X-Ray Diffraction Methods in Polymer Science

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As an example consider the arrangement of molecular chains in an ideal crystal of nylon 66, poly(hexamethylene adipamide), as shown in Figure 1-5[6]. Because of the very great, and indefinite, length of any single molecule, it is manifestly not practicable to select a unit cell in a fashion analogous to that of Figure 1-2 with one, two, or more discrete molecules. However, if we neglect the terminal features of the long molecular chains, it is possible to define a smaller unit cell that contains a discrete number of monomer units. Figure 1-5 shows how we can select a triclinic unit cell that contains the substance of one hexamethylene-adipamide unit, $-HN(CH_2)_6NHCO(CH_2)_4CO-$, as was first shown by Bunn and Garner[6]. We may note that, although one monomer unit lies parallel to each c-edge of the unit cell, any given monomer is shared by the four unit cells that come in contact at this edge, with the result that each cell actually contains the substance of only one monomer unit. We should also observe that one monomer unit may be regarded as associated with each lattice point. Thus one

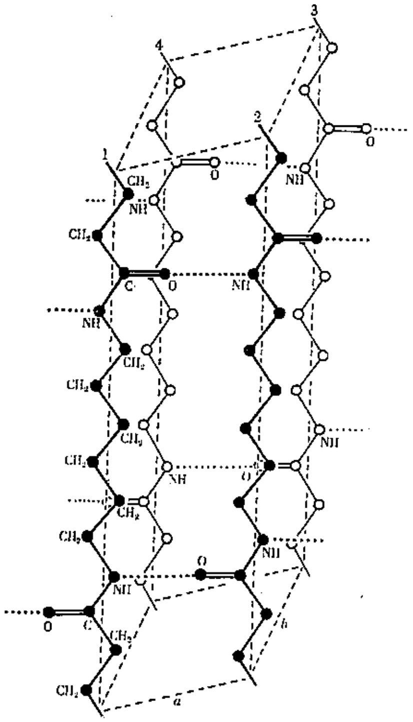


Figure 1-5 Arrangement of molecular chains in nylon 66, poly(hexamethylene adipamide). (Bunn and Garner[6].)

monomer unit is the characteristic *motif* of the nylon 66 structure; the entire ideal crystal consists of a three-dimensional assemblage of a very large number of duplicates of this motif. If the lattice translations (also edge lengths of the unit cell) are a, b, and c, and if we choose to place the first motif at the origin of the triclinic coordinate system, another motif will be found at any point ja, mb, nc, where j, m, n are integers ranging from zero to very large positive or negative values.

Figure 1-6 shows how the molecular arrangement in *cis* 1,4-polybutadiene [7] is based on a c-centered monoclinic unit cell (No. 3 of Figure 1-4) with $a = 4.60$, $b = 9.50$, $c = 8.60$ Å, and the angle $\beta = 109°$. Molecular segments consisting of two monomer residues,

$$—CH_2CH{=}CHCH_2CH_2CH{=}CHCH_2—$$

traverse the cell in the c-direction, one along each c-edge and one at the center of the c-face. When the structure is viewed in its entirety, each cell is seen to contain the substance of two chain segments, or four monomer units. In the *cis* 1,4-polybutadiene structure the

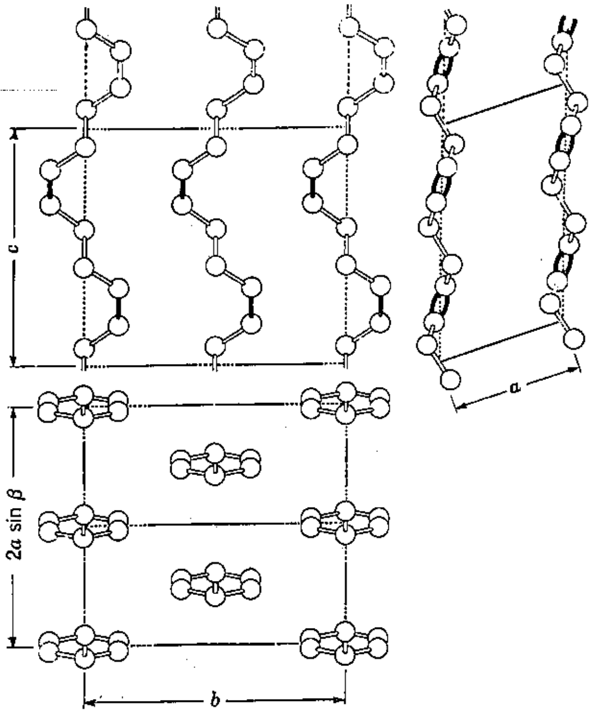
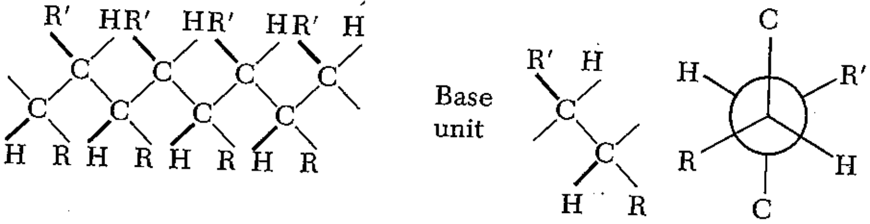


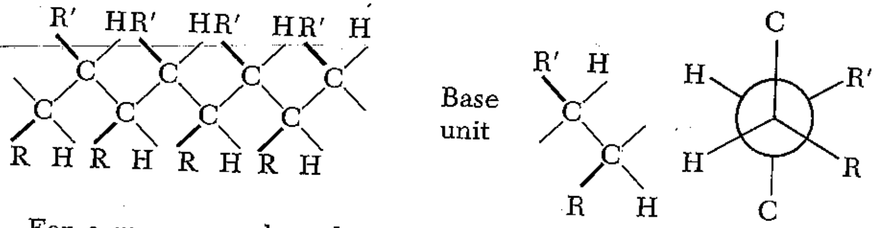
Figure 1-6 Structure of *cis* 1,4-polybutadiene as seen in three projections. Monoclinic unit cell with $a = 4.60$, $b = 9.50$, $c = 8.60$ Å; $\beta = 109°$. (Natta and Corradini [7].)

sites of steric isomerism in each base unit are *opposite.* In a hypothetically extended (zigzag) molecule $(CHRCHR')_n$ the substituents R and R′ are all on the same side of the plane of the chain atoms.

