via cable or waveguide from each antenna of a conventional array, and it may contain, in addition to the cosmic radio data, the other information necessary for the complete analysis of the data.

Transportation and handling of a huge number of magnetic tapes each day represents a formidable task. But with proper coordination and planning for the transportation of magnetic tapes and the use of a multistation playback system, incoming data can be correlated and analyzed with only a few days delay. Similar tasks are handled routinely by the National Aeronautics and Space Administration in evaluating the data that arrive each day from tracking stations throughout the world.

Summary

It is difficult to estimate accurately the cost of constructing a large scientific instrument that involves many techniques. On the other hand, most of the component parts of the VLBA consist of antennas and electronic systems that already exist or are being fabricated. The kind of 25-m antennas being constructed for the VLA will cost about $900,000 each and will work at wavelengths as short as 1 cm. A multifrequency radiometer, hydrogen maser frequency standard, small control computer, control building, and wide-band instrumentation recorder bring the cost to about $1.5 million per element, or $15 million for a ten-element array using tape recorders. A multistation playback facility, with ten recorders and enough correlators to handle all interferometer pairs simultaneously, together with the necessary computers to control the processor and reduce the data, may add $5 million. The total cost is thus about $20 million at current prices, including an adequate supply of magnetic tape. This is comparable to the cost of existing large radio telescopes and arrays.

An array that used a geostationary communication satellite to transmit the data to a real-time correlator would cost $30 million to $50 million more, but this is still within the price range of other space astronomy projects.

It is thus feasible to construct at reasonable cost an intercontinental very long baseline array which has sub-milliarcsecond resolution. This would complement the Very Large Array now being constructed (*4*), which is much more sensitive to objects of low surface brightness. This next step would permit the study of the universe with unprecedented angular resolution.

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22. A committee of radio astronomers has been formed to consider the establishment of a VLBA. Its members include J. J. Broderick, B. F. Burke, B. G. Clark, T. A. Clark, M. H. Cohen, W. C. Erickson, M. S. Ewing, K. I. Kellermann, S. H. Knowles, J. M. Moran, B. Rayhrer, A. E. E. Rogers, D. B. Shaffer, I. I. Shapiro, and G. W. Swenson. We acknowledge the advice and assistance of this group, particularly B. G. Clark, M. H. Cohen, and D. B. Shaffer; however, this article should not be regarded as an output from that committee. We also acknowledge valuable assistance from A. T. Moffet, D. H. Rogstad, and W. Hammond. The National Radio Astronomy Observatory is operated for the National Science Foundation by Associated Universities, Inc.

Spatial Configuration of Macromolecular Chains

Paul J. Flory

The science of macromolecules has developed from primitive beginnings to a flourishing field of investigative activities within the comparatively brief span of some 40 years. A wealth of knowledge has been acquired, and new points of view have illumined various branches of the subject. These advances are the fruits of efforts of many dedicated investigators working in laboratories spread around the world. In a very real sense, I am before you on this occasion as their representative.

In these circumstances, the presentation of a lecture of a scope commensurate with the supreme honor the Royal Swedish Academy of Sciences has bestowed in granting me the Nobel Prize for chemistry is an insuperable task. Rather than attempt to cover the field comprehensively in keeping with the generous citation by the Royal Academy of Sciences, I have chosen to dwell on a single theme. This theme is central to the growth of ideas and concepts concerning macromolecules and their properties. Implemented by methods that have emerged in recent years, researches along lines I shall attempt to highlight in this lecture give promise of far-reaching advances in our understanding of macromolecular substances—materials that are invaluable to mankind.

These polymeric substances are distinguished at the molecular level from other materials by the concatenation of atoms or groups to form chains, often of great length. That chemical structures of this design should occur is implicit in the multivalency manifested by certain atoms, notably carbon, silicon, oxygen, nitrogen, sulfur, and phosphorus and in the capacity of these atoms to enter into sequential combinations. The concept of a chain molecule consisting of atoms covalently linked is as old as modern chemistry. It dates from the origins of the graphic formula introduced by Couper in 1858 and advanced by Kekulé, Loschmidt, and others shortly thereafter. Nothing in chemical theory, either then apparent or later revealed, sets a limit on the number of atoms that may be thus joined together. The rules of chemical valency, even in their most primitive form, anticipate the occurrence of macromolecular structures.

The importance of macromolecular substances, or polymers, is matched by their ubiquity. Examples too numerous to mention abound in biological systems. They comprise the structural materials of both plants and animals. Macromolecules elaborated through processes of evolution perform intricate regulatory and reproductive functions in living cells. Synthetic polymers in great variety are familiar in articles of commerce. The prevailing structural motif is the linear chain of serially connected atoms, groups, or structural units. Departures from strict linearity may sometimes occur through the agency of occasional branched units that impart a ramified pattern to the overall structure. Linearity is predominant in most macromolecular substances, however.

It is noteworthy that the chemical bonds in macromolecules differ in no discernible respect from those in "monomeric" compounds of low molecular weight. The same rules of valency apply; the lengths of the bonds, such as C-C, C-H, and C-O, are the same as the corresponding bonds in monomeric molecules within limits of experimental measurement. This seemingly trivial observation has two important implications: first, the chemistry of macromolecules is coextensive with that of low molecular substances; second, the chemical basis for the special properties of polymers that equip them for so many applications and functions, both in nature and in the artifacts of man, is not therefore to be sought in peculiarities of chemical bonding but rather in their macromolecular constitution, specifically, in the attributes of long molecular chains.

Comprehension of the spatial relationships between the atoms of a molecule is a universal prerequisite for bridging the connection between the graphic formula and the properties of the substance so constituted. Structural chemistry has provided a wealth of information on bond lengths and bond angles. By means of this information the graphic formula, primarily a topological device, has been superseded by the structural formula and by the space model that affords a quantitative representation of the molecule in three dimensions. The stage was thus set for the consideration of rotations about chemical bonds, that is, for conformational analysis of conventional organic compounds, especially cyclic ones. A proper account of bond rotations obviously is essential for a definitive analysis of the spatial geometry of a molecule whose structure permits such rotations.

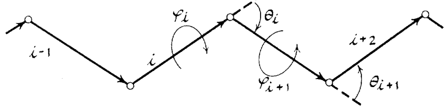


Fig. 1. Representation of the skeletal bonds of a section of a chain molecule showing supplements θ of bond angles, and torsional rotations φ for bonds i, $i+1$, and so on.

The configuration of a linear macromolecule in space involves circumstances of much greater complexity. A portion of such a molecule is shown schematically in Fig. 1. Consecutive bonds comprising the chain skeleton are joined at angles θ fixed within narrow limits. Rotations φ may occur about these skeletal bonds. Each such rotation is subject, however, to a potential determined by the character of the bond itself and by hindrances imposed by steric interactions between pendant atoms and groups. The number and variety of configurations (or conformations in the language of organic chemistry) that may be generated by execution of rotations about each of the skeletal bonds of a long chain, comprising thousands of bonds in a typical polymer, is prodigious beyond comprehension. When the macromolecule is free of constraints, for example, when in dilute solution, all of these configurations are accessible. Analysis of the manner in which such a molecule may arrange itself in space finds close analogies elsewhere in science, such as in the familiar problem of random walk, in diffusion, in the mathematical treatment of systems in one dimension, and in the behavior of real gases.

