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# "SYNTHESIS AND REACTIONS OF MACROMOLECULAR COMPOUNDS"

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NOTES + Bibliographic Material
related to
the LECTURES
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# SYNTHESIS AND REACTIONS OF MACROMOLECULAR COMPOUNDS

The work, ΔF, which has to be performed in the change of a system according to the reaction $A + B \rightarrow C$, or which has to be performed to obtain the reverse reaction, is a measure of the driving force of this reaction. A system can perform work either because its energy becomes smaller through the heat of reaction ΔH (enthalpy), or because its entropy increases by $T \Delta S$ because it goes from a less probable to a more probable state i.e., from an ordered to a disordered (or less ordered) state. If only the internal energy changes, then $\Delta F = \Delta H$; if only the entropy changes, $\Delta F = -T \cdot \Delta S$. In a reaction if the internal energy and also the enthropy change, ΔF is equal to the sum of both, i.e., $\Delta F = \Delta H - T \cdot \Delta S$.

Accordingly, a reaction can occur (ΔF negative) if (1) both the internal energy decreases (ΔH negative) and the entropy increases (ΔS positive); (2) if the internal energy increases (positive ΔH = endothermic reaction), but the entropy increase (positive ΔS) is so large that this effect outweighs the increase in energy; or (3) if there is an entropy decrease (negative ΔS) which is outweighed by simultaneous decrease of the internal energy (negative ΔH = exothermic reaction).

The formation of macromolecules from small molecules (monomers) belongs to this last type of reaction. For example:

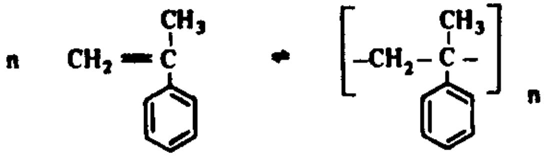
$$n\,CH_2 = CH_2 \rightarrow [-CH_2-CH_2-]_n.$$

Since the polymeric state, in which the monomer residues are tied together into long chains, is always less probable than the state of a completely disordered mixture of the monomer molecules, ΔS must be negative. The formation reaction is, therefore, possible only because it corresponds to the transition of an energy-rich to an energy-poor state (for example, olefin → paraffin) and because all formation reactions of macromolecules are exothermal (negative ΔH).

There are a few exceptions, such as the polymerization of sulfur during which $S_8$ – rings are converted into linear sulfur chains:

$$\boxed{S_4\ S_4} \rightarrow \sim\!\sim S - S - S - S - S - \sim\!\sim$$

The magnitude of the heat of reaction can be quite different with the different reactions which lead to macromolecules. For example, the heat of polymerization of such unsaturated compounds as ethylene, propylene, isobutylene, styrene, vinylchloride, acrylic acid esters, vinyl ethers, and vinyl esters is in the order of 20 kcal/mol. The $\Delta H$ of the polymerization of ethylene oxide, formaldehyde, and the polyaddition of diisocyanates, lies in approximately the same range (30 kcal). In comparison, such polycondensation reactions as occur in the formation of polyamides and polyesters from dicarboxylic acids and amines, i.e., alcohols have a smaller $\Delta H$ (about 4 kcal). On the other hand, we also know of polymerizations that have only a very small $\Delta H$—for example, the polymerization of $\alpha$-methylstyrene. In such a case, the magnitudes of $\Delta H$ and $T \cdot \Delta S$ at 20° C are approximately of the same order, so that the system monomer $\rightleftharpoons$ polymer is in a state of reversible equilibrium.



The higher the temperature, the larger the entropy part $T \cdot \Delta S$ and the greater the oncentration of monomer, which is in an equilibrium state. The lower the emperature, the smaller $T \cdot \Delta S$; therefore, with low temperatures $\Delta F$ becomes egative, and the concentration of the polymer in the equilibrium increases. With he selection of a suitable initiator (lithium alkyls, lithium aryls, and sodium aphthalene in tetrahydrofuran), it is possible through repeated cooling to −70°C nd heating to 40°C to bring about reversible polymerization and depolymeriza-ion. This is similar to altering the temperature of a saturated solution: crystals orm on cooling and dissolve on heating.

In theory all reactions that lead to the formation of macromolecules are quilibrium reactions, but usually the $\Delta H$ values are so large that at ordinary emperatures there is practically no monomer in the system. Only at high emperatures (200°C-300°C) does the entropy term $T \cdot \Delta S$ become so large that epolymerization begins and the monomers distill off—for example, if one heats olymethylmethacrylate (Plexiglas). In other cases (for example, polyacrylonitrile, olyvinylalcohol, or cellulose), certain decomposition reactions begin even below he temperature at which depolymerization can be carried out in a preparative anner. Such decomposition reactions are often combined with discoloration and arbonization.

The temperature at which for a certain monomer $\Delta H = T \cdot \Delta S$ is called the ceiling emperature ($T_c$). At this temperature $\Delta F = 0$, and no further polymerization ccurs. In certain cases one can determine $T_c$ by polymerizing at a number of mperatures and determining the conversion. If one extrapolates the temperature onversion curve to a conversion of O, one obtains the ceiling temperature.

If water or other small molecules are formed in the preparation of a polymer, as r example in the formation of polyesters from glycols and dicarboxylic acids, the ulibrium depends not only on the temperature but also on the concentration of ater. To obtain polymers of a high molecular weight through polycondensation reactions, one must remove the water carefully from the equilibrium. For example, from 146 g of adipic acid and 100 g of hexamethylenediamine on quantitative conversion one obtains 226 g of a polyamide with a molecular weight of $226 \times N_A = 1.361 \times 10^{26}$ (the entire polymeric material is considered a single molecule) and 36 g of water. If one assumes that, on the average, for every 1,000 molecules of adipic acid and diamine (i.e., from 2,000 water molecules) there always remains one molecule of water as $NH_2$ and COOH end groups, then one obtains a polyamide with an average molecular weight of 226,000. To obtain this molecular weight, one actually has to remove 1,999 of a theoretical 2,000 water molecules, i.e., the conversion has to be 99.95%. In the same way, an excess of acid or amide affects the equilibrium. One obtains macromolecules with two $NH_2$ or two carboxyl end groups which cannot find a reaction partner, and therefore a further increase in molecular weight becomes impossible.

One can see from this example that it is not very easy to obtain macromolecular compounds with high molecular weights through polycondensation reactions because the removal of the last traces of water in the reaction mixture is coupled with a number of technical difficulties.[1] This is why industrially produced polycondensates such as polyamides and polyesters (for example, nylon and Dacron) have molecular weights of about 20,000, whereas commercial addition polymers (vinyl polymers such as polymethylmethacrylate, polystyrene, and polyvinylchloride) usually have molecular weights on the order of 200,000.

The fact that a polymerization (or a polycondensation, or polyaddition) is thermodynamically possible (negative $\Delta F$) does not mean that it can occur with a useful reaction velocity, even at normal temperatures. In most cases, one has to use higher temperatures or a catalyst to overcome the potential barrier (whose height is given by the magnitude of the activation energy) which prevents the transition from monomer to polymer.

The many reactions used for the preparation of linear macromolecules can be subdivided into two main groups which differ from each other completely in their kinetics:

1. Polymerization of *unsaturated* olefin monomers or *cyclic* monomers by a *chain reaction:*

$$\text{Initiator} \xrightarrow{\text{Decomposition}} 2 \text{ Radicals } R\cdot$$

$$\text{Radical } R\cdot + \text{Monomer } M \rightarrow R - M\cdot \qquad \text{(Start = Initiation)}$$

$$R - M\cdot + M \rightarrow R - M - M\cdot \rightarrow \text{Chain Radical } R \sim\sim M\cdot \quad \text{(Growth = Propagation)}$$

$$R \sim\sim M\cdot + \cdot M \sim\sim R \rightarrow R \sim\sim M - M \sim\sim R \qquad \text{(Termination)}$$

Depending on the type of initiation, one can differentiate between radical, ionic,

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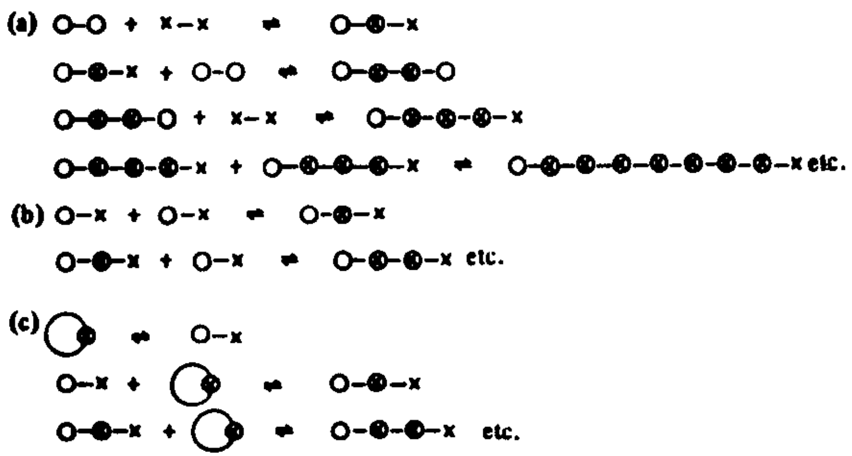
[1] Another reason might be the inability of the polymer coils to penetrate each other (see Section 431).

③

or metal-complex polymerizations. Unsaturated compounds of the type of ethylene and its derivatives, but also such cyclic monomers as ethyleneoxide or trioxane, are easily polymerized according to the above scheme. Of the compounds with C=O double bonds, only formaldehyde leads to relatively stable polymers. Other compounds with CO groups (e.g., acetaldehyde, acetone, and carbon monoxide together with ethylene have also been polymerized, but the resulting polymers are too thermally unstable for any important industrial applications.

II. Polymerization by *stepwise reaction* of monomers with *functional groups*:



O and x are any functional groups which can react with each other to form ⊗, a homopolar main-valence bond. For example:

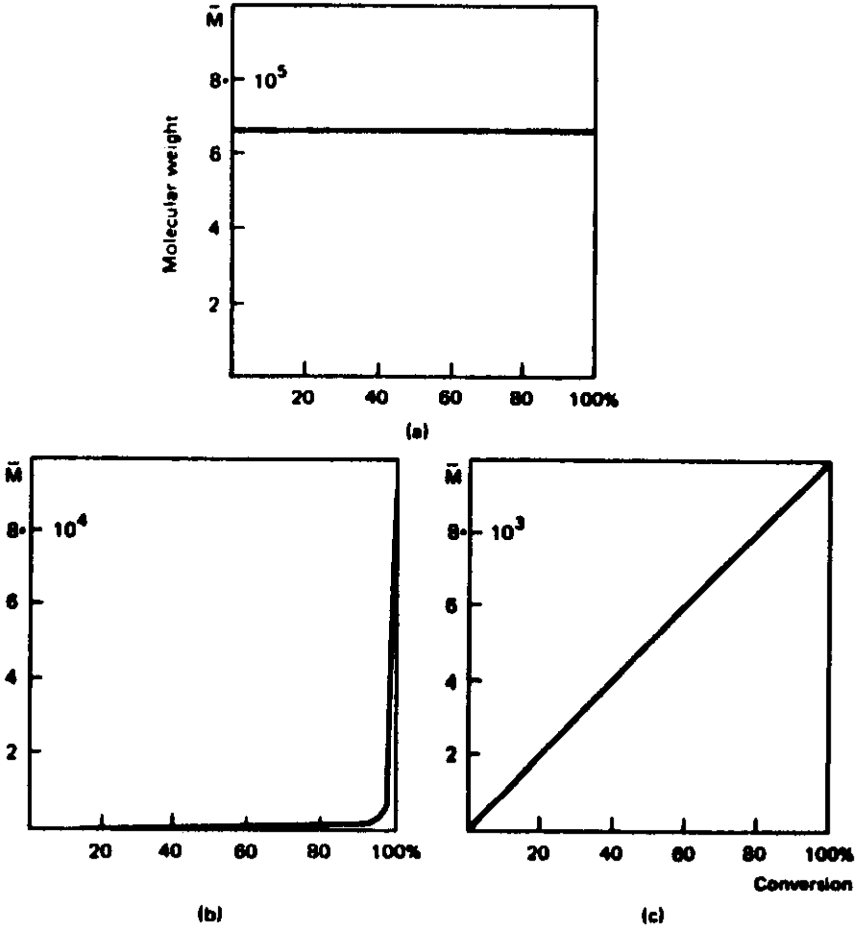
| O | | x |
|---|---|---|
| – OH | + | – COOH |
| – OH | + | – COCl |
| – OH | + | – N = C = O |
| – OH | + | $-CH-CH_2$<br>$\diagdown O \diagup$ |

| O | | x |
|---|---|---|
| $-NH_2$ | + | – COOH |
| $-NH_2$ | + | – N = C = O |
| $-NH_2$ | + | $-COOCH_3$ |

The two different groups, O and x may be, as shown in reaction (a), distributed over two different monomer molecules, (for example, adipic acid and hexamethylenediamine → 6,6–nylon). However, they can also be in one and the same monomer molecule (for example, with ω-amino acids), or they can form a ring in which the two groups are then present within the ring in a condensed form (for example, ε-caprolactam → 6–nylon).

The following are the basic differences between the two types of polymer-forming reactions:

In case I the monomers can react only with the relatively few radicals or ions present but not with each other. By addition of monomers at the few active centers the chain molecules grow very rapidly in a "sudden rush" within a short time span (order of magnitude: 1 second) until they have reached their definitive length by chain termination. Once the growth has been terminated, the formed macromolecules do not participate in the polymerization reaction any more (except where chain transfer reactions occur). This type of chain growth reaction causes the length of the polymer chains to be more or less independent of the degree of conversion (Figure 37a). Just the opposite holds for the other type of reaction, II, which is

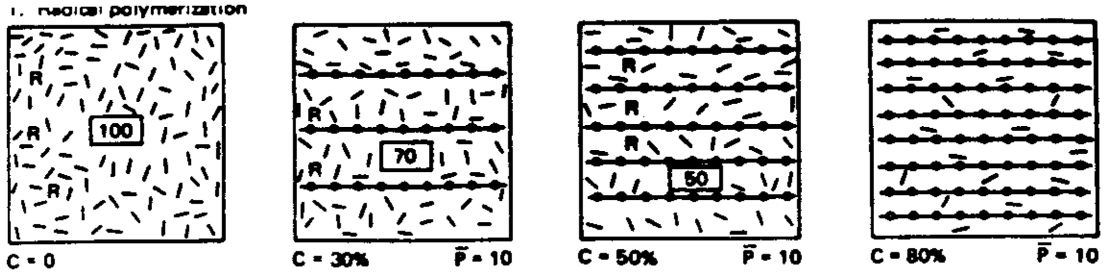


a) with radical polymerizations
b) with polycondensations
c) with living polymerizations and with protein synthesis

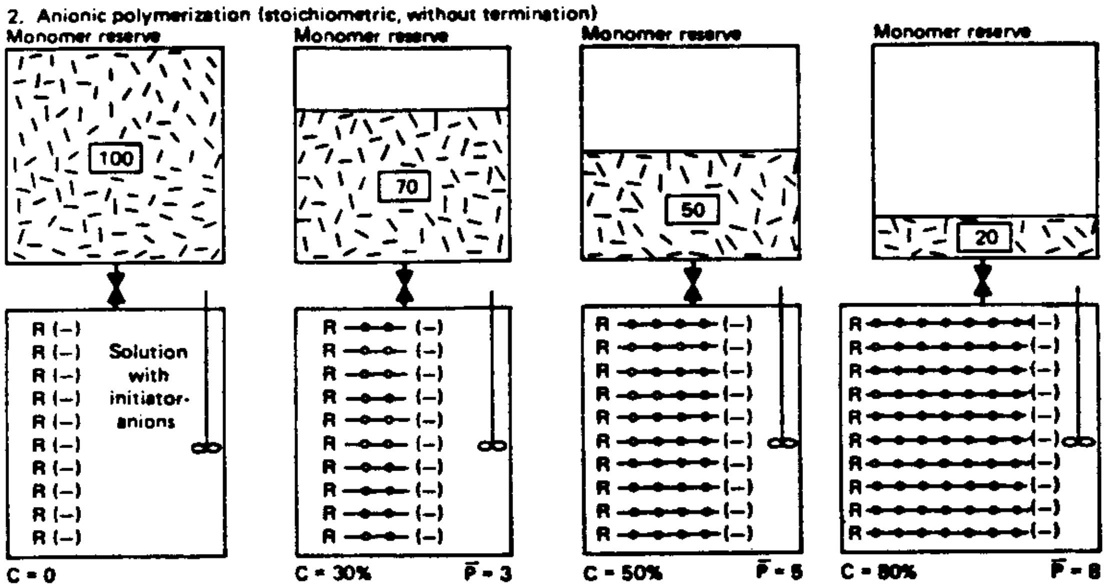
– Dependence of the molecular weight on conversion.

④

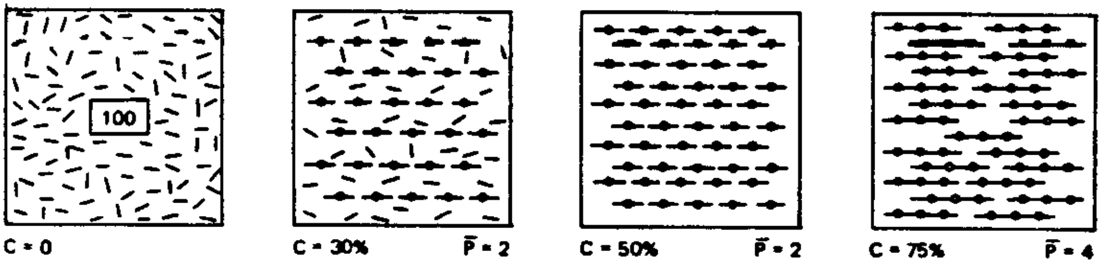
1. Radical polymerization



2. Anionic polymerization (stoichiometric, without termination)

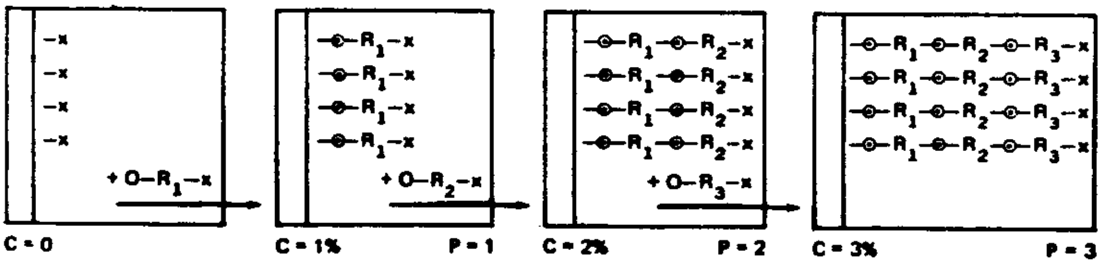


3. Equilibrium condensation



4. Stepwise copolymersynthesis with predetermined monomer sequence (protein synthesis)

For a protein with P = 100:



– Schematic representation of the different possibilities of chain growth with different types of polymer syntheses.

characterized by a very strong dependence of the chain length on the degree of conversion (Figure 37b).

In the case of type II all reaction partners have the same reactivity, and no preferred reaction centers exist. Each monomer molecule can react with each other monomer molecule so that at first (at lower conversions below about 80%) preferably dimers, trimers, and other oligomers are formed. Only at high conversions above 98-99.9%, are long polymer chains formed. Reaction II occurs in a stepwise manner, i.e., it is possible to interrupt the reaction (e.g., by cooling) at any time without affecting the reactivity of the then present chains of oligomers or polymers. The reaction can be continued (e.g., by heating) at any time, and the oligomers and polymers will continue to react with each other.

For both types, the chain-reaction polymerization and the stepwise polycondensation, there is a special case which is characterized by the fact that all chains grow at a constant rate from a constant number of active centers. This leads to a linear relationship between the chain length (i.e., the molecular weight) and the conversion. (Figure 37c).

With the aid of the schematic presentation in Figure 38, it is simple to see the different ways the chain grows in different types of polymer synthesis reactions.

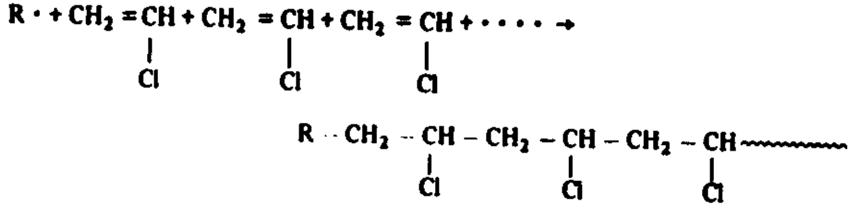
Not all reactions which lead to the formation of macromolecular compounds can be classified without a certain degree of arbitrariness, partly because the reaction mechanism is not completely known in all cases and partly because the reactions of organic synthesis are too numerous to be classified into such a simple four-class scheme. One also should realize that not all reactions which lead to the tying together of molecules are useful for the preparation of macromolecular compounds. Because the purification of polymers, if at all possible, is always difficult and complicated, those reactions which occur without side reactions are preferred, especially by industry, because the removal of side products is always rather expensive. This is also one reason purification of the monomeric starting materials is always carried out with great care.

## SYNTHESIS OF MACROMOLECULES WITH C-C CHAINS THROUGH POLYMERIZATION OF OLEFINIC UNSATURATED COMPOUNDS

Many olefinic unsaturated compounds are able to form chain-like macromolecules through elimination of the double bond, a phenomenon first recognized by Staudinger. Diolefins polymerize in the same manner, however only one of the two double bonds is eliminated. Such reactions occur through the initial addition of a monomer molecule to an initiator radical or an initiator ion by which the active state is transferred from the initiator to the added monomer. In the same way, by means of a chain reaction, one monomer molecule after the other is added

different type of reaction. The polymerization is a chain reaction in two ways: because of the reaction kinetics and because as a reaction product one obtains a chain molecule. The length of the chain molecule is proportional to the kinetic chain length.

One can summarize the process as follows (R· is equal to the initiator radical):



$$R\cdot + \underset{\displaystyle Cl}{CH_2{=}CH} + \underset{\displaystyle Cl}{CH_2{=}CH} + \underset{\displaystyle Cl}{CH_2{=}CH} + \cdots\cdots \rightarrow$$

$$R\cdot\cdot CH_2-\underset{\displaystyle Cl}{CH}-CH_2-\underset{\displaystyle Cl}{CH}-CH_2-\underset{\displaystyle Cl}{CH}\sim\sim\sim$$

One thus obtains polyvinylcholoride from vinylchloride, or polystyrene from styrene, or polyethylene from ethylene, etc.

The length of the chain molecules, measured by means of the degree of polymerization (definition see p. 9), can be varied over a large range through selection of suitable reaction conditions. Usually, with commercially prepared and utilized polymers, the degree of polymerization lies in the range of 1,000 to 5,000, but in many cases it can be below 500 and over 10,000. This should not be interpreted to mean that all molecules of a certain polymeric material consist of chains of 500, or 1,000, or 5,000 monomer units. In almost all cases, the polymeric material consists of a mixture of polymer molecules of different degrees of polymerization. Through such processes, as fractional precipitation and chromatographic methods a polymeric material can be separated into more homogeneous fractions. The greater the number of fractions the more homogeneous they can be made. Often one also specifies a degree of polymerization even for an unfractionated polymer. In such cases, the degree of polymerization is an average, which is defined differently depending on the method used for the determination of the molecular weight. These averages are written $\bar{P}$ or $\bar{M}$ and are usually called $\bar{P}_n$, $\bar{P}_w$ or $\bar{M}_n$, $\bar{M}_w$ (compare Section 3135).

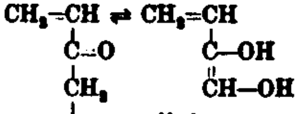
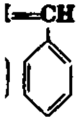
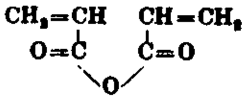
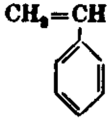
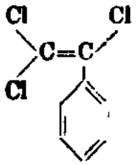
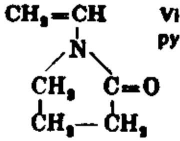
Not all olefinic unsaturated compounds can be polymerized. One basic requirement is a favorable potential difference from the monomer to the polymer (negative ΔH), which can be recognized by the exothermic behavior of the polymerization. The example of α–methylstyrene shows that not even this basic assumption is true for all olefins. In addition, there are some olefins which fulfill this basic condition (i.e., where the polymer presents a thermodynamically more stable condition than the monomer) but which do not polymerize. Thus, polymerization can be prevented by too high an activation energy, if suitable intermediate reactions are absent through which it might be possible to overcome the potential barrier, which surrounds the monomer like a wall. For example, all efforts to polymerize propylene to a real macromolecule were unsuccessful for a

6

this case $TiCl_3/Al(C_2H_5)_3$]. Furthermore, steric reasons or the peculiar case of inhibition (see p. 71) may be responsible for the reluctance of an unsaturated pound to polymerize.

f we arrange the polymerizable olefins on a linear scale, we can put at one end the scale those olefins which are difficult to polymerize (or not at all merizable). At the other end will then be those which have such a great lency to polymerize that it is very difficult to prepare them in a monomerically state–they are stable only in the dark under refrigeration or by addition of ilizers. In between these extremes lie those monomers which polymerize rapidly upon warming or upon addition of suitable initiators (the term "monomer" is for all polymerizable unsaturated compounds and also for any bifunctional pounds used in the synthesis of macromolecules). Table 42 gives some nples of these three groups of unsaturated compounds.

**TABLE** . Examples of unsaturated olefins and vinyl compounds with different tendency for polymerization

| A | | B | | C | |
|---|---|---|---|---|---|
|  | (over 40°C) α-Methyl-styrene | $CH_2=CH_2$ | Ethylene |  $CH_2=CH-C(=O)-CH_2-OH \rightleftharpoons CH_2=CH-C(OH)=CH-OH$ | Hydroxy-methyl-vinyl-ketone |
| $=CH-CH_2-OH$ | Allyl-alcohol (-ester) | $CH_2=CH-CH_3$ | Propylene | $CH_2=C(CN)_2$ | Vinylidene-cyanide (Methylene-malodinitrile) |
| $=CH-CH_2-Cl$ | Allylchloride | $CH_2=C(CH_3)_2$ | Isobutylene | $CH_2=CH-COOH$ | Acrylic acid |
|  | Stilbene | $CH_2=CH-CH=CH_2$ | Butadiene |  | Acrylicanhydride |
| $=CH-Cl$ | Dichloro-ethylene |  | Styrene | $CH_2=C(COOR)_2$ | Methylene malonate |
| $=CH-COOH$ | Maleic-acid | $CH_2=CH-Cl$ | Vinylchloride | $CH_2=CH-NO_2$ | Nitroethylene |
|  | Trichloro-styrene | $CF_2=CF_2$ | Tetrafluoro-ethylene | $CH_2=C(CN)-COOR$ | α-Cyanoacrylate |
| | | $CH_2=CH-O-C(=O)-CH_3$ | Vinylesters | | |
| | | $CH_2=CH-O-R$ | Vinylethers | | |
| | | $CH_2=CH-COOR$ | Acrylic acid-esters | | |
| | | $CH_2=C(COOH)-CH_2-COOH$ | Itaconic acid (esters) | | |
| | | $CH_2=CH-CN$ | Acrylo-nitrile | | |
| | |  | Vinyl-pyrrolidone | | |

**A** Unsaturated compounds which do not polymerize by themselves

**B** Monomers which polymerize under the action of heat, light, or initiators

**C** Monomers which have a particularly strong tendency to polymerize

Polymerization, a chain reaction, occurs according to the same mechanism as the well-known chlorine-hydrogen reaction and the decomposition of phosgene.

The initiation reaction, which consists of the activation of the double bond, can be brought about by heating, irradiation, ultrasonics, or initiators. The initiation of the chain reaction can be observed most clearly with radical or ionic initiators. These are energy-rich compounds which can add suitable unsaturated compounds (monomers) and maintain the activated radical, or ionic, state so that further monomer molecules can be added in the same manner. For the individual steps of this growth reaction one needs only a relatively small activation energy and therefore through a single activation step (the actual initiation reaction) a large number of olefin molecules are converted, as is implied by the term "chain reaction." Because very small amounts of the initiator bring about the formation of a large amount of polymeric material (1:1,000 to 1:10,000), it is possible to regard polymerization from a superficial point of view as a catalytic reaction. For this reason, the initiators used in polymerization reactions are often designated as polymerization catalysts, even though, in the strictest sense, they are not true catalysts because the polymerization initiator enters into the reaction as a real partner and can be found chemically bound in the reaction product, i.e., the polymer. In addition to the ionic and radical initiators there are now metal complex initiators (which can be obtained, for example, by the reaction of titanium tetrachloride or titanium trichloride with aluminum alkyls), which play an important role in polymerization reactions (Ziegler catalysts). The mechanism of their catalytic action is not yet completely clear.

Table 44 shows the type of initiation by which most monomers are polymerized. When the monomer is also commercially polymerized, the preferred initiation is designated with a circle.

**TABLE** . Types of initiation mechanism by which different monomers polymerize.

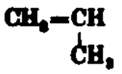
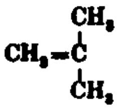
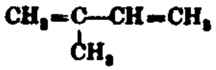
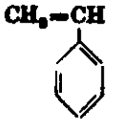
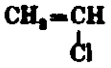
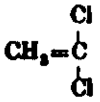
| Monomer | | Polymerization mechanism | | | |
|---|---|---|---|---|---|
| | | radical | anionic | cationic | Metal-complex |
| $CH_2{=}CH_2$ | Ethylene | ⊕ | | + | ⊕ |
|  $CH_2{=}\underset{CH_3}{CH}$ | Propylene | | | + | ⊕ |
| $CH_2{=}CH{-}CH_2{-}CH_3$ | Butylene-1 | | | | ⊕ |
|  $CH_2{=}\overset{CH_3}{\underset{CH_3}{C}}$ | Isobutylene | | | ⊕ | + |
| $CH_2{=}CH{-}CH{=}CH_2$ | Butadiene | ⊕ | + | | ⊕ |
|  $CH_2{=}\underset{CH_3}{C}{-}CH{=}CH_2$ | Isoprene | + | + | | ⊕ |
|  | Styrene | ⊕ | + | + | + |
|  $CH_2{=}\underset{Cl}{CH}$ | Vinylchloride | ⊕ | | | + |
|  $CH_2{=}\overset{Cl}{\underset{Cl}{C}}$ | Vinylidenechloride (Dichloroethylene) | ⊕ | | | |

**TABLE** (Cont'd)

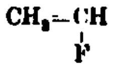
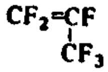
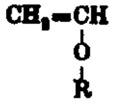
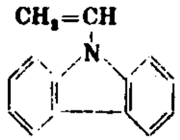
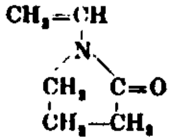
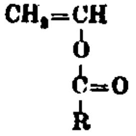
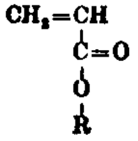
| Monomer | | Polymerization mechanism | | | |
|---|---|---|---|---|---|
| | | radical | anionic | cationic | Metal-complex |
|  $CH_2{=}\underset{F}{CH}$ | Vinylfluoride | ⊕ | | | |
| $CF_2{=}CF_2$ | Tetrafluoroethylene | ⊕ | | | |
|  $CF_2{=}\underset{CF_3}{CF}$ | Perfluoropropylene | ⊕ | | | + |
|  $CH_2{=}\underset{NO_2}{CH}$ | Nitroethylene | + | + | | |
|  $CH_2{=}\underset{\underset{R}{O}}{CH}$ | Vinylethers | | | ⊕ | + |
|  | Vinylcarbazole | ⊕ | | | + |
|  | Vinylpyrrolidone | ⊕ | | + | |
|  $CH_2{=}\underset{\underset{\underset{R}{C=O}}{O}}{CH}$ | Vinyl esters | ⊕ | | | |
|  $CH_2{=}\underset{\underset{\underset{R}{O}}{C=O}}{CH}$ | Acrylic acid esters (acrylates) | ⊕ | | | |

**TABLE** (Cont'd)

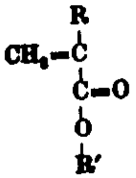
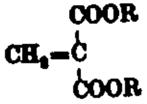
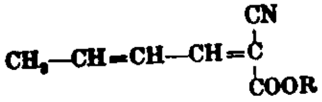
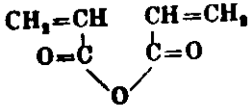
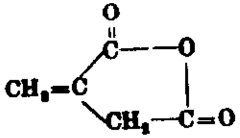
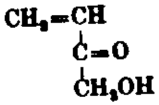
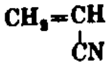
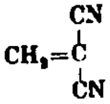
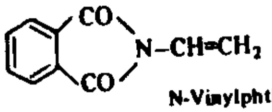
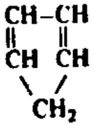
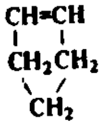
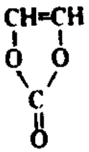
| Monomer | Polymerization mechanism | | | |
|---|---|---|---|---|
| | radical | anionic | cationic | Metal-complex |
|  $CH_2=C(R)-C(=O)-O-R'$ Methacrylates (R=CH$_3$) | ⊕ | + | | + |
| α-Chloracrylates (R = Cl) | + | | | |
| α-Cyanoacrylates (R = CN) | + | + | | |
|  $CH_2=C(COOR)_2$ Methylenemalonates | + | + | | |
|  $CH_3-CH=CH-CH=C(CN)COOR$ α-Cyanosorbates | + | + | | |
|  Acrylicanhydride | + | | | |
|  Itaconicanhydride | + | | | |
|  $CH_2=CH-C(=O)-CH_2OH$ Oxymethylvinylketone | + | | | |
|  $CH_2=CH-CN$ Acrylonitrile | ⊕ | + | | |

**TABLE** (Cont'd)

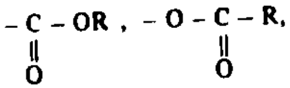
| Monomer | Polymerization mechanism | | | |
|---|---|---|---|---|
| | radical | anionic | cationic | Metal-complex |
|  $CH_2=C(CN)_2$ Vinylidenecyanide | ⊕ | + | | |
|  N-Vinylphthalimide | + | | | |
|  Cyclopentadiene | | | | + |
|  Cyclopentene | | | | + |
|  Vinylenecarbonate | + | | | |

⊕ indicates an industrial process

## Radical Polymerization

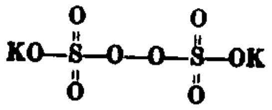
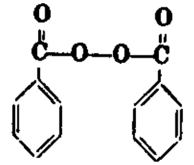
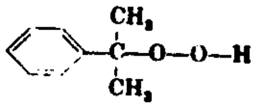
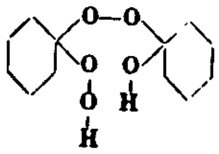
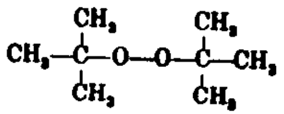
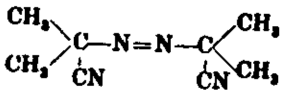
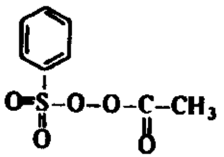
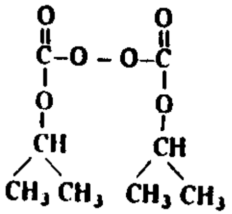
Compounds which readily decompose into free radicals on heating or under the influence of light are usually used as initiators in radical polymerizations. Peroxides and aliphatic azo-compounds in particular have shown themselves as very suitable, and they are therefore produced commercially for use as polymerization initiators. Table 48 shows some of the most common peroxides and azo-compounds.

The following reactions describe the course of a radical polymerization, using as an example a vinyl compound (for example, where R = − $C_6H_5$

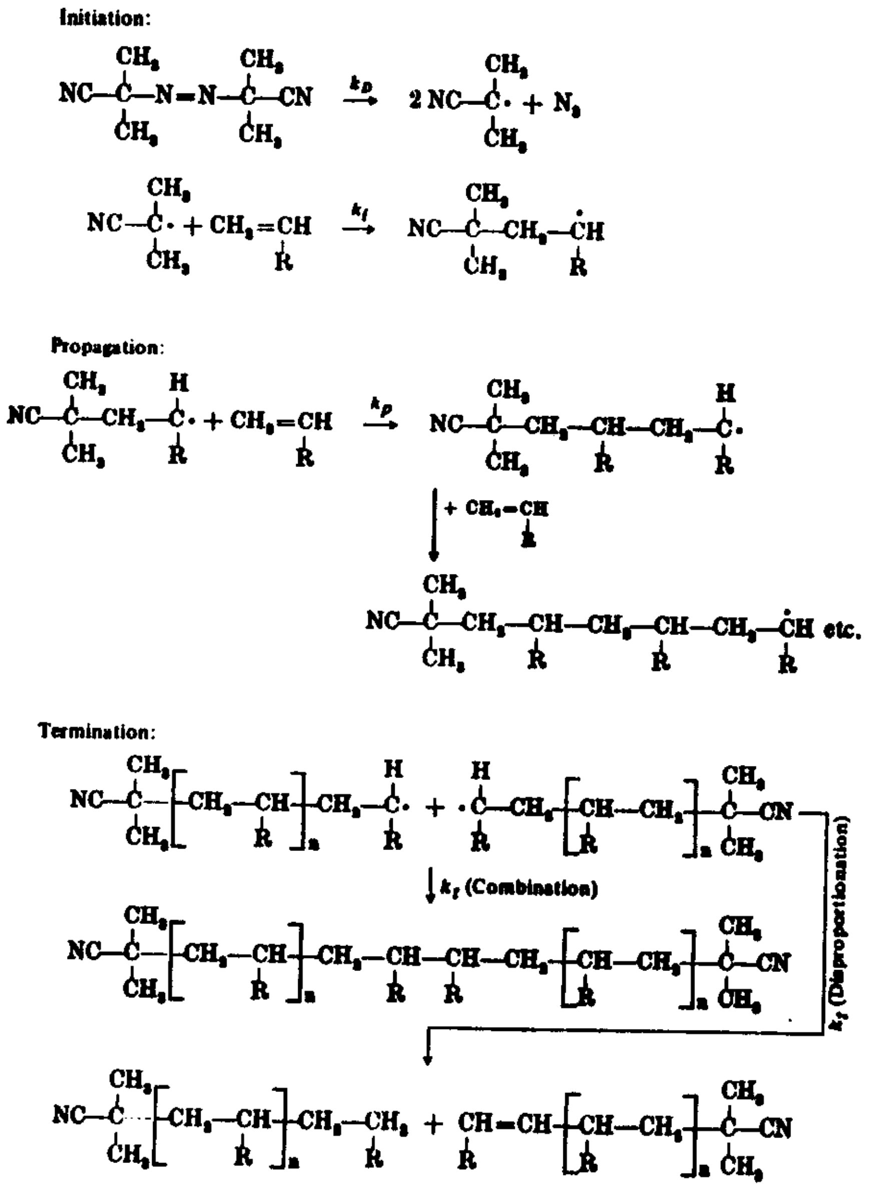


$$-C(=O)-OR\ ,\ -O-C(=O)-R,$$

**TABLE** Initiators for radical polymerization

| Name | Formula | Suitable Polymerization Temperature °C |
|---|---|---|
| Potassiumpersulfate |  $KO-\overset{O}{\underset{O}{S}}-O-O-\overset{O}{\underset{O}{S}}-OK$ | 40—80 |
| Dibenzoylperoxyde (Lucidol) |  | 40—90 |
| Cumenehydroperoxyde |  | 50—100 |
| Cyclohexanoneperoxyde |  | 20—80 |
| Di-t-butylperoxyde |  $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O-O-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$ | 80—150 |
| Azo-bis-isobutyronitrile (Vazo, AIBN) |  | 20—100 |
| Cyclohexylsulfonyl-acetylperoxyde (Percadox ACS) |  | 0–40 |
| Diisopropylpercarbonate (Percadox IPP) |  | 40–80 |

– Cl or – CN) with azobisisobutyronitrile as the initiator. The reactions are valid in principle for all monomers that polymerize by a radical mechanism, even though the individual reaction steps, especially the initiation and termination reactions, may differ in certain cases from the scheme presented here.

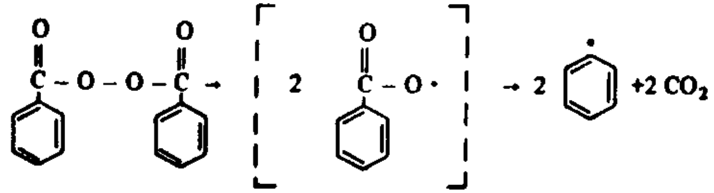


## Chain Initiation

The initiation reaction occurs in two steps: the decomposition reaction of the nitiator and the addition of the first monomer molecule to the radical. Not every adical formed through the decomposition reaction must lead to the starting of a hain. A fraction of the radicals can disappear under certain circumstances also hrough different reactions, e.g., through direct recombination of two radicals or by eaction with atmospheric oxygen or other inhibiting substances, as will be liscussed in greater detail later on.

To determine the radical yield, one has to determine the number of radicals ormed in a given time and the number of polymer chains formed in the same time. he rate of radical formation can be determined by analytical methods, for xample, determination of peroxide. The number of polymer chains can be etermined by molecular weight measurements with a method which gives the umber-average molecular weight (by end-group determination or osmotic pressure easurements).

The rate of the initiation reaction depends on the rate of the initiator ecomposition reaction, i.e., on the half-life of the initiator. This reaction has a igh activation energy (with the most commonly used initiators it is on the order of 0 kcal/mole), and it is therefore strongly temperature dependent. The course of e decomposition reaction and, therefore, the constitution of the radicals which re formed, is often dependent on the nature of the solvent in which the ecomposition occurs. Thus, dibenzoylperoxide decomposes in inert solvents, such benzene, into phenyl radicals under formation of $CO_2$. However, in the presence styrene, where no $CO_2$ formation seems to occur, the apparently intermediate enzoyl radicals start the polymerization.



ydroperoxides may, according to W. Kern, decompose in a bimolecular reaction ith the formation of water:

$$R-O-O-H+H-O-O-R \rightarrow R-O\cdot+R-O-O\cdot+H_2O$$

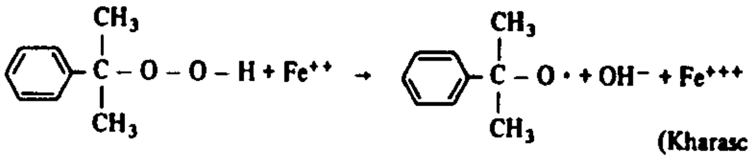
Among the well-known radical formers, azobisisobutyronitrile (available mmercially under the name VAZO in the United States), which has found great e as a foaming agent in the manufacture of foam plastics, decomposes especially iformly and homogeneously to give only a single type of radical. It is therefore ry suitable as an initiator for radical polymerizations, both for scientific (kinetic) vestigations and for industry. With the aid of azobisisobutyronitrile it is possible

to carry out polymerizations already at relatively low temperatures (e.g., 40°C-60°C). Another advantage of azobisisobutyronitrile is that it can be prepared with relatively little danger and can be kept in pure form; because the preparation and use of many peroxides can be very dangerous, one has to keep them either in solution or in suspension. At temperatures of 80°C-90°C, however, even azobisisobutyronitrile decomposes quite violently.

In addition to the rate of decomposition, it is also important to consider the stability of the radicals formed in order to determine the usefulness of a radical-forming compound as a polymerization initiator. Very stable radicals, such as triphenylmethyl and diphenylpicrylhydrazyl, do not show a great tendency to initiate polymerization.

One can reduce the activation energy of the peroxide decomposition reaction and thus increase the rate of decomposition at low temperatures greatly, if one adds reducing agents as "activators"—e.g., sodium hyposulfite, potassium persulfate, amines such as dimethylaniline or hydroxylamine, readily enolizable carbonyl compounds such as ascorbic acid, or metal ions such as $Fe^{++}$ or $Cu^{+}$. This is usually done in the case of emulsion polymerizations, as illustrated by the following reactions:

$$H-O-O-H+Fe^{++} \rightarrow HO\cdot+OH^{-}+Fe^{+++} \quad \text{(Haber-Weiss)}$$



(Kharasch)

(cumene hydroperoxide)

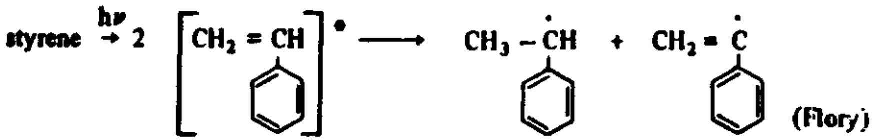
$$R-O-O-H+Cu^{++} \rightarrow R-O-O\cdot+H^{+}+Cu^{+} \quad \text{(Kern)}$$

$$R-O-O-H+Cu^{+} \rightarrow R-O\cdot+OH^{-}+Cu^{++} \quad \text{(Kern)}$$

Such redox systems permit radical polymerizations (especially emulsion polymerizations) at 0°C and even lower temperatures. A large-scale industrial application of redox polymerization is the production of synthetic rubber (SBR), which occurs by emulsion polymerization at temperatures down to − 5°C.

The emulsion polymerization of vinyl compounds by a radical mechanism can also be initiated in the absence of peroxides by salts of such transition metals as $H_2PtCl_6\cdot6H_2O$, $PdCl_2\cdot2H_2O$, $RhCl_3\cdot3H_2O$, or $TiCl_3$. However, these initiators show a specificity toward different monomers. For example, $TiCl_3$, $H_2PtCl_6$, and $PdCl_2$ are good initiators for styrene, but not for methylmethacrylate. $RhCl_3$, on [illegible]

As far as is known today, it is not possible to present a generally valid mechanism for the initiation reaction in photopolymerizations. With certain monomers the molecule is split into many small radicals (e.g., into $\cdot CH_3$, $CH_2{=}\dot{C}H$, and $CH_3{-}\dot{C}{=}O$ for the case of methylvinylketone). With other monomers (for example, methylmethacrylate) a condensation to quinoidal systems occurs. With styrene one assumes that a disproportionation reaction between two activated molecules is possible:



Even less is known about the mechanism of a straight thermal initiation reaction, such as the polymerization of styrene, which has been carried out for over 25 years on a large industrial scale without its being possible up until now to elucidate the mechanism completely.

Often one adds certain sensitizers to a photopolymerization. These sensitizers are compounds which, under ultraviolet radiation, decompose into radicals. Commonly used sensitizers are benzoin and its derivatives, condensed aromatic ring systems, sulfur compounds, azo compounds, etc. Among the last is azobisisobutyronitrile, which is especially useful. The initiation reaction is the same as without UV irradiation, but the difference is that with UV irradiation the decomposition temperature of the initiator is lowered by approximately 50°C to 80°C. In this way, it is possible to bring about radical polymerizations at −10°C to −30°C.

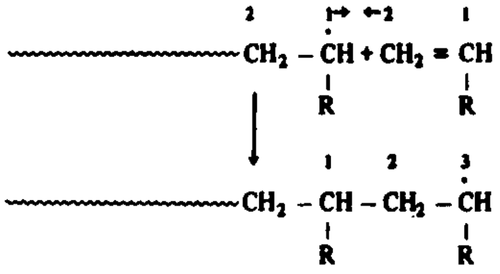
### 2112 Chain Propagation

In contrast to the initiation reaction, the growth or propagation reaction requires a much lower activation energy, and its rate ($v_p$) is therefore also less temperature-dependent than the rate of the initiation reaction. This is important for the dependence of the degree of polymerization on the temperature of polymerization, since the degree of polymerization is proportional to the ratio of the rates of the growth reaction and to the termination reaction (compare pp. 66 and 93).

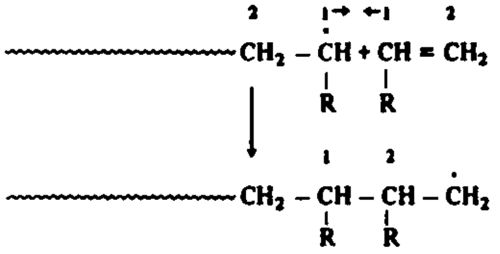
It is surprising that certain unsaturated compounds polymerize rapidly by a free radical mechanism (for example, acrylic esters, vinyl ketone, styrene, vinyl chloride, and a number of other vinyl compounds), whereas other unsaturated compounds polymerize only very slowly or not at all by a free radical mechanism (for example, allylic esters, allyl chloride, maleic esters, and vinyl ether). This happens not because in one case the propagation rate is much lower than in the other case, but rather because the lifetime of the radicals is very much shorter as a result of chain termination or chain transfer.

The addition of vinyl monomers during chain propagation occurs mainly as 1,2-addition so that the substituents are in 1,3-position:

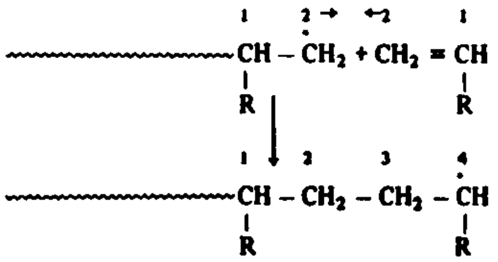
1,2-addition:



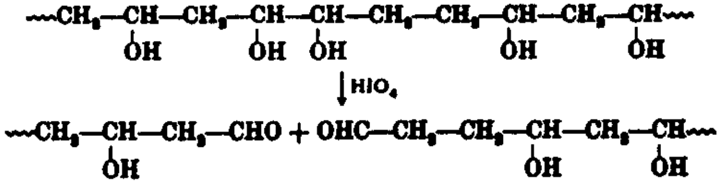
1,1-addition:



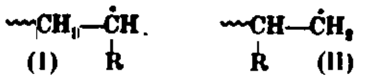
2,2-addition:



The fraction of 1,1- and 2,2-addition is usually so small that it cannot be proved experimentally. Only if there are especially sensitive reactions available, such as chain scission of polyvinylalcohol with periodic acid, is it possible to determine the amount of 1,2-glycol groups.

