Internal Viscosity of Polymers and the Role of Solvent Resistance

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ABSTRACT: A brief review is made of internal viscosity (IV) theories for polymer chain dynamics in dilute solution. The nature of the IV parameter ϕ is discussed, including contributions from both the polymer (ϕ°) and the solvent (ϕ_s). A previous model by Peterlin proposes additivity in the sense $\phi = \phi^\circ + \phi_s$. Here, we present a new interpretation based on the view that the solvent at this level cannot be considered a continuum (as has previously been the case). Arguments based on free-volume constraints to chain rotation lead to a model of the form $\phi = \phi^\circ\phi_s$. This result is compared with recent data on non-Newtonian viscosity (η) of polystyrene Θ solutions that exhibit a previously unreported anomalous dependence on solvent viscosity (η_s). The latter, inconsistent with most theories of chain dynamics, can be explained by a properly formulated IV theory because of $\phi_s(\eta_s)$. Curve-fitting the η data, including the η_s anomaly, with the Bazua–Williams IV theory leads to values of ϕ/f (where f is a "bead" friction coefficient) with temperature dependence and parameter dependence in agreement with the new model for ϕ.

Introduction

The internal viscosity (IV) force in modeling polymer chain dynamics was first suggested by Kuhn and Kuhn[1] and subsequently implemented by Cerf,[2,3] Peterlin,[4,5] and Peterlin and Reinhold[6] to describe linear viscoelastic and optical properties of dilute polymer solutions in dynamic experiments. Important successes for IV theory included the ability to fit high-frequency dynamic rheological data[7,8] and dielectric relaxation data,[9] plus the prediction of nonlinear properties (e.g., non-Newtonian viscosity) that were beyond the scope of most molecular dynamic models. Despite this extended and successful history, the physical meaning of IV continues to be a subject of controversy and the IV model is still not widely accepted. Three reasons for this lack of acceptance are (1) lack of definitive and unambiguous experimental evidence of the existence of an IV force, (2) controversial mathematical features of the formulation of several IV theories, and (3) the historical lack of a unified approach to explaining the origins of the IV force from a molecular point of view, together with a great diversity in recent attempts to do so. While the first two points have been addressed elsewhere,[9-11] the third point is the principal subject here.

Ideally, we would like to model the polymer molecule as a series of monomer units connected by bonds of fixed length with fixed angles between adjacent bonds. Changes of configuration would occur by a series of bond rotations hindered by local energy barriers of various kinds.[9,12] Solvent molecules in this model would be treated as separate particles rather than as a continuum. The complete model of the polymer solution would be the system of all polymer molecules plus all solvent molecules.

At this level of modeling there would be no need for an IV force. All intermolecular and intramolecular forces acting on a particle could be described in terms of potentials which depend only on the distances between that particle and other particles in the system. Curtiss, Bird, and Hassager[13] developed a generalized phase–space kinetic theory that could be used, in principle, to evaluate the distribution function for this system from the Liouville equation. In practice, however, useful results can be obtained only after a series of approximations have been made to simplify the system (i.e., the submolecule approximation and the continuum solvent approximation).

When the submolecule approximation has been made, with the entire chain replaced by a sequence ($i = 0, 1, 2, \ldots N$) of "submolecules" composed of 10–20 monomer units, there is no longer a one-to-one correspondence between system points ("beads") in the mathematical model and actual particles (monomer chain units) in the physical system. Instead, a system point must represent the behavior of many particles. At this level of modeling, the set of forces (contractile and frictional) acting on a bead must approximate the much larger set of intermolecular and intramolecular forces that operate on the monomer units contained within the submolecule.

The contractile force law for the hypothetical "connector" segment between beads is discussed most easily in the two-bead case ("dumbbell"; $i = 0, 1$) where the bead separation vector is **R** and its equilibrium length is b. Rather than being expressed in terms of a simple two-particle potential, contractile ("spring") forces are now given by[12,14]

$$\mathbf{F}_0^{\mathrm{sp}} = -\mathbf{F}_1^{\mathrm{sp}} \equiv \mathbf{F}^{\mathrm{sp}}(\mathbf{R}) = -\kappa T\left(\frac{\partial \ln Z}{\partial \mathbf{R}}\right) = -\kappa T\left(\frac{\partial \ln \psi_0}{\partial \mathbf{R}}\right) \tag{1}$$

in which ψ_0 is the equilibrium distribution function for an equivalent free chain and Z is the configurational partition function for a constrained chain with end-to-end vector **R**. (An expression identical in form with eq 1 but evaluated with the nonequilibrium distribution function ψ produces the so-called Brownian force $\mathbf{F}_i^{\mathrm{B}}$.) This connector force law can be expressed as a function of position coordinates alone. The solvent drag force, however, is represented as a viscous relationship

$$\mathbf{F}_i^{\mathrm{v}} = -f(\mathbf{V}_i - \mathbf{V}_i^{\mathrm{s}}) \tag{2}$$

where **V** and $\mathbf{V}^{\mathrm{s}}$ are velocities of the bead and solvent and f is the friction coefficient. Note that eq 2 is not expressed in terms of a potential that depends on position. Similarly, the IV forces ($\mathbf{F}^{\mathrm{iv}}$) are expressed in terms of velocity differences rather than in terms of a potential.[15]

In most IV theories, IV forces are not intended as a modification to Z used in eq 1. Internal viscosity is used to correct the Rouse–Zimm force balance ($\mathbf{F}^{\mathrm{v}} + \mathbf{F}^{\mathrm{sp}} + \mathbf{F}^{\mathrm{B}} = 0$) for extra solvent drag and kinetic effects associated with deformation rates which cannot be adequately represented by $\mathbf{F}^{\mathrm{v}}$ in eq 2. It would perhaps be logical, then, to express IV as a modified friction force operating on beads rather than on submolecules. However, deformations are associated with submolecules rather than beads,

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and so the IV force must be specified for submolecules even though it is not usually considered part of the contractile force as given by eq 1.