Inquiry into the spatial configuration of these long-chain molecules, fascinating in itself, derives compelling motivation from its close relevancy to the properties imparted by such molecules to the materials comprising them. Indeed, most of the properties that distinguish polymers from other substances are intimately related to the spatial configurations of their molecules, these configurations being available in profusion as noted. The phenomenon of rubberlike elasticity, the hydrodynamic and thermodynamic properties of polymer solutions, and various optical properties are but a few that reflect the spatial character of the random macromolecule. The subject is the nexus between chemical constitution and physical and chemical properties of polymeric substances, both biological and synthetic.

The importance of gaining a grasp of the spatial character of polymeric chains became evident immediately upon the establishment, about 1930, of the hypothesis that they are covalently linked molecules rather than aggregates of smaller molecules, an achievement due in large measure to the compelling evidence adduced and forcefully presented by H. Staudinger, Nobelist for 1953. In 1932 K. H. Meyer (*1*) adumbrated the theory of rubberlike elasticity by calling attention to the capacity of randomly coiled polymer chains to accommodate large deformations owing to the variety of configurations accessible to them. Kuhn (*2*) and Guth and Mark (*3*) made the first attempts at mathematical description of the spatial configurations of random chains. The complexities of bond geometry and bond rotations were poorly understood at the time. Kuhn (*2*) and Guth and Marks (*3*) circumvented these difficulties by taking refuge in the analogy to unrestricted random flights, the theory of which had been fully developed by Lord Rayleigh. The skeletal bonds of the molecular chain were thus likened to the steps in a random walk in three dimensions, the steps being uncorrelated one to another. Restrictions imposed by bond angles and hindrances to rotation were dismissed on the grounds that they should not affect the form of the results.

For a random flight chain consisting of n bonds each of length l, the mean-square of the distance r between the ends of the chain is given by the familiar relation

$$\langle r^2 \rangle = nl^2 \tag{1}$$

The angle brackets denote the average taken over all configurations. Kuhn (*4*) argued that the consequences of fixed bond angles and hindrances to rotation could be accommodated by letting several bonds of the chain molecule be represented by one longer "equivalent" bond, or step, of the random flight. This would require n to be diminished and l to be increased in Eq. 1. Equivalently, one may preserve the identification of n and l with the actual molecular quantities and replace Eq. 1 with

$$\langle r^2 \rangle = C\,nl^2 \tag{2}$$

where C is a constant for polymers of a given homologous series, that is, for polymers differing in length but composed of identical monomeric units. The proportionality between $\langle r^2 \rangle$ and chain length expressed in Eq. 2 may be shown to hold for any random chain of finite flexibility, regardless of the structure, provided that the chain is of sufficient length and that it is unperturbed by external forces or by effects due to excluded volume (see below).

The author is professor of chemistry at Stanford University, Stanford, California. This article is the lecture he delivered in Stockholm, Sweden, 11 December 1974 when he received the Nobel Prize in chemistry. Minor additions and corrections have been made by the author. It is published here with the permission of the Nobel Foundation and will also be included in the complete volume of *Les Prix Nobel en 1974* as well as in the series Nobel Lectures (in English) published by the Elsevier Publishing Company, Amsterdam and New York.

The result expressed in Eq. 2 is of the utmost importance. Closely associated with it is the assertion that the density distribution $W(\mathbf{r})$ of values of the end-to-end vector $\mathbf{r}$ must be Gaussian for chains of sufficient length, irrespective of their chemical structure, provided only that the structure admits of some degree of flexibility. Hence, for large n the distribution of values of r is determined by the single parameter $\langle r^2 \rangle$ that defines the Gaussian distribution.

Much of polymer theory has been propounded on the basis of the Kuhn "equivalent" random flight chain, with adjustment of n and l, or of C, as required to match experimental determination of $\langle r^2 \rangle$ or of other configuration-dependent quantities. The validity of this model therefore invites critical examination. Its *intrinsic artificiality* is its foremost deficiency. Actual bond lengths, bond angles, and rotational hindrances cannot be incorporated in this model. Hence, contact is broken at the outset with the features of chemical constitution that distinguish macromolecular chains of one kind from those of another. The model is therefore incapable of accounting for the vast differences in properties exhibited by the great variety of polymeric substances.

The random flight chain is patently unsuited for the treatment of constitutive properties that are configuration-dependent—for example, dipole moments, optical polarizabilities, and dichroism. Inasmuch as the contribution to one of these properties from a structural unit of the chain is a vector or tensor, it cannot be referenced to an equivalent bond that is a mere line. Moreover, the equivalent bond cannot be embedded unambiguously in the real structure.

Methods have recently been devised for treating macromolecular chains in a realistic manner. They take full account of the structural geometry of the given chain and, in excellent approximation, of the potentials affecting bond rotations as well. Before discussing these methods, however, I must direct your attention to another aspect of the subject. I refer to the notorious effect of volume exclusion in a polymer chain.

At the hazard of seeming trite, I should begin by pointing out that the chain molecule is forbidden to adopt a configuration in which two of its parts, or segments, occupy the same space. The fact is indisputable; its consequences are less obvious. It will be apparent, however, that volume exclusion vitiates the analogy between the trajectory of a particle executing a random flight and the molecular chain, a material body. The particle may cross its own path at will, but self-intersections of the polymer chain are forbidden.

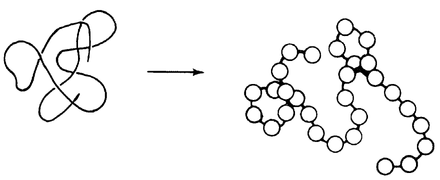


Fig. 2. The effect of excluded volume. The configuration on the left represents the random coil in absence of volume exclusion, the chain being equivalent to a line in space. In the sketch on the right the units of the chain occupy finite domains from which other units are excluded, with the result that the average size of the configuration is increased.

The effect of excluded volume must be dealt with regardless of the model chosen for representation of the chain. In practice, elimination of the effect of volume exclusion is a prerequisite to the analysis of experimental results, as I will explain in more detail later.

The closely related problems of random flights with disallowance of self-intersections and of volume exclusion within long-chain molecules have attracted the attention of many theorists. A variety of mathematical techniques have been applied to the treatment of these problems, and a profusion of theories have been put forward, some with a high order of sophistication. Extensive numerical computations of random walks on lattices of various sorts also have been carried out. Convergence of results obtained by the many investigators captivated by the subject over the past quarter century seems at last to be discernible. I shall confine myself to a brief sketch of an early, comparatively simple approach to the solution of this problem (*5*). The results it yields contrast with its simplicity.

Returning to the analogy of the trajectory traced by a particle undergoing a sequence of finite displacements, we consider only those trajectories that are free of intersections as being acceptable for the chain molecule. Directions of successive steps may or may not be correlated—that is, restrictions on bond angles and rotational hindrances may or may not be operative; this is immaterial with respect to the matter immediately at hand. Obviously, the set of eligible configurations will occupy a larger domain, on the average, than those having one or more self-intersections. Hence, volume exclusion must cause $\langle r^2 \rangle$ to increase. The associated expansion of the spatial configuration is illustrated in Fig. 2. Other configuration-dependent quantities may be affected as well.