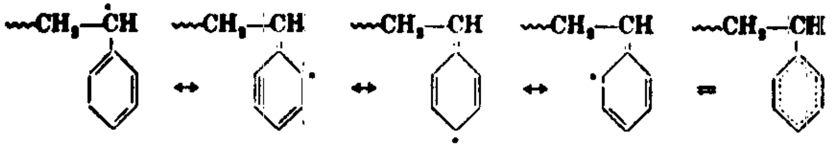


The striking preference of 1,3-addition with radical polymerization can be explained on the basis of the different stability of the two radicals (I) and (II).



$$\sim CH_2-\underset{R}{\overset{\bullet}{C}H}\ \text{(I)} \qquad \sim\underset{R}{CH}-\overset{\bullet}{C}H_2\ \text{(II)}$$

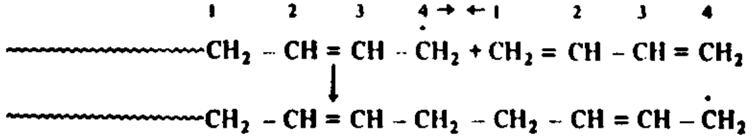
Since with radical (I), the radical is in most cases stablized by resonance, the formation of this radical, which occurs through 1,2-addition (in the sense of the formula of p. 72), is thermodynamically preferred. With a styrene radical, for example, the following mesomeric forms are possible:



In addition to resonance stabilization, steric hindrance can play an important role in the structure of the polymer. Structures which allow a greater mobility will probably be preferred. It is also possible that polarization effects can have an influence on the position in which a monomer adds to the growing chain.

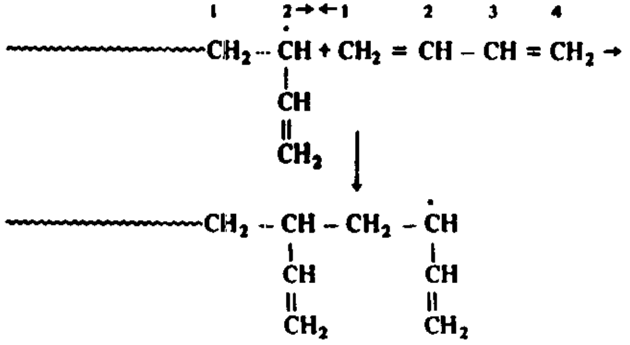
Of special importance is the question of chain structure with dienes (butadiene and isoprene). Propagation can occur as 1,4- and as 1,2-addition.

1,4 – Addition:



$$\sim CH_2 \overset{1}{} - \overset{2}{CH} = \overset{3}{CH} - \overset{4}{\dot{C}H_2} \rightarrow \leftarrow \overset{1}{CH_2} = \overset{2}{CH} - \overset{3}{CH} = \overset{4}{CH_2}$$
$$\downarrow$$
$$\sim CH_2 - CH = CH - CH_2 - CH_2 - CH = CH - \dot{C}H_2$$

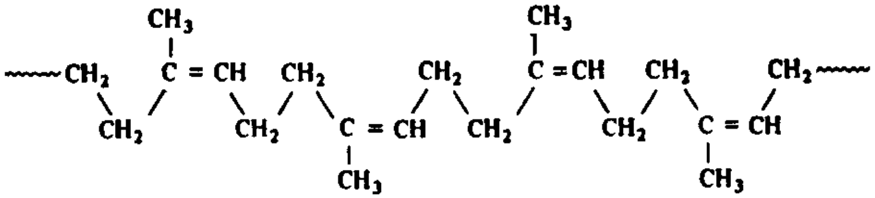
1,2 – Addition:



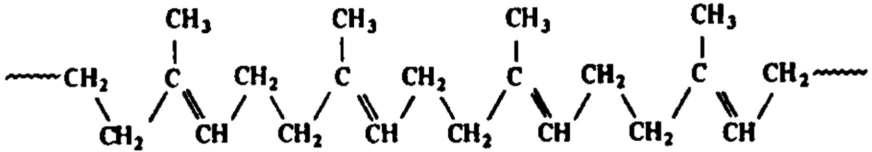
$$\sim \overset{1}{CH_2} - \underset{\substack{|\\ CH\\ \|\\ CH_2}}{\overset{2}{\dot{C}H}} \rightarrow \leftarrow \overset{1}{CH_2} = \overset{2}{CH} - \overset{3}{CH} = \overset{4}{CH_2} \rightarrow$$
$$\downarrow$$
$$\sim CH_2 - \underset{\substack{|\\ CH\\ \|\\ CH_2}}{CH} - CH_2 - \underset{\substack{|\\ CH\\ \|\\ CH_2}}{\dot{C}H}$$

With radical polymerization one obtains chains with a mixed structure, but with nic polymerization one can obtain 1,4- or 1,2-polymers according to the choice of the polymerization conditions. With organo-alkali reagents e.g., phenyllithium in tetrahydrofuran, one obtains mainly, 1,2-polymers, whereas with lithium dispersions or phenyllithium in paraffinic hydrocarbons e.g., heptane as a solvent one obtains mainly 1,4-polymers. The pure crystalline 1,2-polybutadiene which is obtained using an initiator combination of chromium hexacarbonyl and aluminum triethyl turns out to be a hard and tough resin with a crystalline melting point of 131°C. The 1,4-*trans*-polybutadiene is also a hard/tough crystalline compound, whereas the 1,4-*cis*-polybutadiene is a soft and elastomeric material which becomes hard and glassy at temperatures of about – 100°C. This finding shows that, in addition to the chemical constitution, the steric structure of polymers also has a great influence on their properties.

Natural rubber (polyisoprene), as another example, has a pure *cis*-1,4 configuration.



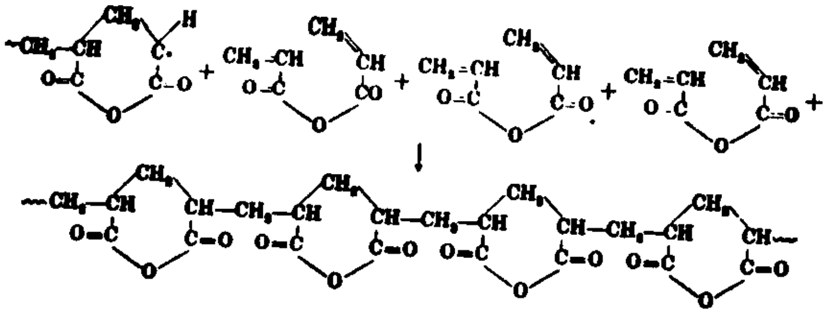
The same polymer with a *trans*-1,4 configuration (guttapercha) is not elastic, but turns out to be a hard and brittle resin.



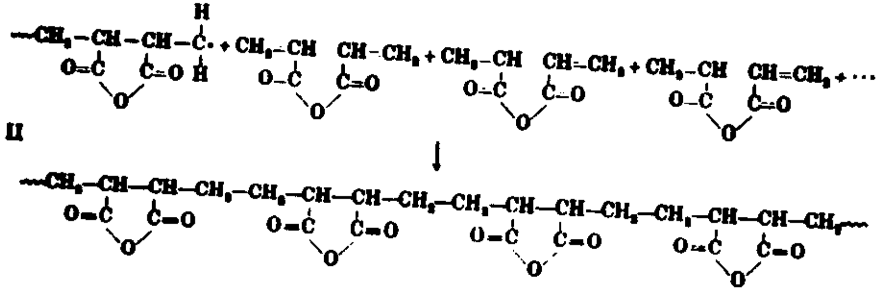
Synthetic rubber (SBR) is a copolymer of butadiene (75%) and styrene (25%) with a mixed structure of 1,2-, and *cis* and *trans* 1,4-butadiene structural units in the chain. With Ziegler-type catalysts (e.g., $TiI_4/Al(C_2H_5)_3$ or $AlR_2Cl/CoCl_2$), or phenyllithium, or lithium in heptane, it is possible to prepare a synthetic rubber from isoprene or from butadiene which has mainly the *cis*-1,4 configuration (see p. 135 ff.). Other examples for different steric structures (isotactic and syndiotactic polymers) will be disucssed in greater detail in the section on polymerization initiated by complex catalysts (section 213).

During the polymerization of vinyl compounds one usually obtains polymers without regular steric structure, i.e., all possible steric configurations are distributed along the polymer chain in a random statistical manner.

A special sort of chain propagation is found with monomers of the type of acrylic anhydride in which two identical double bonds are found in the molecule at such a distance that during the polymerization five-or six-membered rings can be formed.


I

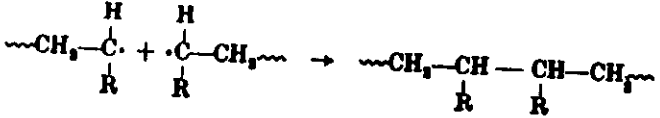
or:


II

In reaction (I) chain growth occurs in the manner of a 1,2-addition (see p. 72) and one should therefore assume that this reaction is preferred. However, it was discovered that the infrared spectrum of polyacrylic acid, which was prepared by the hydrolysis of polyacrylic acid anhydride, differs from the normal polyacrylic acid prepared by polymerization of acrylic acid. This finding cannot be understood in terms of structure (I). One therefore has to leave open the question of which of the two chain structures corresponds to the true structure of polyacrylic acid anhydride. It can be said with certainty only that the structure must be one of the two, because a polymerization of the two double bonds of the acrylic acid anhydride in two *different* polymer chains according to the reaction discussed on page 26 for divinylbenzene cannot occur because polyacrylic acid anhydride is a soluble polymer and can therefore not be cross-linked. With chain growth occurring according to reactions I or II, the reaction is called ring-forming polymerization, or cyclopolymerization.

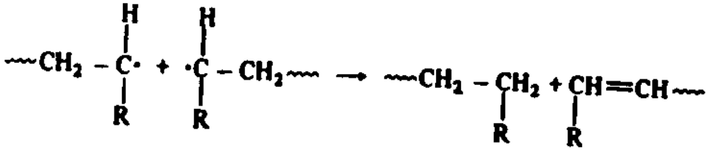
### 2113 Chain Termination

In contrast to ionic polymerization, which under certain circumstances can occur in such a way that no chain termination takes place, radical polymerization must always involve a chain terminator because the radicals of the growing chain always have a strong tendency to react with each other. Two types of reactions are possible: recombination and disproportionation. The recombination consists of the addition of two growing radical chain ends to form a saturated macromolecule:


$$\sim CH_2-\overset{H}{\underset{R}{C}}\cdot + \cdot\overset{H}{\underset{R}{C}}-CH_2\sim \;\rightarrow\; \sim CH_2-\underset{R}{CH}-\underset{R}{CH}-CH_2\sim$$

In certain cases, by means of osmotic molecular weight determination and quantitative end group determination with polymers which had been prepared using radioactive $C^{14}$-containing azobisisobutyronitrile, it was demonstrated that each molecule contains two radioactive end groups. The same results were found for emulsion polymers of styrene which had been prepared by initiation with radioactive potassium persulfate ($S^{35}$). This means that in these quantitatively investigated examples recombination is practically the only termination reaction. The term "recombination" also includes the combination of the growing chain radical with an initiator radical, a reaction which is rather improbable at the beginning of the polymerization as long as there is still a high concentration of monomer but which becomes more and more probable with increasing conversion. (In emulsion polymerization this reaction is the only termination reaction—compare p. 157).

The second reaction which leads to chain termination, called disproportionation, can be described by the following equation:


$$\sim CH_2-\overset{H}{\underset{R}{C}}\cdot + \cdot\overset{H}{\underset{R}{C}}-CH_2\sim \;\rightarrow\; \sim CH_2-\underset{R}{CH_2} + \underset{R}{CH}=CH\sim$$

The reactions for recombination and disproportionation show that recombination leads to macromolecules whose molecular weight is on the average twice that of the growing chain radicals, whereas disproportionation leads to chain molecules of the same average length as that of the chain radicals.

Which of the two termination reactions, recombination or disproportionation, prevails depends both on the type of monomer and on the temperature. Since the recombination reaction, in which the atomic structure of the reaction partners remains unchanged, occurs practically without activation energy, its rate scarcely depends on the temperature. However, in disproportionation a hydrogen atom has to move, and this can not take place without energy. The rate of the disproportionation reaction is therefore temperature dependent. Consequently, disproportionation becomes more important the higher the polymerization temperature. The temperature at which disproportionation becomes significant depends on the individual monomer. With polymerization of styrene, for example, one does not find any disproportionation at 60°C-70°C; with methylmethacrylate, however, disproportionation predominates at this temperature.

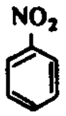
In addition to the so-called natural chain termination reactions, recombination and disproportionation, there are a number of additional possibilities for chain termination, which can be brought about more or less at will either through substances which are unintentionally present during the polymerization or through substances which one intentionally adds at a certain stage of the polymerization in order to stop it. In the first case, we are concerned with impurities which are present in the monomer, or in the solvent, or in other additives such as soaps and protective colloids (in emulsion polymerization), or which are present in the reaction vessel (for example, greases or lubricants in technical polymerizations). Atmospheric oxygen must also be included among the impurities which inhibit the polymerization, which is why radical polymerizations are usually carried out under nitrogen. In the second case, the polymerization is intentionally interrupted toward the end of the reaction. Thus while the radical concentration remains nearly constant, only small amounts of monomer remain at the end of the polymerization, and the chain growth is therefore slowed down. However, the termination reactions occur at the same rate as during the beginning of the polymerization, and therefore polymers with relative low molecular weight are preferably formed (see section on kinetics of radical polymerization). These polymers usually have a detrimental influence on the physical properties of the final product. Also, undesirable side reactions, which at high conversion occur more readily, may be a reason for terminating the polymerization at an earlier stage. This is the case during the synthesis of rubber by emulsion polymerization of butadiene and styrene. This reaction is terminated by the addition of stopping agents such as phenyl-β-naphtylamine to prevent the formation of larger amounts of cross-linked products.

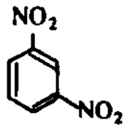
*Inhibitors*

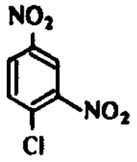
In addition to β–naphtylamine there are a large number of other organic compounds suitable for bringing about chain termination in radical polymerization. These compounds usually react with radicals, either giving rise to saturated molecules or to stable radicals too unreactive to start a new chain.

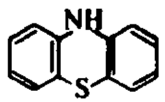
Much more important than bringing about chain termination during polymerization is the use of these compounds during preparation and storage of monomers to prevent polymerization from taking place. One therefore calls chain-terminating substances inhibitors. The following inhibitors, which can be added to a monomer in concentrations of 0.1-0.0001% (0.0001% = 1 ppm = 1 part per million) in order to stabilize it, are especially effective and commonly used:

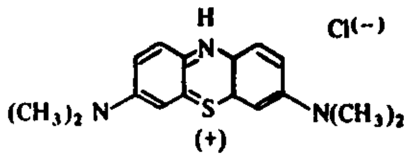

Quinone[2]

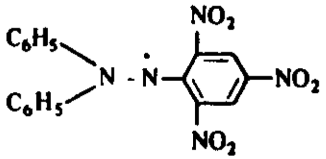

Nitrobenzene


Dinitrobenzene


Dinitrochlorobenzene


Benzothiazine
(Thiodiphenylamine)

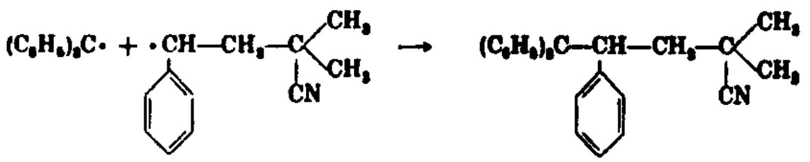

Methylene Blue


Diphenylpicrylhydrazyl
(DPPH)

In addition to these compounds, the following are also active inhibitors: oxygen, NO (one of the most effective inhibitors), numerous nitroso compounds, sulfur compounds, amines, phenols, aldehydes, and carbamates. Some highly reactive monomers can be distilled only under an atmosphere of NO.

Not all inhibitors are equally useful for all monomers and it is often necessary to select the best inhibitor for a certain monomer by trial and error. The technical importance of inhibitors is just as great as that of polymerization initiators, because without inhibitors the production and storage of many monomers on a technical scale would hardly be possible.

The mechanism of inhibition can be understood most clearly if the inhibitor is a radical such as diphenylpicrylhydrazyl, which is so stable that it does not show any tendency to add to unsaturated compounds in order to start a chain. Such radicals combine with initiator radicals or chain radicals under formation of stable saturated compounds. For example:



The prerequisite for an inhibitor radical (i.e., no reaction with monomers, but rapid reaction with active radicals) does not apply to many radicals. In many cases, one finds both inhibitor activity and initiator activity, as, for example, with

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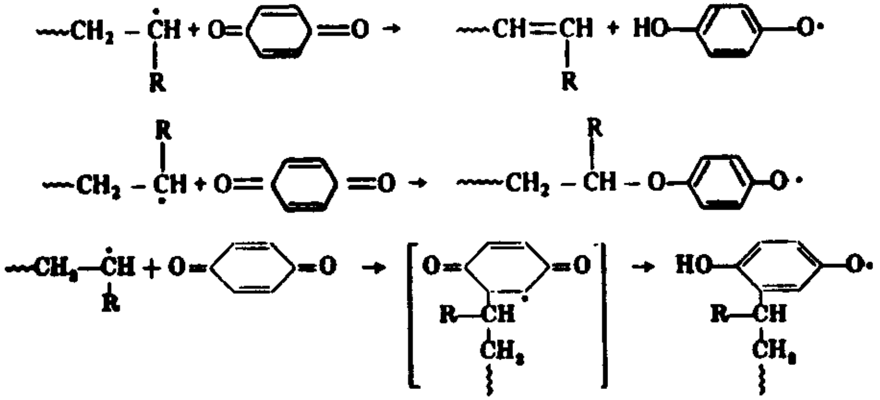
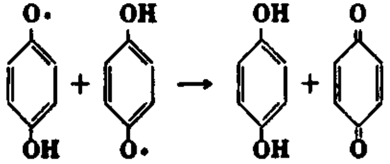
[2] Hydroquinone is not an inhibitor; however, it acts like one, because it reacts with air to form quinone.

triphenylmethyl which may be used to initiate polymerization as well as to inhibit it. In such cases polymerization is not completely prevented, only slowed down.

In theory this overlapping of inhibition and initiation exists with all inhibitors, because, even with the nonradical inhibitors, the inhibition reaction forms free radicals. During the stabilization with quinone, for example, the following reactions may take place:

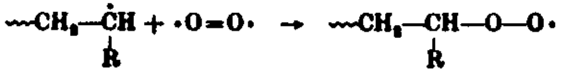


The radicals formed in this way are stabilized by resonance to such an extent that they do not start chains. They disappear partly through disproportionation to quinone and hydroquinone, which explains the formation of hydroquinone observed during the stabilization of styrene with quinone:



The radicals also combine, both with each other and with new chain radicals, and therefore the radicals formed in the inhibition reaction of quinone are themselves inhibitors, i.e., of the same type as DPPH.

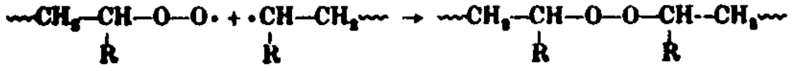
The inhibiting action of oxygen is caused by the biradical character of the oxygen molecule. The first step consists of the addition of oxygen to a chain radical under formation of a peroxide radical:



$$\sim CH_2-\underset{R}{\dot{C}H} + \cdot O{=}O\cdot \rightarrow \sim CH_2-\underset{R}{CH}-O-O\cdot$$

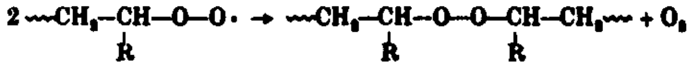
The peroxide radical may react further in different ways:

I



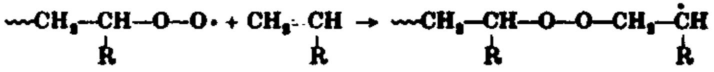
$$\sim CH_2-\underset{R}{CH}-O-O\cdot + \cdot\underset{R}{CH}-CH_2\sim \rightarrow \sim CH_2-\underset{R}{CH}-O-O-\underset{R}{CH}-CH_2\sim$$

II



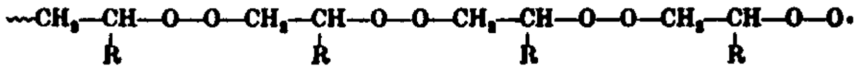
$$2\sim CH_2-\underset{R}{CH}-O-O\cdot \rightarrow \sim CH_2-\underset{R}{CH}-O-O-\underset{R}{CH}-CH_2\sim + O_2$$

III



$$\sim CH_2-\underset{R}{CH}-O-O\cdot + CH_2{=}\underset{R}{CH} \rightarrow \sim CH_2-\underset{R}{CH}-O-O-CH_2-\underset{R}{\dot{C}H}$$

In the first two cases an ordinary peroxide is formed; in case III a polymeric peroxide is formed, because the third reaction is not the final one—the chain radical may react further with oxygen (if sufficient oxygen is present) and, therefore, one may think of oxygen as a comonomer:

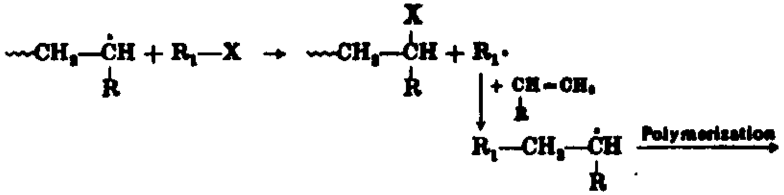


$$\sim CH_2-\underset{R}{CH}-O-O-CH_2-\underset{R}{CH}-O-O-CH_2-\underset{R}{CH}-O-O-CH_2-\underset{R}{CH}-O-O\cdot$$

Such polymeric peroxides with a degree of polymerization between 10 and 40 have been isolated. The oxygen radicals as well as the peroxides occurring as the reaction products are evidently fairly stable at low temperatures, otherwise they could not act as inhibitors. At higher temperatures on the other hand, the peroxides thus formed may decompose again and, if no inhibitor is present, bring about a strong polymerization reaction.

### *Chain Transfer*

One must distinguish between the term "chain" used as a designation for a linear macromolecule, and the chain (=reaction chain) as a kinetic concept. Similarly we must distinguish between the chain growth of a macromolecule during polymerization, where the degree of polymerization is determined by the termination of this chain growth and chain growth in a reaction kinetic sense. Thus the termination of the growth of the chain molecule does not always lead to a termination of the kinetic chain. A growing chain radical may abstract an atom (for example, hydrogen or chlorine) from another molecule and thus become saturated, and the molecule from which the atom has been abstracted will then become a radical and start a new chain. The chain reaction therefore continues, even though the chain growth of the first macromolecule has stopped; i.e., it has transferred the reaction chain to another molecule. This reaction is therefore called a transfer reaction, or just chain transfer:



$$\sim CH_2-\underset{R}{\dot{C}H} + R_1-X \rightarrow \sim CH_2-\overset{X}{\underset{R}{C}H} + R_1\cdot$$

$$R_1\cdot + \underset{R}{CH}{=}CH_2 \rightarrow R_1-CH_2-\underset{R}{\dot{C}H} \xrightarrow{\text{Polymerization}}$$

Chain transfer of this type may occur with the initiator, with the monomer, with the solvent or other compounds which have been added in order to promote chain transfer (modifiers), and with growing or complete polymer chains.

Radical polymerization begins with the decomposition of an initiator molecule I, into two radicals, R·, which very soon after their formation add a monome molecule, M (chain initiation). When the monomer adds, the radical state i transfered from the initiator radical to the added monomer molecule which ca then, in the same fashion, add additional monomer molecules (chain growth). Thi addition continues until two growing chain radicals, R~~~M·, react with each other, either by recombination or by disproportionation (chain termination).

Initiation: $I \xrightarrow{k_d} 2\,R\cdot$ (1)

$R\cdot + M \rightarrow R-M\cdot$ (2

Growth: (propagation) $R-M\cdot + M \rightarrow R-M-M\cdot \xrightarrow{+M} R-M-M-M\cdot$ etc.

or in general: $R\sim\sim M\cdot + M \xrightarrow{k_w} R\sim\sim M-M\cdot$ (3

Termination: $2\,R\sim\sim M\cdot \xrightarrow{k_t} R\sim\sim M-M\sim\sim R$ (recombination)

or

$2\,R\sim\sim M\cdot \xrightarrow{k_t} R\sim\sim MH + R\sim\sim M'$ (disporportionation) (4)

Since the two reactions (1) and (2) are coupled with each other, the effective rate of reaction (2) is determined by the rate of the decomposition reaction (1). In other words, the number of radicals R· which add a monomer molecule according to reaction (2) can be no larger than the number of radicals which are produced by the decomposition of the initiator according to reaction (1). For the simplest case in which all radicals formed by reaction (1) then can react further by reaction (2) with a monomer molecule, this means that the rate of reaction (2), $r_2 = -d(R\cdot)/dt$, is identical to the rate $r_1$ of the initiator decomposition reaction (1), $r_i = d(R\cdot)/dt$:

$$r_2 = -d(R\cdot)/dt = r_1 = d(R\cdot)/dt = -2d[I]/dt = r_i, \qquad (5)$$[3]

where [I] is the initiator concentration in mol/liter, r is the reaction rate in mol/liter/second, and d (R·)/dt is the number of moles R· per liter formed (or used) in 1 second. As we will see with the discussion of the steady-state equilibrium, d(R·)/dt is not identical with the change in the radical concentration d[R·]/dt (see p. 76).

The number of moles of R· formed per second by decomposition of I according to Equation (1), $r_i = d(R\cdot)/dt$, is twice as large as the number of moles of I disappearing per second according to (1), $r_d = -d(I)/dt$. To avoid the factor 2 in the following equations, the rate of the initiation reaction has been defined by $r_i = d(R\cdot)/dt$ and not by $-d(I)/dt$. The rate of reaction (2), $-d(R\cdot)/dt$, is—in the ideal case—identical with the rate of reaction (1), $d(R\cdot)/dt = -2\,d(I)/dt$. It should be noted, however, that the rate constant $k_i = 2\,k_d$ is not identical with the rate constant of reaction (2).

The decomposition of the initiator is a reaction of the first order: $-d(I)/dt = k_d[I]$, and one can therefore write for the rate of the initiation reaction:

$$r_i = 2\,k_d\,[I] = k_i\,[I]. \qquad (6)$$

16

If the radical yield is not quantitative [i.e., if not all radicals formed by reaction (1) subsequently react with monomer according to reaction (2), but only a fraction *f* continues to react], then the rate of the initiation reaction is given by the equation:

$$r_i = -d(R\cdot)/dt = f\cdot k_i[I]. \qquad (6a)$$

For initiators, such as peroxides or azo-compounds, one can determine d(R·)/dt by analytical methods: one determines $-d[I]/dt$, and therefore also $k_i$, from the decrease in the initiator concentration. The determination of the radical yield *f* further requires molecular weight determinations to obtain $\overline{M}_n$.For many polymerizations $f = 1$ or nearly 1.

For the kinetic treatment of the growth reaction (chain propagation), one can disregard the concentration of the radical R-M· which is first formed in reaction (2), because reaction (2) is really only one among many thousands of reaction steps which lead to equivalent radicals R–M·, R–M–M·, R–M–M–M·, and so forth. In general [R~~~M·] represents the concentration of all the growing radicals present in the reaction mixture at any given time *t*. One can therefore write:

$$[R\sim\sim M\cdot] = [R-M\cdot] + [R-M-M\cdot] +$$
$$[R-M-M-M\cdot] + + \cdots = \sum_{n=1}^{n=P} [R(M)_nM\cdot]$$

If there were no chain termination, the radical concentration would increase, beginning with concentration zero, in a continuous manner according to Equation (6). However, the greater the radical concentration becomes, the greater the possibility that two radicals will meet and disappear through recombination. This means that the rate of the termination reaction increases and finally a radical concentration [R~~~M·] will be reached at which, in a given time, just as many radicals will disappear through recombination as there will be new ones formed. Thus the initiation and termination reactions are in a certain phase of dynamic equilibrium (steady state) and the following equation holds:

$$r_i = r_t \qquad (7)$$

Under most of the usual polymerization conditions, the equilibrium condition (steady state) is reached in a short time after the beginning of the polymerization (see fig. 77). Therefore the polymerization occurs with a constant radical concentration according to Equation (3). According to the equation for a second order reaction, the polymerization rate (velocity) may be defined as follows:

$$r_P = r_p = -d[M]/dt = k_p\cdot[M]\cdot[R\sim\sim M\cdot]. \qquad (8)$$

In this equation, $k_p$ is the rate constant of the propagation reaction in liter·mol$^{-1}$·sec$^{-1}$, [M] is the monomer concentration in moles/liter, and [R~~~M·] is the chain radical concentration at the steady state in moles/liter

The polymerization rate $r_P$ (which is identical with the velocity of the propagation reaction, $r_p$) is then obtained in terms of mol·liter$^{-1}$·sec$^{-1}$ (the number of moles of monomer which disappear from one liter per second through addition to the growing chain). $r_p$ may be easily determined experimentally through continous concentration determinations during the polymerization or even more simply by using a dilatometer to measure the increase in density during the polymerization.

During the chain termination reaction two chain radicals $[R\sim\sim M\cdot]$ combine according to Equation (4), or by disproportionation, to a polymer molecule. If $k_t$ is the rate constant of this reaction, one may write according to a second order equation for the velocity of the termination reaction:

$$r_t = -d(R\sim\sim M\cdot)/dt = k_t[R\sim\sim M\cdot]^2. \qquad (9)$$

$-d(R\sim\sim M\cdot)/dt$ is the rate at which the chain radicals are used up by termination reactions, i.e., $-d(R\sim\sim M\cdot)/dt$ = the number of moles $R\sim\sim M\cdot$ which react with each other per second by recombination or disproportionation in a volume of 1 liter of the polymerizing system. Just as with $R\cdot$ (see p 74), it is also true for these chain radicals that $d(R\sim\sim M\cdot)/dt$ is not identical with the change in the radical concentration $d[R\sim\sim M\cdot]/dt$. Whereas according to Equation (9) $-d(R\sim\sim M\cdot)/dt = k_t\,[R\sim\sim M\cdot]^2$, the change in the radical concentration $d[R\sim\sim M\cdot]/dt$ is always the sum of two rates, i.e., the rate of formation $r_i$ and the rate of destruction $r_t$ of the radicals $R\sim\sim M\cdot$:

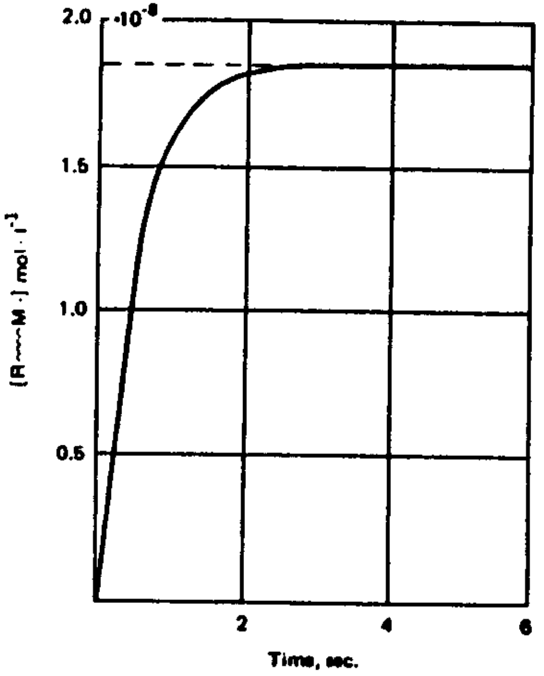
$$\begin{aligned} d[R\sim\sim M\cdot]/dt &= r_i - r_t = d(R\cdot)/dt + d(R\sim\sim M\cdot)/dt \\ &= k_i\,[I] - k_t[R\sim\sim M\cdot]^2. \end{aligned} \qquad (9a)$$

$r_i$ normally remains nearly constant in the first hours of a radical polymerization. $r_t$ is at first equal to zero, and then increases with increasing radical concentration during the beginning of the polymerization ($d[R\sim\sim M\cdot]/dt$ correspondingly becomes smaller) until at the steady state $r_i = r_t$ and $d[R\sim\sim M\cdot]/dt = 0$. The termination rate, $-d(R\sim\sim M\cdot)/dt$, on the other hand continues at a constant rate according to Equation (9).

By integration of Equation (9a), one obtains the radical concentration $[R\sim\sim M\cdot]_t$ at a time *t* after the start of the polymerization:

$$[R\sim\sim M\cdot]_t = ([I]\,k_i/k_t)^{1/2}\ \frac{\exp\left[(4k_ik_t\,[I]^{1/2}\cdot t\right] - 1}{\exp\left[(4k_ik_t\,[I]^{1/2}\cdot t\right] + 1}. \qquad (9b)$$

Equation (9b) yields the curve shown in Figure 77 for a styrene polymerization. It shows that, after two seconds, the radical concentration has already reached its stationary value $[R\sim\sim M\cdot]_s$. One obtains $[R\sim\sim M\cdot]_s$ by setting $r_i$ and $r_t$ equal, according to the steady-state requirement or by setting



$[I] = 1\cdot 10^{-3}$ mol · l$^{-1}$
$k_i = 1.2\cdot 10^{-5}$ sec$^{-1}$
$k_p = 176$ l · mol$^{-1}$ · sec$^{-1}$
$k_t = 7.2\cdot 10^{7}$ l · mol$^{-1}$ · sec$^{-1}$

FIG. " – Increase of the radical concentration immediately after the start of a solution-polymerization of styrene in benzene at 60°C (according to D. MARGERISON and G.C. EAST)

Equation (9a)–which is the first derivative of Equation (9b)–equal to zer the stationary radical concentration $[R\sim\sim M\cdot]_s$ is the maximum v $[R\sim\sim M\cdot]$):

$$d[R\sim\sim M\cdot]/dt = r_i - r_t = 0$$

$$k_t\cdot[R\sim\sim M\cdot]_s^2 = k_i\cdot[I] \text{ and } [R\sim\sim M\cdot]_s = \sqrt{(k_i/k_t)\,[I]}.$$

This calculation shows that $[R\sim\sim M\cdot]_s$ remains constant until the i concentration has begun to decrease. For the polymerization rate one can the according to Equation (8):

$$r_p = k_p\,[M] \cdot \sqrt{(k_i/k_t) \cdot [I]}. \qquad (11)$$

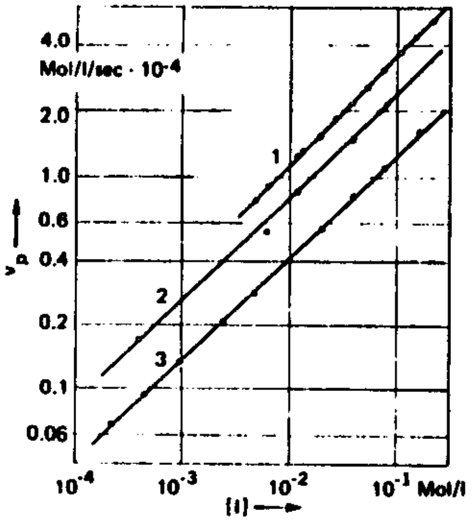
Accordingly, the rate of polymerization depends on the following parameters: 1. The chain-radical concentration [R~~~~M·], which in turn depends on the initiator concentration and the ratio of the reaction rate constants of the initiation and termination reactions $k_i/k_t$; 2. The monomer concentration [M]; and (3) The reaction rate constant of the growth reaction (propagation reaction), $k_p$.

It may at first sight seem surprising that the rate of the overall polymerization, $r_p$, depends not only on $k_i$ and [I], but also on $k_p$ and [M], since it was pointed out earlier that the addition of a monomer to a radical (reaction 2)—considered as an independent reaction—occurs much more rapidly than the formation of the radicals by decomposition of the initiator, and that the rate of a multi-step reaction is determined by the slowest step, i.e., the initiator decomposition. This is true only as long as one considers the reaction up to the addition of one monomer molecule (or, in general, for the addition of a specific number of monomer molecules). But this is not true for a description of the overall total polymerization. As with all chain reactions, the growth reaction here also occurs completely independently of the initiation reaction. This means that once a radical R· is formed, the number of monomer molecules which will add to this radical per second depends only on the rate of the growth reaction, i.e. (for a given set of reaction conditions ([I], [M], [R~~~~M·], etc.), it will depend only on $k_p$. For the polymerization of a monomer with $k_p = 2{,}000$ liters·mol$^{-1}$sec$^{-1}$, therefore 10 times as much polymer will be formed per second and the polymer chains will be 10 times as long, as for a polymerization of a monomer with $k_p = 200$ liters·mol$^{-1}$·sec$^{-1}$. It will be recognized that the molecular weight and the growth rate are dependent upon one other [compare p. 86, Equation (25)]. The automatic influence of $k_p$ on the overall rate of polymerization ($r_p$) therefore holds only for the case where the chains can grow freely and where their length is not limited by a parameter which is independent of $k_p$. If one could limit the molecular weight for example by the addition of a suitable inhibitor, then the rate of such polymerizations would be determined only by the rate of the initiator decomposition.

The same is true if one limits the discussion to a monomer with a definite reaction constant, $k_p$. In this case the rate of polymerization is proportional to the square root of the initiator concentration according to Equation (11):

$$r_p = \text{constant} \cdot \sqrt{[I]}. \qquad (11a)$$

The validity of this relation has been experimentally verified for many monomers (Figure 79). Naturally, this relation holds only for the earlier stages of the polymerization, since the monomer concentration and the initiator concentration changes with continuing polymerization. The linear dependence of the beginning polymerization rate on the monomer concentration, according to Equation (11), has also been experimentally confirmed.



1. Methylmethacrylate with azobisisobutyronitrile at 50°C;
2. Styrene with benzoyl peroxide at 60°;
3. Methylmethacrylate with benzoyl peroxide at 50°C.

FIG. 79 – Dependence of the steady state rate of polymerization on the initiator concentration (double logarithmic plot according to P.J. FLORY, based on measurements of SCHULZ and BLASCHKE, ARNETT and MAYO, GREGG and MATHESON).

$$r_p = \text{constant} \cdot [M]. \qquad (11b)$$

For the region of constant radical concentration (i.e., with constant initiator concentration), the total polymerization rate $r_p$ behaves like a reaction of first order. If the polymerization is carried out on a continuous basis, one can also hold the monomer concentration constant, and this results in a constant yield at a given time.

Normally, if one does not hold [R~~~~M·] and [M] constant by means of special measures, the polymerization rate will decrease with increasing conversion. However, in many cases when a certain conversion has been reached the polymerization rate suddenly increases. This effect, which has been called a gel effect, or an autoacceleration, has been explained in

⑲

termination reaction caused by the high viscosity of the reaction medium (compare p. 89 ff.).

### *The Determination of $r_i$ and $k_p^2/k_t$*

The values $r_i$ and $r_p$ can be determined experimentally: $r_p$ by determination of the conversion and $r_i$ by determination of the rate of decomposition of the initiator for example, by determining the rate at which an inhibitor is consumed in the presence of the monomer and initiator. The inhibitor used most is diphenylpicrylhydrazyl (see also p. 61). From that one can determine the corresponding reaction rate constants, $k_i$ according to Equation (6), and the ratio of $k_p^2/k_t$ according to Equation (11):

$$k_i = \frac{r_i}{[I]} \tag{12}$$

$$\text{and} \quad \frac{k_p}{k_t} = \frac{r_p^2}{[M]^2 [I]\, k_i} \quad \text{or} \quad \frac{k_p}{k_t^{1/2}} = \frac{r_p}{[M]\, [I]^{1/2}\, k_i^{1/2}}\ . \tag{13}$$

If in Equation (13) one replaces $k_i[I]$ by $v_i$ according to Equation (6) one obtains:

$$\frac{k_p^2}{k_t} = \frac{r_p^2}{[M]^2 \cdot r_i} \quad \text{or} \quad \frac{k_p}{k_t^{1/2}} = \frac{r_p}{[M] \cdot r_i^{1/2}}\ . \tag{14}$$

### *The Determination of the Activation Energies*

From the temperature dependence of the reaction rate constants one obtains the activation energies according to the Arrhenius equation:

$$k = k_m \cdot e^{-A/RT} \qquad \text{(Arrhenius Equation)}$$

or

$$\ln k = \ln k_m - \frac{A}{RT} = H_n - \frac{A}{RT}$$

and by multiplication with log e:

$$\log k = H_d - \frac{A}{2.3 \cdot R \cdot T}$$

where A = activation energy, $k_m$ = maximum reaction rate constant, i.e., if all collisions would lead to a reaction; and H = log $k_m$ resp. ln $k_m$ (for $H_d$ resp. $H_n$).
If one applies these equations to the ratio $k_p/k_t^{1/2}$ (i.e., if in the expression $\log k_p/k_t^{1/2} = \log k_p - 1/2 \log k_t$ one replaces the reaction rate constant by the corresponding Arrhenius expressions $\log k_p = H_p - A_p/2.3 \cdot RT$ and $\log k_t = H_t - A_t/2.3 \cdot RT$, one obtains:

$$\log k_p/k_t^{1/2} = (-1/2.3 \cdot RT)(A_p - 1/2 A_t) + (H_p - 1/2 H_t). \tag{15}$$

Thus, one can determine $A_p - 1/2\, A_t$ if one plots $\log k_p/k_t^{1/2}$ versus 1/T. According to Equation (11) one can determine the activation energy of the overall polymerization reaction from this plot. Thus, if in logarithmic Equation (11) one replaces reaction rate constants log $k_p$, log $k_i$, and log $k_t$ by the corresponding Arrhenius expressions H – A/2.3 RT, one obtains:

$$\log r_P/[M] \cdot [I]^{1/2} = H_p + 1/2(H_i - H_t) - (A_p - 1/2 A_t + 1/2 A_i)/2.3\ RT. \tag{16}$$

According to Equation (11), $r_P$ is equal to $k_p \cdot \sqrt{k_i/k_t} \cdot [M] \cdot \sqrt{[I]}$, and one can therefore consider the expression $k_p \cdot \sqrt{k_i/k_t}$ as a sort of reaction rate constant $k_P$ of the overall polymerization reaction:

$$k_p\ \sqrt{k_i/k_t} = k_P = r_P/[M] \cdot [I]^{1/2}. \tag{16a}$$

If one now compares Equation (16) with the Arrhenius expression (p. 80), one sees that in Equation (16) the sum of $A_p + 1/2(A_i - A_t)$ is the activation energy (corresponding to $k_P$) of the overall polymerization reaction:

$$A_P = 1/2 A_i + (A_p - 1/2 A_t) \tag{17}$$

$A_i$ (which is determined from the temperature dependence of $k_i$) is approximately 30 kcal/mole for the usual peroxide and azo initiators. For the expression $A_p - 1/2 A_t$ (determined according to Equation (15) ) values between 4 and 7 kcal/mole were found for different monomers so that $A_P$ according to Equation (17) has a value of the order of from 20 to 22 kcal/mole.

### *Kinetic Chain Length and Degree of Polymerization*

According to Equation (23), $n_M = k_p \cdot [M]$ monomer molecules add to a single radical per second. The number $L_{kin}$ of monomer molecules which are added during the lifetime $\tau$ of a radical is therefore equal to:

$$L_{kin} = n_M \cdot \tau = k_p \cdot [M] \cdot \tau. \qquad (24)$$

The parameter $L_{kin}$ defined by Equation (24) is called the kinetic chain length. If, according to Equation 20, one replaces the average lifetime $\tau$ by the expression $[R\sim\sim M\cdot]/k_t[R\sim\sim M\cdot]^2$, one obtains:

$$L_{kin} = \frac{k_p\,[M]\,[R\sim\sim M\cdot]}{k_t \cdot [R\sim\sim M\cdot]^2} = \frac{k_p \cdot [M]}{k_t \cdot [R\sim\sim M\cdot]} = \frac{r_p}{r_t} = \frac{r_p}{r_t} \qquad (25)$$

If no chain transfer occurs (i.e., if with the end of molecular growth the radical which carries on the reaction also disappears), then the degree of polymerization is equal to the kinetic chain length, or is proportional to it. If chain termination occurs only by disproportionation, then $\bar{P} = \bar{L}_{kin}$. If chain termination occurs only through recombination then $\bar{P} = 2\bar{L}_{kin}$.

If the proportionality factor is smaller than 2, then this is a sign that chain termination occurs to some extent through disproportionation. If there is no linear

dependence between $\bar{P}$ and $\bar{L}_{kin}$ then the size of the molecules is determined r through chain termination but through chain transfer (modifier action).

Propagation reaction rate constants ($k_p$) of different orders of magnitude a according to Equation (25), the reason that not all monomers under the sa reaction conditions yield polymers with the same molecular weight (i.e., the grea $k_p$, and therefore $r_p$, the greater will be the chain length and therefore the hig the molecular weight for corresponding rates of termination. Acrylic esters ($k_p$ 2,090 liters·mol$^{-1}$sec$^{-1}$ at 60°C) polymerize very rapidly; styrene ($k_p$ = 1 liters·mol$^{-1}$sec$^{-1}$) polymerizes relatively slowly. The molecular weight of t polymers obtained from acrylic esters is correspondingly higher than that obtain from styrene under comparable conditions. On the other hand, one should n conclude from Equation (25) that one can simply increase the degree polymerization by increasing $r_p$. Actually, one obtains just the opposite. Th kinetic chain length, and therefore the degree of polymerization, is only increas by an increase of $r_p$ if the termination rate $r_t$ remains unchanged. Most conditio under which the rate of polymerization is increased (for example, by increasing th concentration of the initiator or the temperature) give rise to an increase in th radical concentration $[R\sim\sim M\cdot]$, which enters into Equation (25) as a squa term, and therefore an increase in $r_p$ caused by a corresponding and much great increase in $r_t$ leads to a decrease in the ratio $r_p/r_t$. One sees this immediately if on replaces the ratio in Equation (25) by $k_p \cdot [M]$, and one thus finds–if [M] constant–that the kinetic chain length is inversely proportional to the rate polymerization:

$$L_{kin} = \frac{k_p\,[M]\,[R\sim\sim M\cdot]\;k_p\,[M]}{k_t\,[R\sim\sim M\cdot]^2\,k_p\,[M]}$$

$$= \frac{k_p}{k_t} \cdot \frac{[M]^2}{k_p\,[R\sim\sim M\cdot]\,[M]} = \frac{k_p{}^2}{k_t} \cdot \frac{[M]^2}{r_p} = \text{const.}\,\frac{1}{r_p} \qquad (27$$

To represent this function one usually plots $1/\bar{P}$ against $r_p/[M]^2$. One has t remember however that $\bar{L}_{kin}$ is usually not equal to $\bar{P}$, and one therefore requires proportionality factor K. Furthermore, it is not always possible to neglect chai transfer. One discovers this immediately by the fact that the lines do not pas through the zero point (see Fig. 88). The intercept at the ordinate gives, in thi case, the numerical value of the transfer constant (as long as one only has chai transfer to the monomer), or, a value which is proportional to the transfer constan (for example, $C_{tr} \cdot [\bar{P}]/[M]$, if chain transfer occurs with the polymer o concentration $[\bar{P}]$. If chain transfer occurs with the solvent of concentration [S] then the proportionality factor becomes $C_{tr}[S]/[M]$ (compare pages 63 to 69 anc page 91):

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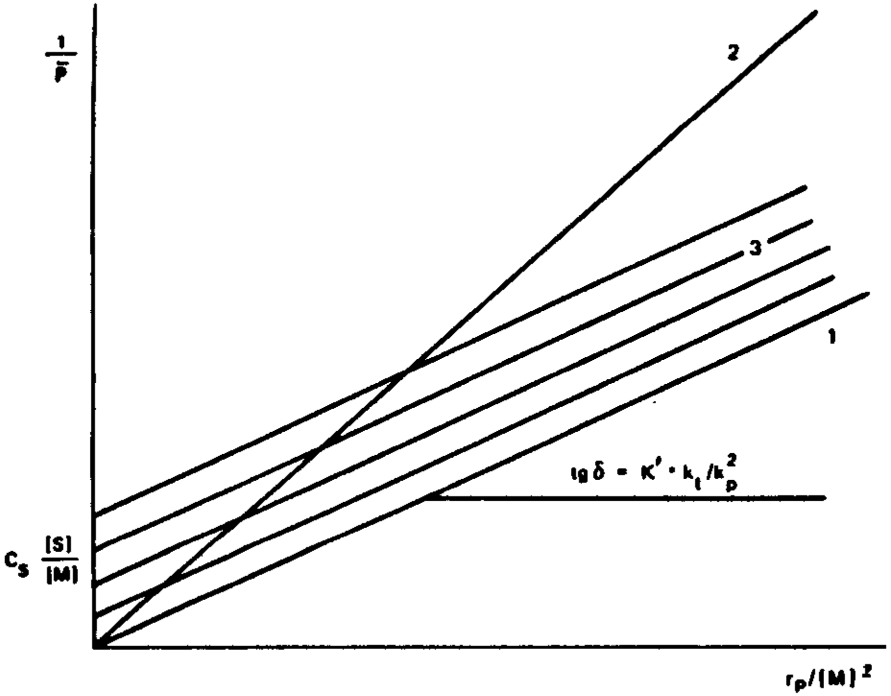

1) Bulk polymerization; termination by disproportionation ($K' \approx 1$)
2) Bulk polymerization; termination by recombination ($K' \approx 2$)
3) Solution polymerization

**FIG. 88** – Dependence of the reciprocal degree of polymerization, $1/\bar{P}$, on $v_p/[M]^2$ according to Equ. (27a)

$$P = K \cdot L_{kin} = K\frac{k_p^2}{k_t} \cdot \frac{[M]^2}{r_p} + \frac{1}{C_s}$$

$$\text{or} \quad \frac{1}{P} = K' \frac{k_t}{k_p^2} \cdot \frac{r_p}{[M]^2} + C_s \frac{[S]}{[M]} \tag{27a}$$

Equation (27a) is identical to Equation (28), which can easily be shown by replacing in both equations $r_p$ and $r_t$ by $k_p \cdot [M] \cdot [R\sim\sim M\cdot]$ and $k_t \cdot [R\sim\sim M\cdot]^2$, and $r_{tr}$ by $k_{tr} \cdot [S] \cdot [R\sim\sim M\cdot]$. If one determines the degree of polymerization $\bar{P}$ at different rates of polymerization $r_p$, or different monomer concentrations, and plots according to Figure 88, $1/\bar{P}$ vs. $r_p/[M]^2$, then the slopes of the lines permit determination of K, and therefore they also give information about the type of chain termination, if $k_p^2/kt$ is known [compare

Equation (13)], or conversely, they permit a determination of $k_p^2/k_t$, if the type of chain termination is known. Furthermore, the value of the intercept at the ordinate gives information about the influence of the chain-transfer reactions (compare p. 91). The validity of Equation (27a) is typical for radical polymerizations and can in certain doubtful cases (for example, for initiation with new initiator systems, or by irradiation) be used for the elucidation of the type of polymerization. In order to vary $r_p/[M]^2$, one can carry out the polymerizations at different temperatures or with increasing concentrations of initiator.

