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"SCHOOL ON POLYMER PHYSICS"

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"SYNTHESIS OF MACROMOLECULES"

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SYNTHESIS OF MACROMOLECULES

n_o MONOMERS —Polymerization→ n MACROMOLECULES

Mol. Weight = M_o

$n \ll n_o$

$\bar{M}_n = \frac{n_o}{n} M_o$

LINEAR STRUCTURES:

A A A A A A A A ⟶ -A-A-A-A-A-A-A-A

-B-A A A B B A B ⟶ -B-A-A-A-B-B-A-B-

BIDIMENSIONAL STRUCTURES

-AA-A-A-A-A-A-A
+
mB
⟶
-A-A-A-A-A-A-A-
B B
B B

TRIDIMENSIONAL STRUCTURES (NETWORKS)

-AAAAAAA- + -B-B-B-B-B-B-B-

nA + mB ⟶

-BBB-B-B-B-
-AAA-A-A-A-
OR
-BAAABBBAAA-
-ABAAAAAA-BBA-

CONCEPTS OF MACROMOLECULES SYNTHESIS

conversion of monomer into polymer vs time (kinetics)
molecular weight vs time (conversion)
side reactions to
- separable byproducts
- nonseparable byproducts (chain irregularities)

average molecular weights and distribution
sequence distribution in copolymers
degree of crosslinking in networks
influence of polymerization mechanism

Specific features

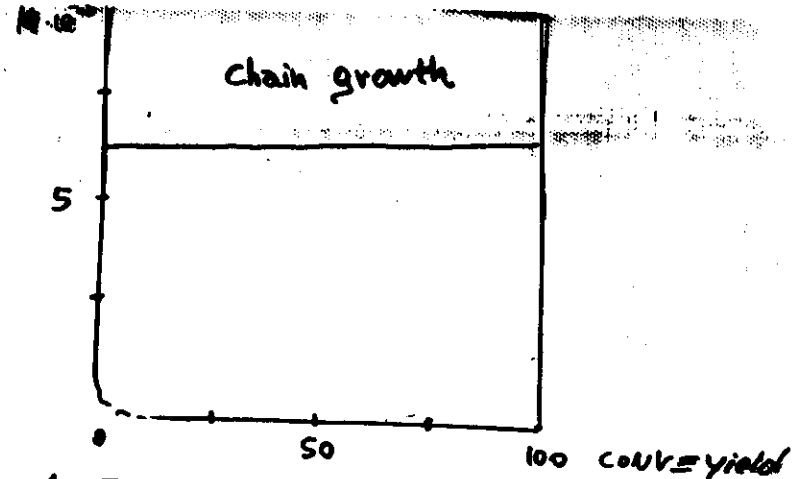
stereoregularity
macromolecules with highly defined structure
monodisperse macromolecules

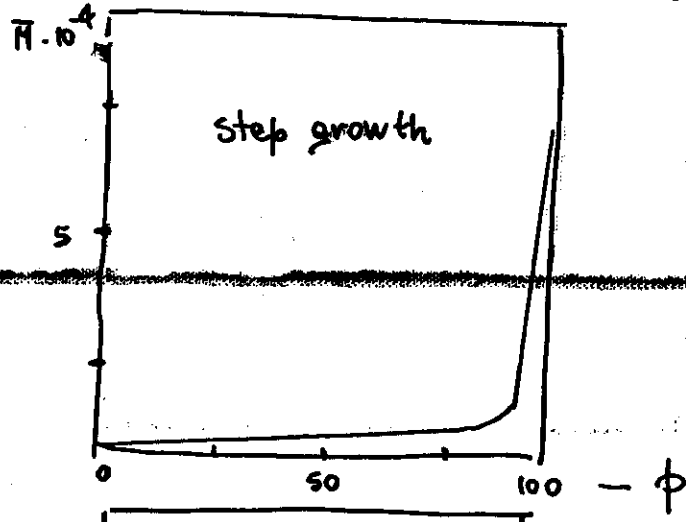
1

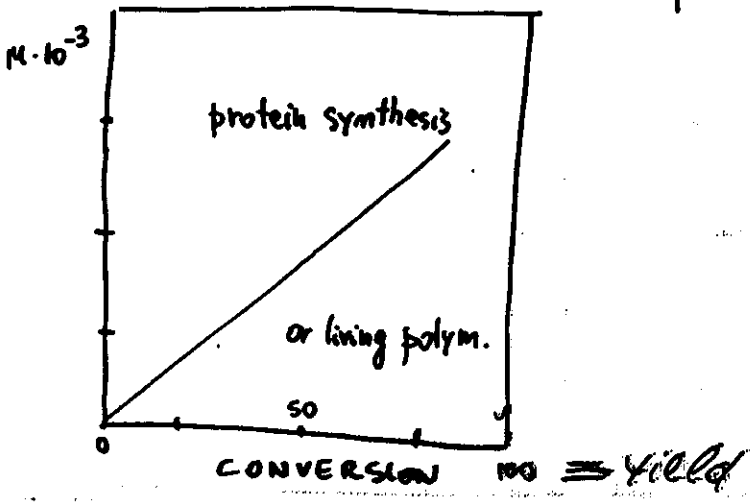
Polymerization Processes

Chain growth { free radical; anionic; cationic } ①, ②

Step growth { polycondensation ③; polyaddition ④ }







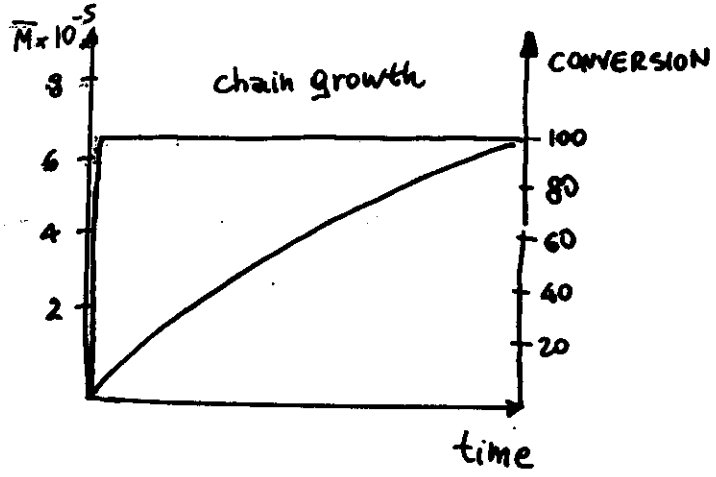
Examples

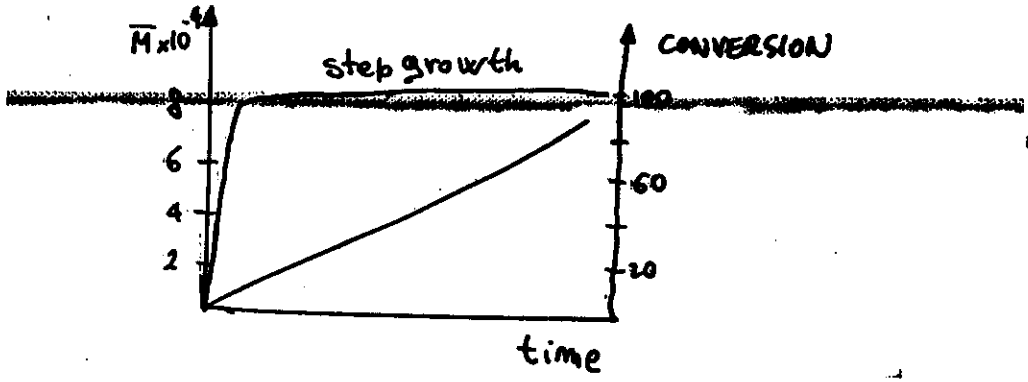
① $n\ CH_2{=}CH$ (C$_6$H$_5$) $\longrightarrow$ $\left[CH_2{-}CH\right]_n$ (C$_6$H$_5$)

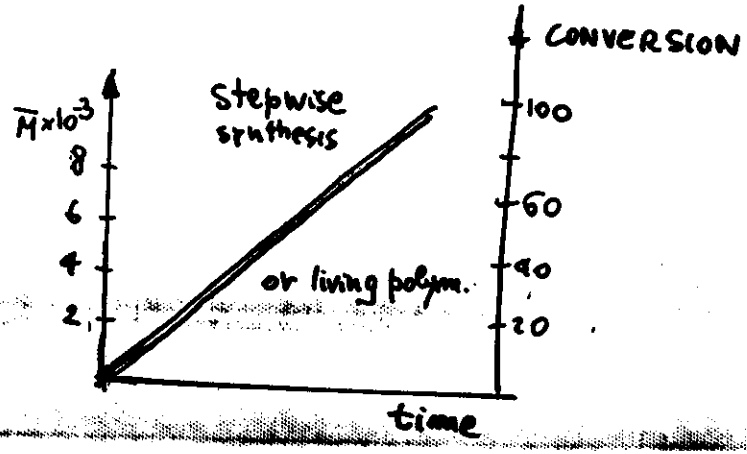
② n  $\xrightarrow{H_2O}$ $n\ HO\left[CH_2{-}CH_2{-}O\right]_m OH$

③ $n\ HOOC{-}(CH_2)_5{-}NH_2 \rightleftharpoons HO\left[OC{-}(CH_2)_5{-}NH\right]_n H + (n-1)H_2O$

④ $OCN{-}(CH_2)_6{-}NCO$ + $HO{-}(CH_2)_4{-}OH$ $\longrightarrow$ $OCN{-}(CH_2)_6{-}\overset{H}{\underset{}{N}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}(CH_2)_4{-}OH$







CHAIN GROWTH

Reazioni di Polimerizzazione a Catena

schema cinetico

1) Inizio di Catena (Initiation)

$$C \xrightarrow{k_i} C^{\bullet}$$

$$C^{\bullet} + M \xrightarrow{k_i} CM^{\bullet}$$

2) Propagazione di catena (Propagation)

$$CM^{\bullet} + M \xrightarrow{k_p} CM_2M^{\bullet}$$

$$CM_{n-2}M^{\bullet} + M \xrightarrow{k_p} CM_{n-1}M^{\bullet}$$

3) Terminazione di Catena (Termination)

$$CM_{n-1}M^{\bullet} \xrightarrow{k_t} CM_n$$

4) Trasferimento di Catena (Transfer)

$$CM_{n-1}M^{\bullet} + T \xrightarrow{k_{tr}} CM_n + T^{\bullet}$$

1. INIZIO DI CATENA

A. Meccanismo radicalico

A1. Con iniziatore

$$I \xrightarrow{k_D} 2\,R\cdot$$

$$R\cdot + M \xrightarrow{k_i} RM\cdot$$

$$\therefore \frac{d[R\cdot]}{dt} = 2k_D[I] - k_i[R\cdot][M] - \sum R_i = 0$$

allo stato stazionario, se R_i indica la velocità della reazione i che consuma $R\cdot$.

se f = efficienza iniziatore

$$f = \frac{k_i[R\cdot][M]}{k_D[I]\cdot 2}$$

$$\boxed{v_i = \text{velocità inizio} = \frac{d[R\text{-}M\cdot]}{dt} = 2f[I]\cdot k_D}$$

