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"CONSTITUTION, CONFIGURATION AND CONFORMATION OF MACROMOLECULES"

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CONSTITUTION, CONFIGURATION AND CONFORMATION OF MACROMOLECULES

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At variance with chemical substances of low molecular mass, the description of the chemical structure of a polymer has a <u>statistical character</u>.

For the presentation of clear concepts, we have to resort to <u>idealized definitions</u>. Real polymers, however, deviate more or less from ideality on the molecular as well as on the bulk levels. Therefore, the definitions that we are going to give may be applied as well to the predominating structural features of real polymer molecules.

In a molecule, the <u>constitution</u> specifies which atoms are bound to each other, and with what type of bonds, without specifying their spacial disposition; the <u>configuration</u> specifies the spacial disposition of the bonds, for a given constitution, without taking into account the multiplicity of spacial dispositions that may arise through rotation around single bonds. The spacial dispositions, arising from the specification of the angles of rotation around single bonds, represent possible <u>conformations</u>.

According to I.U.P.A.C. definitions, a <u>polymer</u> is a substance composed of molecules characterized by the multiple repetition of one or more species of atoms or group of atoms (<u>constitutional units</u>) linked to each other in amounts sufficient to provide a set of properties that do not vary markedly with the addition or removal of one or a few of the constitutional units.

In correspondence to the same elemental composition, it is possible to have many different polymeric materials, which differ in constitution and/or in configuration, henceforth in properties.

To the composition CnH2n correspond polymeric materials so different in physical properties as the low and high density polyethylenes, the crystalline and the amorphous polypropylenes, the rubbery ethylene-propylene copolymers, the polyisobutylene, the crystalline poy-4-methylpentene; they give rise to plastic materials, fibers, rubber; some of the materials have melting points below 0°C, or above 200°C; some of them are always amorphous.

We say that a polymer is a regular polymer if its molecules can be described by only one species of constitutional unit in a single sequential arrangement.

In polyethylene such constitutional repeating unit (CRU) is:

```
-- CH2 --
```

For the polymers of propylene normally produced the constitutional repeating unit is:

```
-- CH -- CH2 --
   |
   CH3
```

Two regular macromolecules CnH2n with the structures above and the same and large n would be constitutional isomers; in fact, the two molecules would have the same composition and

molecular mass, but different constitution.

The ethylene-propylene copolymers normally produced are irregular polymers, since their molecules cannot be described by only one species of constitutional unit, in a single sequential arrangement.

The molecules of such polymers are characterized, from the structural view point, by the multiple repetition, not in a single sequential arrangement, of two species of constitutional units:

```
-- CH2 --     and     -- CH --
                         |
                         CH3
```

The constitution may be characterized by the knowledge (and hence by the specification) of the frequency of occurrence of various types of possible regular sequences of constitutional units (by N.M.R. and/or I.R. methods), for instance:

```
(-- CH2 --)n , n = 2,3,4,5,... or

-- CH -(- CH2 -- CH -)m - , m = 1,2,3,...
   |             |
   CH3           CH3
```

The sequence (-- CH(CH3) --)n with n > 2 in the ethylene-propylene copolymers has frequency of occurrence zero.

In any case, even for perfectly regular polymers, the constitution of the molecules must be described statistically as far as the molecular masses are concerned.

For the molecular masses, physical methods are available, which allow us to determine the mean value in number (Mn) or the mean value in weight (Mw), or other types of mean values of the molecular mass.

A more complete characterization may be obtained only from the determination of the distribution of the molecular masses (for instance, through the methods of gel permeation chromatography).

In real cases, even for a polymer which is substantially regular, such as polyethylene, any given macromolecule is not necessarily completely linear, and branches may be present. In low density polyethylenes, for instance, short branches in the order of magnitude of a few percent may be present; long branches are present in a small number for each macromolecule, but their higher or lower concentration may have important effects -coeteris paribus- on the rheological properties of the polymer.

In vinyl polymers, the enchainment of the monomeric units is prevailingly, but not completely, of the head-to-tail type. More complex, obviously, from the constitutional view point, are the graft and block polymers and, of course, the cross-linked polymers.

A block is a portion of a polymer molecule comprising many constitutional units, that has at least one constitutional or configurational feature not present in the adjacent portions.

A block polymer is a polymer whose molecules consist of blocks connected linearly. The blocks are connected directly or through a constitutional unit that is not part of the blocks.

A graft polymer is a polymer whose molecules have one or more species of block connected to the main chain as side chains,

these side chains having constitutional or configurational features different from the constitutional units comprising the main chain, exclusive of junction points.

For example, if A and B are:

```
-- CH -- CH2 --    (A)        and  -- CH -- CH2 --    (B)
   |                                  |
   CC2CH3                             C6H5
```

a molecule of block polymer could be:

A_k -- B_l -- A_m -- B_n

while a molecule of graft polymer could be:

```
...-- A -- A -- A -- A -- A -- A -- A -- A --...
           |              |
           Bm             Bn
```

A polymer may be regular from the constitutional point of view; however, it may show configurational isomerism.

The configuration of a carbon atom bound to four substituents is tetrahedral; the configuration of a carbon atom bound to three substituents is trigonal planar. Problems of stereoisomerism, that is of configurational isomerism arise whenever, along a chain, we have double bonds or when we have, in the constitutional units, tetrahedral carbon atoms bound to two different substituents, i.e.:

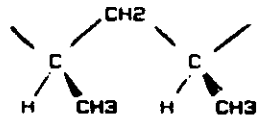
```
 H   CH3                    CH3  H
  \ /                          \ /
   C            ≠               C
(-) / \ (+)                (+) / \ (-)
```

The bonds indicated (+) and (-) are in the plane of the paper sheet; the bond indicated / is above (the chemical symbols are, correspondingly, in bold character), while the bond indicated \ is below the plane of the sheet; the signs indicate that the two bonds are enautiotupic: given two "test" substituents A and B, we have enantiomers if A is bonded in (+) and B in (-) or if A is bonded to (-) and B in (+).

In a polypropylenic chain, whose constitution is specified as follows:

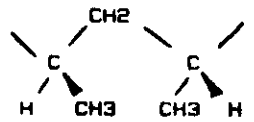
...--CH2--CH(CH3)--CH2--CH(CH3)--CH2--CH(CH3)--...

the two local configurations:



(meso diad, m)

and



(racemic diad, r)

are not equivalent, as in the classic case of racemic and meso tartaric acids.

Stereoregular vinyl polymers can be defined in terms of regular sequences of diads: thus an isotactic vinyl polymer consists entirely of m diads, i.e., it corresponds to the succession of relative configurations:

...m,m,m,m,m,m,m,m,m,..., whereas a syndiotactic vinyl polymer consists entirely of r diads, corresponding to the sequence: ...r,r,r,r,r,r,r,r,r,....

It is interesting to note that the assertion that a diad is m or r is independent of the internal rotations around C--C bonds, which are possible, but do not change the intrinsic

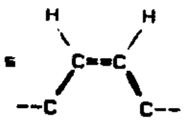
(+) or (-) character of the bonds.

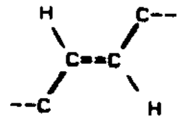
Physical methods (N.M.R.) are available to give the statistical distribution of configurational sequences: triads (m m, m r = r m, r r), tetrads (i.e., m m m or r m m = m m r, and so on...), pentads, and so on.

The physical properties vary with the distribution of configurations.

In vinyl polymers, the degree of isotacticity is strictly connected with the crystallinity. The higher the crystallinity, the more the polymer is isotactic. A polymer is highly isotactic when the percentage of isotactic diads is higher than 95%.

Double bonds along the chain of a polymer constitute another source of stereoisomerism, since they constrain the two atoms, which are partners of the double bond, and the four atoms bonded to them by single bonds to be in a plane. In respect to the polymeric chain, it is possible to have a cis or trans configuration; i.e.:

cis 

; trans 

.

Thus, we may have two stereoregular poybutadienes, with 1-4 enchainment, cistactic and transtactic.

Finally, the properties of polymers, in solution and in the bulk, are connected to the conformations taken by the macromolecules.

For the various constitutions and configurations of the macromolecules, many different dispositions in space of the atoms may occur for each single chain through rotations about single bonds. The theoretical study of the macromolecular conformations is performed with the methods of statistical thermodynamics for the amorphous and solution states; in the crystalline state the conformations of units succeed each other regularly along each chain, correspondingly to minima of internal energy.

References:

I.U.P.A.C. Commission on Macromolecular Nomenclature. Basic Definitions of Terms Relating to Polymers 1974.
Pure Appl. Chem., 40, 477 (1974).