### *Self-Acceleration (Autocatalysis) of the Polymerization (Norrish-Trommsdorf Effect)*

The polymerization rate and the degree of polymerization are not always coupled in such a way that with increasing rate of polymerization the degree of polymerization diminishes. For example, the degree of polymerization can increase if in emulsion polymerization the rate of polymerization is increased by increasing the soap concentration (compare p. 154 ff.). This is also observed during the self-acceleration phase of a radical polymerization at higher conversions. Thus when the conversion with bulk-, or solution-, or pearl-polymerization has reached such a high value that the viscosity of the polymerizing solution has become very high then the mobility of the polymer molecules is hindered so strongly that a collision between two chain-radicals occurs more seldom.

For the kinetics of the polymerization reaction this phenomenon means that th reaction rate constant of the termination reaction, $k_t$($k_t$ = the number of moles pe second of chain radicals disappearing through termination when $[R\sim\sim M\cdot]$ = mole/l), will decrease after the viscosity has reached a certain relatively high value The creation of new radicals R· through initiator decomposition continue undisturbed, however, so that the radical concentration increases over that given b the steady state equilibrium. Therefore according to Equation (10):[4]

$$[R\sim\sim M\cdot]_\eta = (\sqrt{k_i \cdot [I]})\,(1/\sqrt{k_{t(\eta)}}) = \text{Constant} \cdot \quad 1/\sqrt{k_{t(\eta)}} \qquad (27b$$

Whereas normally an increase in the radical concentration (for example, b increasing the temperature or by increasing the initiator concentration) alwa brings about an increase in the termination rate, this is not the case here, where th increase in the radical concentration is effected only by the decrease in the ra constant $k_t$. This becomes clear, if one substitutes Equation (27b) into Equatio (9):

$$d(R\sim\sim M\cdot)/dt = r_t = k_t \cdot [R\sim\sim M\cdot]^2 = k_t \cdot \text{Constant}\,(1/\sqrt{k_t})^2 = \text{Constant} \quad (27$$

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[4] One could ask here whether Equation (10), which is based on the assumption that $r_i = r_t$ still valid. If one remembers that for each new value of $k_{t(\eta)}$ there is again a new stationa equilibrium, with a new radical concentration $[R\sim\sim M\cdot]_\eta$ corresponding to this equ ibrium, one sees that the equation is valid at least for a sufficiently short interval of time. $\sim\sim M\cdot]_\eta$ is the equilibrium radical concentration corresponding to $k_{t(\eta)}$. When $[R\sim\sim M\cdot]_\eta$ is effectively reached, $k_{t\,\text{effective}}$ is always somewhat smaller than $k_{t(\eta)}$, but difference between $k_{t(\eta)}$ and $k_{t(eff)}$ is smaller, the shorter the discussed time interval.

Now we can describe the Norrish-Trommsdorf effect as follows: The slowing down of the reaction rate $r_t$ of the chain termination (caused by increasing viscosity and decreasing $k_t$) causes an increase of $[R\sim\sim M\cdot]$ according to Equation 27b. This increase of $[R\sim\sim M\cdot]$ would suffice exactly to compensate for the slowing down of $r_t$, if the viscosity of the polymerizing system (and thus also $k_t$) could be held constant for a moment. In reality, however, the viscosity continues to rise, effecting again a decrease of $r_t$ and increase of $[R\sim\sim M\cdot]$, etc. Through the compensation mechanism in the sense of Equation (27c), the difference between $r_i$ and $r_t$ remains constant in spite of continuously rising $[R\sim\sim M\cdot]$–values (if the increase of viscosity runs linearly). By this, the non-steady state in the self-acceleration stage of a radical polymerization is distinguished from the non-steady state in the beginning stage of the polymerization.

The unchecked increase in the radical concentration $[R\sim\sim M\cdot]$ has two important results as far as the polymerization reaction and the formed polymers are concerned:

1. The polymerization rate $r_P$ increases rapidly with increasing viscosity because of the Trommsdorf effect ($r_P = k_p \cdot [M] \cdot [R\sim\sim M\cdot]$).
2. The kinetic chain length, and therefore the degree of polymerization, increases with increasing rate of polymerization and constant termination rate ($\bar{L}_{kin} = r_P/r_t$).

For example, if the termination rate constant decreases because of the high viscosity to one-fourth of its normal value, the radical concentration $[R\sim\sim M\cdot]$ increases according to Equation (27b) to twice its value. The result is that also $r_P$ and $L_{kin}$ increase to twice their normal value.

As the polymerization rate and the degree of polymerization increase, one finds an even more rapid increase in the viscosity. This in turn leads to a further increase in the polymerization rate and so on. The result is often that the polymerization "runs away" unless it is possible to remove the heat of polymerization by certain reaction conditions. Because in a high viscosity polymerizing medium the heat exchange is very much restricted, a bulk polymerization carried out on a technical scale always requires certain experimental procedures to remove the heat.

The increase in the kinetic chain length and the resulting increase in the degree of the polymerization during the stage of autocatalysis can be experimentally proved by means of molecular weight determinations. The cause for the Norrish-Trommsdorf effect is basically the same as that which leads to higher degrees of polymerization and higher polymerization rates with emulsion polymerizations, i.e., the partial or complete isolation of the chain radicals from each other (compare pp. 154-163).

### *Kinetics of Chain Transfer and Determination of the Transfer Constants*

Especially in the presence of solvents or modifiers (compare p. 65) one often finds that the growth of a macromolecule is terminated without the disappearance of the radical which carries on the chain reaction. The radical state is actually transferred from the growing chain end to a solvent or modifier molecule from which a new molecule then begins to grow. The molecular chain is terminated; however, the radical chain is not. Thus in such cases the degree of polymerization is determined not only by the chain termination reaction, but also by the chain transfer reaction. With strongly effective modifiers, the chain transfer reaction is actually the one which alone determines the degree of polymerization. This is why the rate of the transfer reaction $r_{tr}$ plays the same role in determining the degree of polymerization as the rate of the termination reaction plays in determining the kinetic chain length. In analogy to Equation (25), one can write:

$$\bar{P} = \frac{r_P}{K \cdot r_t + r_{tr}} \qquad \text{or} \qquad \frac{1}{\bar{P}} = K' \cdot \frac{r_t}{r_P} + \frac{r_{tr}}{r_P} = \frac{1}{\bar{P}_0} + \frac{r_{tr}}{r_P} \qquad (28)$$

$K \cdot r_t/r_P = 1/\bar{P}_0$ is the reciprocal of the degree of polymerization which would be obtained if the polymerization were carried out under the same conditions but without chain transfer. The chain transfer reaction (similar to the propagation reaction; compare p. 73) is a bimolecular reaction between the chain radical and a solvent or modifier molecule. One therefore obtains (if $[S]$ is the solvent or modifier concentration)

$$r_{tr} = k_{tr} [R\sim\sim M\cdot] [S]. \qquad (29)$$

If one then replaces $r_P$ by $k_p \cdot [R\sim\sim M\cdot] [M]$ according to Equation (8), one obtains from Equation (28)

$$\frac{1}{\bar{P}} = \frac{1}{\bar{P}_0} + \frac{k_{tr}\,[R\sim\sim M\cdot]}{k_p\,[R\sim\sim M\cdot]}\,\frac{[S]}{[M]} = \frac{1}{\bar{P}_0} + \frac{k_{tr}\,[S]}{k_p\,[M]}$$

$$= \frac{1}{\bar{P}_0} + C_s \frac{[S]}{[M]} \qquad (30)$$

This equation permits the calculation of the transfer constant $C_s = k_{tr}/k_p$ of technically important solvents and modifiers by varying the ratio $[S]/[M]$ (i.e., the solvent concentration) and determining the molecular weight obtained for each ratio. If one then plots $1/\bar{P}$ versus $[S]/[M]$, one obtains $C_s$ as the slope of the straight line. In order that $1/\bar{P}_0$ remain constant, one has to select the initiator concentration for each solvent concentration in such a way that $r_t/r_P$ remains constant. This is the case if the initiator concentration is changed according to the relation $[I] = \text{const.} \cdot [M]^2$. Especially simple are the conditions during the thermal polymerization of a monomer (without initiator). In that case the initiation

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reaction is bimolecular ($r_i = k_i \cdot [M]^2$), and the ratio $r_t/r_p = r_i/r_p$ is therefore independent of the monomer concentration. Figure 92 shows the effect of increasing the concentration of different solvents on the molecular weight obtained during the thermal polymerization of styrene. The slope of the lines yields, according to Equation (30), the transfer constants $C_s$ listed in Table 66.

One can use Equation (30) (if $C_s$ is known) to calculate the decrease of the molecular weight to be expected during radical polymerization on the addition of certain solvents and modifiers.

For a given $C_s$, the decrease of the degree of polymerization depends only on the ratio $[S]/[M]$. However, one has to take into consideration that this ratio can change significantly if a polymerization is carried out to a high degree of conversion. By addition of monomers during the polymerization, one can counteract such changes occuring in the ratio $[S]/[M]$.

In addition to the above method for the determination of $C_s$-values, there are still other methods. For example, for high values of $C_s$, it might be better to determine the decrease in concentration of the modifier with continuing polymerization. If one then plots log $[S]$ versus log $[M]$ one obtains the transfer constant $C_s$ as the slope of the line $\log [S] = C_s \cdot \log [M]$.

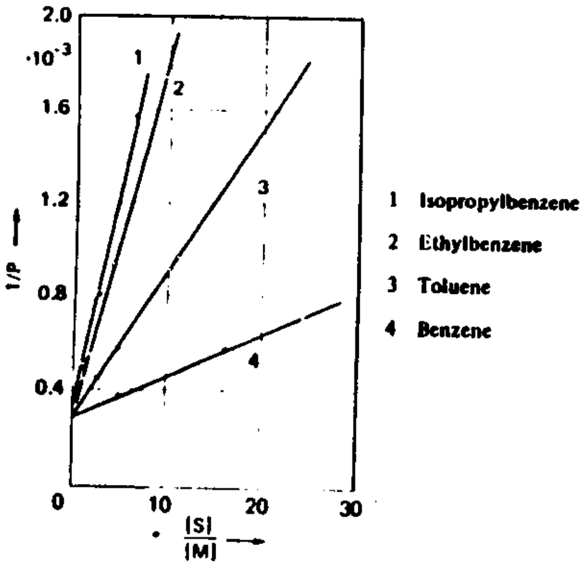

FIG — Dependence of the reciprocal degree of polymerization, 1/P, on the solvent concentration, i.e. [S]/[M] for the polymerization of styrene in different solvents at 100°C (according to Equ. (30) after GREGG and MAYO).

### *Temperature Dependence of the Degree of Polymerization*

Experience indicates that when the temperature of polymerization is increased, the degree of polymerization decreases. This is especially important in polymerizations carried out on a technical scale, where one tries to obtain a well-defined degree of polymerization from one batch to another. One therefore has to maintain a definite temperature in order to obtain a constant degree of polymerization. On the other hand, it is possible by variation of the temperature, and/or by addition of modifiers, to predetermine the value of the degree of polymerization in a relatively convenient way.

The negative temperature coefficient of the degree of polymerization (i.e., of the kinetic chain length $L_{kin}$) results from the value of the activation energy of the different stages of the chain reaction: if one replaces in Equation (25) ($L_{kin} = k_p[M]/k_t[R\sim\sim M\cdot]$) the radical concentration by the expression $\sqrt{(k_i/k_t)\cdot[I]}$ according to Equation (10), one obtains:

$$L_{kin} = \frac{k_p \cdot [M]}{k_t\sqrt{(k_i/k_t)\cdot[I]}} = \frac{k_p \cdot [M]}{\sqrt{k_t \cdot k_i \cdot [I]}} \tag{31}$$

If one takes the logarithm of Equation (31) and replaces the reaction rate constants $k_p$, $k_t$, and $k_i$ by the corresponding Arrhenius expressions $\ln k = \ln k_m - A/RT = H_n - A/RT$, one obtains (see page 81):

$$\ln L_{kin} = -\frac{A_p}{RT} + \tfrac{1}{2}\frac{A_t}{RT} + \tfrac{1}{2}\frac{A_i}{RT} + H_p - \tfrac{1}{2}H_t - \tfrac{1}{2}H_i - \tfrac{1}{2}\ln[I] + \ln[M]$$

By differentiation with respect to T, one obtains the temperature coefficient of the kinetic chain length:

$$d(\ln L_{kin})/dt = (A_p - \tfrac{1}{2}A_t - \tfrac{1}{2}A_i)/RT^2 \tag{32}$$

Since $A_i$ is approximately 30 kcal, but $(A_p - \tfrac{1}{2}A_t)$ is only 4-7 kcal, d (ln $L_{kin}$)/dT and, therefore, also the temperature coefficient of the degree of polymerization is negative. The decrease in the degree of polymerization with increasing temperature results from the fact that the activation energy of the initiation reaction is relatively high compared to the activation energy of the growth reaction. Although the rate of chain growth (propagation) also increases with increasing temperature (which by itself would lead to an increase in the degree of polymerization), the increase in the rate of initiation is the outweighing factor and therefore according to Equation (25) the degree of polymerization decreases.

a polymerization where the degree of polymerization is either constant or eases with an increase in temperature, one therefore would need an initiation tion which has an extremely small activation energy, i.e., one where the rate is pendent of the temperature. Such an initiation reaction is possible by initiation ugh UV irradiation. Thus, with photopolymerization the degree of polymeriza- increases with increasing temperature, provided that strong chain transfer does ause a decrease in the degree of polymerization.

### 2115 Copolymerization

one polymerizes a mixture of different monomers, one usually obtains omolecules whose structure contains all the monomers that are present in the ion mixture.[6] However, one should not expect that these monomers are nt in the same ratio in the polymer molecule as in the monomer mixture. In an me case, (which, however, can not be realized for theoretical reasons (see p. one might even obtain on polymerizing a mixture of two monomers, $M_1$ and polymer molecules which consist exclusively of monomer $M_1$ and other ner molecules which consist exclusively of monomer $M_2$. In such a case one ot obtained a copolymer, but only a mixture of two homopolymers. The other me case (and this is encountered quite frequently) occurs if the copolymeriza- of the monomers is preferred so strongly to the formation of homopolymer independent of the concentration of the monomer mixture, only polymer ules in which the two different monomers alternate regularly are obtained. As as the monomer present in the lower concentration is used up, the erization stops completely, or the monomer present in excess polymerizes ly considerably slower) by itself. Between these two extremes lies the ideal of those copolymers whose macromolecules (with random [statistical] ution of the structural elements) contain exactly the ratio of the two ners present in the monomer mixture. Most of the technically important mers approach this ideal case to a smaller or larger extent.

behavior of a monomer mixture is determined to a large extent by the rate ratio of the rates) of the reactions taking part in chain growth. With a merization involving two different monomers, the growth reactions are the ng four reactions:

$$1.\ R \sim\sim M_1\cdot + M_1 \xrightarrow{k_{11}} R \sim\sim M_1M_1\cdot$$

$$2.\ R \sim\sim M_1\cdot + M_2 \xrightarrow{k_{12}} R \sim\sim M_1M_2\cdot$$

$$3.\ R \sim\sim M_2\cdot + M_2 \xrightarrow{k_{22}} R \sim\sim M_2M_2\cdot$$

$$4.\ R \sim\sim M_2\cdot + M_1 \xrightarrow{k_{21}} R \sim\sim M_2M_1\cdot$$

---

the general structure of copolymers, block-copolymers and graft-copolymers, see pp.

If the reaction rate constant $k_{11}$ for the normal chain growth is much greater than $k_{12}$, and correspondingly $k_{22}$ is very much greater than $k_{21}$, then reactions 2 and 4, which lead to the formation of copolymers, would be practically insignificant and one should obtain block-copolymers or mixtures of homopolymers. On the other hand, if the constants $k_{12}$ and $k_{21}$ are much greater than $k_{11}$ and $k_{22}$, chains with $M_1\cdot$ at the growing chain end add practically only monomer $M_2$, and $R \sim\sim M_2\cdot$ chains add practically only monomer $M_1$, so that copolymers with an alternating sequence of the structural units are formed, independent of the ratio of the monomers present in the monomer mixture. Finally, if $k_{12} = k_{11}$ and $k_{21} = k_{22}$, the frequency with which an $M_1$ or an $M_2$ monomer adds to the chain end is simply determined by their concentration, which leads to the result that the ratio of the two monomers in the monomer mixture is equal to the ratio of the two monomers in the copolymer molecules (ideal copolymerization[7]).

One cannot calculate the rate constants $r_{12}$ and $r_{21}$ from the rate constants $r_{11}$ and $r_{22}$. Therefore, the behavior of a monomer in homopolymerization does not give any indication of its behavior in copolymerization. If one wants to obtain an idea about the behavior of a certain monomer pair during copolymerization, then one experimentally determines the composition of the copolymers with different $[M_1]/[M_2]$ ratios in the monomer mixture. This composition of the copolymers is usually represented by $d[M_1]/d[M_2]$, because the ratio of the monomers in the copolymer is identical with the ratio with which two monomers disappear from the monomer mixture. Since the ratio of the monomers usually changes continuously during polymerization (except with an ideal copolymerization), only investigations in which the polymerization is stopped at low conversions are meaningful.

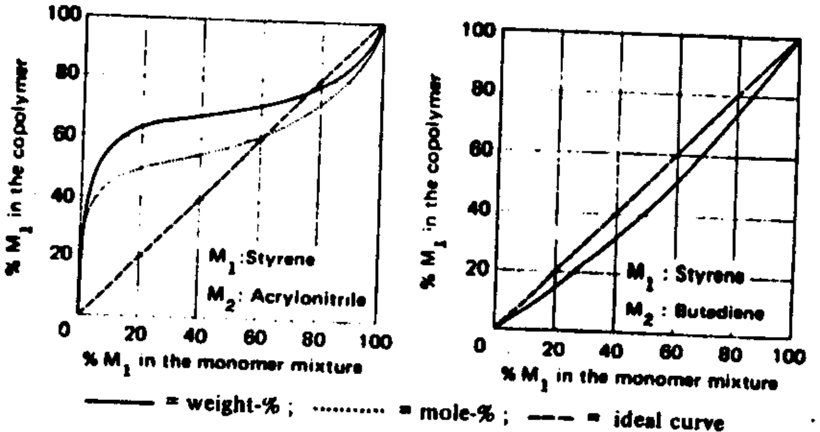

FIG. – Copolymerization diagrams for styrene/acrylonitrile ($r_1$ = 0.4, $r_2$ = 0.03) and styrene/butadiene ($r_1$ = 0.7, $r_2$ = 1.4)

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[7] The description "ideal copolymerization" is used in the literature mostly for systems where the product of the parameters $r_1$ and $r_2$ is equal to 1 (compare p. 112).

Therefore, one interrupts the polymerization with conversions of 5-10% and isolates the copolymer. In many cases one of the monomers contains an atom or functional group which can be determined easily by analytical means. With the aid of this group one can then determine the composition of the copolymer (for example, chlorine with vinyl chloride; or the ester group with acrylic ester or vinyl esters; nitrogen with acrylonitrile or vinyl pyrrolidone; oxygen with vinyl ethers; or a double bond with butadiene). With copolymers of two pure hydrocarbons, such as isobutylene and styrene, or two acrylic esters, the analysis becomes much more complicated. In such cases infrared spectroscopy is useful, or one has to provide one of the monomers with an easily determined atom which, however, does not influence the polymerization behavior of that particular monomer, e.g., $C_{14}$. If one plots the result of such experiments in the form of the composition of the copolymer $d[M_1]/d[M_2]$ versus $[M_1]/[M_2]$, or better, the weight percent or molar percent of $M_1$ in the monomer mixture as a function of the percent of $M_1$ in the copolymer, one obtains characteristic curves whose form is completely analogous to the curves that one obtains for the distillation of binary systems.

Figure 95 shows diagrams for two technically very interesting systems. The dashed curve corresponds to an ideal copolymerization. The curves without inversion correspond to (as we shall see) monomer pairs where one of the monomers reacts more rapidly with its own radical than with the other radical, whereas the second monomer adds more rapidly to the different radical. Inversion curves, such as for the system styrene/acrylonitrile, are typical for monomer pairs which tend to alternating addition. If one obtains curves whose inversions are opposite to those shown in Figure 95, then one has systems where each monomer prefers homopolymerization, and therefore the polymers obtained would be segment- or block-copolymers. (No clearly proven cases are known, see p. 167).

### *Kinetics of Copolymerization*

The interpretation of such curves becomes possible through the following simple considerations. The monomer $M_1$ is used up by the reactions 1 and 4 (p. 94). According to the equation for bimolecular reactions, one can write for the rate at which monomer $M_1$ is used up:

$$-d[M_1]/dt = k_{11}[R\sim\sim\sim M_1\cdot][M_1] + k_{21}[R\sim\sim\sim M_2\cdot][M_1]. \qquad (33)$$

Correspondingly, for the rate of disappearance of monomer $M_2$ we can combine reactions 2 and 3 to give Equation (34):

$$-d[M_2]/dt = k_{12}[R\sim\sim\sim M_1\cdot][M_2] + k_{22}[R\sim\sim\sim M_2\cdot][M_2] \qquad (34)$$

As has been explained on page 75, the radical concentration increases at the beginning of the polymerization because of the decomposition of the initiator, until the termination reaction, whose velocity increases with the square of the radical concentration, reaches the same rate as the initiation reaction (i.e., until just as many radicals disappear per unit time as new ones are formed). With copolymerization (we are considering here only binary systems), there are two types of radicals—$R\sim\sim\sim M_1\cdot$ and $R\sim\sim\sim M_2\cdot$—such that the formation reaction of the one radical is at the same time the disappearance reaction for the other. $R\sim\sim\sim M_1\cdot$ is formed through reaction 4 and disappears through reaction 2. Obviously $R\sim\sim\sim M_1\cdot$ radicals are formed and disappear also through initiation and termination reactions, but the rate of these reactions, compared to the rate of reactions 2 and 4, is so small that it can be disregarded.[8] As is generally true for the relationship between initiation and termination, we can also say for reactions 2 and 4 that the rate of reaction 2 (disappearance of $R\sim\sim\sim M_1\cdot$ radicals) is determined through 4 and vice versa, that the concentration of $R\sim\sim\sim M_1\cdot$ radicals grows according to reaction 4 until the rate of reaction 2 has become equal to that of reaction 4 and therefore just as many radicals $R\sim\sim\sim M_1\cdot$ disappear per unit time as new ones are formed.

$$k_{21}[R\sim\sim\sim M_2\cdot][M_1] = k_{12}[R\sim\sim\sim M_1\cdot][M_2]$$

or

$$[R\sim\sim\sim M_2\cdot] = \frac{k_{12}}{k_{21}} \cdot \frac{[R\sim\sim\sim M_1\cdot][M_2]}{[M_1]} \qquad (35)$$

If one then substitutes this expression for $[R\sim\sim\sim M_2\cdot]$ (with $[R\sim\sim\sim M_1\cdot]$ it would work just as well) in Equation (33) and (34), one obtains:

$$-d[M_1]/dt = k_{11}[R\sim\sim\sim M_1\cdot][M_1] + k_{12}[R\sim\sim\sim M_1\cdot][M_2]$$

and

$$-d[M_2]/dt = k_{12}[R\sim\sim\sim M_1\cdot][M_2] + k_{22}\frac{k_{12}}{k_{21}} \frac{[R\sim\sim\sim M_1\cdot][M_2]^2}{[M_1]}$$

$$= k_{12}[R\sim\sim\sim M_1\cdot][M_2]\left(1 + \frac{k_{22}}{k_{21}}\frac{[M_2]}{[M_1]}\right)$$

If one divides the first equation with the second, one obtains:

$$\frac{-d[M_1]/dt}{-d[M_2]/dt} = \frac{d[M_1]}{d[M_2]} = \frac{k_{11}[M_1]}{k_{12}[M_2]} \cdot \frac{1}{1 + \frac{k_{22}}{k_{21}}\frac{[M_2]}{[M_1]}} + \frac{1}{1 + \frac{k_{22}}{k_{21}}\frac{[M_2]}{[M_1]}}$$

The ratios $k_{11}/k_{12}$ and $k_{22}/k_{21}$ are called the copolymerization parameters, and the symbols used for them are $r_1$ and $r_2$:

$$r_1 = k_{11}/k_{12} \text{ and } r_2 = k_{22}/k_{21}.$$

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[8] If $k_{21}$ is extremely small and/or $[M_1]$ is very small, more radicals $(R\sim\sim\sim M_1\cdot)$ may be formed by decomposition of the initiator than through reaction 4. In that case Equations (33)-(38) no longer apply.

After introduction of these parameters one obtains:

$$\frac{d[M_1]}{d[M_2]} = \frac{r_1[M_1]/[M_2]}{1+(r_2[M_2]/[M_1])} + \frac{1}{1+(r_2[M_2]/[M_1])}$$

$$\frac{d[M_1]}{d[M_2]} = \frac{(r_1[M_1]/[M_2])+1}{(r_2[M_2]/[M_1])+1} \quad \text{(Mayo and Lewis),} \tag{36}$$

where $d[M_1]/d[M_2]$ is the ratio of the rates with which the two monomers $[M_1]$ and $[M_2]$ disappear from the monomer mixture through addition to the growing polymer chains. In the same ratio these monomers will appear as structural units in the chains of the copolymer. Therefore, $d[M_1]/d[M_2]$ is equal to the molar concentration ratio of the structural units in the copolymer. If one designates this ratio with the letter *b* and the molar concentration ratio of the monomers in the monomer mixture with the letter *a*, then:

$$a = \frac{[M_1]}{[M_2]} \quad \text{and, } b = \frac{-d[M_1]/dt}{-d[M_2]/dt} = \frac{d[M_1]}{d[M_2]} \quad \text{or} \quad \frac{m_1}{m_2},$$

and one obtains the copolymerization Equation (36) in the following simple form:

$$b = \frac{r_1 a + 1}{(r_2/a) + 1} \tag{36a}$$

or, if one factors out 1/a, one obtains:

$$b = a\,\frac{r_1 a + 1}{a + r_2} \tag{36b}$$

If, in this equation *a* is replaced by $[M_1]/[M_2]$ and in the numerator 1 is replaced by $[M_2]/[M_2]$, and finally $1/[M_2]$ is factored out, one obtains Equation (36) in a form often found in the literature:

$$\frac{d[M_1]}{d[M_2]} = \frac{m_1}{m_2} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1]+[M_2]}{r_2[M_2]+[M_1]} \tag{36c}$$

Equation (36) describes the composition of the copolymer as a function of the composition of the monomer mixture. One has to remember that *a*, and therefore also *b*, usually changes continuously during a copolymerization (exceptions: ideal copolymerization and those carried out at the azeotrope point, compare p. 104).

In graphical representations of copolymerization reactions one usually plots the concentration of $M_1$ in the monomer mixture versus the concentration of $M_1$ in the polymer chain. As a measure of concentration one uses weight percent or mole percent, and thus the sum of the concentrations becomes 100.:

$$[M_1] + [M_2] = 100 \text{ and } d[M_1] + d[M_2] = 100.$$

For *b* one can write:

$$b = d[M_1]/(100 - d[M_1])$$

This gives the following expression for the molar concentration of structural units of the monomer $M_1$ in the copolymer:

$$d[M_1] = b(100 - d[M_1]) = 100 \cdot b/(1+b) \text{ mole \%} \tag{37}$$

If one substitutes Equation (36a) in Equation (37) one obtains:

$$d[M_1] = (r_1 a + 1)\,100/(r_2/a + r_1 a + 2). \tag{38}$$

The copolymerization equation derived in the preceding paragraphs [Equations (36) and (38)] has demonstrated its general validity. (One assumes, however, that the kinetics underlying this derivation hold true, but this may not always be the case. For example, equilibrium polymerization follows different kinetics, such as the anionic polymerization of α-methyl-styrene). The parameters $r_1$ and $r_2$ are therefore universally used for the characterization of monomer pairs with regard to their behavior in copolymerization (compare Table 107). Depending upon the magnitude of $r_1$ and $r_2$, Equation (38) yields curves similar to those shown in Figures 95a or 95b, which correspond closely to the experimentally determined curves.

### *Determination of the Parameters $r_1$ and $r_2$*

The parameters $r_1$ and $r_2$ can be estimated fairly accurately after a sufficient amount of practice with copolymerization curves from the shape of the curve Conversely, from the values of $r_1$ and $r_2$ one can sketch the behavior of the copolymerization curve. To determine the values for $r_1$ and $r_2$ from the experimentally determined *b* values, one has to try to obtain the copolymerization equation, Equation (36a), as a linear function. This is done by solving Equatior (36a) for $r_2$ or $r_1$ (according to Lewis and Mayo) or, by solving Equation (36a) fo *a*-(*a*/*b*) (according to Fineman and Ross). The solution for $r_2$ yields:

$$r_2 = a\,\frac{r_1 a + 1}{b} - a = r_1\,\frac{a^2}{b} + \left(\frac{a}{b} - a\right). \tag{39}$$

If one then substitutes different values determined from the experimental curve fo *a* and *b*, one obtains a series of straight lines corresponding to different values of $r_1$

as a function of $r_1$. By substituting increasing values for $r_1$ (for example, from 0 to 1)[9] and calculating $r_2$ according to Equation (39), one obtains a family of straight lines which all intersect at a certain point. At this point all $a$ and $b$ values, taken from the experimental curves have the same $r_1$ and $r_2$ values. Therefore, the resulting $r_1$ and $r_2$ values are those which one has to substitute in Equations (36), (37), or (38) to obtain curves identical to those determined experimentally. Figure 100 represents such a graphical $r_1$-$r_2$ determination for the monomer pair styrene/methylmethacrylate. The solution of Equation (36a), or (39) for a-(a/b) gives:

$$a-(a/b) = r_1(a^2/b)-r_2 \qquad (39a)$$

If one now plots the ordinate $a-(a/b)$ against $a^2/b$ as the abscissa, as is shown in Figure 102, one obtains $(-r_2)$ as the intercept at the ordinate and $r_1$ as tangent $\delta$. Figure 102, shows as an example the determination of the r values for the monomer pair, acrylic acid (1)-acrylonitrile (2). The Fineman-Ross procedure is simpler because one only has to calculate a single straight line by substituting the experimentally determined (a/b)-ratios directly in Equation (39a).

A different way of determination of $r_1$ and $r_2$ has been proposed and tested by V. Jaacks. This method uses the integrated copolymerization Equation (36) after reducing it to a very simple form. This is possible if a copolymerization is carried out with a large excess of $M_1$ so that the ratio $[M_1]/[M_2]$ becomes very large and, correspondingly, $[M_2]/[M_1]$ becomes very small. In this case we can neglect the 1 in the numerator of Equation (36), and the denominator of Equation (36) becomes equal to 1:

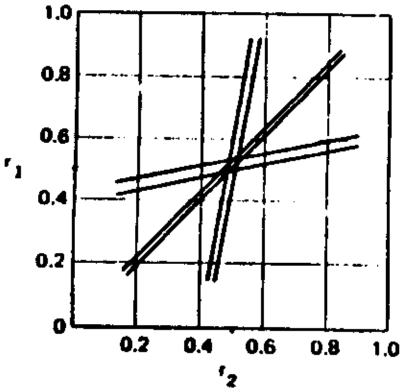

**FIG. 100** – Graphical determination of $r_1$ and $r_2$ according to Equ. (39) for the system styrene/methylmethacrylate ($M_1$ = styrene; $M_2$ = methylmethacrylate) (after LEWIS and MAYO).

$$\frac{d[M_1]}{d[M_2]} = \frac{r_1([M_1]/[M_2]) + 1}{r_2([M_2]/[M_1]) + 1} \qquad (36)$$

$$\Bigg\downarrow \quad \begin{array}{l} [M_1]/[M_2] > 1 \\ [M_2]/[M_1] < 1 \end{array}$$

$$\frac{d[M_1]}{d[M_2]} = r_1[M_1]/[M_2] \quad \text{or} \quad \frac{d[M_1]}{[M_1]} = r_1 \cdot d[M_2]/[M_2] \qquad (36d)$$

That is, with a sufficient excess of $M_1$, the composition of the resulting copolymer is determined only by $r_1$ and is independent of $r_2$.

By integration of Equation (36d) between the limits $[M_1]_o$ and $[M_2]_o$ at the time before starting the copolymerization, and $[M_1]_t$ and $[M_2]_t$ at the time $t$ after the start of the copolymerization, one obtains:

$$\lg \frac{[M_1]_t}{[M_1]_o} = r_1 \cdot \lg \frac{[M_2]_t}{[M_2]_o} \qquad (36e)$$

Equation (36e) describes the course of the whole copolymerization up to high conversions. Therefore, $r_1$ can be calculated by determination of the monomer ratio $[M_1]_t/[M_1]_o$ at any time after starting the copolymerization; the determination can be done in many cases with sufficient precision by gas chromatography. ($[M_2]_t$ is known when $[M_1]_t$ has been determined, because $[M_1]_t + [M_2]_t = 100$.) For a more precise determination of $r_1$, the monomer concentration $[M_1]_t$ is determined at different conversions. If $\lg [M_1]_t/[M_1]_o$ is plotted against $\lg [M_2]_t/[M_2]_o$, one obtains $r_1$ as the slope of the resulting straight line. In the same way, $r_2$ is determined through a copolymerization using a large excess of $M_2$. One cannot say that any one of the described methods is the best, but one has to decide which method is most suitable for a particular case. With time it seems that the Fineman-Ross procedure is often preferred. The Jaacks method has the advantage that it is not necessary to isolate and analyze a series of copolymers with different $[M_1]/[M_2]$ ratios. This is especially important, if there is no characteristic group, which can easily be determined quantitatively, in one of

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[9] From the shape of the copolymerization curves it is possible to select the correct range of $r_1$ values (compare Figures 103, 104, 106, 112 and 113).

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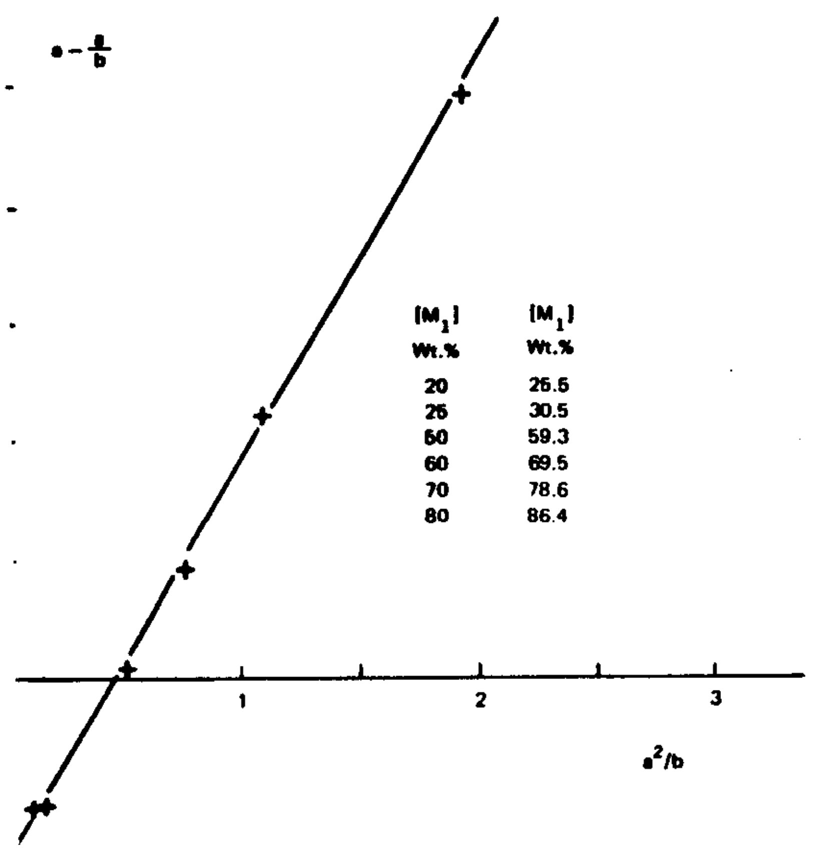

| $[M_1]$ Wt.% | $[M_1]$ Wt.% |
|---|---|
| 20 | 26.5 |
| 25 | 30.5 |
| 50 | 59.3 |
| 60 | 69.5 |
| 70 | 78.6 |
| 80 | 86.4 |

– Graphical determination of $r_1$ and $r_2$ according to FINEMAN and for the system acrylic acid/acrylonitrile.

onomers. A further advantage becomes evident with ternary (and higher) merization. Here, it is not necessary to carry out the copolymerizations two , but they can be determined by three ternary copolymerizations with a xcess of $M_1$, or $M_2$, or $M_3$.

he following section we will discuss the most characteristic polymerization ns in detail.

*s With Inflection Point Curves*

curves shown in Figure 103 are characteristic for cases where both $r_1$ and $r_2$ aller than 1. If one remembers that $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$, one

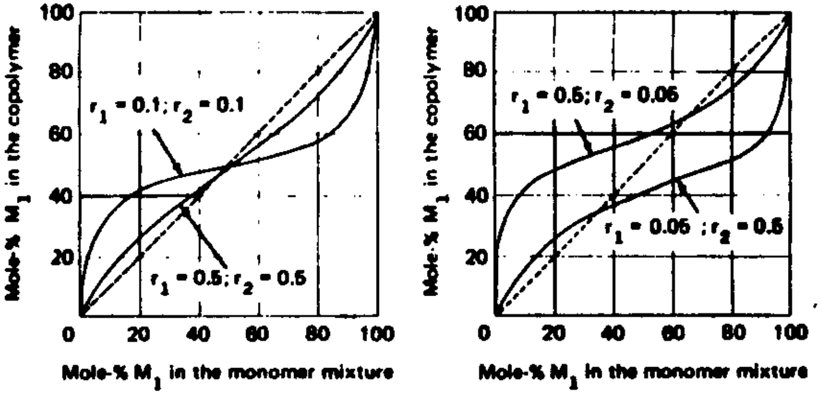

FIG. – Copolymerization curves with inflection-point, $r_1 < 1$ and $r_2 < 1$. ------ = $r_1 = 1$ and $r_2 = 1$.

immediately realizes the kinetic explanation for this behavior, which is that the reaction rate constants $k_{12}$ and $k_{21}$ are larger than $k_{11}$ and $k_{22}$ (i.e., that the addition of the opposite monomer to the radicals $R{\sim\sim}M_1\cdot$ and $R{\sim\sim}M_2\cdot$ occurs more rapidly than the addition of its own respective monomer). Furthermore, the aversion of the radicals to add their own monomers is the greater, the smaller the corresponding $r_1$ or $r_2$ value. If the parameters $r_1$ and $r_2$ are equal and if the molar concentration of the monomers is identical, then the addition of $M_2$ to $R{\sim\sim}M_1\cdot$ occurs more frequently than the addition of $M_1$ to $R{\sim\sim}M_1\cdot$ by the same amount as the addition of $M_1$ to $R{\sim\sim}M_2\cdot$ occurs more frequently than the addition of $M_2$ to $R{\sim\sim}M_2\cdot$. The inflection point lies at 50 mol% $M_1$, and the copolymer molecules contain on the average as many $M_1$ units as $M_2$ units. If the parameters $r_1$ and $r_2$ are not only equal but also much smaller than 1, then one obtains copolymers with regular alternation of $M_1$ and $M_2$ in the chain. The smaller the parameters $r_1$ and $r_2$, the more strictly this alternation of $M_1$ and $M_2$ in the polymer chain is observed (the larger $k_{12}$ and $k_{21}$ are compared to $k_{11}$ and $k_{22}$, respectively). On the other hand, the smaller the difference between the parameters $r_1$ and $r_2$ and 1, the more frequently one finds that $M_1$ adds to ${\sim\sim}M_1\cdot$ and that $M_2$ adds to ${\sim\sim}M_2\cdot$ in addition to alternation. If only $r_2$ is much smaller than 1, but $r_1$ is close to 1 (for example, styrene-acrylonitrile: $r_1 = k_{11}/k_{12} \approx 1/2.5$ and $r_2 = k_{22}/k_{21} = 1/33$), then one finds that ${\sim\sim}M_2\cdot + M_1$-addition and ${\sim\sim}M_1\cdot + M_2$-addition are preferred to ${\sim\sim}M_2\cdot + M_2$- and ${\sim\sim}M_1\cdot + M_1$-addition, respectively. Of these two the ${\sim\sim}M_1\cdot + M_2$-addition is not as strongly preferred as the ${\sim\sim}M_2\cdot + M_1$-addition. This means that one will find a number of sections in the copolymer molecule where two or more styrene residues succeed each other. There will be fewer cases where two or more acrylonitrile residues follow each other in the chain. This behavior shows up in the curve in the following way: the inflection point is no longer at 50 mol% but at higher or lower $M_1$ concentrations (if $r_1$ is greater than $r_2$, it is found at higher $M_1$ concentrations; if $r_1$ is smaller than $r_2$ it is found at lower $M_1$ concentrations).

The inflection point of the curve gives the composition at which the resulting copolymer has the same composition as the monomer mixture. One calls this (just as in the distillation of binary mixtures) an azeotropic composition, or azeotropic concentration, and one can even speak of an azeotropic copolymer.

The azeotropic monomer ratio can be determined immediately by substitution of $r_1$ and $r_2$ in the following equation:

$$[M_1]/[M_2] = (r_2 - 1)/(r_1 - 1). \qquad (39b)$$

In the azeotrope, namely, the concentration ratio *a* of the monomers is equal to the concentration ratio *b* of the monomer units in the copolymer chain. Therefore, if one substitutes $a = b$ in Equation (36b), one obtains:

$$(r_1 a + 1)/(a + r_2) = 1$$

Solving for *a*, this leads to Equation (39a). For industrial purposes the knowledge of this azeotropic concentration is of great interest, because at this ratio the composition of the monomer mixture and of the copolymer does not change during the polymerization reaction. Therefore one can continue the polymerization to very high conversions (98-99%), without the possibility of the polymer's becoming inhomogeneous. On the other hand, if one polymerizes a monomer mixture whose $M_1$ concentration is above or below azeotropic composition, then one first obtains a copolymer whose composition is nearer to that of the azeotrope than that of the monomer mixture, and, with strongly curved diagrams ($r_1$ and $r_2$ much smaller than 1), one even obtains copolymers that are identical with the azeotropic

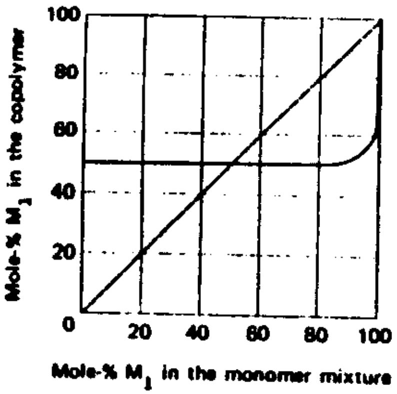

FIG. 104 – Copolymerization diagram for the system styrene/maleicanhydride ($r_1 \approx 0.0095$, $r_2 \approx 0$)

composition over a wide range of mixtures. As one can easily demonstrate by means of the copolymerization curves, the monomer mixture rapidly becomes poorer in that monomer, which was present in lower concentration, and one soon finds that only the other monomer is left, which then polymerizes, if one continues the polymerization, to a homopolymer. One therefore obtains copolymer that corresponds mainly to the azeotropic composition and, in addition, a homopolymer of $M_1$ or of $M_2$. Since with few exceptions different polymers are not miscible, one obtains inhomogeneous mixtures which have poor cohesion and are therefore of little technical importance. Such mixtures result, for example, from the polymerization of styrene-acrylonitrile mixtures which contain less than 65% styrene (azeotropic composition approximately 65:35; compare Figure 95).

Frequently, one of the monomers does not polymerize by itself, or only very slowly, and then $r_1$ or $r_2$ becomes O. In such cases the polymerization stops as soon as the other monomer has been used up by azeotropic copolymerization. This is found to be the case with mixtures of fumaric acid esters and isobutylene, or mixtures of styrene and maleic anhydride. Excess isobutylene, in the one case, and maleic anhydride in the other example, remain as unconverted monomers. If more than 50 mol% styrene is present in the monomer mixture, then one obtains homopolystyrene in addition to the $M_1M_2$ copolymers. Figure 104 shows the copolymerization diagram for the system styrene/maleic anhydride ($r_1 = 0.0095$ and $r_2 \cong 0$), and Table 105 shows the calculation of the curves according to Equation (38).

In this case one finds a degenerate inflection curve where the inflection point is lengthened to an inflexion tangent parallel to the x-axis. The curve shows that over a wide range one obtains copolymer with the same composition of styrene and

**TABLE 105.** Calculation of the copolymerization curve for the system styrene/maleicanhydride from the parameters $r_1 = 0.0095$, and $r_2 = 0$ according to Equ. (38). (All concentrations in mole-%)

| Monomer mixture | | | Copolymer | |
|---|---|---|---|---|
| $[M_1]$ Styrene | $[M_2]$ (Maleic-anhydride) | $a = \frac{[M_1]}{[M_2]}$ | $\frac{(r_1 a + 1)\cdot 100}{\frac{r_2}{a} + r_1 a + 2}$ | $d[M_1]$ |
| 1 | 99 | 0.01 | 100.01/2.0001 | 50 |
| 5 | 95 | 0.05 | 100.05/2.0005 | 50 |
| 10 | 90 | 0.1 | 100.1 /2.001 | 50 |
| 25 | 75 | 0.3 | 100.3 /2.003 | 50 |
| 50 | 50 | 1 | 101/2.01 | 50.3 |
| 75 | 25 | 3 | 103/2.03 | 50.4 |
| 90 | 10 | 9 | 109/2.09 | 52.2 |
| 95 | 5 | 19 | 119/2.19 | 53.4 |
| 97 | 3 | 32 | 132/2.32 | 57.0 |
| 99 | 1 | 99 | 199/2.99 | 66.6 |

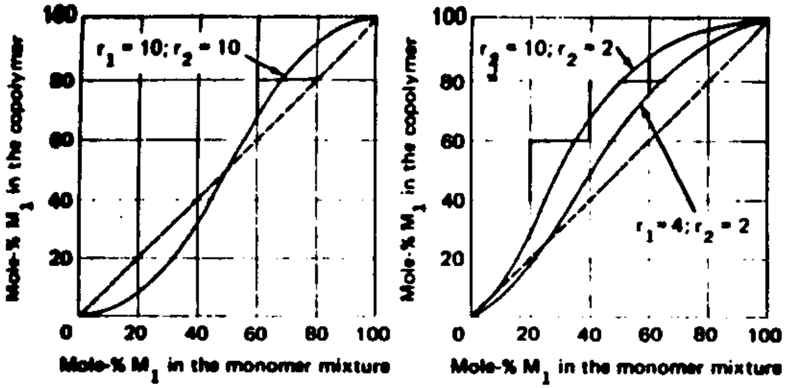

FIG. —Copolymerization diagrams for $r_1 > 1$ and $r_2 > 1$

eic anhydride independent of the composition of the monomer mixture. This is result of the strong alternating tendency[10] of the system ($k_{12}$ much greater $k_{11}$, and $k_{21}$ much greater than $k_{22}$).

f *both* parameters are equal to 0, then one obtains a straight line parallel to the is at $d[M_1]$-concentration = 50%.

his is true for monomer pairs where each of the two monomers is unable to merize by itself (i.e., where $k_{11}$ and $k_{22}$ are equal to zero). The chains of the olymers resulting from such systems have a completely regularly alternating ence of the structural units $M_1$ and $M_2$, regardless of the composition of the omer mixture. The value of systems where $r_1 = 0$ and $r_2 = 0$ for the aration of copolymers with alternating structure depends entirely on the lute magnitude of the corresponding reaction rate constants $k_{12}$ and $k_{21}$. Only he numerical values of $k_{12}$ and $k_{21}$ are of the order of 100 to 1,000 $\cdot mol^{-1} sec^{-1}$ (comparable with the $k_p$ values for styrene, methylmethacry- and vinylacetate) is it possible to produce copolymers with high molecular ht. Thus, while listed values of $r_1 = 0$ and $r_2 = 0$ mean that one *cannot* prepare opolymers from these monomers, the values *do not* mean that copolymers *can* repared since the values of $k_{12}$ and $k_{21}$ may be too small.

t also happens that one of the monomers (for example, maleic anhydride) is not merizable in the usual laboratory experiment, and that $k_{11}$ is not exactly 0, is very small. In that case $r_1$ is only approximately 0 if $k_{12}$ is larger by several ers of 10. However, if $k_{12}$ is only slightly larger than $k_{11}$ (10-100 times), then not 0, but 0.1 to 0.01. A typical example of this kind is the combination icanhydride/stilbene, which has the values $r_1 = 0.03$ and $r_2 = 0.03$. Neither icanhydride nor stilbene forms homopolymers with a high molecular weight. In spite of that, the r values are (within experimental error) different from zero, even though the copolymerization steps occur quite slowly in contrast to the extremely rapid copolymerization of maleicanhydride-styrene ($r_1 = 0$ and $r_2 = 0.01$). The conclusion "$r_1 = 0$ and $r_2 = 0$, therefore the monomers of this pair cannot be homopolymerized" is not reversible, i.e., actual values for $r_1$ and $r_2$ do not imply that the monomers are capable of homopolymerization. $r_1 = 1$ and $r_2 = 1$ simply means that the copolymerization steps do not occur more rapidly than the corresponding homopolymerization steps. With pairs of monomers which do not homopolymerize, or only homopolymerize slowly, the fact that $r_1$ and $r_2$ have finite values simply means that these monomers do not homopolymerize or copolymerize with any preparatively useful rate. Of the almost 1,000 monomer pairs whose parameters have been determined, a considerable fraction belong to this category.

As is discussed later on (see p. 111) the behavior of monomer pairs without azeotrope can readily be explained, expecially of those with symmetrical copolymerization diagrams. A satisfactory explanation can also be given for the behavior of monomer pairs which give a copolymerization curve with an inflection point, such as in Figure 103.

The same considerations lead to the conclusion that monomer pairs for which $r_1>1$ and $r_2>1$ do not exist. If one looks over the known r values (for example, see *Polymer Handbook*, Wiley-Interscience, 1966), there are a few monomer pairs, listed at the end of Table 107, which formally belong to this group. However, it is not clear whether this is due to measurement errors, or if one is here dealing with still unknown effects which determine the rate of the different addition steps. It is striking, however, that systems with $r_1>1$ and $r_2>1$ are more common among the ionic copolymerizations. Monomer pairs with high r values, as will be discussed subsequently, have the tendency to form long sequences. Very large values of $r_1>1$ and $r_2>1$ would therefore indicate that such a system (if it exists) would lead to the synthesis of block copolymers or—in extreme cases— that the two homopolymers (poly-$M_1$ and poly-$M_2$) would be formed side-by-side.