This much is readily evident. Assessment of the magnitude of the perturbation of the configuration and its dependence on chain length require a more penetrating examination.

The problem has two interrelated parts: (i) The mutual exclusion of the space occupied by segments comprising the chain tends to disperse them over a larger volume and (ii) the concomitant alteration of the chain configuration opposes expansion of the chain. Volume exclusion (i) is commonplace. It is prevalent in conventional dilute solutions and in real gases, molecules of which mutually exclude one another. In the polymer chain the same rules of exclusion apply, but treatment of the problem is complicated by its association with (ii).

Pursuing the analogies to dilute solutions and gases, we adopt a "smoothed density" or "mean field" model. The segments of the chain, x in number, are considered to pervade a volume V, the connections between them being ignored insofar as part (i) is concerned. The segment need not be defined explicitly; it may be identified with a repeating unit or some other approximately isometric portion of the chain. In any case, x will be proportional to the number n of bonds; in general $x \neq n$, however. For simplicity, we may consider the segment density ρ to be uniform throughout the volume V; that is, $\rho = x/V$ within V and $\rho = 0$ outside of V. This volume should be proportional to $\langle r^2 \rangle^{3/2}$, where $\langle r^2 \rangle$ is the mean-square separation of the ends of the chain averaged over those configurations *not disallowed* by excluded volume interactions. Accordingly, we let

$$V = A \langle r^2 \rangle^{3/2} \tag{3}$$

where A is a numerical factor expected to be of the order of magnitude of unity.

It is necessary to digress at this point for the purpose of drawing a distinction between $\langle r^2 \rangle$ for the chain perturbed by the effects of excluded volume and $\langle r^2 \rangle_0$ for the unperturbed chain in the absence of such effects. If α denotes the factor by which a linear dimension of the configuration is altered, then

$$\langle r^2 \rangle = \alpha^2 \langle r^2 \rangle_0 \tag{4}$$

Equation 2, having been derived without regard for excluded volume interactions, should be replaced by

$$\langle r^2 \rangle_0 = C n l^2 \tag{2'}$$

where C reaches a constant value with increase in n for any series of finitely flexible chains.

The smoothed density within the domain of a linear macromolecule having a molecular weight of 100,000 or greater (that is, $n > 1000$) is low, only about 1 percent or less of the space being occupied by chain segments. For a random dispersion of the segments over the volume V, encounters in which segments overlap are rare in the sense that few of them are thus involved. However, the expectation that such a dispersion is entirely free of overlaps between any pair of segments is very small for a long chain. The attrition of configurations due to excluded volume is therefore severe.

Because of the low segment density, it suffices to consider only binary encounters. Hence, if β is the volume excluded by a segment, the probability that an arbitrary distribution of their centers within the volume V is free of conflicts between any pair of segments is

$$P_{(i)} \approx \prod_{i=1}^{x} (1-i\beta/V) \approx \exp(-\beta x^2/2V) \qquad (5)$$

Introduction of Eqs. 3 and 4 gives

$$P_{(i)} = \exp(-\beta x^2/2A\,\langle r^2\rangle_0{}^{3/2}\alpha^3) \qquad (6)$$

or, in terms of the conventional parameter z defined by

$$z = (3/2\pi)^{3/2}\,(\langle r^2\rangle_0/x)^{-3/2}\,x^{1/2}\beta \qquad (7)$$

$$P_{(i)} = \exp[-2^{1/2}(\pi/3)^{3/2}A^{-1}z\alpha^{-3}] \qquad (8)$$

Since $\langle r^2\rangle_0$ is proportional to x for long chains (see Eq. 2′), z depends on the square root of the chain length for a given series of polymer homologs.

We require also the possibility $P_{(ii)}$ of a set of configurations having the average density corresponding to the dilation α^3 relative to the probability of a set of configurations for which the density of segments corresponds to $\alpha^3 = 1$. For the former, the mean-squared separation of the ends of the chain is $\langle r^2\rangle$; for the latter it is $\langle r^2\rangle_0$. The distribution of chain vectors $\mathbf{r}$ for the unperturbed chain is approximately Gaussian as noted above. That is to say, the probability that $\mathbf{r}$ falls in the range $\mathbf{r}$ to $\mathbf{r} + d\mathbf{r}$ is

$$W(\mathbf{r})d\mathbf{r} = \text{Const}\exp(-3r^2/2\langle r^2\rangle_0)d\mathbf{r} \qquad (9)$$

where $d\mathbf{r}$ denotes the element of volume. The required factor is the ratio of the probabilities for the dilated and the undilated sets of configurations. These probabilities, obtained by taking the products of $W(\mathbf{r})d\mathbf{r}$ over the respective sets of configurations, are expressed by $W(\mathbf{r})$ according to Eq. 9, with r^2 therein replaced by the respective mean values, $\langle r^2\rangle$ and $\langle r^2\rangle_0$, for the perturbed and unperturbed sets. Bearing in mind that the volume element $d\mathbf{r}$ is dilated as well, we thus obtain

$$P_{\text{ii}} = \left[\frac{(d\mathbf{r})}{(d\mathbf{r})_0}\right] \exp\left[\frac{-3(\langle r^2\rangle - \langle r^2\rangle_0)}{2\langle r^2\rangle_0}\right]$$

$$= \alpha^3\exp[-(3/2)(\alpha^2-1)] \qquad (10)$$

The combined probability of the state defined by the dilation α^3 is

$$P_{(i)}P_{(ii)} =$$

$$\alpha^3\exp[-2^{1/2}(\pi/3)^{3/2}A^{-1}z\alpha^{-3} - (3/2)(\alpha^2-1)] \qquad (11)$$

Solution for the value of α that maximizes this expression gives

$$\alpha^5 - \alpha^3 = 2^{1/2}(\pi/3)^{3/2}A^{-1}z \qquad (12)$$

Recalling that z is proportional to $x^{1/2}\beta$ according to Eq. 7, one may express this result alternatively as follows

$$\alpha^5 - \alpha^3 = Bx^{1/2}\beta \qquad (12')$$

where $B = (\langle r^2\rangle_0/x)^{-3/2}(2A)^{-1}$ is a constant for a given series of polymer homologs.

In the full treatment (*5, 6*) of the problem along the lines sketched briefly above, the continuous variation of the mean segment density with distance from the center of the molecule is taken into account, and the appropriate sums are executed over all configurations of the chain. The squared radius of gyration s^2, that is, the mean-square of the distances of the segments from their center of gravity, is preferable to r^2 as a parameter with which to characterize the spatial distribution (*7*). Treatments carried out with these refinements affirm the essential validity of the result expressed by Eqs. 12 or 12′. They show conclusively (*7, 8*) that the form of the result should hold in the limit of large values of $\beta x^{1/2}$, that is, for large excluded volume or high chain length (or both), and hence for $\alpha >> 1$. In this limit,

$$(\alpha^5-\alpha^3)/z = 1.67$$

according to H. Fujita and T. Norisuye (*8*). For $\alpha < \sim 1.4$, however, this ratio decreases, reaching a value of 1.276 at $\alpha = 1$ (*8, 9*).

