

MOLECULAR STRUCTURE, CONFORMATION AND PROPERTIES OF MACROMOLECULES

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Abstract - The spacio-geometric characteristics of macromolecular chains are discussed from the point of view of the essential connections they provide between chemical constitution and properties. Quantities such as molecular weight, radius of gyration, degree of branching, etc., that characterize the molecule as a whole do not suffice for an understanding of the virtually endless variations in the properties that distinguish one polymer from another. For this purpose it is necessary to examine the chemical structures of the constituent units, taking into account the geometric parameters pertaining to chemical bonds, the conformations accessible to the chain skeleton and the resulting spatial configurations. The physical principles underlying the statistical mechanical treatment of conformations of long chain molecules and of their configuration-dependent properties are summarized. Correlations between bonds of the chain and the range of such correlations provide insights into the spatial characteristics of polymer chains. Persistences expressing the configurational averages of vectors spanning sequences of chain units are particularly useful in this connection. Experimental methods that provide quantitative information on conformation and the correlations between units of the chain are briefly discussed.

INTRODUCTION

Comprehension of relationships between properties of macromolecular substances on the one hand and their chemical structures and physical morphologies on the other is perhaps the most pervasive theme of polymer science. In one or another of its many aspects it engages the efforts of theoreticians, physical chemists and physicists. It is a broad concern of synthesists as well.

The chemical constitution of a polymer requires assessment at two levels. First, (i) it must be characterized at the macro level, where we take account of the overall architecture as expressed in the molecular weight or chain length, the molecular weight distribution, the degree of branching and/or cross-linking, and so forth. Secondly, (ii) at the micro level it is necessary to consider the constitution of the units comprising the polymer chains and the bonds connecting them to one another. In this category are included not only the prosaic composition of the polymer or copolymer in terms of the common names of the units it contains, but also their detailed chemical structures as embodied in stereochemical configurations and the sequential relationships between units.

The role of the molecular constitution at the level (i) is vividly illustrated by the spectrum of properties encompassed by varying the chain length within a given series of polymer homologs. They may vary continuously from oils for those of lowest molecular weight to viscoelastic fluids at intermediate chain lengths, and, eventually to elastic solids if the chain length is very great or if the material is cross-linked to a network. The ranges of properties realized through alterations of the "micro" constitution at the level (ii) may be even more striking. Consider, for example, the marked effect of stereoregularity on the melting point and capacity for crystallization, and on various related properties. Again, the sequencing of units in block copolymers may alter the mechanical properties and the glass transition drastically.

In combination, variations in constitution at levels (i) and (ii) admit of a potential for an almost endless diversity of properties. No other class of materials is comparably versatile in its inherent capacity for constitutional modifications and adjustments, in both scope and detail. These qualities are abundantly manifest in the wide range of properties of existing polymeric materials, not to mention the myriad possibilities as yet unexplored.

This diversity is nowhere demonstrated so emphatically as in biological macromolecules. They provide the fabric of structural form and serve essential functions in all living substance. Their elaboration through eons of trial-and-error evolution far surpasses the modest accomplishments of polymer chemistry, impressive as they are, gained during the span

of less than a century of effort, ostensibly conducted in a more orderly fashion and guided by the professed intelligence of scientists, although sometimes inhibited by their prejudices. Whatever may be the advantages of organized scientific effort, the fact remains that the level of refinement of structure and function in biological macromolecules presents an awesome challenge to polymer science.

Structural description of polymers at the macro level (i) is generic. The relationships that obtain are common to polymers of all kinds. Thus, the relationship between intrinsic viscosity and chain length is generally of the same form for all linear polymers, apart from modifications for rigid chains, for polyelectrolytes, etc. The characterization of branching and cross linking can be set forth without regard for the specific nature of the units comprising the polymer. The theory of rubber elasticity is comprehensive in the sense that it is independent of structural features at the micro level (ii); it suffices to stipulate that the chains comprising the network are random coils,

Both theoretical and experimental methods for dealing with macromolecular architecture at level (i) seem to have reached a fairly advanced stage of maturity. Simple models suffice, insofar as models may be required. The freely jointed chain is generally appropriate for the purpose. The most that is required is the gesture of scaling the bond of this model in such a way as to match a characteristic of the real chain, e.g., its radius of gyration.

The very fact that relationships at level (i) are general renders theory and experiment in this domain incapable of dealing with the multifarious differences that distinguish polymers of various kinds from one another. An understanding of these differences must be sought at level (ii) for they are embedded in details of the molecular structure peculiar to a given polymer and, hence, responsible for the properties that differentiate it from other polymers.

Elucidation of relationships between structure and properties necessitates inquiry into the spatial arrangement of the atoms comprising the chain skeleton and its pendent groups. This is an essential first step in any comprehensive investigation of the connections between molecular structure and properties, not only of polymers but of low molecular substances as well. For the latter, structural parameters consisting of bond lengths and bond angles may suffice to specify the spacio-geometric configuration of the molecule. In chain molecules, and especially in polymers, torsional rotations about skeletal bonds must be taken into account as well. Whereas the structural parameters are fixed within narrow limits, torsional angles often may assume wide ranges of values. The spatial configuration of a chain polymer depends most decisively on these angles, which specify its conformation. For a long chain polymer this set of variables is very large, being equal, approximately, to the number of skeletal bonds. Consequently, the polymer molecule has accessible to it an enormous array of conformations. Characterization of its spatial configuration and of its properties related thereto appears therefore to be a much more complicated task than characterization of a small molecule having at most only a few bonds susceptible to torsional rotations.