Erythro-di-isotactic poly-2-pentene ($R = CH_3$, $R' = C_2H_5$)



Threo-di-isotactic poly-2-pentene ($R = CH_3$, $R' = C_2H_5$)



For a more complete description of the nomenclature and the characterization of modes of stereoregularity in linear polymers the reader is referred to publications of Natta, Farina, and Peraldo [4], Miller and Nielsen [5], Newman [6], and Miller [7, 8].

6-1.2 Conformational Nomenclature

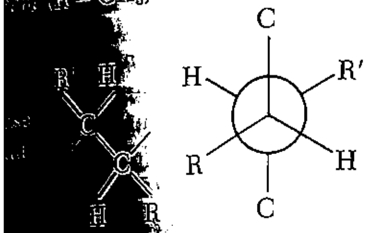
Since the molecular chains of so many natural and synthetic polymers assume helical conformations, at least in the crystalline state, an appropriate system of nomenclature is needed to describe them. Actually, two systems are presently in use, in both of which a helical net of points is generated from an origin point by repetitive rotation through an angle $\Delta\Phi$ accompanied by a translation Δz along the helix axis Z. The first system, which is to be preferred for the description of polymer helices, may be referred to as the *helical point-net* system, and the second is the conventional *crystallographic screw-axis* designation. For the description of these systems we define the following quantities (see Figure 6-1) [9]:

P = Z translation equivalent to one turn of the helix (*pitch* of the helix);

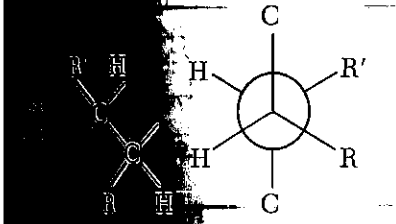
c = crystallographic identity period parallel to Z;

unit are *opposite*. In a hypo-
(CHRCHR')$_n$ the substituents
plane of the chain atoms.

$R = CH_3$, $R' = C_2H_5$)



$R = CH_3$, $R' = C_2H_5$)



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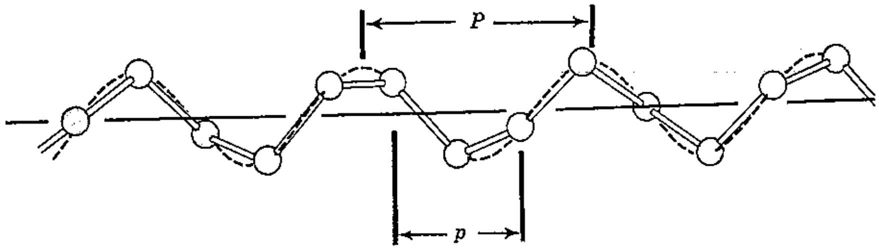

$$\frac{P}{p} = \frac{u}{t} = \text{motifs per turn}$$

Figure 6-1 Helical nomenclature. (Courtesy of E. S. Clark.)

p = Z-axis projection of the distance between consecutive equivalent points on the helix;
u = number of points, or motifs, on the helix corresponding to the period c (an integer);
t = number of turns of the helix in the identity period c (an integer);
$\Delta\Phi$ = projection on a plane perpendicular to Z of the central angle defined by two successive equivalent points on the helix;
γ = a positive integer > 0;
ϵ = a positive integer $\geqslant 0$.

***Helical Point Net* H.** This system has been discussed in detail by Hughes and Lauer [10] and also treated by Nagai and Kobayashi [11]. The symmetry is expressed as u/t, and the operators $\Delta\Phi_H$ and Δz_H are defined by

$$\Delta\Phi_H = 2\pi\frac{p}{P} = 2\pi\frac{t}{u}, \tag{6-1}$$

$$\Delta z_H = p = \frac{c}{u}. \tag{6-2}$$

***Screw Axis* S.** The symmetry is expressed as u_γ, and the rotational and translational operators are defined by

$$\Delta\Phi_S = \frac{2\pi}{u}, \tag{6-3}$$

$$\Delta z_S = \gamma\left(\frac{c}{u}\right). \tag{6-4}$$

The two systems of notation are related by the expression

$$\gamma t = \epsilon u + 1. \tag{6-5}$$

For a given helix the numerical descriptions u/t and u_γ are equivalent ($u = u$ and $t = \gamma$) if a value of ϵ exists such that $\gamma = t$ and $\gamma^2 = t^2 = \epsilon u + 1$.

Figures 6-2 and 6-3 illustrate the application of these notations with the example of polyoxymethylene. The symmetry of the actual polymer is approximately, but not precisely, 9/5 in the H-notation; however, the idealized symmetry 9/5 will be assumed for purposes of illustration. Thus the period c contains nine C–O motifs and five turns of the helix. Figure 6-3 depicts the action of the rotational operator through one identity period. By (6-1) the rotational operation involved is

$$\Delta\Phi_H = 2\pi\frac{t}{u} = \frac{5}{9}\times 360^\circ = 200^\circ.$$

If we commence at A (point 0), a rotation of 200° results in a rotation to C (point 1), accompanied by a translation of

$$p = \frac{c}{u} = \frac{c}{9}$$

[from (6-2)]. Successive operations then take us to points 2, 3, 4, · · ·, 9(0), accompanied by equal translational increments p.