Internal Viscosity Models

While IV research in the 1950s and 1960s was concerned largely with model formulation and predictions, several workers in the 1970s and 1980s became interested in elucidating the molecular origins of IV forces. Kuhn and Kuhn[1] originally proposed that IV forces resulted from intrachain kinetic resistance to bond rotation (at the monomer unit level) through potential energy barriers, which impedes chain deformation by retarding local configurational change. This concept has been retained in most contemporary theories.

Bazua and Williams[16] have applied the intrachain energy barrier concept at the monomer unit level to develop a quantitative IV theory. In this theory, a 3-fold rotational potential (possibly asymmetric) is assigned to each bond along the polymer chain backbone. The energy barrier to a given bond rotation is taken to be the activation energy for an equivalent isomerization reaction. Absolute rate theory is then employed to specify the rates of change to and from a given configuration. At equilibrium these rates are balanced and no net change occurs. When an external force is applied, the potential energy field is biased and a configurational change occurs at a finite (nonequilibrium) net rate in the direction of the applied force. The velocity difference between the end points of a subchain of monomer units is related to the net rate of configurational change, which in turn depends on the applied force. When a tensor expression of this relationship is inverted, an IV force is obtained as a linear function of deformational velocity. The IV coefficient, ϕ, depends on the number of monomer units in a subchain, but not (to a good approximation) on the number of subchains in the macromolecule. Since the Bazua–Williams approach considers only intrachain potential energy terms, the resulting IV coefficient (designated ϕ° in this limit) is independent of solvent viscosity.

Peterlin[17,18] expanded the IV concept to include solvent–polymer interactions as well as intrachain interactions. Solvent viscosity effects are taken into account in a semiquantitative way by examining the motions of monomer units in a short subchain of the macromolecule. Peterlin has reasoned that the fixed bond angle structure will require transverse orbital motions of intermediate monomer units to accompany any change in the distance between the end units. These transverse motions give rise to extra frictional work that is not characterized by f in eq 2. To rectify this discrepancy, the Peterlin formulation adds a term (ϕ_s) proportional to solvent viscosity (η_s) to the solvent-independent $\mathbf{F}^{iv}$ term that was studied by Bazua and Williams; thus, $\phi = \phi^\circ + \phi_s$ according to Peterlin. Then, at high η_s, $\phi \cong \phi_s \propto \eta_s$.

Cerf[19,20] has given a derivation of ϕ from molecular origins. While Peterlin[17,18] and Bazua and Williams[16] consider isolated aspects of bond-level subchain mechanics and apply the resulting IV forces to the Rouse–Zimm coil, Cerf starts from a different point of view. Beginning with a stochastic approach rather than the diffusion equation approach, Cerf expresses the probability of local chain rearrangement as a point function, using a result of Kramers[21] for a particle embedded in a viscous medium, which may escape over a potential barrier. Point functions for the probability of configurational transitions are then used by Cerf in Iwata's[22] master equation for Brownian motion of the polymer chain. A coarse-graining technique smooths Iwata's master equation to a continuous diffusion equation. When terms of this diffusion equation are compared to Rouse–Zimm theory, extra terms arise that Cerf identifies with IV. Like Peterlin, Cerf includes the possibility of both η_s-dependent and η_s-independent contributions to ϕ.

The mode dependence (normal modes $p = 1, 2, \ldots N$) of the IV contribution is a source of some controversy. In the Bazua–Williams model,[10,16] $\mathbf{F}^{iv}$ is initially cast in laboratory coordinates with a scalar coefficient ϕ multiplying deformational velocity differences, a framework that leads directly to a normal-coordinate form $\phi_p = \phi\lambda_p$ where $\lambda_p(p;N)$ is an eigenvalue (consequently, $\phi_p \cong \phi p^2/N^2$ for the lower p/N in the free-draining case). In contrast, the Cerf–Peterlin models[3-6] insert IV only in the normal-coordinate framework, with the ad hoc form $\phi_p = \phi p/N$. These different N dependencies—i.e., molecular weight effects—have still not been resolved. de Gennes[23] has argued that the normal-coordinate formulation can be justified by considering intramolecular segment–segment friction, but this still does not establish the form of $\phi_p(p;N)$.

MacInnes[24] has also applied a coarse-graining technique to stochastic equations to study IV. He uses arguments concerning the relative magnitudes of correlation times (polymer–solvent interaction and intrachain interaction times vs. the selected coarse-graining time) to demonstrate that ϕ should be independent of η_s at low η_s and linearly proportional to η_s at high η_s. The polymer chain is modeled as a series of beads in MacInnes's theory, but the physical interpretation of his beads is somewhat enigmatic. Identification of the bead at a near-monomer level is suggested by the use of rotational potentials to characterize interaction between the $(n-2)$th and $(n+2)$th beads. This results in IV forces proportional to deformational velocity differences between *alternate* beads of the chain rather than between adjacent beads. At the same time, though, a $\mathbf{F}^{sp}$ is introduced that operates between adjacent beads, suggesting a submolecule-level interpretation for each bead.

