

Conformation of Macromolecules

A physical chemistry experiment

In 1949 van Holde and Alberty (1) described in THIS JOURNAL a simple viscosity experiment by which the molecular weight of a linear macromolecule may be determined. This type of experiment is now a classic in the field of high polymers. The purpose of this note is to illustrate how, for linear macromolecules, a judicious extension of the original procedure enables most of the elementary concepts of conformational statistics to be demonstrated.

Theory

Conformational Statistics

The conformation of polymer molecules may be specified by one or more of the parameters which measure their average extension in space. Linear polymers are often characterized by their root-mean-square (r.m.s.) end-to-end distance $\langle r^2 \rangle^{1/2}$, defined by

$$\langle r^2 \rangle^{1/2} = \left(\frac{\sum_i n_i r_i^2}{\sum_i n_i} \right)^{1/2}$$

where n_i is the number of molecules having an end-to-end length (see Fig. 2) of r_i . This definition is clearly unsatisfactory for branched polymers, which are multi-ended, and so resort is also made to the r.m.s. radius of gyration $\langle s^2 \rangle^{1/2}$ which is given by

$$\langle s^2 \rangle^{1/2} = \left(\frac{\sum_i n_i s_i^2}{\sum_i n_i} \right)^{1/2}$$

Here s_i is the radius of gyration of the molecule in the i th conformation such that

$$s_i^2 = \frac{\sum_j m_{ij} x_{ij}^2}{\sum_j m_{ij}}$$

where x_{ij} is the distance of the mass element m_{ij} from the center of mass of the i th conformation.

The simplest model of a linear macromolecule to envisage initially is the volumeless, freely-jointed chain composed of n links ($n \gg \gg 1$), each of length l . Freely jointed simply implies that there are no preferred angles between successive chain links and that restrictions to free rotation about these links are absent. The root-mean-square end-to-end length $\langle r^2 \rangle^{1/2}_{0,f}$ of such a random flight chain is given by (2)

$$\langle r^2 \rangle^{1/2}_{0,f} = ln^{1/2} \quad (1)$$

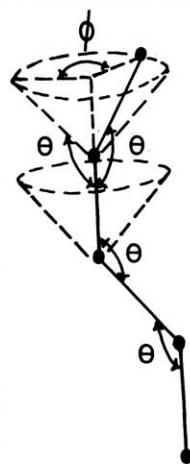


Figure 1. Schematic representation of a short polymer chain showing the valence angle θ and the bond rotational angle ϕ .

For a real macromolecule, allowance must be made for at least three additional properties of the polymer backbone (2): for the bond angles, for restrictions to free rotation about bonds, and for the finite volume of the chain segments. These constraints will be lifted in turn.

First, if the valence angle θ is constant along the backbone (see Fig. 1) then Eyring showed that the r.m.s. end-to-end length becomes

$$\langle r^2 \rangle^{1/2}_{0,f} = ln^{1/2} \left(\frac{1 - \cos \theta}{1 + \cos \theta} \right)^{1/2} \quad (2)$$

where the subscript f denotes free rotation and $0^\circ < \theta < 180^\circ$. When the tetrahedral C—C bond angle is considered, for example, $\cos \theta = -1/3$ and for the freely rotating polymethylene chain $\langle r^2 \rangle^{1/2}_{0,f} = l(2n)^{1/2}$. The influence of restricted valence angle is illustrated in Figure 2.

Second, limitations to free rotation can be incorporated into eqn. (2) through a steric factor σ , giving

$$\langle r^2 \rangle^{1/2}_0 = \sigma \langle r^2 \rangle^{1/2}_{0,f} \quad (3)$$

$$= ln^{1/2} \left(\frac{1 - \cos \theta}{1 + \cos \theta} \right)^{1/2} \left(\frac{1 + \langle \cos \phi \rangle}{1 - \langle \cos \phi \rangle} \right)^{1/2} \quad (4)$$

Equation (4) implies that

$$\sigma = \left(\frac{1 + \langle \cos \phi \rangle}{1 - \langle \cos \phi \rangle} \right)^{1/2}$$

where the averages are taken over all the angles ϕ (see Fig. 1) to which the bond rotations are restricted and $\langle \cos \phi \rangle$ is not too near unity. However, *ab initio* calculation of this short-range steric effect is difficult, and σ is more easily determined experimentally. Commonly its value is in the range 1.5–3.