In the S-system, however, the rotational operation is

$$\Delta\Phi_S = \frac{2\pi}{u} = 40^\circ,$$

accompanied by a translation of

$$\Delta z_S = \gamma\frac{c}{u} = \frac{2c}{9}.$$

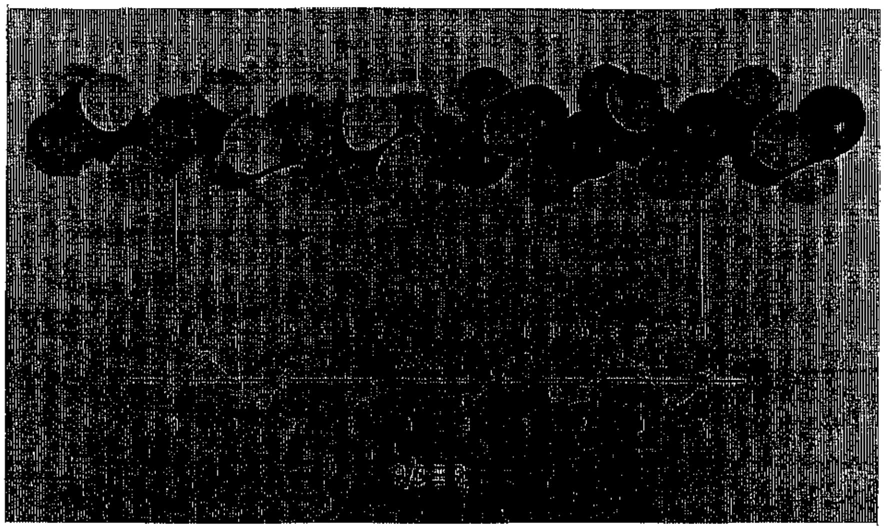

Figure 6-2 Helical conformation of polyoxymethylene. (Courtesy of E. S. Clark.)

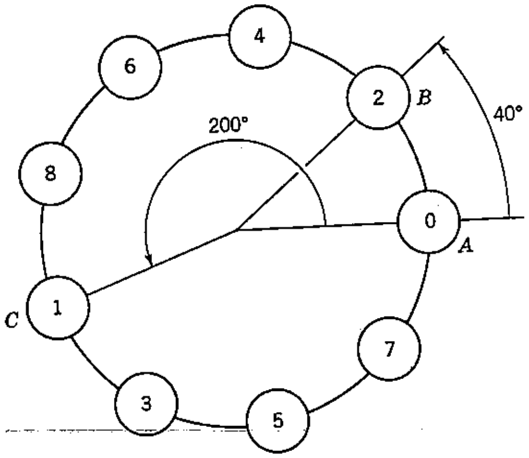

Figure 6-3 Helical conformation 9/5 ≡ 9_2, showing action of rotational operators.

Successive operations, then, take us from 0 to 2, 2 to 4, 4 to 6, etc., to 9(0). The net translation equivalent to the nine operations is in this case $9\times 2c/9$, or $2c$, rather than c as in the case of the helical-point system of nomenclature. Since $\gamma=2$, the screw-axis designation of this helix is 9_2. It follows from (6-5) that the numerical value of ϵ relating the two notations for the polyoxymethylene helix is

$$\epsilon=\frac{\gamma t-1}{u}=\frac{2\cdot 5-1}{9}=1.$$

We may note that, if the carbon and oxygen atoms could be treated as completely equivalent, the helical designations in the two systems would be 18/5 and 18_{11}.

It is important to observe that in the above systems of nomenclature all the atoms that constitute one unit of structure (*true base unit* in tacticity parlance and usually also the *monomer unit*) are termed the *motif* and are represented by one point on the helix. The radial and azimuthal coordinates of the component atoms with respect to some arbitrary origin are not specified. A more complete description of helical structure and its diffraction effects is presented in Appendix 1 and in Section 6-1.6.

The helical-point-net nomenclature has been adopted by Miller and Nielsen [12, 13] and by Miller [14] in their valuable tabulations of crystallographic data for various polymers, a recent edition of which comprises Appendix 3 of the present monograph. In his more recent editions of the tables Miller prefixes the symbol u/t with the number n of *skeletal* atoms in the chain motif. At the same time he employs the format $n * u - t$ in order to permit direct photo-offset reproduction of the computer printout.

Internal-Rotation Angles[15]. A useful way of describing the conformation of the main polymer chain is to specify the sequence of internal-rotation angles. Referring to Figure 6-4, we consider any three successive chain bonds, L_1, L_2, and L_3. The internal-rotation angle σ is then the angle defined by the two planes L_1L_2 and L_2L_3, which is seen to express the conformation of the chain around the bond L_2. We adopt the convention that σ is positive if, looking along L_2 from L_1, we see that L_1 must be rotated clockwise by an angle σ, which is less than 180°, in order that it superpose L_3. This is completely equivalent to saying that if we look along L_2 from L_3, we see that L_3 must be rotated clockwise through the angle σ to superpose it on L_1. Counterclockwise rotations of less than 180° are designated negative.

Bunn's Notation[16, 17]. In the course of early studies of polymer chain structures, in particular vinyl polymers, Bunn suggested the following scheme of nomenclature for the most commonly encountered single-bonded carbon-chain conformations. The orientation of a given bond with respect to the *two preceding bonds* in the chain is designated A, B, or C as follows:

A = *trans* $(\sigma = 180°)$,

B = left *gauche* $(\sigma = +60°)$,

C = right *gauche* $(\sigma = -60°)$.

