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Introduction

1.1 Background

Polymers of high molecular weight have now been accepted as respectable members of the molecular community. This situation was not always true.(1) It is now recognized, however, that polymer molecules possess the unique structural feature of being composed of a very large number of chain units that are covalently linked together. This property is common to all macromolecules despite their diverse origin, their widely differing chemical and stereochemical structures and uses and function. It is, therefore, possible to study this class of substances from a unified point of view that encompasses the relatively simpler polymers prepared in the laboratory, as well as the more complex ones of nature. The characteristic thermodynamic, hydrodynamic, physical, and mechanical properties possessed by high polymeric substances can be explained, in the main, by their covalent structure and the attendant large size of the individual molecules.

Although one is dealing with molecules that contain thousands of chain bonds, macromolecular systems still retain the ability to exist in different states. This property is common to all substances, high polymers included. Two states of matter that are observed in monomeric substances, the liquid and crystalline states, are also found in polymers. The liquid or amorphous state is characterized by some amount of rotation about the single bonds connecting the chain atoms in the polymer. Hence, in this state a single polymer molecule can assume a large number of spatial conformations. The bonds in a collection of such chain molecules in the liquid state, adopt statistical orientations and their centers of gravity are randomly arranged relative to one another. The structural units of a collection of such molecules in this state are arranged in a random, disoriented array and are essentially uncoordinated with one another. However, under appropriate conditions of either temperature, pressure, stress, or solvent environment, a spontaneous ordering of portions of the chain molecules can take place. This ordering results from the strong preference of the chain bonds to assume a set of highly favored specific orientations or rotational states. Therefore, in contrast to the amorphous or liquid polymer, the individual molecules now exist in a state of conformational order. The individual ordered chains, or more specifically portions of them, can then be organized into a regular three-dimensional array with the chain axes usually being parallel to one another, although a few exceptions have been found. The structure of the individual molecules may be such that they are fully extended, or they could be in a helical conformation, or they may fold back upon one another, as circumstances dictate. The significant factor is that a state of three-dimensional order is developed that in its major aspects closely resembles the crystalline state of monomeric substances. This general structural arrangement of the constituent molecules is termed the crystalline state of polymers. Since in virtually all cases the ordering process is not complete, this state is more properly termed a semi-crystalline one.

It is axiomatic that an individual polymer molecule that possesses a high degree of chemical and structural regularity among its chain elements is capable of undergoing crystallization. Indeed, crystallization has been observed in a wide variety of such polymers. It is found, moreover, that a significant amount of structural irregularity can be tolerated without preventing the crystallization process. However, even for a polymer possessing a highly regular structure, conditions must be found that are kinetically favorable for crystallization to occur in the allotted observation time. For example, poly(isobutylene), a polymer of apparently regular structure, can be easily crystallized by stretching. For a long time this polymer was not thought to be crystallizable without the application of an external stress. However, it has been demonstrated that crystallinity can be induced merely by cooling. Many months must elapse, at the optimum temperature, before the development of the crystalline state can be definitely established. Kinetic factors, therefore, are quite important. It is thus not surprising that some polymers thought to have a regular structure have not as yet been crystallized.

The understanding of the structure and properties of semi-crystalline polymers involves many different experimental techniques, scientific disciplines and theoretical approaches. The totality of the problem, and the interrelation between its different facets, are shown schematically in Fig. 1.1.(2) Essentially, all properties are controlled by the molecular morphology, that in turn is determined by the crystallization mechanisms. Information about mechanisms is obtained from studies of crystallization kinetics. In order to interpret kinetics, the equilibrium requirements need to be established. It has long been recognized that the crystalline state that is actually observed in polymers, more often than not represents one that is not at equilibrium and can be considered to be metastable. However, knowledge of the equilibrium requirements is vital to understanding all aspects of the crystallization process and the final state that eventually evolves. Based on the overview

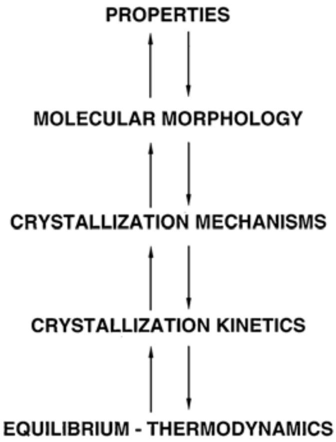

Fig. 1.1 Schematic representation and interrelation of problem areas in the study of crystalline polymers.(2)

given by the schematic of Fig. 1.1, the study of crystalline polymers divides itself naturally into three parts. Therefore, in this work the first of these, Equilibrium Concepts, comprise Volume 1. Volume 2 is concerned with Crystallization Kinetics and Mechanisms. Molecular Morphology and Properties are treated in Volume 3.