TABLE . Copolymerization Parameters*

| $M_1$ | $M_2$ | $r_1$ | $r_2$ | Temp. |
|---|---|---|---|---|
| Both Parameters = 1 | (ideal Monomer pairs) | | | |
| Methylmethacrylate | Vinylidenechloride | 1.0 | 1.0 | 60° |
| Vinylacetate | Isopropenylacetate | 1.0 | 1.0 | 75° |
| Acrylonitrile | Glycidylacrylate | 1.0 | 1.0 | 60° |
| Butylacrylate | Acrylonitrile | 1.0 | 0.92 | 56°E** |

* For a comprehensive tabulation see BRANDRUP-IMMERGUT, Polymer Handbook, Interscience Publishers 1966.

** E = Emulsion/polymerization

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The condition for the formation of an alternating copolymer chain structure, namely, $_1 \cong r_2$ is always met with very small $r_1$ and $r_2$ values ($r_1<1$ and $r_2<1$). Therefore, in the ple of styrene/maleic anhydride, where $r_1 = 0.0095$ and $r_2 = 0$, we can write that $r_1 \cong 0$.

**TABLE** [illegible]**. (Cont'd)**

| $M_1$ | $M_2$ | $r_1$ | $r_2$ | Temp. |
|---|---|---|---|---|
| Butylacrylate | N-Methylolacrylamide | 0.87 | 0.61 | -- |
| Ethylacrylate | Acrylonitrile | 0.95 | 0.44 | 80° |
| Styrene | Ethylacrylate | 0.80 | 0.20 | 70° |
| Butylmethacrylate | Methacrylonitrile | 0.70 | 0.50 | 80° |
| Butylmethacrylate | Styrene | 0.64 | 0.63 | 50° |
| Butadiene | Methylacrylate | 0.76 | 0.05 | 50° E |
| Styrene | Methylmethacrylate | 0.50 | 0.50 | 60° |
| Methacrylonitrile | Methylmethacrylate | 0.65 | 0.67 | 60° |
| Styrene | 4-Vinylpyridine | 0.70 | 0.54 | 60° |
| N-Vinylpyrrolidone | Vinylenecarbonate | 0.70 | 0.40 | 60° |
| Styrene | Glycidylacrylate | 0.60 | 0.17 | 60° |
| Vinylacetate | Allylacetate | 0.60 | 0.50 | 60° |
| Glycidylmethacrylate | Styrene | 0.53 | 0.44 | 60° |
| Styrene | Methylacrylate | 0.75 | 0.20 | 70° |
| Styrene | Butylacrylate | 0.76 | 0.15 | 60° |
| Styrene | Butylacrylate | 0.48 | 0.15 | 25° |
| Methacrylic acid | Butadiene | 0.53 | 0.20 | 50° E |
| Vinylchloride | N-Vinylpyrrolidone | 0.53 | 0.38 | -- |
| 2-Fluorobutadiene | Acrylonitrile | 0.60 | 0.07 | 50° |
| Butadiene | Methylmethacrylate | 0.53 | 0.06 | 5° E |
| N-Vinylpyrrolidone | Vinylacetate | 0.44 | 0.38 | 70° |
| Glycidylmethacrylate | Styrene | 0.44 | 0.35 | 60° |
| Diethylfumarate | Vinylchloride | 0.47 | 0.12 | 60° |
| Diethylfumarate | Vinylacetate | 0.44 | 0.01 | 60° |
| Styrene | Acrylonitrile | 0.41 | 0.03 | 75° |
| Methacrylonitrile | α-Methylstyrene | 0.35 | 0.12 | 80° |
| Vinylidenechloride | Butylmethacrylate | 0.35 | 0.22 | 70° |
| Acrylic acid | Styrene | 0.35 | 0.22 | 70° |
| Butadiene | Methacrylonitrile | 0.36 | 0.04 | 5° E |
| Butadiene | Acrylonitrile | 0.35 | 0.05 | 50° E |
| Styrene | Itaconicanhydride | 0.30 | 0.20 | 70° |
| Styrene | Methacrylonitrile | 0.25 | 0.25 | 80° |
| Styrene | Diethylfumarate | 0.30 | 0.07 | 60° |
| Ethylacrylate | 2-Vinylpyridine | 0.20 | 0.20 | 75° |
| Isoprene | Acrylonitrile | 0.30 | 0.05 | 50° |
| Styrene | Acrylicanhydride | 0.17 | 0.10 | 35° |
| Vinylacetate | Maleicanhydride | 0.055 | 0.003 | 75° |
| Isopropenylacetate | Maleicanhydride | 0.032 | 0.002 | 75° |
| Vinylchloride | Maleicanhydride | 0.3 | 0.008 | 75° |
| Stilbene | Maleicanhydride | 0.03 | 0.03 | 60° |
| $r_1 < 1, r_2 = 0$ | | | | |
| Styrene | β-Nitrostyrene | 0.4 | 0 | 80° |
| Styrene | Fumarodinitrile | 0.2 | 0 | 60° |
| Vinylacetate | Fumarylchloride | 0.14 | 0 | 70° |
| Styrene | Maleianhydride | 0.01 | 0 | 60° |

**TABLE** [illegible]**. (Cont'd)**

| $M_1$ | $M_2$ | $r_1$ | $r_2$ | Temp. | |
|---|---|---|---|---|---|
| $r_1 = 0, r_2 = 0$ | | | | | |
| Maleicanhydride | 2-Chlorallylacetate | 0 | 0 | 120° | |
| Diethylfumarate | Isobutylene | 0 | 0 | 70° | |
| Poly-(ethyleneglycol-fumarate) | n-Amylvinylether | 0 | 0 | 60° | |
| $r_1 > 1, r_2 > 1$ | | | | | |
| Acrylonitrile | N-Octadecylacrylamide | 1.10 ± 0.035 | 1.44±0.019 | 60° | |
| N-Methylolacrylamide | Methylacrylate | 1.9 ± 0.7 | 1.3 ±0.7 | -- | |
| Isoprene | Styrene | 2.05 | 1.38 | 50° | |
| Allylbenzoate | Allylchloride | 2.5 | 1.25 | 60° | |
| Acrylonitrile | Dodecylacrylate | 3.2 ± 0.5 | 1.3 ±0.1 | 60° | |
| Methylvinylketone | α(2-Cyanoethyl)-acrylonitrile | 5.05 ± 0.95 | 1.24±0.75 | -- | |
| Ethylacrylate | Na-acrylate | 5.7 | 1.5 | 50° | |
| Ionic and Metal – Complex-Copolymerization | | | | | |
| Isoprene | Butadiene | 1.0 | 1.0 | -20° | $AlR_2Cl$/Co-Complex |
| p-Chlorostyrene | Isobutylene | 1.0 | 1.0 | 0 | $AlBr_3$ in Hexane |
| p-Chlorostyrene | Isobutylene | 1.2 | 8.6 | 0 | $SnCl_4$ in Hexane |
| Ethylene | Propylene | 15.7 | 0.11 | 75° | $TiCl_3/AlR_3$ |
| p-Methoxystyrene | Styrene | 100 | 0.01 | 0° | $SnCl_4$ |
| Styrene | p-Chlorostyrene | 2.2 | 0.45 | 0° | $SnCl_4$ in Nitrobenzene |
| Isobutylene | Styrene | 9.0 | 2.0 | -90° | $AlCl_3$ in $CH_3Cl$ |
| 2-Chloroethylvinylether | Styrene | 36 | 3 | | cationic |
| p-Methoxystyrene | 2-Chloroethylvinylether | 5 | 45 | | cationic |
| Isoprene | Styrene | 1.92 | 0.54 | 80° | radical |
| Isoprene | Styrene | 5.9 | 0.03 | 20° | with Butyllithium (anionic) |
| Isoprene | Styrene | 1.88 | 0.66 | 22° | initiated with γ-rays |

### ***Diagrams Without Azeotrope***

With the other large group of monomer pairs, one of the radicals prefers to add the opposite monomer, whereas the second radical prefers to add its own monomer. Thus either $k_{11}/k_{12} = r_1 > 1$ and $k_{22}/k_{21} = r_2 < 1$, or conversely $k_{11}/k_{12} = r_1 < 1$ and $k_{22}/k_{21} = r_2 > 1$.

Figures 112 and 113 show typical diagrams for such cases. The curves are symmetrical (with regard to the 45°-line), if $r_2$ is smaller than 1 by the same factor by which $r_1$ is greater than 1 (or vice versa), i.e., if $r_1 \cdot r_2 = 1$. For such systems in the literature the indication "ideal copolymerization" is mostly used. This, however, is not justified, because those systems are not characterized by any particular theoretical or practical condition. The case that the curves in the diagrams for ($r_1 \cdot r_2 = 1$)-systems are symmetrical with regard to the 45°-line is simply one of many imaginable and real ways in which pairs of monomers can behave during copolymerization. But among all these possibilities, there is only a single solution for which the copolymers and the corresponding monomer mixtures have, over the entire range of mixtures, the same composition, and that is the 45°-line with $r_1 = 1$ and $r_2 = 1$. Therefore, only this case can meaningfully be called "ideal copolymerization."

As long as the $r_1$ and $r_2$ values are only slightly different from 1, (for example, $r_1 = 0.8$ and $r_2 = 1.2$), the resulting copolymer has nearly the same composition as that of the monomer mixture for all ratios of the two monomers in the monomer mixture. On the other hand, if the deviations from 1 are considerable (curves deviating very much from the diagonal), then during polymerization one of the two monomers is rapidly enriched. For example, if $r_1 = 5$ and $r_2 = 0.2$, then one has the following situation: if with a 50/50 monomer mixture an $M_1^\bullet$ radical is at the end of the chain, then the addition of another $M_1$ monomer occurs 5 times as rapidly as the addition of a monomer $M_2$. Then if a monomer $M_2$ adds, on the average after 5 $M_1$-additions, the resulting $M_2^\bullet$ radical also adds a monomer $M_1$ 5 times as rapidly as a monomer $M_2$ (because $k_{22}/k_{21} = 1/5$). Thus, among 6 $M_2^\bullet$ radicals there is on the average only a single one that adds a monomer $M_2$. Whatever radical is present at the chain end, monomer $M_1$ will always be preferred in the ratio of 5 to 1. Consequently, of each 6 structural units in the resulting copolymer, on the average 5 will be $M_1$ units. Thus, the copolymer obtained from a 50/50 monomer mixture with the values $r_1 = 5$ and $r_2 = 0.2$ will consist of 83.3% of $M_1$ units. This can also be demonstrated by observing the resulting copolymerization diagram (see Figure 84/1). The further the parameters deviate from 1, the more the structure of the copolymer approaches that of $M_1$ homopolymer. With $r_1 = 100$ and $r_2 = 0.01$, a 50/50 monomer mixture would yield a copolymer consisting of 99% of $M_1$ units. If one allows the polymerization of this mixture to go to high conversion, then the composition of the monomer mixture increases rapidly from 50/50 to 70/30, 90/10, and 95/5 until finally only pure monomer $M_2$ remains, because monomer $M_1$ is used up much more rapidly than monomer $M_2$. Thus, one obtains with increasing $M_2$ monomer concentration during copolymerization copolymers with increasing $M_2$ structural units until finally, if the polymerization is continued, a pure homopolymer of $M_2$ is formed. The result of such a copolymerization is in almost all cases an inhomogeneous mixture of $M_1$–$M_2$ copolymer with increasing amounts of $M_2$ units (from 1-99%) and varying amounts of $M_2$ homopolymer. In practice, in the case described above, one says that the monomer $M_2$ does not enter into the chain, and one helps the situation by adding the more slowly used up monomer in high concentration and continuing the addition of the more rapidly used up monomer during copolymerization in such a way that a concentration of the monomer mixture which yields the desired copolymer is maintained. From the diagrams one can in each case determine the experimental conditions required. (compare section on "preparative copolymerization", p. 126).

Often one faces the problem of introducing certain functional groups in low concentration into a polymer by means of copolymerization. In such cases it is useful to look at the $r_1$, $r_2$ values first and draw the diagram, or, if the $r_1$, $r_2$ values are not known, to carry out sufficient copolymerizations to obtain the diagram and to determine the $r_1$, $r_2$ values.

Another possibility for copolymerizing two monomers with unsuitable $r_1$, $r_2$ values into a copolymer is to use a third monomer. One can usually prepare

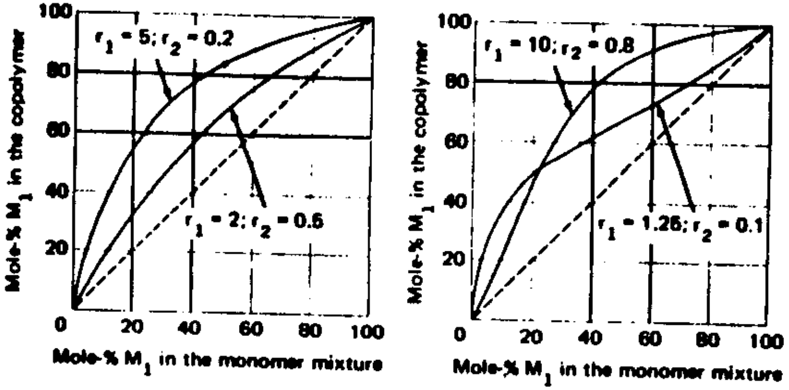

FIG. — Copolymerization diagrams without inflection-point. $r_1 > 1$, $r_2 < 1$.

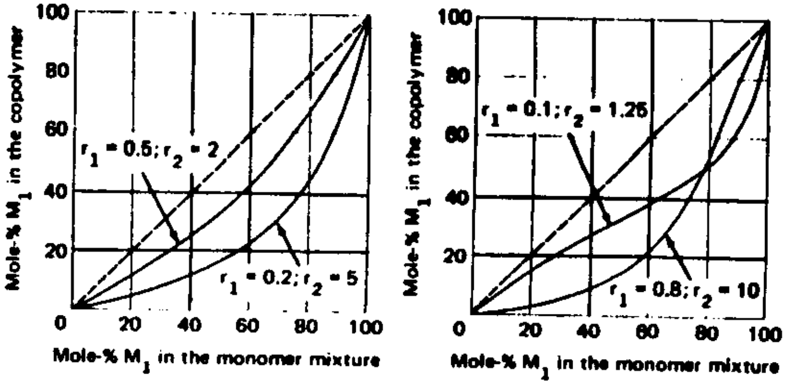

FIG. 113 – Copolymerization diagrams without inflection-point. $r_1 < 1$, $r_2 > 1$.

copolymers of styrene and vinylcarbazole only with great difficulty. However, by the addition of a small amount of acrylonitrile, it becomes very simple to prepare homogeneous copolymers (terpolymers).

Table 107 shows a number of monomer pairs with their $r_1$ and $r_2$ values. They are arranged according to the extent to which they deviate from 1. With the large majority of the monomer pairs the values of $r_1$ are between 1 and 2 and those of $r_2$ are between 1 and 0.1. Furthermore, the deviation in general favors values <1. The $r_1$ and $r_2$ values in Table 107 are valid for radical polymerization (with the exception of those at the end of the table). Even though the mechanism of ionic polymerization is different from that of radical polymerization, the basic scheme in both cases involves a chain reaction, and ionic copolymerization can be described in the same form and by the same copolymerization equation as radical copolymerization. As the few examples at the end of Table 107 demonstrate, ionic copolymerization parameters usually differ greatly from 1. It is also curious that the combination $r_1 > 1$ and $r_2 > 1$ is observed with the cationic rather than the anionic copolymerizations. No explanation for this can be given at this time, however. A series of monomers can be polymerized both by a radical and an ionic mechanism (for example, styrene) or can at least be copolymerized by both mechanisms (for example, vinylethers). The parameters are then different for the same monomer pair, and it is therefore possible to use copolymerization reactions to determine the type of initiation involved (for example, with radiation polymerization).

The accuracy of the numerical $r_1$ and $r_2$ values varies greatly depending on the accuracy of the different analytical methods used for the different copolymerizations. (At the end of the book the same monomer pairs are listed once more in alphabetical sequence and with an indication of the error limits. A complete collection of known $r_1$ and $r_2$ values can be found in the *Polymer Handbook*, Wiley-Interscience, 1966.)

### *Copolymerization Equations for Limiting Cases*

For the limiting cases discussed previously, the copolymerization equation [Equation (36)] takes on simpler forms which are summarized below:

**1. Ideal copolymerization:**

**Conditions:** $r_1 = 1$

$r_2 = 1$

**Equation:**

$$b = \frac{r_1 a + 1}{r_2/a + 1} = \frac{a + 1}{1/a + 1} = a$$

$$m_1 = [M_1]$$

2. At the azeotrope point:

Conditions: $a = b$

Equation:

$$b = a = \frac{r_1 a + 1}{(r_2/a) + 1} = \frac{r_1 b + 1}{(r_2/b) + 1}$$

$$b(r_2/b + 1) = r_1 b + 1$$

$$r_2 + b = r_1 b + 1$$

$$r_2 - 1 = r_1 b - b = b(r_1 - 1)$$

$$b = (r_2 - 1)/(r_1 - 1)$$

3. Strictly alternating copolymerization:

Conditions: $r_1 = 0$

$r_2 = 0$

Equation: $b = 1$

$m_1 = 50\%$

4. Symmetrical copolymerization curves

a) with azeotrope:

Conditions: $r_1 = r_2 < 1$

Equation: $$b = \frac{r_1 a + 1}{(r_1/a) + 1}$$

b) Without azeotrope:

Conditions: $\frac{k_{11}}{k_{12}} = \frac{k_{21}}{k_{22}}$ or, $r_1 = \frac{1}{r_2}$ or, $r_1 \cdot r_2 = 1$

Equation: $$b = \frac{r_1 a + 1}{(1/r_1 a) + 1} = \frac{r_1 a + 1}{(1/r_1 a)(1 + r_1 a)} = r_1 \cdot a$$

### *Structure of Copolymers*

#### *Mean Sequence Length*

The mean number of structural units of $M_1$ in a sequence is always larger by 1 than the ratio of the number of $(M\cdot_1 + M_1)$-additions to the number of $(M\cdot_1 + M_2)$-additions. It is determined by the ratio between the rates of the two addition steps $(v_{11}/v_{12}) + 1$. For instance, if in the above example $v_{11}$ is 5 times as large as

$v_{12}$, in an average time interval the two monomers are used up at a rate of 5/1 (with $[M_1]/[M_2] = 1$). Also the monomers are added in that ratio to the growing chain and therefore in a given time $t$, 5 $M_1$-monomers and 1 $M_2$-monomer will add to the radical $\sim\sim M\cdot_1$. This leads to a sequence of (5/1) + 1 = 6 $M_1$ structural units:

$$\sim\sim M_2 - M\cdot_1 + 5\,M_1 + 1\,M_2 \rightarrow$$
$$\sim\sim M_2 - M_1 - M_1 - M_1 - M_1 - M_1 - M_1 - M\cdot_2$$

If $v_{11}/v_{12} = 3/1$, then one obtains sequences of four units:

$$\sim\sim M_2 - M\cdot_1 + 3\,M_1 + 1\,M_2 \rightarrow \sim\sim M_2 - M_1 - M_1 - M_1 - M_1 - M\cdot_2$$

and if $v_{11}/v_{12} = 1/1$ one obtains sequences consisting of two units:

$$\sim\sim M_2 - M\cdot_1 + M_1 + M_2 \rightarrow \sim\sim M_2 - M_1 - M_1 - M\cdot_2$$

or in general: the mean sequence length $\bar{l}_1$ (i.e., the average number of $M_1$ units combined into a sequence) is given by the following equation:

$$\bar{l}_1 = \frac{v_{11}}{v_{12}} + 1 = \frac{k_{11}\cdot[M_1]\cdot[R\sim\sim M\cdot_1]}{k_{12}\cdot[M_2]\cdot[R\sim\sim M\cdot_1]} + 1 = \frac{k_{11}}{k_{12}}\cdot\frac{[M_1]}{[M_2]} + 1 =$$
$$r_1\cdot\frac{[M_1]}{[M_2]} + 1 = r_1 a + 1 \tag{39c}$$

Similarly one obtains a relation for the average length of the $M_2$ sequence:

$$\bar{l}_2 = \frac{v_{22}}{v_{21}} + 1 = \frac{k_{22}\cdot[M_2]\cdot[R\sim\sim M\cdot_2]}{k_{21}\cdot[M_1]\cdot[R\sim\sim M\cdot_2]} + 1 = \frac{k_{22}}{k_{21}}\cdot\frac{[M_2]}{[M_1]} + 1 =$$
$$= r_2\cdot\frac{[M_2]}{[M_1]} + 1 = (r_2/a) + 1 \tag{39d}$$

As one can immediately see, the average length of the $M_1$ or $M_2$ sequences, is quivalent to the composition of the copolymer chain (i.e., the ratio of the tructural units in the chain $m_1/m_2 = d[M_1]/d[M_2]$ is identical with the ratio of he mean sequence lengths):

$$\frac{d[M_1]}{d[M_2]} = \frac{\bar{l}_1}{\bar{l}_2} = \frac{r_1[M_1]/[M_2] + 1}{r_2[M_2]/[M_1] + 1} = \frac{r_1 a + 1}{(r_2/a) + 1} \tag{39e}$$

The identity of Equations (36) and (39a) shows that in this way one can derive the opolymerization equation simply and clearly.

### *Sequence Length Distribution*

The copolymerization equation describes the overall composition $m_1/m_2$ of a copolymer as a function of the monomer mixture composition $[M_1]/[M_2]$ and the parameters $r_1$ and $r_2$. There are, of course, many chain structures possible for a given overall composition. These can be regular and irregular, and they differ from each other by the length of the $M_1$ and $M_2$ sequences, respectively. However, since the different addition steps occur at random, it is possible with simple statistical considerations to establish a relationship between the r values and the probability with which $M_1$ or $M_2$ sequences of increasing length occur in a copolymer molecule:

If the probability that a chain-radical $\sim\sim M_2\text{-}M_1^{\cdot}$ [11] adds a monomer molecule $M_1$ (forming a $M_1$-$M_1$ sequence) is given by $W_{11}$, then the probability that this process immediately occurs again forming a 3 $M_1$ sequence is given by $W_{11}^2$; that it then occurs a third time (forming a 4 $M_1$ sequence) is given by $W_{11}^3$, and so forth. Therefore the probability for the creation of an $M_1$-$M_1$ sequence with n $M_1$ structural units is equal to $W_{1(n)} = W_{11}^{n-1}$. This sequence is of course an *open* sequence of undetermined length, because the further addition of monomers is not excluded. For a *closed* sequence within the chain, one still always needs the addition of a monomer $M_2$ given by the probability $W_{12}$. Therefore, the probability for the existence of a closed sequence with n units of the same type $M_1$ is given by:

$$W_{1(n)} = W_{11}^{n-1}\cdot W_{12} = W_{11}^{n-1}\cdot(1 - W_{11}) \tag{39f}$$

How do we obtain $W_{11}$, the probability that a chain-radical $\sim\sim M_2\text{-}M_1^{\cdot}$ adds a monomer molecule $M_1$? The probability W for the occurence of an event is defined by the ratio W = number of favorable cases/number of all possible cases. For example, the probability of obtaining a 6 on casting a die is given by 1/6 (among six possible cases, the favorable case exists only once). In the previous case we were concerned with the addition of the monomers $M_1$ and $M_2$ to the chain radical $\sim\sim M_2\text{-}M_1^{\cdot}$. The number of favorable cases (i.e., the addition of monomer $M_1$ to $\sim\sim M_2\text{-}M_1^{\cdot}$)[12] is proportional to the rate $v_{11} = k_{11}\cdot[R\sim\sim M\cdot_1]\cdot[M_1]$. And the number of all possible cases (i.e., the addition of a monomer $M_1$ or a monomer $M_2$ to $\sim\sim M_2\text{-}M_1^{\cdot}$), is proportional to the sum $v_{11} + v_{12}$.

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[11] The probability of throwing a 6 with a die that has six faces is 1/6; the probability of throwing two 6's in a row, is $(1/6)^2$, because the combination 6-6 is one of 36 possible combinations, i.e., 1/36; the possibility of throwing three 6's in a row is $(1/6)^3$, because the combination 6-6-6 is one of 216 possible combinations, etc.

[12] Obviously the probability that other chain radicals $\sim\sim M_1$, such as $\sim\sim M_2 - M_1 - M_1$, $\sim\sim M_2 - M_1 - M_1$ add a monomer $M_1$, is the same in all cases, but we are interested here only in additions to $\sim\sim M_2 - M_1$, because only in this case is the number of addition steps indentical with the number of $M_1$ in the increasing $M_1$ sequence.

This explanation for the behavior of different monomers in radical polymerization is based on the attempt by Alfrey and Price to provide a quantitative description, with the aid of two parameters, for *each* monomer rather than for a monomer *pair*. These parameters are called Q and *e*. For the rate constant $k_{xy}$ for the addition of a monomer $M_y$ to the radical $\sim\sim M_x^{\bullet}$ according to the reaction:

$$\sim\sim M_x^{\bullet} + M_y \xrightarrow{k_{xy}} \sim\sim M_x - M_y^{\bullet},$$

the following expression can be written:

$$k_{xy} = P_x \cdot Q_y \cdot e^{-e_x \cdot e_y} \qquad \text{(a)}$$

$P_x$ is a proportionality factor which is characteristic of the state of the radical $\sim\sim M_x^{\bullet}$. $Q_y$ is a measure for the reactivity of the monomer $M_y$ and thus a measure for the willingness of the monomer $M_y$ to form the radical $\sim\sim M_x{-}M_y^{\bullet}$ by reaction with $\sim\sim M_x^{\bullet}$. Since this readiness to form a radical ending in $M_y$ is the greater, the greater the resonance stabilization of $\sim\sim M_y^{\bullet}$, $Q_y$ must be also a measure for the resonance stabilization of the radical $\sim\sim M_y^{\bullet}$ produced. The quantities $e_x$ and $e_y$ describe the polarization of the two radicals ($\sim\sim M_x^{\bullet}$ and $\sim\sim M_y^{\bullet}$) and the two monomers ($M_x$ and $M_y$) resulting from the substituents (–Cl, –OH, –COOR, –CN, etc.) on the monomers. As a simplification, it is assumed that the corresponding radicals and monomers have the same polarity and therefore the same *e* value. $e_x$ is therefore the polarity of the radical $\sim\sim M_x^{\bullet}$ and also of the monomer $M_x$. The same holds also for $e_y$, of course. With the aid of Equation (a) one can write the ratios $k_{11}/k_{12} = r_1$ and $k_{22}/k_{21} = r_2$, so that the quantity $P_1$, which in both cases refers to the radical $\sim\sim M_1^{\bullet}$, disappears and one obtains Equation (b):

$$r_1 = \frac{k_{11}}{k_{12}} = \frac{P_1 \cdot Q_1 \exp\,\{-e_1 \cdot e_1\}}{P_1 \cdot Q_2 \exp\,\{-e_1 \cdot e_2\}} = \frac{Q_1}{Q_2}\ \exp\ \{-e_1(e_1 - e_2)\} \qquad \text{(b)}$$

and correspondingly for $r_2$:

$$r_2 = \frac{k_{22}}{k_{21}} = \frac{Q_2}{Q_1}\ \exp\ \{-e_2(e_2 - e_1)\}\,. \qquad \text{(c)}$$

These equations permit us to calculate the Q and *e* values for single monomers from the $r_1 - r_2$ values, provided we have one monomer for which Q and *e* have been arbitrarily established. Price chose styrene as the standard monomer with the values Q = 1 and *e* = –0.8. One can now calculate the Q and *e* values of any monomer that has been copolymerized with styrene from the $r_1$ and $r_2$ values of the copolymerization of styrene with that particular monomer. Knowing the Q and *e* values of these various monomers, one can then calculate Q and *e* for any monomer that has been copolymerized with these monomers (i.e., where $r_1$ and $r_2$ are given in the literature). Conversely, knowing Q and *e* for any two monomers, we can calculate the $r_1 - r_2$ values for this monomer pair, whether or not they have ever been copolymerized. This is very useful, since it allows prediction of the copolymerization behavior of any two monomers for which Q and *e* are known. While the predicted behavior is not always exactly like the

35

TABLE 139. Selected Q and e values*

| | e | Q |
|---|---|---|
| Isobutylvinylether | −1.77 | 0.023 |
| t-Butylvinylether | −1.58 | 0.15 |
| p-Dimethylaminostyrene | −1.37 | 1.51 |
| α-Methylstyrene | −1.27 | 0.98 |
| Isoprene | −1.22 | 3.33 |
| n-Butylvinylether | −1.20 | 0.087 |
| Na-Methacrylate | −1.18 | 1.36 |
| Ethylvinylether | −1.17 | 0.032 |
| N-Vinylpyrrolidone | −1.14 | 0.14 |
| Allylacetate | −1.13 | 0.028 |
| 2-Chloroallylacetate | −1.12 | 0.53 |
| p-Methoxystyrene | −1.11 | 1.36 |
| 1,3-Butadiene | −1.05 | 2.39 |
| Indene | −1.03 | 0.36 |
| p-Methylstyrene | −0.98 | 1.27 |
| Isobutylene | −0.96 | 0.033 |
| Styrene (reference standard) | −0.80 | 1.00 |
| Propylene | −0.78 | 0.002 |
| Vinylisocyanate | −0.70 | 0.16 |
| Vinylenecarbonate | −0.65 | 0.00073 |
| p-Iodostyrene | −0.40 | 1.17 |
| m-Chlorostyrene | −0.36 | 1.03 |
| p-Chlorostyrene | −0.33 | 1.03 |
| p-Styrene sulfonic acid | −0.26 | 1.04 |
| n-Butylmethacrylate | −0.23 | 0.72 |
| Vinylacetate | −0.22 | 0.026 |
| Ethylene | −0.20 | 0.015 |
| p-Cyanostyrene | −0.21 | 1.86 |
| 4-Vinylpyridine | −0.20 | 0.82 |
| n-Hexylmethacrylate | −0.12 | 0.70 |
| Na-acrylate | −0.12 | 0.71 |
| Vinylsulfonic acid | −0.02 | 0.093 |
| Glycidylmethacrylate | 0.10 | 0.85 |
| Allylchloride | 0.11 | 0.056 |
| n-Nonylmethacrylate | 0.14 | 0.91 |
| Ethylmethacrylate | 0.17 | 0.56 |
| Vinylchloride | 0.20 | 0.044 |
| Ethylacrylate | 0.22 | 0.52 |
| Allylalcohol | 0.29 | 0.052 |
| Vinylidenechloride | 0.36 | 0.22 |
| N-Methylolacrylamide | 0.36 | 0.43 |
| p-Nitrostyrene | 0.39 | 1.63 |
| Methylmethacrylate | 0.40 | 0.74 |
| Methylcinnamate | 0.49 | 0.12 |
| Methylacrylate | 0.60 | 0.42 |

*(For a comprehensive tabulation see L.J. YOUNG in "Polymer Handbook", Interscience Publishers, 1966).

# Ionic Polymerization

## 4.1 General characteristics

Radical-initiated polymerizations are generally non-specific, but this is not true for ionic initiators, since the formation and stabilization of a carbonium ion or carbanion depends largely on the nature of the group R in the vinyl monomer $CH_2{=}CHR$. For this reason cationic initiation is usually limited to monomers with electron-donating groups which help to stabilize the delocalization of the positive charge in the π-orbitals of the double bond. Anionic initiators require electron withdrawing substituents ($-CN$, $-COOH$, $-CH{=}CH_2$, *etc.*) to promote the formation of a stable carbanion, and when there is a combination of both mesomeric and inductive effects the stability is greatly enhanced.

As these ions are associated with a counter-ion or gegen-ion the solvent has a profound influence. Chain propagation will depend significantly on the separation of the two ions and this separation will also control the mode of entry of an adding monomer. Also, the gegen-ion itself can influence both the rate and stereochemical course of the reaction. While polar and highly solvating media are obvious choices for ionic polymerizations, many cannot be used because they react with and negate the ionic initiators. This is true of the hydroxyl solvents, and even ketones will form stable complexes with the initiator to the detriment of the reaction. As solvents of much lower dielectric constant have to be used, the resulting close proximity of the gegen-ion to the chain end requires that one must treat the propagating species as an *ion pair*, but even in low polarity media such as methylene chloride, ether, THF, nitrobenzene, *etc.*, the ion pair separation can vary sufficiently for the effects to be distinguishable.

Ionic-initiated polymerizations are much more complex than radical reactions. When the chain carrier is ionic, the reaction rates are rapid, difficult to reproduce, and yield high molar mass material at low temperatures by mechanisms which are often difficult to define.

Complications in the kinetic analysis can arise from co-catalyst effects where small quantities of an inorganic compound, such as water, will have an unexpectedly large influence on the polymerization rate.

Initiation of an ionic polymerization can occur in one of four ways involving essentially the loss or gain of an electron $e^-$ by the monomer to produce an ion or radical ion.

| | |
|---|---|
| (a) $M + I^+ \rightarrow MI^+$ | Cationic |
| (b) $M + I^- \rightarrow MI^-$ | Anionic |
| (c) $M + e^- \rightarrow {}^{\cdot}M^-$ | Anionic |
| (d) $M - e^- \rightarrow {}^{\cdot}M^+$ | Cationic (charge transfer) |

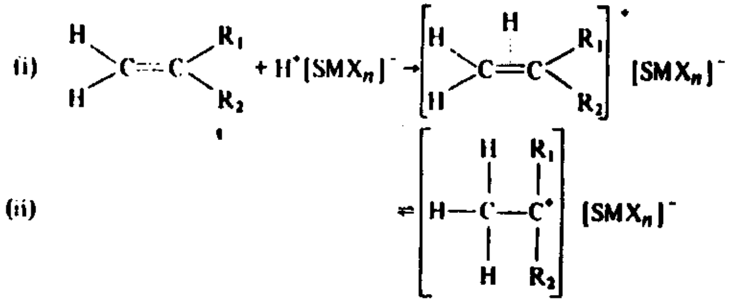
## 4.2 Cationic polymerization

Ionic polymerizations proceed by a chain mechanism and can be dealt with under the general headings that were used for the radical reactions: initiation, propagation, and termination. A common type of cationic initiation reaction is that represented in (a) where $I^+$ is typically a strong Lewis acid. These electrophilic initiators are classed in three groups: (1) classical protonic acids or acid surfaces – $HCl$, $H_2SO_4$, $HClO_4$; (2) Lewis acids or Friedel-Crafts catalysts – $BF_3$, $AlCl_3$, $TiCl_4$, $SnCl_4$; (3) carbonium ion salts.

The most important initiators are the Lewis acids $MX_n$, but they are not particularly active alone and require a co-catalyst SH to act as a proton donor. In general

$$MX_n + SH \rightleftharpoons [SMX_n]^- H^+$$

and a probable initiation mechanism is the two-step process.



Where step one is the rapid formation of a π-complex and step two is a slow intramolecular rearrangement. While the need for a co-catalyst is recognized it is often difficult to demonstrate, and a useful reaction which serves this purpose is the polymerization of isobutylene. This reaction proceeds rapidly when trace quantities of water are present but remains dormant under anhydrous conditions.

The active catalyst - co-catalyst species required to promote this reaction is

$$BF_3 + H_2O \rightleftharpoons H^+[BF_3OH]^-,$$

and the complex reacts with the monomer to produce a carbonium ion chain carrier which exists as an ion pair with $[BF_3OH]^-$.

$$H^+[BF_3OH]^- + (CH_3)_2C{=}CH_2 \rightarrow (CH_3)_3C^+[BF_3OH]^-$$

The type of co-catalyst also influences the polymerization rate because the activity of the initiator complex depends on how readily it can transfer a proton to the monomer. If the polymerization of isobutylene is initiated by $SnCl_4$, the acid strength of the co-catalyst governs the rate, which decreases in the co-catalyst order: acetic acid > nitroethane > phenol > water.

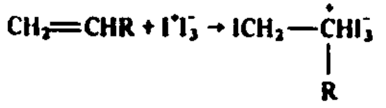
Other types of initiator are less important; thus strong acids protonate the double bond of a vinyl monomer

$$HA + CH_2{=}CR_1R_2 \rightarrow A^-CH_3C^+R_1R_2,$$

while iodine initiates polymerization with the ion pair

$$2I_2 \rightarrow I^+I_3^-$$

which forms a stable $\pi$-complex with olefins such as styrene and vinyl ethers.



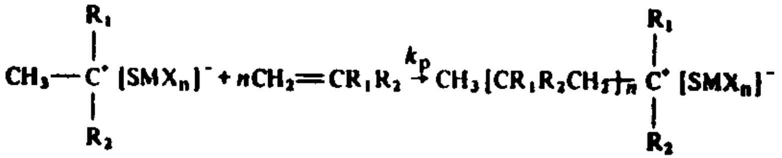
$$CH_2{=}CHR + I^+I_3^- \rightarrow ICH_2{-}\underset{R}{\overset{+}{C}}HI_3^-$$

A recent suggestion that it may be a charge transfer mechanism has not been fully substantiated.

High energy radiation is also thought to produce cationic initiation, but this may lead to fragmentation and a mixture of free radical and cationic centres.

### 4.3 Propagation by cationic chain carriers

Chain growth takes place through the repeated addition of a monomer in a head-to-tail manner, to the carbonium ion, with retention of the ionic character throughout.



$$CH_3{-}\underset{R_2}{\overset{R_1}{C^+}}[SMX_n]^- + nCH_2{=}CR_1R_2 \xrightarrow{k_p} CH_3[CR_1R_2CH_2]_n\underset{R_2}{\overset{R_1}{C^+}}[SMX_n]^-$$

The mechanism depends on the *counterion*, the *solvent*, the *temperature*, and the *type of monomer*. Reactions can be extremely rapid when strong acid initiators such as $BF_3$ are used, and produce long chain polymer at low temperatures. Rates tend to be slower when the weaker acid initiators are used and a polymerization with $SnCl_4$ may take several days. Useful reaction temperatures are in the range 170 to 190 K and both molar mass and reaction rate decrease as the temperature is raised.

Propagation also depends greatly on the position and type of the gegen-ion associated with the chain carrier. The position of the gegen-ion can be altered by varying the dielectric constant of the solvent and large changes in $k_p$ can be obtained as shown in table 4.1 for a perchloric acid initiated polymerization of styrene in several media.

TABLE 4.1. Cationic polymerization of styrene in media of varying dielectric constant $\epsilon$

| *Solvent* | $\epsilon$ | *Catalyst* | $k_p$ <br> $dm^3\ mol^{-1}\ s^{-1}$ |
|---|---|---|---|
| $CCl_4$ | 2.3 | $HClO_4$ | 0.0012 |
| $CCl_4 + (CH_2Cl)_2$ (40/60) | 5.16 | $HClO_4$ | 0.40 |
| $CCl_4 + (CH_2Cl)_2$ (20/80) | 7.0 | $HClO_4$ | 3.20 |
| $(CH_2Cl)_2$ | 9.72 | $HClO_4$ | 17.0 |
| $(CH_2Cl)_2$ | 9.72 | $TiCl_4/H_2O$ | 6.0 |
| $(CH_2Cl)_2$ | 9.72 | $I_2$ | 0.003 |

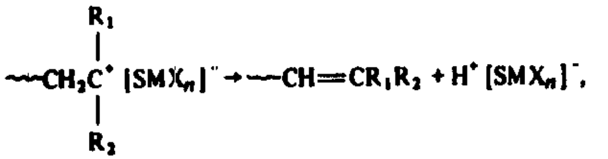
It has been suggested that the various stages of the ionization producing carbonium ions can be represented as

$$\underset{\text{covalent}}{RX} \rightleftharpoons \underset{\text{intimate ion pair}}{R^+X^-} \rightleftharpoons \underset{\text{solvent separated ion pair}}{R^+//X^-} \rightleftharpoons \underset{\text{free ions}}{R^+ + X^-}.$$

The increasing polarity of the solvent alters the distance between the ions from an intimate pair, through a solvent separated pair to a state of complete dissociation. As free ions propagate faster than a tight ion pair, the increase in free ion concentration with change in dielectric constant is reflected in an increase in $k_p$. The separation of the ions also lowers the steric restrictions to the incoming monomer, so that free ions exert little stereo-regulation on the propagation and too great a separation may even hinder reactions which are assisted by co-ordination of the monomer with the metal in the gegen-ion. To the first approximation it can be stated that as the dielectric constant of the medium increases, there is a linear increase in the polymer chain length and an exponential increase in the reaction rate, but in some cases the bulk dielectric of the medium may not determine the effect of the solvent on an ion in its immediate environment. This leads to deviations from the simple picture. The nature of the gegen-ion affects the polymerization rate. Larger and less tightly bound ions lead to larger values of $k_p$, hence a decrease in $k_p$ is observed as the initiator changes from $HClO_4$ to $TiCl_4 . H_2O$ to $I_2$, for the reaction of styrene in 1,2-dichloro-ethane.

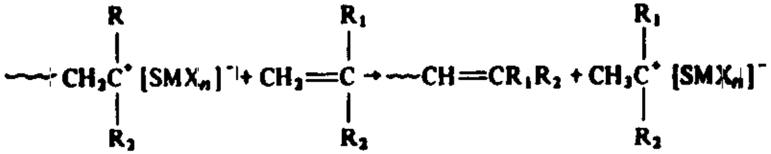
### 4.4 Termination

The termination reaction in a cationic polymerization is less well defined than for the radical reactions, but is thought to take place either by a unimolecular rearrangement of the ion pair



$$\sim\sim CH_2\overset{R_1}{\underset{R_2}{C^+}}\,[SMX_n]^- \rightarrow \sim\sim CH{=}CR_1R_2 + H^+\,[SMX_n]^-,$$

or through a bimolecular transfer reaction with a monomer



$$\sim\sim CH_2\overset{R}{\underset{R_2}{C^+}}\,[SMX_n]^- + CH_2{=}\overset{R_1}{\underset{R_2}{C}} \rightarrow \sim\sim CH{=}CR_1R_2 + CH_3\overset{R_1}{\underset{R_2}{C^+}}\,[SMX_n]^-$$

The first involves hydrogen abstraction from the growing chain to regenerate the catalyst-co-catalyst complex, while the second re-forms a monomer-initiator complex, thereby ensuring that the kinetic chain is not terminated by the reaction. In the unimolecular process, actual covalent combination of the active centre with a catalyst-co-catalyst complex fragment may occur giving two inactive species. This serves to terminate the kinetic chain and reduce the initiator complex and, as such, is a more effective route to reaction termination.

### 4.5 General kinetic scheme

Many cationic polymerizations are both rapid and heterogeneous which makes the formulation of a rigorous kinetic scheme extremely difficult. At best, one of general validity can be deduced, but this should not be applied indiscriminately. Following the steady-state approach outlined for radical reactions, the rate of initiation $\nu_i$ of a cationic reaction is proportional to the catalyst-co-catalyst concentration $c$ and the monomer concentration $[M]$.

$$\nu_i = k_i c[M] \tag{4.1}$$

Termination can be taken as a first-order process in contrast to the free radical mechanisms, and

$$\nu_t = k_t[M^+] \tag{4.2}$$

Under steady-state conditions, $\nu_i = \nu_t$ and

$$[M^+] = k_i c[M]/k_t. \tag{4.3}$$

This gives an overall polymerization rate $\nu_p$ of

$$\nu_p = k_p[M][M^+] = (k_p k_i/k_t)c[M]^2 \tag{4.4}$$

and a chain length of

$$x_n = \nu_p/\nu_t = (k_p/k_t)[M], \tag{4.5}$$

if termination, rather than transfer, is the dominant process. When chain transfer is significant,

$$x_n = k_p/k_{tr}. \tag{4.6}$$

Although not universally applicable, this scheme gives an adequate description of the polymerization of styrene by $SnCl_4$ in ethylene dichloride at 298 K.

### 4.6 Energetics of cationic polymerization

Having established a kinetic scheme, some explanation for the increase in overall rate with decreasing temperature may be forthcoming. The rate is proportional to $(k_i k_p/k_t)$ so the overall activation energy $E$ is given by

$$E = E_i + E_p - E_t, \tag{4.7}$$

and for the chain length

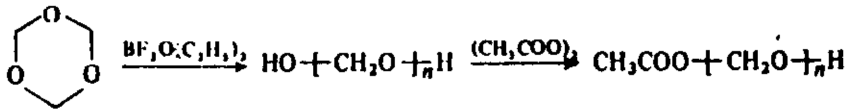
$$E_x = E_p - E_t. \tag{4.8}$$

Propagation in a cationic polymerization requires the approach of an ion to an uncharged molecule in a relatively non-polar medium and as this is an operation with a low activation energy, $E_p$ is much less than $E_i$, $E_t$, or $E_{tr}$. Consequently $E$ is normally in the range −40 to +60 kJ $mol^{-1}$, and when it is negative, the rather unexpected increase in $k_p$ is obtained with decreasing temperature. It should be noted, however, that not all cationic polymerizations have negative activation energies; the polymerizations of styrene by trichloroacetic acid in nitromethane and by 1,2-dichloroethylene have $E$ equal to +57.8 kJ $mol^{-1}$ and +33.6 kJ $mol^{-1}$ respectively.

The chain length, on the other hand, will always decrease as the reaction temperature rises because $E_t$ is always $> E_p$.

### 4.7 Experimental cationic polymerization

A typical cationic reaction can be demonstrated by the polymerization of trioxan to form polyformaldehyde and using boron trifluoride etherate as initiator. The polymer formed can then be stabilized by acetylating the terminal hydroxyl group



with acetic anhydride.

The catalyst solution of $BF_3O(C_2H_5)_2$ (2 $cm^3$) in benzene (40 $cm^3$) is prepared and thoroughly dried over calcium hydride before starting the polymerization. A mixture of cyclohexane (12 $cm^3$), previously dried over calcium hydride, and 10.0 g of trioxan, recrystallized from methylene chloride, is added to a dry test tube. The tube is loosely stoppered and placed in a thermostat bath at 340 K. The catalyst solution (0.15 $cm^3$) is then added to the reaction mixture using a syringe, and the tube recapped. The reaction proceeds rapidly and polymer forms in about 5 min, after which time the bath temperature is lowered to 320 K for about 30 min. The product is separated by filtration and washed with isopropanol containing 10 per cent aqueous ammonia, then dried in *in vacuo* at 330 K overnight. The polyformaldehyde is soluble in dimethyl formamide.

### 4.8 Stable carbonium ions

Many of the uncertainties inherent in Friedel-Crafts catalyst-co-catalyst systems can be removed if stable, well defined, initiators are used. Bawn and his co-workers have made use of triphenyl methyl and tropylium salts of the general formula $Ph_3C^+X^-$ and $C_7H_7^+X^-$ where $X^-$ is a stable anion such as $ClO_4^-$, $SbCl_6^-$, and $PF_6^-$.

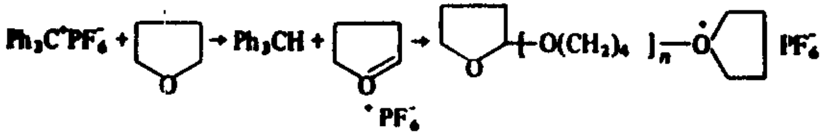
Initiation occurs by one of three mechanisms:

(i) Direct addition: $I^+ + CH_2{=}CHR \rightarrow ICH_2{-}\overset{+}{C}HR$

(ii) Hydride extraction: $I^+ + CH_2{=}CHR \rightarrow IH + CH{=}\overset{+}{C}H{-}R$

(iii) Electron transfer: $I^+ + CH_2{=}CHR \rightarrow I^{\cdot} + {}^{\cdot}[CH_2{=}CHR]^+$

The reaction of trityl hexafluorophosphate and tetrahydrofuran (THF) has been shown to proceed without evidence of a termination reaction and a "living" cationic system can be obtained. The reaction takes place below room temperature.



The effect of the counter-ion is a noticeable factor in the elimination of the termination reaction and neither $SbCl_6^-$ nor any other anion studied has proved as good as $PF_6^-$.

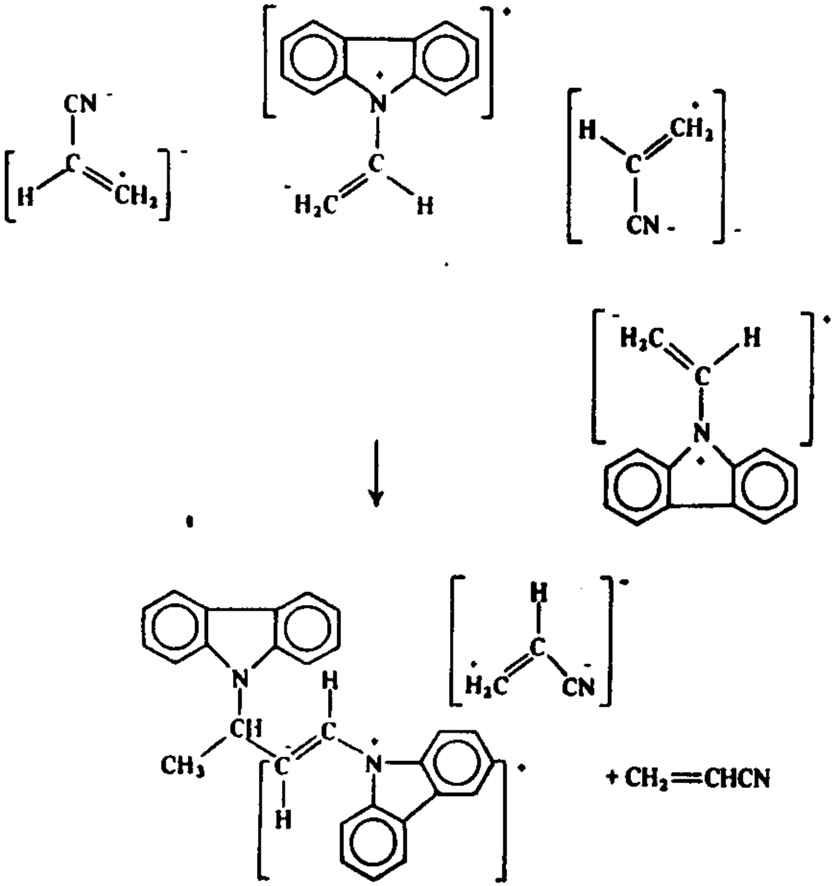
Other similar non-terminating systems have been identified, but the influence of the anion on the efficiency of the system to produce "living" polymers varies from monomer to monomer.