I.U.P.A.C. Commission on Macromolecular Nomenclature. Stereochemical Definitions and Notations relating to Polymers
Pure Appl. Chem., 53, 733 (1981)

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R.W. Lenz anf F. Ciardelli (eds.), Preparation and Properties of Stereoregular Polymers, 317-352. D. Reidel Publishing Company (1979)

APPENDIX TO LECTURE NOTES OF PROF. CORRADINI

A basic computer program for calculating cartesian coordinates from internal coordinates (Dunitz)

```
9 DIM A(8,100),Q(2,100)
10 PRINT
25 I=0
26 F=.0174533
30 FOR S=1 TO 7
35 LET A(S,0)=0
40 NEXT S
45 A(0,0)=1
50 A(4,0)=1
55 A(8,0)=1
60 Q(0,0)=0
65 Q(1,0)=0
70 Q(2,0)=0
74  PRINT "Atomo vicino"
75 LPRINT "Atomo vicino";
76 INPUT N:LPRINT N
77 IF N=999 GOTO 299
78 INPUT W,T,R:LPRINT W,T,R
79 IF I=0 GOTO 261
95 IF I>2 GOTO 140
100 IF I<2 GOTO 120
105 T=0
110 M=1
115 GOTO 155
120 W=0
125 T=180-T
130 M=0
135 GOTO 155
140 M=N-1
155 N=M
160 B0=-COS(W*F)
165 B1=-SIN(W*F)
170 B5=-SIN(T*F)
175 B8=COS(T*F)
180 B3=-B1*B8
185 B4=B0*B8
190 B6=B1*B5
195 B7=-B0*B5
200 B2=0
205 A(0,I)=A(0,M)*B0+A(1,M)*B3+A(2,M)*B6
210 A(1,I)=A(0,M)*B1+A(1,M)*B4+A(2,M)*B7
215 A(2,I)=A(0,M)*B2+A(1,M)*B5+A(2,M)*B8
220 A(3,I)=A(3,M)*B0+A(4,M)*B3+A(5,M)*B6
225 A(4,I)=A(3,M)*B1+A(4,M)*B4+A(5,M)*B7
230 A(5,I)=A(3,M)*B2+A(4,M)*B5+A(5,M)*B8
235 A(6,I)=A(6,M)*B0+A(7,M)*B3+A(8,M)*B6
240 A(7,I)=A(6,M)*B1+A(7,M)*B4+A(8,M)*B7
245 A(8,I)=A(6,M)*B2+A(7,M)*B5+A(8,M)*B8
250 Q(0,I)=Q(0,M)+A(0,I)*R
```

```
255 Q(1,I)=Q(1,M)+A(3,I)*R
260 Q(2,I)=Q(2,M)+A(6,I)*R
261 PRINT
262 LET I1=I+1
265 LPRINT I1,Q(0,I),Q(1,I),Q(2,I)
266 PRINT I1,Q(0,I),Q(1,I),Q(2,I)
270 LET I =I+1
275 GOTO 74
299 PRINT
300 LPRINT " batti 1 se vuoi cominciare un'altra
conformazione"
310 INPUT Z
315 IF Z=1 GOTO 10
320 END
```

A basic computer program for calculating interatomic distances and angles and torsion angles from crystal coordinates (Dunitz)

```
4 PRINT
5 LPRINT "geometria molecolare"
6 PRINT "geometria molecolare"
10 DIM X(60),Y(60),Z(60)
15 LPRINT "A,b,c,alfa,beta,gamma"
16 PRINT "A,b,c,alfa,beta,gamma"
20 INPUT A1,A2,A3,W1,W2,W3
25 P=3.14159/180
26 LPRINT A1;A2;A3;W1;W2;W3
30 C1= COS (W1*P)
31 C2= COS (W2*P)
32 C3= COS (W3*P)
33 S3= SIN (W3*P)
35 M6= (C1-C3*C2)/S3
37 V=SQR (1-C1*C1-C2*C2-C3*C3+2*C1*C2*C3)
39 M9 =V/S3
45 PRINT "i,x(i),y(i),z(i),i=0 per l'ultimo atomo"
46 INPUT I, X(I), Y(I), Z(I)
47 LPRINT I; X(I); Y(I); Z(I)
48 IF I=0 GOTO 75
49 U=A1*X(I)+A2*Y(I)*C3+A3*Z(I)*C2
50 V=A2*Y(I)*S3+A3*Z(I)*M6
51 W=A3*Z(I)*M9
52 X(I)=U
55 Y(I)=V
57 Z(I)=W
58 GOTO 46
75 PRINT "lunghezza legame: i1,i2,0,0"
76 PRINT "angolo di legame: i1,i2,i3,0"
77 PRINT "angolo di torsione: i1,i2,i3,i4"
78 LPRINT "lunghezza legame: i1,i2,0,0"
```



```
79 LPRINT "angolo di legame: i1,i2,i3,0"
80 LPRINT "angolo di torsione: i1,i2,i3,i4"
85 INPUT T1, T2, T3, T4
86 LPRINT T1; T2; T3; T4
100 E(1)=X(T2)-X(T1)
105 E(2)=Y(T2)-Y(T1)
110 E(3)=Z(T2)-Z(T1)
115 F=1
120 D1=SQR(E(1)*E(1)+E(2)*E(2)+E(3)*E(3))
121 D=D1
125 GOSUB 325
133 IF T3=0 GOTO 499
135 E(4)= X(T3)-X(T2)
140 E(5)= Y(T3)-Y(T2)
145 E(6)=Z(T3)-Z(T2)
150 F=4
155 D2=SQR(E(4)*E(4)+E(5)*E(5)+E(6)*E(6))
156 D=D2
160 GOSUB 325
165 C4=-(E(1)*E(4)+E(2)*E(5)+E(3)*E(6))
170 S4=SQR (1 -C4*C4)
175 A4=ATN (S4/C4)/P
176 IF A4 >0 GOTO 180
177 A4=A4+180
180 IF T4=0 GOTO 497
185 E(7)=X(T4)-X(T3)
190 E(8)=Y(T4)-Y(T3)
195 E(9)=Z(T4)-Z(T3)
200 F=7
205 D3=SQR(E(7)*E(7)+E(8)*E(8)+E(9)*E(9))
210 D=D3
215 GOSUB 325
220 C5=-(E(4)*E(7)+E(5)*E(8)+E(6)*E(9))
225 S5=SQR (1 -C5*C5)
230 A5=ATN (S5/C5)/P
231 IF A5 >0 GOTO 250
232 A5=A5+180
250 U1=(E(2)*E(6)-E(3)*E(5))
252 U2=(E(3)*E(4)-E(1)*E(6))
254 U3=(E(1)*E(5)-E(2)*E(4))
256 V1=(E(5)*E(9)-E(6)*E(8))
258 V2=(E(6)*E(7)-E(4)*E(9))
260 V3=(E(4)*E(8)-E(5)*E(7))
265 C6=(U1*V1+U2*V2+U3*V3)/(S4*S5)
270 S6=(E(1)*V1+E(2)*V2+E(3)*V3)/(S4*S5)
275 A6 =ATN(S6/C6)/P
280 IF A6>0 GOTO 290
281 IF S6<0 GOTO 300   < 282 A6 = A6+180
284 GOTO 300
290 IF C6>0 GOTO 300
292 A6=A6-180
299 PRINT
300 LPRINT "t("T1;T2;T3;T4;") ="A6
301 LPRINT "w("T2;T3;T4;") ="A5
```

```
302 LPRINT "d("T3;T4;") ="D3
303  PRINT "t("T1;T2;T3;T4;") ="A6
304  PRINT "w("T2;T3;T4;") ="A5
305  PRINT "d("T3;T4;") ="D3
306 GOTO 497
325 FOR J=F TO F+2
327 E(J)=E(J)/D
329 NEXT J
331 RETURN
496 PRINT
497 LPRINT "w("T1;T2;T3;") ="A4
498 LPRINT "d("T2;T3;") ="D2
499 LPRINT "d("T1;T2;") ="D1
500  PRINT "w("T1;T2;T3;") ="A4
501  PRINT "d("T2;T3;") ="D2
502  PRINT "d("T1;T2;") ="D1
510 PRINT
512 GOTO 85
515 END
1000 INPUT A,B,C,D,E,F
```


PRESENT STATUS OF THE CONFIGURATIONAL AND CONFORMATIONAL ANALYSIS OF STEREOREGULAR POLYMERS

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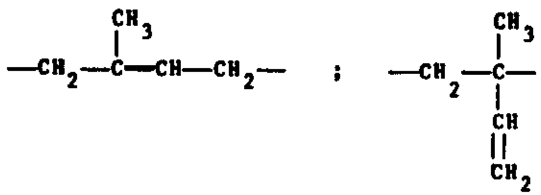
CONSTITUTIONAL AND CONFIGURATIONAL ISOMERISM IN MACROMOLECULES(1)

In a molecule the constitution specifies which atoms are bonded to each other and with what kind of bonds, without considering their spatial dispositions; the configuration specifies the spatial disposition of the bonds, for an assigned constitution, without taking into account the molteplicities of the spatial dispositions, that may arise by rotation around single bonds. The spatial dispositions which arise from the specification of the internal rotation angles around single bonds represent possible conformations.

From any single monomer, different constitutional units may arise during the polimerization. Consider, for instance, the monomer isoprene; even in the case of a regular enchainment, the monomeric units may join the growing chain according to the three different constitucns which are indicated:



1,4 ; 1,2

R. W. Lenz and F. Ciardelli (eds.), Preparation and Properties of Stereoregular Polymers, 317-352.
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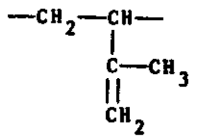
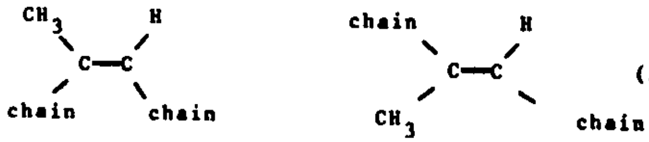


(1)

3,4

Consider now the 1,4 regular enchainment. Yet, a regular polymer having this constitution may have still two different configurations for the double bond along the chain:



(2)

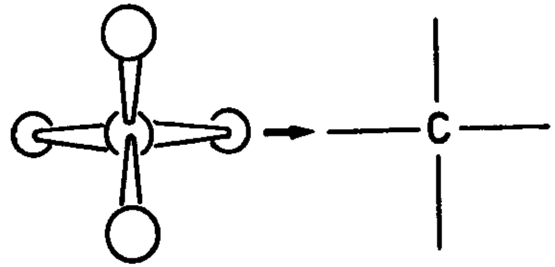
cis-configuration *trans*-configuration

If all the units along the chain are *trans* or if all the units along the chain are *cis*, the polymer is called tactic: in the first case *trans*-tactic, in the second case *cis*-tactic. It may be noted that, in the case of 1,4 polyisoprene, these two possibilities correspond to guttapercha and natural rubber respectively; tactic polymers of isoprene are naturally occurring polymers.