Two recent theories have given a somewhat different interpretation to IV. In the model of Allegra[25] and Allegra and Ganazzoli,[26,27] IV arises because subchains of the macromolecule are temporarily cast into a nonequilibrium distribution of (small scale) configurations following a deformation. This hypothesis leads to a departure from the equilibrium partition function and, hence, a departure from the entropy spring force given in eq 1. Absolute rate theory arguments, similar to those of Bazua and Williams,[16] are used to express the nonequilibrium deviation from $\mathbf{F}^{sp}$ in terms of $\mathbf{F}^{iv}$. The resulting integro–differential equation (incorporating local memory/elastic effects by means of the integral) then replaces the usual diffusion equation.

Adelman and Freed[28] derive generalized Langevin equations of motion for the Rouse modes. They then show that "memory" terms in these equations account for deviations from Rouse–Zimm dynamics and associate these terms with IV. Anharmonic mechanisms are proposed to give rise to internal friction and mode coupling which can be represented by an IV force term with $\phi_p = \phi p/N$. This latter result gives some theoretical support for the Peterlin–Cerf formulation; however, anharmonic mechanisms may be associated with a non-Gaussian distribution function and consequently a nonlinear entropic spring force, and it is not clear how to treat this problem and IV simultaneously.

It is evident that there is considerable theoretical support for the existence of IV but also considerable diversity of opinions as to its origins. The theories are not mutually exclusive, and all of the proposed mechanisms may contribute to a generic IV force. The more general theories, such as those of Cerf[19,20] and Adelman and Freed,[28] are the most rigorous and the most convincing in demonstrating the justification for using IV within the Rouse–Zimm framework. Simulations of molecular dynamics by Fixman[29] also lend support, showing that stress calculations for a linear chain having constant bond lengths, fixed bond angles, and a threefold bond rotation potential (but no explicit internal viscosity force term) resemble predictions made for Rouse–Zimm models that incorporate IV. However, for all this support, there remains no convenient or well-accepted way to predict the magnitude of ϕ.

Theory

General Considerations. Two possible sources of the IV force have gained wide acceptance: (a) internal resistance to local polymer configurational change, resulting from intrachain energy barriers to bond rotation (leading to ϕ° when operating alone), and (b) external resistance to local configurational change, due to the presence of a viscous solvent (leading to ϕ_s when operating alone). Workers dealing with IV models have often assumed, following Peterlin,[17,18] that these two resistances would be separate *additive* contributions to ϕ, but the present development challenges that assumption. (Contrary evidence was also available earlier,[9] such as the effective activation energies for fast relaxations in polymer solutions being additive over the activation energies of polymer bond rotation and solvent viscosity.) We will use the Bazua–Williams model as a basis to develop an alternative representation for ϕ which unifies the concepts of an internal rotational potential and an external solvent resistance. In the process of formulating this theory we will also examine two of the key assumptions of the Peterlin treatment, namely that (1) solvent-dependent and solvent-independent contributions to the IV force are additive and (2) a continuum treatment of the solvent is appropriate.

The Bazua–Williams IV theory[16] develops, in a rigorous way, the relationship between rates of individual configurational-state transitions and the overall rate of deformation of a segment of the polymer chain. The rates for configurational-state transitions are determined from absolute rate theory with activation energies obtained from the potential function for bond rotation. At equilibrium these rates are balanced so that no net change of configuration occurs. When an external force is applied to a chain segment, however, the bond rotational potential is biased in the direction of the applied force. At the bond level this causes an imbalance in the rates of configurational-state transitions and a net rate of change of configuration which corresponds to a finite deformational velocity at the submolecule level. The vectorial relationship between the net rates of configurational change for individual bonds and the relative velocity of the ends of a chain segment is established by multiplying the individual rates by a series of geometry-related tensors that transform the resultant motions from the coordinate system of each bond to the laboratory coordinate system. These rates are then ensemble-averaged to determine the overall deformational velocity of the segment.

The Bazua–Williams theory does not include hindrance to bond rotation from the surrounding solvent. We may anticipate, however, that this effect will be very important when the polymer molecules is dissolved in a viscous solvent. In this case, a chain bond must simultaneously satisfy two conditions to complete a transition: (1) It must have sufficient energy to surmount the the rotational potential barrier. (2) It must overcome the resistance of the solvent either by having extra energy or by finding itself adjacent to a void space so that, for that particular transition, the solvent resistance is zero. This second condition will greatly reduce the rates of all configurational-state transitions. The presence of a viscous solvent will not affect the rotational potential functions or the amount by which they are biased by an external force, however, and the geometry of the chain will certainly remain unchanged. Therefore the BW theory can be modified to account for the effects of a viscous solvent by simple modifications of the previous rate expressions for configurational change.[16]

The nature of these modifications will depend on whether the solvent is treated as a continuum or as a collection of discrete particles. If the radius of the solvent molecules, r_s, is small compared to r_p, the scale of the polymer's rotating unit (i.e., the bond and its associated structural elements), the continuum approximation may be invoked by assigning a friction factor to each rotating unit. This approximation has commonly been used in the work of others, but not with the necessary justification (i.e., $r_s \ll r_p$). When the solvent molecules are of a size comparable to or larger than the rotating polymer bond, the continuum approximation is not appropriate and a more refined theory of the liquid state must be applied. The molecular dimensions of most (if not all) viscous solvent molecules fall into the second category, so we will base our treatment on this case.