A2 Iniziazione termica[1]

$$2M \xrightarrow{k} \cdot M\text{—}M\cdot$$

$$\cdot M\text{—}M\cdot + M \longrightarrow M\cdot + MM\cdot$$

$$v_i = k[M]^2$$

A3) Con radiazioni

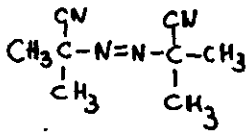
I) $M + h\nu_0 \longrightarrow M\cdot$

$$v_i = \Phi_M \varepsilon_M I_0$$

II) Con fotosensibilizzatore (c)

$$v_i = \Phi_c \varepsilon_c I_0$$

k_D per alcuni iniziatori

iniziatore	solvente	T(°C)	k_D (sec^{-1})
	CCl_4	60	$4,0\times10^{-6}$
	benzene	60	$8,5\times10^{-6}$
		100	$1,5\times10^{-3}$
	Acetone	50	$4,3\times10^{-7}$
		70	$2,6\times10^{-5}$
	Benzene	70	$1,2\times10^{-5}$
		100	$2,5\times10^{-4}$

B) INIZIAZIONE ANIONICA

B1 Attacco di una base sul monomero

$$B^{\ominus} + M \rightarrow [B-M]^{\ominus}$$

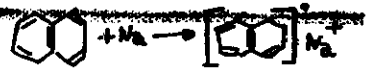
$$B^{\ominus} + CH_2=\underset{R}{\underset{|}{CH}} \rightarrow \left[B-CH_2-\underset{R}{\underset{|}{CH}}\right]^{\ominus}$$

effetto stabilizzante di R sul carbanione

$$-NO_2 > -\dot{C}O > -\dot{S}O_2 > -\dot{C}O_2 > -CN > C_6H_5 \simeq -CH=CH_2 \gg -CH_3$$

B2 Trasferimento di un elettrone da un donatore al doppio legame

$$e + M \rightarrow [M]^{\cdot}$$



$$[M]^{\cdot} + [M]^{\cdot} \rightarrow {}^{\ominus}M-M^{\ominus}$$

$$[M]^{\cdot} + M \rightarrow {}^{\ominus}M-M^{\cdot}$$

Velocità inizio dipende dal solvente

I. Solvente idrocarburico

I. Litio alchili sono associati

$[EtLi]_6$, $[nBuLi]_6$
$[tBuLi]_4$, $[sBuLi]_4$
$[MeLi]_2$, $[PhCH_2Li]_2$

nessuna induzione

$P^{\ominus}Li^{\oplus}$ può dare aggregati misti

C) INIZIAZZIONE CATIONICA

$$HA + M \xrightarrow{k_i} A^{\ominus} + HM^{\oplus}$$

$$V_i = d[HM^{\oplus}]/dt = k_i[HA][M]$$

C1. Acidi di Lewis (MeX_n)

$$HX + MeX_n + CH_2=\underset{R}{\underset{|}{CH}} \xrightarrow{k_i} CH_3\overset{\oplus}{\underset{R}{\underset{|}{CH}}}\ \overset{\ominus}{MeX_{n+1}}$$

$$HCl + AlCl_3 + CH_2=C(CH_3)_2 \xrightarrow{k_i} CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}\overset{\oplus}{} \cdot AlCl_4^{\ominus}$$

C2. Acidi protonici

$$H^{\oplus}B^{\ominus} + CH_2=CHR \xrightarrow{k_i} CH_3-\overset{\oplus}{\underset{R}{\underset{|}{CH}}}\ \overset{\ominus}{B}$$

C3. Iodio

$$2I_2 \rightleftharpoons I^{\oplus}I_3^{\ominus}$$

$$I^{\oplus}I_3^{\ominus} + CH_2=\underset{OR}{\underset{|}{CH}} \xrightarrow{k_i} ICH_2\overset{\oplus}{\underset{OR}{\underset{|}{\overset{H}{\underset{|}{C}}}}}\ I_3^{\ominus}$$

C4. Sali di carbocationi stabili

$C_7H_7^{\oplus}SbCl_6^{\ominus}$ $\quad$ $Ph_3C^{\oplus}ClO_4^{\ominus}$

$$Ph_3C^{\oplus} + CH_2=\underset{OR}{\underset{|}{CH}} \rightarrow \begin{cases} Ph_3C^{\cdot} + [CH_2=CHOCH_2R]^{\oplus} \\ Ph_3CH + CH_2=CH-\overset{\oplus}{O}=CHR \\ Ph_3CCH_2\overset{\oplus}{C}H-OCH_2R \leftrightarrow \underset{CPh_3}{\underset{|}{CH}}Cl-\overset{\oplus}{\underset{R}{\underset{|}{CH_2}}} \end{cases}$$

2. PROPAGAZIONE DI CATENA

A) RADICALICA

$$\sim M\cdot + M \xrightarrow{k_p} \sim MM\cdot$$

$$V_p = -d[M]/dt = k_p [\sim M\cdot][M]$$

B) ANIONICA

EFFETTO solvente anche in questo stadio

I) Solventi non polari

$$(R\sim MLi)_2 \overset{K_e}{\rightleftharpoons} 2\, R\sim MLi$$

$$R\sim MLi + M \xrightarrow{k_p} R\sim MMLi$$

$$V_p = -d[M]/dt = k_p \cdot K_e^{1/2}[(R\sim MLi)_2]^{1/2}[M]$$

II) Solventi polari

$$\sim M^{\ominus}\,B^{\oplus} \overset{K_D}{\rightleftharpoons} \sim M^{\ominus} + B^{\oplus}$$

$$+M \downarrow k_p \qquad +M \downarrow k_p^{\ominus}$$

$$\sim MM^{\ominus}\,B^{\oplus} \rightleftharpoons \sim MM^{\ominus} + B^{\oplus}$$

$$V_p = -d[M]/dt = \{k_p[\sim M^{\oplus}] + k_p^{\ominus}[\sim M^{\ominus}]\}[M]$$

C) CATIONICA

$$\sim M^{\oplus}\,A^{\ominus} \rightleftharpoons \sim M^{\oplus} + A^{\ominus}$$

$$+M \downarrow k_p \qquad +M \downarrow k_p^{\oplus}$$

$$\sim MM^{\oplus}\,A^{\ominus} \rightleftharpoons \sim MM^{\oplus} + A^{\ominus}$$

α = grado dissociazione = $[\sim M^{\oplus}]$

$$V_p = -d[M]/dt = k_{p_{oss}} \cdot [I][M]$$

$$k_{p_{oss}} = \alpha\, k_p^{\oplus} + (1-\alpha)\, k_p$$

C') PSEUDO CATIONICA

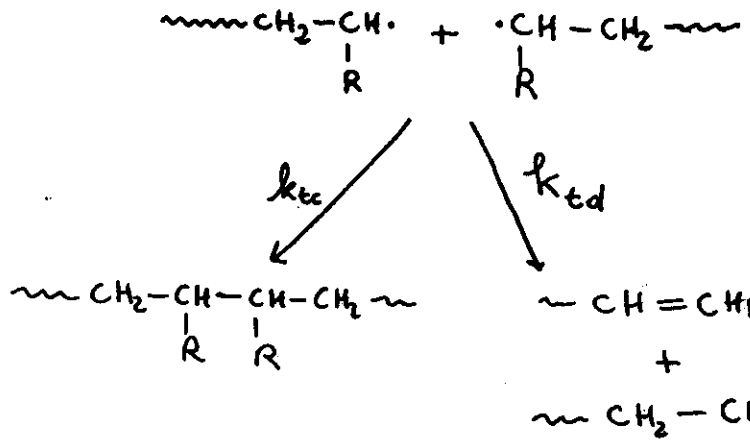
$$\sim St^{\oplus} + ClO_4^{\ominus} \rightleftharpoons \sim St^{\oplus}\,ClO_4^{\ominus} \rightleftharpoons \sim St{-}OClO_3$$

ioni liberi — coppia ionica — ESTERE COVALENTE

Lo stadio lento a temperatura amb. è dovuto a propagazione via estere covalente o ad una bassa conc. di coppia ionica?

3) TERMINAZIONE DI CATENA

A) RADICALICA



$$V_t = k_t [\sim M\cdot]^2$$

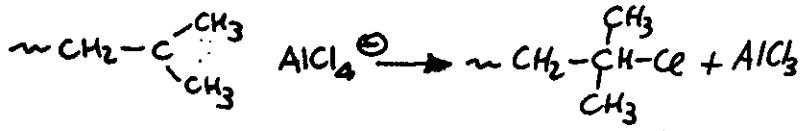
dove $k_t = \alpha k_{tc} + (1-\alpha) k_{td}$

B) ANIONICA

Le reazioni di terminazione mancano in condizioni di elevata purezza; esse devono essere effettuate deliberatamente.

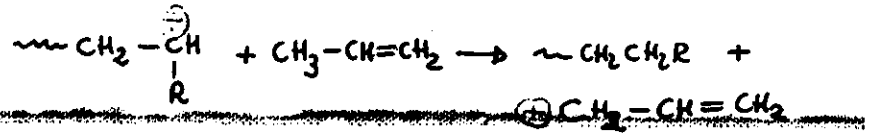
C) CATIONICA

C1. neutralizzazione di carica

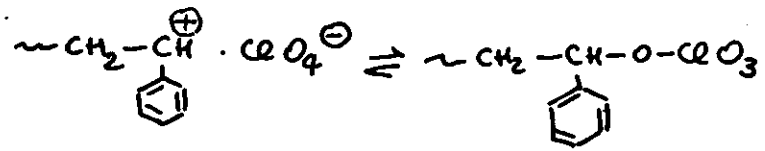


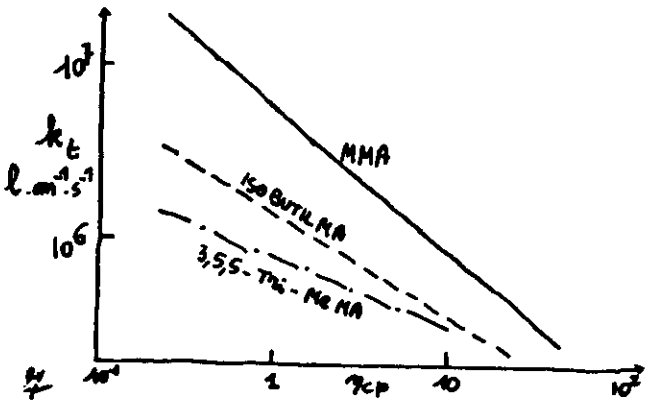
può diventare una reazione di trasferimento, perché $AlCl_3$ può iniziare una nuova catena.