Many important properties of polymeric systems reside in the details of the conformation of the individual chains. This is particularly true with regard to their crystallization behavior. Hence it is appropriate that, before embarking on a discussion of the major subject at hand, attention be given to the general principles involved in determining the conformation of individual long chain molecules and the nature of the liquid state.

1.2 Structure of disordered chains and the liquid state

The spatial geometry of a long chain molecule depends on the bond distances between the chain atoms, the valence angles, and the hindrance potentials for internal rotation about single bonds. The conformation of a given chain backbone (fixed bond lengths and valence angles) is completely specified by the rotation angles about each of its single bonds. The large number of conformations available to a given molecule results from the permissible variations in the rotational angles among the skeletal bonds. These conformations differ from one another according to the value of the rotational angle for each individual bond.

As a convenient starting point in developing the statistical methods that are needed to analyze chain conformation, and for the purpose of calculating the dimensions of real molecules, a highly hypothetical model of a chain made up of completely freely rotating single bonds and bond angles is assumed. The geometric

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properties of such a chain model can be calculated exactly as long as long-range intramolecular interactions involving pairs of units remotely separated along the chain contour are neglected.(3) The geometry of the chain can be conveniently described either by the distance between the chain ends or by the distance of a chain element from the center of gravity of the molecule. Because of the large number of different conformations available to a molecule, a distribution of end-to-end distances is calculated. This distribution function is Gaussian, and the mean-square end-to-end distance is found to be $\langle r^2\rangle_{0f} = nl^2$. Here l is the length and n the number of links in the chain. The subscripts designate that we are dealing with an isolated, freely jointed chain. It has also been shown that for such a chain the root-mean-square distance of an element from the center of gravity $\langle s^2\rangle_{0f}^{1/2}$ and $\langle r^2\rangle_{0f}$ are related by $\langle s^2\rangle_{0f}^{1/2} = \langle r^2\rangle_{0f}^{1/2}/6$. For the chain model assumed, these linear dimensions depend on the square root of the number of bonds and hence are many times smaller than the extended length of the macromolecule. The most frequent conformations expected in the liquid state will, therefore, be those that are highly coiled. Calculations of the dimensions of freely rotating chains have also been made for cases where more than one kind of bond and valence angle are present.(3,4) Hence, it is possible for a comparison to be made between the actual dimensions of many real chains and their freely rotating counterparts.

In a real chain, the freedom of internal rotation and thus chain dimensions are tempered by the hindrance potential associated with a given bond, as well as steric interferences and interactions between neighboring substituents attached to the main chain atoms. Also of concern is the question of whether the bond rotations of neighboring bonds are independent or interdependent with one another. The hindrance potentials (for single bonds in polymer chains) are expected to resemble those of similar bonds in monomeric molecules.(5,6,7) For example, a threefold symmetric potential is appropriate to describe the rotational states of ethane. However, the potential for the central bond of butane needs to be modified. Although three minima still exist in the potential function all are not of equal energy. The lowest one is for the planar or trans configuration. The other two minima represent gauche forms, which are obtained by rotations of ±120° from the trans position. The two gauche forms are of the same energy and exceed that for the trans form by about 500 to 800 cal mol^{-1}. It has been assumed that a similar potential function is applicable to the hindered rotation of bonds in the long chain polyethylene molecule. Hence, for this polymer the lowest energy form is the planar all-trans configuration which corresponds to the fully extended chain. Although the trans state is energetically favored, gauche states are allowed at favorable temperatures so that it is still possible to generate highly irregular conformations.