One should not conclude from the comparison of molecules in the respective categories that interpretation of properties of polymers at the molecular level is necessarily more complicated and difficult than the same task for a low molecular substance. Indeed, the opposite may be the case. Although the polymer molecule is obviously of much greater complexity, because of its size it imposes structural relationships extending to a higher level of organization. If the goal is to understand properties of matter in terms of chemical constitution, then the extent of subdivision of the substance considered into molecules is not of over-riding importance. Whether it consists of a large number of small molecules or of a smaller number of larger ones should make little difference. In fact, the continuity of a polymeric chain offers the advantage of partially alleviating the universal difficulties attending treatment of intermolecular interactions in three dimensions in condensed systems. Thus, if the characterization of the substance consisting of a collection of many molecules replaces the traditional objective of the chemist of characterizing the molecule, considered to be the ultimate entity, then the alleged complexities of polymeric substances will be seen to be illusory.

Moreover, owing to the linearity of polymer chains they may be treated as one-dimensional statistical mechanical systems, and such systems are amenable to exact methods. The large number of variables (i.e., torsional angles) required to specify a conformation notwithstanding, averages over these variables may readily be evaluated by dealing with them sequentially. Statistical mechanical averages of the properties of a polymer molecule of specified structure consequently may be treated quite rigorously and with an accuracy comparable to that attainable with small molecules.

CONFORMATIONAL ANALYSIS AND CONFIGURATIONAL STATISTICS

The potentials affecting torsional rotations ϕ about single bonds of the chain backbone usually possess several minima separated by barriers at least several times the thermal energy kT . Often, as in polymethylene chains, the potentials are threefold, with minima at

or near $\varphi=0$ and $\pm 2\pi/3$, i.e., the locations of the trans (t) and gauche (g^+ and g^-) conformations, respectively. If the minima are well defined, a tangible physical basis exists for adoption of the rotational isomeric state (RIS) scheme (1) that replaces continuous ranges of torsional angle φ by a small set of discrete values. These "states" may usually be identified with the minima in the torsional potential. Even in those instances where the torsional potential is small and does not exhibit well defined minima, the RIS scheme finds justification as a device for replacing the configuration integral over φ by a sum over discrete values. In any case, the RIS approach offers far-reaching advantages of mathematical tractability and computational simplicity. The criteria pertaining to its usage have been discussed in detail (2,3). It must suffice to note here that both the number and locations of these artificial states are arbitrary. Hence, in principle, any degree of refinement is possible.

The potential affecting rotation about a given bond usually depends on the rotations of its neighbors. Seldom does this interdependence extend beyond first neighbors (although the influence thereof may be transmitted over a much greater range through the effect of each successive bond on its immediate neighbor). This circumstance is of major significance. Its physical effect is to enhance the range of correlation of bond directions, sometimes to a marked extent. It necessitates treatment of the bond torsions as a mutually interdependent set of variables.

Consider, for example, the vinyl polymer chain shown in Fig. 1. Its conformational energy can be formulated as the sum of energies associated with assignments of the torsion angles

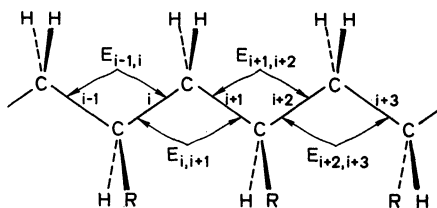


Figure 1. Pairwise conformational energies in an isotactic vinyl polymer chain.

φ_i consecutively for bonds $i=2$ to $n-1$, rotations about terminal bonds 1 and n being of no consequence. The energy that is attributed to the assignment of φ_i takes account of all interactions determined by φ_i in conjunction with assignments φ_h for all preceding bonds $h < i$. Interactions dependent on angles φ_h with $h > i$ are taken into account at the appropriate later step. Inasmuch as it suffices to consider first neighbors only, the combined energy of a conformation specified by the complete set $\{\varphi\}$ of torsional angles may be expressed as the sum of the pairwise terms indicated in Fig. 1. That is,

$$E_{\{\varphi\}} = \sum_{i=2}^{n-1} E_{i-1,i} \quad (1)$$

where $E_{i-1,i}$ is a function of φ_{i-1} and φ_i . The Boltzmann factor that weights the contribution $Z_{\{\varphi\}}$ of this chain configuration to the partition function Z may therefore be expressed as a product of factors according to

$$\exp(-E_{\{\varphi\}}/kT) = \prod_{i=2}^{n-1} \exp(-E_{i-1,i}/kT) .$$

It follows that $Z_{\{\varphi\}}$ can be written as a product of statistical weights $\xi_{i-1,i}$ for consecutive bond pairs; i.e.,

$$Z_{\{\varphi\}} = \prod_{i=2}^{n-1} \xi_{i-1,i} ; \quad \xi_{i-1,i} = \exp(-E_{i-1,i}/kT) \quad (2)$$

where $\xi_{i-1,i}$ depends on φ_{i-1} and φ_i . Thus, the separability of the energy into a sum of terms for bond pairs allows the term $Z_{\{\varphi\}}$ for the configuration $\{\varphi\}$ to be expressed as the product of a set of factors, one for each bond pair.