From the previous example we have seen that a problem of configurational isomerism arises whenever we have a double bond along the chain. Another case in which a problem of configurational isomerism arises is the case in which we have along the chain a carbon atom which is further bonded to two different groups, S and L. Here are represented the two possible cases which may arise for two successive constitutionally equivalent carbon atoms –C(S)(L)– along the chain, that have a simmetrically constituted connecting group(if any):

diad *m* diad *r* (3)

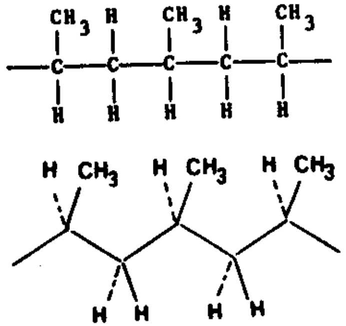
This representation of the space disposition of bonds, around these carbon atoms, is a modified Fisher projection, where the bonds at each carbon atom are seen as a projection of a tetrahedral arrangement, so that the two vertical bonds go in the direction of the observer, and the two horizontal bonds go in the direction away from the observer:



(4)

Stereosequences terminating in tetrahedral stereoisomeric centres at both ends, and which comprise two, three, four, five etc. consecutive centres of that type, may be called diads, triads, tetrads, pentads, etc., respectively. As indicated in the formulas (3), the diad *m* is defined as that with identical substituents on the same side in respect to the backbone in Fisher projection, and diad *r* is defined as that with identical substituents in the opposite sides in respect to the backbone, in the same projection.

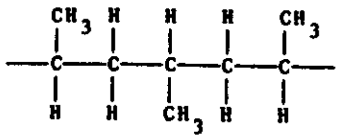
All definitions in polymers refer to ideal situations, so an "ideal" isotactic vinyl polymer is a polymer caracterized by a succession of <u>all</u> *m* diads; an "ideal" syndiotactic vinyl polymer is a polymer which is caracterized by a succession of <u>all</u> *r* diads. According to these conventions, the isotactic polymer of propylene can be indicated:



(Fisher projection)

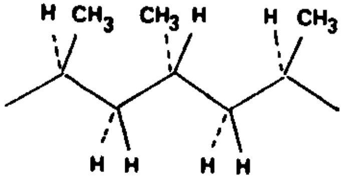
(5)

(reference to a zig-zag planar conformation) while the syndiotactic polymer will be indicated:



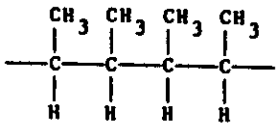
(Fisher projection)

(6)



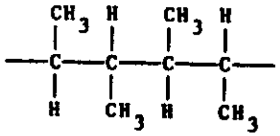
(reference to a zig-zag planar conformation)

The first definition of an isotactic polymer was made with reference to a zig-zag planar conformation. Take, however, the case of polyethylidene; the isotactic polymer will be represented, in the modified projection, as follows:



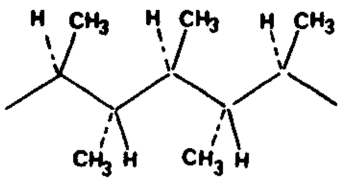
(7)

while the syndiotactic polymer in the same representation:



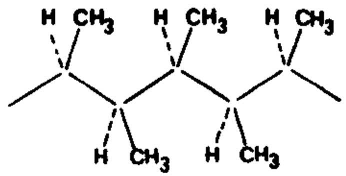
(8)

Note that, if you represent the chain in its zig-zag planar conformation, the result will be:



(9)

isotactic polymer

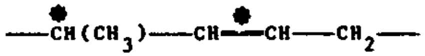


(9)

syndiotactic polymer

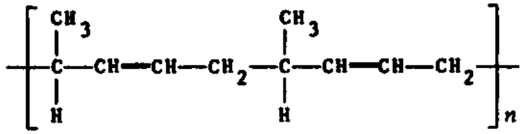
where the successive methyl groups are on opposite sides, in respect to the plane of the zig-zag, in the isotactic polymer, and on the same side in the syndiotactic polymer; instead opposite conclusions, for analogue representations, are reached in the case of isotactic and syndiotactic polypropylene.

Consider, now, the case of polypentadiene, in the 1,4 enchainment:



(10)

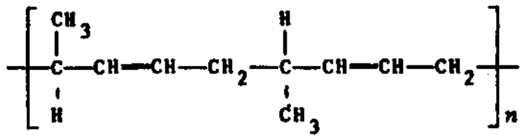
and suppose that only one of the two sites of stereoisomerism ✱, in each constitutional unit in one sequence, has defined stereochemistry. We can have the isotactic polymer:



(11)

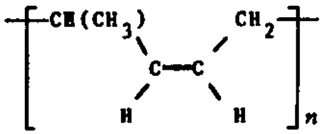
(configuration of the double bond unknown or not defined)

the syndiotactic polymer:



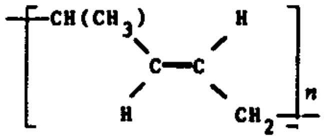
(12)

the *cis*-tactic polymer:

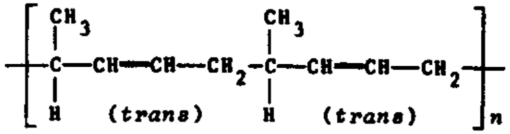


(13)

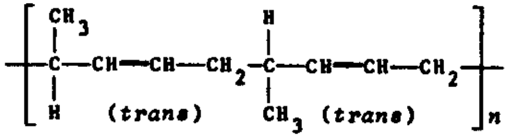
(configuration of the tertiary carbon atom unknown or not defined)
the *trans*-tactic polymer:


(14)

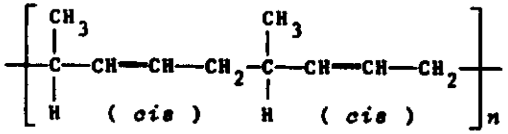
If both the sites of stereoisomerism have defined stereochemistry, the polymer is defined stereoregular. So stereoregular polymers are:


(15)

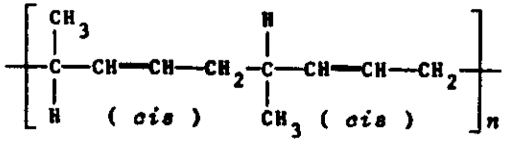
isotranstactic


(16)

syndiotranstactic


(17)

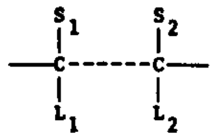
isocistactic


(18)

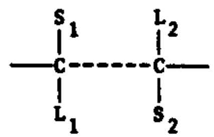
syndiocistactic

In general, according to the IUPAC definitions, a *regular* polymer is a polymer which is built up of identical constitutional units, which are called constitutional repeating units. A polymer is called *tactic* if at least one site of stereoisomerism in each constitutional unit has a regular stereochemistry. A polymer is called, instead, *stereoregular* when the molecules can be described in terms of only one species of configurational unit, having defined configuration at all the sites of stereoisomerism in the main chain, in a single sequential arrangement. Thus, a stereoregular polymer is always a tactic polymer, but a tactic polymer need not always stereoregular, because a tactic polymer need not have all sites of stereoisomerism with defined stereochemistry. The polymers (11),(12),(13),(14) are tactic, the polymers (5),(6),(7),(8),(15),(16),(17),(18) are both tactic and stereoregular.

For the designation of relative configurations inside of a given monomeric unit, with two non-constitutionally equivalent carbon atoms of the main chain, bearing substituents S_1,L_1 and S_2,L_2 respectively, a further convention (which is taken from the chemistry of carbohydrates) is used:

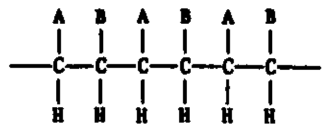

erythro
relative configuration

(19)

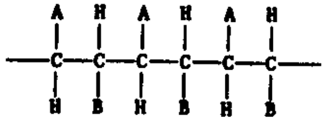

threo
relative configuration

where $S_1 \neq S_2$ and/or $L_1 \neq L_2$ and L precedes S according to the Cahn, Ingold, and Prelog rule of precedence.

The possible stereoregular polymers which may arise from units of the previous kind are, in the case that S_1 ($=S_2$) is a hydrogen atom and $L_1 = A \neq L_2 = B$:

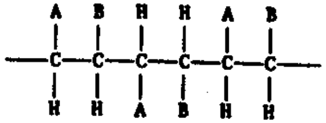

(20)

erythro-diisotactic



(21)

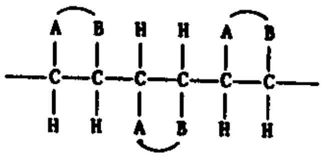
threo-diisotactic



(22)

disyndiotactic

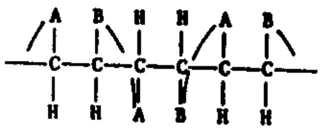
it is possible to get an *erythro* and a *threo* diisotactic polymers whereas there is only one disyndiotactic polymer. But in the case, in which the substituents, A and B, are joined in a ring it is possible to distinguish two cases for the disyndiotactic polymer; the first case in which the rings join two atoms on the same side of the Fisher projection (the polymer is then named *erythro*-disyndiotactic):



(23)

erythro-disyndiotactic

the second case in which the rings join two atoms in the opposite sides of the Fisher projection (the polymer is then named *threo*-disyndiotactic):



(24)

threo-disyndiotactic

THEORETICAL ASPECTS OF CONFORMATIONAL ANALYSIS

Internal coordinates(2)

The space form of the chain of a polymer depends on bond distances, on bond angles, and on dihedral angles: parameters which are called internal coordinates; the number of internal coordinates necessary to describe a chain with n atoms is $3n-6$. Fig. 1 shows as in a given chain bond lengths, bond angles, and internal rotation angles are most appropriately designated.