For polymers whose chain structures are more complex than that of polyethylene the simple potential function described above needs to be modified. However, the potential functions are still characterized by minima that represent the low energy, highly favored rotational states. Hence, for real chains the angular position of each bond may be considered to occur effectively in one of the available minima. Bond rotations are thus limited to angular values that lie within fairly narrow ranges that can be regarded as discrete states. This approximation has been termed the rotational isomeric state. With this model an elegant mathematical apparatus is available that allows for a quantitative description of the chain conformation and can take into consideration the interdependence of rotational potentials on the states of neighboring bonds.(7,8,9) The partition function of the chain can be calculated using the method of the one-dimensional Ising lattice that was developed for the treatment of ferromagnetism.(7,8,9) From this calculation, the average dimensions of the single, isolated real chain can be deduced as well as the angular position of the energy minima. The chain dimensions are conveniently characterized by their characteristic ratios defined as $C_n = \langle r^2 \rangle_0 / nl^2$, where n represents the number of chain bonds and $\langle r^2 \rangle_0$ the actual mean-square end-to-end distance of an isolated chain unperturbed by long-range intramolecular interactions. The characteristic ratio is a measure of the spatial domain of the chain and will obviously be greater than that of the freely jointed chain. The C_n value can be obtained experimentally by several different physical chemical methods. In the disordered or liquid state individual chains are said to adopt a statistical conformation, since the conformation is governed by the rules of statistical mechanics. A compilation of values for C_∞, characteristic of an infinitely long chain, is given in Table 1.1 for a set of representative polymers. A more complete set of data can be found elsewhere.(9a)

Usually, there is good agreement between the experimentally determined values of C_∞ and the theoretical expectations. For the polymers listed, C_∞ values range from about 2 to 20, significantly greater than what would be calculated for a free rotating or freely jointed chain. Freely jointed, or rotating chains do not give either a good or a universal representation of the spatial characteristics of real chains. There is a certain element of arbitrariness in calculating C_∞ for chains that contain rings in the backbone because of the ambiguity in specifying the required single or virtual bonds.(10) For example, depending on the virtual bond chosen, C_∞ for poly(ethylene terephthalate) is calculated to be either 4.70 or 5.45. To avoid this ambiguity the spatial extent of the chain can also be expressed as $(\langle r^2 \rangle_0 / M)_\infty$. This latter quantity is calculated to be 0.93 Å^2 g mol^{-1} for poly(ethylene terephthalate), a value that is comparable to the experimentally determined one.

Polymers that have C_∞ values in the range listed in Table 1.1 are considered to be "flexible" chains. These values are in marked contrast to another class of polymers, such as the poly(p-phenylene amides) and the corresponding polyesters, where NH is replaced by O. For these polymers C_∞ values are calculated to be in the range of 125–225.(11) Although for sufficiently high molecular weights these polymers can

Table 1.1. *Values of C_∞ for some representative polymers*[a]

Polymer	T °C	C_∞	Reference
Poly(methylene)	138–142	6.6–6.8	a,b,c,d
	140	7.9^b	e
	25	8.3	f
Poly(tetrafluoroethylene)	327	9.8^b	g
	325	8 ± 2.5	h
Poly(isobutylene)	24	6.6	i
	24	7.2^b	j
Poly(oxyethylene)	35–45	4.0^b	k
	30	4.0–5.5^b	l
		4.0–5.6	l
Poly(dimethyl siloxane)	20.0, 22.5	6.35–7.7^b	m
Poly(hexamethylene adipamide)	25	5.9	n
	25	6.10^b	o
Poly(caproamide)	25	6.08^b	o
1,4 Poly(isoprene)			
cis	50	3.84^b, 4.55^b, 4.92^b	p,q
	50	4.7	r,s
trans	50	6.60^b, 6.95^b	r
	56	6.60, 7.4	s,t,u
Poly(propylene)			
isotactic	140	4.2^b	v
syndiotactic	140	11^b	v
atactic	140	5.5^b, 5.3^b	v,w
Poly(methyl methacrylate)			
isotactic	27.6, 26.5	9.1–10.0, 10.0^b	x,y,z
syndiotactic	8, 35	6.5, 7.2	y
		7.2^b	aa
atactic	4–70	6.9 ± 0.5	bb,cc, dd,ee
Poly(styrene)			
isotactic	30	11	ff,gg
syndiotactic	30	15–30^b	hh
atactic	30	10	gg,ii, jj,kk
Poly(L-proline)	30	14 (water)	ll
		18–20 (organic solvents)	ll
Poly(L-glycine)	30	2^b	mm
Poly(L-alanine)	30	9^b	mm

[a] Experimental values are given for C_∞ except when otherwise noted.
[b] Calculated values for C_∞.