### 4.9 Cationic charge transfer initiation

Initiation of polymerization by mechanism (d) of section 4.1 requires that the monomer concerned is a nucleophile with respect to the electron acceptor which may be a halogen, a metal cation in a high oxidation state, nitrogen peroxide, sulphur dioxide, or an organic molecule with an electrophilic group. The extent of the interaction between the donor D and the acceptor A determines the relative magnitudes of the constants in the equilibria

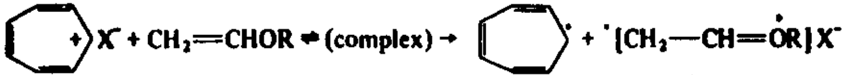
$$D + A \overset{k_1}{\rightleftharpoons} [D\ldots A \leftrightarrow D^{\delta+}\ldots A^{\delta-}] \overset{k_2}{\rightleftharpoons} [D^+A^-] \overset{k_3}{\rightleftharpoons} {}^{\cdot}D^+ + {}^{\cdot}A^-,$$

but the condition $k_1 \gg k_2$, $k_3$ usually predominates, except for powerful donor-acceptor pairs. When the monomer is the donor its character determines the most propitious acceptor to initiate the reaction, thus N-vinyl carbazole can be polymerized in the presence of relatively weak acceptors such as sulphur dioxide, tetrachloroethylene, or acrylonitrile, where the intense colours usually associated with charge-transfer complexes rarely develop. Medium to strong acceptors, *o*-chloroanil, tetranitromethane, *etc.*, can also be used. Ellinger has suggested the following scheme with acrylonitrile as the electrophile and where all charges are actually partial changes.



Vinyl ethers are different because they generally require a much more positive reaction with complete electron transfer to a strong acceptor, *e.g.* $P_2O_5$, triethanolamine, or tetracyanoethylene.

Some initiators may lead to propagation by both radical and cationic mechanisms. Most notable among these are the tropylium salts, studied by Bawn and Ledwith, who have suggested that the salt forms a charge-transfer complex with the monomer. This eventually dissociates to produce a tropyl radical and a monomer cation radical where $X^-$ may be $SbCl_6^-$ or $BF_4^-$.



The cation radical can dimerize or form a di-cation to propagate the chain, although this has not yet been proved conclusively. However, it has been shown that the polymerizations initiated by the tropylium salts are undoubtedly cationic in nature.

## 4.10 Anionic polymerization

The polymerization of monomers with strong electronegative groups – acrylonitrile, vinyl chloride, styrene, and methyl methacrylate – can be initiated by either mechanism (b) or (c) of section 4.1.

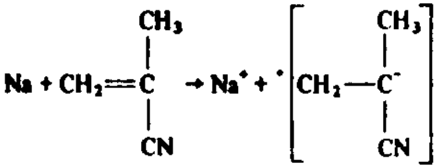
In (b) an ionic or ionogenic molecule is required, capable of adding the anion to the vinyl double bond and so create a carbanion.

$$CX \rightarrow C^+ + X^-$$
$$X^- + M \rightarrow MX^-$$

The gegen-ion $C^+$ may be inorganic or organic and typical initiators include $KNH_2$, *n*-butyl lithium, and Grignard reagents (alkyl magnesium bromides).

If the monomer has a strong electron withdrawing group, then only a weakly positive initiator (Grignard) will be required for polymerization, but when the side group is phenyl or the electronegativity is low, a highly electropositive metal initiator, such as a lithium compound, is needed.

Mechanism (c) is the direct transfer of an electron from a donor to the monomer to form a radical anion. This can be accomplished by means of an alkali metal, and Na or K can initiate the polymerization of butadiene and methacrylonitrile; the latter reaction is carried out in liquid ammonia at 198 K.



$$Na + CH_2{=}\underset{CN}{\overset{CH_3}{C}} \rightarrow Na^+ + {}^{\bullet}\left[CH_2{-}\underset{CN}{\overset{CH_3}{C^-}}\right]$$

The anionic reactions have characteristics similar in many ways to the cationic polymerizations. In general they are rapid at low temperatures but are slower and less sensitive to changes in temperature than the cationic reactions. Reaction rates depend on the dielectric constant of the solvent, the resonance stability of the carbanion, the electronegativity of the initiator, and the degree of solvation of the gegen-ion. Many anionic polymerizations have no formal termination step but are sensitive to traces of impurities and as carbanions are quickly neutralized by small quantities of water, alcohol, carbon dioxide, and oxygen these are effective terminating agents. This imposes the need for rather rigorous experimental procedures to exclude impurities when anionic polymerizations are being studied and a few of these procedures will be mentioned later.

## 4.11 Polymerization of styrene by $KNH_2$

One of the first anionic reactions studied in detail was the polymerization of styrene in liquid ammonia, with potassium amide as initiator, reported by Higginson and Wooding. This serves to illustrate the general mechanism encountered and has the added interest that it is one of the few reactions involving free ions rather than ion pairs. Polymerizations were performed at 240 K in a highly polar medium, liquid ammonia.

Initiation is a two-step process; the dissociation of the potassium amide, first into its constituent ions, followed by addition of the anion to the monomer to create an active chain carrier.

$$KNH_2 \rightleftharpoons K^+ + {:}NH_2^-$$
$${:}NH_2^- + CH_2{=}CHC_6H_5 \xrightarrow{k_i} H_2NCH_2{-}\overset{-}{\underset{..}{C}}HC_6H_5$$

The second step is rate determining so that

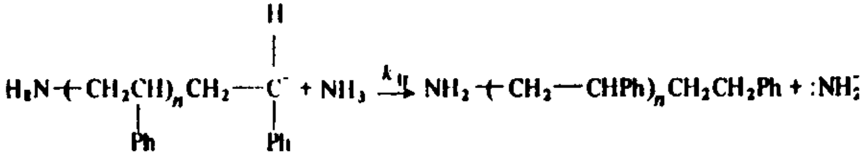
$$v_i = k_i c[M], \qquad (4.9)$$

where $c$ is the concentration of the ion ${:}NH_2^-$.

Propagation is then the usual addition of monomer to the carbanion and the rate is given by

$$v_p = k_p[M][M^-]. \qquad (4.10)$$

Termination of the growing chain occurs when there is transfer to the solvent with regeneration of the amide ion, which is usually capable of initiating another chain



$$H_2N{-}\!\!\left(CH_2\underset{Ph}{CH}\right)_n CH_2{-}\underset{Ph}{\overset{H}{C^-}} + NH_3 \xrightarrow{k_{tr}} NH_2{-}\!\!\left(CH_2{-}CHPh\right)_n CH_2CH_2Ph + {:}NH_2^-$$

The rate of termination is then

$$v_t = k_{tr}[M^-][NH_3]. \qquad (4.11)$$

The assumption of steady-state conditions gives an expression for the concentration of propagating polycarbanions,

$$[M^-] = (k_i/k_{tr})c[M]/[NH_3], \tag{4.12}$$

giving

$$v_p = (k_p k_i/k_{tr})c[M]^2/[NH_3] \tag{4.13}$$

and

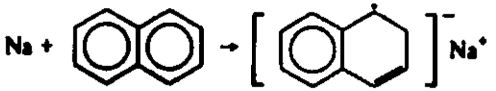
$$x_n = (k_p/k_{tr})[M]/[NH_3]. \tag{4.14}$$

The activation energy for the transfer process is larger than that for propagation and so the chain length decreases with increasing temperature, but as the overall activation energy for the reaction is positive, +38 kJ mol$^{-1}$, the reaction rate decreases with decreasing temperature.

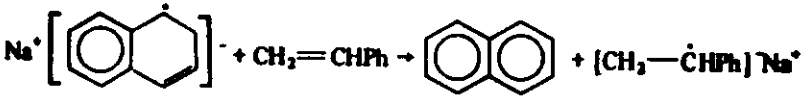
## 4.12 "Living" polymers

The reaction scheme proposed for the initiation with potassium amide contains no formal termination step and if all the impurities which are liable to react with the carbanions are excluded from the system, propagation should continue until all monomer has been consumed, leaving the carbanion intact and still active. This means that if more monomer could be introduced, the active end would continue growing unless inadvertently terminated. These active polycarbanions were first referred to as "living" polymers by Swarc.

One of the first "living" polymer systems studied was the polymerization of styrene initiated by sodium naphthalene. The initiator is formed by adding sodium to a solution of naphthalene in an inert solvent, tetrahydrofuran.



The sodium dissolves to form an addition compound and, by transferring an electron, produces the green naphthalene anion radical. Addition of styrene to the system leads to electron transfer from the naphthyl radical to the monomer to form a red styryl radical anion.



It is thought, a dianion is finally formed capable of propagating from both ends.

$$Na^{+-}[PhCHCH_2CH_2CHPh]^-Na^+$$

Note that the absence of both a termination and a transfer reaction means that if no accidental termination by impurity occurs the chains will remain active indefinitely.

The validity of this assumption has been demonstrated (i) by adding more styrene to the "living" polystyryl carbanions, and (ii) by adding another monomer such as isoprene, to form a block copolymer.

The existence of "living" polymers was originally demonstrated by Swarc using an all-glass apparatus of the type shown in figure 4.1.

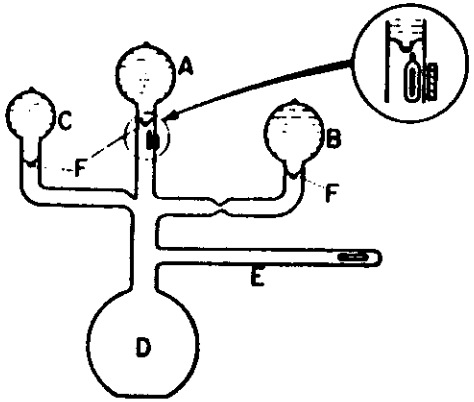


FIGURE 4.1. Apparatus similar to that used by Swarc to demonstrate the existence of "living" polymers. The insert shows the arrangement of the internal and external magnets in relation to a break seal.

The components of the reaction were subjected to stringent purification procedures and sealed in the apparatus under vacuum. The green solution of the initiator, sodium naphthalene, in THF was contained in B and introduced into D by rupturing the break-seal using a glass-encased magnet with a sharp tip, contained in the apparatus. The magnet can be held in position by a second magnet taped in position on the exterior surface of the glass tubing. Pure styrene from C was then admitted to the reactor and an immediate colour change from green to red was observed which persisted after the rapid reaction was complete. The viscosity of the reaction mixture was tested by tipping it into the side arm E, after rotation to the vertical position, and timing the fall of a piece of metal encased in glass, through the medium. The apparatus was returned through 90° to its original position and a fresh solution of styrene in THF, having the same concentration as the reaction mixture, was added from bulb A. A marked increase in viscosity indicated further growth of the existing chains (rather than new ones being formed) and the red colour of the polystyryl ion was retained. In a second experiment, isoprene was contained in bulb A and when added, formed a block copolymer with the styrene. Analysis of the product showed that no polyisoprene was formed, again substantiating the concept of a "living" polymer. The use of "living" polymers is now a standard method of preparing block copolymers as well as the more unusual star-shaped and comb-branched polymers.

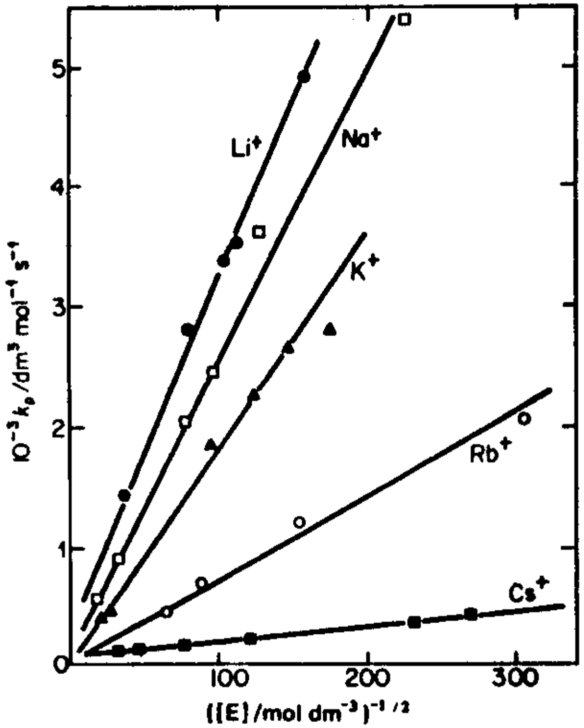
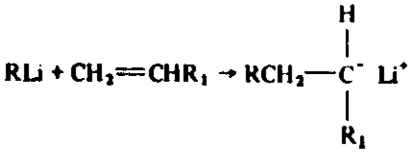


**FIGURE 4.2.** Behaviour of the experimental propagation rate constant $k_p$ as a function of the concentration [E] of "living ends" for various salts of "living" polystyrene in tetrahydrofuran at 298 K. (From data by Swarc.)

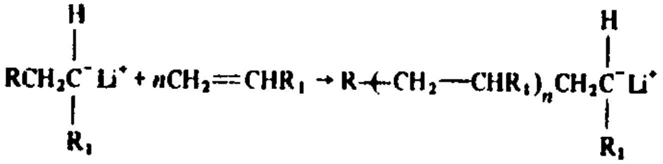
### 4.13 Metal alkyl initiators

The organo-lithium derivatives, such as *n*-butyl lithium, are particular members of this group of electron deficient initiators. In general, the initiation involves addition to the double bond of the monomer



$$RLi + CH_2{=}CHR_1 \rightarrow RCH_2{-}\underset{R_1}{\overset{H}{C^-}}\ Li^+$$

and propagation is then



$$RCH_2\underset{R_1}{\overset{H}{C^-}}\ Li^+ + nCH_2{=}CHR_1 \rightarrow R{-}(CH_2{-}CHR_1)_nCH_2\underset{R_1}{\overset{H}{C^-}}\ Li^+$$

Kinetic analysis of the reactions shows that the initiation is not a simple function of the basicity of R, however, owing to the characteristic tendency for organo-lithium compounds to associate and form tetramers or hexamers. The kinetics are usually complicated by this feature, which is solvent dependent, and consequently fractional reaction orders are commonplace.

The alkyl lithiums have proved commercially useful in diene polymerization and some steric control over the polymerization can be obtained.

### 4.14 Solvent and gegen-ion effects

Both the solvent and the gegen-ion have a pronounced influence on the rates of anionic polymerizations. The polymerization rate generally increases with increasing polarity of the solvent, for example, $k_p = 2.0$ dm$^3$ mol$^{-1}$ s$^{-1}$ for the anionic polymerization of styrene in benzene, but $k_p = 3800$ dm$^3$ mol$^{-1}$ s$^{-1}$ when the solvent is 1,2-dimethoxyethane.

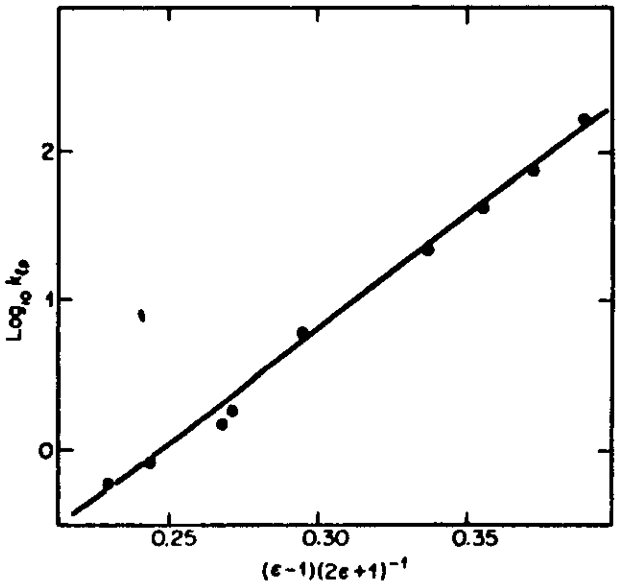


FIGURE 4.3. The propagation rate constant $k_{lp}$ for the polystyryl-lithium ion pair plotted as a function of the dielectric constant of the reaction medium. (Adapted from Bywater and Worsfold.)

# Step-growth Polymerization

The classical subdivision of polymers into two main groups was made around 1929 by W. H. Carothers, who proposed that a distinction be made between polymers prepared by the stepwise reaction of monomers and those formed by chain reactions. These he called:
(1) *Condensation polymers*, characteristically formed by reactions involving the elimination of a small molecule, such as water, at each step; and
(2) *Addition polymers*, where no such loss occurred.

While these definitions were perfectly adequate at the time, it soon became obvious that notable exceptions existed and that a fundamentally sounder classification should be based on a description of the chain growth mechanism. It is preferable to replace the term condensation with step-growth or step-reaction. Reclassification as *step-growth* polymerization, now logically includes polymers such as polyurethanes, which grow by a step reaction mechanism without elimination of a small molecule.

In this chapter we shall examine the main features of step-growth polymerization, beginning with the simpler reactions which produce linear chains exclusively. This type of polymerization is used to produce some of the industrially important fibres such as the nylons and terylene. A brief discussion of the more complex branching reactions follows to illustrate how the thermosetting plastics are formed.

## 2.1 General reactions

In any reaction resulting in the formation of a chain or network of high molar mass, the functionality (see section 1.3) of the monomer is of prime importance. In step-growth polymerization, a linear chain of monomer residues is obtained by the stepwise intermolecular condensation or addition of the reactive groups in bifunctional monomers. These reactions are analogous to simple reactions involving monofunctional units as typified by a polyesterification reaction involving a diol and a dibasic acid,

$$\mathrm{HO{-}R{-}OH + HOOC{-}R'{-}COOH = HO{-}R{-}OCO{-}R'{-}COOH + H_2O}$$

If the water is removed as it is formed, no equilibrium is established and the first stage in the reaction is the formation of a dimer which is also bifunctional. As the reaction proceeds, longer chains, trimers, tetramers, and so on, will form through other esterification reactions, all essentially identical in rate and mechanism, until ultimately the reaction contains a mixture of polymer chains of large molar masses $M$. However, the formation of samples with significantly large values of $M$ is subject to a number of rather stringent conditions which will be examined in greater detail later in this chapter.

Two major groups, both distinguished by the type of monomer involved, can be identified in step-growth polymerization. In the first group two polyfunctional monomers take part in the reaction, and each possesses only one distinct type of functional group as in the esterification reaction, or more generally:

$$\mathrm{A{-}A + B{-}B \rightarrow \!\!\left( A{-}AB{-}B \right)\!\!}$$

The second group is encountered when the monomer contains more than one type of functional group such as a hydroxyacid (HO—R—COOH), represented generally as A—B where the reaction is

$$n\mathrm{A{-}B} \rightarrow -\!\!\left( \mathrm{AB} \right)\!\!-_n$$

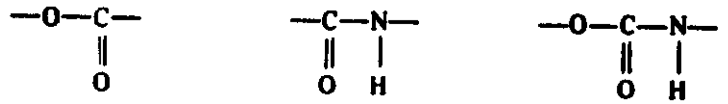
or

$$n(\mathrm{HO{-}R{-}COOH}) \rightarrow \mathrm{H}\!\left( \mathrm{ORCO} \right)_{n}\mathrm{OH}.$$

A large number of step growth polymers have the basic structure

$$-\square-\mathrm{R}-\square-\mathrm{R}-\square-\mathrm{R}-$$

where R can be $\left(\mathrm{CH_2}\right)_x$ or  and the link $-\square-$ is one of three important groups:



$$\underset{\text{ester}}{-\mathrm{O}-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-} \qquad \underset{\text{amide}}{-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\underset{\underset{\mathrm{H}}{|}}{\mathrm{N}}-} \qquad \underset{\text{urethane}}{-\mathrm{O}-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\underset{\underset{\mathrm{H}}{|}}{\mathrm{N}}-}$$

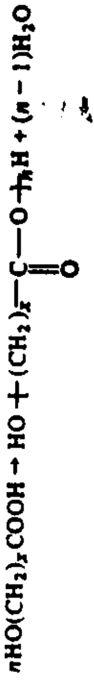
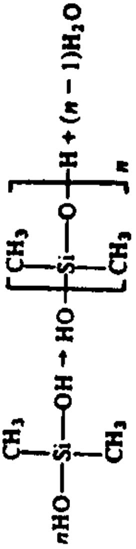
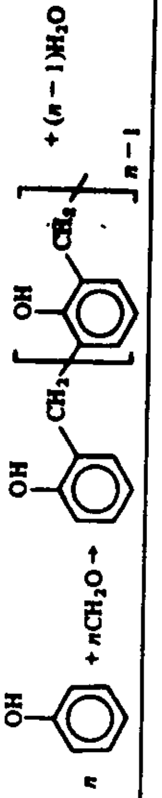
ester amide urethane

Other links and groups are involved in these reactions and some typical step-reaction polymers are shown in table 2.1.

## 2.2 Reactivity of functional groups

One basic simplifying assumption proposed by Flory, when analysing the kinetics of step-growth systems, was that all functional groups can be considered

**TABLE 2.1. Typical step-growth polymerization reactions**

| *Polymer* | *Reaction* |
|---|---|
| Polyester |  $n\mathrm{HO(CH_2)_xCOOH \rightarrow HO{+}(CH_2)_x{-}\underset{\underset{O}{\|}}{C}{-}O{+}_nH + (n-1)H_2O}$ |
| Polyamide | $n\mathrm{NH_2{-}R{-}COOH \rightarrow H{+}NH{-}R{-}CO{+}_nOH} + (n-1)\mathrm{H_2O}$<br>$n\mathrm{NH_2{-}R{-}NH_2} + n\mathrm{HOOC{-}R'{-}COOH \rightarrow H{+}NH{-}R{-}NHCO{-}R'{-}CO{+}OH} + (2n-1)\mathrm{H_2O}$ |
| Polyurethanes | $n\mathrm{HO{-}R{-}OH + OCN{-}R'{-}NCO \rightarrow {+}OR{\cdot}O{\cdot}CONH{-}R'{-}NH{\cdot}CO{+}_n}$ |
| Polyanhydride | $n\mathrm{HOOC{-}R{-}COOH \rightarrow HO{+}OC{-}R{-}CO{\cdot}O{+}_nH} + (n-1)\mathrm{H_2O}$ |
| Polysiloxane |  $n\mathrm{HO{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}OH \rightarrow HO}\left[\mathrm{\underset{CH_3}{\overset{CH_3}{Si}}{-}O}\right]_n\mathrm{H} + (n-1)\mathrm{H_2O}$ |
| Phenol-formaldehyde |  |

monomer or polymer species with equal ease.

The progress of the reaction can be illustrated in figure 2.1 where after 25 per cent reaction the number average chain length $x_n$ is still less than two because monomers, being the most predominant species, will tend to react most often, and the reaction is mainly the formation of dimers and trimers. Even after 87.5 per cent of the reaction $x_n$ will only be about eight and it becomes increasingly obvious that if long chains are required, the reaction must be pushed towards completion.

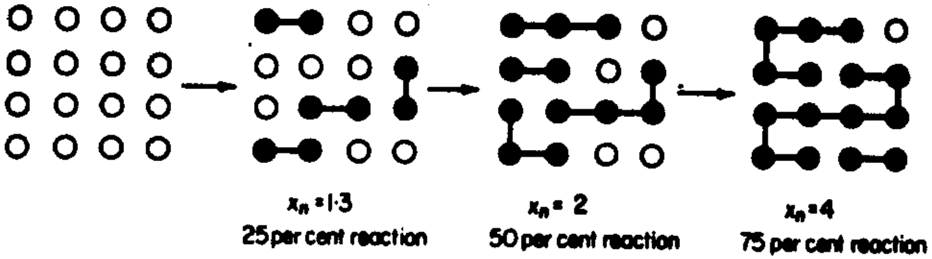


FIGURE 2.1. Diagrammatic representation of a step-growth polymerization.

### 2.3 Carothers equation

W. H. Carothers, the pioneer of step-growth reactions, proposed a simple equation relating $x_n$ to a quantity $p$ describing the extent of the reaction for linear polycondensations or polyadditions.

If $N_0$ is the original number of molecules present in an A–B monomer system and $N$ the number of all molecules remaining after time $t$, then the total number of functional groups of either A or B which have reacted is $(N_0 - N)$. At that time $t$ the extent of reaction $p$ is given by

$$p = (N_0 - N)/N_0 \quad \text{or} \quad N = N_0(1 - p). \tag{2.1}$$

If we remember that $x_n = N_0/N$, a combination of expressions gives the *Carothers equation*,

$$x_n = 1/(1 - p). \tag{2.2}$$

This equation is also valid for an A–A + B–B reaction when one considers that in this case there are initially $2N_0$ molecules.

The Carothers equation is particularly enlightening when we examine the numerical relation between $x_n$ and $p$; thus for $p = 0{\cdot}95$ (*i.e.* 95 per cent conversion), $x_n = 50$ and when $p = 0.99$, then $x_n = 100$. In practical terms, it has been

$(CH_2)_4CO \}_n$ the value of $M_n$ has to be about 12000 to 13 000 g $mol^{-1}$ if a high tenacity fibre is to be spun, and as this corresponds to $x_n = 53$ to 58, the polymerization has to proceed beyond 95 per cent completion. Similarly for polyesters derived from ω-hydroxydecanoic acid, $H\{O(CH_2)_9CO\}_nOH$, $x_n$ of about 150 is optimum for good fibres and so $p$ must exceed 0.99.

### 2.4 Control of the molar mass

Quite obviously the control of the molar mass of the product of these reactions is very important. Very high molar mass material may be too difficult to process, while low molar mass polymer may not exhibit the properties desired in the end product, and one must be able to stop the reaction at the required value of $p$. Consequently the reactions are particularly demanding with respect to the purity of the reagents and accurate control of the amount of each species in the mixture is cardinal. It is symptomatic of these critical requirements that only four types of reaction usefully produce linear polymers with $M_n > 25000$ g $mol^{-1}$.

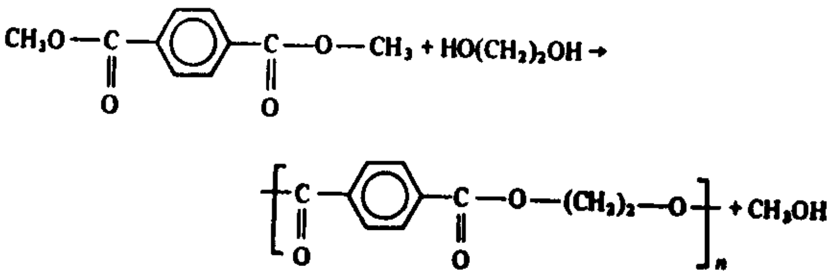
(1) *Schotten-Baumann reaction.* This involves the use of an acid chloride in an esterification or amidation; for example the so-called "nylon rope trick" reaction is an interfacial condensation between sebacoyl chloride and hexamethylenediamine, producing a polyamide known as nylon-6,10.

$$nClCO(CH_2)_8COCl + nH_2N(CH_2)_6NH_2 \rightarrow \{CO(CH_2)_8CONH(CH_2)_6NH\}_n + (2n-1)HCl$$

The bifunctional acyl chloride is dissolved in $CCl_4$ and placed in a beaker. An aqueous alkaline solution of the bifunctional amine is layered on top and the nylon-6,10 which forms immediately at the interface can be drawn off as a continuous filament until the reagents are exhausted. The reaction has an $S_N2$ mechanism with the release of a proton to the base in the aqueous phase; the condensation is a successive stepwise reaction by this $S_N2$ route.

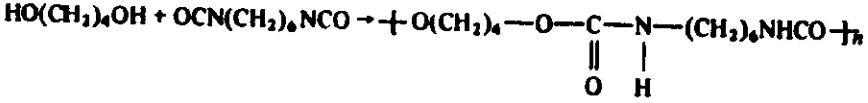
(2) *Salt dehydration.* Direct esterification requires high purity materials in equimolar amounts because esterifications rarely go beyond 98 per cent completion in practice. To overcome this, hexamethylene diamine and a dibasic acid such as adipic acid can be reacted to produce a nylon salt, hexamethylene diammonium adipate. A solution of 0.5 mol diamine in a mixture of 95 per cent ethanol (160 $cm^3$) and distilled water (60 $cm^3$) is added to 0.5 mol diacid dissolved in 600 $cm^3$ of 95 per cent ethanol over a period of 15 min. The mixture is stirred for 30 min during which time the nylon salt precipitates as a white crystalline solid. This can be recrystallized and should melt at 456 K. The pure salt can be converted into a polyamide by heating it under vacuum in a sealed tube, protected by wire gauze, at about 540 K in the presence of a small quantity of the diacid, *e.g.* 10 g salt to 0.55 g adipic acid is a suitable mixture. If a lower molar mass is desired, a monofunctional acid can replace the adipic acid and act as a chain terminator.

(3) *Ester interchange.* An alternative reaction is a trans-esterification in the presence of a proton donating or weak base catalyst such as sodium methoxide, *e.g.*



In this way ethylene glycol and dimethyl terephthalate produce terylene. Ester interchange is the most practical approach to polyester formation because of the faster reaction rate and use of more easily purified products. The formation of poly(ethylene terephthalate) is essentially a two-stage process. The first stage, at 380 to 470 K, is the formation of dimers and trimers, each with two hydroxyl end-groups, and during this formation the methanol is being distilled off. To complete the reaction the temperature is raised to 530 K and condensation of these oligomers produces a polymer with large $M_n$. The major advantage is that the stoichiometry is self-adjusting in the second stage.

(4) *Step polyaddition* (*Urethane formation*). Polyurethanes with large $M_n$ can be prepared using a method based on the Wurtz alcohol test. In the presence of a basic catalyst, such as a diamine, ionic addition takes place, for example between 1,4-butanediol and 1,6-hexanediisocyanate:



$$HO(CH_2)_4OH + OCN(CH_2)_6NCO \rightarrow \{O(CH_2)_4-O-\underset{\underset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-(CH_2)_6NHCO\}_n$$

This reaction produces a highly crystalline polymer, but a vast number of urethanes can be formed by varying the reactants and a series of polymers covering a wide spectrum of properties can be prepared.

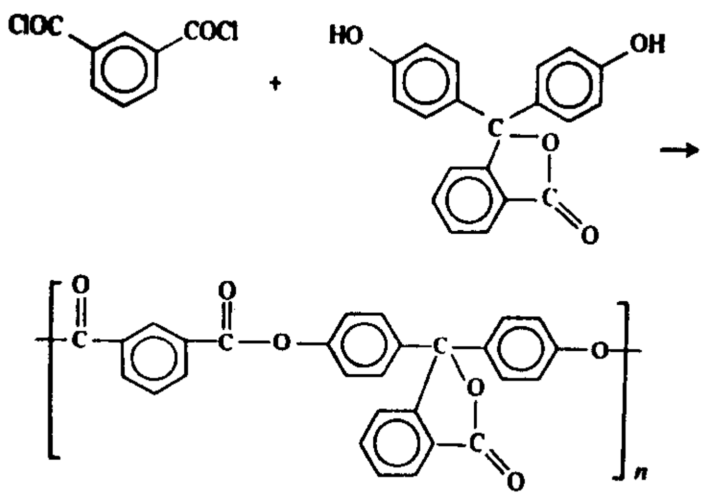
### 2.5 Stoichiometric control of $M_n$

Often it is preferable to avoid production of high molar mass polymer and control can be effected by rapidly cooling the reaction at the appropriate stage or by adding calculated quantities of monofunctional materials as in the preparation of nylon-6,6 from the salt.

More usefully, a precisely controlled stoichiometric imbalance of the reactants in the mixture can provide the desired result. For example, an excess of diamine over an acid chloride would eventually produce a polyamide with two amine of further growth when the acid chloride was totally consumed. This can be expressed in an extension of the Carothers equation as,

$$x_n = (1 + r)/(1 + r - 2rp), \tag{2.3}$$

where $r$ is the ratio of the number of molecules of the reactants. Thus for a quantitative reaction ($p = 0.999$) between $N$ molecules of phenolphthalein and $1.05N$ molecules of terephthaloyl chloride to form poly(terephthaloyl phenolphthalein)



The value of $r = N_{AA}/N_{BB} = 1/1.05 = 0.952$

and $x_n = (1 + 0.952)/(1 + 0.952 - 2 \times 0.999 \times 0.952) \approx 39$,

rather than 1000 for $r = 1$. This reaction is an interfacial polycondensation whose progress may be followed by noting the colour change from the red phenolphthalein solution to the colourless polyester. The interface can remain stationary in the experiment but the uniformity of the polymer is improved by increasing the reaction surface using high-speed stirring.

The corresponding equation for a monofunctional additive is similar to equation (2.3) only now $r$ is defined as the ratio $N_{AA}/(N_{BB} + 2N_B)$ where $N_B$ is the number of monofunctional molecules added.

### 2.6 Kinetics

The assumption that functional group reactivity is independent of chain length can be verified kinetically by following a polyesterification. The simple esterification is an acid catalysed process where protonation of the acid is followed by interaction with the alcohol to produce an ester and water. If significant polymer formation is to be achieved, the water must be removed continuously from the reaction to displace the equilibrium and the water eliminated can be used to estimate the extent of the reaction. Alternatively the rate of disappearance of carboxylic groups can be measured by titrating aliquots of the mixture.

A typical apparatus is shown in figure 2.2 consisting of a reaction kettle, a Dean and Stark trap to collect the water, a stirrer, $N_2$ inlet, and thermometer. The reaction can be illustrated using ethylene glycol and adipic acid. A mixture of decalin (35 cm$^3$) and adipic acid (1 mol) is placed in the kettle and the trap is filled with decalin. The mixture is heated to 420 K and glycol (1 mol), preheated to this temperature, is added, followed by an acid catalyst such as $p$-toluene sulphonic acid (1 mmol.). Nitrogen is bubbled rapidly through the mixture which is quickly raised to reflux temperature. The water level in the trap is noted at regular intervals and small aliquots of the reaction mixture can be withdrawn, weighed, diluted with acetone, and titrated with methanolic KOH. If an activation energy is required, the temperature can be raised several times and the reaction followed for a time at each new temperature.

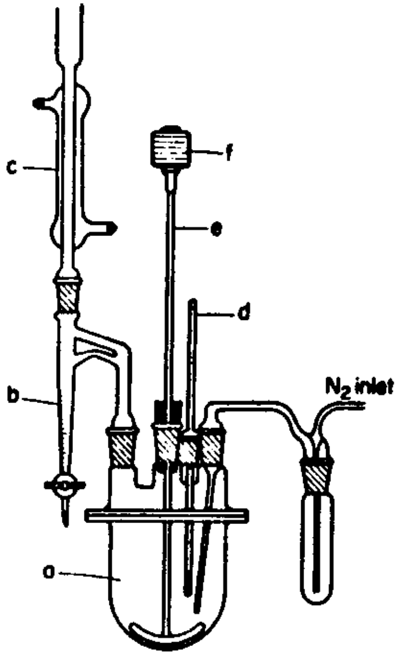


FIGURE 2.2. Apparatus suitable for polycondensation reactions: a, the reaction kettle; b, Dean and Stark trap; c, condenser; d, thermometer; e, stirrer; f, stirring motor.

*Self-catalysed reaction.* If no acid catalyst is added, the reaction will still proceed because the acid can act as its own catalyst. The rate of condensation at any time $t$ can then be derived from the rate of disappearance of —COOH groups and

$$-\mathrm{d}[\mathrm{COOH}]/\mathrm{d}t = k[\mathrm{COOH}]^2[\mathrm{OH}]. \tag{2.4}$$

The second order [COOH] term arises from its use as a catalyst and $k$ is the rate constant. For a system with equivalent quantities of acid and glycol the functional group concentration can be written simply as $c$ and

$$-\mathrm{d}c/\mathrm{d}t = kc^3 \tag{2.5}$$

This expression can be integrated under the conditions that $c = c_0$ at time $t = 0$ and

$$2\,kt = 1/c^2 - 1/c_0^2. \tag{2.6}$$

The water formed is removed and can be neglected. From the Carothers equation it follows that $c = c_0(1-p)$, leading to the final form

$$2c_0^2kt = 1/(1-p^{e})^{2} - 1. \tag{2.7}$$

*Acid-catalysed reaction.* The uncatalysed reaction is rather slow and a high $x_n$ is not readily attained. In the presence of a catalyst there is an acceleration of the rate and the kinetic expression is altered to

$$-\mathrm{d}[\mathrm{COOH}]/\mathrm{d}t = k'[\mathrm{COOH}][\mathrm{OH}], \tag{2.8}$$

which is kinetically first order in each functional group. The new rate constant $k'$ is then a composite of the rate constant $k$ and the catalyst concentration which also remains constant. Hence

$$-\mathrm{d}c/\mathrm{d}t = k'c^2, \tag{2.9}$$

and integration gives finally

$$c_0k't = 1/(1-p) - 1. \tag{2.10}$$

Both equations have been verified experimentally by Flory as shown in figure 2.3.

## 2.7 Molar mass distribution in linear systems

The creation of long chain polymers by the covalent linking of small molecules is a random process, leading to chains of widely varying lengths. Because of the random nature of the process, the distribution of chain lengths in a sample can be arrived at by simple statistical arguments.

The problem is to calculate the probability of finding a chain composed of $x$ basic structural units in the reaction mixture at time $t$, for either of the two reactions

$$x\,\mathrm{A{-}A} + x\,\mathrm{B{-}B} \rightarrow \mathrm{A{-}A}[\mathrm{B{-}BA{-}A}]_{x-1}\mathrm{B{-}B},$$

$$\text{or } x\,\mathrm{A{-}B} \qquad \rightarrow \mathrm{A}\!+\!\mathrm{BA}\!+_{x-1}\!\mathrm{B},$$

*i.e.* to calculate the probability that a functional group A or B has reacted. For the sake of clarity we can consider one of the functional groups to be carboxyl and determine the probability that $(x-1)$ carboxyl groups have reacted to form a chain. This is $p^{x-1}$, where $p$ is the extent of the reaction, defined in equation (2.1).

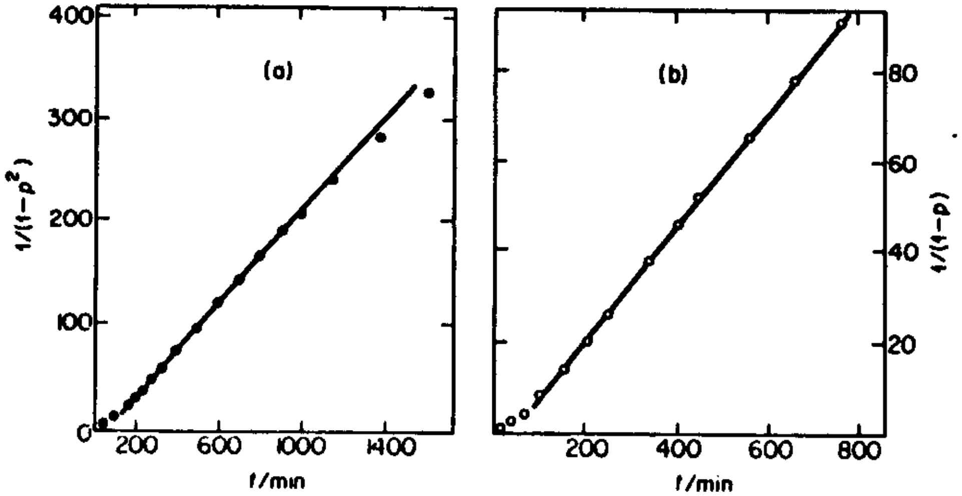


FIGURE 2.3. (a) Self-catalysed polyesterification of adipic acid with ethylene glycol at 439 K; (b) polyesterification of adipic acid with ethylene glycol at 382 K, catalysed by 0.4 mole per cent of $p$-toluene sulphonic acid. (From data by Flory.)

It follows that if a carboxyl group remains unreacted the probability of finding this uncondensed group is $(1-p)$ and so the probability $P_x$ of finding one chain $x$ units long (*i.e.* an $x$-mer) is

$$P_x = (1-p)p^{x-1}. \tag{2.11}$$

As the fraction of $x$-mers in any system equals the probability of finding one; the total number $N_x$ present is given by

$$N_x = N(1-p)p^{x-1}, \tag{2.12}$$

where $N$ is the total number of polymer molecules present in the reaction. Substitution of the Carothers equation (2.2) gives

$$N_x = N_0(1-p)^2p^{x-1}, \tag{2.13}$$

where $N_0$ is the total number of monomer units present initially. The variation of $N_x$ for various values of $p$ and $x$ is shown in figure 2.4. A slightly different set of curves is obtained if the composition is expressed in terms of mass fraction $w$, in this case $w_x = xN_x/N_0$ to give

$$w_x = x(1-p)^2 p^{x-1}, \qquad (2.14)$$

Both reveal that very high conversions are necessary if chains of significant size are to be obtained and that while monomer is normally the most numerous species, the proportion of low molar mass material decreases as $p$ exceeds 0.95.

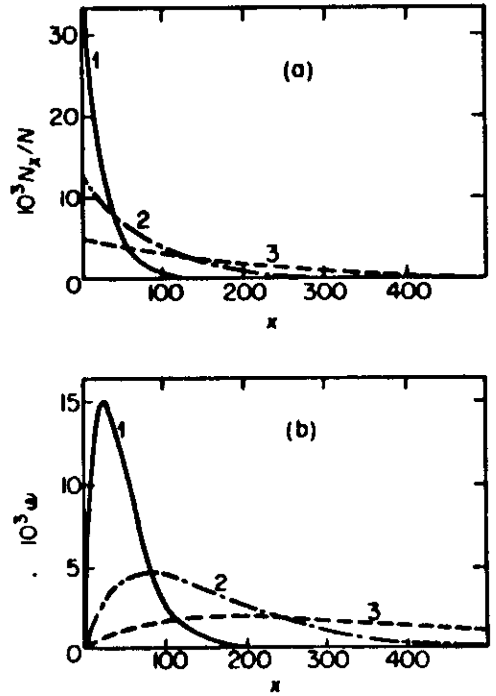


FIGURE 2.4. (a) Number fraction distribution curves for linear step growth polymerizations. Curve 1, $p = 0.9600$; Curve 2, p = 0.9875; Curve 3, $p = 0.9950$. (b) Corresponding weight fraction distributions for the same system.

### 2.8 Average molar masses

Number and weight average molar masses can be calculated from the equations if $M_0$ is taken as the molar mass of the repeat unit. Thus

$$M_n = N_x \Sigma(M_0 N_x)/N = M_0/(1-p), \qquad (2.15)$$

and

$$M_w = M_0(1+p)/(1-p). \qquad (2.16)$$

It can be seen that a heterogeneity index ($M_w/M_n$) for the most probable distribution when $p = 1$ is

$$(M_w/M_n) = \{M_0(1+p)/(1-p)\}\{(1-p)/M_0\} = 2. \qquad (2.17)$$

### 2.9 Characteristics of step-growth polymerization

It might be appropriate at this stage to summarize the main features of the step-reactions.

(1) Any two molecular species in the mixture can react.

(2) The monomer is almost all incorporated in a chain molecule in the early stages of the reaction, *i.e.* about 1 per cent of monomer remains unreacted when $x_n = 10$. Hence polymer yield is independent of the reaction time in the later stages.

(3) Initiation, propagation, and termination reactions are essentially identical in rate and mechanism.

(4) The chain length increases steadily as the reaction proceeds.

(5) Long reaction times and high conversions are necessary for the production of a polymer with large $x_n$.

(6) Reaction rates are slow at ambient temperatures, but increase with a rise in temperature although this has little effect on the chain length of the final product.

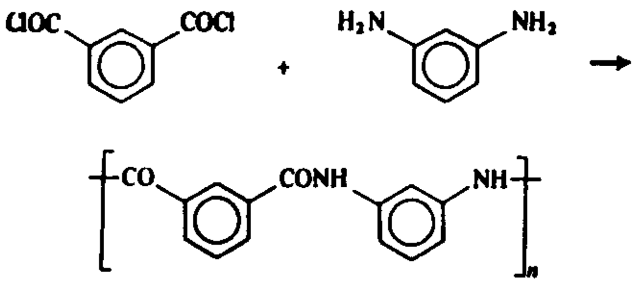
(7) Activation energies are moderately high and reactions are not excessively exothermic.

### 2.10 Typical step-growth reactions

Reactions are normally carried out in bulk in the temperature range 420 to 520 K to encourage fast reactions and promote the removal of the low molar mass condensation product. Activation energies are about 80 kJ mol$^{-1}$.

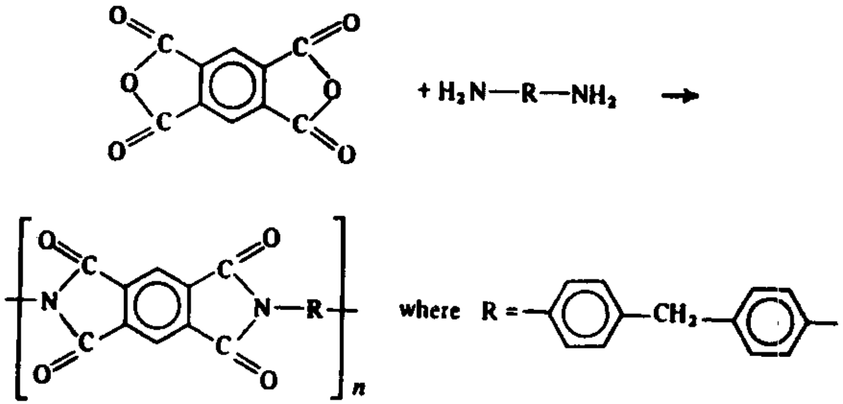
*Low temperature polycondensations.* The advantages of high temperature reactions are partly counteracted by the increasing danger of side-reactions, and room temperature reactions using highly energetic reactants provide routes to a variety of polymers. The use of the Schotten–Baumann reaction for polyamides has already been outlined. This is an example of an unstirred interfacial reaction in which the diamine is soluble in both phases and diffuses across the interface into the organic layer where polymerization takes place. Continuous polymer production is achieved by withdrawing the film formed at the interface to allow continued diffusion of the reactants. Alternatively, the continuity of the polymerization reaction can be maintained by stirring the system vigorously; this ensures a constantly changing interface and increases the surface area available for the reaction. As both methods are diffusion controlled the need for stringent stoichiometric control is obviated.

When the diamine used is aromatic only low molar mass polymer is formed because of the lower reaction rates. To produce longer chains, conditions must be readjusted so that both phases are polar and miscible and vigorous high-speed stirring of the system is necessary. This is used in the reaction between isophthaloyl chloride and *m*-phenylene diamine,



These aromatic polyamides are particularly versatile materials and of considerable interest.

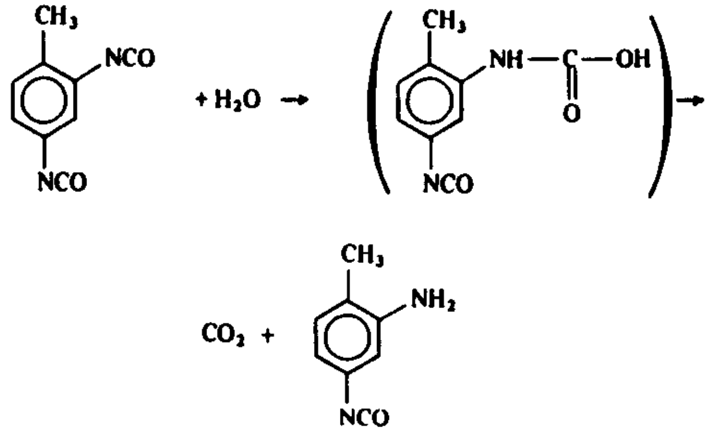
The ultimate extension to a homogeneous system with inert polar solvents is used in the synthesis of polyimides. Poly(methylene 4,4'-diphenylene pyromellitamide acid) is prepared by mixing equal amounts of pyromellitic dianhydride and bis(4-aminophenyl methane) in N,N'-dimethylformamide



The reaction is maintained at 288 K, with stirring, for an hour and the polymer is isolated by precipitation in vigorously stirred water.

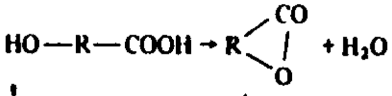
Polysulphonamides, polyanhydrides, and polyurethanes can also be formed in homogeneous low temperature reactions.

*Polyurethanes.* An important and versatile family of polymers, whose diverse uses include foams, fibres, elastomers, adhesives, and coatings, is formed by the interaction of diisocyanates with diols to give chains with the characteristic $+\!\mathrm{NHCOO}\!+$ link. Unfortunately the polymerizations are prone to side-reactions and an excess of the diisocyanate is often necessary initially to react with impurities in the system. Property variations in the product can be obtained through a suitable choice of starting materials. Thus high melting temperature compounds can be prepared if phenyl groups are incorporated in the chain by using biphenylene diisocyanate, whereas flexible elastomeric chains are formed if long $+\!\mathrm{CH_2}\!+_x$ sequences are present. The side-reaction of the isocyanate group with water can be utilized to make foams. Liberation of $CO_2$ in a viscous polymerizing medium blows it up into an expanded cellular form; the rigidity or flexibility of the foam can be controlled by the chain flexibility of the polymer, and foam density by the amount of $CO_2$ liberated.



## 2.11 Ring formation

The assumption so far has been that all bifunctional monomers in step-growth reactions form linear polymers. This is not always true and competitive side reactions such as cyclization may occur, as with certain hydroxyacids which may form lactones, or lactams if an amino acid is used.



$$\mathrm{HO—R—COOH} \rightarrow \mathrm{R}\langle{}^{\mathrm{CO}}_{\mathrm{O}}\rangle + \mathrm{H_2O}$$

lactone

To gauge the importance of such reactions consideration must be given to the thermodynamic and kinetic aspects of ring formation. A study of ring strain in cycloalkanes has shown that 3 and 4 membered rings are severely strained but that this decreases dramatically for 5, 6, or 7 membered rings, then increases again up to 11 before decreasing for very large rings. In addition to the thermodynamic stability, the kinetic feasibility of two suitable functional groups being in juxtaposition to react must also be considered. This probability decreases with increasing ring size and again 5, 6, or 7 membered rings are favoured and will form in preference to a linear chain when possible.

### 2.12 Ring opening polymerizations

In contrast to ring formation, an important group of polymer producing reactions involve ring opening. The kinetics are similar to step-growth and the reactions are sometimes called step-addition, but in most cases a catalyst is required. An important example is the polymerization of ε-caprolactam to give nylon-6. The reaction is catalysed by water, at 520 K, but will also proceed in the presence of a strong base such as an alkali metal or metal amide. With HC.

as catalyst, a series of cyclic lactams showed the following reaction rates of linear polymerization: 8 > 7 > 11 ≫ 5 or 6 membered rings. Similarly lactones will polymerize when treated with aqueous alkaline solutions but the 5 and 6 membered rings are resistant to cleavage and polymer formation.

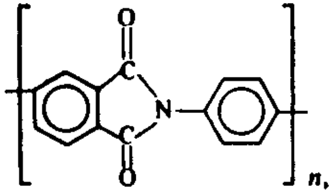
### 2.13 High temperature polymers

While many of the more common polymers are remarkably resistant to chemical attack and are stable when subjected to mechanical deformation, few can withstand the destructive effects of intense heat. Recent work has centred on the synthesis of chains incorporating: (i) thermally unreactive aromatic rings; (ii) resonance stabilized systems; (iii) crosslinked "ladder" structures; and (iv) protective side groups in an attempt to improve the thermal stability.