It is important to know which is the appropriate convention which is used to measure internal rotation angles. Take, for example, three successive bonds L_1, L_2, and L_3 (fig. 2). If you look in the direction of L_2 from the side of L_3, the dihedral angle is that from which we have to rotate the bond L_3 in order to superpose it to

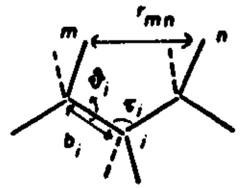


Fig. 1. Symbols used for: bond lengths, bond angles, internal rotation angles and distance between nonbonded atoms.

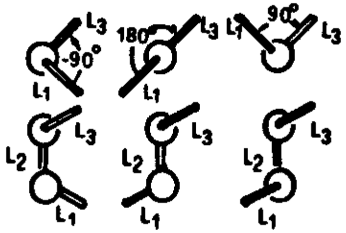


Fig. 2. Convention used to measure internal rotation angles.

L_1, describing the smaller angle possible. If the rotation is in the clockwise direction the angle is positive, viceversa it is negative; thus possible values of dihedral angles are included in the range (-180°,180°). It is easy to see that the same result would be obtained if, always looking in direction of L_2, but from the side of L_1, you measure the dihedral angle from which we have to rotate L_1 in order to superpose it to L_3.

Special names and symbols are attributed to the following internal rotation angles:

trans or *antiperiplanar* (T) for 180°
anticlinal (A) for |120°|
gauche or *synclinal* (G) for |60°|
cis or *symperiplanar* (C) for 0°

A sign can be appended to the symbol, to indicate whether the internal rotation angle is plus or minus, while a prime may indicate an internal rotation angle which is slightly displaced from the exact corresponding value. The notation G , $\bar{G}$; A , $\bar{A}$ (and T , $\bar{T}$; C , $\bar{C}$ whenever the torsion angles are not exactly equal to 180° and 0°, respectively) are reserved for the designation of enantiomorph conformations, i.e. conformations of opposite but unspecified sign.

Internal potential energy(2)

The comprehension of the spatial relationships among the atoms of a molecule, which is the object of conformational analysis, is a universal prerequisite in the establishement of the connections between the graphic formula and the properties of a substance. The relevancy is even greater in the case of long chain molecules where the phemenomenon of rubber elasticity, the hydrodynamic and thermodynamic properties of the solutions, the rheology of the melts reflect the caracter of random coil of a single macromolecule, whereas many useful properties of polymers reflect their ability to crystallize.

The intramolecular potential energy is very important in determining the conformations of the macromolecules, both in the crystalline state and in the amorphous or solution state. In turn, the potential energy may be taken, in general, as a sum of terms of the kind: stretching, bending, torsion, nonbonded,electrostatic:

$$E = E_s + E_b + E_t + E_{nb} + E_{el} \qquad (25)$$

For small displacements from the minimum energy value, the stretching energy may be taken as:

$$E_s = \frac{1}{2} k_s (b-b_\circ)^2 \qquad (26)$$

and an analogous formula may be used for the bending energy:

$$E_b = \frac{1}{2} k_b (\tau-\tau_\circ)^2 \qquad (27)$$

where $b_\circ$ and $\tau_\circ$ are the values of bond distances and angles chosen as energetic minima, and k_s and k_b constants depending on the particular kind of bonds. The k_s value in formula(26) is such as to prohibit displacements of the bond distances from $b_\circ$ greater than a few percent. In fact, bond distances as determined from X-ray diffraction experiments, are generally almost constant in going from one molecule to another, if we refer to atoms in similar electronic environments.

The bending energy parameters, which are used by Flory(3), in a consistent way with the non bonded parameters, which we shall indicate later on, are reported in table 1. It is seen that a deviation of 5° from the minimum energy values does not imply very large energy differences; such differences are always lower than RT, at room temperature (this is indicated in the third column of the table).

Most researchers, performing conformational analysis, use also a torsion term, which for single C–C bonds not adjacent to a double bond (for instance, ethane) is:

$$E_t = \frac{1}{2} E_\circ^{\prime} (1 + \cos 3\theta) \qquad (28)$$

while for single bonds adjacent to a double bond (for

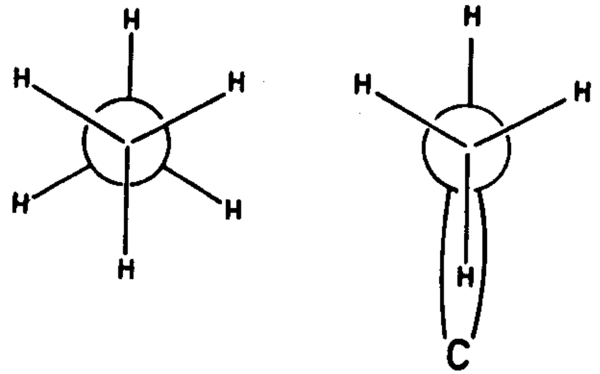
Table 1. Bending energy parameters used by Flory.

Bond angle	k_b (kcal mol^{-1}deg^{-2})	E (δτ=5°)
<CCC	0.044	0.55
<CCH	0.029	0.36
<HCH	0.024	0.30

instance, propylene) is:

$$E_t = \frac{1}{2} E_s'' (1 - \cos 3\theta) \qquad (29)$$

For his calculations, Flory takes $E_s' = 2.8$ kcal/mol and $E_s'' = 1.98$ kcal/mol. Take note that the relative positions of two hydrogen atoms in ethane are *trans* and *gauche* for the minimum energy value, while in the case of the methyl group of propylene the minimum energy relative positions of the hydrogen atoms of the methyl group, in respect to the carbon atom joined by a double bond, are *anticlinal* or *cis*, depending on the minus sign which appears in the formula(29):



The nonbonded energies arise from the interactions between atoms which are not directly bonded and are taken to depend only on the distances r_{mn} (fig. 1) between each pair of atoms m and n, of species i and j. For the nonbonded energies two kinds of functions are generally used:

$$E_{nb} = \frac{d_{ij}}{r_{mn}^{12}} - \frac{e_{ij}}{r_{mn}^{6}} \qquad \text{Lennard-Jones}$$

(31)

$$E_{nb} = a_{ij}\exp(-b_{ij}r_{mn}) - c_{ij}/r_{mn}^{6}$$

Buckingham

Some indicative data for contact types given by Flory are indicated in table 2. Similar data given by Scott and Scheraga(4) are indicated in table 3. A tabulation of the values of the function is given in the table 4.

When dipoles are present in the molecules (for instance, in the case of CO and NH groups in amides), Scott and Scheraga(4) include the electrostatic term of Eq.(25), by localizing partial charges on the atoms (table 5).

Table 2. Nonbonded parameters used by Flory.

Interacting pair	$d_{ij}\ 10^{-3}$ (kcal mol^{-1} Å^{12})	e_{ij} (kcal mol^{-1}Å^{6})	r_{min} (Å)
C,C	398	366	3.6
C,H	57	128	3.1
H,H	7.3	47	2.6

Table 3. Nonbonded parameters used by Scott and Scheraga

Interacting pair	$d_{ij}\ 10^{-3}$ (kcal mol^{-1}Å^{12})	e_{ij} (kcal mol^{-1}Å^{6})	r_{min} (Å)
C,C	286	370	3.4
C,H	38	128	2.9
H,H	4.46	46.7	2.4

Table 4. Values of the Lennard-Jones functions for different values of distances between the atoms. The energies are given in kcal mol^{-1}.

with Flory parameters			
r_{mn}(Å)	E(C,C)	E(C,H)	E(H,H)
1.6	–	–	23.1
1.8	333.28	45.51	4.93
2.0	91.45	11.92	1.05
2.2	27.73	3.31	0.15
2.4	8.98	0.89	-0.05
2.6	2.99	0.18	-0.08
2.8	0.95	-0.02	-0.07
3.0	0.25	-0.07	-0.05
3.2	0.00	-0.07	-0.04
3.4	-0.07	-0.06	-0.03
3.6	-0.08	-0.05	-0.02
3.8	-0.08	-0.04	-0.01
with Scott and Scheraga parameters			
r_{mn}(Å)	E(C,C)	E(C,H)	E(H,H)
1.6	–	–	13.06
1.8	236.35	29.08	2.48
2.0	64.04	7.28	0.36
2.2	18.98	1.83	-0.06
2.4	5.90	0.37	-0.12
2.6	1.80	-0.02	-0.10
2.8	0.46	-0.10	-0.08
3.0	0.03	-0.10	-0.05
3.2	-0.10	-0.09	-0.04
3.4	-0.12	-0.07	-0.03
3.6	-0.11	-0.05	-0.02
3.8	-0.09	-0.04	-0.02

Table 5. Partial charges on the atoms of amide group used by Scott and Scheraga.

Atom	Charge(in units of e)
H	+0.272
N	-0.305
C	+0.449
O	-0.416

Calculation of distances between the atoms(5)

The calculation of the potential energy of a disposition of atoms is possible if we know the coordinates of the atoms in a cartesian system in order to get all the distances between the atoms, which are essential in the calculation of the nonbonded energy terms. One possible way to get the relevant cartesian coordinates of a molecule, as a function of its internal coordinates, is now indicated.