Free Volume. Since solvent molecules are similar in scale to the rotating units of the polymer chain, mechanisms for configurational change must involve the structure of the solvent as well as that of the polymer chain. Fortunately, a straightforward approach to this problem is suggested by free-volume theories (Haward[30]) and significant-structure theories (Eyring[31]) of the liquid state.

These theories depict the liquid state as a partially ordered collection of molecules in which there is a distribution of accessible void spaces or "free volume". Motions of an individual molecule are constrained by the presence of surrounding molecules, but a positional change may occur if the molecule is situated next to a sufficiently large void space. This concept may easily be applied to rotating units of the polymer chain by postulating that a change of configuration $C_i \rightarrow C_j$ can occur only when a void space of volume v_{ij}^* is accessible to the rotating unit or units involved in the change.

The earlier prediction[16] of rates of configurational-state changes (R_{ij}°) applies in the absence of solvent molecules; when solvent molecules are present, the rates are reduced according to the probability of finding sufficient accessible free volume for the changes to occur. Specifically, the rate R_{ij} for $C_i \rightarrow C_j$ is reduced in terms of $P(v_{ij}^*)$, the simultaneous probability of an accessible void space larger than the minimum required volume v_{ij}^*:

$$R_{ij} \equiv P(v_{ij}^*)R_{ij}^\circ = P(v_{ij}^*)P(C_i)k_{ij} \exp[\Delta E_{ij}/\kappa T] \quad (3)$$

Thus, the total rate is a *product* of a solvent-dependent probability and a solvent-independent probability. The function $P(C_i)$ is the probability of finding the rotating bond in configurational state i; k_{ij} is a rate constant; and ΔE_{ij} is the amount by which the chain rotational potential energy barrier deviates from its equilibrium value due to an imposed force.

We will illustrate this in terms of a generic chain of carbon–carbon backbone bonds having three configurational states: t, g^+, and g^-. The spatial locations of these states are close to being symmetric about the axis of the bond. Transitions $C_i \rightarrow C_j$ between any pair of adjacent states traverse arcs that are roughly equal; therefore, they will require approximately the same accessible void volume, v_{ij}^*. If we restrict our attention to polymers with identical bond units such as polyethylene, we may consider the v_{ij}^* for all $C_i \rightarrow C_j$ and for all bonds of the chain to be equal to each other, hereafter designated v^*. Similarly, all $P(v_{ij}^*)$ will be equal to the single value $P(v^*)$. For this case the rates given by eq 3 can be multiplied by the appropriate geometric tensors and summed, as described by eq 35 and 42 of Bazua and Williams.[16] The result of this procedure is a modified expression for $\mathbf{V}^d$, the submolecule deformational velocity:

$$\mathbf{V}^d = P(v^*)(\mathbf{V}^d)^\circ = P(v^*)(\mathbf{A} \cdot \mathbf{F}^d) \qquad (4)$$

where $\mathbf{F}^d$ is the deformational force and $\mathbf{A}$ is a matrix that emerges naturally from the summation cited above.[16] Averaging eq 4, followed by inversion to solve for $\mathbf{F}^d$ ($=\mathbf{F}^{iv}$), leads directly to the overall IV coefficient ϕ:

$$\phi = \phi^\circ / P(v^*) \qquad (5)$$

To complete the analysis, an expression for $P(v^*)$ is needed. Cohen and Turnbull[32] have evaluated this probability in connection with their theory of self-diffusion in liquids and glasses:

$$P(v^*) = \exp\left[\frac{-\gamma v^*}{v_f}\right] \qquad (6)$$

where the constant γ is a number close to unity and the accessible solvent free volume v_f is defined as $v_f = v_s(T) - v_s(0)$. Here, $v_s(T)$ is the average volume per solvent molecule at prevailing temperature T, and $v_s(0)$ is the volume per solvent molecule at 0 K. Note that v^* will be a property of the solute polymer. A volume equal to that of an isolated rotating unit would be sufficient to allow rotation of a single bond of the chain segment. In a polymer, however, the portions of the chain segment that sequentially follow the rotating unit execute a cooperative configurational change[9] for which the total required volume is given approximately by

$$v^* \equiv q v_1 \qquad (7)$$

where v_1 is the volume occupied by a single rotating bond unit and q is the number of units that actively participate in the deformation. The probability of finding an accessible voidage greater than or equal to v^* is then, from eq 6 and 7,

$$P = \exp\left(\frac{-q\gamma v_1}{v_f}\right) \qquad (8)$$

A given bond may rotate, however, if it is in any one of q positions, so the desired probability of rotation is approximately

$$P(v^*) \cong q \exp\left[\frac{-q\gamma v_1}{v_f}\right] \qquad (9)$$

Equation 9 can be combined with eq 5 to give

$$\phi = q^{-1}[\exp(+q\gamma v_1/v_f)]\phi^\circ \qquad (10)$$

where ϕ° is IV due to internal chain energy barriers alone. Note that eq 10 predicts that solvent effects are *multiplicative* with chain energy-barrier effects, unlike the *additive* dependence employed by Cerf–Peterlin theory.

It is not easy to make an a priori determination of the parameter q. The shortest sequence of chain units that can undergo a self-contained extension is a triad of bonds, so the lower limit for q is 3. We might expect q to be somewhat larger than this lower limit but much smaller than the number of bonds in a submolecule (~20). Since q is determined solely from the geometry of the polymer chain, it should be independent of the physical properties of the solvent. Using geometric arguments Peterlin[18] has estimated $q = 5$ for a polyethylene-like chain.