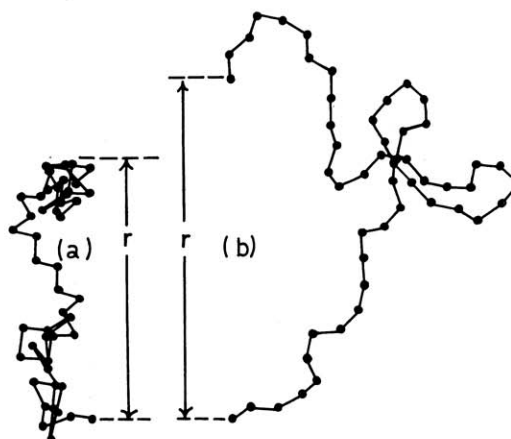


Figure 2. The end-to-end length r of a fifty link chain in a 2-D random walk for (a) a freely jointed chain and (b) a chain with the valence angle restricted to $90^\circ \leq \theta \leq 180^\circ$. After (2).

Third, the finite segmental volumes of real molecules expand their sizes to larger than that calculated from $\langle r^2 \rangle_0^{1/2}$. One index of this long-range intramolecular expansion is α , where

$$\langle r^2 \rangle^{1/2} = \alpha \langle r^2 \rangle_0^{1/2} \quad (5)$$

Here the omission of the subscript zero signifies finite segmental volumes.

Those dimensions of a polymer molecule which are determined solely by bond lengths, by bond angles, and by restrictions to free rotation are termed the unperturbed dimensions and designated by the subscript zero. One example of such dimensions, which are usually taken to be independent of or unperturbed by the nature of the solvent, is obviously $\langle r^2 \rangle_0^{1/2}$. Another example is the unperturbed r.m.s. radius of gyration $\langle s^2 \rangle_0^{1/2}$, which for linear random coil macromolecules is related to $\langle r^2 \rangle_0^{1/2}$ through

$$\langle s^2 \rangle_0^{1/2} = (\langle r^2 \rangle_0 / 6)^{1/2} \quad (6)$$

It has previously been mentioned that the finite segmental volumes of real molecules increase their size to larger than the unperturbed. This can be counteracted by dissolving the macromolecules in somewhat poorer solvents. When the dimensional contraction resulting from the poorer solvency exactly cancels the increase in size due to the finite segmental volumes, the solvent is termed a theta (Θ) solvent. Clearly, macromolecules adopt their unperturbed conformations in Θ -solvents, as, for example, does polystyrene in cyclohexane at 34°C. When, however, polymers are dissolved in good solvents, such as when polystyrene is dissolved in toluene, segment-solvent contacts are energetically more favorable than segment-segment contacts. The macromolecules accordingly expand to maximize such contacts, consistent with their attainment of the minimum Gibbs free energy state. The expansion factor α then exceeds unity.

Viscosity

Let η_0 = viscosity of the solvent, η = viscosity of the solution, and c_2 = polymer concentration. The important derived viscosity functions are listed in the table. The intrinsic viscosity (also termed the limiting viscosity number) is usually assumed to be shear independent. The polymer concentration may be expressed in grams per deciliter; units of $[\eta]$ then become dl/g.

The presence of the dissolved macromolecules in the solution increases the energy dissipation in laminar flow over that for the pure solvent. This is a consequence of the perturbation of the solvent flow by the polymer segments. Flexible linear macromolecules in solution behave hydrodynamically as though they were solvent-impermeable cores with peripheral solvent-

permeable segments. The Kirkwood-Riseman theory (3) for the intrinsic viscosity of such macromolecules, of molecular weight M_2 , yields

$$[\eta] = \Phi \langle r^2 \rangle_0^{3/2} / M_2 \quad (7)$$

where Φ is a universal constant. The best value of Φ predicted theoretically for a polymer of homogeneous molecular weight is 2.84×10^{21} , where $[\eta]$ is expressed in dl/g and $\langle r^2 \rangle_0^{1/2}$ is in cm. Experimentally Φ has been found to lie in the range $(2.0-2.5) \times 10^{21}$ for unfractionated and partially fractionated polymers, with perhaps the best value to-date being $2.1 (\pm 0.2) \times 10^{21}$. Equation (7) is easily (4) transformed into the Flory-Fox formulation by inserting eqn. (5),

$$[\eta] = \Phi \alpha^3 \langle r^2 \rangle_0^{3/2} / M_2 = K \alpha^3 (M_2)^{1/2} \quad (8)$$

where $K (= \Phi \langle r^2 \rangle_0^{3/2} / M_2^{3/2})$ is a constant for a given polymer.