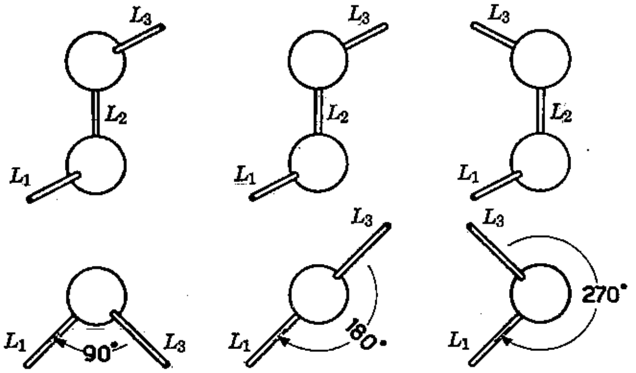

Figure 6-4 Conventions for the specification of internal-rotation angles σ. (Natta, Corradini, and Bassi[15].)

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With Tadokoro[18] we now simplify the nomenclature by replacing *A*, *B*, and *C* with *T*, *G*, and $\overline{G}$, respectively. These three basic bond sequences in single-bonded carbon chains, represented in projection in Figure 6-5, are the only ones that are permitted by the principle of staggered bonds. When the chain motif, or geometrical repeating unit, comprises more than one bond sequence of the same kind, it is denoted by the appropriate numerical subscript; for example, T_2, $(TG)_3$, etc. Mixed modes such as $TGT\overline{G}$ or $(TG)_2(T\overline{G})_2$ may also be specified.

On the basis of idealized bond distances and angles we may expect characteristic identity periods to be observed for a number of single-bonded carbon-chain conformations as follows:

Mode	Identity Period (Å)	Mode	Identity Period (Å)
T_2	2.5	$(TG)_3$	6.2
T_4	5.0	$(T\overline{G})_3$	6.2
$TGT\overline{G}$	4.4	$T_3GT_3\overline{G}$	8.8
G_4	3.6	$(TG)_2(T\overline{G})_2$	8.5

Five of these conformations are depicted in Figure 6-6. If substituent groups of appreciable size are attached to alternate carbon atoms in the chain, the ideally tetrahedral angles in the chain tend to open up a little, thus increasing the identity periods somewhat; for example, the observation of periods between 6.2 and 6.7 Å in vinyl polymers indicates the chain form to be $(TG)_3$ or $(T\overline{G})_3$, which are left- and right-handed isotactic helices, respectively. On the other hand, periods slightly larger than 5.0 Å in vinyl polymers are indicative of simple syndiotactic placements based on the chain form T_4. An example of chain form T_4 with alternate left- and right-hand

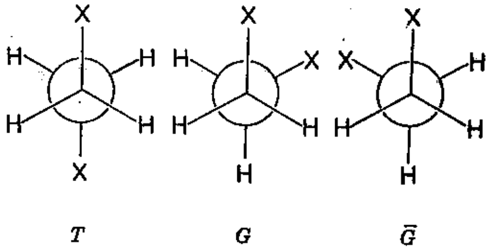

Figure 6-5 The three bond sequences in single-bonded carbon chains that conform to the principle of staggered bonds: *T*, *trans*; *G*, left *gauche*; $\overline{G}$, right *gauche*. (Tadokoro [18].)

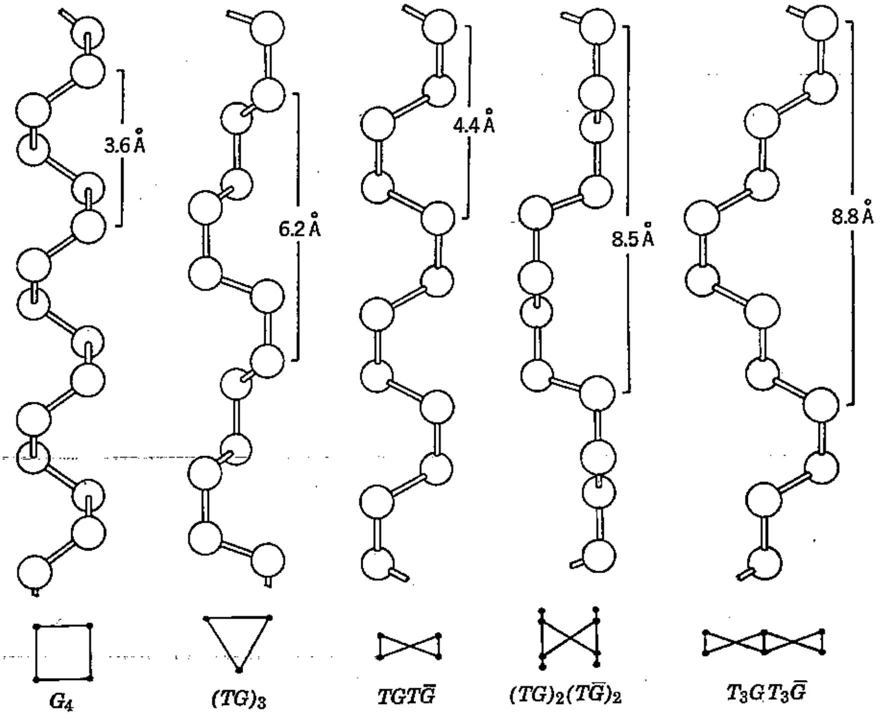

Figure 6-6 Five chain conformations based on the T, G, and $\overline{G}$ staggered bond orientations of Figure 6-5. (After Bunn [16].)

placement of substituent groups is supplied by syndiotactic poly(vinyl chloride) (see Figure 1-11), which displays an axial identity period of 5.1 Å [19]. Figure 6-7 shows a good example of a $(TG)_3$ structure, that of isotactic polystyrene [17, 20], which shows an axial periodicity of 6.65 Å. We may note that in H and S helical notation $(TG)_3$ structures are designated 3/1 and 3_1, respectively. Some additional examples of $(TG)_3$ structures with their observed periodicities are: polypropene, 6.50 Å; poly-1-butene, 6.50 Å; poly-1-pentene, 6.49 Å; poly(N,N-dibutyl acrylamide), 6.3 Å; 1,2-poly-1,3-butadiene, 6.5 Å; and poly(butyl vinyl ether), 6.30 Å.

