Macromolecules **1993**, *26*, 643–646

Free Volume Interpretation of the Polymer Effect on Solvent Dynamics

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Received August 6, 1992; Revised Manuscript Received November 4, 1992

ABSTRACT: Morris et al. pointed out that the free volume concept is inadequate to reconcile the experimentally observed dynamic behavior that Aroclor 1248 shows in Aroclor/polystyrene or Aroclor/1,4-polybutadiene dilute solution. The present paper shows that if the concentration dependence of the thermal expansivity of the free volume is taken into account, Fujita's free volume theory can be made consistent with the main features of these data, though not perfectly.

Introduction

In analyzing concentration-dependence data for the dynamic properties of polymer solutions, it is usually assumed that dynamic properties of the solvent such as its friction factor are not modified by the presence of polymer molecules, at least in the dilute regime. Recently, there has been a growing interest in the extent to which this assumption is valid. Thus, working on dilute solutions of polystyrene (PS), 1,4-polybutadiene (1,4-PB), and polyisoprene (PI) in Aroclor 1248, a mixture of polychlorinated biphenyls, Lodge and co-workers[1-3] observed that the translational diffusion coefficient and the rotational relaxation time of the solvent molecule as evaluated by such techniques as pulsed-field-gradient nuclear magnetic resonance (PFG-NMR), oscillatory electric birefringence (OEB), and depolarized Rayleigh scattering (DRS) varied markedly with the polymer concentration. It seems difficult to understand these observations unless the friction factor of Aroclor 1248 changes upon addition of the polymer.

Morris et al.[1] and von Meerwall et al.[2] tried to interpret their experimental data in terms of the free volume concept, actually using the free volume theory formulated by Fujita[4] for the solvent mobility in polymer solutions. They found it difficult to reconcile Fujita's theory with the main features of the data. The present paper points out that the interpretation of the data by Fujita's theory is greatly improved if one factor neglected in their formulations is taken into account. It is the concentration dependence of the thermal expansivity of the fractional free volume in the solution.

Basic Quantities and Relations

We consider the dilute regime of a solution consisting of a polymer and a pure solvent. With $\tau_s(T,c)$ and $D_s(T,c)$ denoting, respectively, the rotational relaxation time and the translational diffusion coefficient of the solvent molecule at temperature T and polymer mass concentration c, we introduce the dimensionless quantities $\zeta_\tau(T,c)$ and $\zeta_D(T,c)$ defined by

$$\zeta_\tau(T,c) = \tau_s(T,c)/\tau_s(T,0) \qquad (1)$$

$$\zeta_D(T,c) = D_s(T,0)/D_s(T,c) \qquad (2)$$

Furthermore, we define $Q_\tau(T)$ and $Q_D(T)$ by

$$Q_\tau(T) = \lim_{c\to 0} [\ln \zeta_\tau(T,c)]/c \qquad (3)$$

$$Q_D(T) = \lim_{c\to 0} [\ln \zeta_D(T,c)]/c \qquad (4)$$

It seems reasonable to assume that the translational and rotational mobilities of a solvent molecule are affected in the same way by temperature and concentration, though one may suspect that the assumption with respect to concentration is dubious for elongated molecules. Then it follows that $\zeta_\tau(T,c) = \zeta_D(T,c)$ and hence

$$Q(T) \equiv Q_\tau(T) = Q_D(T) \qquad (5)$$

When looking at a polymer solution by classical hydrodynamics, we treat the solvent as a continuum in which polymer molecules are dispersed. The viscosity parameter that enters into the Navier–Stokes hydrodynamic equations for the solution is the viscosity η_s of this continuum. Usually, η_s is taken equal to the viscosity of the pure solvent, with the tacit assumption that the solvent friction factor remains unchanged in the presence of polymer molecules. If this assumption is removed, η_s has to be treated as function of c as well as T; i.e., $\eta_s = \eta_s(T,c)$. What hydrodynamics allows us to calculate for a polymer of given length and architecture is not the "experimental" intrinsic viscosity $[\eta](T)$ (defined as $\lim_{c\to 0} [\eta(T,c) - \eta_s(T,0)]/[\eta_s(T,0)c]$) but the "theoretical" intrinsic viscosity $[\eta]_{\text{theor}}(T)$ defined by