The general utility of the foregoing result derived from the most elementary considerations is thus substantiated by elaboration and refinement of the analysis, the quantitative inaccuracy of Eqs. 12 and 12′ in the range $1.0 \leq \alpha \leq 1.4$ notwithstanding. The relationship between α and the parameter z prescribed by these equations, especially as refined by Fujita and Norisuye (*8*), appears to be well supported by experiment (*10, 11*).

The principal conclusions to be drawn from the foregoing results are the following: The expansion of the configuration due to volume exclusion increases with chain length *without limit* for $\beta > 0$; for very large values of $\beta x^{1/2}$ relative to $(\langle r^2\rangle_0/x)^{3/2}$, it should increase as the one-tenth power of the chain length. The sustained increase of the perturbation with chain length reflects the fact that interactions between segments that are remote in sequence along the chain are dominant in affecting the dimensions of the chain. It is on this account that the excluded volume effect is often referred to as a long-range interaction.

The problem has been treated by a variety of other procedures (*9–12*). Notable among these treatments is the self-consistent field theory of Edwards (*12*). The asymptotic dependence of α on the one-tenth power of the chain length, and hence the dependence of $\langle r^2\rangle$ on $n^{6/5}$ for large values of the parameter z, has been confirmed (*12*).

The dilute solution is the milieu chosen for most physicochemical experiments conducted for the purpose of characterizing polymers. The effect of excluded volume is reflected in the properties of the polymer molecule thus determined and must be taken into account if the measurements are to be properly interpreted. The viscosity of a dilute polymer solution is illustrative. Its usefulness for the characterization of polymers gained recognition largely through the work of Staudinger and his collaborators.

Results are usually expressed as the intrinsic viscosity $[\eta]$, defined as the ratio of the increase in the relative viscosity η_{rel} by the polymeric solute to its concentration c in the limit of infinite dilution. That is,

$$[\eta] \equiv \lim_{c\rightarrow 0}[(\eta_{\text{rel}} - 1)/c]$$

the concentration c being expressed in weight per unit volume. The increment in viscosity due to a polymer molecule is proportional to its hydrodynamic volume, which in turn should be proportional to $\langle r^2\rangle^{3/2}$ for a typical polymer chain. Hence, $(\eta_{\text{rel}} - 1)$ should be proportional to the product of $\langle r^2\rangle^{3/2}$ times the number density of solute molecules given by c/M, where M is the molecular weight. It follows that

$$[n] = \Phi\langle r^2\rangle^{3/2}/M \qquad (13)$$

where Φ is a constant of proportionality (*6, 13*). Substitution from Eq. 4 and rearrangement of the result gives

$$[n] = \Phi(\langle r^2\rangle_0/M)^{3/2}M^{1/2}\alpha^3 \qquad (13')$$

The ratio $\langle r^2\rangle_0/M$ should be constant for a series of homologs of varying molecular weight, provided, of course, that the molecular weight, and hence the chain length, is sufficiently large.

If the excluded volume effect could be ignored, the intrinsic viscosity should vary proportionally to $M^{1/2}$. Since, however, α increases with M, a stronger dependence on M generally is observed. Often the dependence of $[\eta]$ on molecular weight can be represented in satisfactory approximation by the empirical relation

$$[\eta] = KM^a \qquad (14)$$

where $0.5 \leq a \leq 0.8$. Typical results are shown by the upper sets of data in Figs. 3 and 4 for polystyrene dissolved in benzene (*14*), and for poly(methyl methacrylate) in methyl ethyl ketone (*15*), respectively. Values of α^3 are in the range 1.4 to 5. At the asymptote for chains of great length and large excluded volume β, the exponent a should reach 0.80 according to the treatment given above. Although this limit is seldom reached within the accessible range of molecular weights, the effects of excluded volume can be substantial. They must be taken into account in the interpretation of hydrodynamic measurements (*13, 16*). Otherwise, the dependences of the intrinsic viscosity and the translational friction coefficient on molecular chain length are quite incomprehensible.

Measurement of light scattering as a function of angle, a method introduced by the late P. Debye, affords a convenient means for determining the mean-square radius of gyration. Small-angle scattering of x-rays (and lately of neutrons) offers an alternative for securing the same information. From the radius of gyration, one may obtain the parameter $\langle r^2 \rangle$ upon which attention is focused here. The results are affected, of course, by the perturbation due to excluded volume. Inasmuch as the perturbation is dependent on the solvent and temperature, the results directly obtained by these methods are not intrinsically characteristic of the macromolecule. Values obtained for $\langle r^2 \rangle$ from the intrinsic viscosity by use of Eq. 13, or by other methods, must also be construed to be jointly dependent on the macromolecule and its environment.

If the factor α were known, the necessary correction could be introduced readily to obtain the more substantive quantities, such as $\langle r^2 \rangle_0$ and $\langle s^2 \rangle_0$, that characterize the macromolecule itself and are generally quite independent of the solvent. Evaluation of α according to Eqs. 11 and 12 would require the excluded volume β. This parameter depends on the solvent in a manner that eludes prediction. Fairly extensive experimental measurements are required for its estimation, or for otherwise making correction for the expansion α.

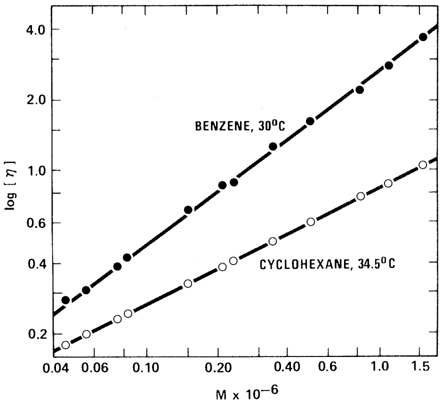


Fig. 3. Intrinsic viscosities of polystyrene fractions plotted against their molecular weights on logarithmic scales in accordance with Eq. 14. The upper set of data was determined in benzene, a good solvent for this polymer. The lower set of data was determined in cyclohexane at the Theta point. The slopes of the lines are $a = 0.75$ and 0.50, respectively. [From the results of Altares, Wyman, and Allen (*14*)]

All these difficulties are circumvented if measurements on the polymer solution are conducted under conditions such that the effects of excluded volume are suppressed. The resistance of atoms to superposition cannot, of course, be set aside. But the consequences thereof can be neutralized. We have only to recall that the effects of excluded volume in a gas comprising real molecules of finite size are exactly compensated by intermolecular attractions at the Boyle temperature (up to moderately high gas densities). At this temperature the real gas masquerades as an ideal one.

For the macromolecule in solution, realization of the analogous condition requires a relatively poor solvent in which the polymer segments prefer self-contacts over contacts with the solvent. The incidence of self-contacts may then be adjusted by manipulating the temperature or the solvent composition (or both) until the required balance is established. Carrying the analogy to a real gas a step further, we require the excluded volume integral for the interaction between a pair of segments to vanish; that is, we require that $\beta = 0$. This is the necessary and sufficient condition (*5, 6, 13*).