The manner in which each φ_i enters two consecutive factors is especially noteworthy. It underlines the basis for application of matrix algebraic methods, which greatly facilitate elaborations of the mathematical formulation that allow evaluation of a wide range of

measurable physical properties as averages over all conformations. These properties include moments of the chain vector \underline{r} , e.g., the persistence vector $\underline{g} = \langle \underline{r} \rangle$, the characteristic ratio $C_n = \langle r_n^2 \rangle / n l^2$, higher moments such as $\langle r^4 \rangle$ and $\langle r^6 \rangle$; the mean-square radius of gyration $\langle s^2 \rangle$; the mean-square dipole moment $\langle \mu^2 \rangle$ for a chain with dipoles embedded in its various units in any locally specified orientation; radiation scattering functions describing the scattered intensity as a function of angle (more precisely, of the scattering vector) with applications to small angle X-ray and neutron scattering; optical anisotropy as observed by depolarized light scattering, electric birefringence, magnetic birefringence and strain birefringence. The theoretical scheme is applicable also to the treatment of stereochemical equilibrium in vinyl polymers containing loci of chirality, to cyclization equilibrium, to the estimation of NMR chemical shifts according to the incidence of various local conformations, and to rotational isomerization in an elastomeric system under stress. All of these properties and characteristics can be treated realistically with full account of the local chain structure and conformation-dependent interactions. The methodology is rigorous and lends itself to refinement virtually to any desired degree of precision.

The formal scheme briefly described is designed for isolated polymer molecules. More specifically, it addresses the polymer chain at high dilution where intermolecular interactions vanish and in a Theta solvent where perturbations due to intramolecular interactions are null. The effects of the profusion of intermolecular interactions incident on a polymer molecule in the amorphous state, in total absence of diluent, has been the subject of widely divergent conjectures, often with little regard either for compelling experimental results or for the insights offered by theory. An abundance of evidence, reviewed elsewhere (4) and confirmed definitively by small angle neutron scattering, shows the spatial configuration to be the same, within limits of experimental error (less than 5% in the r.m.s. radius of gyration) as for the unperturbed chain in dilute solutions (5-8). These results and other supporting evidence (4) may be readily understood if one recognizes that the copious intermolecular interactions, attractive and repulsive, occurring in the bulk amorphous polymer should be neutral with respect to conformation, i.e., these interactions should be insensitive to conformation, hence the average conformation is little affected by them (4,9).

It is the broader implications of these results that are important here, for they show that calculations carried out for polymer chains in isolation, and complementary experiments conducted on dilute solutions, are relevant under a much wider range of conditions. They apply to bulk amorphous polymers where the connections between structure and properties are of special importance. In some respects the results deduced for the idealized environment of the infinitely dilute solution are applicable also to semicrystalline polymers.

PERSISTENCE VECTORS

The moments of the end-to-end vector \underline{r}_n for a sequence of n bonds afford the most universal quantities with which to characterize the average configuration of a chain. The average of the square of \underline{r}_n as embodied in the characteristic ratio $C_n = \langle r_n^2 \rangle / n l^2$ is widely used for this purpose. The related quantity $\langle s_n^2 \rangle / n l^2$, where $\langle s_n^2 \rangle$ is the square of the radius of gyration averaged over all configurations of the chain of n bonds, is sometimes preferred.

The configurational average of \underline{r}_n itself, a little used quantity which we call the persistence vector (3,10) defined by $\underline{g}_n = \langle \underline{r}_n \rangle$, is perhaps most instructive on the characteristics of the spatial configurations of chain molecules of a given kind. We consider \underline{r}_n in a reference frame defined by the first two bonds of the chain in the manner shown in Fig. 2. The x-axis

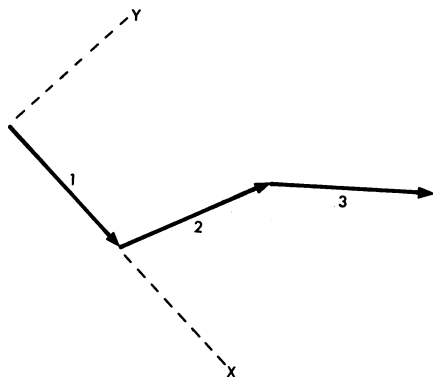


Figure 2. Coordinate system defined by the first two bonds of a chain.

is taken along the first bond; the y-axis is in the plane of the first two bonds, its direction making an acute angle with the second bond; the z-axis, perpendicular to this plane, completes a right-handed cartesian coordinate system. Then

$$\underline{a}_n = \sum_{i=1}^n \langle \underline{l}_i \rangle \quad (3)$$

where $\langle \underline{l}_i \rangle$ is the configurational average of bond vector \underline{l}_i in the reference frame of the initial bond defined in Fig. 2; i.e., the components of $\langle \underline{l}_i \rangle$ are the projections, averaged over all configurations of the chain, of bond vector \underline{l}_i on the respective axes of this coordinate system.

The persistence vector \underline{a}_m for a sequence of m bonds within a chain of $n > m$ bonds may be defined equivalently. This vector for a finite sequence in the interior of a very long chain generally differs from \underline{a}_n for a finite chain of $n=m$ bonds owing to end effects (2). The difference usually is small, however, and distinctions between finite chains and sequences of the same length embedded within very long chains are not required. Hence, in practice, persistence vectors \underline{a}_n calculated for finite chains usually may be assumed to apply to internal sequences as well.