Notes to Table 1.1 (*cont.*)
References
a. Chiang, R., *J. Phys. Chem.*, **70**, 2348 (1966).
b. Stacy, C. J. and R. L. Arnett, *J. Phys. Chem.*, **69**, 3109 (1965).
c. Nakajima, A., F. Hamada and S. Hayashi, *J. Polym. Sci.*, **15C**, 285 (1966).
d. Chiang, R., *J. Phys. Chem.*, **69**, 1645 (1965).
e. Han, J., R. L. Jaffe and D. Y. Yoon, *Macromolecules*, **30**, 7425 (1997).
f. Fetters, L. J., W. W. Graessley, R. Krishnamoorti and D. J. Lohse, *Macromolecules*, **30**, 4973 (1997).
g. Smith, G. D., R. L. Jaffe and D. Y. Yoon, *Macromolecules*, **27**, 3166 (1994).
h. Chu, B., C. Wu and W. Beck, *Macromolecules*, **22**, 831 (1989).
i. Fox, T. G., Jr., and P. J. Flory, *J. Am. Chem. Soc.*, **73**, 1909 (1951).
j. Suter, U. W., E. Saiz and P. J. Flory, *Macromolecules*, **16**, 1317 (1983).
k. Mark, J. E. and P. J. Flory, *J. Am. Chem. Soc.*, **87**, 1415 (1965).
l. Smith, G. D., D. Y. Yoon and R. L. Jaffe, *Macromolecules*, **26**, 5213 (1993).
m. Crescenzi, V. and P. J. Flory, *J. Am. Chem. Soc.*, **86**, 141 (1964).
n. Saunders, P. R., *J. Polym. Sci., A*, **2**, 3765 (1964).
o. Flory, P. J. and A. D. Williams, *J. Polym. Sci., Pt. A*-2, **5**, 399 (1967).
p. Abe, Y. and P. J. Flory, *Macromolecule*s, **4**, 230 (1971).
q. Tanaka, S. and A. Nakajima, *Polym. J.*, **3**, 500 (1972).
r. Mark, J. E., *J. Am. Chem. Soc.*, **88**, 4354 (1966).
s. Wagner, H. and P. J. Flory, *J. Am. Chem. Soc.*, **74**, 195 (1952).
t. Mark, J. E., *J. Am. Chem. Soc.*, **89**, 829 (1967).
u. Poddabny, Pa, E. G. Erenburg and M. A. Eryomina, *Vysokomal. Soedin. Ser. A*, **10**, 1381 (1968).
v. Suter, U. W. and P. J. Flory, *Macromolecules*, **8**, 765 (1975).
w. Alfonso, G. C., D. Yan and Z. Zhou, *Polymer*, **34**, 2830 (1993).
x. Krause, S. and E. Cohn-Ginsberg, *J. Phys. Chem.*, **67**, 1479 (1963).
y. Schulz, G. V., W. Wunderlich and R. Kirste, *Makromol. Chem.*, **75**, 22 (1964).
z. Jenkins, R. and R. S. Porter, *Polymer*, **23**, 105 (1982).
aa. Vacatello, M. and P. J. Flory, *Macromolecules*, **19**, 405 (1986).
bb. Fox, T. G., *Polymer*, **3**, 111 (1962).
cc. Schultz, G. V. and R. Kirste, *Z. Physik Chem.* (*Frankfurt*), **30**, 171 (1961).
dd. Chinai, S. N. and P. J. Valles, *J. Polym. Sci.*, **39**, 363 (1959).
ee. Vasudevon, P. and M. Santoppa, *J. Polym. Sci. A-2*, **9**, 483 (1971).
ff. Krigbaum, W. R., D. K. Carpenter and S. Newman, *J. Phys. Chem.*, **62**, 1586 (1958).
gg. Kurata, M. and W. H. Stockmayer, *Fortschr. Hochpolym. Forsch.*, **3**, 196 (1963).
hh. Yoon, D. Y., P. R. Sundararajan and P. J. Flory, *Macromolecules*, **8**, 776 (1975).
ii. Krigbaum, W. R. and P. J. Flory, *J. Polym. Sci.*, **11**, 37 (1953).
jj. Altares, T., D. P. Wyman and V. R. Allen, *J. Polym. Sci., A*, **2**, 4533 (1964).
kk. Orofino, T. A. and J. W. Mickey, Jr., *J. Chem. Phys.*, **38**, 2513 (1963).
ll. Mattice, W. L. and L. Mandelkern, *J. Am. Chem. Soc.*, **93**, 1769 (1971).
mm. Brant, D. A., W. G. Miller and P. J. Flory, *J. Mol. Biol.*, **23**, 47 (1967).