C2. formazione di un catione stabile



C3. formazione di specie covalenti





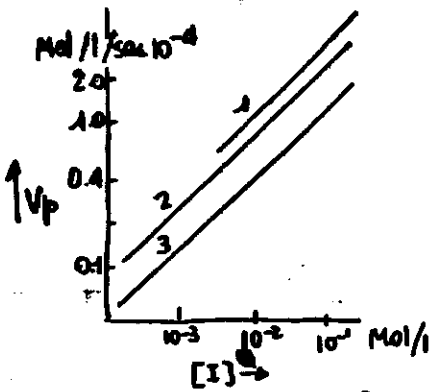
4). TRASFERIMENTO DI CATENA

A) RADICALICA

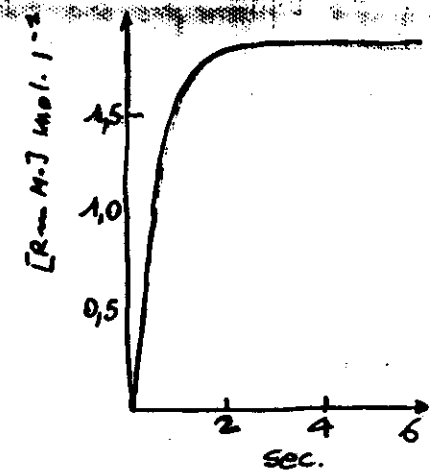
$$\sim M\cdot + S \xrightarrow{k_{tr}} \sim M + S\cdot$$

$$V_{tr} = k_{tr}[\sim M\cdot][S]$$

S = monomero, o iniziatore, o solvente o trasferitore



1. MMA con AIBN, 60°C
2. ST con Bz_2O_2, 60°C
3. MMA " , 60°C



B) ANIONICA

non comuni od inesistenti (V. CATIONICHE)

C) CATIONICA

$$\sim M^{\oplus} + S' \xrightarrow{k_{tr}} \sim M + S'^{\oplus}$$

S' = monomero, catalizzatore, co-catalizzatore, solvente o impurezza

$$V_{tr} = k_{tr}[\sim M^{\oplus}][S']$$

Lunghezza cinetica della catena e grado di polimerizzazione

$$\bar{\nu}_0 = \tau \cdot r_M = \tau \cdot k_p [M]$$

$$\tau = \frac{[R\sim M\cdot]}{V_t} = \frac{1}{k_t [R\sim M\cdot]}$$

$$\bar{\nu}_0 = \frac{k_p [M] [R\sim M\cdot]}{V_t} = \frac{V_p}{V_t}$$

con trasferimento di catena

$$\tau = \frac{[R\sim M\cdot]}{V_t + V_{tr}}$$

$$\bar{\nu} = \frac{k_p [M] [R\sim M\cdot]}{V_t + V_{tr}}$$

$$\bar{\nu} = \frac{V_p}{V_t + V_{tr}}$$

$$\frac{1}{\bar{\nu}} = \frac{1}{\bar{\nu}_0} + \frac{V_{tr}}{V_p} = \frac{1}{\bar{\nu}_0} + \frac{k_{tr}}{k_p}\frac{[S]}{[M]}$$

$$\frac{1}{\bar{\nu}} = \frac{1}{\bar{\nu}_0} + C_S \frac{[S]}{[M]}$$

Dipendenza del grado di polimerizzazione dalla temperatura

$$\bar{\nu} = k_p [M] / k_t [R\sim M\cdot]$$

$$[R\sim M\cdot] = \sqrt{k_d [I]/k_t}$$

$$\bar{\nu} = k_p [M] / \sqrt{k_d \cdot k_t \cdot [I]}$$

$$\frac{d \ln \bar{\nu}}{dT} = + \frac{E_p}{RT^2} + \frac{1}{2}\frac{E_t}{RT^2} + \frac{1}{2}\frac{E_d}{RT^2}$$

$E_d \sim 30$ kcal/mol.

$E_p - \frac{1}{2} E_t \simeq 4\text{-}7$ kcal

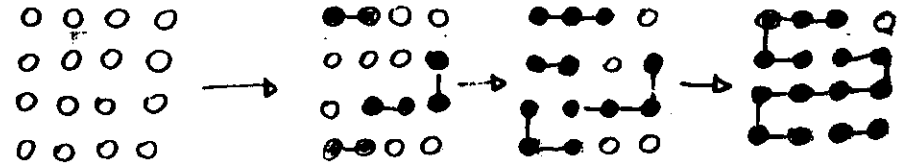
$$\frac{d \ln \bar{\nu}}{dT} = \frac{1}{RT^2}\left[-\frac{E_d}{2} + \left(E_p - \frac{1}{2}E_t\right)\right] < 0$$

$\bar{\nu} \leq \bar{X}_M \leq 2\bar{\nu}$ decresce con T

Policondensazione — Polycondensation

1) $A-B \longrightarrow \sim A-B-A-B \sim$

2) $A-A + B-B \longrightarrow \sim A-A-B-B \sim$



$X_m = 1$ — 25% reaz $X_m = 1,3$ — 50% reaz $X_m = 2$ — 75% reaz $X_m = 4$

$p = 0$ — $p = 0.25$ — 0.50 — 0.75

(p) = grado di avanzamento della reazione

Caso 1 $\quad \overline{X}_m = \frac{N_0}{N} = \frac{N_0}{(1-p)N_0} = \frac{1}{1-p}$

Caso 2 $\quad \overline{X}_m = \frac{N_0^A + N_B^0}{N^A + N^B}$

Se $N_0^A = N_B^0$

$$\boxed{\overline{X}_m = \frac{1}{1-p}}$$

MOLI AA	MOLI BB	ov MOLI AB	MOLI NE FORMATE	$\overline{X}_m$	p
1	1	2	1	2	0,5
2	2	4	3	4	0,75
5	5	10	9	10	0,90
10	10	20	19	20	0,95
50	50	100	99	100	0,99
100	100	200	199	200	0,995

se nel caso 2

$N_0^A \neq N_0^B \qquad N_0^A / N_0^B = r$

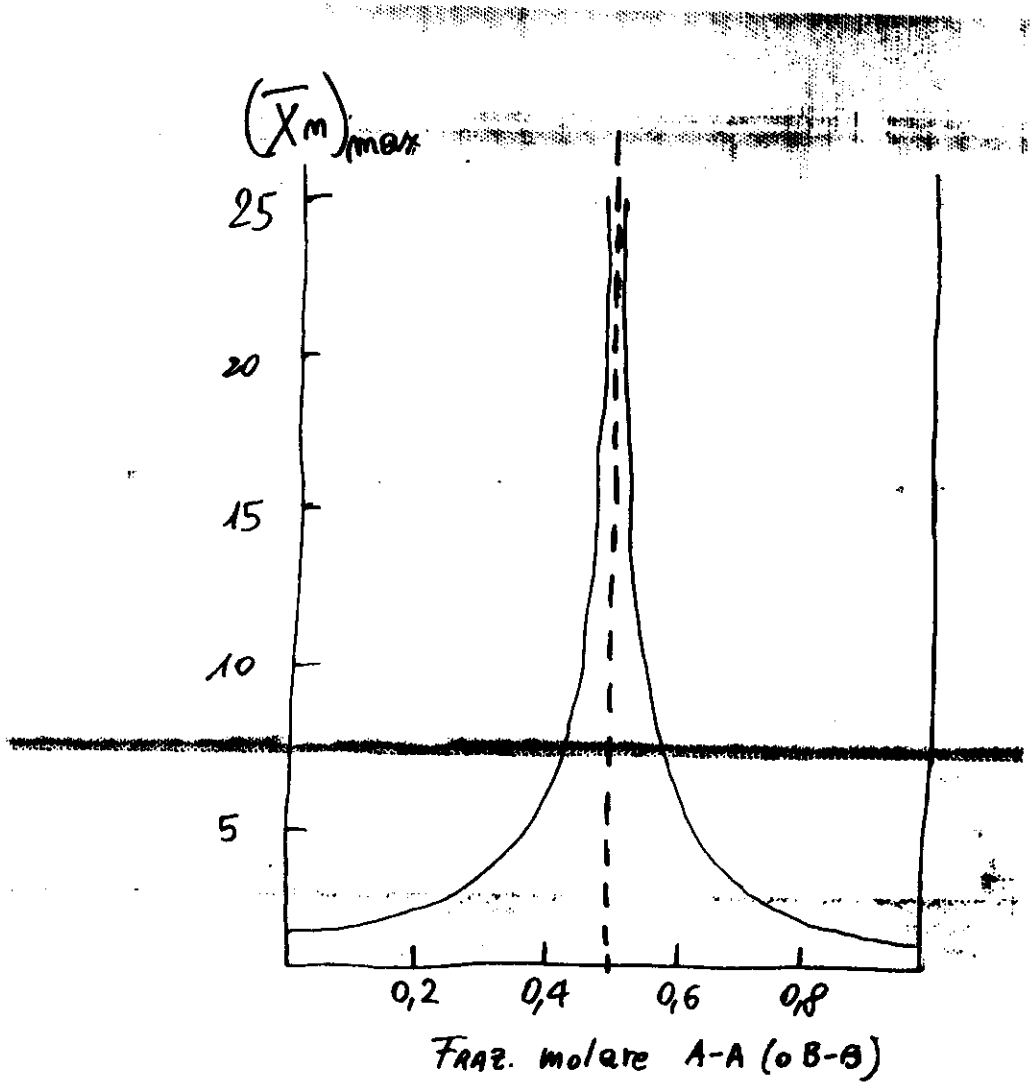
$N_{tot} = N_0^A (1-p) = r N_B^0 (1-p)$

$N_B = N_0^B - p_A N_0^A = N_0^B (1 - r p_A)$

$$\boxed{\overline{X}_m = \frac{1+r}{1+r-2r p_A}}$$

$r < 1$

MOLI AA	MOLI BB	r	$(\overline{X}_m)_{max}$
1	2	0,5	3
2	3	0,66	5
50	51	0,98	101
100	101	0,99	201
1	1	1	GRANDE QUANTO SI VUOLE



Policondensazione lineare

CINETICA DELLA POLICONDENSAZIONE

$$-COOH + \cdot OH \xrightarrow{k} -\overset{O}{\overset{\|}{C}}-O- + H_2O$$

reazione autocatalitica:

$$-\frac{d[COOH]}{dt} = k[COOH]^2[OH] = kc^3$$

$$\frac{1}{(1-p)^2} = 2c_o^2 kt + 1$$

reazione catalizzata

$$-\frac{dc}{dt} = k'c^2$$

$$\frac{1}{1-p} = c_o k' t + 1$$

Distribuzione pesi molecolari

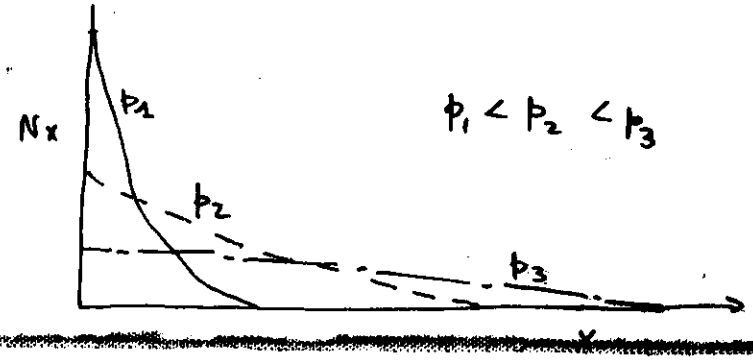
$$x\ A-A + x\ BB \longrightarrow A-A-[B-B-A-A]_{x-1}-B-B$$

$$x\ A-B \longrightarrow A-[B-A]_{x-1}-B$$

Fraz. molare molecole con x unità:

$$N_x = 1 \cdot (1-p)\, p^{x-1} = \text{Molar fraction}$$

$$n_x = n_0 (1-p)^2 p^{x-1} = \text{total number}$$



$p_1 < p_2 < p_3$

$$\overline{X}_m = \frac{\sum x N_x}{} = x(1-p)\, p^{x-1}$$

$$\sum_1^{\infty} x\, p^{x-1} = \frac{1}{(1-p)^2}$$

$$\overline{X}_m = \frac{1}{1-p}$$

Grado polim. medio ponderale

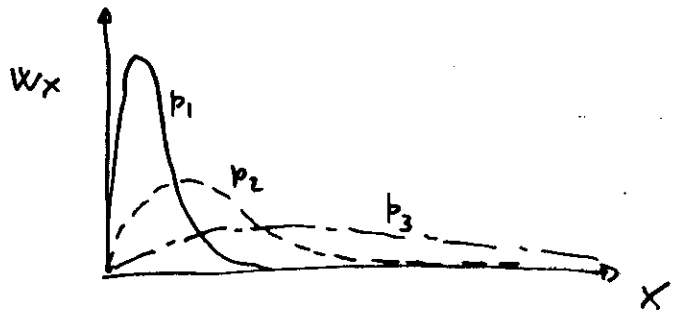
$$\overline{X}_w = \sum w_x \cdot x = \sum x^2 p^{x-1} (1-p)^2$$

$$\sum^{\infty} x^2 p^{x-1} = \frac{1+p}{(1-p)^3}$$

$$\overline{X}_w = \frac{1+p}{1-p}$$

Fraz. ponderale

$$w_x = x\,(1-p)^2\, p^{x-1} \quad \text{weight Fraction}$$



$$\frac{\overline{X}_w}{\overline{X}_m} = 1 + p$$

M.W. Dispersity

con $0 \le p \le 1$

PROBLEMS FOR THE SYNTHESIS OF MACROMOLECULES WITH HIGH STRUCTURAL REGULARITY

A. MAIN POINTS

1. UNITS ENCHAINMENT (HEAD-TO-TAIL ...)
2. MOLECULAR WEIGHT DISPERSION
3. STEREOREGULARITY
4. SEQUENCE DISTRIBUTION IN COPOLYMER