Polymethylene

Persistence vectors may readily be calculated by use of the methods briefly described above. Results for polymethylene (PM) chains of varying length n are shown by the filled circles in Fig. 3, taken from the work of Yoon in collaboration with the author (11). The x-component $\langle x \rangle$ of \underline{a} is plotted on the abscissa and the y-component $\langle y \rangle$ on the ordinate for chains having the numbers n of bonds indicated with the points. For an achiral chain such as polymethylene the z-component must vanish in the averaging process. Hence the evolution of the persistence vector can be represented in two dimensions. The calculations were carried out on the basis of three rotational states using statistical weights appropriate for a temperature of 140°C. The point for $n=2$, i.e., for the terminus of a chain of two bonds, is fixed according to definition of the coordinate system of reference. The point for $n=3$ is the resultant of averaging over the rotation about bond 2; for $n=4$, rotations about bonds 2 and 3 are simultaneously averaged; and so forth. As n increases, contributions of successively added bonds decrease. They remain appreciable up to $n \approx 25$. Thus, bonds separated by as many as 20-25 intervening bonds are appreciably correlated. With further increase in length of the chain this correlation vanishes, as indeed it must for any chain of finite flexibility when free of external constraints.

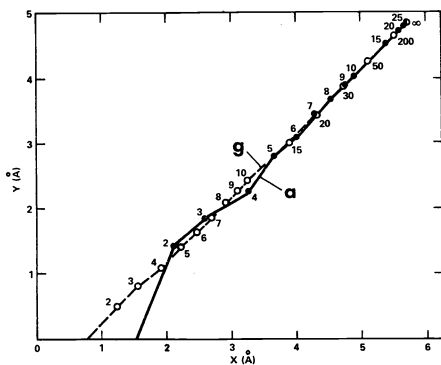


Figure 3. Filled circles represent ends of persistence vectors \underline{a} for the number n of bonds indicated with each point. Open circles are average centers of gravity $\langle \underline{g} \rangle$ for chains having the indicated numbers of bonds. Vectors are represented in the xy plane of the coordinate system defined as in Fig. 2 by the first two bonds of the chain. From ref. 11.

The open circles in Fig. 3 show mean centers of gravity for chains of the labeled lengths n . As $n \rightarrow \infty$ they must necessarily converge to the same limit \underline{a}_∞ as the persistence vectors. The convergence is much slower, of course.

It is noteworthy that the persistence of the PM chain is nearly as pronounced in the y -direction as in the direction, x , of the initial bond; see Fig. 3. In the limit $n \rightarrow \infty$, these components are $\langle x_\infty \rangle = 5.75 \text{ \AA}$ and $\langle y_\infty \rangle = 4.86 \text{ \AA}$; the magnitude of the persistence vector in this limit is $a_\infty = 7.53 \text{ \AA}$. The former component, $\langle x_\infty \rangle$, corresponds to the persistence length according to its definition for the hypothetical persistent, or worm-like, chain (12). The

transverse component $\langle y \rangle$ (as well as $\langle z \rangle$) vanishes for this model chain, in sharp contrast to the real chain.

The second moment of r_n , i.e., $\langle r_n^2 \rangle$, and the characteristic ratio $C_n = \langle r_n^2 \rangle / n l^2$ could be calculated from the persistence vectors \underline{a}_m with $m \leq n$, in the approximation that \underline{a}_m for a sequence of m bonds within a chain may be identified with \underline{a}_n for a chain having a total of $n=m$ bonds. Thus, apart from the small error arising from this generally trivial approximation, the family of persistence vectors determines the characteristic ratio.

The persistence vectors vividly portray the correlations between bonds of the chain. These correlations, persisting over ranges of 20-25 bonds in the PM chain, are due to the combined effects of narrowly restricted bond angles, preferences for one rotational isomer (trans, in this case) over others, and the interdependence of rotations about neighboring bonds. The persistence would be reduced to less than half the values in Fig. 3 if rotation were free (or the several rotational states were of equal energy); see ref. 11. The correlation between bonds then falls off steeply as $(\cos \theta)^n \approx 1/3^n$, where θ is the supplement of the bond angle. Obviously, torsional preferences and interdependence of torsional rotations greatly increase the ranges of correlation, and likewise the magnitude of the persistence vector for a long chain.

Comparison with the freely jointed chain is even more striking. In this case, the persistence is just the first bond, regardless of the length n of the chain. Transverse components are necessarily null. Obviously, the qualities of the real chain expressed in its persistence vectors cannot be incorporated satisfactorily into artificial models.

Poly(dimethylsiloxane). As a second example, consider the chain of the common silicone polymer, $[\text{Si}(\text{CH}_3)_2\text{O}]_n/2$. The bond angles in this chain, $\tau_{\text{Si}} = 110^\circ$ and $\tau_{\text{O}} = 143^\circ$, differ markedly. This is a dominant factor affecting the character of its configuration (2,13). The rotational potentials are believed to be small, hence rotational states are not well defined by them. Averages may nevertheless be evaluated by choice of discrete rotational states, three in number, as a device for approximating integrals over rotation angles. The trans conformation (t) is preferred (13); gauche rotations of opposite sign about silicon, denoted by g^+ and g^- , are strongly precluded by steric interactions between the bulky neighboring $\text{Si}(\text{CH}_3)_2$ groups. The corresponding rotations $|g^+g^-|$ about oxygen appear to be tolerated to a limited extent.

Persistence vectors (14) referred to an initial Si-O bond are shown by the filled circles in Fig. 4 for PDMS chains having the indicated numbers of skeletal bonds, proceeding to the right from the initial bond. Convergence is somewhat more rapid than for the PM chain. In the limit, $a_\infty = 7.35 \text{ \AA}$. The y-component decreases with n , falling to a very small value. Average centers of gravity are again shown by open circles.