As specified before, the space form of a molecule depends on $3n$-6 internal coordinates. Take as an example a succession of five atoms, as indicated in fig.3. In this case the internal coordinates, which characterize the space form of such chain, correspond to four bond distances (b_2, b_3, b_4, b_5), three bond angles (τ_2, τ_3, τ_4), two dihedral angles (θ_3, θ_4).

We can put the first atom 1 at the origin of the cartesian system, the next atom 2 may be disposed with the b_2 bond in the direction of the x-coordinate, and it is also possible to fix the atom 3 in the x-y plane. The coordinates of the first atom will be indicated as a column vector as follows:

$$\begin{vmatrix} x_1 \\ y_1 \\ z_1 \end{vmatrix} = \begin{vmatrix} 0 \\ 0 \\ 0 \end{vmatrix}$$

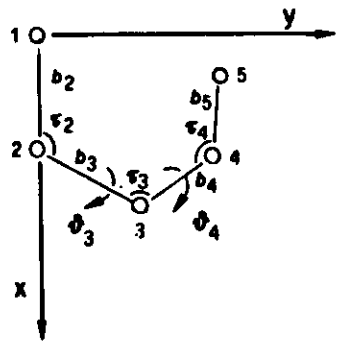


Fig. 3.A succession of five atoms in the cartesian system described in the text.

The coordinates of the second atom are indicated as:

$$\begin{vmatrix} x_2 \\ y_2 \\ z_2 \end{vmatrix} = \begin{vmatrix} b_2 \\ 0 \\ 0 \end{vmatrix}$$

The coordinates of the third atom may be obtained by summation of two vectors:

$$\begin{vmatrix} x_3 \\ y_3 \\ z_3 \end{vmatrix} = \begin{vmatrix} -\cos\tau_2 & -\sin\tau_2 & 0 \\ \sin\tau_2 & -\cos\tau_2 & 0 \\ 0 & 0 & 1 \end{vmatrix} \begin{vmatrix} b_3 \\ 0 \\ 0 \end{vmatrix} + \begin{vmatrix} x_2 \\ y_2 \\ z_2 \end{vmatrix} =$$

$$= \begin{vmatrix} -b_3\cos\tau_2 + b_2 \\ b_3\sin\tau_2 \\ 0 \end{vmatrix}$$

In order to get the coordinates of the atom 4, we have to sum the vector (x_3, y_3, z_3) to a vector whose coordinates depend on the internal rotation angle θ_3 and on the bond angle τ_3, so that we obtain:

$$\begin{vmatrix} x_4 \\ y_4 \\ z_4 \end{vmatrix} = \underset{\sim}{A}_2^{\tau} \begin{vmatrix} 1 & 0 & 0 \\ 0 & \cos\tau_3 & -\sin\tau_3 \\ 0 & \sin\tau_3 & \cos\tau_3 \end{vmatrix} \begin{vmatrix} -\cos\theta_3 & -\sin\theta_3 & 0 \\ \sin\theta_3 & -\cos\theta_3 & 0 \\ 0 & 0 & 1 \end{vmatrix} \times$$

$$\times \begin{vmatrix} b_4 \\ 0 \\ 0 \end{vmatrix} + \begin{vmatrix} x_3 \\ y_3 \\ z_3 \end{vmatrix}$$

where:

$$\underset{\sim}{A}_2^{\tau} = \begin{vmatrix} -\cos\tau_2 & -\sin\tau_2 & 0 \\ \sin\tau_2 & -\cos\tau_2 & 0 \\ 0 & 0 & 1 \end{vmatrix}$$

In the same way the coordinates of the atom 5 are obtained as follows:

$$\begin{vmatrix} x_5 \\ y_5 \\ z_5 \end{vmatrix} = \underset{\sim}{A}_2^{\tau}\, \underset{\sim}{A}_3^{\tau\theta} \underset{\sim}{A}_4^{\tau\theta} \begin{vmatrix} b_5 \\ 0 \\ 0 \end{vmatrix} + \begin{vmatrix} x_4 \\ y_4 \\ z_4 \end{vmatrix}$$

where:

$$\underset{\sim}{A}_j^{\tau,\theta} = \begin{vmatrix} 1 & 0 & 0 \\ 0 & \cos\tau_j & -\sin\tau_j \\ 0 & \sin\tau_j & \cos\tau_j \end{vmatrix} \begin{vmatrix} -\cos\theta_j & -\sin\theta_j & 0 \\ \sin\theta_j & -\cos\theta_j & 0 \\ 0 & 0 & 1 \end{vmatrix}$$

For the general case of a chain of j atoms we get the formula (which can easily programmed for computer calculation):

$$\underset{\sim}{x}_j = \underset{\sim}{A}_2^{\tau}\, \underset{\sim}{A}_3^{\tau,\theta} \cdots \underset{\sim}{A}_{j-1}^{\tau,\theta}\, \underset{\sim}{b}_j + \underset{\sim}{x}_{j-1} \qquad (32)$$

where

$$\underset{\sim}{x}_j = \begin{vmatrix} x_j \\ y_j \\ z_j \end{vmatrix} \quad \text{and} \quad \underset{\sim}{b}_j = \begin{vmatrix} b_j \\ 0 \\ 0 \end{vmatrix}$$

THE CONFORMATION OF POLYMERIC CHAINS IN THE CRYSTALLINE STATE

Equivalence principle(6)

In a system of polydisperse polymer molecules (as it is the case for synthetic polymers, where the molecules are never all alike, even in the case of $M_w/M_n = 1$), the crystalline state (which implies threedimensional long range order) may be conceived only in the approximation of not taking into account the terminals of the molecules (that is considering the molecules of infinite length) and implies in general, with exceptions which will be cited later on, the repetition of identical units along the chain axis.

The fig. 4 is a representation of the structure of cellulose, as given for the first time by Meyer(7).

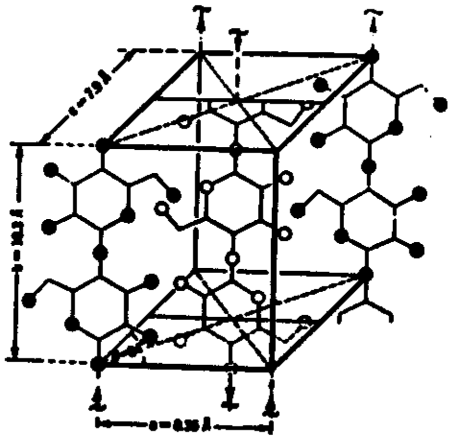


Fig. 4. Representation of the structure of cellulose as given by Meyer.

The concept of macromolecule had been given a few years before by Staudinger(8) in 1924 and was not accepted immediately. Many people continued to think of polymers as "colloidal" associations of small molecules. The fact that the unit cell of cellulose was small could have been taken as an evidence of the non macromolecular character of that material and it was important, at the time, the establishement of the idea that a molecule (in the case of chain molecules) needed not be confined to a unit cell, but could span many unit cells in sequence along the chain axis.

If we need to have repetition of identical units along the chain of a polymer, it is clear that, at least in principle, prerequisites for the crystallizability of a polymer are:

1) regularity of chemical constitution
2) regularity of configuration (stereoregularity) for long sequences of monomeric units.

As we shall see, an exception may arise because of isomorphism of monomeric units having different constitutions or configurations and/or conformations, which we shall discuss in the lecture "The crystalline structure of addition polymers. Research problems".

It may be seen that the repetition of identical units (repeating units) along the chain axis in the crystalline state implies the so called "equivalence principle" which can be formulated as follows:

The chain needs to be built up of structural units, which take geometrically equivalent positions in respect to an axis.

As we shall see, such structural units are in general a fraction of the repeating units. While a repeating unit may correspond even to a large number of monomeric units (f.i., in helical polymers), the structural unit corresponds very often to one monomeric unit, even though this is not necessarily so. For instance in the case of 1,4 *trans* or 1,4 *cis* polybutadiene, the structural unit corresponds to one half a monomeric unit, while in the case of polydimethyl-ketene in the ketonic enchainment, the structural unit corresponds to two monomeric units. A similar occurrence may explain the conflicting observations on crystalline gels of isotactic polystyrene, which are reported in(9) and we shall discuss in the above cited lecture.

Line repetition groups(6)

The only simmetry operators which have a translational component and which are compatible with chain repetition are:

t translation $\vec{c}$ along z (chain axis);

c glide-plane (translation $\frac{1}{2}\vec{c}$ along z associated with a mirror on a plane containing z);

s screw (helical) repetition of M units in N turns (translation $\vec{c}/M$ along z plus rotation $2\pi N/M$ around z). In the case of the helical repetition we use the terms: unit height (h) for the translation $|\vec{c}/M|$, unit twist (t) for the rotation $2\pi N/M$, number of residues per turn (n) for the ratio M/N.

Other symmetry operators which are compatible with a chain repetition are: r_n, $2\pi/n$ rotation around the chain axis; i , center of symmetry; m , plane of symmetry perpendicular to the chain axis; d , plane of symmetry parallel to the chain axis; 2 , two-fold rotation perpendicular to the z axis.

Some of them are just indicated for theoretical reasons. For instance rotations around the chain axis for a single chain may be thought of only for very particular constitutional repeating units and very particular values of $2\pi/n$. A rotation of 180° may occur if we have two chains winding up on the same chain axis, but does not refer to the conformation of one single chain. In fact, not all the symmetry elements are compatible with a given constitution and configuration of a polymer chain; for instance, whenever the unit has a directional character, symmetry elements like 2 and - and $\bar{1}$ are ruled out automatically. The translational symmetry elements and the further symmetry elements which we have indicated (excluding r_0) may be combined into the chain repetitions groups, indicated in table 6.