6-1.3 Factors That Determine Chain Conformation

As the result of numerous studies Natta, Corradini, and Ganis [21, 22] have concluded that in crystalline linear polymers (a) the monomeric units, or motifs, occupy geometrically equivalent positions in relation to the axis of the macromolecule (*equivalence*

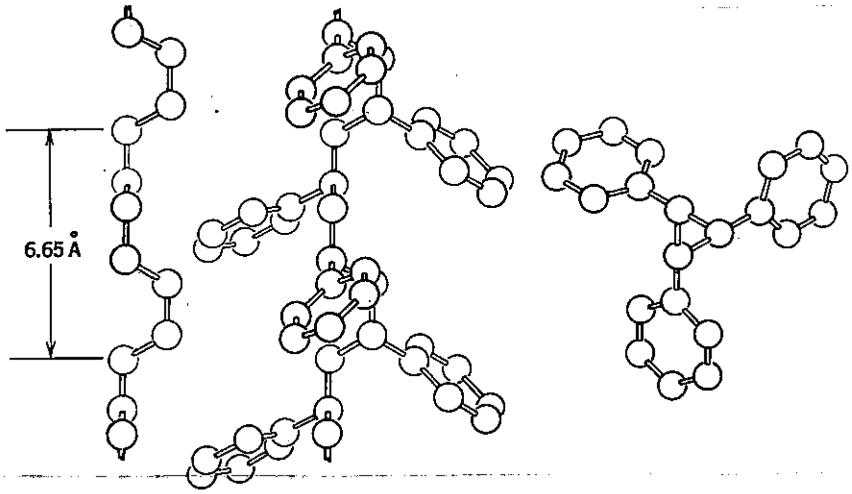

Figure 6-7 Left: the chain $(TG)_3$. Center and right: side and end views of the isotactic polystyrene molecule. (Bunn and Howells [17].)

postulate) and (b) the conformation actually assumed approaches the one of *minimum potential energy* that would be assumed by an *isolated* macromolecule conforming to the symmetry restriction (a). This means that chain-packing considerations ordinarily play only a secondary role in governing the conformations that are assumed by the molecular chains in the crystalline state. Important exceptions are polymers such as polyamides in which adjacent molecular chains are linked together by hydrogen bonds, which strongly influence the conformation adopted by the individual molecule.

So far as consistent with other stereochemical constraints a carbon-chain macromolecule "strives" (a) to assume normal bond lengths and angles, and (b) to adopt a conformation that satisfies the principle of staggered bonds (see again Figure 6-5) while at the same time permitting the molecules to pack together in a manner that permits comfortable intermolecular van der Waals contacts. It is evident that this is simply an alternative and somewhat more detailed way of expressing the minimum-potential-energy postulate. It should be emphasized that actual linear macromolecules, especially those characterized by bulky substituent groups, cannot simultaneously satisfy all of these geometrical criteria, with the result that appreciable deviations from ideality will be observed. The foregoing principles were first extensively invoked in the investigation and prediction of polymer structure by C. W. Bunn and co-workers [16, 17, 23].

Two classic examples of linear polymers in which the adoption of helical conformations minimizes overcrowding of substituent groups are polyisobutene and polytetrafluoroethylene, respectively; that is,

$$[-\mathrm{CH_2C(CH_3)_2}-]_n \quad \text{and} \quad (-\mathrm{CF_2CF_2}-)_n.$$

In stretched polyisobutene [23–25] the methyl groups on alternate carbon atoms would be only 2.54 Å apart if the chain possessed a fully extended, planar zigzag conformation with normal tetrahedral bond angles. The situation is relieved by (a) adoption of an 8/5 helical conformation and (b) opening and closing of alternate tetrahedral angles in the main chain such that

$$\mathrm{CH_2}\!\angle = 126^\circ \quad \text{and} \quad (\mathrm{CH_3})_2\mathrm{C}\!\angle = 107^\circ,$$

which is equivalent to alternating internal-rotation angles of 102.5 and 51°. This chain conformation, depicted in Figure 6-8, is remarkably well defined by one of the best known polymer diffraction patterns. (See again Figure 1-3.)

In polytetrafluoroethylene [26–28] the relatively small fluorine-atom substituents, with a van der Waals radius of 1.4 Å, would nevertheless cause overcrowding in a planar zigzag conformation since they are substituents on all, rather than alternate, carbon atoms. Below the 19°C transition temperature there occurs a small twist of 20° about every chain bond, resulting in a 13/6 helix, which together with an opening up of the chain bond angles to 116° increases the shortest $F \cdots F$ distance to an acceptable value of 2.7 Å. The conformation of the polytetrafluoroethylene molecule is shown in Figure 6-9.

6-1.4 Randomly Oriented Systems

The importance of this section lies in its applicability to polymers possessing less than three-dimensional order and especially to noncrystalline specimens. Randomness of orientation, a state sometimes

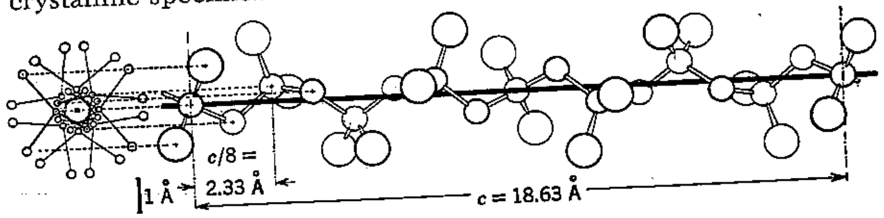

Figure 6-8 The 8/5 helix of the polyisobutene molecule. Small circles = $\mathrm{CH_2}$; large circles = $\mathrm{CH_3}$. (Liquori [25].)