The persistence vector obtained if O-Si is chosen as the initial bond is quite different. On this basis, $\langle y_\infty \rangle = 6.95 \text{ \AA}$ is greater than $\langle x_\infty \rangle = 4.71 \text{ \AA}$, and $a_\infty = 8.40 \text{ \AA}$. In comparing these results with those for PM, one should note that the length of the Si-O bond is 1.64 \AA compared with 1.53 \AA for C-C.

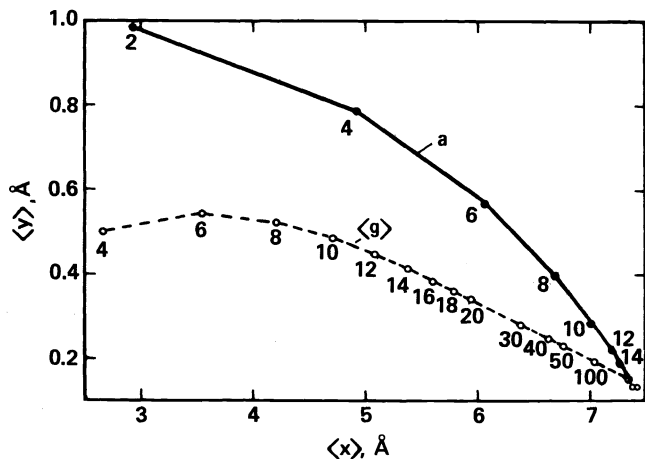


Figure 4. Persistence vectors (filled circles) and mean centers of gravity (open circles) for poly(dimethylsiloxane)'s of the chain lengths indicated, Si-O being chosen as the initial bond. From ref. 14. See legend to Fig. 3.

Vinyl Polymers

The presence of chiral elements in these chains admits of a finite z-component of \underline{g}_n . Hence, the persistences must be represented in three dimensions. In Fig. 5 the projections of \underline{g}_n on the xy and xz planes are shown by filled and open circles, respectively, for isotactic polypropylene (PP), the CHR-CH₂ bond being taken as the initial one (15). The calculations were carried out using a five-state RIS scheme with statistical weights estimated principally from conformational energy calculations (16). The preferred conformation for a dyad is approximately |tg|, (or its converse |gt|), the actual torsions being ca. 15° and 105°, respectively. Regular repetition of this conformation generates the familiar Natta-Corradini 3₁ helix. Vestiges of this arrangement are evident in Fig. 5, especially in the xz projection. Beyond n=16 correlations with the initial bond pair (that define the coordinate system of reference) are very small and convergence of \underline{g} to its limit is approached. At this limit, the x, y, and z components of \underline{g}_∞ are 3.20, 4.55 and 1.61Å, respectively, giving $|\underline{g}_\infty| = 5.79\text{Å}$.

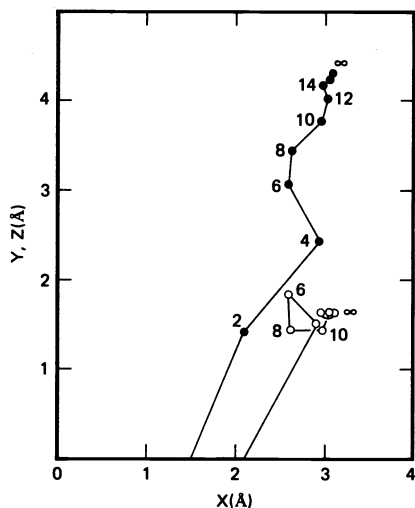


Figure 5. Projections of persistence vectors for isotactic polypropylene on the xy (filled circles) and on the xz planes (open circles). The number n of bonds is indicated with each point. From ref. 15.

Persistence vectors calculated (15) for isotactic polystyrene (PS) are presented similarly in Fig. 6. Calculations of the conformational energy as a function of bond torsion angles recommend a two-state scheme consisting of t and g states at $\phi=10^\circ$ and 110° , respectively (17); the gauche rotation \bar{g} of opposite character is effectively suppressed by steric interactions. The conformation $|10^\circ, 110^\circ| \approx |tg|$ is preferred (17), but with frequent interruptions by |tt|. The tendency to perpetuate the 3₁ helix is evident. The influence of neighbor dependence is more pronounced than in PP. Hence, correlations extend over a longer range in the PS chain, convergence is slower and $|\underline{g}_\infty| = 13.0\text{Å}$ is larger.

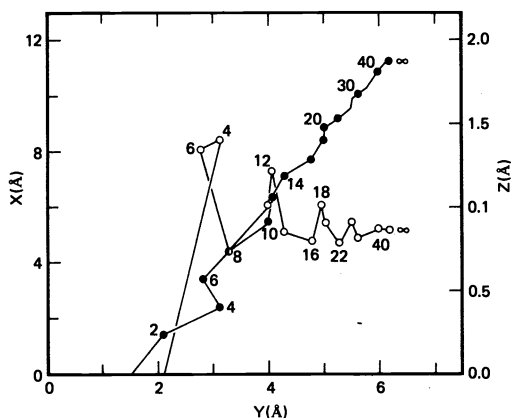


Figure 6. Projections of the persistence vectors for isotactic polystyrene. See legend to Fig. 5. From ref. 15.

The preference for the extended $|tt|$ conformation in the syndiotactic forms of both PP (16) and PS (17) leads to larger persistence vectors and slower convergence than for the isotactic chains (Figs. 5 and 6). The magnitudes $|g_{\infty}|$ calculated for the respective syndiotactic chains are 12.7\AA and 18.4\AA .