Table 6. Possible Chain Repetition Groups.

s(M/N)1	Isotactic polypropylene	*s*(3/1)1
particular case *t*1	1,4-*trans*-polyisoprene, Mod α	*s*(1/1)=*t*1
s(M/N)2	Syndiotactic polypropylene	*s*(2/1)2
particular case *t*2	–	
tm	Nylon 77	
td	–	
tc	1,4-*cis*-polyisoprene	
ti	Ethylene-butene-2 isotactic alternating copolymer	
s(2/1)*m*	*trans*-polypentenamer	
s(2/1)*d*	Nylon 6 (planar chain conformation)	
tdm	–	
tid	Nylon 66 (planar chain conformation)	
tcm	Syndiotactic 1,2-polybutadiene	
tic	*cis*-1,4-polybutadiene	
s(2/1)*dm*	Polymethylene	

Thus, for example, the repetition group of the chain of isotactic polypropylene (fig. 5), which is a threefold helix, may be indicated as *s*(3/1)1 , where the symbol *s* indicates the helical repetition, the symbol 3/1 the repetition of three units in one pitch and the further symbol 1 indicates that there is no further symmetry element but the identity which, according to the crystallographyc rules, is indicated with 1.

The symbol for syndiotactic polypropylene may be indicated with *s*(2/1)2 (fig. 5), and shows that neighbouring structural units are repeated through the operation of twofold axes perpendicular to the chain axis and each pair of units is repeated according to a helix containing two pairs in one pitch.

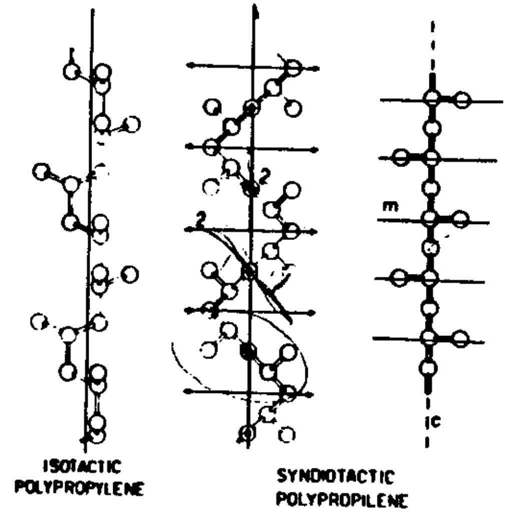


Fig. 5. Different conformations of polypropylene chains: isotactic (*s*(3/1)1 group) and syndiotactic (*s*(2/1)2 and *tcm* groups).

The symbol *ti* applies for the isotactic alternate copolymer of ethylene and butene-2 (fig. 6a); in this case the only symmetry element together with the translation is a center of symmetry.

In the case of polymethylene almost all of the symmetry elements which have been indicated previously are present; the appropiate symbol is *s*(2/1)*dm* (fig. 6b) , but a center of symmetry and a glide plane are also present because they are generated by combination of the symmetry elements indicated in the symbol (the screw axis 2/1 and the mirror planes *d* and *m*).

In the case of *cis*-1,4-polybutadiene the symbol is *tic*. The center of symmetry and the glide plane are both indicated, but these symmetry elements, combined together, generate also a twofold axis perpendicular to the chain axis.

The chain conformation of the four stereoregular polymers, which may arise from the polymerization of 1,3

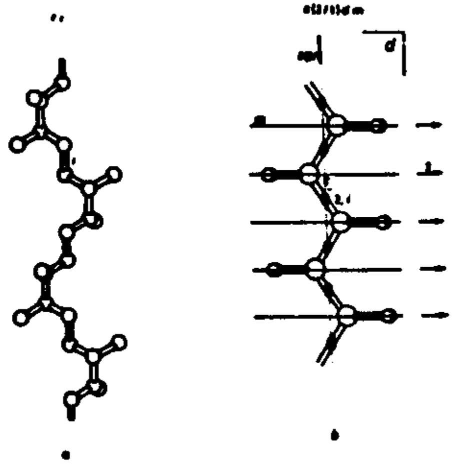


Fig. 6. Chain conformation and symmetry elements for: a) Isotactic alternate copolymer of ethylene and butene-2. b) Polymethylene.

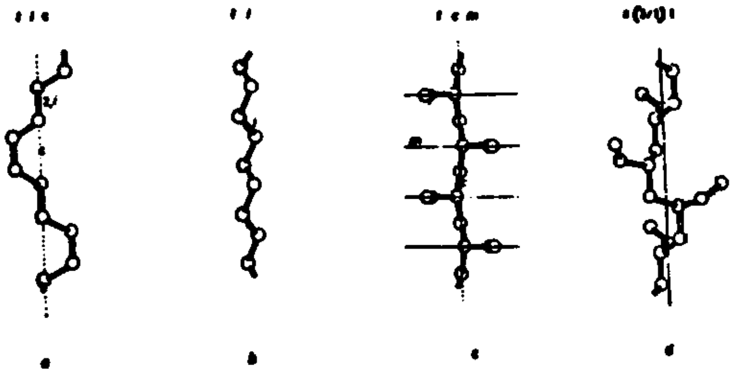


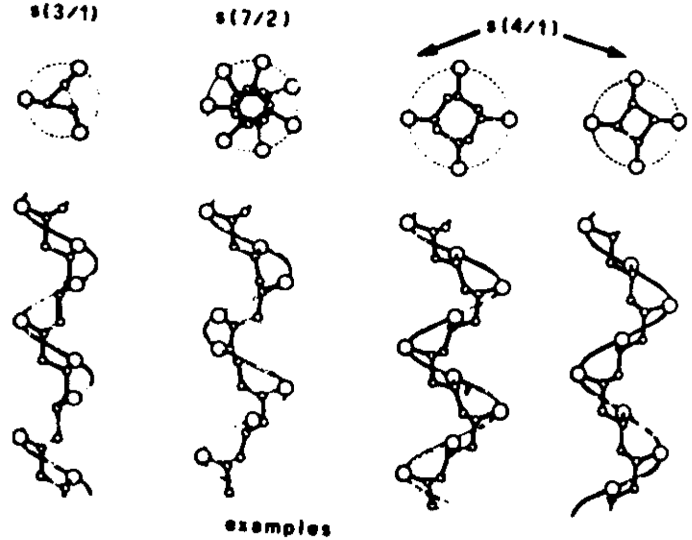
Fig. 7. Conformations of the four stereoregular polymers of 1,3-butadiene with symmetry elements: a) *cis*-1,4 b) *trans*-1,4 c) syndiotactic 1,2 d) isotactic 1,2

butadiene, are indicated together with the appropriate chain repetition groups and the symmetry elements which are present in the chain in fig. 7. As said before, both in the case of 1,4-*cis* or 1,4-*trans* polybutadiene the indipendent structural unit is built up of only half a monomeric unit, because of the symmetry elements which are present along the chain.

Isotactic polymers get generally a helical structure with a number of monomeric units per pitch which ranges between 3 and 4; some examples are indicated in fig. 8.

Some selected examples of conformational energy calculations

Now we report the results of a conformational analysis which was performed on isotactic and syndiotactic polypropylene many years ago (more refined calculations on isotactic polymers performed by us lately, will be reported in the lecture "The crystalline structure of addition polymers. Research problems").



O= $-CH_3, -C_2H_5$ O= $-CH_2-CH-(CH_3)_2$ O= $-CH-(CH_3)_2C_2H_5$ O-⟨phenyl⟩-F

Fig. 8. Chain conformations of some isotactic polymers.

To study the conformations in the crystalline state, the calculations were performed on the basis of the equivalence principle, by taking into account the possible variations of the internal rotation angles (bond angles and bond length being kept constant) and making the assumption that the structural unit was coincident with one monomeric unit. In such a case, it is easy to see that the isotactic polymer must be built by a succession of units in which a pair of different internal rotation angles θ_1 and θ_2 is repeated along the chain; whereas the chain of the syndiotactic polymer must be built up by a succession of the type $\theta_1, \theta_1, \theta_2, \theta_2, \theta_1, \theta_1, \ldots$ Consequently contour plots of the internal energy E as a function of two dihedral angles (θ_1 and θ_2), are sufficient to establish the conformation or conformations of minimum internal energy.

The fig. 9 shows, for isotactic polypropylene, two minima that correspond to the chain conformations $(TG_+)_3$ (left-handed helix) and $(G_-T)_3$ (right-handed helix) found in the crystalline state.[3]

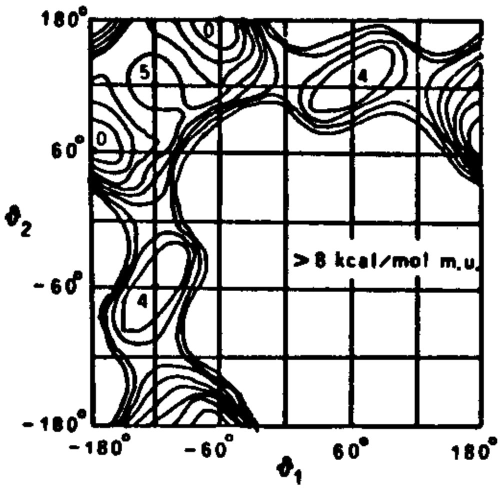


Fig. 9. Contour plot of internal energy E, as a function of two dihedral angles of the backbone for isotactic polypropylene.

The fig. 10 shows, for syndiotactic polypropylene, three minima in the energy map, two of which corresponding to a right-handed helix and a left-handed helix, while the third corresponding to a trans planar conformation.

This is in accordance with the fact that syndiotactic polypropylene is polymorphous. In fact, it can get two different crystalline forms, which differ because of the chain conformation (fig. 5).