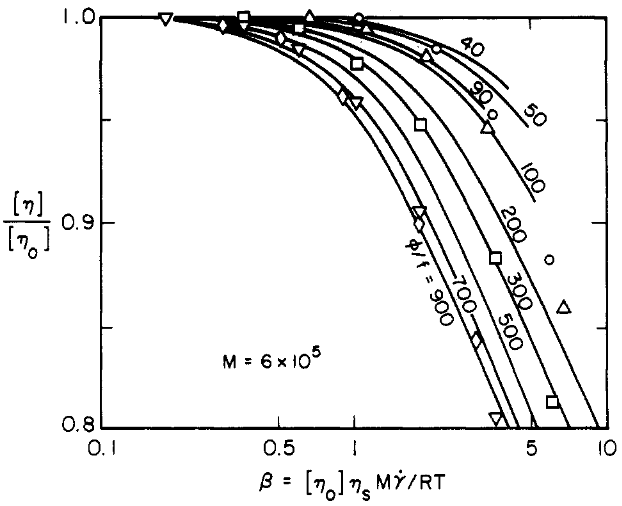

Figure 1. Reduced-variable display of non-Newtonian intrinsic viscosity for Θ solutions of monodisperse polystyrene with $M = 6 \times 10^5$. Each curve represents a different solvent viscosity; from left to right, in units of Pa·s: 0.22 (◇), 0.45 (▽), 5.1 (□), 8.7 (△), 27.4 (○) for data.[34] Solid lines give the predictions of eq 12 with the designated values of ϕ/f and the exact eigenvalues using $h^* = 0.15$ (and $N = M/M_{sub} = 258$).

Experimental Confirmation

The internal viscosity theory proposed in eq 10 can be tested by experimentally determining ϕ for a given polymer solute in solvents that give a range of values for v_1/v_f. According to eq 10, a plot of such data in the form ln ϕ vs. v_1/v_f should be linear. Furthermore, the magnitudes of q and ϕ° determined from such a plot should be physically reasonable.

Most often, ϕ has been determined in the past from dynamic viscosity experiments. However, when such data have been obtained with Θ solutions (for which the Gaussian chain statistics required by the theory are valid), the η_s magnitudes have been small—near 1 mPa·s—and have had very restrictive range (hence, limited v_1/v_f range). The use of solvents with higher η_s, such as chlorinated biphenyls (e.g., the Aroclors from Monsanto) for polystyrene, has always led to non-Gaussian statistics, so those data are inappropriate to apply here. Both types of conflict were overcome by the development of a new class of Θ solvents,[33] composed of a blend of low-molecular-weight polymer (the same kind as used for the high-molecular-weight solute) with a monomeric diluent. These blends produce Θ solvents even when large amounts of diluent (up to 70%) are present and also over a wide range of temperatures. Variation of the solvent blend ratio or the temperature causes a wide range of η_s and v_1/v_f to occur.

We recently conducted experiments using this strategy.[34] With two solvent blends of polystyrene/styrene (in 0.5/0.5 and 0.625/0.375 ratios w/w) and a monodisperse polystyrene solute of $M = 6 \times 10^5$, solutions were prepared at several concentrations and their non-Newtonian viscosities $\eta(\dot{\gamma})$ measured over a range of temperatures; here, $\dot{\gamma}$ is shear rate. Extrapolation to the dilute limit produced the intrinsic viscosities $[\eta(\dot{\gamma})]$ at each temperature, corresponding to a different value of η_s in each case. These data are plotted in dimensionless form, as shown in Figure 1, with the variable β:

$$\beta = \frac{[\eta_0]\eta_s M\dot{\gamma}}{RT} \qquad (11)$$

Plots of $[\eta]/[\eta_0]$ vs. β are predicted by most theories to accommodate all the η_s and $\dot{\gamma}$ dependence in such experiments. However, Figure 1 shows that an additional η_s dependence resides in the data; as η_s increases, the onset of non-Newtonian effects in these reduced variables is delayed to higher β. Such behavior

Table I
Experimentally Determined Parameters

system	η_s, Pa·s	ϕ/f	v_1/v_f
series I, 8 °C	27.4	40	3.15
series I, 16.5 °C	8.7	90	3.00
series I, 24 °C	5.1	300	2.88
series II, 24 °C	0.46	700	2.69
series II, 40 °C	0.22	850	2.47

has apparently never been seen before, presumably because η_s values were too small or covered too narrow a range or both. Our contention is that this phenomenon is a manifestation of IV in a general sense and also that it can be explained quantitatively by the theory presented above.

Values for ϕ/f were determined by comparing experimental $[\eta(\beta)]/[\eta_0]$ to the prediction[10]

$$\frac{[\eta(\beta)]}{[\eta_0]} = 1 - (1 - 2\epsilon) \sum_{p=1}^{N} \left[\frac{\lambda_p \phi/f}{(\lambda_p \sum_{k=1}^{N} \lambda_k^{-1})(1 + \lambda_p \phi/f)} \right] \tag{12}$$

where N is the number of submolecules and the dimensionless angular velocity of the coil, ϵ, is given implicitly by

$$\sum_{p=1}^{N} \left[\frac{1 - 2\epsilon}{1 + \lambda_p \phi/f} - \frac{2\beta^2 \epsilon}{[\lambda_p \sum_k \lambda_k^{-1}]^2 + 4\beta^2 \epsilon (\lambda_p \phi/f)(1 + \epsilon \lambda_p \phi/f)} \right] = 0 \tag{13}$$

The exact eigenvalues λ_p were obtained from Lodge and Wu,[35] using for interpolation between their tabulated values the functions recommended by Thurston.[36] This curve-fitting process was employed by McAdams[37,38] to fit an even larger set of data on similar fluids, yielding $N = 258$ and $h^* = 0.15$, where h^* is the hydrodynamic interaction parameter, and these parameters were used here.