These approaches have met with considerable success. Aromatic polycarbonates, polyethers, and polysulphones are useful in situations where drastic temperature fluctuations are encountered but they are still only stable up to about 570 K and beyond this most fail.

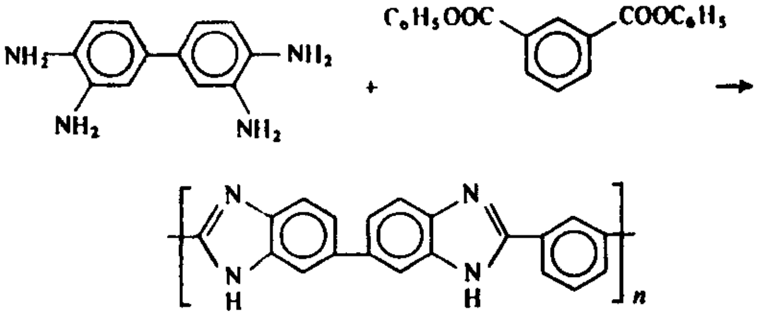
For greater temperature stability different ring systems have been tried. Fibres from aromatic polyamides are capable of maintaining about 50 per cent of the ambient tensile strength when heated to 550 K. They also have the added advantage that they are extremely difficult to ignite and can be used to make excellent fire resistant clothing.

The polyimides

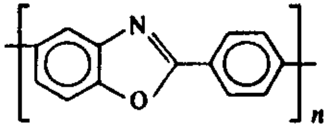


prepared in low temperature polycondensation reactions, constitute a further group some of whose members can withstand temperatures of up to 800 K. These are used in high temperature environments where lubricants cannot be used and are produced as sleeve bearings, valve seatings, and compressor vanes in jet engines. They are also excellent insulators but suffer from the disadvantage that they are normally intractable in common organic solvents and present manufacturing difficulties.

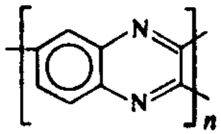
This problem is not met with in the polybenzimidazoles; these polymers are soluble yet retain their characteristic high temperature resistance and good mechanical response. They can be prepared in a two phase melt condensation reaction involving the diphenyl ester of a dibasic acid and a tetra-functional amine, *e.g.* polybenzimidazole,



This is an example of a semi-ladder polymer and the polybenzoxazoles

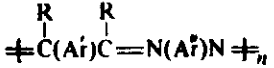


and polyquinoxalines



also fall into this category.

These structures derive their thermal stability from the high resonance energy of the aromatic and heterocyclic groups incorporated in the chain. In addition to these, polymeric azomethines with typical structures



$$\left[\overset{R}{\overset{|}{C}}(Ar)\overset{R}{\overset{|}{C}}{=}N(Ar)N\right]_n$$

## 6.1 Polymerization using Ziegler-Natta catalysts

Stereoregular polymerizations carried out in homogeneous systems, using essentially polar monomers whose ability to co-ordinate with the catalyst-complex imposes a stereospecific mechanism on the addition, have been dealt with above. As the polarity of the monomer decreases, however, the ability to control the configuration of the incoming monomer decreases and atactic polymers result.

The work carried out by Ziegler on organometallic catalyst systems, culminating in the discovery that ethylene can be polymerized at ambient temperatures and atmospheric pressure, opened the way to the preparation of stereoregular $\alpha$-olefins. Ziegler found that the polyethylene obtained, using a catalyst formed by mixing solutions of triethyl aluminium and titanium tetrachloride, was a highly linear crystalline polymer, as opposed to the branched more amorphous material obtained at high pressures. This stimulated Natta to further work, and he and his co-workers demonstrated that highly crystalline linear polymers from propylene, 1-butene, and a number of other $\alpha$-olefins, could be prepared using modified catalysts of the Ziegler type. It was also found that the crystallinity in these polymers arose from their highly stereoregular structure.

The systems were in all cases heterogeneous and the active initiators are now known by the general name *Ziegler-Natta* catalysts. This encompasses a vast number of substances prepared from different combinations of organometallic compounds where the metal comes from the main Groups I, II, or III and is combined with the halide or ester of a transition metal (Groups IV to VIII). Table 6.3 contains a number of the common components of the Ziegler-Natta catalysts but this list is far from exhaustive.

These catalysts tend to control two features, (a) the rate and (b) the specificity of the reaction, but this varies from reaction to reaction and only a judicious choice of catalyst can effect control over both of these aspects.

Unfortunately the insolubility of the catalyst poses the problems that the kinetics are hard to reproduce and the reaction mechanisms are difficult to formulate with real confidence. This means that the choice of a suitable catalyst for a system is somewhat empirical and very much trial and error, until optimum conditions are established.

It is useful to remember that both heterogeneous and homogeneous catalysts exist in the Ziegler-Natta group but the latter only yield atactic or occasionally syndiotactic polymers from non-polar monomers. As only the heterogeneous Ziegler-Natta catalysts produce isotactic poly-$\alpha$-olefins, these have received most attention. The interest in this type of system has been immense, as evidenced by the vast quantity of published material, and it was most fitting that both Ziegler and Natta were recognized for their work by being awarded jointly the Nobel Prize for chemistry in 1963.

TABLE 6.3. Components of Ziegler-Natta Catalysts

| *Metal Alkyl or Aryl* | *Transition metal compounds* |
|---|---|
| $(C_2H_5)_3Al$ | $TiCl_4$; $TiBr_3$ |
| $(C_2H_5)_2AlCl$ | $TiCl_3$; $VCl_3$ |
| $(C_2H_5)AlCl_2$ | $VCl_4$; $(C_5H_5)_2TiCl_2$ |
| $(i\text{-}C_4H_9)_3Al$ | $(CH_3COCHCOCH_3)_3V$ |
| $(C_2H_5)_2Be$ | $Ti(OC_4H_9)_4$ |
| $(C_2H_5)_2Mg$ | $Ti(OH)_4$; $VOCl_3$ |
| $(C_4H_9)Li$ | $MoCl_5$; $CrCl_3$ |
| $(C_2H_5)_2Zn$ | $ZrCl_4$ |
| $(C_2H_5)_4Pb$ | $CuCl$ |
| $((C_6H_5)_2N)_3Al$ | $WCl_6$ |
| $C_6H_5MgBr$ | $MnCl_2$ |
| $(C_2H_5)_4AlLi$ | $NiO$ |

## EXPERIMENTAL DEMONSTRATION

Before dealing with the mechanism of catalysis and the nature of the catalyst in greater depth, a description of a laboratory preparation of polyethylene will be given to demonstrate the use of such systems.

***Preparation of the catalyst.*** This is prepared from either aluminium triethyl or aluminium diethyl chloride in combination with titanium tetrachloride. The main disadvantage in using aluminium alkyls is that they ignite spontaneously in air and, to avoid this hazard, must be handled in an inert atmosphere.

A safer procedure is to use amyl lithium which can be prepared from lithium wire and amyl chloride. Petroleum ether (50 $cm^3$) is stirred in a three-necked flask and degassed under a stream of nitrogen, which is first purified by passing through a pyrogallol and sodium hydroxide train to remove oxygen. Lithium wire (3 g) is added, followed by 2 $cm^3$ of a solution of amyl chloride (20.7 $cm^3$) in petroleum ether (25 $cm^3$). This is stirred vigorously until the solution becomes turbid (LiCl) and then the remaining amyl chloride solution is added slowly over a period of 20 min to the reaction flask now being cooled in an ice-bath. The reaction mixture turns blue-brown and after 2.5 h it is filtered under nitrogen through glass wool into a graduated flask to remove unreacted Li. The filtrate is allowed to settle and the supernatant liquid is analysed by hydrolysing an aliquot with water and titrating the LiOH formed with 0.1 M HCl. The amyl lithium solution can be stored for some days at 273 K.

***Reaction.*** The catalyst is prepared *in situ*. An apparatus similar to that in figure 6.2 is used. The reaction kettle (1 $dm^3$) is charged with 400 $cm^3$ petroleum ether and 0.05 mol lithium amyl. Anhydrous $TiCl_4$ (2 $cm^3$) is added and the formation of the catalyst as a brownish-black precipitate is complete in 20 min. The formation is accompanied by a rise in temperature of about 10 K. Ethylene is then passed into the stirred mixture and polyethylene forms immediately. The reaction can be allowed to continue for 30 min, then the catalyst is destroyed by the addition of butanol (40 $cm^3$). The polymer is filtered, washed with a 1:1 mixture of HCl and methanol, and dried at 350 K. It has a high degree of crystallinity, a higher density, and a melting temperature some 20 to 30 K higher than samples prepared using high pressure techniques.

The apparatus shows a syringe in position which may be used if the more inflammable aluminium alkyl catalysts are used, as these are often handled in hydrocarbon solvents.

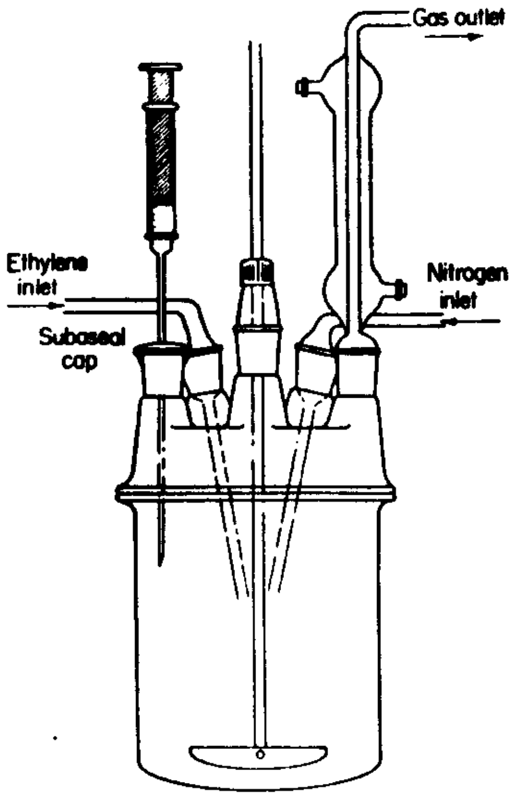


FIGURE 6.2. Apparatus for polymerization of ethylene.

### 6.11 Nature of the catalyst

Frequently the product of a Ziegler-Natta polymerization is sterically impure and can be preferentially extracted to give two products – a highly crystalline stereoregular fraction, and an amorphous atactic one. This may be attributed to the size of the catalyst particles as stereoregularity is enhanced by having large particles, whereas a finely divided catalyst tends to produce an amorphous polymer.

The crystal form of the catalyst is also important and the violet $\alpha$, $\gamma$, and $\delta$ forms of $TiCl_3$ produce a greater quantity of isotactic polypropylene when combined with an aluminium alkyl, than the brown $\beta$-structure. As the active sites for heterogeneous polymerizations are believed to be situated on the crystal surfaces, the structure is all important. In the layered structure of $\alpha$-$TiCl_3$, where every third $Ti^{3+}$ ion in the lattice is missing, a number of Cl vacancies occur on the surface to maintain electrical neutrality in the crystal. The $Ti^{3+}$ on the surface is then only 5-co-ordinated leaving a vacant d-orbital, ☐, and an active site is created when an alkyl group replaces a chloride ion to form $TiRCl_4$ ☐. (See diagrams page 123.)

In $\beta$-$TiCl_3$, the linear chains form bundles in which some Ti ions are surrounded by five $Cl^-$ ions and some by only four $Cl^-$. This means that the steric control at the sites with two vacancies is now less rigid and stereoregulation is much poorer.

Catalyst composition affects both stereoregulation and polymer yield. Thus $Ti^{3+}$ is a more active producer of isotactic polypropylene than $Ti^{4+}$ or $Ti^{2+}$, while an increase in the length of the associating alkyl group decreases the efficiency of stereoregular placements. Varying the transition metal and the associated aluminium compounds in the catalysts also influences the nature of the product.

### 6.12 Nature of active centres

Most of the experimental evidence points to propagation taking place at a carbon to transition metal bond with the active centre being anionic in character. Free radical reactions are considered to be non-existent in the Ziegler-Natta systems because neither (i) chain transfer nor (ii) catalyst consumption occurs. The active centres also live longer than radicals and resemble "living" polymer systems in many ways, one being that block copolymers can be produced by feeding two monomers alternatively into the system.

While a number of reaction mechanisms have been suggested, two are worth considering in detail. These are based on the view that the active centres are localized rather than migrating and that the $\alpha$-olefin is complexed at the transition metal centre prior to incorporation into the chain, *i.e.* growth is always from the metal end of the growing chain.

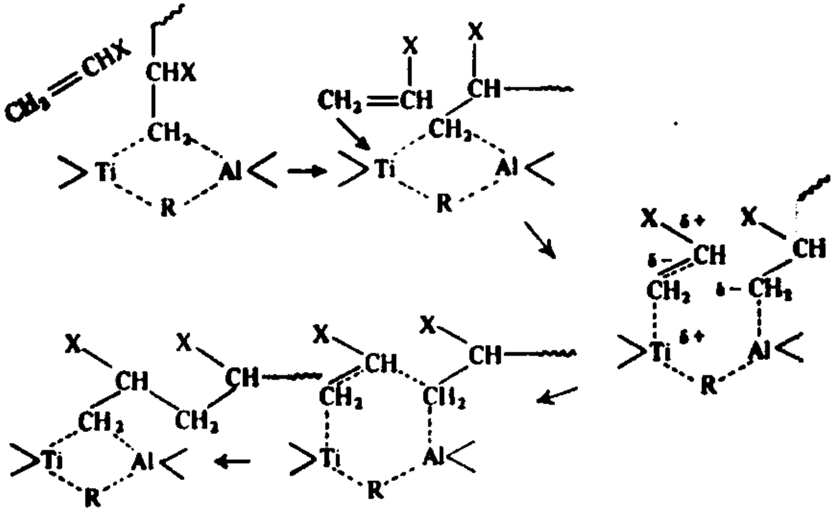
The active species are then considered to be either *bimetallic* or *monometallic*.

### 6.13 Bimetallic mechanism

Natta and his associates have postulated a mechanism involving chain propagation from an active centre formed by the chemisorption of an electropositive metal alkyl of small ionic radius on the co-catalyst surface. This yields an electron deficient bridge complex such as IX and chain growth then emanates from the C–Al bond.

IX

It is suggested that the nucleophilic olefin forms a π-complex with the ion of the transition metal and, following a partial ionization of the alkyl bridge, the monomer is included in a six-membered ring transition state. The monomer is then incorporated into the growing chain between the Al and the C allowing regeneration of the complex.

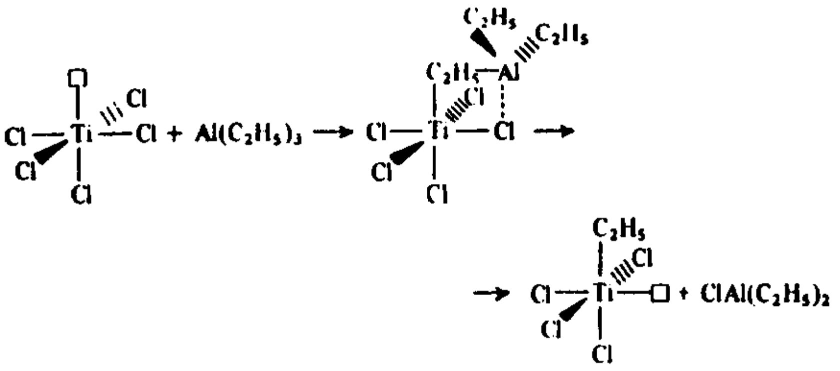


While a limited amount of experimental evidence does lend support to this concept, major objections have been voiced by Ziegler, who is of the opinion that as dimeric aluminium alkyls are inefficient catalysts in the "Aufbau" reaction, the Ti–Al complex is not likely to be the effective catalytic agent. Other more recent work also favours the second and simpler alternative, the monometallic mechanism.

### 6.14 Monometallic mechanism

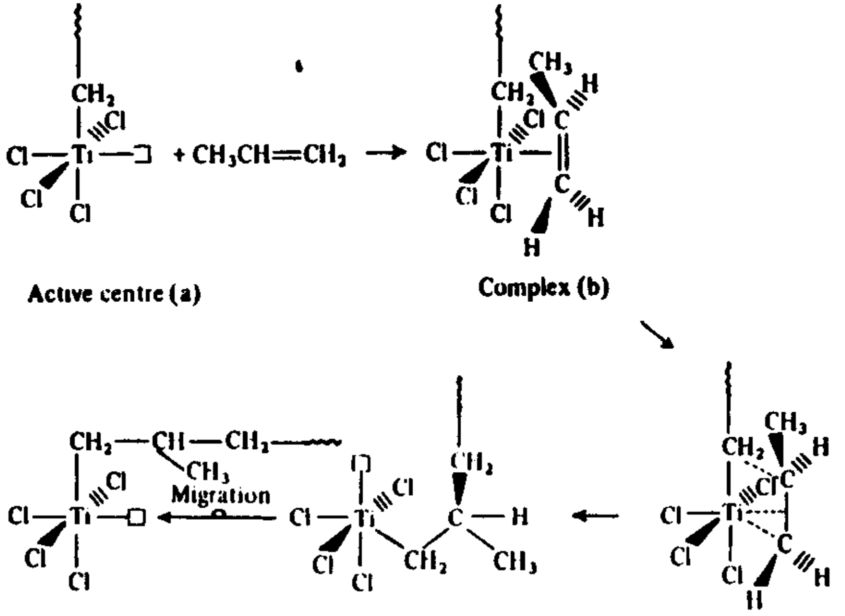
Majority opinion now favours the concept that the d-orbitals in the transition element are the main source of catalytic activity and that chain growth occurs at the titanium-alkyl bond. The ideas now presented are predominantly those of Cossee and Arlman, and will be developed using propylene as the monomer.

The first stage is the formation of the active centre illustrated here using $\alpha$-$TiCl_3$ as catalyst. The suggestion is that alkylation of the 5-co-ordinated $Ti^{3+}$



ion takes place by an exchange mechanism after chemisorption of the aluminium alkyl on the surface of the $TiCl_3$ crystal. The four chloride ions remaining are the ones firmly embedded on the lattice and the vacant site is now ready to accommodate the incoming monomer unit. The reaction is confined to the crystal surface and the active complex is purely a surface phenomenon in heterogeneous systems.

The attacking monomer is essentially non-polar but forms a π-complex with the titanium at the vacant d-orbital. A diagram of a section of the complex



Active centre (a)

Complex (b)

New Active centre

Active centre (d)

Transition state (c)

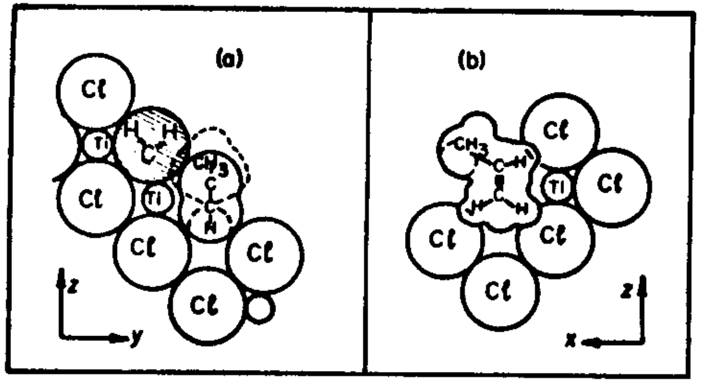


FIGURE 6.3. Cross-sectional diagrams of the propylene-catalyst complex through (a) the $y-z$ plane and (b) the $x-z$ plane of the octahedral structure. (Adapted from Bawn and Ledwith.)

shows that the propylene molecule is not much bigger than a chloride ion and consequently the double bond can be placed adjacent to the Ti ion and practically as close as the halide. After insertion of the monomer between the Ti–C bond, the polymer chain then migrates back into its original position ready for a further complexing reaction.

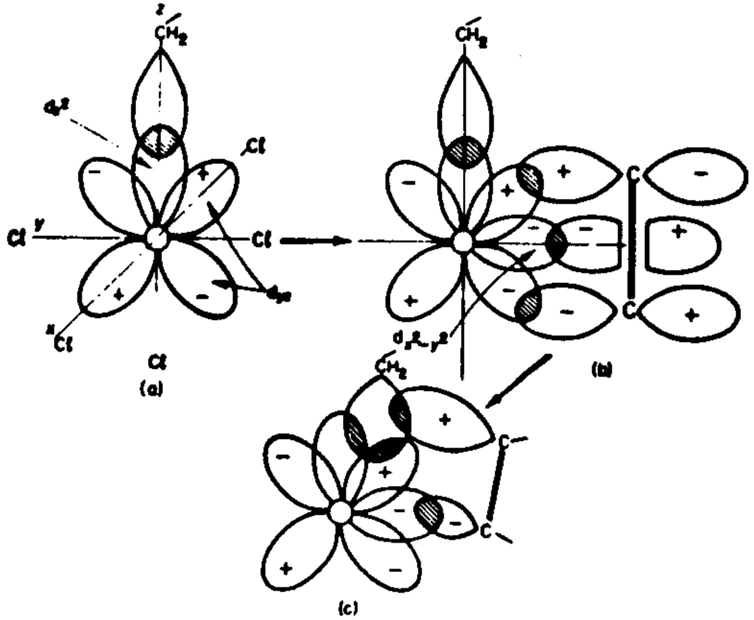


FIGURE 6.4. Representation of the relevant orbital overlap in (a) the active centre, (b) the titanium-olefin complex, and (c) the transition state.

The reactivity of the active centre is attributed primarily to the presence of d-orbitals in the transition metal. The initial state of the active centre shows that the $=CH_2$ group will be capable of considerable distortion from its equilibrium position, because of the availability of adjacent d-orbitals. Complexing (b) takes place when the π-bonding orbitals of the olefin overlap with the vacant $d_{x^2-y^2}$ orbital of the $Ti^{3+}$ while at the same time the π*-antibonding orbitals can overlap the $d_{yz}$ orbitals of the $Ti^{3+}$. Formation of the transition state is aided by the ability of the $=CH_2$ group to migrate by partial overlap with the $d_{z^2}$, $d_{yz}$, and π*-orbitals.

The main features of the monometallic mechanism are: (1) an octahedral vacancy on the $Ti^{3+}$ is available to complex the olefin; (2) the presence of an alkyl to transition metal bond at this site is required; and (3) the growing polymer chain is always attached to the transition metal.

## 6.15 Stereoregulation

To obtain a stereoregular polymer, the chemisorption of the monomer on the catalyst surface must be controlled so that the orientation of the incoming monomer is always the same. Examination of models shows that a molecule such as propylene will fit into the catalyst surface in only one way if a position of closest approach of the double bond to the $Ti^{3+}$ ion is to be achieved. This places the $=CH_2$ group pointing into the lattice and for steric reasons the orientation of the $-CH_3$ group to one side is preferred. This determines the configuration of the monomer during the complexing stage and is always the same. Repeated absorption of the monomer in this orientation, prior to reaction, leads to an isotactic polymer.

For the Cossee-Arlman mechanism to operate, migration of the vacant site back to its original position is necessary, else an alternating position is offered to the chemisorbed monomer and a syndiotactic polymer would result. This implies that the tacticity of the polymer formed depends essentially on the rates of both the alkyl shift and the migration. As both of these will slow down when the temperature is decreased, formation of syndiotactic polymer should be favoured at low temperatures, and syndiotactic polypropylene can in fact be obtained at 203 K.

(55) → (60)

# RECENT DEVELOPMENTS IN STEREOREGULATION BY ZIEGLER-NATTA POLYMERIZATION OF α-OLEFINS

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## 1. INTRODUCTION

Since its discovery a great deal of work has been done for understanding the mechanism of Ziegler-Natta polymerization of α-olefins. In spite of this almost 25 years old activity many points do not appear entirely clarified and firmly established. Indeed these catalysts join unique and very interesting properties to a very large complexity. Thus the field is under constant development and also the aspects generally accepted (1) are often put in debate.For istance the α-olefin insertion in a transition metal-carbon bond, considered as one of the fixed step of the mechanism, has been questioned very recently by proposing (2) a mechanism proceeding via a 1,2 hydrogen shift from the α-carbon of the growing chain and formation of metallocycle and carbene intermediates. Even if this last proposal does not explain end group nature, particularly when using $AlPh_3$, large predominance of primary insertion in isotactic polymerization and different role of growing chain end and metal complex in the steric control, it however indicates that several problems are still open as discussed in other chapters.

In the present chapter we shall limit ourself to discuss the basic stereochemical features of α-olefins polymerization, which appear rather well understood. Stereochemistry of iso- and syndiotactic polymerization has been indeed interpreted not on the ground of mechanistic speculations but on the basis of polymer structure analysis, that is of firm experimental bases. Reversely these conclusions can be used to check any chemical mechanism which must explain also stereochemistry of resulting macromolecules.

*R. W. Lenz and F. Ciardelli (eds.), Preparation and Properties of Stereoregular Polymers, 73–83.*

Steric interactions responsible for stereospecific polymerization may occur between monomer and either catalytic complex or last unit of the growing chain (3). The former has supposed to be responsible for isotactic propagation because of its inherently chiral structure as shown by the high crystallinity (4) and by the separation in fractions with opposite optical activity (5) of the polymers from racemic α-olefins. On the other side this hypothesis and the determining role of growing chain end in syndiotactic propagation have been demonstrated by copolymerizing differently substituted α -olefins (6).

Propylene is the only α -olefin which can be polymerized to either isotactic or syndiotactic polymers by means of Ziegler - Natta catalyst. The stereochemistry of the two types of stereospecific polymerization has been elucidated by structural analysis of polymerization products (mainly propylene homopolymers and ethylene-propylene copolymers) obtained in the presence of different catalytic systems (7).

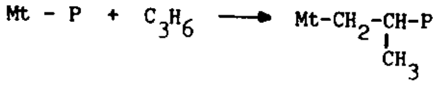
## 2.STEREOREGULATION IN POLYMERIZATION OF α-OLEFINS TO ISOTACTIC POLYMERS

High resolution $^1$H- and $^{13}$C-NMR of polypropylene and of ethylene-propylene copolymers as well as determination of enantiomers distribution in polymers from racemic α-olefins demonstrated that the catalytic complex is responsible for the isotactic enchainment. This implies the chiral (racemic)structure of the catalyst which at present seems to be adequately proved as discussed in the two following sections.

### 2.1 NMR Study of propylene and ethylene-propylene copolymers.

In the case of isotactic polymerization it has been observed that the overal stereochemical mechanism of addition to the double bond is cis (8,9). Indeed NMR analysis of polymers obtained in the presence of isotactic catalysts from cis- and trans-ld$_1$-propene indicated that erythro-diisotactic polymers are obtained from the former and threo-diisotactic polymers from the latter.

The polymerization is highly regiospecific: only head-to-tail einchained monomer units are detected in highly isotactic polymers and only odd methylene sequences are detected in ethylene/propylene copolymers (10-12). The insertion of all propylene units into the reactive metal-carbon bond is primary (or antimarkownikow)



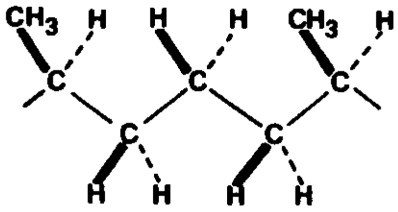
$$\text{Mt} - \text{P} + C_3H_6 \longrightarrow \text{Mt-CH}_2\text{-}\underset{\substack{|\\ CH_3}}{\text{CH}}\text{-P}$$

as determined by detailed analysis of the end groups (13,14).

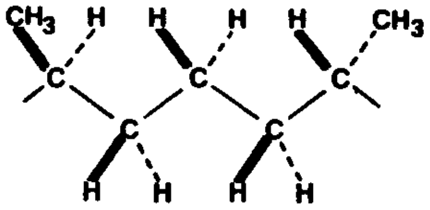
The steric control is due to the chirality of the catalytic sites rather than to the chirality of the growing chain end. This conclusion has been achieved on the basis of the following considerations:

i) The statistic of the stereochemical sequences of the substituted carbon atoms in propylene homopolymers is substantially described by the "enatiomorphic-sites model" elaborated by Shelden and Furukawa (10,15). This model assumes that the configuration of adding monomer is determined primarily by the configuration of the catalyst, whereas the configuration of the growing chain has only a negligible effect.

ii) The steric control is transmitted across isolated ethylene units as shown by $^{13}$C-NMR analysis of the stereochemical environment of ethylene units in ethylene-propylene copolymers of low ethylene content. Indeed copolymerization of enriched ethylene-1 $^{13}$C with propylene in the presence of catalysts capable of highly isotactic control gives polymers showing only two ethylene resonances for the $CH_2$-$CH_2$-$CH_2$-groups, thus suggesting the presence of only meso (A) or racemic (B) situation (11,12,16).



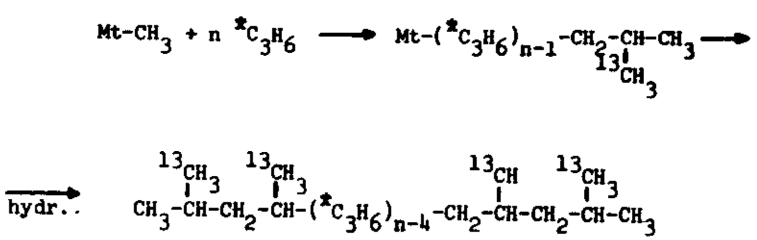
(A)



(B)

The two peaks detected in sample obtained with isotactic-specific catalyst were assigned to meso ethylene units. This result clearly indicates that insertion of ethylene in the growing chain does not change configuration of propylene units according to control of the stereochemistry of the addition by the catalytic metal complex; only in this situation in fact the stereoregulation can be transmitted across the achiral ethylene unit.

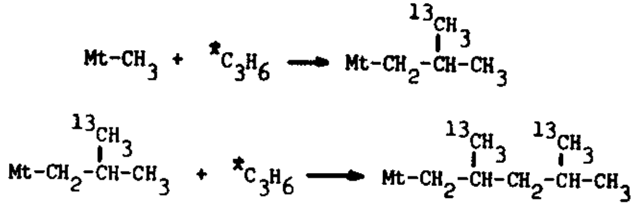
iii) Determination of the stereochemistry of end groups is a third manner of grasping the problem of origin of steric control in isotactic polymerization. As observed by Carman and coworkers (17) the carbon atoms of the two methyls of the isopropyl group of branched hydrocarbons are diastereotopic and show different $^{13}C$ shifts . Work in progress (14) suggests that when 3-$^{13}C$ enriched propylene ($^*C_3H_6$) is polymerized in the presence of $TiCl_3/Al(CH_3)_3/Zn(CH_3)_2$ catalytic system, the $^{13}C$ enriched carbon atoms of the two isopropyl end groups of the resulting isotactic macromolecules are both in an erythro relationship.



$$Mt\text{-}CH_3 + n\ {}^*C_3H_6 \longrightarrow Mt\text{-}({}^*C_3H_6)_{n-1}\text{-}CH_2\text{-}\underset{^{13}CH_3}{CH}\text{-}CH_3 \longrightarrow$$

$$\xrightarrow[\text{hydr.}]{} CH_3\text{-}\underset{}{\overset{^{13}CH_3}{CH}}\text{-}CH_2\text{-}\overset{^{13}CH_3}{CH}\text{-}({}^*C_3H_6)_{n-4}\text{-}CH_2\text{-}\overset{^{13}CH}{CH}\text{-}CH_2\text{-}\overset{^{13}CH_3}{CH}\text{-}CH_3$$

(as defined in references 18 and 19) with respect to the methyl substituents of the respective first neighbouring monomer unit. In the above scheme the isopropyl group arising from Mt-chain hydrolysis in on the left and the one formed by insertion of propylene in the Mt-$CH_3$ bond, at the beginning of the polymerization, is on the right. Thus the first and second units inserted are subjected to the same isotactic steric control, despite nor the starting methyl group nor the isobutyl group formed by insertion of the first propylene



$$Mt\text{-}CH_3 + {}^*C_3H_6 \longrightarrow Mt\text{-}CH_2\text{-}\overset{^{13}CH_3}{CH}\text{-}CH_3$$

$$Mt\text{-}CH_2\text{-}\overset{^{13}CH_3}{CH}\text{-}CH_3 + {}^*C_3H_6 \longrightarrow Mt\text{-}CH_2\text{-}\overset{^{13}CH_3}{CH}\text{-}CH_2\text{-}\overset{^{13}CH_3}{CH}\text{-}CH_3$$

molecule are chiral.

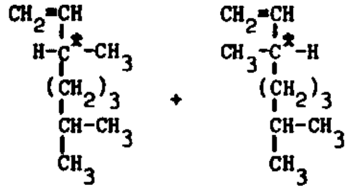
The driving force of 5 Kcal/mole evaluated for the isotactic

propagation (20) is to assign to the asymmetric structure of the active sites in the catalytic complex.

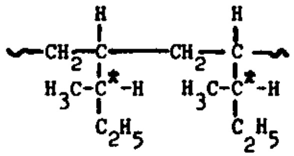
## 2.2. Polymerization of chiral α-olefins

Results obtained by polymerizing racemic α-olefins having the asymmetric C-atom in α to the bouble bond in the presence of the same type of catalysts are consistent with the above conclusion.

Isotactic polymers of racemic 3,7-dimethyl-1-octene can be separated in fractions having optical activity of opposite sign by elution on an optically active crystalline support consisting of poly-[(S)-3-methyl-1-pentene] (21). The separation degree F even for highly isotactic fractions is not higher



racemic 3,7-dimethyl-1-octene



isotactic poly-[(S)-3-methyl-1-pentene]

than 40% (22),but a very similar value has been obtained by submitting to elution under the same conditions a 1/1 mixture of isotactic poly-[(S)-and poly-[(R)-3,7-dimethyl-1-octene] (Table 1)(23). As in this last case the intrinsic separability D is 100%, the separation efficiency of the method E=F/D is lower than 40%. Accordingly the intrinsic separability of the highly isotactic polymer from racemic 3,7-dimethyl-1-octene must be higher than 90%, indicating for each macromolecule an average enantiomeric purity of the same order of magnitude. These results exclude the formation of statistical and block copolymers of the two antipodes and are rather consistent with the formation of macromolecules consisting of long sections of units derived from the same antipode connected by isolated mistakes as shown below. Such a structure can be formed only if the catalytic complex is able to distinguish between the to

$$n\ (R + S) \longrightarrow RRRSRRRRRRR + SSSRSSSSSS$$

[R and S represent (R)- and (S)-3,7-dimethyl-1-octene,respectively]

Table 1

Separation in Fractions with Opposite Optical Rotation of Polymers from Racemic 3,7-Dimethyl-1-octene and of an Equimolar Mixture of Homopolymers of the Two Antipodes (23).

| Sample submitted to elution on poly-(S)-3-methyl-1-pentene | Separation degree,% F | Intrinsic Separability,% D |
|---|---|---|
| Poly-[(R)(S)-3,7-dimethyl-1-octene] | 33.6 | 91 |
| Equimolar mixture of Poly-[(R)-and Poly-[(S)-3,7-dimethyl-1-octene] | 37.0 | 100 |

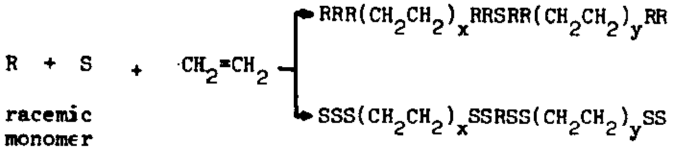
antipodes, its capability being maintained even if a "wrong" monomer insertion occurs. Moreover the random copolymers of 3,7-dimethyl-1-octene with ethylene have been separated in fractions having optical rotation with opposite sign (24). The separation degree F attained (25) was only slightly lower than for the polymers from racemic 3,7-dimethyl-1-octene (Table 2).

Table 2

Separation Degree F in Fractions Having Opposite Optical Rotation for Polymers of Racemic 3,7-Dimethyl-1-octene and for its Copolymer with Ethylene.

| Polymer | F% |
|---|---|
| Poly-[(R)(S)-3,7-dimethyl-1-octene] | 27 - 34 |
| (R)(S)-3,7-dimethyl-1-octene/ Ethylene 56/44 copolymer | 23 - 29 |

It is reasonable to expect that the efficiency E of the separation is lower for the ethylene copolymer; thus the intrinsic separability D of this last is probably higher than that observed indicating that insertion of ethylene in the growing chain does not affect the stereoselectivity of a single site towards the two monomer antipodes. The process can be represented as below, where R and S indicate (R)- and (S)-3,7-dimethyl-1-octene, respectively:



$$\underset{\text{racemic monomer}}{R + S} + CH_2{=}CH_2 \rightarrow \begin{cases} RRR(CH_2CH_2)_xRRSRR(CH_2CH_2)_yRR \\ SSS(CH_2CH_2)_xSSRSS(CH_2CH_2)_ySS \end{cases}$$

In this case also, the only explanation possible is that the catalytic site is able to distinguish between the R- and S-monomer, the assistance from the growing chain being vanishing small if any.

According to the previous presentation heterogenous Ziegler-Natta catalysts capable of isotactic propagation should have a racemic structure with chiral site of both levo and dextro configuration. It appeared very attractive to attempt the preparation of catalytic systems containing sites of a single chirality only by using optically active components. We have to say that up to now this goal has been only partially achieved starting with optically active metal alkyls (26) or using optically active electron donors (27) for catalyst preparation. These systems are indeed able to induce preferential polymerization of a monomer antipode but the "stereoelectivity" is not very high, the enantiomeric prevalence in the polymer being lower than 20%, while from the separation data we could expect that a real chiral site is able to distinguish between the two antipodes up to more than 90%.

Rather an interesting application of the chiral structure of active sites is obtained by copolymerizing a racemic α-olefin with an optically active one (28). In this case we have actually a terpolymerization with two monomers having the same absolute configuration (for instance R) and a third monomer having opposite configuration (S). As the two (R)-monomer will polymerize on the centers of the same chirality they yield a copolymer, whereas the (S)-monomer forms a homopolymer:

| R + S | + R' | ⟶ SSSSSS | + RR'RRRR'R'R |
|---|---|---|---|
| racemic monomer | optically active monomer | (S)-homopolymer | (R)(R')-copolymer |

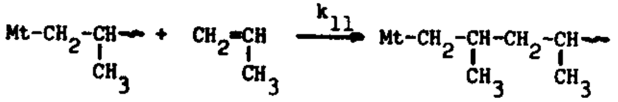
|R and S represent (R)- and (S)-3,7-dimethyl-1-octene respectively and R' is (R)-3-methyl-1-pentene|

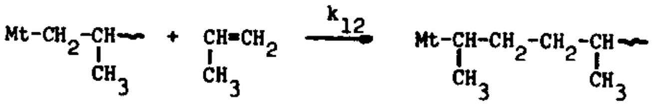
The final product, because of different solubility of homopolymer and copolymer can be separated in fractions of opposite optical rotation by simple solvent extraction.

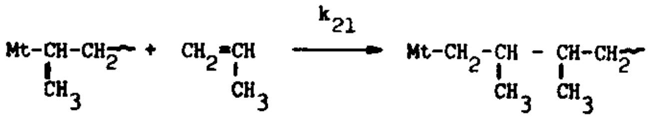
## 3. Polymerization of propylene to syndiotactic polymers

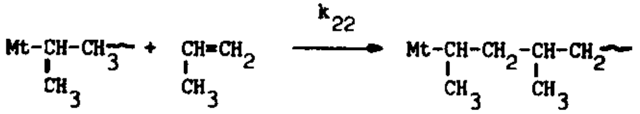
The best way to obtain syndiotactic polypropylene is the low temperature polymerization in the presence of homogeneous vanadium based catalysts (29). Also, in this case the overall stereochemical mechanism of addition to the double bond is cis (30) as for isotactic propagation, but this seems to be the only common feature of the two types of stereospecific polymerization of propylene.

The presence of "head-to-head" and "tail-to-tail" units in addition to the head-to-tail ones in propylene homopolymers (11,32), and of a number of even methylene sequences in ethylene/propylene copolymers (11,31,33-35) denotes lack of regiospecificity. As a consequence the syndiotactic polymerization of propylene is conveniently described as a binary copolymerization (11, 31, 36) between "head-to-tail" and "tail-to-head" oriented monomer molecules:


$$\text{Mt-CH}_2\text{-}\underset{CH_3}{CH}\sim + CH_2{=}\underset{CH_3}{CH} \xrightarrow{k_{11}} \text{Mt-CH}_2\text{-}\underset{CH_3}{CH}\text{-CH}_2\text{-}\underset{CH_3}{CH}\sim \qquad [11]$$


$$\text{Mt-CH}_2\text{-}\underset{CH_3}{CH}\sim + \underset{CH_3}{CH}{=}CH_2 \xrightarrow{k_{12}} \text{Mt-}\underset{CH_3}{CH}\text{-CH}_2\text{-CH}_2\text{-}\underset{CH_3}{CH}\sim \qquad [12]$$


$$\text{Mt-}\underset{CH_3}{CH}\text{-CH}_2\sim + CH_2{=}\underset{CH_3}{CH} \xrightarrow{k_{21}} \text{Mt-CH}_2\text{-}\underset{CH_3}{CH} - \underset{CH_3}{CH}\text{-CH}_2\sim \qquad [21]$$


$$\text{Mt-}\underset{CH_3}{CH}\text{-CH}_3\sim + \underset{CH_3}{CH}{=}CH_2 \xrightarrow{k_{22}} \text{Mt-}\underset{CH_3}{CH}\text{-CH}_2\text{-}\underset{CH_3}{CH}\text{-CH}_2\sim \qquad [22]$$

The step [22] has been shown to be the only one syndiotactic specific (11,31,32), the prevailingly syndiotactic structure of the chains indicating that:

$$k_{11}/k_{12} < k_{22}/k_{21}$$

and

$$k_{11}k_{22}/k_{12}k_{21} > 1$$

The stereochemical sequences of the prevailingly syndiotactic polymers follow a perturbed first order Markov model (a strictly first order Markov model should be expected from the propagation step [22]) (20). The secondary (or Markownikow) regiospecificity of the step [22] turns primary across ethylene units with contemporary decrease of the syndiotactic content. Syndiotactic control is therefore lost whenever the last unit is achiral.

These facts together with the alternating tendence of syndiotactic specific catalysts in the copolymerization of ethylene with propylene and 1-butene as well as the higher syndiotactic content of propylene/1-butene copolymers than the corresponding propylene/ethylene copolymers (6) indicate that the syndiospecific propagation is controlled by the steric interactions between the last chiral unit of the growing chain end and the incoming monomer. These conclusions are confirmed by the results obtained by detailed analysis of the macromolecules end groups (14). It is of interest to remark that a driving force of less than 2 Kcal/mole has been estimated for syndiotactic polymerization control (20), appreciably lower than for the isotactic polymerization.

Recently a polymerization mechanism assuming pentacoordinate catalytic complexes has been proposed which accounts for a number of stereochemical details concerning this type of polymerization (37).

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# RECENT DEVELOPMENTS IN THE POLYMERIZATION OF OLEFINS WITH ORGANOMETALLIC CATALYSTS

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Abstract - Some recent developments in basic research on the polymerization of olefins to linear polymers are reviewed, including progress in preparation of catalytic systems, advances in knowledge about the mechanism of polymerization and attempts to control molecular weight distribution.
For the catalytic systems of the type $TiCl_4/MgCl_2/AlR_3$/Lewis bases indirect methods for the characterization of the active centers are considered. Dissimilarities in the time dependence of the rate of polymerization and changes in the productivity as a function of the Lewis base-to-aluminum alkyl ratio indicate that ethylene and propylene polymerize, at least in a large part, on different active centers. However, productivity of the highly stereospecific centers synthesizing isotactic poly($\alpha$-olefin)'s is of the same order of magnitude for ethylene and propylene.

## INTRODUCTION

The polymerization of olefins to linear polymers continues to be one of the most investigated areas in polymer science. This interest from the industrial and the academic laboratories is justified by both the practical interest and by the numerous unsolved problems in this field.
In this short survey we plan to summarize the recent main progress in catalyst preparations as well as the advancements in the understanding of the polymerization steps and of the characterization of the catalytic active centers.
We have tried to emphasize the basic aspects of the research in this field but we have not attempted to review exhaustively all the literature and particularly the patent literature which has appeared in the field.

## TRENDS IN RESEARCH ON NEW CATALYTIC SYSTEMS

Since its start in the early fifties, the polymerization of ethylene and $\alpha$-olefins was carried out with supported transition metal oxides ($MoO_3 \cdot CoO$ reduced with hydrogen (1) or $CrO_3$ on $Al_2O_3/SiO_2$ support reduced with olefins during the polymerization (2) or with mixtures of transition metal compounds with organometallic compounds of the main group metals (metallorganische Mischkatalysatoren) (3) or of the transition metals (4-6).
Soluble two component (7-10) and, later, single component (11) catalytic systems were also used, particularly for the polymerization of ethylene.
Developments have taken place in all the mentioned directions as shown in Table 1. In the field of the soluble catalysts, the most spectacular developments concern the two component catalysts obtained from bis(cyclopentadienylzirconium) or titanium derivatives and aluminoxanes (18-20). With the zirconium catalytic systems productivities of up to $3 \cdot 10^6$ g PE/g Zr·h·bar have been obtained. But with both systems, titanium and zirconium, only completely atactic polypropylene is produced (18, 28). This type of catalytic system can also be used for the production of statistical copolymers

TABLE 1. Organometallic Catalysts for Polymerization of Olefins

| Catalyst precursor | Polymerization Conditions Monomer | Temperature °C | Pressure Atm | Productivity gP/gMt·h·bar | Ref. |
|---|---|---|---|---|---|
| a) Soluble Catalysts | | | | | |
| $Ti(CH_2C(CH_3)_3)_4$ | $C_2H_4$ | 80 | 2.1 | 19 | 12 |
| $Ta(=CHCMe_3)(H)(PMe_3)_3I_2$ | $C_2H_4$ | 0 | 1 | 0.3 | 14 |
| $Lu(\eta^5-C_5Me_5)_2Me\cdot Et_2O$ | $C_2H_4$ | 40 | 43 | 380 | 16 |
| | $C_3H_6$ | 17 | 0.25 | 4 | 16 |
| $Cp_2ZrR'_2/[-Al(R)O-]_n$ | $C_2H_4$ | 90 | 8 | 3'100'000 | 18 |
| | $C_3H_6$ | 5 | 8 | 2'000 | 19 |
| $Cr(CH_2C(CH_3)_3)_4/AlEt_3$ | $C_2H_4$ | 50 | 2.1 | 1'700 | 13 |
| b) Supported Single Component Catalysts | | | | | |
| $Zr(CH_2-C(CH_3)_2C_6H_5)_4/Al_2O_3/H_2$ | $C_2H_4$ | 150 | 2.8 | 2'775 | 29 |
| $Zr(CH_2-C(CH_3)_2-C_6H_5)_4/SiO_2/H_2$ | $C_2H_4$ | 150 | 2.8 | 942 | 29 |
| $Ti(CH_2C(CH_3)_3)_4/SiO_2$ | $C_2H_4$ | 90 | 2.1 | 48 | 12 |
| | $C_3H_6$ | 50 | 2.8 | 3.1 | 12 |
| $Cr(CH_2C(CH_3)_3)_4/SiO_2$ | $C_2H_4$ | 80 | 2.1 | 5'770 | 13 |
| $Zr(CH_2-C(CH_3)_2C_6H_5)_4/Al_2O_3$ | $C_3H_6$ | 50-70 | 8 | 400 | 30 |
| $Hf(CH_2-C_6H_5)_4/Al_2O_3$ | $C_3H_6$ | 75 | 26 | 60 | 30 |
| c) Supported Two Component Catalysts | | | | | |
| $TiCl_4/MgCl_2/AlR_3$ | $C_2H_4$ | 60 | 0.25 | 50'000 | 23 |
| | $C_3H_6$ | 60 | 1.0 | 14'500 | 23 |
| | $C_4H_8$ | 60 | 0.5 | 9'500 | 24 |
| $TiCl_4/MnCl_2/AlR_3$ | $C_3H_6$ | 60 | 1.0 | 14'700 | 25 |
| $TiCl_4/SiO_2/MgR_2/AlR_3$ | $C_2H_4$ | 102 | 12.5 | 34'000 | 26 |

of ethylene and α-olefins (18). The lutetium (16,17) and tantalum (14,15) catalysts have mainly been used to investigate the basic aspects of the polymerization of olefins and will be discussed later.

Interesting developments have taken place in the field of single component heterogeneous catalysts, the main progress being the use of catalysts containing pre-formed metal-to-carbon bonds. Pioneering research in this field was carried out by the I.C.I. laboratories in the early seventies (29-31). Very active catalysts for the polymerization of ethylene which remain active up to 300°C have been obtained by supporting tetraneophylzirconium on $Al_2O_3$ (21). No highly stereospecific catalyst of this type has been described up to now for the production of isotactic α-olefins. However, particularly interesting stereoblock polypropylenes can be produced with supported zirconium catalysts (22).

In the field of supported two component catalysts the use of activated $MgCl_2$ (32) or $MnCl_2$ (33) as support has effected a substantial progress in the production of polyethylene (32-35) and isotactic polypropylene and polybutene (33,36,37). Using titanium catalysts of the type $TiCl_4/MgCl_2/AlR_3$, productivities of the order of 50'000 g polymers/g Ti·h·bar at 60° can easily be achieved for polyethylene (23). For isotactic polypropylene, high stereospecificities (>95% of heptane insoluble polymer) and productivities higher than $10^4$ g polymer/g Ti·h·bar can be obtained using catalytic systems of the type $TiCl_4/MgCl_2/AlR_3$/Lewis base (25, 38).

In order to decrease the chlorine content of the polymer more complicated systems of the type $SiO_2/MgCl_2/TiCl_4/AlR_3$ have been proposed (26, 27).

## ADVANCES IN KNOWLEDGE ABOUT THE MECHANISM OF THE POLYMERIZATION OF α-OLEFINS

The mechanism of the polymerization of olefins via organometallic catalysts includes the following three main steps which will be discussed separately:

a) Formation of catalytic centers from the precursors of the catalyst
b) Monomer insertion into a metal-to-carbon bond
c) Chain termination

Basic knowledge of the three steps is still rather scarce, although the insertion mechanism was already experimentally established in the fifties (39, 40).

### a) Formation of the Catalytic Species

Single component heterogeneous catalysts are believed to contain Mt-R or Mt-H groups anchored to the support via oxygen bridges (41, 31). However the number of R groups bound to each catalytically active metal atom, the degree of coordinative unsaturation and even the oxidation state of the transition metal atoms present in the catalytically active centers are unknown. No substantial progress has been made in the understanding of the formation of the catalytic centers in heterogeneous two component catalytic systems. It appears that centers having very different structures are generated when the supported transition metal compounds are in contact with metal alkyls (28, 42). As we shall discuss later, some of these centers rapidly decompose after formation, others remain active for hours. Their Lewis acidities are very different and furthermore there are centers with different degrees of coordinative unsaturation. The processes which lead to the formation of the different centers can be rather different and probably consist of a number of steps.