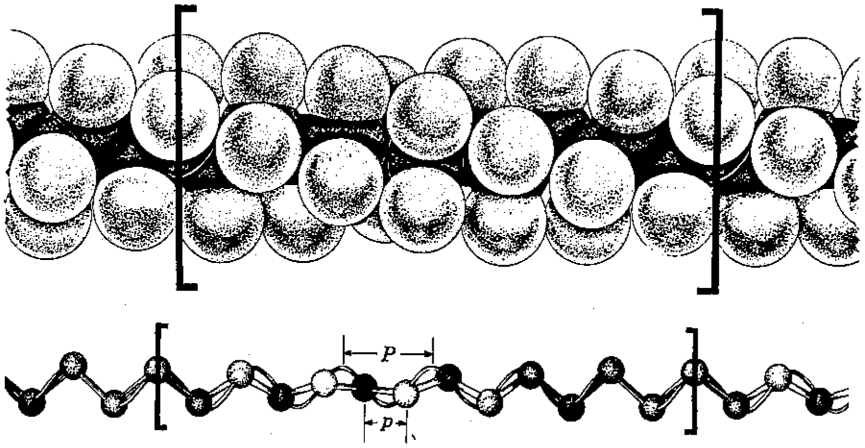

Figure 6-9 Molecular conformation of polytetrafluoroethylene: top – repeat unit of one molecule; bottom – carbon skeleton showing 13/6 helix. (Clark and Muus [27].)

referred to as *isotropic*, signifies that one orientation of a molecule or molecular element, such as a monomer residue, is as probable as any other and, furthermore, that the number of such orientations is very large from the point of view of statistics. The mathematical basis of x-ray scattering by such systems is presented in condensed form in Appendix 1, and more detailed treatments are given in the literature [29–32].

The x-ray pattern of a system characterized by orientational randomness is spherically symmetrical and can be mathematically transformed, or inverted, into a radial-distribution function, which specifies the atomic or electronic density as a function of the distance from every atom or electron in the system regarded successively as the origin. Thus the method is capable of giving information relative to the magnitudes but not the directions of the interatomic vectors, which constitutes such a severe limitation that only infrequent applications have been made to polymer structures.

The testing of alternative structure models by radial-distribution analysis can be performed in two ways, which in a formal sense are equivalent. First, the Fourier transform of the normalized experimental intensity curve $i(S)$ [see Appendix 1, (T-17)] may be compared with the radial-distribution curve calculated for the model in question or, second, the calculated and experimental intensity curves may be compared directly. On the basis of considerable practical experience Arndt and Riley [33] concluded that the second method is capable of revealing finer structural distinctions than the first. They attribute this to the fact that the effects of small structural variations tend to be concentrated in one portion of the $i(S)$ curve, particularly the region $1 < S < 3.5$, which is precisely the portion of the intensity curve that can be measured most accurately. On the other hand, Riley [34] considers the first method to be well suited to more rapid diagnosis, thereby providing a convenient means of narrowing down the field of choice preliminary to more detailed analysis based on the $i(S)$ curve. We shall now give condensed accounts of two investigations—the first illustrating the comparison of observed and calculated radial-distribution curves, and the second, and more precise, illustrating the comparison of $i(S)$ curves.

Conformation of Poly(hexamethylene adipamide) [35]. With the aim of devising procedures that would prove useful in cellulose analysis, Bjørnhaug, Ellefsen, and Tønnesen [35] compared the experimental radial-distribution curves of selected synthetic linear polymers with curves calculated for various models. Debye-Scherrer patterns were recorded with both Cu$K\alpha$ and Mo$K\alpha$ radiations monochromatized with a rock-salt crystal. The patterns were analyzed with a microphotometer and converted to intensity curves in electron units by standard procedures [29, 36]. These investigators made use of Finbak's electronic distribution function [36], which has the form of (T-17) (Appendix 1) but differs from it in that $i(S)$ is defined as $I(S) - Nf^2$ rather than $[I(S) - Nf^2]/Nf^2$. The removal of the factor $1/Nf^2$ has the beneficial effect of virtually eliminating the adverse effects of small errors in the intensity curve at large values of S. The electronic distribution may be expressed as

$$\sigma(r) = \frac{2r}{\pi}\int_0^\infty S\,[I(S) - Nf^2]\sin rS\,dS. \tag{6-6}$$

Limitations of space permit us to describe only the results obtained by Bjørnhaug, Ellefsen, and Tønnesen for poly(hexamethylene adipamide). The solid line of Figure 6-10*a* is the experimental $\sigma(r)$ curve of a randomly oriented specimen, whereas the dotted line is the $\sigma(r)$ curve calculated for a fully extended planar zigzag conformation of poly(hexamethylene adipamide) with a repetition period of 17.4 Å [37]. It will be noticed that there are rather large-scale areas of disagreement even though the individual maxima in the two functions agree on a detailed scale. Figure 6-10*b* is the function obtained by smoothing out the difference curve obtained from the two curves of part *a*. Since the calculated curve of Figure 6-10*a* takes no account

ethylene glycol with a number of
series of such polyesters with
acid residue, $—CO(CH_2)_nCO—$,
a concurrent variation in steps of
overall contraction of the monomer
fully extended zigzag value
deformation occurred in the acid
probable that (a) the very constant
increase in n would not be main-
tion of 0.5 Å would tend to increase

of the cross sections of the unit cells
polyethylene perpendicular to the
shows them both to be rectangles
are Figures 6-38 and 6-40):