In Figure 1, the curves drawn through the data represent the predictions of eq 12 and 13 for the specified values of ϕ/f. At low η_s, the data are well matched by the high-ϕ/f curves. For higher η_s, lower values of ϕ/f are indicated, and data departures from the IV curves become more evident as η_s is increased. McAdams and Williams[38] have noted similar deviations between data and IV-predicted curve shapes, which they attribute to non-Gaussian extension of the polymer coil. The results shown in Figure 1 are consistent with that explanation, since non-Gaussian behavior is expected to occur at earlier β for lower values of ϕ/f (i.e., for higher η_s).

Quite apart from the quality of the curve fits in Figure 1 is the unmistakable trend for ϕ/f to decrease as η_s (and hence f) increases. (A similar trend emerges from fitting various forms of the nonlinear Peterlin–Cerf model to such data, though values of ϕ/f characterizing the curves would differ from those in Figure 1.) This shows that ϕ is not necessarily proportional to η_s as is commonly believed,[9,39] but that other factors beyond the continuum parameter η_s are involved at the molecular level. The fact that low-η_s solvents come closest to yielding $\phi \propto \eta_s$ suggests that this proportionality characterizes the local diffusion phenomenon when adequate free volume exists. Deviations with high-η_s solvents (as in Figure 1) must be attributed to diffusion that is free-volume limited.

Values for ϕ/f are determined by matching the IV predictions to low-β data for high η_s and to a broader range of β for lower η_s; both ϕ/f and η_s are listed in Table I, along with the η_s-related parameter v_1/v_f calculated as described in the Appendix. Since f is directly proportional to η_s, the dependence of $(\eta_s\phi/f)$ on η_s should arise only through change in v_f, according to eq 10. The dependence of $(\eta_s\phi/f)$ on v_1/v_f is examined in Figure 2. Except for the point at $v_1/v_f = 2.88$, the relationship between ln $(\eta_s\phi/f)$ and v_1/v_f is almost perfectly linear, which confirms eq 10 as written in the form

$$\log\left[\eta_s\left(\frac{\phi}{f}\right)\right] = \frac{q\gamma}{2.3}\left(\frac{v_1}{v_f}\right) + \log\left[\frac{\eta_s}{f}\left(\frac{\phi^\circ}{q}\right)\right] \tag{14}$$

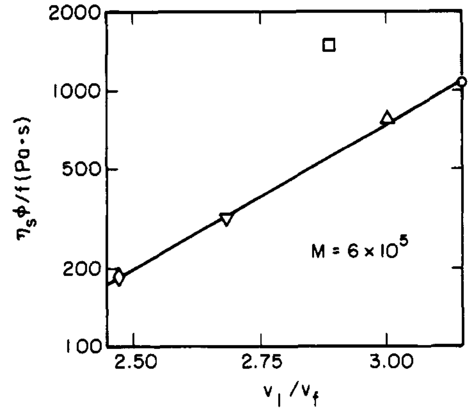

Figure 2. Data for ϕ/f from Figure 1, displayed as suggested by eq 10 and 14.

The factor η_s/f has been inserted on both sides of the equation but grouped differently to illustrate data analysis.

Using the least-squares correlation line in Figure 2 we obtain from the slope $\gamma q = 2.64$ and from the intercept $\phi^\circ = 0.264q(f/\eta_s)$ in SI units. The use of $\gamma = 0.525$ (see the Appendix) gives $q = 5.03$. This value agrees almost exactly with Peterlin's[18] estimate $q = 5$, which was determined from the geometry of C–C bonding along the polymer chain backbone. A crude Stokes' law estimate for f is $6\pi R\eta_s = 3.8 \times 10^{-9}\eta_s$ (m). Together with $q = 5$, this leads to $\phi^\circ = 5.0 \times 10^{-9}$ kg/s. This value is close to experimental values for ϕ ranging from 10^{-9} kg/s to 10^{-8} kg/s, which Peterlin[18] has cited as limiting, η_s-dependent IV coefficients.

The Bazua–Williams theory,[16] however, predicts $\phi^\circ = 3.7 \times 10^{-13}$ kg/s for polyethylene, substantially smaller than 5×10^{-9} kg/s extracted from this polystyrene data. Reasons for this apparent disagreement may include (1) the effect on ϕ° of higher energy barriers to rotation due to greater steric hindrance in the PS chain than in PE or (2) the effect of additional η_s-independent IV mechanisms (such as the propagation effect proposed by Allegra[25]) that are not included in the Bazua–Williams formulation.