Some progress has been made in understanding the formation of single component and two component soluble catalytic species. For $[C_5(CH_3)_5]_2Lu(CH_3)\cdot O(C_2H_5)_2$ which polymerizes propylene, the activation process is believed to be the dissociation of the diethyl ether molecule with formation of the coordinatively unsaturated species $[C_5(CH_3)_5]_2Lu(CH_3)$ (16); no precise information is available for the activation of $[P(CH_3)_3]_3(I)_2(H)Ta{=}CH{-}C(CH_3)_3$ which polymerizes ethylene at 0°C (14,15); part of the complex remains unaltered during the polymerization.

Concerning the two component soluble catalytic species, the system $(C_5H_5)_2TiCl(C_2H_5)/AlCl_2(C_2H_5)$ has been investigated in depth (43-48). A two step activation mechanism (Scheme 1) (47) is in good agreement with the kinetic data. However the structures of the "inactive" (C) and of the active complex (C*) remain unknown.

The formation of the highly active catalytic centers obtained from $(C_5H_5)_2Zr(CH_3)_2$ and $[-Al(CH_3)O-]_n$ is still under investigation and the detailed structure of the active species is still unknown (18).

Scheme 1. Equilibria for the Formation of Active Centers

$$(C_5H_5)_2TiRCl + 1/2[AlCl_2(C_2H_5)]_2 \xrightleftharpoons{K_1} C$$

$$C + (AlEtCl_2)_2 \xrightleftharpoons{K_2} C^* + X$$

C : Al : Ti = 1 : 1 (inactive primary complex)

C* : Al : Ti = 1 : 1 (active complex in polymerization)

b) Monomer Insertion into Metal-to-Carbon Bonds

Advancement in the basic knowledge of the chain growth obtained with heterogeneous catalysts is very slow, due to the intrinsic nature of catalytic heterogeneous processes. In practice the process may involve a number of steps, some of which are indicated in Scheme 2. Furthermore, due to the large difference in structure and reactivity among the catalytic centers (28,42), the number of steps involved and the, probably different, related specific rates, the interpretation of the kinetic measurements on a molecular basis is extremely uncertain.

Scheme 2.

$$M_d \rightleftarrows M_a$$

$$M_a \rightleftarrows M_a^*$$

$$Mt\text{-}(M)_n\text{-}R + M_a^* \longrightarrow Mt\text{-}(M)_{n+1}\text{-}R$$

$M_d$ : monomer dissolved in reaction medium

$M_a$ : monomer adsorbed on surface of the catalyst

$M_a^*$ : monomer adsorbed on active center

M : inserted monomeric unit

Further uncertainties are created by the difficulty in determining the actual concentration of the active centers per unit weight of catalyst and its variation with time (49-54). Despite this complicated situation, some kinetic aspects of the polymerization appear to be deceivingly simple. For instance, the total amount of polymer produced in the polymerization of propylene with a $TiCl_4/MgCl_2/Al(i\text{-}C_4H_9)_3$ catalytic system at 60° is proportional to the partial pressure of propylene over a relatively large interval (0.25 bar to 7.74 bar, Figure 1a). However, if the productivities of different types of diastereomeric polymers are considered separately, a non-linear behavior is evident (Figure 1b).

More promising is the investigation of the soluble catalytic systems for experimental observations carried out during the period in which there is no precipitation of polymer. With reasonable assumptions, the rate of chain growth at 10°C could be calculated for the polymerization of ethylene with the catalytic system obtained from $(C_5H_5)_2TiCl(C_2H_5)$ and $AlCl_2(C_2H_5)$ (46). In the first polymerization steps, the rate of chain growth decreases from 120-140 ℓ/mol·sec for the insertion of ethylene into a $Ti\text{-}C_2H_5$ bond to 47 ℓ/mol·sec for insertion into a $Ti\text{-}C_6H_{13}$ bond.

For the above catalytic system, a picture of the polymerization of ethylene emerges which is substantially different from that of the radical polymerization, the ratio between the rate of formation of active centers and the rate of chain growth being much higher than one in the first case and much lower than one in the second case, at comparable temperatures.

No π-olefin complex was detected in this system; furthermore, the change in chain growth rate with growing chain length indicates that insertion of the monomer rather than formation of catalyst-to-monomer complex is the step with the slowest specific rate constant in the process. From these two facts it appears that either the formation of the π-olefin complex is thermodynamically unfavored and is not present in detectable concentration or the formation of the π-olefin complex does not play a role in insertion of monomer, at least in this case. A low value of equilibrium constant for the formation of the π complex was found by Ballard and coworkers in the polymerization of ethylene with the catalytic system $Zr[CH_2Si(CH_3)_3]_4$ (55).

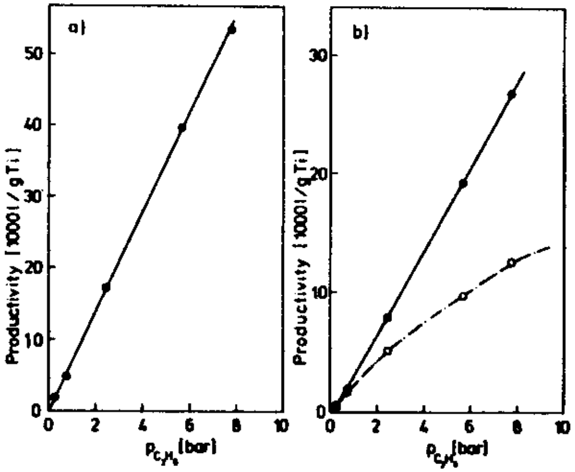
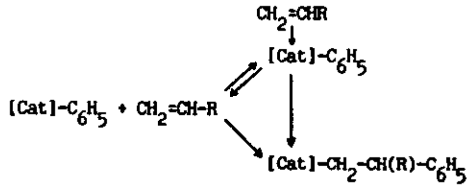


Fig. 1. Productivity (P)(ℓ/g titanium) of the $MgCl_2/TiCl_4/AlR_3$ catalytic system in the polymerization of propylene at different partial pressures of propylene.
a) overall productivity (●); b) productivity referred to the ether soluble fraction (●) and productivity referred to the heptane insoluble fraction (o). Reaction conditions: 8,0 mmoles $Al(i\text{-}C_4H_9)_3$ in 600 ml heptane at 333 K; runs of 2 h.

The mechanism of the insertion reaction with some titanium-aluminum systems was proved by Natta and coworkers already in the fifties (Scheme 3) (39,40), the only aspect remaining unclarified being the possibility of the formation of an intermediate π complex preceding the actual insertion.

Scheme 3

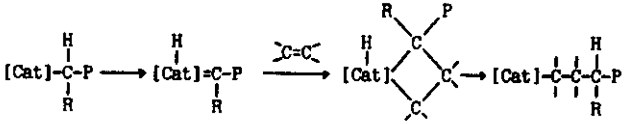


R = H, alkyl

While it seems likely that with heterogeneous catalysts, adsorption of the monomers on the catalyst precedes the actual insertion (56,57), the formation of a π-olefin complex as postulated by Cossee (58-60) has received no experimental confirmation and has recently been challenged also on theoretical grounds (61).

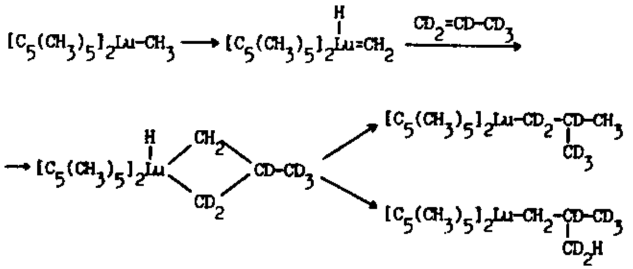
Some authors (62,63) have postulated that when a hydrogen atom is present on the carbon atom in an α-position with respect to the metal atom, it is possible that the insertion of the olefins occurs through a carbene intermediate. This interesting additional possibility for the insertion of the olefins into a Mt-CH< bond (Scheme 4a) has been subjected to experimental verification: in the copolymerization of $C_2D_4$ with $C_2H_4$ using a $(C_5H_5)_2TiCl(C_2H_5)/AlCl_2(C_2H_5)$ catalytic system, virtually no isotope effect was observed ($k_{pH}/k_{pD}$ = 1.04 ± 0.03), (64) contrary to expectations from the model of the carbene intermediate (62,63).

Scheme 4a



In the investigation of the dimerization of propylene with the $[C_5(CH_3)_5]_2$-Lu-$CH_3$ catalytic systems (Scheme 4b) (16) only chains containing $CH_3$ groups have been obtained, while $-CD_2H$ groups should be present, according to the model of carbene intermediate, unless the cleavage of the metallacyclobutane ring is completely regioselective.

Scheme 4b



On the other hand ethylene is readily polymerized at 0° using $[P(CH_3)_3]_3(I)_2(H)Ta{=}CHC(CH)_3)_3$ as catalyst precursor (14,15) as expected from the model of the carbene intermediate.

Recent research on the insertion of α-olefin into metal-to-carbon bonds has confirmed the remarkable regioselectivity of the process (Table 2).

Insertion of the 1-2 type has been confirmed for 3-methyl-1-pentene(67) and propylene (66) as monomers with the catalytic system δ-$TiCl_3/Al(C_2H_5)_2Cl$ as well as for the supported system $TiCl_4/MgCl_2/AlR_3$/ethylbenzoate (66). The same type of insertion was confirmed in the case of propylene for the soluble system $[C_5(CH_3)_5]_2Lu{-}CH_3$ (16) and seems very likely for the soluble system $(C_5H_5)_2Ti(CH_3)_2/[-Al(CH_3)O-]_n$ (28).

Apparently insertion of the 2-1 type and/or low regioselectivity are peculiarities of soluble catalytic systems of vanadium (65).

The stereospecificity of the insertion of the monomer in the first step of polymerization of propylene was investigated using $Al(^{13}CH_3)_2X$ (X=Cl or I) or $Al(^{13}CH_2CH_3)_3$ (66). As shown in Table 3 the stereospecificity of the first insertion was always lower than that of the following steps of polymerization. However, in the polymerization of propylene a remarkable increase in the stereospecificity was observed for δ-$TiCl_3/AlR_2X$ systems with R = $CH_3$ going from X = Cl to X = I (65-67). Furthermore, an increase was found going from $Al(CH_3)_2Cl$ to $Al(C_2H_5)_3$ (66). The stereospecificity in the first step of polymerization is similar using δ-$TiCl_3$ or $TiCl_4/MgCl_2$ as the solid component of the catalyst (66). Similar results have been obtained using rac.- or (S)-3-methyl-1-pentene as monomers (67).

TABLE 2. Regioselectivity in α-Olefin Insertion

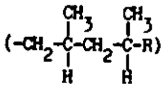
| Olefin | Catalyst precursor | Type of prevailing insertion | $CH_2$-$CH_2$ sequences g/100g polymer | Ref. |
|---|---|---|---|---|
| Propylene | $(C_5(CH_3)_5)_2Lu(CH_3)\cdot O(C_2H_5)_2$ | 1-2 | - | 16,17 |
| Propylene | $(C_5H_5)_2Ti(CH_3)_2/(-Al(R)O-)_n$ | 1-2 | - | 28 |
| Propylene | δ-$TiCl_3/Al(C_2H_5)_2Cl$ | 1-2 | <1 | 66 |
| Propylene | $TiCl_4/MgCl_2/Al(C_2H_5)_3$/EB a) | 1-2 | - | 66 |
| Propylene | $VCl_4/Al(C_2H_5)_2Cl$/Anisole b) | 2-1 | 3.3 | 65 |
| 3-Methyl-1-pentene | δ-$TiCl_3/Al(CH_3)_3/Zn(CH_3)_2$ | 1-2 | - | 67 |

a) Ethylbenzoate
b) at -78°C

TABLE 3. Stereoregulation in the First Polymerization Step of Propylene (66)

| Catalytic System | mm triads molar fraction | [e]a) | R |
|---|---|---|---|
| $TiCl_3/Al(^{13}CH_3)_2Cl$ | 0.76 | 0.50 | $^{13}CH_3$ |
| $TiCl_3/Al(^{13}CH_3)_2I$ | 0.82 | 0.75 | $^{13}CH_3$ |
| $TiCl_3/Al(^{13}CH_2CH_3)_3Zn(^{13}CH_2CH_3)_2$ | 0.91 | 0.79 | $^{13}CH_2CH_3$ |
| $TiCl_4/MgCl_2/EB/Al(^{13}CH_2CH_3)_3/Zn(^{13}CH_2CH_3)_2$ | 0.89 | 0.80 | $^{13}CH_2CH_3$ |

a) molar fraction of erythro terminal groups



$(-CH_2-\overset{CH_3}{\underset{H}{C}}-CH_2-\overset{CH_3}{\underset{H}{C}}-R)$

These results show that in agreement with other experimental data (28), stereospecificity in the polymerization of α-olefins is connected with the presence of chiral catalytic centers (68). However, since the stereospecificity in the first step of polymerization is also connected with the size of the alkyl group bound to the catalytic center, it appears that the bulkiness of the last inserted monomeric unit bound to the catalyst plays an important role in stereoregulation. This is in keeping with predictions from the stereochemical models proposed by Corradini and coworkers (69-71).

The stereoregularity of polypropylenes measured on the basis of the content of meso pentads is closely connected to the type of the catalytic system used in the polymerization (Table 4).

TABLE 4. Isotactic Pentads in Polypropylenes Obtained with Different Catalytic Systems

| Catalyst precursor | Polymer fractions |  |  |  |  |  | Ref. |
|---|---|---|---|---|---|---|---|
|  | Ether soluble |  | Heptane soluble |  | Heptane insoluble |  |  |
|  | % | mmmm % | % | mmmm % | % | mmmm % |  |
| $Cp_2Ti(CH_3)_2/[-Al(CH_3)O-]_n$ | 100 | 6 | - |  | - |  | 18 |
| $Zr(CH_2-C(CH_3)_2-C_6H_5)_4/Al_2O_3$ | 47 | 14 | 53 b) | 56.7 | - |  | 22 |
| $TiCl_4/MgCl_2/Al(iC_4H_9)_3$ | 36.0 | 15.1 | 28.2 | 51.4 | 35.4 | 84.0 | 72 |
| $TiCl_4/MgCl_2/Al(iC_4H_9)_3/LB$ a) | 3.3 | 8.1 | 5.9 | 39.7 | 90.4 | 88.9 | 72 |

a) LB = $C_6H_5COOC_2H_5$; LB/$AlR_3$ = 0.8

b) Ether insoluble fraction

The minimum content in meso pentads was observed in the polypropylenes obtained with the soluble catalytic systems $(C_5H_5)_2Ti(CH_3)_2/[-Al(CH_3)O-]_n$ (18-20, 28). Of the heterogeneous catalytic systems, single component catalysts do not yield highly stereoregular polymers. Most of these data come from the patent literature (21) and it is not clear if the relatively low stereoregularity in the non-fractionated polymer is connected to the absence of highly stereospecific centers in these catalysts.

With the $MgCl_2$ supported $TiCl_4$ catalyst, the low percent of meso pentads in the non-fractionated polypropylenes is clearly due to the presence of centers yielding atactic polypropylene in addition to stereospecific centers; in fact, highly isotactic polypropylenes with meso pentads content above 90% can be obtained by modifying the catalytic systems with the addition of Lewis bases. In Table 5 the meso pentads content as well as the percentage of some other relevant pentads are shown for fractions obtained using the catalytic system $TiCl_4/MgCl_2/AlR_3$ in the absence and in the presence (LB/Al = 0,8) of a Lewis base (72). The presence of the Lewis base completely changes the diastereomeric composition of the polymers, as shown by the percentage of the different fractions obtained in either case. Furthermore, in the ether soluble and in the ether insoluble/heptane soluble fractions, the ratio between the meso and the racemic pentads substantially decreases in the presence of a Lewis base, showing that in this type of catalyst the few centers which produce syndiotactic polypropylenes have not been modified or poisoned by the Lewis base.

It has been proven experimentally (73, 74) that the Lewis bases act in two ways; i.e. by poisoning the non-stereospecific centers which have lower Lewis acidities than the stereospecific ones or by transforming non-stereospecific centers into stereospecific ones by coordination to one of the vacant coordination sites.

TABLE 5. Steric Irregularities in Polypropylenes Obtained with $TiCl_4/MgCl_2$ Catalysts in the Presence and in the Absence of Lewis Bases

| Polymer Fraction | Catalytic System |  |  | mmmm | mmmr | mrrm | rrrr |
|---|---|---|---|---|---|---|---|
|  |  | % | [η]* | % | % | % | % |
| Acetone insoluble, | A | 36.0 | 0.75 | 15.1 | 9.9 | 8.4 | 11.9 |
| Ether soluble | B | 3.3 | 1.07 | 8.1 | 7.1 | 10.4 | 15.5 |
| Ether insoluble, | A | 28.2 | 1.25 | 51.4 | 9.8 | 7.9 | 6.0 |
| Heptane soluble | B | 5.9 | 1.41 | 39.7 | 8.9 | 5.6 | 15.3 |
| Heptane insoluble, | A | 12.1 | 1.45 | 76.4 | 7.1 | 4.8 | 0.4 |
| Trimethylpentane soluble | B | 8.7 | 1.10 | 85.6 | 4.8 | 2.4 | 0.7 |
| Trimethylpentane insoluble, | A | 6.9 | 2.29 | 84.1 | 4.2 | 3.4 | 0.0 |
| Octane soluble | B | 13.4 | 1.34 | 88.9 | 3.5 | 2.0 | 0.6 |
| Octane insoluble | A | 15.4 | 2.39 | 88.2 | 3.0 | 2.5 | 0.5 |
|  | B | 68.3 | 4.03 | 88.9 | 3.5 | 2.0 | 0.6 |

A : 40 mg $MgCl_2/TiCl_4$ (2,8% Titanium)
B : 455 mg $MgCl_2/TiCl_4$ (2,8% Titanium); 10.6 mM Ethyl benzoate
Polymerization Conditions: 600 ml heptane; 2,7 bar (0.88 M) $C_3H_6$; 13.3 mM $Al(i-Bu)_3$; 60°C; 2 h; 1000 RPM. Steric pentad fractions determined by $^{13}C$ NMR. *[η] in dl/g (tetraline at 135°).

c) Chain Termination

The investigation of the polymerization of propylene with the $[C_5(CH_3)_5]_2Lu-CH_3$ (17) soluble catalytic system has shown that there are two other possible chain terminations (Scheme 5e,f) in addition to the four well-known reactions (Scheme 5a,b,c,d). As early as 1960 the elimination of the 3-methyl group in trineopentylaluminum was observed (75), but this mechanism has never been considered as one of the possible chain terminations in the polymerization of propylene.

Scheme 5. Chain Termination

a) $Mt-CH_2-CH(R)-P \longrightarrow Mt-H + CH_2{=}C(R)-P$

b) $Mt-CH_2-CH(R)-P + CH_2{=}CH-R \longrightarrow Mt-CH_2-CH_2-R + CH_2{=}C(R)-P$

c) $Mt-CH_2-CH(R)-P + H_2 \longrightarrow Mt-H + CH_3-CH(R)-P$

d) $Mt-CH_2-CH(R)-P + Me(C_2H_5)_n \longrightarrow Mt-CH_2-CH_3 + Me(C_2H_5)_{n-1}CH_2-CH(R)-P$

e) $Mt-CH_2-CH(CH_3)-P \longrightarrow Mt-CH_3 + CH_2{=}CH-P$

f) $Mt-CH_2-CH(CH_3)-P + CH_2{=}CH-CH_3 \longrightarrow Mt-CH_2-CH{=}CH_2 + CH_3-CH(CH_3)-P$

Chain termination by hydride transfer to the monomer (Scheme 5b) does not play any role in the dimerization of propylene with aluminumalkyls (76) but it seems to play a role in the polymerization of propylene with the $TiCl_4/MgCl_2/AlR_3$ catalytic system. In fact no change in the average molecular weight in the isotactic fraction was observed when the partial pressure of propylene was increased from 0.5 to 7.7 bar (Fig. 2) (23,80) and this can

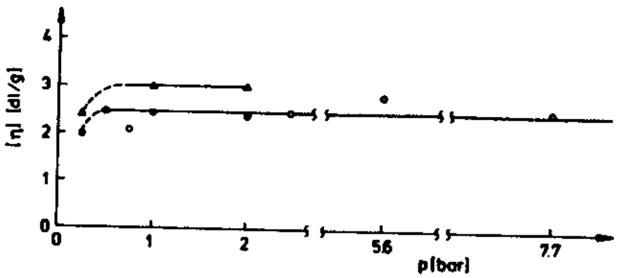
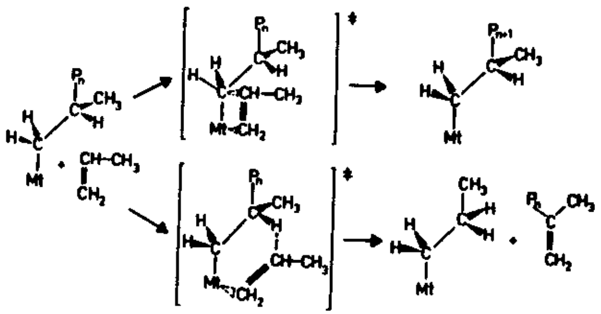


Fig. 2. Intrinsic viscosity of the heptane insoluble fraction of polypropylenes obtained at different $P_{C_3H_6}$.
▲ $TiCl_4/MgCl_2$, TMEDA/Al = 0.2, 2.8% Ti. ● $TiCl_4/MgCl_2$, 2.8% Ti.
o $TiCl_4/MgCl_2$, 2.6% Ti. Reaction conditions in Fig. 1.

be taken as an indication that monomer concentration influences both growth and termination reactions in the same way. Only at very low propylene concentrations was a decrease in average molecular weight noticed.
A six member transition state similar to the one proposed for the dimerization of propylene in presence of a nickel complex (77,78) is believed to be responsible for this type of termination (79). Scheme 6 shows the similar transition states for insertion and chain termination by hydride transfer to the monomer, where the position of the monomer alone has been altered by rotation.

Scheme 6: Possible Structure of the Transition States for Insertion and Chain Termination in $C_3H_6$ polymerization



In the $MgCl_2/TiCl_4/AlR_3$ catalytic system the reaction of chain termination induced by aluminumalkyl does not seem to be significant at least under the chosen reaction conditions. In fact the increase by a factor of 200 of the concentration of aluminumalkyl led to only small decreases in the average molecular weights of the heptane soluble and heptane insoluble fractions. The increase in concentration of aluminumalkyl caused an increase in the heptane insoluble fractions and a decrease in the ether soluble fractions as well as in the overall productivities (23) (Table 6).

TABLE 6. Effect of the $AlR_3$ Concentration on the Diastereomeric Composition of the Polypropylene Prepared with the Catalytic System $TiCl_4/MgCl_2/Al(iC_4H_9)_3$

| $Al(iBu)_3$ mmoles l | Al/Ti molar ratio | Productivity (gPP/gTixhxbar) | Polypropylene Fractions | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | acetone soluble | | diethylether soluble | | heptane soluble | | heptane insoluble | |
| | | | % | (η) dl/g | % | (η) dl/g | % | (η) dl/g | % | (η) dl/g |
| 0.7 | 10 | 9305 | 3.3 | n.d. | 44.1 | .80 | 23.5 | 1.08 | 28.1 | 2.19 |
| 3.3 | 53 | 9090 | 3.2 | n.d. | 40.5 | .81 | 24.7 | 1.25 | 31.7 | 2.45 |
| 13.3 | 196 | 7720 | 1.3 | n.d. | 35.9 | .82 | 24.6 | 1.22 | 38.2 | 2.42 |
| 33.3 | 573 | 6656 | 3.1 | n.d. | 32.9 | .80 | 23.5 | 1.14 | 40.5 | 2.36 |
| 133.3 | 2230 | 5445 | 2.9 | n.d. | 32.6 | .65 | 18.8 | 1.08 | 45.7 | 2.29 |

Polymerization conditions: $p(C_3H_6)$ = 1.0 bar, T = 333K, Ti-content = 2.80%, solvent: 600 ml n-heptane, polymerization time = 2 h.

Chain termination by hydrogen (96,97) was investigated using different catalytic systems (81,82); particularly relevant are the results obtained in the chain termination by hydrogen in the polymerization of ethylene and propylene with a $TiCl_4/MgCl_2/AlR_3$ catalytic system (Figure 3) (83).

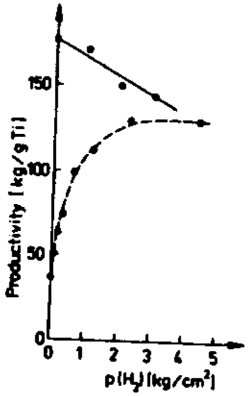


Fig. 3. Productivity of ethylene (●) and propylene (o) as a function of $p_{H_2}$; reaction conditions:
$C_2H_4$: p = 5.0 atm, T = 333 K, t = 1.0 h $[Al(C_2H_5)_3]$ = 10 mM
$C_3H_6$: p = 3.0 atm, T = 343 K, t = 0.5 h $[Al(C_2H_5)_3]$ = 5 mM

While the productivity of polyethylene is decreased by increasing the partial pressure of hydrogen up to 4 atm, with the same catalyst there is a three fold increase in productivity of polypropylene when the partial pressure of hydrogen is increased from 0 to 3 atm. This can be rationalized as-

suming that ethylene is polymerized at least in large part by centers which are substantially different from the centers which polymerize propylene. We shall discuss this point further in the section dedicated to the characterization of the catalytic centers of this type of supported catalyst.
For propylene the decrease in molecular weight fits the equation proposed for the traditional catalysts ($\bar{M}_v^0/\bar{M}_v = 1 + K(p_{H_2})^{1/2}$) (84,85).

## CONTROL OF MOLECULAR WEIGHT DISTRIBUTION IN LINEAR POLYOLEFINS

This problem is attracting more and more attention because molecular weight distribution controls some important properties of poly(α-olefin)'s.
An exhaustive review on this subject by U. Zucchini and G. Cecchin (86) has recently been published; therefore only a few remarks will be made here on this subject.
As shown in Table 7 polydispersity in linear polyethylenes can vary over a broad range ($\bar{M}_w/\bar{M}_n$ = 1.07-10), depending on the catalytic system used. In general, low polydispersity is only obtained with soluble catalysts at low temperatures. The typically high polydispersity obtained with heterogeneous catalysts is at least in part related to the variety of chemical nature of the active centers. In the polymerization of propylene the use of $MgCl_2$ to support $TiCl_4$ catalysts does not seem to influence polydispersity, but more data are needed to confirm this point.

TABLE 7. Polydispersity of Polyethylenes Obtained with Soluble, Traditional, $SiO_2$-$Al_2O_3$ Supported and $MgCl_2$ Supported Titanium Catalysts

| Catalytic System | Temperature °C | $\bar{M}_n$ $10^{-3}$ | $\bar{M}_w/\bar{M}_n$ | Ref. |
|---|---|---|---|---|
| $Cp_2TiEtCl/AlEtCl_2$ | 0 a) | - | 1.81 | 87 |
| $Cp_2TiCl_2/AlEt_2Cl$ | 5 b) | - | 1.07 | 88 |
| α-$TiCl_3$·0.3 $AlCl_3/AlEt_3$ | 70 | 340 | 8.0 | 89 |
| $TiCl_4/SiO_2$-$Al_2O_3/AlEt_3$ | 70 | 300 | 10.0 | 89 |
| $TiCl_4/MgCl_2/AlEt_3$ | 75 | 15 c) | 6.2 | 86 |

a) in toluene; Al/Ti = 1-10
b) in benzene
c) in the presence of hydrogen

According to Zucchini and Cecchin (86) the polydispersity in polyolefins is influenced, among other factors, by the type of transition metal, and, in the two component catalytic system, by the type of main group metal alkyl, by the nature of the carrier and by the temperature of polymerization. Due to this situation a rational approach for controlling polydispersity is not feasible at present. A better knowledge of the structure of the catalytic centers, the synthesis of catalysts which contain only a few types of well defined active centers and a much deeper understanding of the mechanism and kinetics of polymerization are required. An empirical approach with selected catalytic systems has produced some success in controlling the polydispersity of linear polyethylenes and in many laboratories further research is in progress to obtain similar control of polydispersity of polypropylenes.

## CHARACTERIZATION OF THE ACTIVE CENTERS IN THE ORGANOMETALLIC CATALYSTS FOR THE POLYMERIZATION OF OLEFINS

The characterization of the active centers in catalytic systems is one of the main problems still to be solved in homogeneous and heterogeneous catalysis. In view of the low concentrations and of the very high reactivities of the active centers direct physico-chemical measurements yield only relatively little information. Indirect methods, such as the investigations of the structure and the composition of the reaction products, of the time dependence of the reaction rate, studies of model reactions and studies of the reactions leading to the formation and disappearance of the catalytic centers has yielded more interesting information, at least in the polymerizations of ethylene and α-olefins. The most interesting recent results have been obtained with the catalytic systems of the type $TiCl_4/MgCl_2/AlR_3$ which give well reproducible results and can be reversibly modified by the use of suitable Lewis bases (23)(28).
Indeed, the systematic investigation of the influence of the Lewis base to $AlR_3$ ratios (r) on the productivity of catalyst (28), on the time dependence of productivity (90), on the diastereomeric composition of the polymers(28) and on the stereoelectivity in the polymerization of racemic α-olefins (42, 91) has yielded new and very interesting information.
We shall first examine the information arising from the investigation of the time dependence of the overall productivity of polyethylene and poly(α-olefin)'s as a function of (r) and then we shall discuss the information obtained from the study of the diastereomeric composition of the poly(α-olefin) as a function of (r). Information arising from the use of Lewis bases with different structures have already been published (92) and will not be considered here.

### a) Polymerization of Ethylene and of α-Olefins with the Catalytic System $TiCl_4/MgCl_2/AlR_3$ in the Absence and in the Presence of a Lewis Base

Ethylene and α-olefins are polymerized very rapidly by the $TiCl_4/MgCl_2/AlR_3$ catalytic system. In our experiments the rates of polymerization after one hour are 50'000 ℓ/gTi·h for ethylene, 400 ℓ/gTi·h for propylene and 200 ℓ/gTi·h for 1-butene, respectively.
A closer examination of the time dependence of the polymerization rate shows that for ethylene the rate reaches a limiting value after 40 min and remains constant for at least one additional hour (Figure 4a). On the contrary, with propylene a rate maximum is reached after few seconds and then

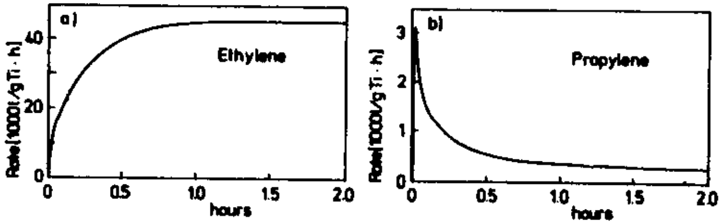


Fig. 4. Time dependence of the rate of polymerization of ethylene and propylene: a) $p_{C_2H_4}$ = 0.25 bar, b) $p_{C_3H_6}$ = 1.0 bar; polymerization conditions in Fig. 1

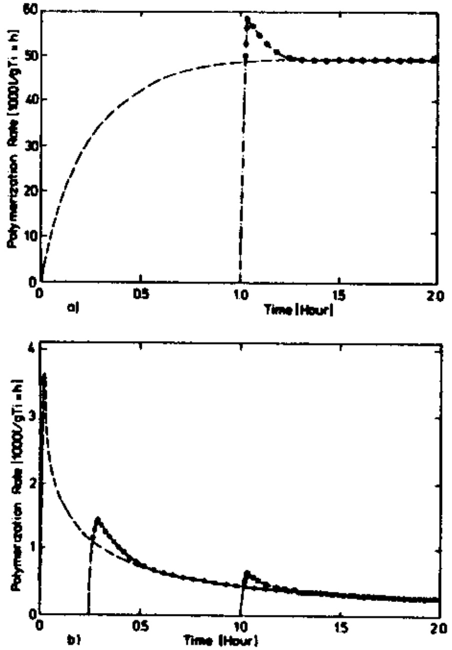


Fig. 5. Influence of catalyst aging on the rate of polymerization of ethylene and propylene a) $C_2H_4$, aging time 1 h, $p_{C_2H_4}$ = 0.25 bar b) $C_3H_6$ aging time 0.25 and 1 h, $p_{C_3H_6}$ = 1.0 bar

it rapidly decreases, reaching a nearly constant value after about one hour (Figure 4b). In both cases, the change in rate with time can be attributed to the formation or disappearance of active centers. In fact, the measurements of concentration of active centers at different times made by Giannini and coworkers (93) and by Keii and coworkers (57) show that there is a rapid decrease with time in the concentration of the catalytic centers that polymerize propylene. Furthermore, when monomer was added to the catalytic system after one hour, the same rate was observed (Fig. 5) as preparing the catalyst in presence of monomer, showing that the presence of either monomer does not influence the rate of formation or of disappearance of the active centers. If the change in productivity at constant concentration of monomer is taken as an indication of a change in concentration of active centers, the variation with time in the overall productivity at different $AlR_3$ concentrations (Fig. 6) indicates at least in the case of propylene that the $AlR_3$ takes part in both the formation and the inactivation of active centers.

In agreement with the experiments of Kashiwa and Yoshitake (94) who succeeded in re-generating the active centers by treating the catalyst with chlorine, and from analysis of the curve of Figure 5b, it appears that inactivation of the catalytic centers is a bimolecular process which leads to Ti species with lower oxidation states. In agreement with the proposal of Keii et al., (57) a complexation equilibrium between aluminum alkyl in so-

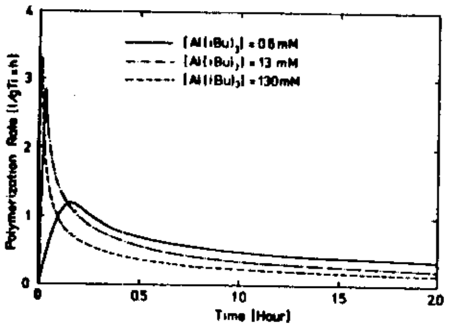


Fig. 6. Time dependence of the rate of polymerization at different concentrations of aluminum alkyl; polymerization conditions: $P_{C_3H_6}$ = 1.0 bar, T = 333 K, t = 2 h, $TiCl_4/MgCl_2$, 2.8% Ti, solvent = heptane

lution and adsorbed on the surface of solid catalyst should exist. This adsorbed aluminum alkyl should favor both the alkylation of titanium (this is supposed to be one of the steps in the synthesis of the catalytic centers for the polymerization of propylene) and the bimolecular inactivation of those catalytic centers.

The experiments show that the centers for the polymerization of ethylene are much more stable than the centers for the polymerization of propylene, but in order to characterize them, further research is necessary. A comparison of the decrease in the rate of polymerization of ethylene with that of propylene, both in the presence of ethylbenzoate as a Lewis base (Fig. 7), shows that on the average the centers for the polymerization of ethylene are stronger Lewis acids than the centers which polymerize propylene.

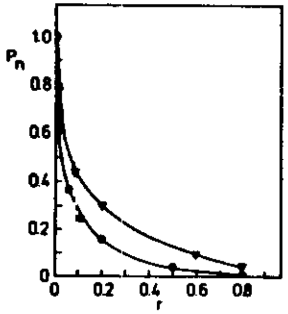


Fig. 7. Normalized productivities (Pn) of polyethylene (●) and polypropylene (▼) at different ethylbenzoate-to-aluminum alkyl ratios (r). Reaction conditions in Fig. 1, $P_{C_2H_4}$ = 0.25 bar

The change in the time dependence of the rate of polymerization of ethylene for different values of (r) (Fig. 8) confirms these results.

Furthermore, in Fig. 8 it is shown that at high values of (r) ((r) = 0.8) the changes in time dependence of the rates of polymerization for propylene and for ethylene are very similar, and their productivities are of the same order of magnitude.

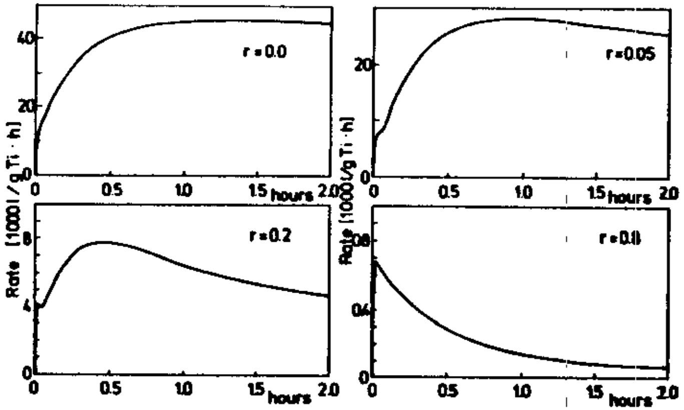


Fig. 8. Time dependence of the rate of polymerization of ethylene at different ethylbenzoate-to-aluminum ratios (r). Reaction conditions in Fig. 7.

Therefore, we conclude that ethylene is also polymerized by the catalytic centers which polymerize propylene. However in the absence of Lewis base most of the ethylene is polymerized by catalytic centers which do not polymerize propylene or polymerize it only at a very low rate.
Giannini and Guastalla (83) demonstrated the effect of hydrogen on the productivity of the catalytic system $TiCl_4/MgCl_2/AlR_3$ and it appears that for the polymerization of ethylene the catalytic centers are not, or are only slowly re-generated after reaction with hydrogen, while for the polymerization of propylene the presence of metal-to-hydrogen bonds generated by the addition of hydrogen slows down the bimolecular deactivation of the catalytic centers. This is further evidence of the remarkable differences in the two types of centers.

### b) Information about the Catalytic Centers Arising from the Diastereomeric Composition of the Polymers of α-Olefins

The analysis of the diastereomeric composition of the poly(α-olefin)'s yielded important information about the catalytic centers. However, it must be emphasized that as in kinetic controlled multistep reactions all the information from the composition of reaction products concerns the transition state with the highest energy (95)(Fig. 9). In order to organize the above information, we assumed that this transition state corresponds to the insertion of the α-olefin into the metal-to-growing chain bond as schematically represented in Fig. 10.

Fig. 9. Free energies of two possible transition states in polymerization of propylene with heterogeneous catalysts to isotactic polymer.

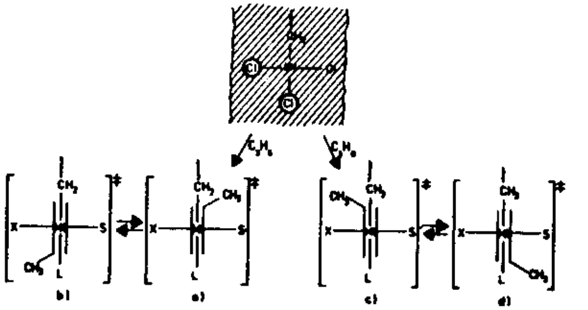


Fig. 10. Simplified model of the transition state of the insertion of propylene. Condition for 1-2 insertion: L>>CH ; isospecific centers: X>>S; unspecific centers $X \gtrsim S$

This representation is based on the experimentally proved chiral nature of the catalytic centers; it rationalizes on the basis of the different steric hindrance of the ligands S, X and L to the approach of the monomer, the 1-2 regioselectivity (large size of L with respect to the $CH_2$ group of the growing chain) and the stereospecificity (large difference in size between X and S). In the above framework, the previously described active centers which polymerize ethylene but not (or very slowly) propylene should have substituents S and X, which both exert a high steric hindrance in the direction of the approach of monomers, thus hindering the polymerization of α-olefins but not of ethylene. The stereoregulating effect of the Lewis base is shown in Fig. 11 and is connected to the presence of active centers with two vacant sites. The same scheme also rationalizes the stereoelectivity obtained in the polymerization of racemic α-olefins in the presence of chiral Lewis bases (74).

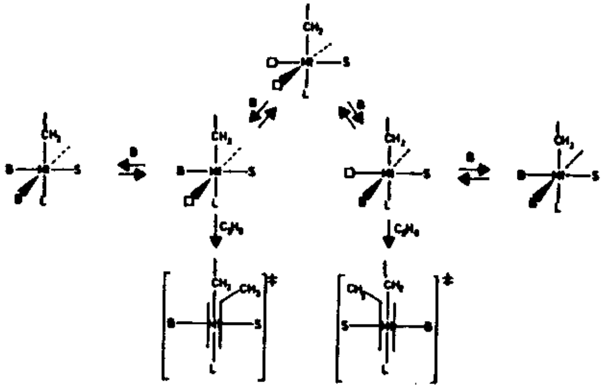


Fig. 11. Simplified model of a possible stereoregulating effect of the Lewis base (B)

According to the results obtained by polymerising non-chiral and racemic olefins at different Lewis base-to-aluminium alkyl ratios six classes of active centers have been postulated in the $TiCl_4/MgCl_2/AlR_3/LB$ catalytic systems (74).
Using the schematic representation of the transition states reported in Fig. 10 and 11, which does not contradict the model of active centers which was recently proposed by Corradini and coworkers (69-71), we are now extending our own research to Lewis bases with different structure (92), with the hope of obtaining further information about the structure of the catalytic centers and about shape and dimension of the L, X and S groups coordinated to the transition metals.

## FINAL REMARKS

After the rapid development of new highly active and highly stereospecific catalytic systems in the seventies, which brought about remarkable improvements in the industrial processes for the production of linear polyolefins, the main goals of industrial research in the field are now to develop new processes for the production of copolymers of ethylene and α-olefins to replace the usual high pressure polyethylenes, and to control polydispersity and morphology of polymers and copolymers of olefins in order to obtain products with varied tailor-made properties for the different end-uses.
Basic research is directed towards having a better knowledge of the structures of the catalytic centers and of the methods for synthesizing catalysts containing catalytic centers with similar structures and catalytic properties. The detailed research on the $TiCl_4/MgCl_2/AlR_3$ catalytic systems, in keeping with the research on heterogeneous catalysts, shows how broad the above field is and how far we are from a detailed understanding of the interplay between the steric and electronic factors which the activity and specificity of the catalytic centers are based on.
Detailed knowledge about the synthesis of the active centers in soluble and insoluble catalysts is still lacking, even though some general aspects, such as the formation of transition metal-to-carbon bonds, have been confirmed.
Concerning chain growth and chain termination, the basic knowledge acquired in the fifties, mainly by Natta and his group, are still valid and the substantial differences between radical polymerization and the polymerization of olefins by polyinsertion into metal-to-carbon bond have been completely confirmed by the detailed kinetic investigations of the polymerization of olefins in homogeneous phase.

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Chapter

# Reactions of Macromolecules

## 23.1. Basic Principles

### 23.1.1. Review

Reactions are often carried out on macromolecules in order to elucidate their chemical structure.

Macromolecular transformations are also of scientific and commercial interest. They can be used for the manufacture of new compounds, particularly in cases where no monomer exists (vinyl alcohol as the enolic form of acetaldehyde) or where the monomer polymerizes with difficulty or not at all (e.g., vinyl hydroquinone). In these cases, derivatives such as vinyl acetate or vinyl hydroquinone ester are polymerized and the polymers are then saponified to poly(vinyl alcohol) and poly(vinyl hydroquinone), respectively. Other processes of industrial importance are conversions of inexpensive macromolecular compounds such as cellulose into new materials (cellulose acetate, cellulose nitrate, etc.), manufacture of ion-exchange resins, and dyeing with reactive dyestuffs. All of these reactions lead to a definite product. If the degree of polymerization is retained, then they are called polymer analog reactions.

Undesirable reactions are among those that occur during the more or less long-term applications of macromolecular materials exposed to the influence of atmospheric conditions (air, water, light, etc.). This aging, as it is called, to form undesirable products not only causes the constitution of the monomeric units to change (for example, through oxidation); it may also lower the degree of polymerization through oxidative degradation or hydrolysis. In a few cases, however, the molecular weight is increased by simultaneously occurring cross-linking reactions. Since the decrease in the degree of polymerization usually predominates, this undesired reaction is often described simply as "degradation." The term "degradation" should really be confined to reactions where a decrease in the degree of polymerization occurs with retention of the original constitution.

The reactions and properties of macromolecules are determined by chemical structure and molecular size. Consequently, it is convenient to use these parameters instead of, for example, mechanisms to classify macromolecular reactions. Distinction is made among catalyses, isomerizations, polymer analog conversions, chain extension, and degradation reactions according to whether the chemical structure, the molecular weight, and/or the degree of polymerization are retained or changed.

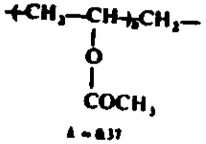
### 23.1.2. *Molecules and Chemical Groups*

Macromolecular reactions proceed more or less similarly to those of low-molecular-weight compounds. Special features are seen through the neighboring group effect and the whereabouts of the "by-products."

In low-molecular-weight chemistry, side reactions only lead to a diminishing of the yield of the main product. In macromolecular chemistry however, side reactions can involve the same molecule, since each macromolecule possesses many reactive groups. Consequently, main and by-products cannot be separated from each other by the more or less simple separation processes used in low-molecular-weight chemistry. Thus, in contrast to low-molecular-weight chemistry, yield (with respect to molecules) must be sharply distinguished from conversion (with respect to reactive groups) when dealing with macromolecular reactions.

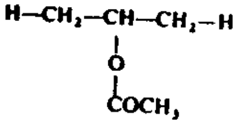
The reactivity of macromolecular and low-molecular-weight groups is about the same when neighboring group effects are taken into consideration.

Isopropyl acetate, and not ethyl acetate or vinyl acetate, is thus the more suitable model compound for considering the hydrolysis of poly(vinyl acetate) with sodium hydroxide in acetone/water (75:25) at 30°C, as can be seen from the rate constants:



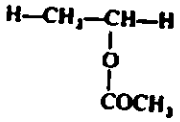
$-(CH_2-\underset{\substack{|\\O\\|\\COCH_3}}{CH})_nCH_2-$

$k = 0.37$



$H-CH_2-\underset{\substack{|\\O\\|\\COCH_3}}{CH}-CH_2-H$

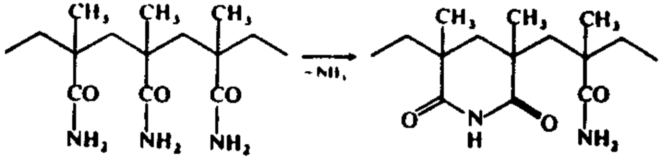
$k = 0.57$



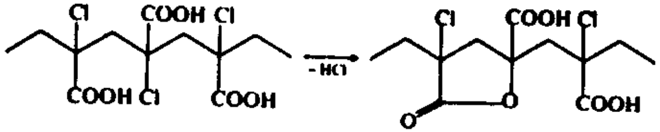
$H-CH_2-\underset{\substack{|\\O\\|\\COCH_3}}{CH}-H$

$k = 3.5\ dm^3\ mol^{-1}\ min^{-1}$

If there is only a small number of reactive groups per macromolecule, the environment of these groups is not changed as the reaction proceeds. The macromolecular chain simply acts as a diluent. Of course, neighboring group effects can also play a role, especially if five- and six-membered cyclic transition states can be formed. An example of this is the partial imidization of poly(methacrylamide) at temperatures above 65°C:


(23-1)

or lactone formation in the polymerization of chloracrylic acid in water:


(23-2)

Even with a very low macromolecular concentration, the reactive groups are present at a quite high local concentration, since they are locally confined by being attached to the macromolecule. Most macromolecules form coils in solution (see Chapter 4). The concentration of reactive groups is very high within the coils; it is virtually zero outside.

The following example illustrates this situation: A 1% solution of ethyl acetate ($M = 88$ g/mol) represents a solution of 0.11 mol/dm$^3$ with respect to acetate groups. A 1% solution of poly(vinyl acetate) with $M = 10^6$ g/mol is also about 0.11 molar with respect to acetate groups ($M_u = 86$ g/mol). However, in a coil of spherical shape and homogeneous density the number of groups per unit volume is given by

$$\frac{X_n}{V_p} = \frac{M/M_u}{4\pi r^3/3} \qquad (23\text{-}3)$$

Consequently, a local concentration of $3.5 \times 10^{20}$ groups/cm$^3$, or 0.55 mol of acetate groups/dm$^3$, is obtained for $r = 20$ nm.

The environment can have a decisive influence on the course of a reaction in macromolecular chemistry, altering not only the rate but also the optimum obtainable yield. At equal concentrations, the probability for intramolecular reactions of coil molecules is greater in poor solvents (low second virial coefficient) than in good solvents (high second virial coefficient). Ring-forming reactions therefore occur preferentially in poor solvents.

+7

In every case of polymer analog reactions on unipolymers, a copolymer is first formed at incomplete yield. If this copolymer is insoluble in the solvent, then it precipitates, and no further conversion may be achieved because of the inaccessibility of the potentially convertible groups. The resulting conversion product contains a heterogeneous distribution of the newly introduced groups. In order to obtain homogeneous products, therefore, it is necessary that the solvent employed for the reaction be one in which the intermediate and end product will dissolve.

In extreme cases, block copolymers or polymer mixtures result from reactions of this kind. In the hydrogenations of poly(styrene) with Raney nickel as catalyst, the groups close to the catalyst are preferentially hydrogenated. First, a block of hexahydrostyrene (vinyl cyclohexane) units is formed in a poly(styrene) chain. If the block is large enough, then it will be incompatible with the polystyrene blocks (on incompatibility, see Section 6.6.6). Because of the resulting partial phase separation, only these block copolymer chains remain close to the catalyst, and these chains are first fully hydrogenated, while other chains consist entirely of polystyrene units. Thus, although hydrogenation in itself takes place randomly, the influence of the environment leads to polymer mixtures. Chains are in a highly ordered state in crystalline polymers. Diffusion is therefore slow in crystalline regions. In partially crystalline polymers, consequently, the reactions occur predominantly in the amorphous regions. Since the orientation of the chains also ensures that access is made more difficult, it is possible to obtain different yields with solid polymers according to the degree and kind of morphologically influencing pretreatment. On the other hand, solvents may swell the solid polymer, so that higher yields are possible.

## 23.2. *Macromolecular Catalysts*

By definition, catalysts are substances that make a reaction possible by lowering the activation energy barrier or strongly accelerating a reaction, under the condition that the catalyst remain unchanged at the end of the reaction. Consequently, neither the chemical structure nor the molecular weight of the catalyst is altered.