The presence of two substituents in poly(methyl methacrylate) (PMMA) introduces steric overlaps that are both severe and unavoidable in any conformation. They expand the skeletal bond angle at the methylene carbon to ca. 124° (18); the angle at the substituted carbon is ca. 110° . The accessible conformations are adequately approximated by two rotational states at $\varphi=0^\circ$ and 120° ; the $|tt|$ conformation is preferred over $|tg|$ or $|gt|$ for both meso (isotactic) and racemic (syndiotactic) dyads (19).

Projections of persistence vectors calculated for isotactic and syndiotactic PMMA (15) in the xy and yz planes are shown in Figs. 7 and 8, respectively. The slower convergence for the syndiotactic polymer is a consequence of stronger preference for $|tt|$; this conformation is perpetuated for an average sequence of about nine dyads in the syndiotactic chain, compared with three dyads in the isotactic chain (19). The inequality of skeletal angles is responsible for the tendency to spiralize, prominently evident in Fig. 8 for the syndiotactic PMMA chain.

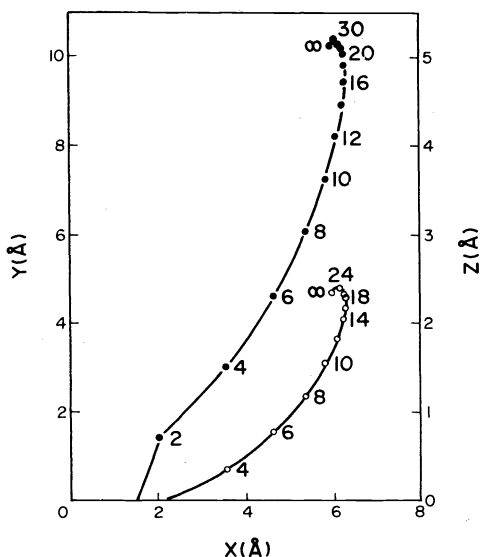


Figure 7. Projections of the persistence vectors for isotactic PMMA. See legend to Fig. 5. From ref. 15.

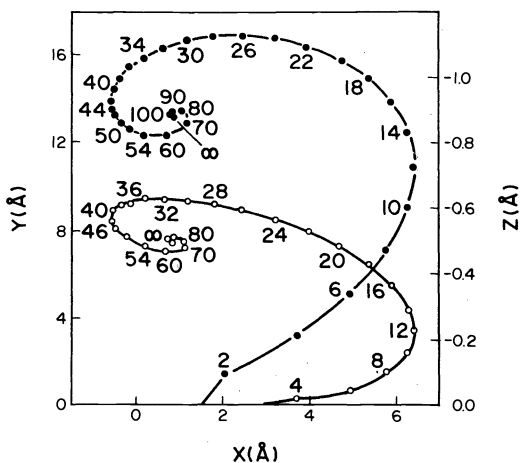


Figure 8. Projections of the persistence vectors for syndiotactic PMMA. See legend to Fig. 5. From ref. 15.

The latter feature causes the length $|g_n|$ of the persistence vector for both isotactic and syndiotactic PMMA to pass through maxima with increase in chain length before reaching their limiting values of 11.7\AA and 13.0\AA , respectively; see Figs. 7 and 8. For the former the

decline beyond the maximum occurring in the vicinity of $n=30$ is small; for the latter chain $|\bar{x}_n|$ oscillates before converging. This unusual feature that arises from the inequality of the skeletal bond angles and the marked preference of the syndiotactic chain for the $|tt|$ conformation is manifested also in the ratio $\langle r^2 \rangle_0 / nl^2$, which rises to a maximum with n , then decreases to its limit (19). Moreover, $\langle y \rangle$ exceeds $\langle x \rangle$ for both isotactic and syndiotactic PMMA.

These peculiarities of the persistence vectors of PMMA chains, especially the slow convergence of \bar{a}_n , the tendency to spiralize and the oscillation of $|\bar{a}_n|$ with n , have important implications with regard to the spatial configuration. They are strikingly manifested in the small angle X-ray (20) and neutron (6) scattering functions for syndiotactic PMMA (21).

p-Phenylene Polyamides and Polyesters

Typical of the class of highly extended p-phenylene polyesters and polyamides is poly(p-benzamide) (PBA) shown in Fig. 9. Its spatial geometry can be described by virtual bond vectors, shown by heavy dashed lines in the figure, that join successive carbonyl carbon atoms. Skeletal bond angles at carbonyl and at nitrogen differ by $\delta = \theta_1 - \theta_2 \approx 10^\circ$, θ_1 and θ_2 being the supplements of the respective bond angles (22,23); see Fig. 9. Directions of successive phenylene axes, shown by light dashed lines, are inclined to one another at the angle δ . In the conformation of maximum extension shown in Fig. 9, deviations of direction due to this difference are compensated by alternating successive units between "up" and "down" positions. Alternate phenylene axes are then parallel, the virtual bonds are in planar zig-zag array and the chain follows a rectilinear axis.

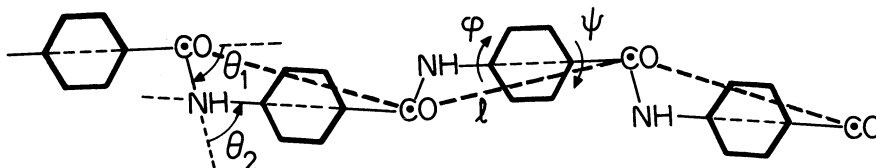


Figure 9. The poly(p-benzamide) (PBA) chain in its fully extended conformation. Virtual bonds are shown by dashed heavy lines. Skeletal bond angle supplements θ_1 and θ_2 at the carbonyl carbon and at nitrogen, respectively, and the torsion angles φ and ψ are indicated. Successive phenylene axes are inclined at angles $\pm \delta = \pm(\theta_2 - \theta_1)$ to one another.