B. ACTUAL SITUATION

1. strictly respected only in polycondensation and stepwise synthesis; substantially valid for most chain polymerizations particularly Ziegler-Natta
2. Substantially respected in living polymerization (anionic, group transfer)
3. Ziegler-Natta and stepwise synthesis
4. Alternating copolymerization and stepwise synthesis

ZIEGLER-NATTA POLYMERIZATION

INITIATION

$$TiCl_4 + Al(C_2H_5)_3 \longrightarrow \{Ti - C_2H_5$$

$$\{Ti - C_2H_5 + CH_2=CH_2 \longrightarrow \{Ti - CH_2 - CH_2 - C_2H_5$$

PROPAGATION

$$\{Ti - CH_2 - CH_2 - C_2H_5 + n\, CH_2=CH_2 \xrightarrow{k_p}$$

$$\longrightarrow \{Ti\left(CH_2 - CH_2\right)_{n} CH_2CH_2C_2H_5$$

$$v_p = k_p [M][C^*]$$

TRANSFER

$$\{Ti - CH_2CH_2 \sim C_2H_5 \;\begin{cases} \xrightarrow{H_2} \{Ti - H + CH_3CH_2 \sim C_2H_5 \\ \qquad \downarrow C_2H_4 \\ \xrightarrow{CH_2=CH_2} \{Ti - C_2H_5 + CH_2=CH \sim C_2H_5 \\ \xrightarrow{Al(C_2H_5)_3} \{Ti - C_2H_5 + (C_2H_5)_2Al - CH_2 \sim \end{cases}$$

ASSOCIAZIONE ITALIANA DI SCIENZA
E TECNOLOGIA DELLE MACROMOLECOLE

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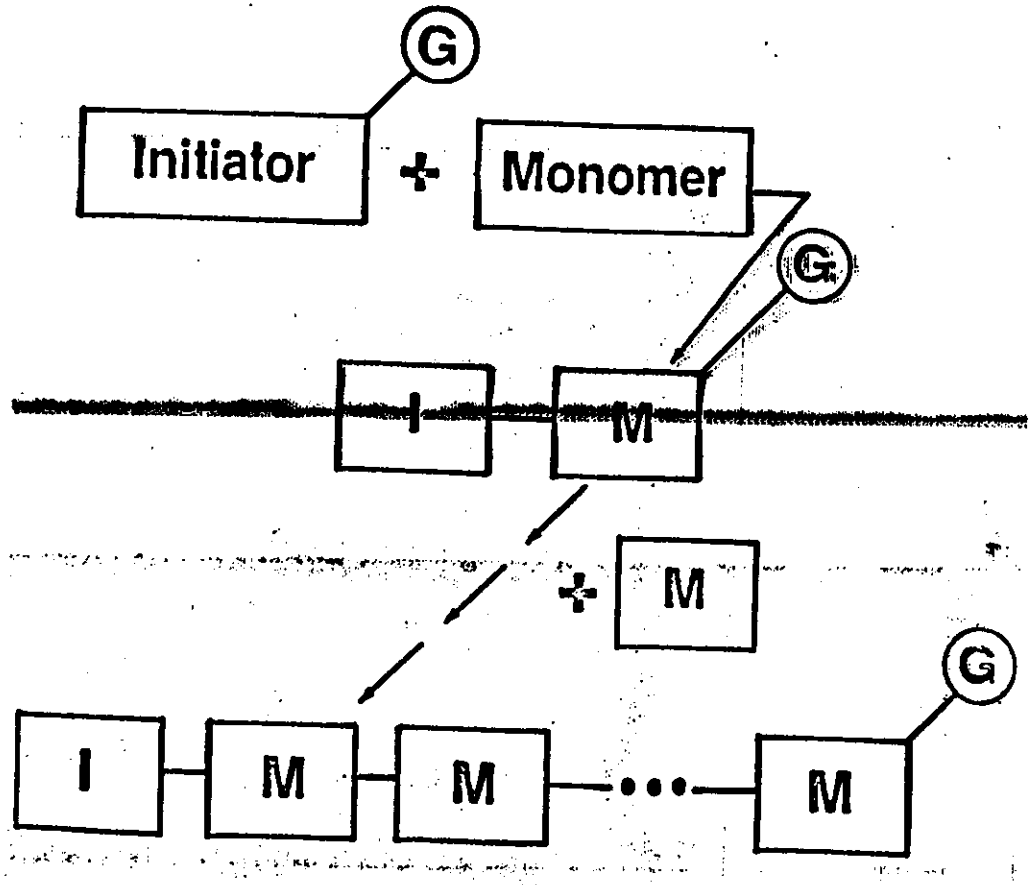
GROUP TRANSFER

Polymerization

Schematic of Group Transfer Polymerization

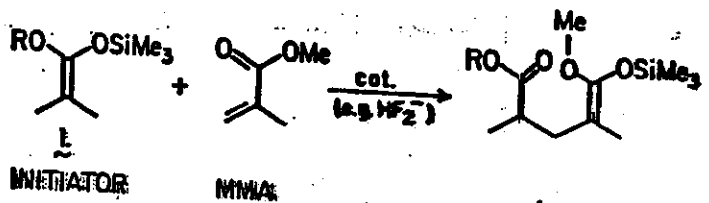


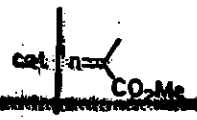
*The special initiator (I) with a silicon containing group (G) adds to the monomer (M) and simultaneously transfers the silicon group to the opposite end of the monomer.

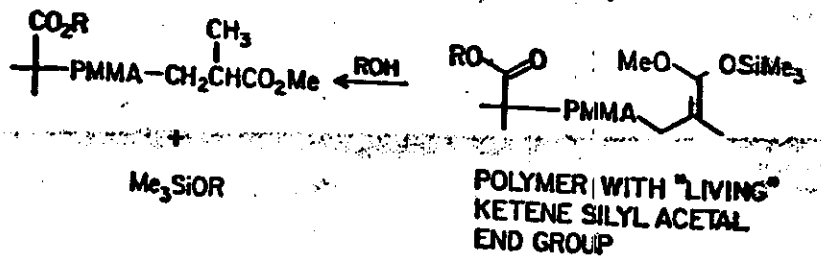
1

GROUP TRANSFER POLYMERIZATION

GROUP TRANSFER POLYMERIZATION IS THE SEQUENTIAL CATALYZED MICHAEL ADDITION OF KETENE SILYL ACETALS (1) TO α, β–UNSATURATED ESTERS, NITRILES, OR CARBOX–AMIDES.







2

CHARACTERISTICS OF GROUP TRANSFER POLYMERIZATION

POLYMERIZATION OF METHYL METHACRYLATE IS RAPID AND EXOTHERMIC IN TEMPERATURE RANGE –100° TO +110°C GIVING QUANTITATIVE YIELD OF POLYMER.

MOLECULAR WEIGHT SHOWS NARROW DISPERSITY. TYPICALLY $\bar{M}w/\bar{M}n$ = 1.1 TO 1.4

THE DEGREE OF POLYMERIZATION IS CONTROLLED BY THE RATIO OF MONOMER OF INITIATOR.

KETENE SILYL ACETAL END GROUP IS STABLE AND MAY BE USED FOR FURTHER REACTIONS OR FOR PREPARING BLOCK POLYMERS BY CHANGING MONOMER FEED.

3

CATALYSTS FOR GROUP TRANSFER POLYMERIZATION

NUCLEOPHILIC CATALYSTS:

$HF_2^{\ominus}$, $CN^{\ominus}$, $N_3^{\ominus}$, $F_2SiMe_3^{\ominus}$

SOLVENTS: Tetrahydrofuran, Toluene, Acetonitrile

LEWIS ACID CATALYSTS:

$ZnCl_2$, $ZnBr_2$, ZnI_2, R_2AlCl, $(R_2Al)_2O$

SOLVENTS: Toluene, Halogenated hydrocarbons

PREPARATION OF $(Me_2N)_3S^{\ominus}HF_2^{\ominus}$ CATALYST ("$TASHF_2$")

$$(Me_2N)_3S^{\oplus}F_2SiMe_3^{\ominus} + \tfrac{1}{2}\,H_2O \longrightarrow (Me_2N)_3S^{\oplus}HF_2^{\ominus} + \tfrac{1}{2}\,(Me_3Si)_2O$$

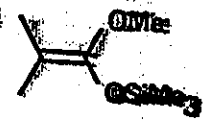
CATALYST REQUIREMENTS

NUCLEOPHILIC CATALYSTS MAY BE USED AT <<1% OF INITIATOR
LEWIS ACID CATALYSTS SHOULD BE USED AT ≥10% OF INITIATOR

4

TYPICAL PROCEDURE FOR GROUP TRANSFER POLYMERIZATION

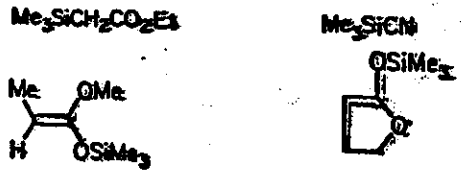
EQUIPMENT AND REAGENTS MUST BE DRY. TO 20 ml THF, 0.01 mmol $TASHF_2$ AND 8.5 mmol



UNDER ARGON OR NITROGEN FEED 360 mmol METHYL METHACRYLATE AT RATE TO MAINTAIN DESIRED TEMPERATURE. QUENCH WITH METHANOL, AND EVAPORATE OR PRECIPITATE PMMA IN QUANTITATIVE YIELD. $\overline{M}n$ 4300 $\overline{M}w$ 5300 (THEORY 4340)

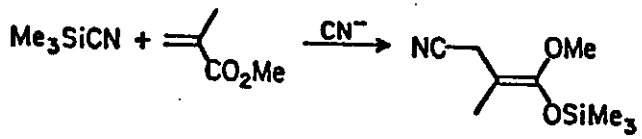
OTHER GROUP TRANSFER POLYMERIZATION INITIATORS

EXAMPLES

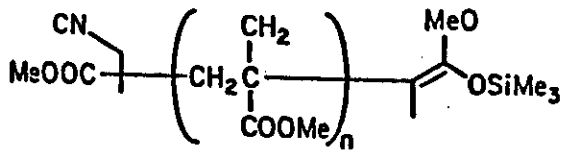


INITIATION WITH Me_3SiCN

TRIMETHYLSILYL CYANIDE, WITH CYANIDE ION CATALYST, INITIATES GROUP TRANSFER POLYMERIZATION OF METHYL METHACRYLATE WITH A PROLONGED INDUCTION PERIOD.