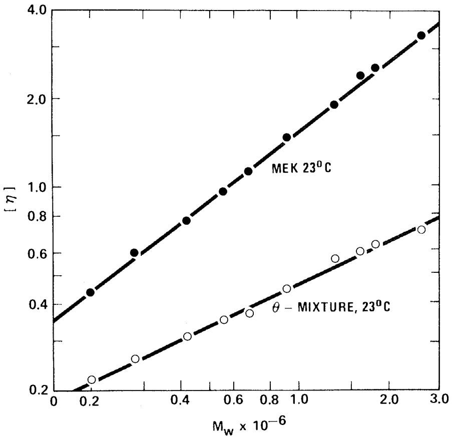


Fig. 4. Intrinsic viscosities of fractions of poly(methyl methacrylate) according to Chinai and Samuels (*15*) plotted as in Fig. 3. The upper set of points was measured in methyl ethyl ketone, a good solvent. The lower set was determined in a mixture of methyl ethyl ketone and isopropanol at the Theta point. Slopes are $a = 0.79$ and 0.50, respectively.

As has been already noted, estimation of the value of β is difficult; the prediction of conditions under which β shall precisely vanish would be even more precarious. However, the "Theta point," so-called, at which this condition is met is readily identified with high accuracy by any of several experimental procedures. An excluded volume of zero connotes a second virial coefficient of zero, and hence conformance of the osmotic pressure to the celebrated law of J. H. van't Hoff. The Theta point may be located directly from osmotic pressure determinations, light scattering measured as a function of concentration, or determination of the precipitation point as a function of molecular weight (*6, 13*).

The efficacy of this procedure, validated a number of years ago with the collaboration of T. G. Fox, W. R. Krigbaum, and others (*13, 17, 18*) is illustrated in Figs. 3 and 4 by the lower plots of data representing intrinsic viscosities measured under ideal, or Theta conditions (*6*). The slopes of the lines drawn through the lower sets of points are exactly ½, as required by Eq. 13′ when $\beta = 0$ and hence $\alpha = 1$. The excellent agreement here illustrated has been abundantly confirmed for linear macromolecules of the widest variety, ranging from polyisobutylene and polyethylene to polyribonucleotides (*19*). At the Theta point the mean-square chain vector $\langle r^2 \rangle_0$ and the mean-square radius of gyration $\langle s^2 \rangle_0$ invariably are found to be proportional to chain length.

A highly effective strategy for characterization of macromolecules emerges from these findings. By conducting experiments at the Theta point, the disconcerting (albeit interesting) effects of excluded volume on experimentally measured quantities may be eliminated. Parameters, such as $\langle r^2 \rangle_0$ and $\langle s^2 \rangle_0$, that are characteristic of the molecular chain are thus obtained. They are found to be virtually independent of the nature of the "Theta solvent" selected. Having eliminated the effects of long-range interactions, one may turn attention to the role of short-range features: structural geometry, bond rotation potentials, and steric interactions between near-neighboring groups. It is here that the influences of chemical architecture are laid bare. If the marked differences in properties that distinguish the great variety of polymeric substances, both natural and synthetic, are to be rationally understood in fundamental, molecular terms, this must be the focus of future research.

Rigorous theoretical methods have recently become available for dealing realistically with short-range features peculiar to a given structure. Most of the remainder of this article is devoted to a brief overview of these methods. Although the field is comparatively new and its exploration has only begun, space does not permit a digest of the results already obtained.

The broad objective of the methods to which we now turn attention is to treat the structure and conformations accessible to the chain molecule in such a manner as will enable one to calculate configuration-dependent quantities and to average them over all conformations, or spatial configurations, of the unperturbed chain. The properties under consideration are constitutive; they represent sums of contributions from the individual units, or chemical groupings, comprising the chain. In addition to $\langle r^2\rangle_0$ and $\langle s^2\rangle_0$, they include: mean-square dipole moments; the optical anisotropies underlying strain birefringence, depolarized light scattering, and electric birefringence; dichroism; and the higher moments, both scalar and tensor, of the chain vector **r**. Classical statistical mechanics provides the basis for evaluating the configurational averages of these quantities. Since bond lengths and bond angles ordinarily may be regarded as fixed, the bond rotations φ are the variables over which averaging must be carried out. The procedure rests on the rotational isomeric state scheme, the foundations for which were set forth in large measure by Volkenstein (*20*) and his colleagues (*21*) in Leningrad in the late 1950's and early 1960's. It is best explained by examples.

Consider rotation about an internal bond of an *n*-alkane chain. As is now well established (*22, 23*), the three staggered conformations, *trans* (t), *gauche-plus* (g^+), and its mirror image *gauche-minus* (g^-), are of lower energy than the eclipsed forms. The t and g^- conformations of *n*-butane are shown in Fig. 5. The energies of the eclipsed conformations separating t from g^+ and t from g^- are about 3.5 kcal mol^{-1} above the energy of the *trans* conformation. Hence, in good approximation, it is justified to consider each bond to occur in one of three rotational isomeric states centered near (but not necessarily precisely at) the energy minima associated with the three staggered conformations (*20–24*). The *gauche* minima lie at an energy of about 500 cal mol^{-1} above *trans*. Each of the former is therefore disfavored compared to the latter by a "statistical weight" factor we choose to call $\sigma \approx \exp(-E_g/RT)$, where E_g is about 500 cal mol^{-1}; thus, $\sigma \approx 0.5$ at $T = 400$ K.

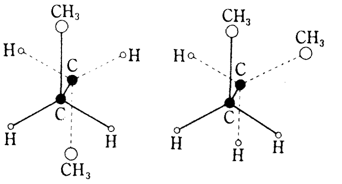


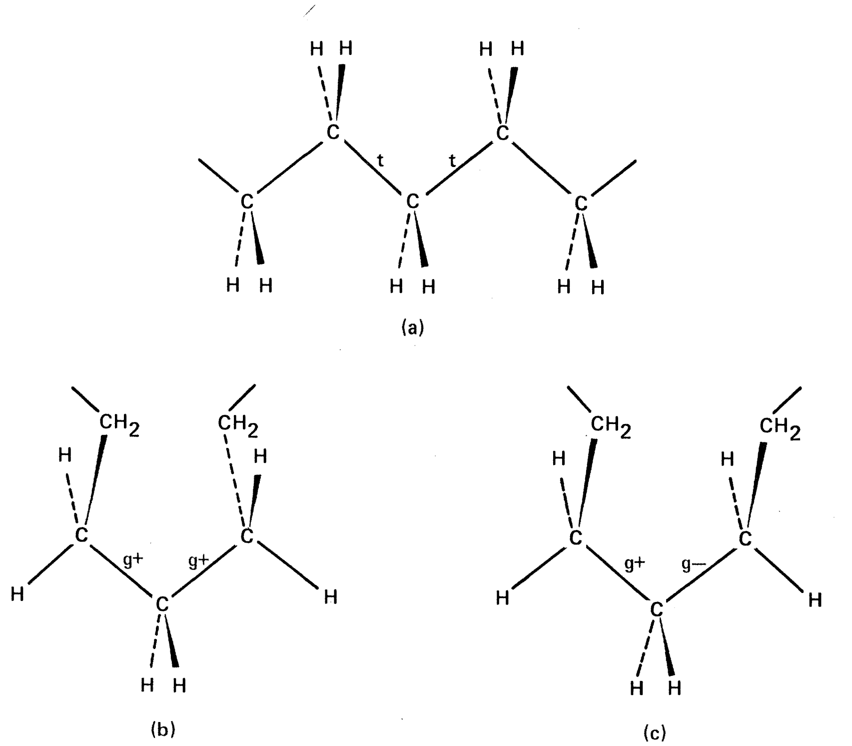
Fig. 5. Two of the staggered conformations for *n*-butane: *trans* on the left and *gauche-minus* on the right.