Rotations φ and ψ about the phenylene axes (see Fig. 9) destroy this perfect regularity. They impart deviations in the directions of the phenylene axes and introduce displacements transverse to the course of the chain trajectory (22,23). Nevertheless, the structural geometry of the PBA chain enforces an over-riding preference for propagation in the direction of the phenylene axis of the unit considered.

The rotations φ and ψ are mutually independent apart from the effect, probably small, of dipole-dipole interactions between the neighboring amide groups (22). Inasmuch as the torsional potentials specifically affecting φ and ψ are twofold, they have no effect on the persistence vector. Consequently, it can be calculated directly from the structural geometry. We thus find $\langle x_\infty \rangle = 410 \text{ \AA}$, corresponding to the combined length of 64 units; the y-component of \bar{a}_∞ is negligible and the z-component is identically zero. For the corresponding polyester, poly(p-hydroxybenzoic acid) (PHB), $\delta = 7.4^\circ$ and $\langle x_\infty \rangle = 740 \text{ \AA}$ corresponding to 116 units.

Higher moments of the chain vector \bar{x}_n , defined by $\langle x^p \rangle = \langle x_x^p x_y^p x_z^p \rangle$ where $p_x + p_y + p_z = p$, reflect characteristics of the spatial distribution. Those that contain odd powers p_y or p_z of y or z vanish owing to symmetry. The non-vanishing moments depend on the potentials affecting torsional rotations (22).

The non-vanishing second moments, expressed as the ratios $\langle x^2 \rangle / nl^2$, $\langle y^2 \rangle / nl^2$ and $\langle z^2 \rangle / nl^2$, are shown in Fig. 10 where they are plotted against n (23). For comparatively short chains $\langle x^2 \rangle / nl^2$ is much greater than the other two ratios. They converge to the same limit $C_\infty/3$, however. At small n the pronounced persistence in the direction of the initial phenylene axis is dominant. The configuration bears resemblance to a rod with only minor articulations. As the chain length increases, rotations $\varphi + \psi$ about the phenylene axis introduce random deviations in the direction of the chain. Eventually, under the cumulative effect of these rotations, correlation with the initial bond vanishes and the configuration approaches that of an isotropic random coil.

The approach to random-coil character can be quantified by analysis of the numerical values of the various moments of rank $p=2, 3$ and 4 (23). Through comparison of these moments with those for a Gaussian coil modeled by a freely jointed chain, one may deduce the number m of units of the real chain that correspond, in the asymptotic limit $1/n \rightarrow 0$, to one bond of the

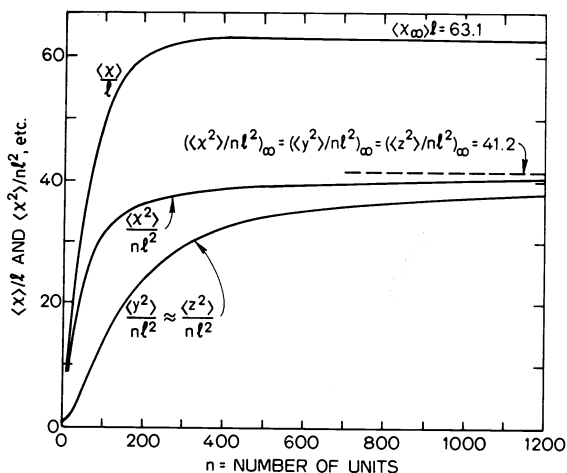


Figure 10. Persistence length and mean squared second moments for PBA chains presented as ratios $\langle x \rangle/l$, $\langle x^2 \rangle/nl^2$, etc., and plotted against the number n of units; $l(=6.50\text{\AA})$ is the length of the virtual bond. The asymptote common to the three second moment ratios is shown by the dashed horizontal line. From ref. 23.

model (11). We thus find $m=240$ units for PBA. For the corresponding polyester PHB, $m=450$ units (23). These values far exceed $m=20$ for PM(11), $m=17$ for PDMS (14) and $m=22$ for L-polypeptides (24). The contrast is accentuated if the lengths of the repeat units are taken into account: 6.50\AA for the virtual bond of PBA compared with a bond length of 1.53\AA in PM, for example.

Analysis of moments affords a rigorous means of tracing the transition from rodlike to random coil character with increase of chain length. The results briefly described are pertinent to the formation of liquid crystalline phases in polymers of the types considered and in their solutions.

EXPERIMENTAL CHARACTERIZATION OF AVERAGE CHAIN CONFORMATION AND SPATIAL CONFIGURATION

The established methods for determining quantities such as the radius of gyration and characteristic ratio - quantities falling in category (1) discussed at the outset - provide essential information on the spatial configuration. Light scattering and viscosity methods, often in combination with gel-phase chromatography, are the ones most commonly used for this purpose. While it may be argued that comparison of results obtained by these well established methods with predictions based on the structure and conformational parameters applicable to the given chain should suffice for a comprehensive analysis of the spatial character of the chain, additional methods often are desired if for no reason other than for corroboration. Methods that assess the conformation over short sequences of the chain especially are desired. Those that measure a constitutive property comprising vectorial or tensorial contributions whose sum is sensitive to conformation, and for which the range of correlation is small compared to the length of the chain, meet this requirement.