be treated as statistical coils, they are in fact highly extended, asymmetric chains. We shall be concerned here primarily with flexible type chains.

The discussion of chains in statistical conformation is based on the properties of individual, isolated chains. Except for crystallization from very dilute solution the crystallization process involves a collection of such chains. The question can

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then be raised as to the relation between the conformation of an isolated chain and that when present in a collection of such chains in the molten or liquid state. Flory has argued on theoretical grounds (12) that polymers in an undiluted melt should be essentially unperturbed, i.e. the chain dimensions should be the same as the isolated chain devoid of long-range intramolecular interaction and thus correspond to the θ condition. This conclusion is based on the premise that although a molecule in the bulk state, or in concentrated solutions, interferes with itself, it has nothing to gain by expanding. The reason is that the decrease in interaction with itself that would occur is compensated by increased interference with its neighbors. Hence, the chain prefers to remain in the θ condition. This theoretical expectation is borne out by experiment. Small-angle neutron scattering measurements of the radii of gyration of many polymers in the bulk are in close agreement with the values for the isolated, unperturbed chain, as determined under θ conditions.(13–18)

The discussion of the liquid state up to this point has been a fairly idealized one, since only the conformation and spatial extent of the chains have been taken into account. Other factors, not as easily susceptible to calculation, also need to be considered. These factors principally involve a description of topological structures such as chain entanglements, loops and knots being among the possibilities. Such structures can be expected in a collection of random long chain molecules in the liquid state and should play a major role in the crystallization process. Unfortunately, the quantification of such topological defects has been difficult. Only chain entanglements, characterized by the molecular weight between entanglements, M_e, have been given quantitative meaning by indirect measurements. It is assumed the points of entanglement acts as crosslinks. Then elementary rubber elasticity theory can be applied to the measured plateau modulus.(19) Values of M_e for selected polymers are given in Table 1.2.(20,21).

There is a considerable variation in the M_e values among the different polymers. The values range from 830 g mol^{-1} for linear polyethylene to as high as 12 000 g mol^{-1} for poly(dimethyl siloxane). The main factors governing M_e are the flexibility of the chain and the presence of branches. From a topological viewpoint, branches and their length are known to affect the entanglement density.(21) The difference in M_e's between polyethylene and the poly(propylenes) can be explained on this basis. Irrespective of the M_e value, the entanglement density will be significant for high molecular weight chains.

1.3 The ordered polymer chain

Under suitable conditions the allowable rotational states can be restricted. A given bond or sequence of bonds will be limited to rotational angles that correspond to the lowest minima in the potential function describing the hindrance to rotation.

Table 1.2. *Molecular weight between entanglements for selected polymers*[a]

Polymer	T °C	M_e (g mol^{-1})
Polyethylene	140	830
Poly(propylene) atactic	140	4600
	25	3500
atactic[b]	30–240	7050
isotactic[b]	170–220	6900
syndiotactic[b]	170–220	2170
Poly(2-methyl-1,3-pentadiene)	25	4700
Poly(1,4-cis-isoprene)	25	3100
Poly(isobutylene)	140	7300
	25	5700
Poly(dimethyl siloxane)	140	12000
	25	9600
Poly(ethylene oxide)	140	1600
Poly(ethylene terephthalate)	275	1200
Poly(carbonate)	200	1300
Poly(capolactam)	270	2000
Poly(oxymethylene)	200	2100
Poly(phenylene oxide)	220	2700–3600
Poly(tetrafluoroethylene)	380	3700

[a] Data taken from Ref. (20) where a more comprehensive table can be found.