A complication arises from the fact that the potentials affecting bond rotations usually are neighbor dependent; that is, the potential affecting φ_i depends on the rotations φ_{i-1} and φ_{i+1}. Bond rotations cannot, therefore, be treated independently (*20, 21, 24, 25*). The source of this interdependence in the case of an *n*-alkane chain is illustrated in Fig. 6, showing a pair of consecutive bonds in three of their nine conformations. In the conformations tt, tg^+, g^+t, tg^-, and g^-t, the two methylene groups pendant to this pair of bonds are well separated. For *gauche* rotations g^+g^+ and g^-g^- of the same hand (Fig. 6b), these groups are proximate but not appreciably overlapped. Semiempirical calculations (*21, 24, 26, 27*) show the intramolecular energy for these two equivalent conformations to be very nearly equal to the sum (about 1000 cal mol^{-1}) for two well-separated *gauche* bonds; that is, the interdependence of the pair of rotations is negligible. In the remaining conformations, g^+g^- and g^-g^+, the steric overlap is severe (Fig. 6c). It may be alleviated somewhat by compromising rotations, but the excess energy associated therewith is nevertheless about 2.0 kcal mol^{-1}. Hence, a statistical weight factor $\omega \approx \exp(-2000/RT)$ is required for each such pair (*24, 26, 28*). Inspection of models in detail shows that interactions dependent upon rotations about three, four, or five consecutive bonds are disallowed by interferences of shorter range and hence may be ignored (*24*). It suffices therefore to consider first neighbors only.

The occurrence of interactions that depend on pairs of skeletal bonds is the rule in chain molecules. In some of them, notably in vinyl polymers, such interactions may affect most of the conformations. Hence, interdependence of rotations usually plays a major role in determining the spatial configuration of the chain. The rotational isomeric state approximation, whereby the continuous variation of each φ is replaced by discrete states, provides the key to mathematical solution of the problem posed by rotational interdependence (*20, 21, 24, 25*).

It is necessary therefore to consider the bonds pairwise consecutively, and to formulate a set of statistical weights for bond i that take account of the state of bond i-1. These statistical weights are conveniently presented in the form of an array, or matrix, as follows:

$$\mathbf{U}_i = \begin{bmatrix} u^{tt} & u^{tg^+} & u^{tg^-} \\ u^{g^+t} & u^{g^+g^+} & u^{g^+g^-} \\ u^{g^-t} & u^{g^-g^+} & u^{g^-g^-} \end{bmatrix}_i \qquad (15)$$

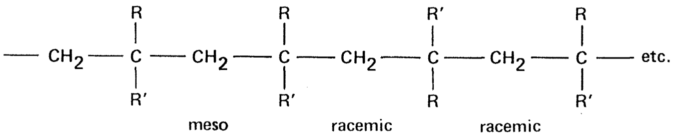


(a)

(b)

(c)

Fig. 6. Conformations for a pair of consecutive bonds in an *n*-alkane chain. (a), tt; (b), g^+g^+; (c), g^+g^-. Wedged bonds project forward from the plane of the central bonds; dashed bonds project behind this plane.



$$-CH_2-\underset{R'}{\overset{R}{C}}-CH_2-\underset{R'}{\overset{R}{C}}-CH_2-\underset{R}{\overset{R'}{C}}-CH_2-\underset{R'}{\overset{R}{C}}-\text{etc.}$$

Fig. 7. A vinyl polymer chain shown in projection in its planar (fully extended) conformation. If the substituents R and R′ differ (for example, if R = C_6H_5 and R′ = H as in polystyrene), diastereomeric dyads must be distinguished as indicated for the stereochemical structure shown.

where the rows are indexed in the order t, g^+, g^- to the state of bond $i - 1$, and the columns are indexed to the state of bond i in the same order. According to the analysis of the alkane chain conformations presented briefly above, $\mathbf{U}_i$ takes the form (*24, 26, 28*)

$$\mathbf{U}_i = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix}_i \qquad (16)$$

for any bond $1 < i < n$.

A conformation of the chain is specified in the rotational isomeric state approximation by stipulation of the states for all internal bonds 2 to $n - 1$ inclusive; for example, by $g^+ttg^-g^-$, and so on. Owing to the threefold symmetry of the terminal methyl groups of the alkane chain, rotations about the terminal bonds are inconsequential and hence are ignored. The statistical weight for the specified conformation of the chain is obtained by selecting the appropriate factor for each bond from the array (*15*) according to the state of this bond and of its predecessor, and taking the product of such factors for all bonds 2 to $n - 1$. In the example above this product is $u^{g^+}\ u^{g^+t}\ u^{tt}\ u^{tg^-}\ u^{g^-g^-}$, and so on. It will be obvious that the first superscripted index in one of the factors u must repeat the second index of its predecessor since these indices refer to the same bond.

The configuration partition function, representing the sum of all such factors, one for each conformation of the chain as represented by the scheme of rotational isomeric states, is

$$Z = \sum_{\text{all states}} u_2 u_3 \cdots u_i \cdots u_{n-1}, \qquad (17)$$

where the subscripts are serial indexes. Each u_i must be assigned as specified above. The sum, which extends over all ordered combinations of rotational states, may be generated identically as the product of the arrays $\mathbf{U}_i$ treated as matrices. That is, according to the rules of matrix multiplication

$$Z = \prod_{i=1}^{n} \mathbf{U}_i \qquad (18)$$

where $\mathbf{U}_1$ = row (1,0,0) and $\mathbf{U}_n$ = column (1,1,1). Matrix multiplication generates products precisely of the character to which attention is directed at the close of the preceding paragraph. Serial multiplication of the statistical weight matrices generates this product for each and every conformation of the chain, and Eq. 18 with the operators $\mathbf{U}_1$ and $\mathbf{U}_n$ appended gives their sum.

The foregoing procedure for evaluation of Z is a minor variant of the method of Kramers and Wannier (*29*) for treating a hypothetical one-dimensional ferromagnet or lattice. A number of interesting characteristics of the chain molecule can be deduced from the partition function by application of familiar techniques of statistical mechanics. I shall resist the temptation to elaborate these beyond mentioning two properties of the molecule that may be derived directly from the partition function, namely, the incidences of the various rotational states and combinations thereof, and the equilibrium constants between isomeric structures of the chain in the presence of catalysts effectuating their interconversion. Vinyl polymers having the structure shown in Fig. 7 with $R' \neq R$ afford examples wherein the study of equilibria between various diastereomeric forms arising from the local chirality of individual skeletal bonds has been especially fruitful (*30*).

Consider the evaluation of a configuration-dependent property for a given configuration, or conformation, of the chain. Since the configuration is seldom "given," the problem as stated is artificial. Its solution, however, is a necessary precursor to the ultimate goal, which is to obtain the average of the property over all configurations. A property or characteristic of the chain that will serve for illustration is the end-to-end vector $\mathbf{r}$. Suppose we wish to express this vector with reference to the first two bonds of the chain. For definiteness, let a Cartesian coordinate system be affixed to these two bonds with its X_1-axis along the first bond and its Y_1-axis in the plane of bonds 1 and 2, as shown in Fig. 8. The vector $\mathbf{r}$ is just the sum

$$\sum_{i=1}^{n} \mathbf{l}_i$$

of all of the bond vectors $\mathbf{l}_i$, each expressed in this reference frame.