Polyethylene
$a = 7.40$ Å
$b = 4.93$ Å

rial structure might appropriately
of molecular chains in two dimen-
[86]. Two ways of arranging the
as indicated in Figure 6-35. These
jected to several modes of bond-
lar zigzag in order to effect the
while at the same time preserving
molecular contact distances. The
demonstrate (a) that only models
ations in the glycol residue were
arrangement of Figure 6-35a rather
degree of agreement between the

of the atomic coordinates was
to confirm the essential correct-
to this point as well as to accom-
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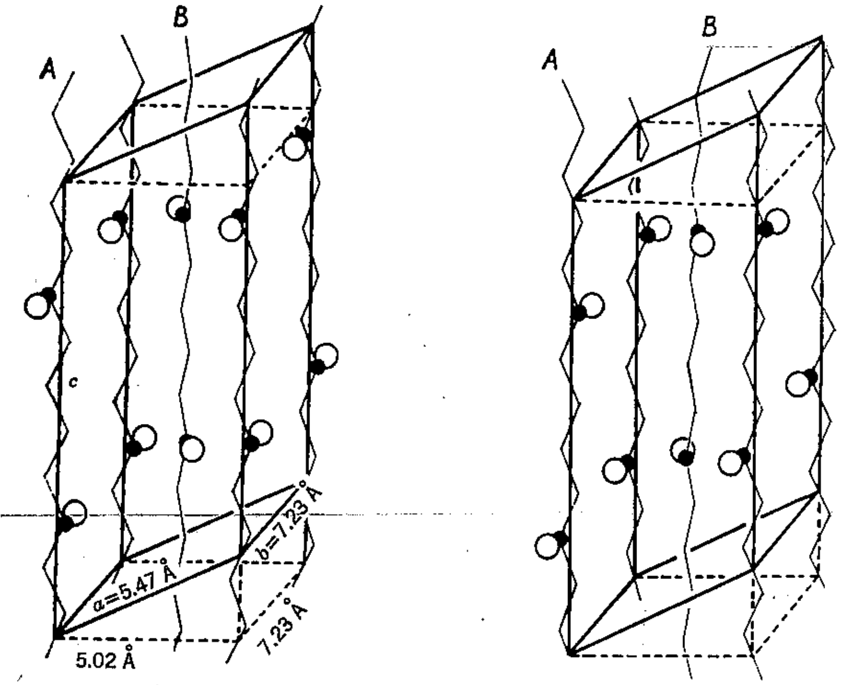
(x, y, z) in the following three



(a) (b)

Figure 6-35 Unit cell of poly(ethylene adipate) and the two possible orientations of the molecular chain. (Turner-Jones and Bunn [84].)

1. With y and z fixed and x variable.
2. With x and z fixed and y variable.
3. With x and y fixed and z variable.

One of these line Fouriers, defined by $x = -0.073$, $y = 0.025$, z, is shown in Figure 6-36. Its significance in terms of the main-chain conformation can be appreciated by relating it to Figures 6-37, 6-38, and 6-39. If the conformation were truly planar zigzag, the line $(-0.073, 0.025, z)$ would pass close to the centers of atoms C_4, C_2, C_1, O_1, and C_3 successively. The fact that the C_1 peak is relatively weak confirms that the (glycol) carbon atoms are considerably displaced from the lines paralleling c on which the remaining chain atoms are situated.

Improved agreement with the experimental structure factors was now achieved by including in the calculated structure factors the contributions of the methylene hydrogen atoms placed in their expected tetrahedral positions relative to, and at a distance of 1.09 Å

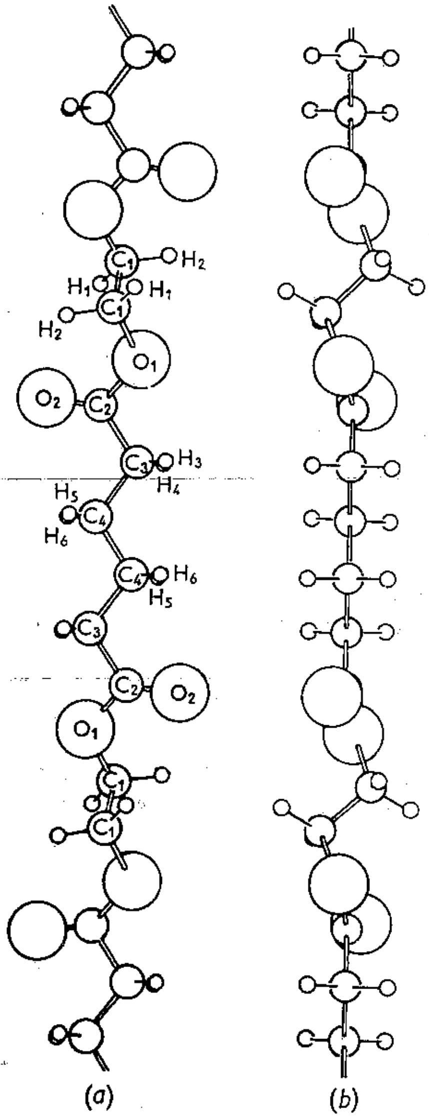


Figure 6-37 Chain configuration of poly(ethylene adipate) viewed (*a*) perpendicular and (*b*) parallel to the plane of the adipate chain. (Turner-Jones and Bunn [84].)

The pronounced displacement of the C_1 atoms from the molecular plane is clearly evident in Figures 6-37*b* and 6-38.