Peterlin's works[17,18] appear to be the only previous source of a quantitative estimate of the solvent contribution to ϕ. In those works the solvent-dependent IV force was determined from the amount of extra frictional work required to move bonded chain units through transverse orbits during a deformational process. Peterlin assumed that the solvent could be treated as a continuum for the purpose of estimating this frictional work and calculated $\phi/f \cong 2$. This value agrees well with values needed to match the Peterlin–Cerf IV theories ($\phi_p = \phi p/N$) to certain linear experimental data.[7,8]

Our much larger values of ϕ/f are in line with those of McAdams,[37,38] who reported $\phi/f \cong 300$ to fit the Bazua–Williams IV model[10] ($\phi_p = \phi\lambda_p$) to oscillatory and steady-shear data for polystyrene solutes of M = 233 000–1 800 000. The ϕ/f magnitudes obtained from these two theories (Peterlin-Cerf and Bazua–Williams) apparently differ so greatly because they are tied to formulations that differ in the p dependence of ϕ_p, and this in turn reflects basically different M dependence in their predictions. Data presented here shed no light on this question directly, since only one polymer (hence, one M and one N) is involved. While the M dependence of neither phenomenological theory has yet been confirmed, the evidence presented here would seem to support the Bazua–Williams formulation used to make predictions in Figure 1. The large values of ϕ/f are entirely consistent with our new free-volume interpretation of η_s effects in ϕ, and the plausibility of numerical values for the parameters in that model (extracted from data) supports the entire pattern as well.

Finally, it is prudent to recognize a few points of uncertainty. Conclusions are based on a relatively limited set of data (Figure 2), and the IV model curve-fits to non-Newtonian viscosity (Figure 1) are not as good for high-η_s data as for low-η_s data. It is also conceivable that some artifacts might arise from using a solvent that is itself a polymer solution; e.g., the increased macroscopic η_s might not reflect a correspondingly increased f. However, the polymer used in these solvents has such a low molecular weight

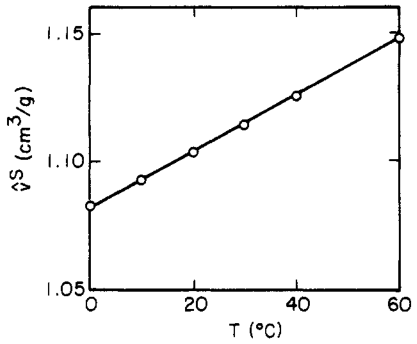

Figure 3. Specific volume of styrene,[40] displayed as suggested by eq 15 for use in determining free volume $\hat{v}_f = \hat{v}_s - \hat{v}_s(0)$.

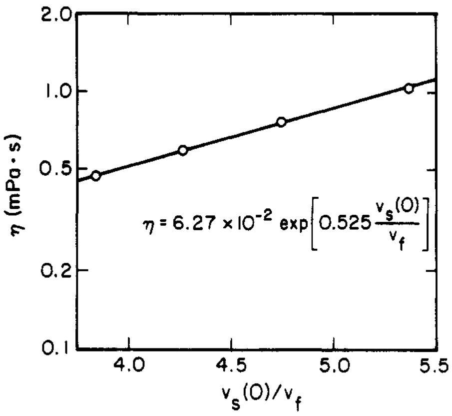

Figure 4. Viscosity of styrene,[40] displayed as suggested by eq 16 for determining γ.

that mechanical artifacts are believed absent from the present data. This was demonstrated earlier for the linear Newtonian limit,[33] and it is likely also true for these small departures from Newtonian behavior. While it seems plausible that a chain bond rotation in the vicinity of an excess of styrene solvent molecules would proceed differentially (and faster) than if the bond were surrounded by an excess of the low-M polystyrene molecules, these local excesses should be small and random. Thus, the observed behavior of the high-M solute chain should be independent of such details in a stochastic sense, and a model that invokes average free volume should be appropriate for characterizing this situation.

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Appendix: Evaluation of Parameters

Equation 10 requires knowlege of γ and v_1/v_f for determination of ϕ. Here we use simple methods to estimate these properties for the M = 600 000 PS solute/solvent blend systems used in the experiments.[34]

Properties of Pure Styrene. Specific volume data[40] for styrene ($\hat{v}^S$, here identified as solvent $\hat{v}_s$) are plotted in Figure 3 for the temperature range 0 °C ≤ T ≤ 60 °C. The linear $\hat{v}_s(T)$ relationship for this temperature range is given by

$$\hat{v}^S = \hat{v}_s = 0.7791 + (1.11 \times 10^{-3})T \qquad (15)$$

with T in K and $\hat{v}_s$ in cm³/g. The occupied volume of styrene, $\hat{v}_s(0)$ = 0.912 cm³/g, is estimated by using the additive group contribution procedure recommended by Haward.[30] Finally, γ is determined by plotting log η as a function of $\hat{v}_s(0)/\hat{v}_f \equiv \hat{v}_s(0)/[\hat{v}_s(T) - \hat{v}_s(0)] = v_s(0)/v_f$. According to free-volume theory,[30] this relationship should be linear:

$$\log \eta = A + 2.303\gamma\hat{v}_s(0)/v_f \qquad (16)$$

Figure 4 confirms eq 16 with $\eta_s(T)$ data from ref 40. The value γ = 0.525 is thereby obtained.

Properties of Polystyrene. The specific volume of pure monodisperse polystyrene is given by[40]

$$\hat{v}^{PS} = 0.767 + (5.5 \times 10^{-4})T + (643 \times 10^{-4})\ T/M \qquad (17)$$

when $T > T_g$ (as is the case in this plasticized blend). The occupied volume is estimated[30] to be $\hat{v}^{PS}(0)$ = 0.820 cm³/g. Since each styrene repeat unit contributes two backbone bonds, with the average molecular weight per bond being $M_S/2$ = 52, this value for occupied specific volume can be converted to the needed volume per bond by

$$v_1 = v_1^{PS} = \frac{\hat{v}^{PS}(0)M_S/2}{N_A} = 7.08 \times 10^{-23}\ \text{cm}^3 \qquad (18)$$

where N_A is Avogadro's number. In the absence of better information, γ to be used in eq 10 is taken to be the same as for styrene (0.525).