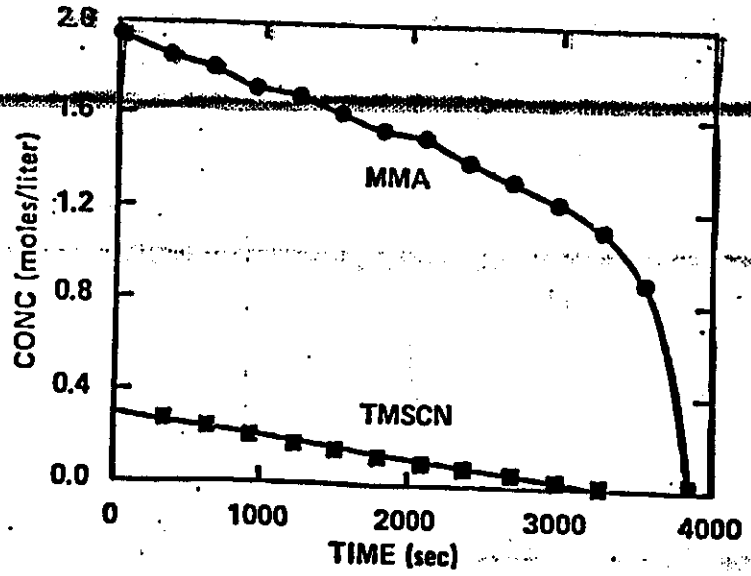
nMMA



INDUCTION PERIOD IS CAUSED BY INHIBITION OF POLYMERIZATION BY TRIMETHYLSILYL CYANIDE INITIATOR. THE INHIBITION RESULTS FROM COMPLEXATION OF $CN^{\ominus}$ CATALYS⁻ BY THE TRIMETHYLSILYL CYANIDE.

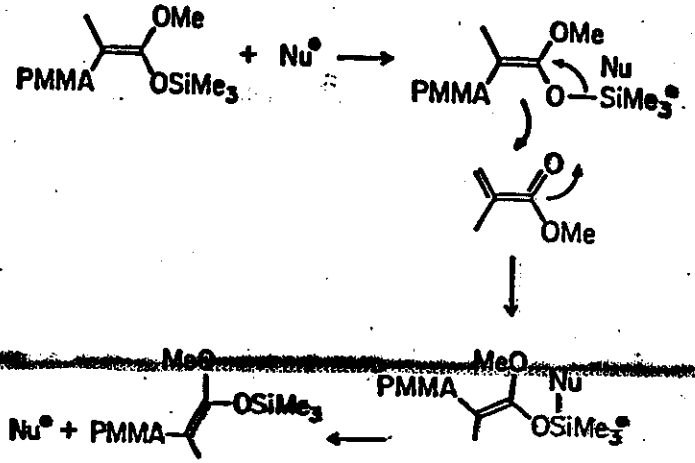
WHEN ALL OF THE TRIMETHYLSILYL CYANIDE IS CONSUMED, RAPID POLYMERIZATION OCCURS AS OBSERVED BY ^1H NMR KINETIC STUDIES.

TMSCN + 6MMA + CN^-

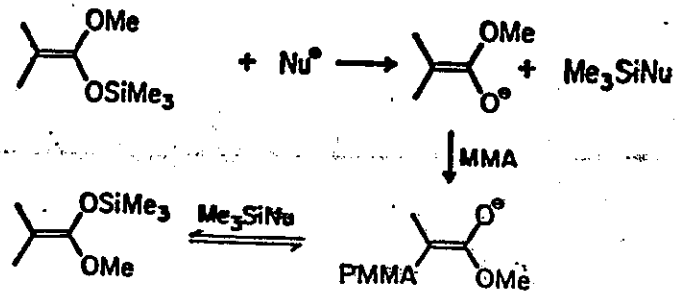


MECHANISM OF GROUP TRANSFER POLYMERIZATION

Associative Intramolecular Silyl Transfer Mechanism

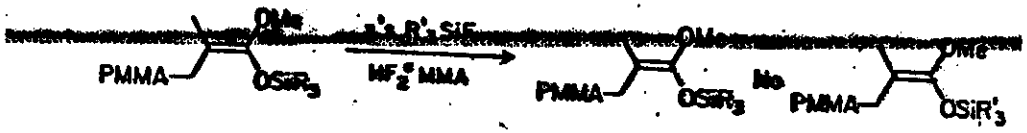


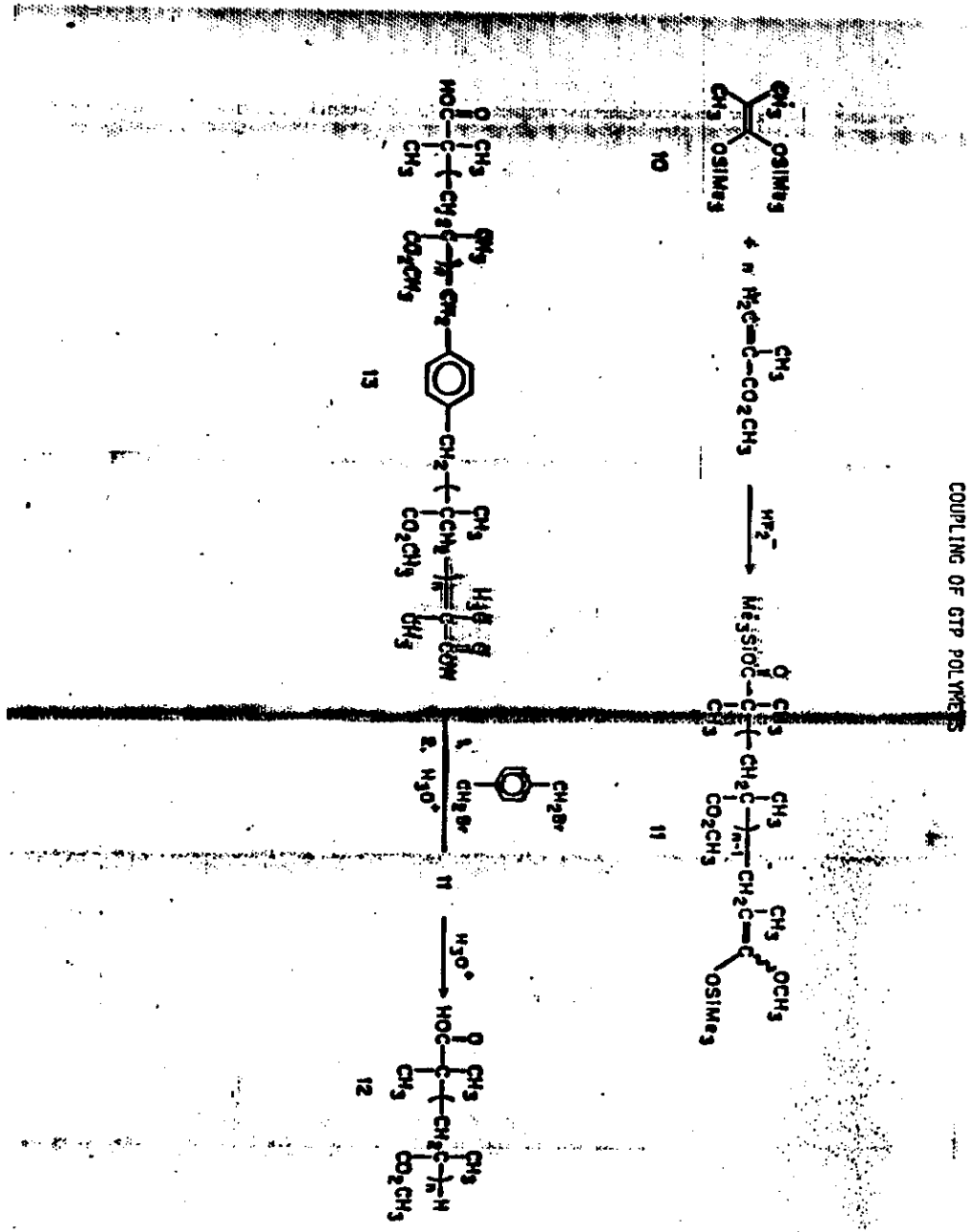
Dissociative Mechanism



EVIDENCE FOR ASSOCIATIVE MECHANISM

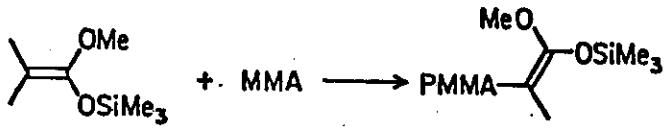
LACK OF EXCHANGE OF TRIALKLYSILYL GROUPS OF POLYMER AND EXTERNAL R_3SiNu DURING POLYMERIZATION IS CONSISTENT WITH ASSOCIATIVE MECHANISM AND INCONSISTENT WITH DIS-SOCIATIVE MECHANISM.





BLOCK POLYMERS

SINCE GROUP TRANSFER POLYMERS ARE "LIVING" (ie THEY CONTAIN A REACTIVE KETENE SILYL ACETAL TERMINUS) CHANGING THE MONOMER FEED TO A NEW MONOMER PRODUCES A NEW BLOCK. THE SIZE OF EACH BLOCK CAN BE ACCURATELY CONTROLLED.



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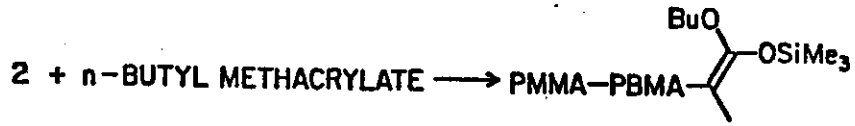

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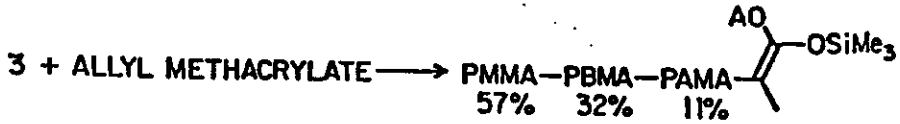


Mn 3800 Mw 4060 (THEORY 4060)
Tg = −19°, +38°, and + 108°C

Reazioni di Macromolecole

1. Reazioni senza variazione del grado di polimerizzazione
   - 1.1. Trasformazioni nella catena principale
   - 1.2. Trasformazioni catene laterali

2. Reazioni con aumento del grado di polimerizzazione
   - 2.1. Copolimeri a blocchi
   - 2.2. Copolimeri ad innesto
   - 2.3. Reticolazioni

3. Reazioni con diminuzione del grado di polimerizzazione
   - 3.1. Depolimerizzazione a stadi
   - 3.2. Depolimerizzazione statistica

Reticolazione e peso molecolare delle macromolecole primarie

1. Polimero monodisperso (DP = X)

p_m = probabilità che una unità sia coinvolta nella reticolazione

allora

$\varepsilon = p_m (X-1)$ = probabilità che in una macromolecola ci sia una reticolazione

Il valore critico per la reticolazione di tutte le macromolecole è $\varepsilon_{critico} = 1$

Quindi

$$\boxed{(p_m)_{crit} = \frac{1}{X-1} \simeq \frac{1}{X}}$$

2. Polimero polidisperso

$\varepsilon_i = p_m (w_m)_i (X_i - 1)$ $\quad w_m$ = frac. peso X_i

$\bar{\varepsilon} = \Sigma_i \varepsilon_i = \Sigma_i p_m (w_m)_i (X_i - 1) = p_m \Sigma_i (w_m)_i (X_i - 1)$