Obviously by measuring the intrinsic viscosity $[\eta]_\Theta$ of a macromolecule in a Θ -solvent, its unperturbed r.m.s. end-to-end length can be calculated from

$$\langle r^2 \rangle_0^{1/2} = ([\eta]_\Theta M_2 / \Phi)^{1/3} \quad (9)$$

The expansion factor in good solvents may be determined from viscosity measurements using

$$\alpha_\eta = ([\eta] / [\eta]_\Theta)^{1/3} \quad (10)$$

where the subscript η signifies the method of measurement.

Equation (8) suggests, and experiments confirm, that the molecular weight can be estimated in a Θ -solvent ($\alpha = 1$) from an expression of the form

$$[\eta]_\Theta = K_\Theta^* (M_2)^{1/2} \quad (11)$$

The value of the constant K_Θ^* for polystyrene in cyclohexane at 34°C is found experimentally (5) to be $8.2 (\pm 0.2) \times 10^{-4}$ for polymers in the molecular weight range of $(2-400) \times 10^4$. The more general form of eqn. (8) can also be recast into the empirical Mark-Houwink relationship,

$$[\eta] = K^* M_2^a \quad (12)$$

where normally $0.5 \leq a < 1$ and both a and K^* are constants for a given molecular weight range of a particular polymer. Results for linear polystyrene in the molecular weight range $(1-5) \times 10^5$ in toluene at 34°C yield (6)

$$K^* = 1.15 \times 10^{-4}$$

and

$$a = 0.72$$

The foregoing theories are best applied to rigorously monodisperse molecular weight polymers. When applied to polydisperse systems, rather complicated averages result. For example, the viscosity average molecular weight $\langle M_v \rangle$ derived from the application of the Mark-Houwink equation is

$$\langle M_v \rangle = \left(\frac{\sum_i n_i M_i^{1+a}}{\sum_i n_i M_i} \right)^{1/a} \quad (13)$$

where n_i is the number of macromolecules of molecular weight M_i . $\langle M_v \rangle$ obviously varies with the exponent a but since $0.5 \leq a < 1$, it lies somewhere between the

Derived Viscosity Functions

Name	Viscosity symbol	Definition	Comments
Relative Specific	η_{rel} η_{sp}	η / η_0 $(\eta - \eta_0) / \eta_0$	Dimensionless ratio Increment due to all solute molecules
Reduced	η_{red}	η_{sp} / c_2	Increment per unit solute concentration at a given concentration
Intrinsic	$[\eta]$	$\lim_{c_2 \rightarrow 0} \eta_{red}$	Eliminates solute intermolecular interactions

number average ($\langle M_N \rangle = \sum_i n_i M_i / \sum_i n_i$) and the weight average ($\langle M_w \rangle = \sum_i n_i M_i^2 / \sum_i n_i M_i$) molecular weight. The value of $\langle M_V \rangle$ measured in good solvents is often within 20% of the value of $\langle M_w \rangle$.

The reduced viscosity at finite polymer concentrations may be expanded in the binomial form

$$\eta_{sp}/c_2 = [\eta] + k'[\eta]^2 c_2 \quad (14)$$

where k' , termed the Huggins constant, for uncharged flexible polymers in good solvents is commonly ~ 0.35 – 0.40 .