The mean-square dipole moment $\langle \mu^2 \rangle$ for a chain of ν units in each of which a dipole moment μ_0 is embedded is such a property. In formal analogy to the chain vector \mathbf{r}_n , the molecular dipole moment μ_ν is the vector sum of the μ_0 ; the quantity measured, being the configurational average of the square of the magnitude of the molecular moment, is conveniently expressed as the ratio $\langle \mu^2 \rangle / \nu \mu_0^2$, which is the analog of the characteristic ratio. Unlike the bond vectors \mathbf{r}_i that comprise \mathbf{r} , the individual moment vectors μ_0 usually are not directed along the skeletal bonds. Examples are PDMS, poly(vinyl chloride) and poly(p-chlorostyrene). Investigations (25) on the first of these polymers have succeeded in tracing the course of the mean-square dipole moment as a function of the chain length from the lowest oligomers to the high polymer. In the latter two vinyl polymers the dipoles μ_0 are preferentially directed transverse to the main-chain axis. Moreover, the dipoles tend to be oriented in opposition to one another, with the result that the ratio $\langle \mu^2 \rangle / \nu \mu_0^2$ is less than unity (26,27). The stereosequence affects both the mutual orientations of successive dipoles in a given conformation and the incidences of various conformations. Hence, effects of stereochemical constitution are manifested in the dipole moments (25-27).

Properties that depend on tensor contributions from individual units of the chain are more sensitive to conformation and stereochemical sequence. Those that depend on the optical

anisotropy provide the principal examples, namely, depolarized Rayleigh scattering, electric birefringence, strain birefringence and magnetic birefringence. Each of these depends on an invariant (for a given conformation) of the anisotropic part $\hat{\alpha}$ of the optical polarizability tensor or on the combination of this tensor with the molecular dipole moment, with the end-to-end vector \underline{r} or with the magnetic anisotropic tensor. In order to proceed, it is assumed that the tensor $\hat{\alpha}$ can be formed as the sum of contributions $\hat{\alpha}_0$ of the individual units. The contributions being tensors of second rank, their sum is sensitively dependent on their mutual orientations, and hence on the chain conformation. The particular invariant must, of course, be averaged over all conformations of the chain.

Mathematical methods are well in hand for performing the computations required to evaluate the depolarized scattering, the Kerr constant for electric birefringence, the stress-optical coefficient and the Cotton-Mouton constant for magnetic birefringence (2,28). Numerical calculations demonstrate the marked dependences of these properties on conformation, and also on stereochemical configuration (29). Such calculations rest on the premise that the contributions of the $\hat{\alpha}_0$ for the various units are locally invariant to conformation and that inductive effects of the polarizations in nearby units may be neglected. The severity of the approximations involved in adopting these premises is not well understood. The range of their validity needs to be established through further experiments if the potentialities of these methods are to be exploited.

Recent advances in X-ray and neutron scattering techniques offer especially attractive possibilities for probing the spatial configuration. Measurements at intermediate angles, i.e., in the range corresponding to Bragg distances of 10-50Å, can provide information on the correlations over comparatively short sequences of units. The application of these methods is illustrated by the experiments of Kirste and his coworkers on PMMA (6,20,21).

Other methods applicable in this area include NMR, especially of ^{13}C but including also proton resonances. Both coupling constants and "through space" interactions affecting chemical shifts are relevant.

Stereochemical equilibria in oligomers of vinyl polymers (30-32) and, recently, on vinyl polymers themselves (33), offer information unsurpassed in precision by any other method currently available. This method rests securely on the premise that the relative thermodynamic stabilities of different diastereomers are determined by the conformational interactions operating in each of them. Hence, the same parameters describing these interactions are applicable both to the analysis of conformations and to stereochemical equilibria. The most definitive results on the conformation in polystyrene (30), polypropylene (31) and poly(vinyl chloride) (32) have been made available by application of this method.

All of the experimental methods briefly cited are applicable, in principle, to oligomers as well as to polymers. They may serve, therefore, to bridge the gap between low molecular substances and macromolecules. An abundance of evidence assures that the same parameters describing conformational interactions are applicable throughout the range. In no validated instance do these interactions in polymers differ from those occurring in low molecular analogs. That this rule should hold is implicit in the quantitative equivalence of chemical bonding in macromolecules and in small molecules. Consequently, basic conformational characteristics of small molecules are at once transferable to polymers. Conversely, the wealth of information becoming available in this area from investigations on polymers can greatly enrich the understanding of conformations in molecules in general.

CONCLUSIONS

Means are at hand for treating a wide range of configuration-dependent properties of polymer chains in terms of their detailed structures and with full account of conformational interactions. The procedure is not strictly deductive as would be the case if the conformational energy could be calculated accurately and reliably from first principles, i.e., from quantum mechanics. Rather, the parameters that characterize conformational interactions (e.g., the statistical weights) must be deduced by resort to semi-empirical methods and adjusted to render calculations in agreement with experiment. The rotational isomeric state scheme affords a basis for calculating various properties, otherwise unrelated, from the same set of parameters. This scheme, and the procedures that implement it, therefore are correlative rather than deductive.

The connections between chemical structure and properties of long-chain macromolecules can be treated without compromise of the rigor attainable with low molecular analogs. The supposed complexities presented by the large number of bonds in the macromolecule are more illusory than real. They are easily overcome by use of RIS theoretical methods.

Comprehension of the spatial configuration of the polymeric chain is essential to an understanding of its properties, both in solution and in bulk. Persistence vectors joining chain sequences of various lengths afford insights into the nature of the configurations peculiar to a given polymer.

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