$\bar{\varepsilon} = p_m \Sigma_i \{(w_m)_i X_i - (w_m)_i\} = p_m [\underbrace{\Sigma_i (w_m)_i X_i}_{\bar{X}_w} - \underbrace{\Sigma_i (w_m)_i}_{1}]$

quindi

$$\bar{\varepsilon} = p_m (\bar{X}_w - 1)$$

$$\boxed{(p_m)_{crit} \simeq 1/\bar{X}_w}$$

Reticolazione di Polimeri

ad es. con perossidi

$RO{-}OR \longrightarrow 2\,RO^{\bullet}$

$RO^{\bullet} + PH \longrightarrow ROH + P^{\bullet}$

$2\,P^{\bullet} \longrightarrow P{-}P$

$2\,P^{\bullet} \longrightarrow P_H + P_{-H}$

si può avere anche degradazione di $P^{\bullet}$

$\sim CH_2{-}CHX{-}CH_2{-}CHX{-}CH_2{-}\overset{\bullet}{C}X{-}CH_2{-}CHX\sim$

Reticolazione | Scissione

$+ \sim CH_2{-}\overset{\bullet}{C}X\sim$

$\sim CH_2{-}CHX{-}CH_2{-}CH_2{-}CHX{-}CH_2{-}CX{-}CH_2CHX\sim$

$-CH_2{-}C(X)-$

$\sim CH_2{-}CHX{-}CH_2{-}\overset{\bullet}{C}HX$

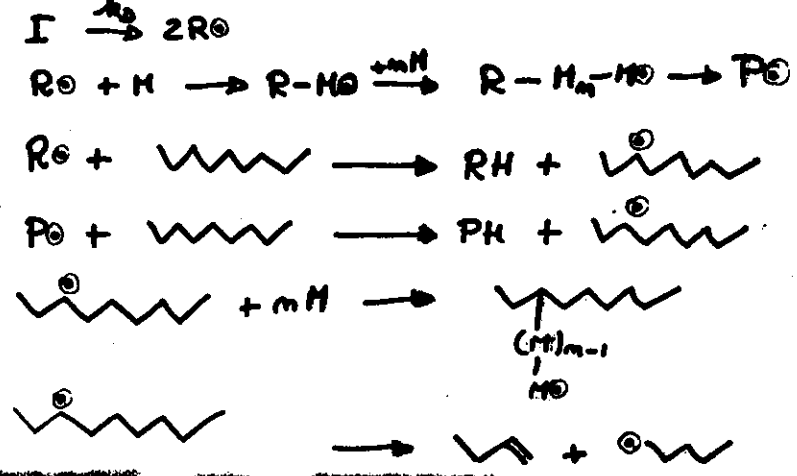
$+$

$CH_2{=}CX{-}CH_2{-}CHX-$

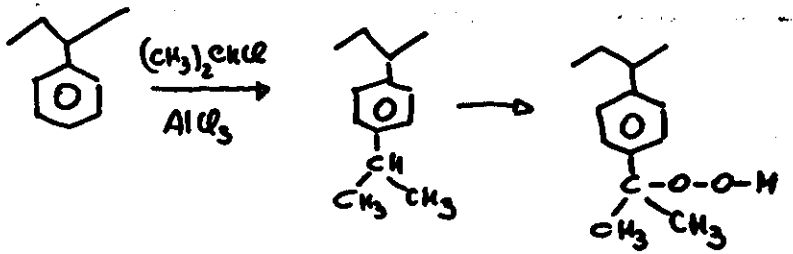
L'EFFICIENZA DELLA RETICOLAZIONE DIPENDE DAL POLIMERO

Sintesi di copolimeri ad innesto per via radicalica

1. Trasferimento di catena



2. Gruppi reattivi sulla catena



3. Metodi fotochimici e radiochimici

Elevata concentrazione dei gruppi reattivi in un omopolimero

1. Soluzione 1% in peso di etilacetato

$CH_3COOC_2H_5$: P.M. = 88

molarità : 0,11 moli/litro

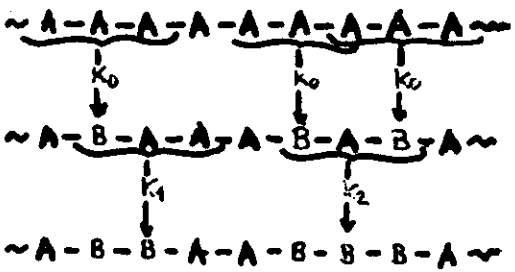
2. Soluzione 1% in peso di PVA ($\bar{M}_n = 10^6$)

$-CH_2-\underset{\underset{COCH_3}{|}}{\underset{|}{CH}}-$: P.M. = 86

molarità $\sim$ 0,11 moli/litro

In un gomitolo omogeneo a sfera di volume V ($r = 20\,nm$) si trovano pero

$$\frac{\bar{M}_n/86}{V} = \frac{\bar{M}_n/86}{\frac{4}{3}\pi r^3} \simeq 0{,}55 \text{ moli/litro}$$



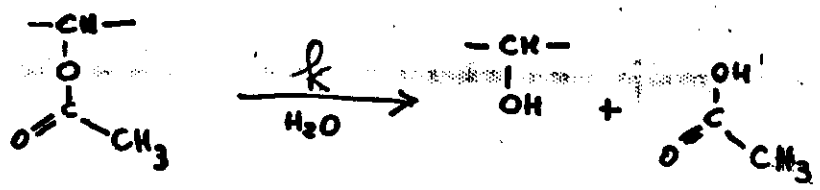
Effetti del gruppo vicino	$k_0 = k_1 = k_2$	$k_0 < k_1 < k_2$	$k_0 > k_1 > k_2$
cinetica	casuale	autoacce-lerazione	autoritardo
conversione	quantitativa	quantita-tiva	limitata
eterogeneità composizione	moderata	elevata	bassa
distribuzione unità A e B	statistica	blocchi di B	B isolato in blocchi di A

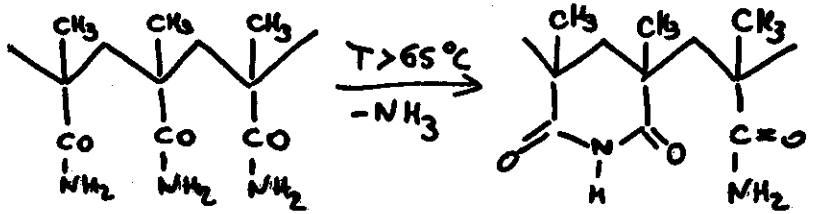
Frazione F di gruppi non reagiti nella reazione bifunzionale di sostituenti:

OMOPOLIMERO

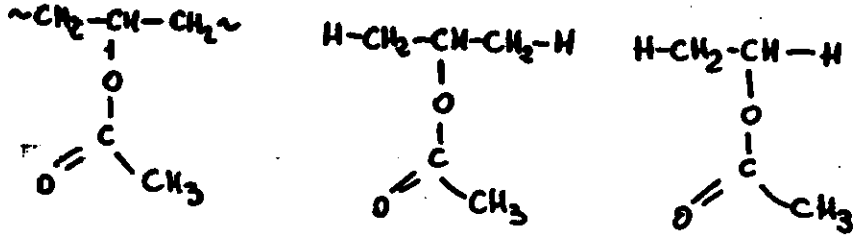
Concatenamento	Posizione gruppi	Numero gruppi per residuo	F
TC	1,3	2	$1/2e = 0{,}184$
TC	1,3	1	$1/e^2 = 0{,}135$
TT/CC (ALT.)	1,2	2	0,5
TT/CC/TC (STAT.)	1,2+1,3	2	0,312

Le interazioni tra unità vicinali sono determinanti quando portano ad uno stato di transizione a ciclo di 5 o 6 membri

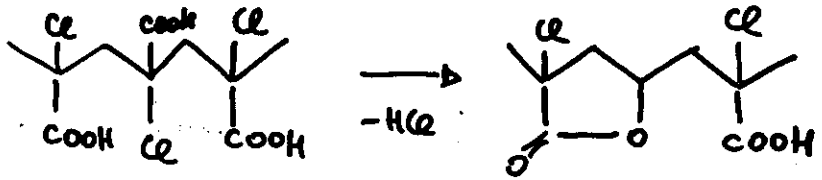




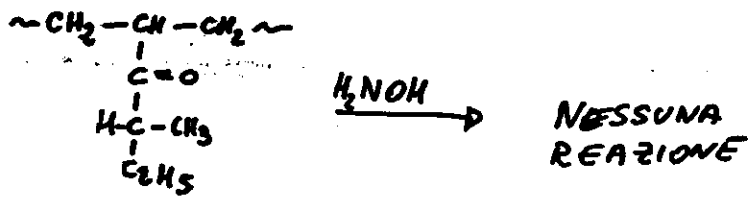
immide

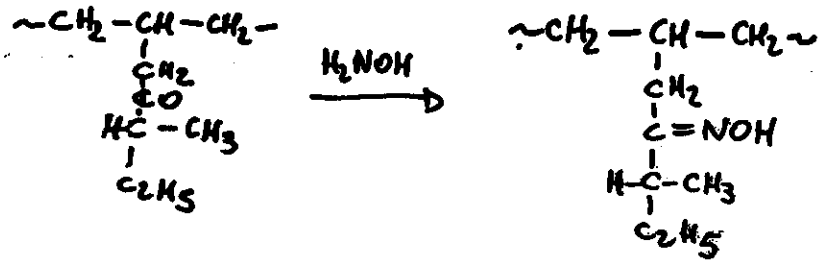


k	0,37	0,57	3,5



Lattone





Fattori che determinano la diversa reattività di un gruppo funzionale in macromolecole ed in analoghi monomerici ~

a)- Diverso intorno strutturale; inclusi effetti sterici

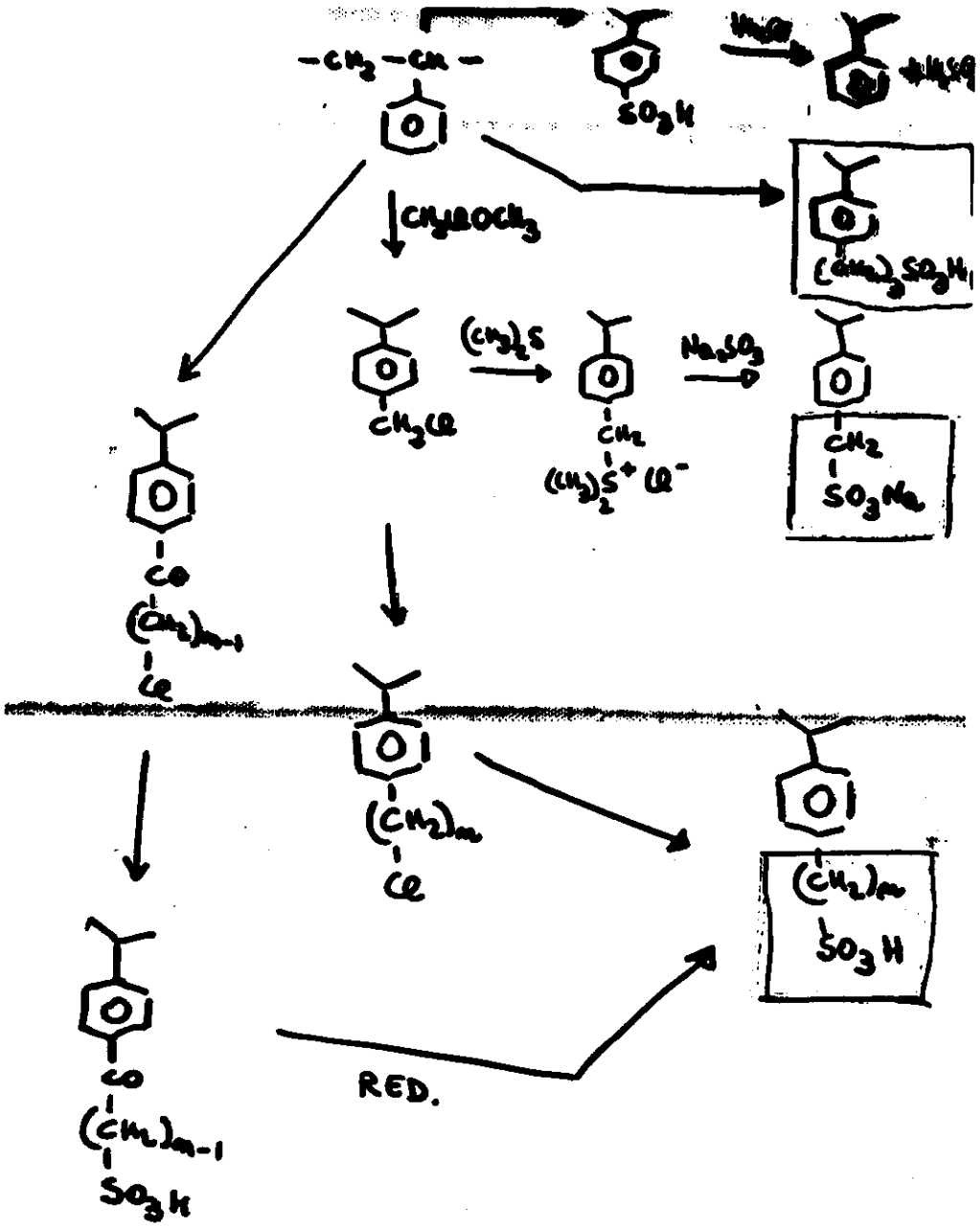
b)- Presenza di gruppi vicinali nel polimero