In order to facilitate the task of transforming every bond vector to the reference frame affiliated with the first bond, it is helpful to define a reference frame for each skeletal bond of the chain. For example, one may place the axis X_i along bond i, the Y_i-axis in the plane of bonds $i - 1$ and i, and choose the Z_i-axis to complete a right-handed Cartesian system. Let $\mathbf{T}_i$ symbolize the transformation that, by premultiplication, converts the representation of a vector in reference frame $i + 1$ to its representation in the preceding reference frame i. Then bond i referred to the initial reference frame is given by

$$\mathbf{T}_1\mathbf{T}_2 \cdots \mathbf{T}_{i-1}\mathbf{l}_i$$

where $\mathbf{l}_i$ is presented in reference frame i. The required sum is just

$$\mathbf{r} = \sum_{i=1}^{n} \mathbf{T}_1 \cdots \mathbf{T}_{i-1}\mathbf{l}_i \qquad (19)$$

This sum of products can be generated according to a simple algorithm. We first define a "generator" matrix $\mathbf{A}_i$ as follows (*31, 32*)

$$\mathbf{A}_i = \begin{bmatrix} \mathbf{T}_i & \mathbf{l}_i \\ \mathbf{0} & 1 \end{bmatrix}, 1 < i < n \qquad (20)$$

together with the two terminal matrices

$$\mathbf{A}_1 = [\mathbf{T}_1 \quad \mathbf{l}_1] \qquad (21)$$

$$\mathbf{A}_n = \begin{bmatrix} \mathbf{l}_n \\ 1 \end{bmatrix} \qquad (22)$$

In these equations $\mathbf{T}_i$ is the matrix representation of the transformation specified above and $\mathbf{0}$ is the null matrix of order 1×3. The desired vector $\mathbf{r}$ is generated identically by taking the serial product of the $\mathbf{A}$'s; that is

$$\mathbf{r} = \prod_{i=1}^{n} \mathbf{A}_i \qquad (23)$$

as may easily be verified from the elementary rules of matrix multiplication. Each generator matrix $\mathbf{A}_i$ depends on the length of bond i and, through $\mathbf{T}_i$, on both the angle θ_i between bonds i and $i + 1$ and on the angle of rotation φ_i about bond i (see Fig. 1).

In order to obtain the average of $\mathbf{r}$ over all configurations of the chain, it is necessary to evaluate the sum over all products of the kind given in Eq. 23 with each of them multiplied by the appropriate statistical weight for the specified configuration of the chain; see Eq. 17. That is,

$$\langle \mathbf{r} \rangle_0 = Z^{-1} \sum u_2 u_3 \cdots u_{n-1} \mathbf{A}_1 \mathbf{A}_2 \cdots \mathbf{A}_n \tag{24}$$

where the sum includes all configurations. This sum can be generated by serial multiplication of matrices defined as follows:

$$\mathcal{A}_i = \begin{bmatrix} u^{tt}\mathbf{A}^t & u^{tg^+}\mathbf{A}^{g^+} & u^{tg^-}\mathbf{A}^{g^-} \\ u^{g^+t}\mathbf{A}^t & u^{g^+g^+}\mathbf{A}^{g^+} & u^{g^+g^-}\mathbf{A}^{g^-} \\ u^{g^-t}\mathbf{A}^t & u^{g^-g^+}\mathbf{A}^{g^+} & u^{g^-g^-}\mathbf{A}^{g^-} \end{bmatrix} \quad 1 < i < n \tag{25}$$

$$\mathcal{A}_1 = [\mathbf{A}_1 \quad \mathbf{0} \quad \mathbf{0}] \tag{26}$$

$$\mathcal{A}_n = \text{column } (\mathbf{A}_n, \mathbf{A}_n, \mathbf{A}_n) \tag{27}$$

Then (*31*)

$$\langle \mathbf{r} \rangle_0 = Z^{-1} \prod_{i=1}^{n} \mathcal{A}_i \tag{28}$$

The matrix $\mathcal{A}_i$ comprises the elements of $\mathbf{U}_i$ (see Eq. 15) joined with the $\mathbf{A}$ matrix for the rotational state of bond i as prescribed by the column index. It will be apparent that serial multiplication of the $\mathcal{A}_i$ according to Eq. 28 generates the statistical weight factor $u_2 u_3 \cdots u_{n-1}$ for every configuration of the chain in the same way that these factors are generated by serial multiplication of the statistical weight matrices $\mathbf{U}_i$ in Eq. 18. Simultaneously, Eq. 28 generates the product of $\mathbf{A}$'s (see Eq. 23) that produces the vector $\mathbf{r}$ for each configuration thus weighted. The resulting products of statistical weights and of $\mathbf{A}$'s are precisely the terms required by Eq. 24. The terminal factors in Eq. 28 yield their sum.

With greater mathematical concision (*31, 32*)

$$\mathcal{A}_i = (\mathbf{U}_i \otimes \mathbf{E}_3) \| \mathbf{A}_i \|, \quad 1 < i < n \tag{29}$$

$$\mathcal{A}_1 = \mathbf{U}_1 \otimes \mathbf{A}_1 \tag{30}$$

$$\mathcal{A}_n = \mathbf{U}_n \otimes \mathbf{A}_n \tag{31}$$

where $\mathbf{E}_3$ is the identity matrix of order three, $\otimes$ signifies the direct product, and $\| \mathbf{A}_i \|$ denotes the diagonal array of the matrices A_i^t, A_i^{g+}, and A_i^{g-}.

A characteristic of the chain commanding greater interest is the quantity $\langle r^2 \rangle_0$ introduced in earlier discussion. For a given configuration of the chain, r^2 is just the scalar product of $\mathbf{r}$ with itself; that is,

$$r^2 = \mathbf{r} \cdot \mathbf{r} = \sum_{i=1}^{n} l_i^2 + 2 \sum\sum_{i<j} \mathbf{l}_i \cdot \mathbf{l}_j \tag{32}$$

If each bond vector $\mathbf{l}_i$ is expressed in its own reference frame i, then

$$r^2 = \sum_{1}^{n} l_i^2 + 2 \sum\sum_{i<j} \mathbf{l}_i^T \mathbf{T}_i \mathbf{T}_{(i+1)} \cdots \mathbf{T}_{j-1} \mathbf{l}_j \tag{33}$$

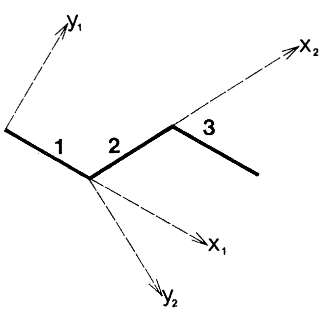


Fig. 8. Specification of the coordinate axes affixed to each of the first two bonds of the chain: X_1Y_1 for bond 1, and X_2Y_2 for bond 2.

where $\mathbf{l}_i^T$ is the transposed, or row form of vector $\mathbf{l}_i$. These sums can be evaluated by serial multiplication of the generator matrices (*24, 33*).

$$\mathbf{G}_i = \begin{bmatrix} 1 & 2\mathbf{l}^T\mathbf{T} & l^2 \\ \mathbf{0} & \mathbf{T} & \mathbf{l} \\ 0 & \mathbf{0} & 1 \end{bmatrix}_i \quad 1 < i < n \tag{34}$$

That is,

$$r^2 = \prod_{1}^{n} \mathbf{G}_i \tag{35}$$

where $\mathbf{G}_1$ has the form of the first row, and $\mathbf{G}_n$ that of final column of Eq. 34. Evaluation of $\langle r^2 \rangle_0$ proceeds exactly as set forth above for $\langle \mathbf{r} \rangle_0$ (*32, 33*).