This polymorphism is different from the case of isotactic polypropylene, which is also polymorphous, but in which, in the different crystalline forms, always a threefold helix is observed; or from the case of polybutene-1 which is also polymorphous, but the different helices observed correspond, however, to the same region of minimum of the conformational energy map. Instead in the case of syndiotactic polypropylene, as shown before, the two different crystalline forms correspond to chain conformations which are widely separated in the conformational energy map.

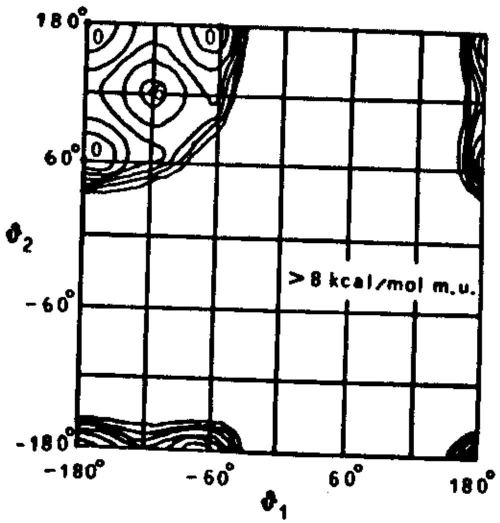


Fig. 10. Contour plot of internal energy E, as a function of the two dihedral angles of the backbone for syndiotactic polypropylene.

THE CONFORMATION OF POLYMERIC CHAINS IN SOLUTION AND IN THE MELT(10)

The rotational isomeric model for liquid hydrocarbons

The conformations of the macromolecules, in the absence of the constraints imposed by neighbouring molecules in an ordered crystalline state, need not be and are not regular.

The repartition of the bonds of a polymer, for an isolated chain with n carbon atoms, between different conformations may be evaluated by the methods of statistical mechanics. A complication arises because the energy associated to a given conformational state of bond i may not be assumed to depend only on its internal rotation angle θ_i, but it depends in general also on the internal rotation angles of all the neighbouring bonds. In the approximation in which this dependence is restricted to next-neighbour internal rotation angles only and in the absence of flexible lateral groups, the treatment is simplified as follows. A statistical weight can be appended to bond i:

$$u_i = \exp\{-[E(\theta_i) + E(\theta_{i-1}, \theta_i)]/RT\} \qquad (33)$$

where $E(\theta_i)$ represents the intrinsic torsional potential of the bond and the nonbonded interactions which depend exclusively on θ_i, while $E(\theta_{i-1}, \theta_i)$ includes the nonbonded interactions which depend jointly on the two internal rotation angles θ_{i-1} and θ_i. The dependence of energy on θ_{i+1} is included in the statistical weight relative to the bond i+1. The conformational partition function is, then, given formally by:

$$Z_{conf} = \sum_{\{\theta\}} \prod_{i=2}^{n-2} u_i$$

where the summation is taken over all the conformations of the macromolecule.

The problem can be further simplified taking into account only a discrete number of rotational states (which are chosen in general to be coincident with conformational potential energy minima), in the calculation of the partition function. This is the rotational isomeric model, first proposed by Volkenstein and principally developped by Flory and his school.

Firstly we consider the application of this model to the molecule of n-butane. In fig. 11 the conformational energy as a function of the dihedral angle C_1-C_2-C_3-C_4,

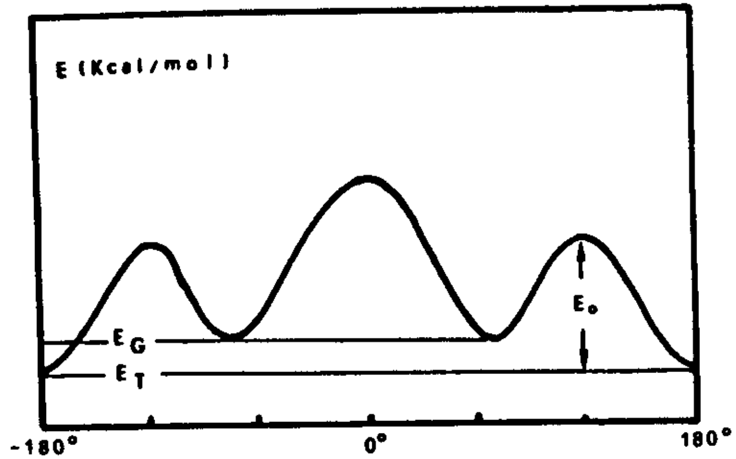


Fig. 11. Conformational energy of n-butane as function of the dihedral angle C_1-C_2-C_3-C_4.

is represented (this is a first approximation, in so far as the possible variation of the bond angles and of the torsion angles adjacent to the methyl groups is not considered).

The shape of the curve may be explained in terms of the previous considerations as arising from an intrinsic torsional potential and the interaction between the nonbonded methyl groups. There are three minima of the energy, corresponding to T, G_+, G_- conformations, the last two being energetically equivalent. For the evaluation of the partition function these are chosen as rotational isomeric states, and their statistical weights are:

$$u_T = \exp(-E_T/RT) \quad ; \quad u_{G_+} = u_{G_-} = \exp(-E_G/RT)$$

taking E_T=0 the partition function is:

$$Z_{conf} = 1+2\sigma \qquad \text{with } \sigma = \exp\{-(E_G-E_T)/RT\}$$

In the case of n-pentane, in an approximation similar to that used in the case of n-butane, the energy may be evaluated as a function of the two dihedral angles θ_{23} and θ_{34}. It is important to note that we cannot neglect the interactions between nonbonded atoms that depend on both θ_{23} and θ_{34} values jointly. In particular, if the two dihedral angles assume the values G_+ and G_-

(or G_- and G_+) in one sequence, the two terminal methyl groups approach each other to a distance much shorter than their Van der Waals radius ; the conformational energy is then widely larger than $2E_G$.

On the basis of the isomeric rotational approximation, we consider only the conformations generated by combining, in all possible ways the conformations T, G_+, G_- which refer to the first dihedral angle (θ_{23}) with the conformations T, G_+, G_- which refer to the second dihedral angle. We attribute to each resulting conformation a statistical weight and represent them with the table

	T	G_+	G_-
T	1	σ	σ
G_+	σ	σ^2	$\sigma^2\omega$
G_-	σ	$\sigma^2\omega$	σ^2

where the selected conformations for the two successive bonds are indicated with the relative symbols.

In this table we made the assumption that, excluding the sequences G_+G_- or G_-G_+, the interactions that depend on both dihedral angles jointly are negligible. The first element of the table is, then, 1 because the energy of a T conformation (and therefore of a TT conformation) is taken as equal to zero; moreover $\sigma = \exp(-\Delta E/RT)$, where ΔE is the energy difference between a *gauche* and a *trans* conformation. With the term ω we take into account the repulsive extra-energy E_ω of G_+G_- and G_-G_+ conformations (being $E_\omega = -RT\ln\omega$), that we discussed before.

The conformational partition function, being the sum of all the terms appearing in the table, may be written for n-pentane, in the rotational isomeric approximation, as:

$$Z_{conf} = 1 + 4\sigma + 2\sigma^2 + 2\sigma^2\omega$$

For a linear hydrocarbon of n atoms, the number of terms to be summed, in the approximation of three rotational isomeric states for each bond, is 3^{n-3}, a number that becomes high very rapidly; therefore the use of a matrix formulation of the partition function is necessary.

We note that, for the n-butane, it is possible to write:

$$Z_{conf} = 1+2\sigma = \overline{\underline{1 \quad \sigma \quad \sigma}} \begin{vmatrix} 1 \\ 1 \\ 1 \end{vmatrix}$$

Moreover the partition function of n-pentane which is the sum of all the elements of the table reported may be written as the following product:

$$Z_{conf} = \overline{\underline{1 \quad \sigma \quad \sigma}} \begin{vmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{vmatrix} \begin{vmatrix} 1 \\ 1 \\ 1 \end{vmatrix}$$

In general for a linear hydrocarbon of n atoms, it is possible to see that the partition function is:

$$Z_{conf} = \overline{\underline{1 \quad \sigma \quad \sigma}} \begin{vmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{vmatrix}^{n-4} \begin{vmatrix} 1 \\ 1 \\ 1 \end{vmatrix} \qquad (35)$$

Polyethylene and isotactic polymers(11)

The conformational partition function of a polyethylenic chain of n atoms may be written, according to the results of the previous paragraph:

$$Z_{conf} = \overline{\underline{1 \quad \sigma \quad \sigma}} \begin{vmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{vmatrix}^{n-4} \begin{vmatrix} 1 \\ 1 \\ 1 \end{vmatrix}$$

Matrix methods, in the case of n large, bring to the conclusion that:

$$Z_{conf} \approx \lambda_1^n \qquad (36)$$

where λ_1 is the largest root of the secular equation (in other words the largest eigenvalue) for the matrix of the statistical weights:

$$\begin{vmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{vmatrix} \qquad (37)$$

For instance, taking $\omega = 0$, the secular equation is:

$$\det \begin{vmatrix} 1-\lambda & \sigma & \sigma \\ 1 & \sigma-\lambda & 0 \\ 1 & 0 & \sigma-\lambda \end{vmatrix} = 0 \qquad (38)$$

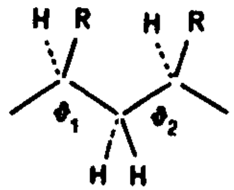
and the largest root is: $\lambda_1 = \frac{1}{2}(1 + \sigma + \sqrt{1+6\sigma+\sigma^2})$.