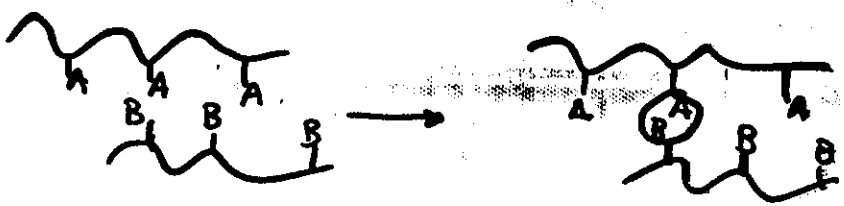
c)- Diversa interazione con il solvente

d)- Difficile omogeneità di sistemi macromolecolari nel corso della reazione

e)- Alta concentrazione locale dei gruppi in un omopolimero

f)- Interazione tra gruppi diversi (vicini o lontani) in copolimeri





Reazioni con aumento del $\overline{DP_n}$

1. Formazione di copolimeri a blocchi

BLOCK COPOLYMERS

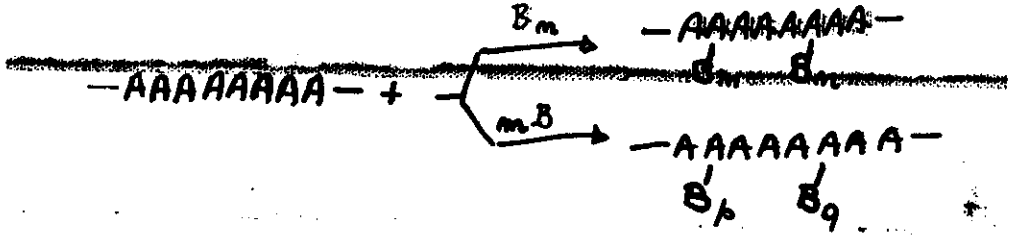
$$-(A)_m^- + m\,B \longrightarrow -(A)_m(B)_m$$

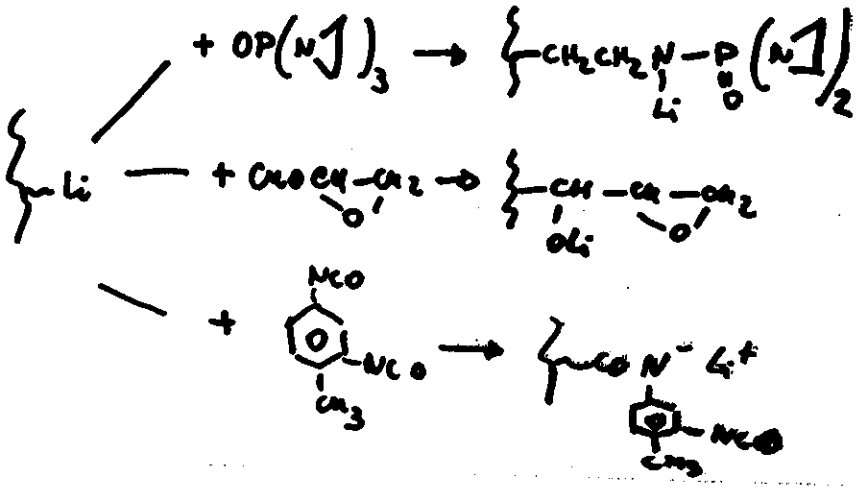
$$-(A)_m^- + (B)_m^- \longrightarrow -(A)_m(B)_m$$

A	B
-anidride	-OH $-NH_2$
-acido (COOH)	-OH -N<
-isocianato	-OH $-NH_2$, -NHR
-epossido	$-NH_2$, -NHR
-idrogenosilano	>C=C< $CH_2=CH-Si$<

2. Formazione di Copolimeri ad innesto

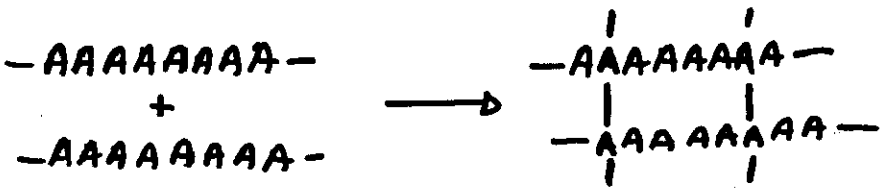
GRAFT COPOLYMERS





Reazioni di reticolazione

CROSSLINKING



Reazioni senza variazione del $\bar{D}P_n$

Reazione: ~A~ ⟶ ~B~

1. Conversione completa

$(A)_n$ — Reazione / Polimerizz. → $(B)_n$ omopolimero

$n\,B$

2. Conversione parziale

$(A)_n$ — Reazione / Copolim. → $(A)_m(B)_p$ copolimero

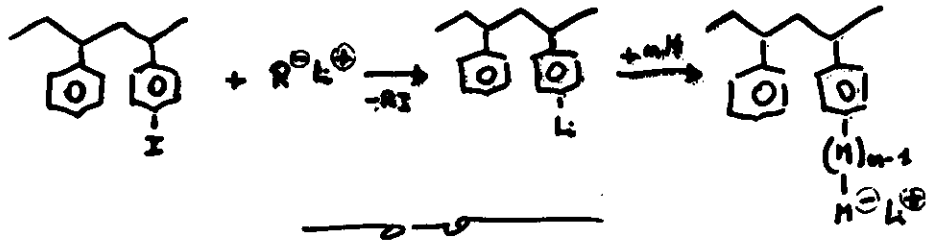
$mA + pB$

(La distribuzione delle unità A e B dipende dal metodo)

N.B. La reazione rimane l'unico metodo di sintesi se il monomero B non è disponibile o polimerizzabile

Sintesi di copolimeri ad innesto per via ionica

1.



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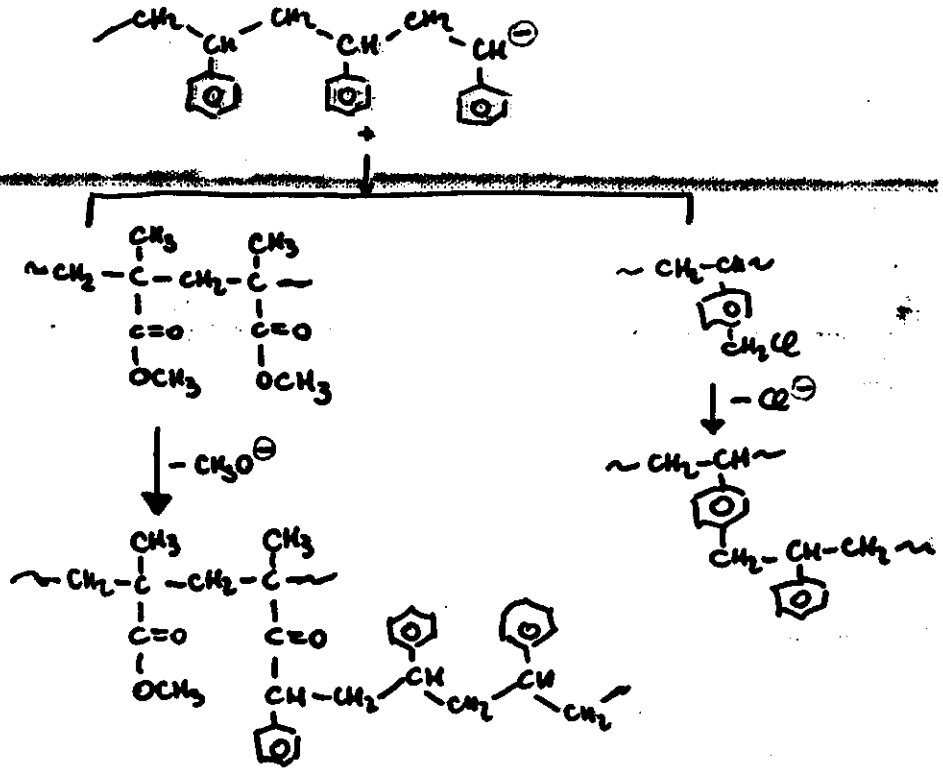
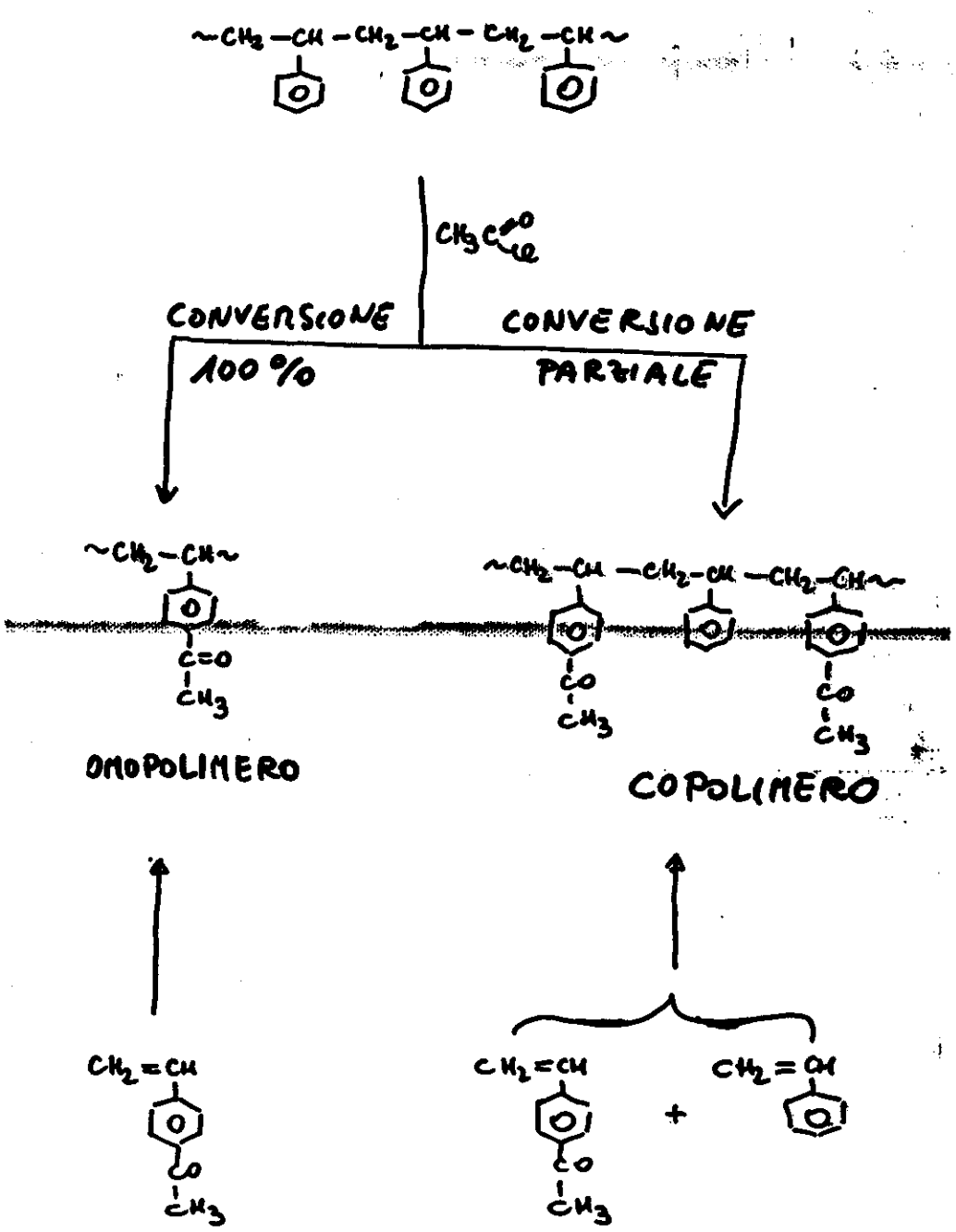




COPOLIMERIZZAZIONE

Interessa essenzialmente lo stadio di propagazione.