Free Volume of Blended Solvents. The chemical similarity of styrene and polystyrene suggests that the mixture free volume $\hat{v}_f^{mix}$ for a blended solvent can be obtained by a simple additive mixing rule:

$$\hat{v}_f^{mix} = w_S\hat{v}_f^S + w_{PS}\hat{v}_f^{PS} \qquad (19)$$

where w_S and w_{PS} are the weight fractions of styrene and polystyrene, respectively. While eq 19 gives free volume on a mass basis, eq 10 requires free volume per solvent molecule. This is approximated by neglecting minor complications arising from the low-M polymer fraction and calculating the free volume per styrene (solvent) unit as

$$v_f = \frac{\hat{v}_f^{mix}M_S}{N_A} \qquad (20)$$

Values for v_1/v_f obtained by using eq 19 and 20 and the expressions for pure component properties listed above are those given in Table I.

Registry No. Polystyrene (homopolymer), 9003-53-6.

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EPR Application to Polymers. 3. EPR Studies of Poly(phenylacetylene) Using Different Nitroxide Spin Probes

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ABSTRACT: EPR line-shape analysis of spin-probed poly(phenylacetylene) in the slow-motional region has been performed in the temperature range 77-258 K where the outermost hyperfine extrema are separable. Two approaches were used to obtain the rotational correlation time, τ_R. In the first approach, the rotation is assumed to be isotropic, and τ_R was calculated by using the empirical formula $\tau_R = a(1 - S)^b$ for the three models of rotation, namely Brownian, moderate jump, and strong jump. The results showed that, depending on the model of rotation, activation energy of rotation decreased by a factor of three in going from the Brownian model to the strong jump model. In the second approach, the line shapes were simulated by using the stochastic Liouville theory of slow-motional effects on EPR spectrum. A systematic method has been developed to determine the axis of rotation, the anisotropy of rotation, and the model of rotation. All four spin probes used (Tempone, doxylcyclohexane, doxylcholestane, and Tempo palmitate) were found to undergo anisotropic reorientation. The model of rotation for Tempone was found to be moderate jump, while the models for the other three were Brownian. The apparently low activation energies (0.3-1.1 kcal/mol) calculated from EPR line-shape simulations in the low-temperature region have been explained in terms of the spin probes rotating in the "holes" of dimensions comparable to those of the probe in the polymer matrices. A comparison of the two approaches for calculating τ_R emphasizes the fact that accurate τ_R values of nitroxide spin probes in poly(phenylacetylene) could best be obtained from a simulation of EPR line shapes employing magnetic parameters determined from their rigid-limit spectra at 77 K.

Introduction

Many studies have been made on synthetic polymers using paramagnetic spin probes embedded in polymer matrices to study the molecular motions of the host polymers.[1] Experimental evidence has shown that the molecular motions of the probe are closely related to those of the host polymer.[2-9] We have used a nitroxide spin probe to study line-shape changes in poly(phenylacetylene)[10] and found that the nitroxide spin probe exhibited anisotropic rotation whose anisotropy increased as temperature decreased. In a recent study Meurisse et al.[11] studied the molecular motion of nitroxide spin probes in two aromatic-aliphatic polyesters and found that the ESR spectra of the nitroxide probes can be explained in terms of a change in the anisotropic rotation of the probes as they pass through the crystal-mesophase transition.

The objective of the present work is to examine the effect of temperature and different nitroxide spin probes on probing poly(phenylacetylene). In particular, we focus much of our attention on the lower temperature, slower tumbling spectra (5×10^{-9} s $< \tau_R < 10^{-7}$ s), in part because this is a region wherein the inhomogeneous proton broadening is of less significance in the spectral simulations. In this region, the typical nitroxide slow-motional spectrum has two well-separated outer hyperfine extrema with an overlapped central region. We have used two approaches to calculate the rotational correlation time. In the first approach, we used the simplified method of estimating correlation time[12] using separate deviations of high-field and low-field positions from the rigid-limit values. In the second approach, we determined the magnetic parameters of four nitroxide spin probes in poly(phenylacetylene) at 77 K and calculated the correlation times by a computer simulation[13] of experimental line shapes using the stochastic Liouville theory.

The reason for choosing two approaches to calculate the rotational correlation time is as follows. In the first approach, τ_R was calculated from an empirical formula assuming that the rotation is isotropic and the model of rotation is known. Since neither of these two conditions is known a priori, the resulting τ_R and the activation energy values may not be reliable. In the second approach, the correlation times were determined from a computer simulating of experimental line shapes. A systematic method for determining the axis and the anisotropy of rotation and the model of rotation was given. The activation energies determined from the second approach were compared with those obtained from the empirical formula in an effort to find a correlation between the two approaches.

Experimental Section

The poly(phenylacetylene) was prepared, purified, and spin probed as described earlier.[10] The nitroxide spin probes were obtained from Molecular Probes, Junction City, OR. EPR spectra were recorded on a Bruker ER 200D-SRC spectrometer interfaced with an Aspect 2000 data system. The temperature was controlled by a Bruker ER 4111 VT variable temperature unit to 1 °C. The

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