[b] Eckstein, A., J. Sahm, C. Friedrich, R. D. Maier, J. Sassmannshausen, M. Bochmann and R. Mülhaupt, *Macromolecules*, **31**, 135 (1998).

Consequently, a highly ordered chain structure is evolved with the concomitant loss of the conformational versatility that characterizes the disordered chain and the liquid state. For example, the trans state represents the bond orientation with the lowest energy in polyethylene. When successive bonds in the chain assume this orientation, a fully extended planar zigzag conformation results, as is illustrated in Fig. 1.2. From the multitudinous number of conformations available to the chain in the liquid state only one ordered structure survives that is characteristic of the crystal. An extended planar, or nearly planar, ordered conformation is characteristic of many polymers including polyamides, polyesters, cellulose derivatives, polydienes, and one of the low energy forms of the polypeptides.

The rotational states allowed for vinyl polymers derived from monomer units of the type —CH_2—CH_2R— depend on the configurations of the successive

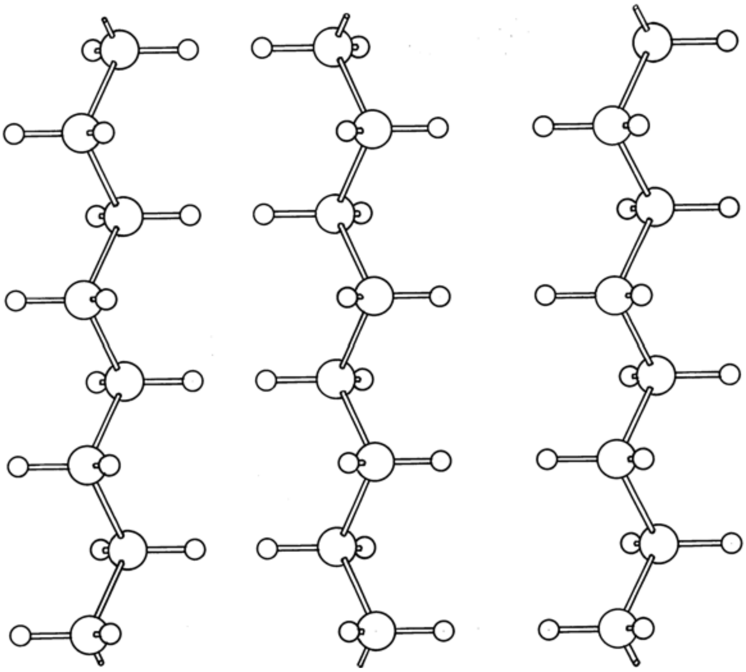

Fig. 1.2 Representation of ordered structure of portions of polyethylene chains. (From Natta and Corradini (22))

asymmetric carbon atoms bearing the substituent. For an isotactic polymer, wherein the substituent bearing carbon possesses the same tetrahedral configuration, the planar zigzag chain is excluded because of the steric interfaces between the neighboring R groups. In the trans state, successive substituent groups are within 2.5 to 2.6 Å of each other. This is not an allowed distance since it results in gross overcrowding. The crowding problem can be alleviated by having alternate bonds assume gauche positions. In this geometric pattern, the substituent groups are adequately separated. If the required rotations are executed in a regular manner so that the sequence of trans–gauche bond orientations is followed, then a helical chain structure is formed. Since there are two gauche positions, if the rotations are always executed in the same direction, either a right-handed or left-handed helix can be generated with the same molecule. If the substituent group is not too bulky, then it is found that the helix contains three chemical repeating units for each geometrical repeating unit. A helix of this type is illustrated in Fig. 1.3a.(22) This helical form allows the substituent groups to be sufficiently far apart. As examples, the nearest distances between nonbonded carbon atoms now become 3.2 Å in isotactic polypropylene and 3.3 Å in isotactic polystyrene.

Polymers containing bulkier side-groups require more space, so that much looser helices are formed. Typical examples of the latter type are illustrated in Fig. 1.3b, c, and d. These structures give rise to larger repeating units. For example,