$$[\eta]_{\text{theor}} = \lim_{c\to 0} [\eta(T,c) - \eta_s(T,c)]/[\eta_s(T,c)c] \qquad (6)$$

where $\eta(T,c)$ denotes the viscosity of the solution at T and c. It should be noted that, though conveniently referred to as solvent viscosity, $\eta_s(T,c)$ is not an experimentally measurable property. von Meerwall et al.[2] have shown that $[\eta]_{\text{theor}}$ is related to the $[\eta](T)$ by

$$[\eta](T) = [\eta]_{\text{theor}}(T) - [\eta_e](T) \qquad (7)$$

where $[\eta_e](T)$ is defined by

$$\eta_s(T,c) = \eta_s(T,0)\{1 + [\eta_e](T)c + ...\} \qquad (8)$$

Thus, $[\eta_e]$ represents the strength of the effect that the solvent viscosity undergoes by addition of a polymer at the limit of infinite dilution. It may be either positive or negative, depending on the system.

We assume that the Einstein–Debye relation is valid for solvent at finite dilution; i.e., $\tau_s(T,c) \sim \eta_s(T,c)/T$ (this implicitly assumes that the solvent viscosity is proportional to the solvent friction factor). Then, with eq 1, we obtain

$$\eta_s(T,c)/\eta_s(T,0) = \zeta_\tau(T,c) \qquad (9)$$

Substituting eq 8 and referring to eqs 3 and 5, we find

$$[\eta_e](T) = Q(T) \qquad (10)$$

This indicates that, differing from $\eta_s(T,c)$, $[\eta_e](T)$ can be

0024-9297/93/2226-0643$04.00/0

estimated from measurement of either rotational relaxation or translational diffusion of the solvent as a function of c.

Since the difference $\eta(T,c) - \eta_s(T,c)$ is a measure of the energy loss due to the polymer molecule, $[\eta]_{\mathrm{theor}}$ is always positive. Previous hydrodynamic calculations show that $[\eta]_{\mathrm{theor}}$ for a series of homologous polymers in a given solvent increases monotonically with increasing chain length, starting from a value near the Einstein value for rigid spheres (0.025 cm^3/g). Thus, it follows from eq 7 that for a system in which $[\eta_e]$ is considerably larger than 0.025 cm^3/g, $[\eta]$ turns to be negative in the region of short chains. Though not all, this explains why some previous authors[5] obtained negative intrinsic viscosities for oligomers.

Free Volume Theory

Fujita's free volume theory[4] postulates that the solvent mobility $m_s(T,c)$ (inversely proportional to the solvent friction factor) and the chain-segment mobility $m_p(T,c)$ in a polymer solution at temperature T and concentration c are related to the fractional free volume $f(T,c)$ in the solution by

$$\ln m_s(T,c) = A_s - B/f(T,c) \tag{11}$$

$$\ln m_p(T,c) = A_p - 1/f(T,c) \tag{12}$$

where f is the free volume per unit volume of solution and A_s, A_p, and B are constants. We note that in the framework of Fujita's theory eq 12 is the definition of f. Depending on whether the mobility refers to rotation or translation, we have to interpret the parameter A accordingly. Furthermore, the value of B, a free parameter, may depend on the motional modes of the solvent and chain segment.

We consider the behavior of $f(T,c)$ at temperature T as $T_g(c) < T < T_g(c) + 100$ °C, where $T_g(c)$ is the glass transition temperature of the solution considered, and assume that $f(T,c)$ depends linearly on T in this temperature range. With $\alpha(c)$ being the thermal expansivity of the fractional free volume at concentration c, this assumption is expressed by

$$f(T,c) = f_g(c) + \alpha(c)[T - T_g(c)] \tag{13}$$

where $f_g(c)$ is the fractional free volume in the solution at $T = T_g(c)$. Applying eq 13 to $c = 0$, subtracting the result from eq 13, and postulating the rule of thumb that the glass transition occurs at an isofractional free volume (see the Remarks section), we obtain

$$f(T,c) = f(T,0) + [\alpha(c) - \alpha(0)]T - [\alpha(c)T_g(c) - \alpha(0)T_g(0)] \tag{14}$$