The nature of the deformation from the fully extended planar chain configuration, which affects only the glycol residue, can be quantita-

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Figure 6-38
Bunn [84].)

tively defi
angles (ref

Plane D

$C_4C_3C_2$
$C_3C_2O_1$
$C_2O_1C_1$

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O_1—C_2 bon
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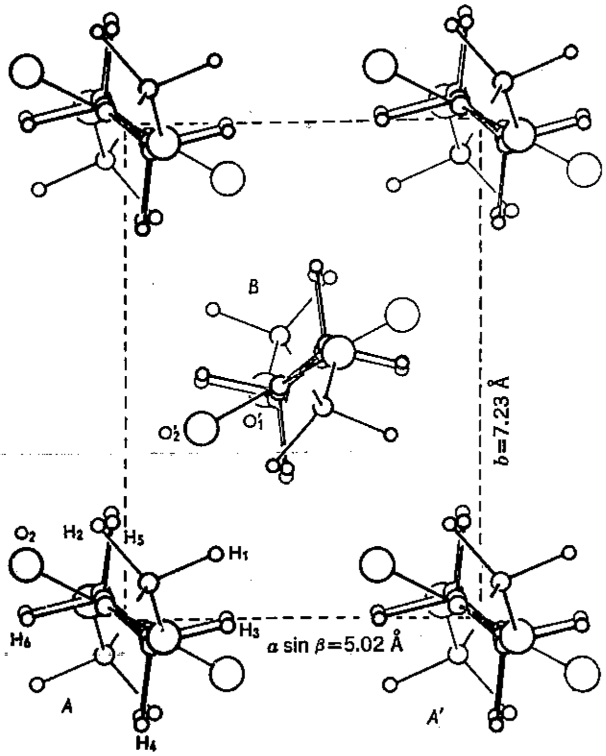

Figure 6-38 Arrangement of the molecules in the *c*-projection. (Turner-Jones and Bunn [84].)

tively defined by means of the following three internal-rotation angles (refer again to "Internal-Rotation Angles" in Section 6-1.2):

Plane L_1L_2	Plane L_2L_3	Rotation about	σ (degrees)
$C_4C_3C_2$	$C_3C_2O_1$	C_3C_2	170
$C_3C_2O_1$	$C_2O_1C_1$	C_2O_1	162
$C_2O_1C_1$	$O_1C_1C_1^*$	O_1C_1	−114

In this tabulation C_1^* is centrosymmetrically related to C_1. For the fully extended conformation σ is of course always 180°. In addition to the choice of these internal-rotation angles, a shortening of the $O_1—C_2$ bond length from the initial value of 1.43 to 1.37 Å was required in order to satisfy the monomeric identity period of 11.72 Å without a decided worsening of the agreement between the observed

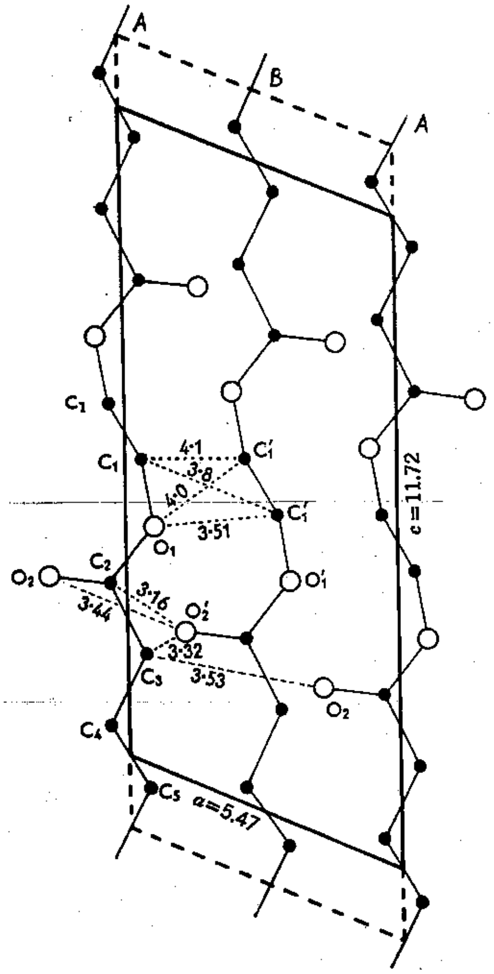

Figure 6-39 Arrangement of the molecules in the *b*-projection. All distances are in angstroms. (Turner-Jones and Bunn [84].)

and calculated structure factors. A shortening of the CO—O bond of similar amount has been observed in ester groups of other structures.

Within the expected limits of about ±0.25 Å the shorter distances between carbon and oxygen atoms in adjacent molecules agree with the sums of the atomic van der Waals radii involved. The three shortest distances are $C_2 \cdots O_2' = 3.16$, $C_3 \cdots O_2' = 3.32$, and $C_4 \cdots O_2' = 3.35$ Å, which may be compared with the sum of Pauling's van der Waals radii [88]:

Figure 6-40
(Courtesy of E

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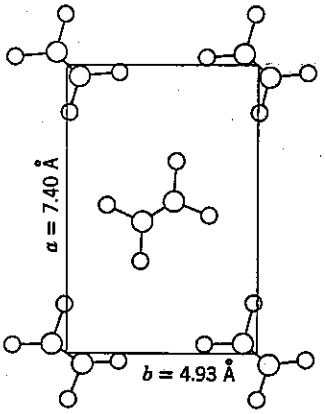

Figure 6-40 Arrangement of the molecules of polyethylene in the *c*-projection. (Courtesy of E. S. Clark.)

$$2.0(CH_2) + 1.4(O) = 3.4\ \text{Å}.$$

The closest methylene · · · methylene approaches are 3.80 and 4.10 Å, as compared with the van der Waals radius of 2.0 Å.

6-2.2 Further Illustrative Structures

In addition to the general references dealing with structure that are cited at the end of this chapter, from the available literature we may make a few specific selections as follows:

Structure	Investigator
Poly(ethylene terephthalate)	Daubeny, Bunn, and Brown [87]
Nylon 6	Holmes, Bunn, and Smith [89]
Nylon 77	Kinoshita [90]
Isotactic polypropene	Natta and Corradini [91]
Isotactic poly-1-butene	Natta, Corradini, and Bassi [92]

GENERAL REFERENCES

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D. R. Davies, "X-Ray Diffraction Studies on Polypeptide Conformations," *Progr. Biophys.*, 15, 189 (1965).

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