Matrix methods of the kind illustrated are the basis for the evaluation of various thermodynamical properties. For instance, the frequency of occurrence of *gauche* states in a polyethylenic chain is given by:

$$f_G = \frac{1}{n}\frac{\partial \ln Z}{\partial \ln \sigma} = \frac{\partial \ln \lambda_1}{\partial \ln \sigma} \qquad (39)$$

If E_G-E_T = 500 cal/mol and T = 400 K (about the melting temperature of the polyethylene), that is σ = 0.5, f_G=40%. Assumption of independence among bond rotations would have given, as for the case of n-butane, $\lambda_1 = 1+2\sigma$ and the fraction of *gauche* bonds, with the same σ value is $f_G = 2\sigma/(1+2\sigma)$ = 50%.

A simplified treatment of the conformation of isotactic polymers in solution can be made in the following way, that we shall discuss for two extreme cases: the case of polypropylene and that of polystyrene. We start from the identification of the minimum internal energy conformations available for a piece of a chain of the kind:



(40)

In the case of polypropylene, the conformational map shows only two minimum internal energy conformations : TG_+ and G_-T. If these conformations are present in a long sequence, they produce a left-handed helix and a right-handed helix respectively (fig. 9). The perpetuation of such helicoidal sequences can be interrupted by a pair of internal rotation angles (θ_x and θ_y), in two different ways, if we go in the sense from the left to the right in the chains below indicated. If we go from a left-handed to a right-handed helix: (fig. 12)

$$....|TG_+|TG_+|TG_+|T\theta_x|\theta_y T|G_-T|G_-T|G_-T|....$$

the possible minimum energy pairs for the angles θ_x and θ_y may be taken in the rotational isomeric approximation as corresponding approximately to A_+G_- and G_+A_- conformations, with energy of the order E^{w} = 2.5 kcal/mol, the corresponding statistical weight being $\omega = \exp(-E^{w}/RT)$. If we go from a right-handed to a left-handed helix:

$$....|G_-T|G_-T|G_-T|G_-\theta_x|\theta_y G_+|TG_+|TG_+|TG_+|....$$

the pair θ_x θ_y may assume the low energy conformation TT. There is no increase of the energy at the inversion of the spiralization sense and the corresponding statistical weight may be taken as 1 (fig. 13). We can write now a simplified matrix of statistical weights analogous to (37), written for polyethylene, but relative to pairs of bonds. The compacted matrix has the form:

	G_-T	TG_+
G_-T	1	1
TG_+	2ω	1

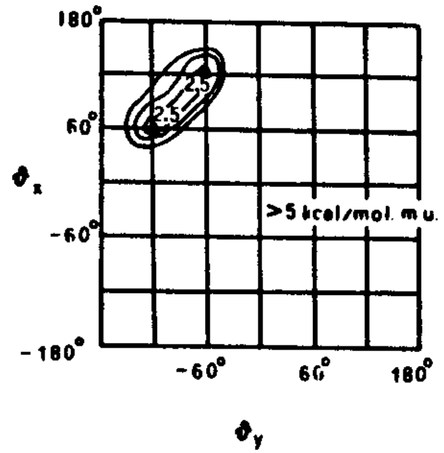


Fig. 12. Conformational energy map for the sequence: $....|TG_+|TG_+|T\theta_x|\theta_y T|G_-T|G_-T|....$

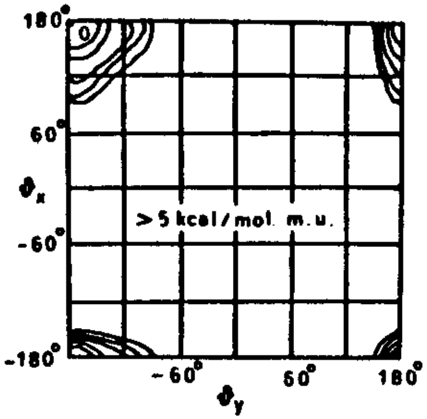


Fig. 13. Conformational energy map for the sequence: $\ldots|G_-T|G_-T|G_-\theta_x|\theta_yG_+|TG_+|TG_+|\ldots$

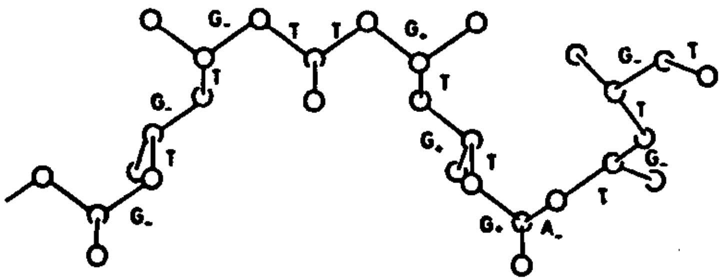


Fig. 14. A model for the chain of isotactic polypropylene in solution θ or in the melt.

and for a chain of n monomeric units with n large:

$$Z = \text{spur}\begin{vmatrix} 1 & 1 \\ 2\omega & 1 \end{vmatrix}^n = (1 + \sqrt{2\omega})^n$$

where spur is the sum of diagonal elements.
The fraction of the inversions in the spiralization sense is $f_i = \sqrt{2\omega}/(1+\sqrt{2\omega})$, and, if T = 450 K, f_i = 25 %.
A resulting model for the chain in solution is indicated in fig. 14.

In the case of isotactic polystyrene or of polyacrylates, other effects must be taken into account. In particular, together with the conformations TG_+ and G_-T, for a piece of chain of the kind (40), also conformations near to TT planar are available. Without discussing the more complicated rotational isomeric model which result, it is interesting to explain why conformations near to the TT planar are possible for polystyrene and more unlikely for a polymer such as polypropylene.

Consider a piece of chain in the conformation TT, for isotactic polypropylene and for isotactic polystyrene, with the bond angles and the relevant distances indicated in fig. 15; in both we can see that the distances and hence the interactions energy between late-

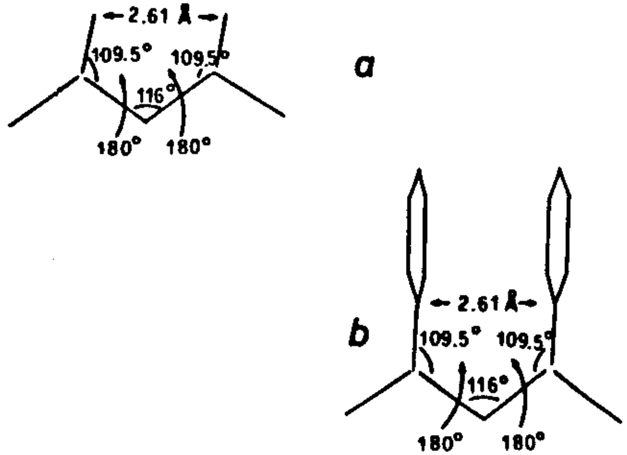


Fig. 15. Pieces of chains in the conformation TT for: a) isotactic polypropylene b) isotactic polystyrene

ral groups are prohibitive. If we change the two internal rotation angles by as much as 10°, as illustrated in fig. 16, the increase of the torsion term of the energy is very small. But, while in the case of polypropylene the distance between methyl groups is still energetically prohibitive, in the case of polystyrene such distance refers to interactions between carbon atoms which are "nude"; moreover a good part of the 36 distances between the carbon atoms of the phenyl groups (if we take them staggered in respect to the chain) is attractive.

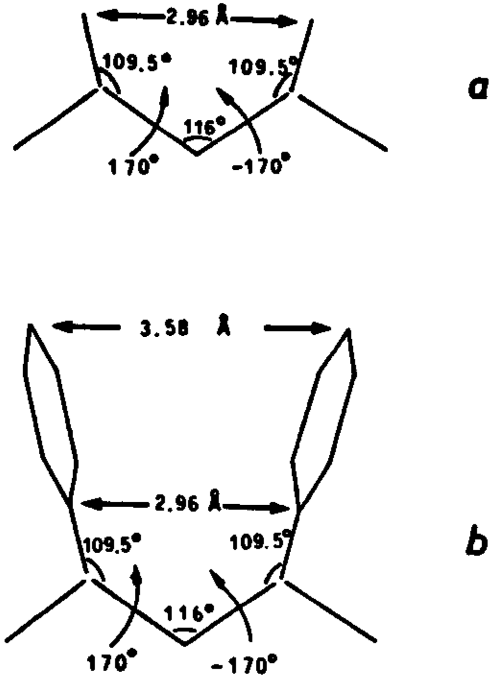


Fig. 16. Pieces of chains in the nearly TT (170°;-170°) conformation for:
a) isotactic polypropylene b) isotactic polystyrene

Finally we want to point out that an application of the rotational isomeric model to a polymer is the evaluation of the portion of the entropy of melting, which depends on the conformational freedom which the chains acquire in the melt. The conformational contribution to the difference in entropy may be evaluated, again by standard methods of statistical mechanics, as:

$$S_{conf} = k \ln Z_{conf} + \frac{T}{Z_{conf}} \frac{dZ_{conf}}{dT} \quad (41)$$

where Z_{conf} is the conformational partition function, easily evaluated in the rotational isomeric approximation. Some data calculated by Tonelli(12) for various polymers are reported in table 7.

Table 7. Comparison between the experimental entropy of fusion at constant volume and calculated conformational contribution to the entropy of fusion.

Polymer	$(\Delta S_m)_v$ (e.u./mole of monomer)	S_{conf}
Polyethylene	1.77	1.76
Polyoxymethylene	2.8	3.00
Polyoxyethylene	4.22	5.10
1,4-*cis*-polyisoprene	1,7	5.41
1,4-*trans*-polyisoprene	5.1	5.47
1,4-*cis*-polybutadiene	5.96	5.52
Polyethyleneterephthalate	8.2	7.51
Polytetrafluoroethylene	0.76	1.6
Nylon-6	11.5	11.91

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