Experimental

The experimental measurements to be made are very simple: the intrinsic viscosity of polystyrene in cyclohexane and in toluene is determined at 34°C. For the purposes of developing this experiment, a broad molecular weight sample of polystyrene, from the National Bureau of Standards, Washington, D. C., was examined; $\langle M_w \rangle$ determined by light scattering was reported to be 257,800 (± 930) with $\langle M_w \rangle : \langle M_N \rangle = 2.1:1$. Bradbury (7), however, has described in THIS JOURNAL conditions for the bulk polymerization of styrene which yield polymer of comparable molecular weight. Fractionation by the method of Bianchi and Magnasco (6) is desirable but not essential. The measurement of intrinsic viscosity has been described previously (1) and only minor points deserve comment. First, dissolution of polystyrene in cyclohexane at 34°C is facilitated by a short exposure to low intensity ultrasonic radiation; once formed, the solution should be maintained at that temperature. Second, a Cannon-Fenske viscometer with a flow time for water of ~ 7 min is suitable for this molecular weight polymer, when studied at concentrations in the range 0.1–0.5 g/dl.

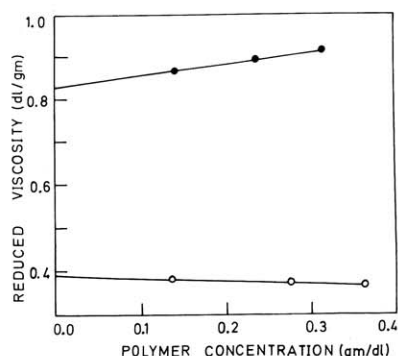


Figure 3. Plots of reduced viscosity versus polymer concentration for polystyrene at 34°C in toluene (solid circles) and cyclohexane (open circles).

Results and Calculations

An example of student results is given in Figure 3. The intrinsic viscosity measured in cyclohexane was 0.390 dl/g, which compares favorably with the N.B.S. value of 0.395 dl/g. The value increased in toluene, as the polystyrene expanded, to 0.835 dl/g. From the data, more than ten derived quantities may be calculated. These are listed below, together with the numerical values, placed in parentheses, for the standard polystyrene

(1) calculate $\langle M_V \rangle$ from both eqn. (11) (226,000) and from eqn. (12) (230,000)

(2) compute an average value for $\langle r^2 \rangle_0^{1/2}$ from eqn. (9) (348 Å). The best value of M_2 to insert into this equation is $\langle M_N \rangle$ but since it is usually unknown, the value of $\langle M_V \rangle$ measured in cyclohexane will suffice. The average of $\langle r^2 \rangle_0^{1/2}$ so calculated will differ by less than 20% from that derived from $\langle M_N \rangle$

(3) calculate an average value for $\langle s^2 \rangle_0^{1/2}$ from eqn. (6) (142 Å)

(4) estimate an average value for $\langle r^2 \rangle^{1/2}$ in toluene using eqn. (7) (448 Å). Again the value of $\langle M_V \rangle$ measured in cyclohexane is used for M_2

(5) calculate an average value of α_n in toluene at 34°C from eqn. (10) (1.29). A literature value (6) for α_n for well-fractionated polystyrene of comparable molecular weight is 1.25

(6) determine an average number of bonds per molecule ($\langle n \rangle$) from the value of $\langle M_V \rangle$ in cyclohexane (4350)

(7) calculate a value for $\langle r^2 \rangle_0^{1/2}$ from eqn. (2) taking the C—C bond length as 1.54 Å and $\theta = 109^\circ 28'$ (145 Å)

(8) estimate σ from eqn. (3) (2.4). This may be compared with the literature value (8) of ~ 2.4

(9) compute an average for the fully-stretched, planar zig-zag length of the macromolecule using $\langle n \rangle$ (5470 Å). Calculate what percentage of this contour length $\langle r^2 \rangle_0^{1/2}$ is (6.4%)

(10) determine the least squares value of k' in toluene using eqn. (14) (+0.35). No reliance can in general be placed on student values of k' determined in Θ -solvents.

Discussion

These calculations demonstrate that, from few experimental data, the numerical values of many macromolecular characteristics of a sample of polystyrene can be determined. In addition to the molecular weight, the contour length, the unperturbed dimensions, the expansion factor, the chain flexibility index, and the Huggins constant are all calculable. The numbers in addition highlight the colloidal nature of high polymer solutions, even in the random coil conformation. Any viscosity procedure suffers as yet from the disadvantage of not being absolute: prior calibration by other methods (e.g., light scattering or osmometry) is necessary. For this experiment, as commonly happens, the requisite data are readily available in the literature.

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