The foregoing method enjoys great versatility. The chain may be of any specified length and structure. If it comprises a variety of skeletal bonds and repeat units, the factors entering into the serial products have merely to be fashioned to introduce the characteristics of the bond represented by each of the successive factors. The mathematical methods are exact; the procedure is free of approximations beyond that involved in adoption of the rotational isomeric state scheme. With judicious choice of rotational states, the error involved here is generally within the limits of accuracy of basic information on bond rotations, nonbonded interactions, and so forth.

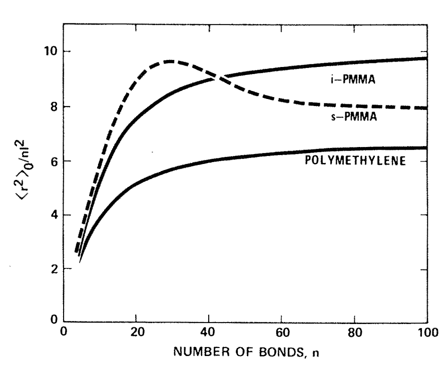


Fig. 9. Characteristic ratios $\langle r^2 \rangle_0/nl^2$ plotted against the number of bonds n in the chain for polymethylene, and for isotactic and syndiotactic poly(methyl methacrylate)'s. [From the calculations of Abe *et al.* (*26*) and of Yoon (*34*)]

Other molecular properties that may be computed by straightforward adaptation of these methods (*24, 32*) include the (i) higher scalar moments such as $\langle r^4 \rangle_0$ and $\langle r^6 \rangle_0$; (ii) the moment tensors formed from $\mathbf{r}$; (iii) the mean-squared radius of gyration

$$\langle s^2 \rangle_0 = (n+1)^{-2} \sum_i \sum_j \langle r_{ij}^2 \rangle$$

(iv) the optical polarizability and its invariants that govern the optical anisotropy as manifested in depolarized light scattering, in strain birefringence, and in electric birefringence; (v) x-ray scattering at small angles; and (vi) chemical shifts observed by nuclear magnetic resonance.

For illustration, characteristic ratios $\langle r^2 \rangle_0/nl^2$ are plotted in Fig. 9 against the numbers n of bonds for n-alkanes and for isotactic and syndiotactic poly(methyl methacrylate) (PMMA). Isotactic PMMA is represented by the formula in Fig. 7 with R = COOCH and R′ = CH_3, and with all dyads of the meso form, that is, with R occurring consistently above (or below) the axis of the chain. In the syndiotactic stereoisomer, the substituents R and R′ alternate from one side to the other, all dyads being racemic.

For the alkane and the isotactic PMMA chains the characteristic ratios increase monotonically with chain length, approaching asymptotic values for $n \approx 100$ bonds. This behavior is typical. For syndiotactic PMMA, however, the characteristic ratio passes through a maximum at intermediate values of n, according to these computations by Yoon (*34*). This behavior can be traced (*34*) to the inequality of the skeletal bond angles in PMMA in conjunction with the preference for *tt* conformations in the syndiotactic chain (*35*). The maximum exhibited in Fig. 9 for this polymer is thus a direct consequence of its constitution. This peculiarity manifests itself in the small angle scattering of x-rays and neutrons by predominantly syndiotactic PMMA of high molecular weight (*36*). Scattering intensities are enhanced at angles corresponding, roughly, to distances approximating $\langle r^2 \rangle_0^{1/2}$ at the maximum in Fig. 9. This enhancement, heretofore considered anomalous, is in fact a direct consequence of the structure and configuration of syndiotactic PMMA.

It is thus apparent that subtle features of the chemical architecture of polymeric chains are manifested in their molecular properties. Treatment in terms of the artificial models much in use at present may therefore be quite misleading.

The analysis of the spatial configurations of macromolecular chains presented above is addressed primarily to an isolated molecule as it exists, for example, in a dilute solution. On theoretical grounds, the results obtained should be equally applicable to the molecules as they occur in an amorphous polymer, even in total absence of a diluent. This assertion follows unambiguously from the statistical thermodynamics of mixing of polymer chains (*5, 6, 37*), including their mixtures with low molecular diluents. It has evoked much skepticism, however, and opinions to the contrary have been widespread. These opposing views stem primarily from qualitative arguments to the effect that difficulties inherent in the packing of long chains of consecutively connected segments to space-filling density can only be resolved either by alignment of the chains in bundle arrays, or by segregation of individual molecules in the form of compact globules. In either circumstance, the chain configuration would be altered drastically.

Whereas dense packing of polymer chains may appear to be a distressing task, a thorough examination of the problem leads to the firm conclusion that macromolecular chains whose structures offer sufficient flexibility are capable of meeting the challenge without departure or deviation from their intrinsic proclivities. In brief, the number of configurations that the chains may assume is sufficiently great to guarantee numerous combinations of arrangements in which the condition of mutual exclusion of space is met throughout the system as a whole. Moreover, the task of packing chain molecules is not made easier by partial ordering of the chains or by segregating them (*6, 37*). Any state of organization short of complete abandonment of disorder in favor of creation of a crystalline phase offers no advantage, in a statistical-thermodynamic sense.

Theoretical arguments aside, experimental evidence is compelling in showing that the chains occur in random configurations in amorphous polymers, and further that these configurations correspond quantitatively with those of the unperturbed state discussed above (*38*). The evidence comes from a variety of sources: from investigations on rubber elasticity, chemical cyclization equilibria, thermodynamics of solutions and, most recently, from neutron scattering studies on protonated polymers in deuterated hosts (or vice versa) (*39*). The investigations last mentioned go further. They confirm the prediction made 25 years ago that the excluded volume perturbation should be annulled in the bulk amorphous state (*5*). The excluded volume effect is therefore an aberration of the dilute solution, which, unfortunately, is the medium preferred for physicochemical characterization of macromolecules.

Knowledge gained through investigations, theoretical and experimental, on the spatial configuration and associated properties of random macromolecular chains acquires added significance and importance from its direct, quantitative applicability to the amorphous state. In a somewhat less quantitative sense, this knowledge applies to the intercrystalline regions of semicrystalline polymers as well. It is the special properties of polymeric materials in amorphous phases that render them uniquely suited to many of the functions they perform both in biological systems and in technological applications. These properties are intimately related to the nature of the spatial configurations of the constituent molecules.

Investigation of the conformations and spatial configurations of macromolecular chains is motivated therefore by considerations that go much beyond its appeal as a stimulating intellectual exercise. Acquisition of a thorough understanding of the subject must be regarded as indispensable to the comprehension of rational connections between chemical constitution and those properties that render polymers essential to living organisms and to the needs of man.

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