1. $\sim M_1^{\bullet} + M_1 \xrightarrow{k_{11}} \sim M_1M_1^{\bullet}$
2. $\sim M_1^{\bullet} + M_2 \xrightarrow{k_{12}} \sim M_1M_2^{\bullet}$
3. $\sim M_2^{\bullet} + M_2 \xrightarrow{k_{22}} \sim M_2M_2^{\bullet}$
4. $\sim M_2^{\bullet} + M_1 \xrightarrow{k_{21}} \sim M_2M_1^{\bullet}$

dove $\bullet$ indica una specie attiva: radicale o catione od anione

$$-\frac{d[M_1]}{dt} = k_{11}[\sim M_1^{\bullet}][M_1] + k_{21}[\sim M_2^{\bullet}][M_1] =$$

$$= [M_1]\{k_{11}[\sim M_1^{\bullet}] + k_{21}[\sim M_2^{\bullet}]\}$$

$$-\frac{d[M_2]}{dt} = [M_2]\{k_{22}[\sim M_2^{\bullet}] + k_{12}[\sim M_1^{\bullet}]\}$$

Stato stazionario della copolimerizzazione

occorre $v_2 = v_4$

cioè

$$k_{12}[\sim M_1^{\bullet}][M_2] = k_{21}[\sim M_2^{\bullet}][M_1]$$

Equazione di copolimerizzazione (Mayo e Lewis)

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

dove

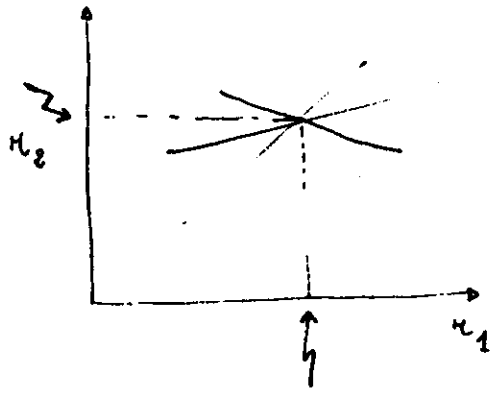
$r_1 = k_{11}/k_{12}$ e $r_2 = k_{22}/k_{21}$

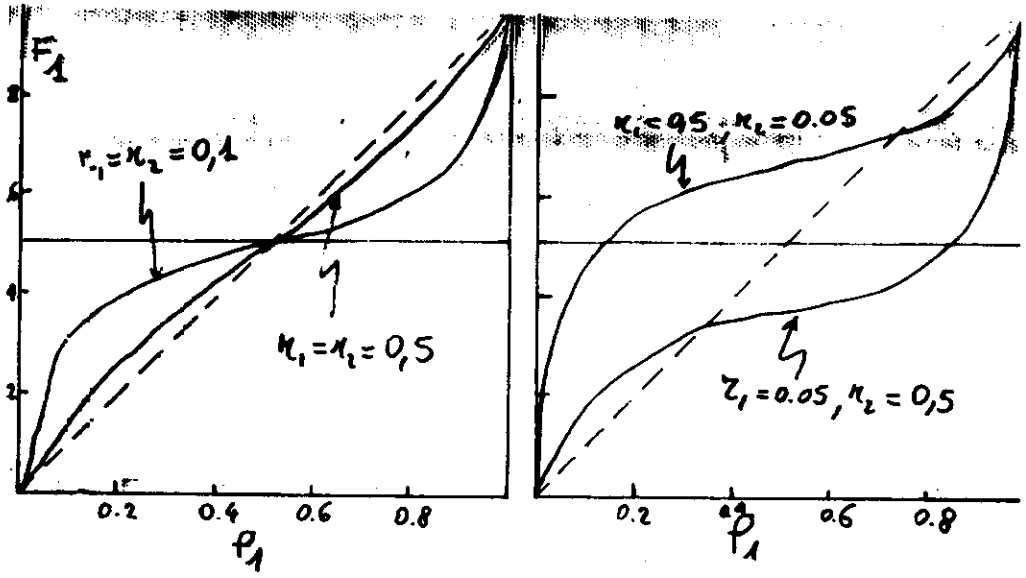
rapporti di reattività

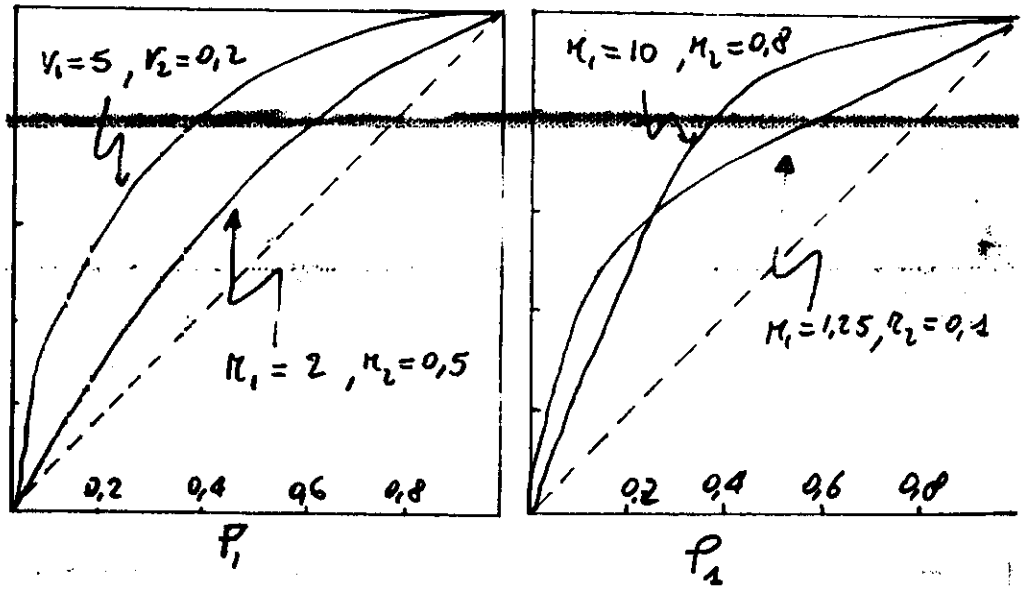
se $a = [M_1]/[M_2]$ e $b = d[M_1]/d[M_2]$

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

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







F_1 = Frazione mol. M_1 nel polimero = $\dfrac{d[M_1]}{d[M_1] + d[M_2]}$

$f_1 = \dfrac{[M_1]}{[M_1] + [M_2]}$

Equazioni di copolimerizzazione per casi limite

1. Ideale

A. $r_1 = r_2 = 1 \qquad b = a$

$$d[M_1] = [M_1] \quad e \quad d[M_2] = [M_2]$$

B. $r_1 \times r_2 = 1$ (statistico)

$$\frac{k_{11}}{k_{12}} \cdot \frac{k_{22}}{k_{21}} = 1 \qquad \frac{k_{11}}{k_{12}} = \frac{k_{21}}{k_{22}}$$

2 - Al punto azeotropico

$$a = b \qquad b = \frac{r_2 - 1}{r_1 - 1}$$

3 - Copolimerizzazione alternata

$r_1 = 0 \qquad r_2 = 0 \qquad b = 1$

Lunghezza media delle sequenze

$$\bar{l}_1 = \frac{v_{11}}{v_{12}} + 1 = r_1 a + 1$$

$$\bar{l}_2 = \frac{r_2}{a} + 1 \qquad \frac{d[M_1]}{d[M_2]} = \frac{\bar{l}_1}{\bar{l}_2}$$

Costanti di velocità assolute ($l \cdot mol^{-1} \cdot sec^{-1}$) per l'addizione di monomeri a radicali

Monomero \ Radicale	~CH₂-CH• (C₆H₅)	~CH₂-C•(CH₃)(CO₂CH₃)	~CH₂-CH•(CO₂CH₃)	~CH₂-CH•(OCOCH₃)
STIRENE	176	806	11500	370.000
MMA	335	367	232	250.000
MA	229	3670	2090	37000
VA	3,2	18,3	233	3700

Schema Q/e

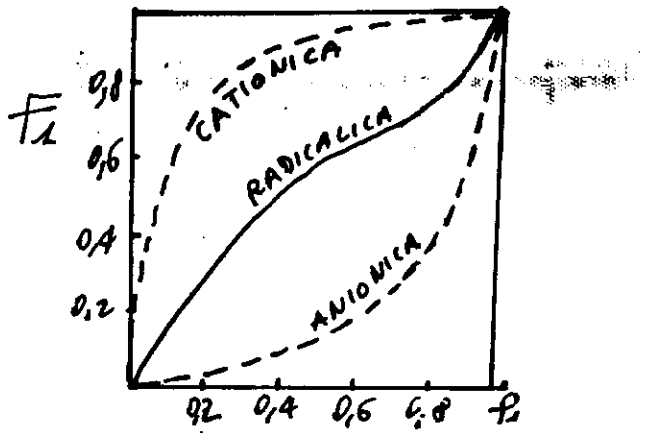
$$\sim M_x^{\bullet} + M_y \xrightarrow{k_{xy}} \sim M_x M_y^{\bullet}$$

$$k_{xy} = P_x \cdot Q_y \cdot e^{-e_x \cdot e_y}$$

$$r_1 = \frac{Q_1}{Q_2} \cdot e^{-e_1(e_1 - e_2)}$$

$$r_2 = \frac{Q_2}{Q_1} e^{-e_2(e_2 - e_1)}$$

$$r_1 \cdot r_2 = e^{-(e_1 - e_2)^2}$$



STIRENE / METIL METACRILATO

COPOLIMERIZZAZIONE STEREOSELETTIVA

$n\,(R+S) \longrightarrow -RRRRR- + -SSSSS-$

$k_{RR} \gg k_{RS} \qquad r_R \gg 1$

$k_{SS} \gg k_{SR} \qquad r_S \gg 1$

osservata per monomeri chirali

1) olefine racemo con cat. Ziegler/Natta

2) $CH_2=CH-R$ con cat eterogenei e/o stereospecifici

3) $R-\underset{\underset{\underset{O}{\|}}{C}-O}{\overset{*}{C}H}-NH-CO$ con basi