Macromolecular catalysts are thus macromolecules that possess catalytically effective groups. Whether and to what extent these catalytic groups are more effective than their low-molecular-weight counterparts depends on the positioning of these catalytic groups relative to each other in the macromolecule. This relative positioning is especially important with bifunctional catalysis. Such a bifunctional catalysis occurs, for example, in the joint action of a nucleophilic and an electrophilic reagent on a substrate. Bifunctional catalysis is held to be responsible for the high efficiency of enzymes.

*Figure 23-1.* Arrangement of cooperatively operating catalytic positions in hormones and enzymes. (A) Continuate word, (B) discontinuate word.

A distinction is made with hormones and enzymes between a "continuate word" positioning and a "discontinuate word" positioning of catalytically effective groups (Figure 23-1). With "continuate word" positioning, the sequence of the effective groups is important, whereas with "discontinuate word" positioning, the topology is important. The former case can be described as one of two-dimensional stereochemistry, whereas the latter case is one of three-dimensional stereochemistry. High activities, or effectivities, and specificities are only to be expected with "discontinuate word" positioning.

A similar method of classification can be used for the catalytically effective groups of synthetic polymers. The effectivity of conventionally produced graft copolymers and random copolymers is relatively small, because only few of the catalytically effective groups are correctly positioned relative to each other (Figure 23-2). However, the correct positioning can be achieved when cross-linking agents with scissionable groups are used. For example, the ester of 2,3-*O*-*p*-vinyl phenyl boric acid and D-glycerinic *p*-vinyl anilide can be copolymerized with divinyl benzene in acetonitrile. After removal of glycerinic acid, the cross-linked polymer possesses free amino and free boric acid groups, which are maintained in the correct position to each other by the cross-linked carrier (Figure 23-3). The polymer produced can effect an antipodal separation of D,L-glycerinic acid and D,L-glycerinaldehyde. Similar effects can be expected for catalytically

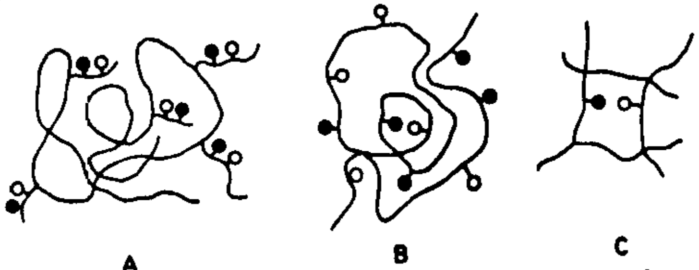


*Figure 23-2.* Arrangement of cooperatively operating catalytic positions in (A) graft copolymers; (B) random copolymers; and (C) conformationally prearranged (before introduction into polymer) groups.

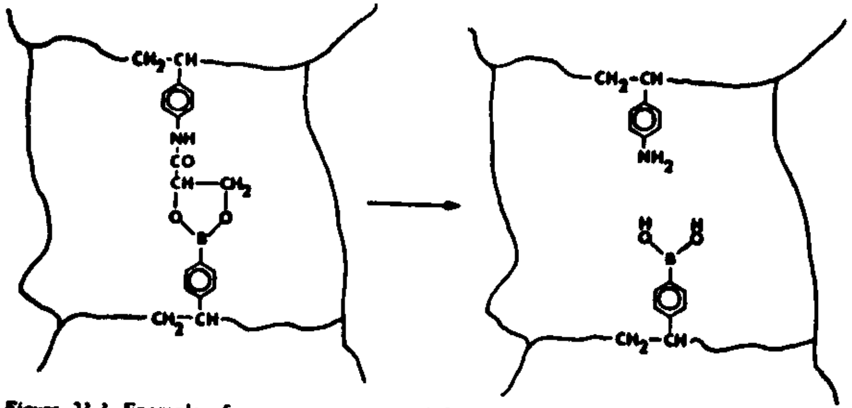
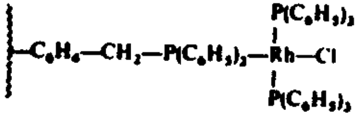


*Figure 23-3.* Example of a group prearranged for cooperative catalytic effectivity before introduction into the polymer.

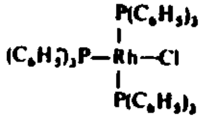
effective groups. The proximity of the two catalytically active groups can produce more entropically favorable conditions for reactions with the substrate: Essentially termolecular reactions behave as bimolecular reactions.

The selectivity of a macromolecular catalyst depends on the size of the substrate as well as on hydrophobic effects. It becomes increasingly difficult for proper contact between catalytically effective groups and the substrate with increasing substrate size for otherwise identical reaction conditions. Thus, the "polymer" rhodium catalyst (I) hydrogenates cyclododecene five times more slowly than it does cyclohexene. This substrate size effect is not observed with the analogous "isolated" low-molecular-weight compound (II):



$$-C_6H_4-CH_2-P(C_6H_5)_2-\overset{P(C_6H_5)_3}{\underset{P(C_6H_5)_3}{Rh}}-Cl$$

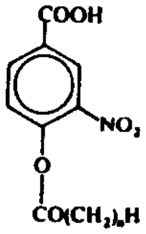
(I)



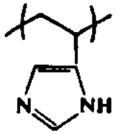
$$(C_6H_5)_3P-\overset{P(C_6H_5)_3}{\underset{P(C_6H_5)_3}{Rh}}-Cl$$

(II)

Saponification of type (III) esters with poly(vinyl imidazole) (IV) as catalyst proceeds about 1000 times faster than saponification with imidazole (V) as catalyst. In addition, the polymer-catalyzed reaction is autocatalytic. The saponification rate increases with the length of the acyl residue (by a factor of 25 from $n = 1$ to $n = 17$). Obviously, increased methylene chain length leads to increasing intramolecular association of the polymer, which is acylated in an intermediate step of the reaction.



(III)



(IV)

(V)

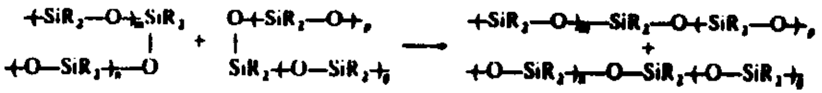
Semiconducting polymers are used as catalysts in dehydrogenation, oxidation, and decomposition reactions. The basis of their effectiveness is as yet not understood. Obviously, only such polymers possessing an aromatic structure that can change to a quinone structure, and vice versa, are catalysts for dehydrogenation reactions. For example, with such catalysts, cyclohexanol is converted exclusively to cyclohexanone at 250°C and cyclohexene is converted to benzene at 350°C without the disproportionation to benzene and cyclohexane usually observed with palladium catalysts.

## 23.3. *Isomerizations*

Isomerizations are defined as reactions that occur with change in the chemical structure but without change in the number-average degree of polymerization.

### 23.3.1. *Exchange Equilibria*

Segments can be interchanged between two polymer chains, as, for example, with polysiloxanes:



$$\begin{array}{c} -(SiR_2-O)_m-SiR_2 \\ | \\ -(O-SiR_2)_n-O \end{array} + \begin{array}{c} O-(SiR_2-O)_p \\ | \\ SiR_2-(O-SiR_2)_q \end{array} \longrightarrow \begin{array}{c} -(SiR_2-O)_m-SiR_2-O-(SiR_2-O)_p \\ + \\ -(O-SiR_2)_n-O-SiR_2-(O-SiR_2)_q \end{array} \qquad (23\text{-}4)$$

These equilibria are also called exchange equilibria. They occur particularly readily in chains with heteroatoms. Besides poly(dimethyl siloxane), polyamides, polyesters, polyacetals, and polyurethanes can be quoted as examples. Exchange equilibria occur readily in all of these compounds because the activation energy for reactions of this kind is low in chains with heteroatoms. In carbon chains, the activation energy needed is much higher, since there are neither electron vacancies, free electron pairs, nor incomplete electron shells. Generally, however, the reactions leading to the establishment of an equilibrium can be appropriately catalyzed, for example, with sulfuric acid in poly(dimethyl siloxane). The reactions are termed transamidations, transacetalations, etc., and, in the special case of polysiloxanes, equilibrations.

The reaction enthalpy of such exchange reactions is zero, since the same kinds of bonds are exchanged. Consequently, the reaction entropy, that is, the arrangement possibilities of the chains, is controlling. If, for example, pentene-2 is converted with the catalyst $WCl_6/C_2H_5OH/C_2H_5AlCl_2$ at room temperature, then within a few minutes a mixture of 25 mol % butene-2, 50 mol % pentene-2, and 25 mol % hexene-3 is obtained. This composition exactly fulfills the statistical expectations for a random exchange of double bonds. This reaction is also known as olefin metathesis.

Olefin metathesis can be used to synthesize macromolecules. If cycloolefins are treated with the above-mentioned catalyst system, then large rings are obtained by ring expansion polymerization. Thus, the cyclic hydrocarbons $C_{10}H_{16}$, $C_{15}H_{24}$, etc., up to the 120-membered ring (15-mer) can be isolated from the reaction with cyclopentene. It can be assumed that the experiments with small initiator concentrations give polymers which represent ring-shaped macromolecules without end groups. The mechanism is not yet fully understood. The intermediate formation of a complex between the olefinic double bond and the tungsten atom or a carbene intermediary are possibilities under discussion.

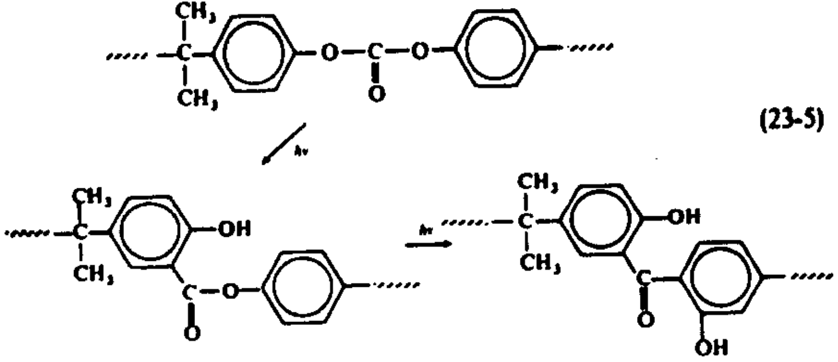
In exchange reactions between linear macromolecules, the number-average molecular weight remains constant because the number of molecules is not changed by the reaction. When the initial material has a narrow molecular-weight distribution, however, the weight-average molecular weight increases until a value of $\bar{X}_w = 2\bar{X}_n - 1$ is obtained. The same value of $\bar{X}_w$ is obtained in polycondensation [see equation (17-26)], which is understandable since the position of an equilibrium is independent of the path leading to it. Exchange equilibria are not always industrially desirable. For example, quite narrow distributions are obtained in the anionic polymerization of ε-caprolactam. However, subsequent processing of this polymer leads to exchange equilibria that increase the weight-average molecular weight and therefore the melt viscosity. Consequently, the processing rate (e.g., in melt spinning) must be continuously regulated.

The exchange equilibrium position can be displaced when certain sequences preferentially crystallize. Both glycols are randomly incorporated in the polycondensation of terephthalic acid with *cis*- and *trans*-1,4-cyclohexyl dimethylol. The melting point of this random copolymer depends on the *trans* content. If ester exchange catalysts are added and the material is heated to just below the melting point, then the melting point of the polyester increases and its solubility decreases: A block copolymer with long, crystallizable *trans* sequences is formed by the ester exchange reaction.

### 23.3.2. *Constitutional Transformations*

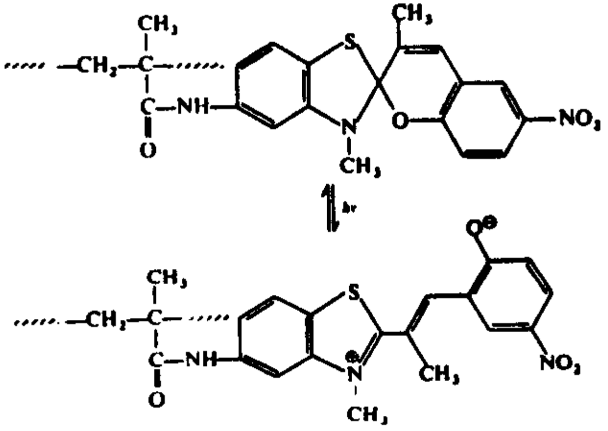
Of the many possible isomerization reactions of monomeric units, only those initiated by light have been studied in detail.

The action of light can induce a Fries rearrangement in aromatic polyesters:



(23-5)

These processes are called photochromic if considerable color changes occur during the photoisomerization. Poly(methacrylates) with certain spiropyran groups become colored on irradiation with light and subsequently decolorize slowly in the dark:



(23-6)

### 23.3.3. *Configurational Transformations*

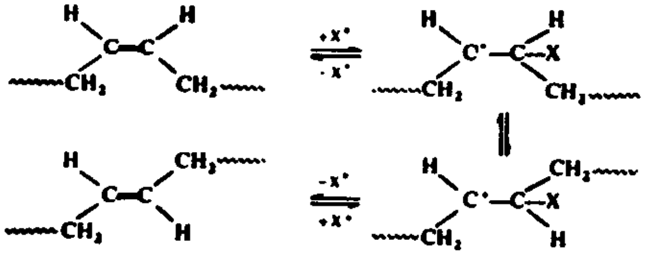
The position of the configurational equilibrium depends on differences in the energy contents of the configurational and geometric isomers:

$$\Delta G_{iso} = G_a - G_b = -RT \ln K_{iso} = -RT \ln \frac{[a]}{[b]} \qquad (23\text{-}7)$$

Here *a* and *b* are the isomers; for example, R and S isomers of optically active compounds or *cis* and *trans* isomers.

An isomerization leads to equal amounts of both isomers when their energy contents are equal. This special case is known as racemization. An example of this is the isomerization of α-amino acids.

Polydienes can be made to undergo a *cis–trans* isomerization. Through addition of free radicals X' to the double bond, this bond can rotate freely. On subsequent elimination of the free radical, the reformed double bond can take up a new position:

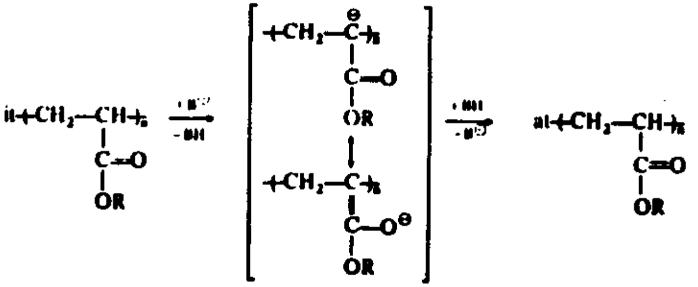


(23-8)

Such free radicals X' are produced by irradiating organobromides, organosulfides, or mercaptans, or by the action of UV light on $Br_2$. Alternatively, the isomerization can proceed via charge transfer complexes with sulfur or selenium. In this way, *cis*-1,4-poly(butadiene) is isomerized at 25°C to an equilibrium product containing 77% *trans* bonds. Thus, with $K_{iso} = 77/23 = 3.35$, equation (23-7) gives $\Delta G_{iso} = -3.0$ kJ/mol.

The tetrahedral state of the carbon atoms first must be destroyed in the isomerization of iso- and syndiotactic polymers. For this, however, bonds (either main-chain bonds or bonds from the main chain to substituents) must be destroyed. The most probable state occurs on reformation of destroyed bonds, that is, polymers with the ratio of iso- to syndiotactic diads corresponding to the conformational equilibrium are formed.

The isomerization of it/st polymers can only rarely be achieved. Destruction of chain bonds requires a high activation energy and also leads to an undesired degradation of the polymer in the majority of cases. Consequently, it/st isomerizations without undesirable side reactions are only rarely observed. An example of one of these rare cases is the isomerization of it-poly(isopropyl acrylate) with catalytic amounts of sodium isopropylate in dry isopropanol. A transitory carbanion is formed on the α-carbon atom by the action of the base, and this carbanion is a mesomer of its enolate form. This results in conformational changes on reformation of the original constitution, and an "atactic" polymer is formed:



(23-9)

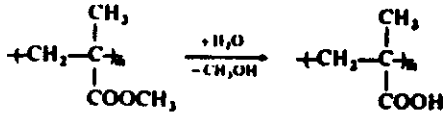
The configurational equilibrium observed in solution can be displaced when one isomer can be removed from the equilibrium, by, for example, crystallization. For example, when 1,4-poly(butadienes) of high *trans* content are dosed with trace amounts of an all-*trans* poly(butadiene), a decrease in the *trans* content is initially observed: Subsequently, however, the *trans* content increases again. It is assumed that a *trans* isomerization occurs at the crystalline–amorphous interface, whereby the longer *trans* sequences are incorporated into the crystal lattice and thereby removed from the equilibrium. A new equilibrium is then established by producing more new *trans* sequences.

## 23.4. *Polymer Analog Conversions*

### 23.4.1. *Review*

The constitution of the monomeric unit is changed but the degree of polymerization remains constant in polymer analog reactions. Chain analog reactions are a special case where the end groups are transformed but the constitution of the monomeric units is retained.

An example of a polymer analog reaction is the saponification of poly(methyl methacrylate) to poly(methacrylic acid):

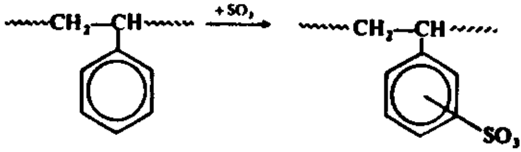


$$+CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}+_n \xrightarrow[-CH_3OH]{+H_2O} +CH_2-\underset{COOH}{\overset{CH_3}{C}}+_n \qquad (23\text{-}10)$$

In industry, polymer analog reactions are carried out on a large scale to produce polymers that cannot be synthesized directly from their monomers. Examples of this are the saponification of poly(vinyl acetate)

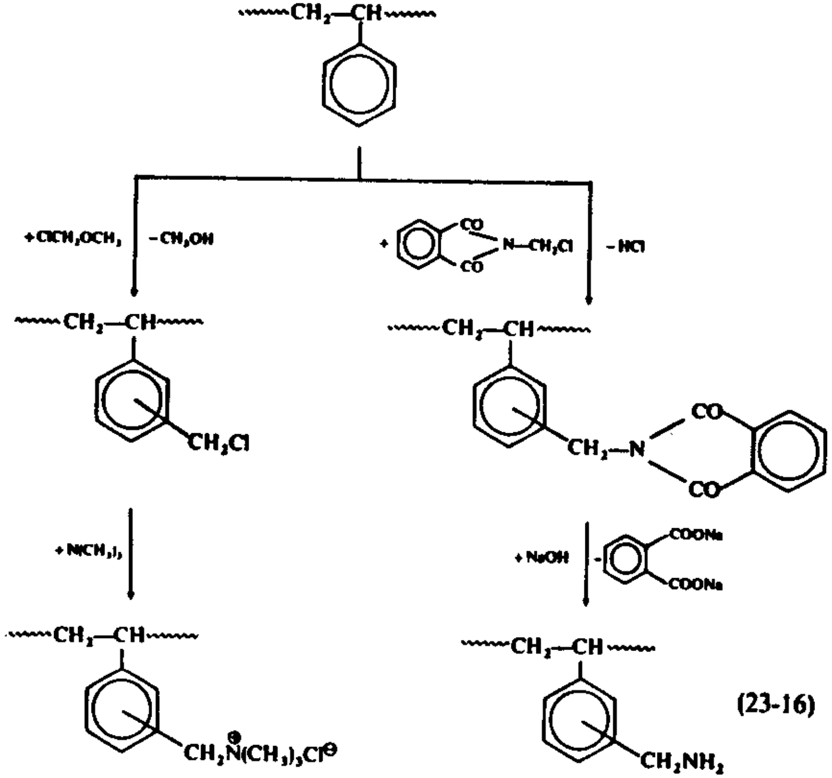
#### 23.4.3.2. *Ion-Exchange Resins*

Ion-exchange resins are cross-linked polyelectrolytes. The majority of commercial products consist of a basic framework of cross-linked "copolymers" of styrene with divinyl benzene. Cross-linked poly(styrene) is particularly suitable for the synthesis of ion-exchange resins because the introduction of various ionically dissociating groups into the phenyl ring occurs easily. Reaction with $SO_3$ produces a strongly acidic cation-exchange resin:



(23-15)

and treatment with chlorodimethyl ether followed by quaternization, or conversion with *N*-chloromethyl phthalimide, gives strongly basic anion-exchange resins:



(23-16)

Weakly acidic cation-exchange resins are obtained by copolymerizing divinyl benzene with acrylic esters. The ester groups are then saponified with alkali. Many other types are known besides these types; for example, those based on phenol/formaldehyde resins, cellulose, etc.

Ion-exchange resins prepared in this way swell considerably in water, thus giving the dissociating groups more accessibility. The exchange of the dissociating, low-molecular-weight ions of the resins is an equilibrium reaction, so that water containing salt can be completely freed of salt by passing through a cation- and an anion-exchange resin with the polyions $(\text{poly})^-$ or $(\text{poly})^+$, respectively:

$$\begin{array}{c}(\text{poly})^-H^+ + Na^+ \rightleftharpoons (\text{poly})^-Na^+ + H^+ \\ (\text{poly})^+OH^- + Cl^- \rightleftharpoons (\text{poly})^+Cl^- + OH^- \\ \hline (\text{poly})^-H^+ + (\text{poly})^+OH^- + NaCl \rightleftharpoons (\text{poly})^-Na^+ + (\text{poly})^+Cl^- + H_2O \end{array} \qquad (23\text{-}17)$$

The spent ion-exchange resins are then regenerated by acid or alkali treatment.

The exchange capacity is determined by the number of dissociating groups per monomer unit and the degree of cross-linking. The higher the degree of cross-linking, the greater will be the $pK_a$ value of the polyacids (decreased accessibility). Macroporous ion-exchange resins possess particularly good ion-exchange capacities, because they have a strong gel structure which does not swell (see Section 2.4.2).

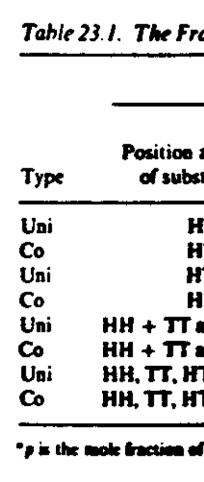
The acid strength of the cross-linked polyacids falls with the size of the hydrated gegenions. The hydrated lithium ion is larger than the hydrated rubidium ion, so that the apparent acid strength of cross-linked polyacids is greater in the presence of rubidium ions than in the presence of lithium ions. This is exactly the reverse of the situation for non-cross-linked polyacids, where acid strength depends on the size of the unhydrated ions.

This effect is probably due to the structure of water in the gel, which is most probably different from the water structure within the coil. According to proton magnetic resonance measurements, the water within the gel in poly(styrene sulfonic acid) is less ordered than that outside the gel. Since the degree of order varies with the density of cross-linking, this discovery could also explain why the selectivity of an ionized gel with respect to ions goes through a maximum with increasing cross-link density.

### 23.4.4. *Ring-Forming Reactions*

#### 23.4.4.1. *Polymer Analog Conversions*

Ring-shaped substituents are produced when bifunctional reagents react with neighboring monofunctional groups on polymers. An example of this is the conversion of poly(vinyl alcohol) with aldehydes to poly(vinyl acetal):



(23-18)

If the reaction is irreversible and occurs randomly, some individual hydroxyl groups cannot react. If reactions can only occur between neighboring hydroxyl pairs, then a 100% conversion can never be obtained. The reaction between aldehyde and hydroxyl groups on different polymer molecules can be largely avoided by working in dilute solutions, and reactions between distant hydroxyl groups on the same molecule can mostly be prevented by working with good solvents.

The maximum achievable conversion in this reaction depends on whether all monomeric units are joined head to tail with each other. If all the reacting groups are situated on the 1,3 positions relative to each other, then, theoretically, $1/e^2$ of the groups cannot react (see the appendix to this chapter). This corresponds to a maximum theoretical conversion, or yield, of 86.5%. Yields of 85.8% for chloroacetaldehyde, 85.0% for palmitinaldehyde, and 83% for benzaldehyde have been obtained and show good agreement with the theoretical figure. If the aldehyde contains ionizable groups, then the yield decreases strongly because of the neighboring group effect, i.e., to 44% for *o*-benzaldehyde sulfonic acid and to 36% for 2,4-benzaldehyde disulfonic acid.

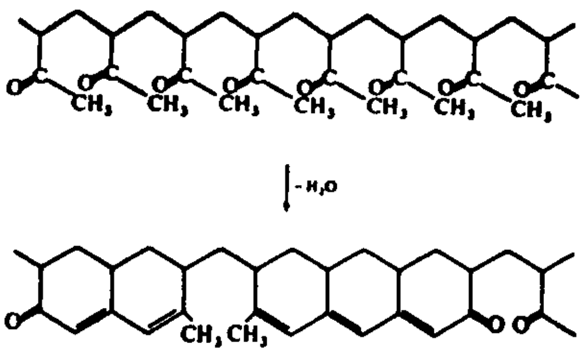
Similar calculations are applicable to copolymers of a monomer 1 with reactive groups and monomer 2 with nonreactive groups. Only a fraction $p$ of the monomer 1 can react. This fraction can be calculated from the probability $p_{11}$ that constitutive monomer 1 diads occur in the copolymer [see equation (22-4)]. For copolymers, the expression $\exp(-2p_{11})$ is inserted in place of the expression $1/e^2 = \exp(-2)$, which is valid for unipolymers.

The situation is different for the reaction between two neighboring groups without the participation of an additional low-molecular-weight reagent. An example of this is the intramolecular elimination of water from poly(vinyl methyl ketone). If only head-to-tail bonds occur, then in this case $1/(2e) = 18.4\%$ of the reactive groups will not react (see also Table 23-1):

*Table 23.1. The Fraction $f$ of Unreacted Groups in the Bifunctional Bonding of Substituents R in Unipolymers or Azeotropic Copolymers*[a]

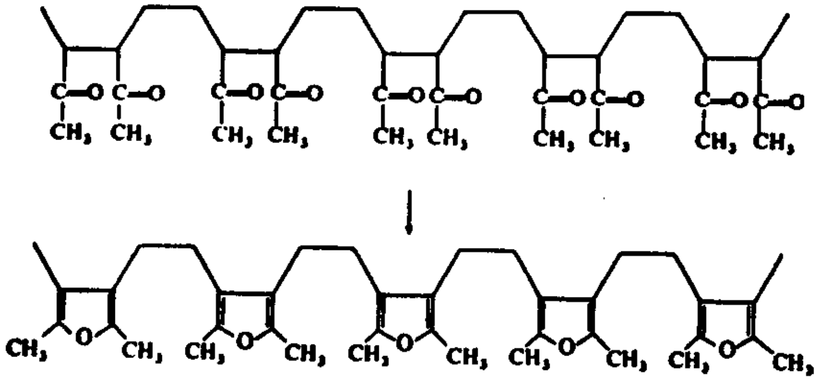
| | Polymer | | Reaction | | Fraction $f$ of unreacted groups | | |
|---|---|---|---|---|---|---|---|
| Type | Position and order of substituents | Order of base units in copolymer | Position of reacting substituents | Number of reactable groups per mer | General | $p = 0$ | $p = 1$ |
| Uni | HT | — | 1.3 | 2 | $1/2e$ | — | 0.184 |
| Co | HT | Random | 1.3 | 2 | $1 - p + (2/9)p^3 - \cdots$ | 1 | 0.184 |
| Uni | HT | — | 1.3 | 1 | $1/e^2$ | — | 0.135 |
| Co | HT | Random | 1.3 | 1 | $1/e^{2p}$ | 1 | 0.135 |
| Uni | HH + TT alternating | — | 1.2 | 2 | 0.5 | — | 0.500 |
| Co | HH + TT alternating | Random | 1.2 | 2 | $1 - 0.5p$ | 1 | 0.500 |
| Uni | HH, TT, HT (random) | — | 1.2 + 1.3 | 2 | 0.312 | — | 0.312 |
| Co | HH, TT, HT (random) | Random | 1.2 + 1.3 | 2 | $1 - (3/4)p + (5/72)p^3 - \cdots$ | 1 | 0.312 |

[a] $p$ is the mole fraction of copolymer groups capable of reacting. H, head; T, tail; Uni, unipolymer; Co, copolymer.



(23-19)

Of course, with pure head-to-tail or tail-to-tail polymers, all of the substituents can still react, but polymers of different constitution are produced:

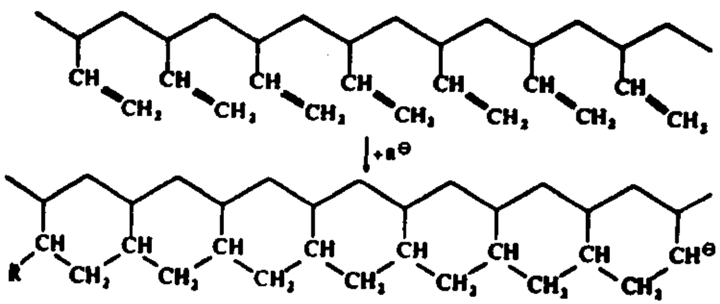


(23-20)

### 23.4.4.2. Two-Step Transannular Reactions

Purely randomly occurring transannular reactions cannot lead to very long sequences of transannular rings [see, for example, (23-19)] since a maximum yield may not be exceeded. The case of a two-step transannular reaction caused by a polymerization reaction is more favorable.

In the first step a polymer chain with regularly ordered substituents is produced, and in the second step the substituents themselves are polymerized. An example of this is the polymerization of butadiene to 1,2-poly(butadiene), which is then cyclized by polymerization of the vinyl groups:

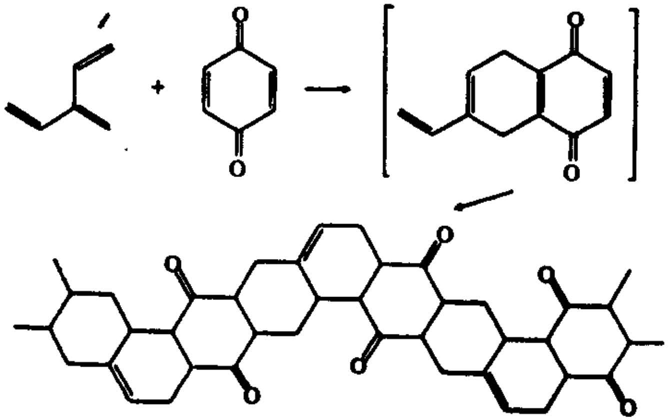


(23-21)

Other examples include the transannulation of poly(vinyl isocyanate) and poly(acrylonitrile).

In these reactions, polymerizations initiated by free radicals or anions are to be preferred over those initiated by cations, since the latter tend to give frequent transfer reactions. For example, in the cyclization of natural rubber with the aid of concentrated acids of Lewis acids, only three transannular rings on the average are obtained [see reaction (25-20)].

Complete sequences of transannular rings give what are known as ladder polymers, because they look like ladders with steps. Of course, ladder polymers can also be produced by one-step transannular reactions. An example of this is the Diels–Alder polymerization of 2-vinyl butadiene and *p*-quinone:



(23-22)

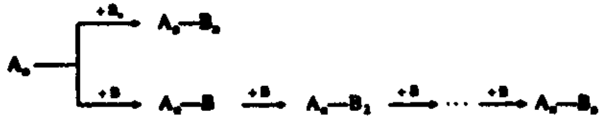
## 23.5. Chain Extension, Branching, and Cross-Linking Reactions

The degree of polymerization of the macromolecule increases in chain extension, branching, and cross-linking reactions. According to the chain structure of the newly produced macromolecule, distinction is made among block-copolymer-forming reactions, grafting reactions, and cross-linking reactions (leading to cross-linked networks). In block formation reactions, one or both ends of a chain will be extended by one or two blocks of a different monomer. Here, strictly speaking, the chain remains unbranched. In graft reactions, side chains are formed on individual monomeric units in a polymer chain. The graft polymer is branched. In cross-linking reactions, the primary polymer molecules (macromolecules initially present before cross-linking) are cross-linked together to a single molecule.

Block formation reactions and graft reactions are nearly always carried out with different monomers. Block and graft polymers are therefore copolymers. Cross-linking reactions, on the other hand, can also be carried out in the absence of a second monomer or polymer. Besides addition polymerization reactions, polycondensation and polyinsertion reactions can be used with all three types of reactions.

## 23.5.1 Block Copolymerization

Block copolymers can be produced from the coupling of already existing blocks from the addition of monomer to an already existing block containing other monomer units, i.e.



$$A_n \begin{cases} \xrightarrow{+B_n} A_n\text{—}B_n \\ \xrightarrow{+B} A_n\text{—}B \xrightarrow{+B} A_n\text{—}B_2 \xrightarrow{+B} \cdots \xrightarrow{+B} A_n\text{—}B_n \end{cases} \qquad (23\text{-}23)$$

Which block copolymer forming process should be used depends on the structure of the required block copolymer as well as on the polyreactions that will lead to its formation. It is convenient to distinguish between two-block copolymers $A_nB_m$, three-block copolymers $A_nB_mA_n$, and multiblock copolymers $(A_nB_m)_p$. Multiblock copolymers with short $A_n$ and $B_m$ blocks are also known as segmented or segment copolymers.

All of the more important methods of producing block copolymers with long blocks utilize the "living" polymer method. To obtain definitive block lengths, the growing chain ends may not undergo termination or transfer reactions. Consequently, anionic polymerizations are more suitable than cationic polymerizations (see also Chapter 18).

The strategies used to produce block copolymers can be well demonstrated with the example of a three-block copolymer, $(\text{styrene})_m(\text{butadiene})_n(\text{styrene})_m$, which is commercially available as a thermoplastic elastomer (see Sections 5.5.4 and 25.3.11) This three-block copolymer can best be produced in a *two-stage process with bifunctional initiators*. Sodium naphthalide or dilithium compounds can be used as initiators (see Section 18.1). Styrene is added on to the dianion produced ${}^{\ominus}B_n^{\ominus}$ and ${}^{\ominus}S_mB_nS_m^{\ominus}$ is formed. The initiators mentioned above, however, are only effective in tetrahydrofuran and other ethers. But butadiene blocks of only limited *cis*-1,4 content are produced in these solvents, and this has an undesirable effect on the thermoplastic elastomer (glass-transition temperature is too high). Consequently, well-dissolving aromatic dilithium compounds are preferably used in the presence of small amounts of aromatic ethers. After formation of the diene blocks, dimethoxyethane is added and the styrene polymerization is carried out in this solvent. Undesired termination reactions lead, in this case, to either poly(butadiene) unipolymer or to two-block copolymers $A_mB_n$. Poly(butadiene) only increases the matrix fraction of the thermoplastic elastomers (see Section 5.5.4) and consequently does not have a deleterious effect on desired properties. The process can be pictured from the following reaction scheme:

$${}^{\ominus}R^{\ominus} + nB \longrightarrow {}^{\ominus}B_{n/2}RB_{n/2}^{\ominus} \xrightarrow{+2mA} {}^{\ominus}A_m(B_{n/2}RB_{n/2})A_m^{\ominus} \qquad (23\text{-}24)$$

In a *two-stage process with monofunctional initiators*, a two-block copolymer is first produced and this is then coupled in the center to give a three-block copolymer:

$$\begin{gathered} R^{\ominus} + mA \longrightarrow RA_m^{\ominus} \xrightarrow{+0.5nB} RA_mB_{n/2}^{\ominus} \\ 2RA_mB_{n/2}^{\ominus} + X \longrightarrow RA_m(B_{n/2}XB_{n/2})A_mR \end{gathered} \qquad (23\text{-}25)$$

If, for example, butyl lithium is used as initiator, then the $C_4H_9A_mB_{n/2}^{\ominus}Li^{\oplus}$ compound produced can be coupled with $X = COCl_2$ to form a three-block copolymer. In general, this process leads to a higher fraction of two-block copolymers than the two-stage process with bifunctional initiators.

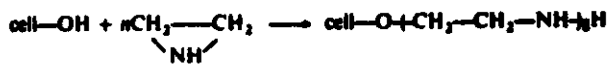
*Three-stage processes* also use monofunctional initiators, but do not require a coupling stage:

$$R^{\ominus} + mA \longrightarrow RA_m^{\ominus} \xrightarrow{+nB} RA_mB_n^{\ominus} \xrightarrow{+mA} RA_mB_nA_m^{\ominus} \qquad (23\text{-}26)$$

However, there is an increased probability for undesired termination reactions because of the three separate propagation steps.

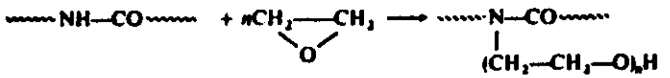
## 23.5.2. Graft Copolymerization

Some polymers already contain reactive groups that can initiate a graft polymerization. The hydroxyl groups in cellulose initiate the polymerization of ethylene imine:



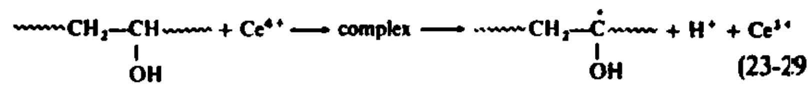
$$\text{cell—OH} + n\,\underset{\text{NH}}{CH_2\text{—}CH_2} \longrightarrow \text{cell—O}\!\left(CH_2\text{—}CH_2\text{—}NH\right)_{\!n}H \qquad (23\text{-}27)$$

and the amide groups in polyamides react with ethylene oxide:



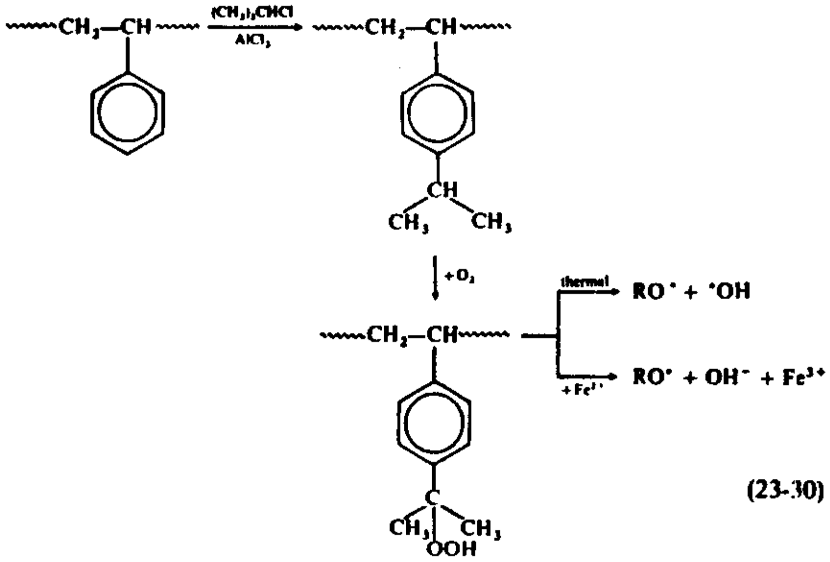
$$\sim\text{NH—CO}\sim + n\,\underset{\text{O}}{CH_2\text{—}CH_2} \longrightarrow \sim\underset{(CH_2\text{—}CH_2\text{—}O)_nH}{\underset{|}{\text{N}}}\text{—CO}\sim \qquad (23\text{-}28)$$

With poly(vinyl alcohol), it is possible to produce free radicals which start the polymerization of vinyl monomers:



$$\sim\!\sim CH_2{-}\underset{\displaystyle OH}{\underset{|}{CH}}\sim\!\sim + Ce^{4+} \longrightarrow \text{complex} \longrightarrow \sim\!\sim CH_2{-}\underset{\displaystyle OH}{\underset{|}{\dot{C}}}\sim\!\sim + H^+ + Ce^{3+} \qquad (23\text{-}29)$$

If there are no groups of this type, then they can often be introduced by a suitable polymer analog reaction on the polymer. The polymerization of monomers onto poly(styrene) is readily achieved, for example, when some phenyl nuclei are first isopropylated and then converted to hydroperoxide. The formation of hydroperoxide is aided by the addition of free-radical-forming agents (peroxides), since the primary reaction ($RH + O_2 \rightarrow R^{\cdot} + {}^{\cdot}OOH$) is very slow (see Section 24.2.1). The hydroperoxide decomposes thermally into an RO$^{\cdot}$ radical and an HO$^{\cdot}$ radical, both of which initiate the polymerization of vinyl monomers. The HO$^{\cdot}$ radical causes unwanted unipolymerization as well as the desired graft polymers. These unipolymers are difficult to separate from the copolymer mixture, and thus it is impossible to determine the graft yield with any certainty. In addition, unipolymers and copolymers are generally incompatible over wide areas of the copolymer composition, causing a deterioration in the mechanical properties. The hydroperoxide radical can be decomposed chemically, however, when the $^{\cdot}$OH radical is not formed, and only the RO$^{\cdot}$ radical is left to initiate polymerization:

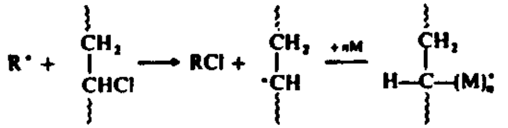


(23-30)

In many cases, however, it is impossible to start a graft copolymerization by including or forming specific groups in the chain. Reactive sites

are therefore produced at the same time as the monomer to be grafted is introduced. These methods work under drastic conditions and are therefore nonspecific and inapplicable to many polymers. Frequently, it is questionable whether or not actual graft reactions have occurred, and degradation is generally unavoidable.

One universally applicable method of grafting (with respect to substrate) is by chain transfer. A radical P$^{\cdot}$ (polymer free radical) or R$^{\cdot}$ (initiator free radical) abstracts, for example, an H or Cl atom and forms a macroradical, which initiates the polymerization of the added monomer:

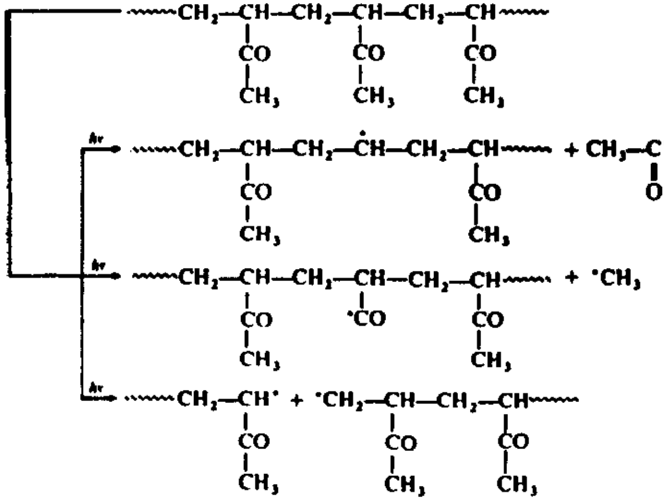


$$R^{\cdot} + \begin{matrix}\wr\\ CH_2\\ |\\ CHCl\\ \wr\end{matrix} \longrightarrow RCl + \begin{matrix}\wr\\ CH_2\\ |\\ {}^{\cdot}CH\\ \wr\end{matrix} \xrightarrow{+nM} \begin{matrix}\wr\\ CH_2\\ |\\ H{-}C{-}(M)_n^{\cdot}\\ \wr\end{matrix} \qquad (23\text{-}31)$$

The transfer constants of the polymer free radicals P$^{\cdot}$ are relatively low, however, so that the graft yield will be very small. The macroradicals are therefore formed through an addition of initiator radicals R$^{\cdot}$.

The initiator concentration must be high in this reaction. However, only initiator radicals that can transfer to polymer are effective (see Section 20.3.4). The question of whether the macroradical formed initiates the polymerization of the added monomer depends on the resonance stabilization and polarity of macroradical and monomer. The effectiveness can therefore be estimated using the *Q–e* scheme. Unipolymers are also formed in every case in which this grafting method is used. Industrially, this method is used to synthesize certain types of ABS polymers (Section 25.2.6.2).

Still fewer polymers can be activated directly with ultraviolet light. An example of such a case is poly(vinyl methyl ketone):



$$\sim\!\sim CH_2{-}\underset{COCH_3}{CH}{-}CH_2{-}\underset{COCH_3}{CH}{-}CH_2{-}\underset{COCH_3}{CH}\sim\!\sim$$
$$\xrightarrow{h\nu} \sim\!\sim CH_2{-}\underset{COCH_3}{CH}{-}CH_2{-}\dot{C}H{-}CH_2{-}\underset{COCH_3}{CH}\sim\!\sim + CH_3{-}\underset{O}{\underset{\|}{C^{\cdot}}} \quad (\rightarrow \dot{C}H_3 + CO)$$
$$\xrightarrow{h\nu} \sim\!\sim CH_2{-}\underset{COCH_3}{CH}{-}CH_2{-}\underset{{}^{\cdot}CO}{CH}{-}CH_2{-}\underset{COCH_3}{CH}\sim\!\sim + {}^{\cdot}CH_3 \qquad (23\text{-}32)$$
$$\xrightarrow{h\nu} \sim\!\sim CH_2{-}\underset{COCH_3}{CH^{\cdot}} + {}^{\cdot}CH_2{-}\underset{COCH_3}{CH}{-}CH_2{-}\underset{COCH_3}{CH}\sim\!\sim$$

The polymer is simultaneously degraded, however. In addition, unipolymers are produced.

The formation of macroradicals by $\gamma$ rays is also not specific. The free radicals are formed in both amorphous and crystalline areas of irradiated solid, crystalline polymers. In the amorphous area, the free radicals can recombine at $T > T_G$, causing the polymer to become cross-linked. The free radicals in the crystalline region, on the other hand, cannot migrate readily and recombine very slowly. If irradiation is carried out in the presence of the monomer to be grafted, then both macro and monomer free radicals are formed, both of which initiate the polymerization of the monomer. The undesirable formation of unipolymers can be minimized, however, by a suitable polymer–monomer choice. Halogen compounds, for example, give a high $G_{R^\cdot}$ value, whereas aromatic compounds give a low value (Section 21.2.1). The irradiation of poly(vinyl chloride) in the presence of styrene thus gives a high yield of graft copolymer along with a very small amount of poly(styrene).

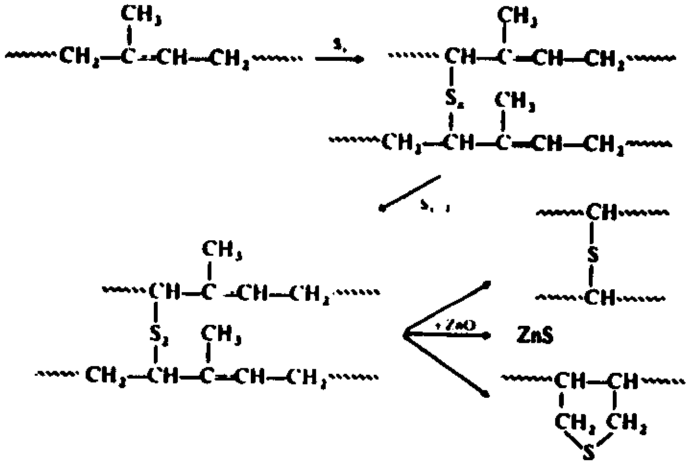
If macroradical recombination is very slow, then it is also possible to irradiate first and add the monomer for grafting after the irradiation. For this, the chosen temperature must be such that the rate of mutual deactivation of trapped free macroradicals is lower than the rate of initiation of growing chains with the second monomer. Consequently, the graft yield is especially high in the region of the glass-transition temperature.

### 23.5.3. Cross-Linking Reactions

In cross-linking, the individual molecular chains are bonded together into "infinitely large" molecules. The macromolecules present before cross-linking takes place are called primary molecules. Undesirable cross-linking often occurs in graft polymerizations. Intentional cross-linking (controlled cross-linking), on the other hand, is of great commercial importance. It can be carried out by polycondensation or addition polymerization reactions, according to the constitution of the primary molecules. Examples of cross-linking by polycondensation are what is called the curing of phenol, amino, and epoxy resins (see Sections 26.3, 28.2, and 26.2.3.2).

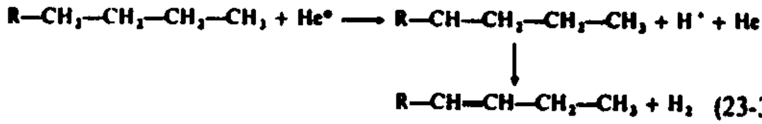
Cross-linking by addition polymerization is also used to a considerable extent. Unsaturated polyesters are cross-linked by copolymerization with styrene or methyl methacrylate. Cross-linking soft, natural rubber with sulfur gives the normally used hard, vulcanized rubber. Ethylene/propylene rubbers can be cross-linked with peroxides. The cross-linking of elastomers is also called "vulcanization," since the classic cross-linking of natural rubber, *cis*-1,4-poly(isoprene), uses heat and sulfur, which were the elements assigned to the god Vulcan.

In the vulcanization of polydienes with sulfur, sulfur bonds are formed [see reaction (23-33)]. In the uncatalyzed reaction, approximately one cross-linking bond is formed for every 50 sulfur atoms added. In catalyzed reactions, (with ZnO, pyridine derivatives, thiuram sulfides, etc.), this number decreases to ~1.6. Natural rubber can also be vulcanized cold, however, with $S_2Cl_2$ or MgO. Basically, all reactions are suitable for cross-linking if the attacking agent is at least bifunctional:

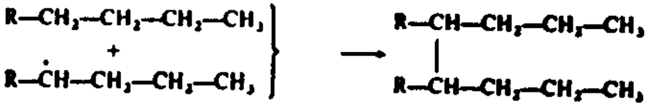


(23-33)

Surface cross-linking can be achieved by the so-called CASING process (cross-linking by activated species of inert gases), in which an inert gas is activated, for example, by microwaves (He⟿He*), and then allowed to react with the surface of the polymer:



$$\mathrm{R{-}CH_2{-}CH_2{-}CH_2{-}CH_3 + He^* \longrightarrow R{-}\dot{C}H{-}CH_2{-}CH_2{-}CH_3 + H^\cdot + He \;\downarrow\; R{-}CH{=}CH{-}CH_2{-}CH_3 + H_2} \qquad (23\text{-}34)$$



$$\left.\begin{array}{c}\mathrm{R{-}CH_2{-}CH_2{-}CH_2{-}CH_3}\\+\\\mathrm{R{-}\dot{C}H{-}CH_2{-}CH_2{-}CH_3}\end{array}\right\} \longrightarrow \begin{array}{l}\mathrm{R{-}CH{-}CH_2{-}CH_2{-}CH_3}\\\quad|\\\mathrm{R{-}CH{-}CH_2{-}CH_2{-}CH_3}\end{array} + \mathrm{H^\cdot}\ \text{etc.} \qquad (23\text{-}35)$$

The polymer is not degraded by this low-energy irradiation. The process time is short (~1 s) and the cross-link yield is high. Of course, only the surface is cross-linked, to a depth of 50–100 nm.

For cross-linking by