At low polymer concentration, $\alpha(c)$ and $T_g(c)$ may be expanded in powers of c as

$$\alpha(c) = \alpha(0) + \alpha' c + ... \tag{15}$$

$$T_g(c) = T_g(0) + Q_g c + ... \tag{16}$$

where

$$Q_g = \lim_{c\to 0} [T_g(c) - T_g(0)]/c \tag{17}$$

Substituting eqs 15 and 16 into eq 14 gives

$$f(T,c) = f(T,0) - \{\alpha(0)Q_g - \alpha'[T - T_g(0)]\}c + ... \tag{18}$$

With this expression for $f(T,c)$, it follows from the appropriate equations above that

$$\lim_{c\to 0} \{\ln [m_s(T,0)/m_s(T,c)]\}/c = B\{\alpha(0)Q_g - \alpha'[T - T_g(0)]\}/[f(T,0)]^2 \tag{19}$$

With the Einstein relation $D_s \sim Tm_s$, the left-hand side of this equation is equal to $Q_D(T)$, defined by eq 4. Hence we obtain with eq 5

$$Q(T) = B\{\alpha(0)Q_g - \alpha'[T - T_g(0)]\}/[f(T,0)]^2 \tag{20}$$

where

$$f(T,0) = f_g(0) + \alpha(0)[T - T_g(0)] \tag{21}$$

which is obtained from eq 13. It is the concentration-dependence term in eq 15 that von Meerwall et al.[2] neglected in their application of Fujita's free volume theory. Hence their equation for $Q(T)$ lacks the second term in the numerator in eq 20. As will be shown below, this term makes a significant contribution to the temperature dependence of $Q(T)$.

Data Analysis

We introduce $P(T)$, defined by

$$P(T) \equiv \{1 + [\alpha(0)/f_g(0)][T - T_g(0)]\}^2 Q(T) \tag{22}$$

This quantity can be evaluated as a function of temperature from experimental data for $Q(T)$ if information about the solvent-related parameters $\alpha(0)$, $f_g(0)$, and $T_g(0)$ is available. With eq 20, eq 22 can be written

$$P(T) = \{B\alpha(0)/[f_g(0)]^2\}\{Q_g - [\alpha'/\alpha(0)][T - T_g(0)]\} \tag{23}$$

Therefore, when $P(T)$ is plotted against $T - T_g(0)$, the data points should follow a straight line, and the parameters B and α' can be evaluated from the intercept and slope of the line if, in addition to $\alpha(0)$ and $f_g(0)$, the value for Q_g is known from separate information.

To check the predicted linearity between $P(T)$ and T with available $Q(T)$ data[1-3,6-9] for PS, PI, and 1,4-PB in Aroclor 1248, we choose 0.025 for $f_g(0)$ as usually made (it should be noted that this numerical value is meaningful only when f is defined by eq 12) and take 7×10^{-4} °C^{-1} and -44 °C for the $\alpha(0)$ and $T_g(0)$ of Aroclor 1248, respectively. Figure 1 shows the resulting plots of $P(T)$ vs $T - T_g(0)$.

It is seen that the data for each system conform fairly well to the prediction over the indicated range of temperature. The straight lines show visual fits to the data points, made by intentionally neglecting the unfilled points indicated by arrows. With 20, -26, and -72 cm^3 °C/g derived for Q_g of PS, PI, and 1,4-PB in Aroclor 1248, respectively, from the paper of von Meerwall et al.,[2] the values of B and $\alpha'/\alpha(0)$ determined from these straight lines are as follows: $B = 0.491$ (PS), 1.34 (PI), and 1.03 (1,4-PB); $\alpha'/\alpha(0)$ (in cm^3/g) $= -2.18$ (PS), -0.301 (PI), and -0.770 (1,4-PB).

Though it is a free parameter in the framework of Fujita's theory, B may be compared to the parameter ξ in the Vrentas–Duda free volume theory,[10] in which ξ is defined as the specific critical hole volume for the solvent relative to that for the polymer segment. The above B values suggest that the chain segment of relatively inflexible PS be significantly greater than those of flexible PI and 1,4-PB.

The slopes of the straight lines in Figure 1 are definitely nonzero, indicating that, in general, α varies with concentration even in the dilute regime, contrary to what was assumed by von Meerwall et al.[2] Interestingly, the sign of α' is negative for all three systems. However, it is not

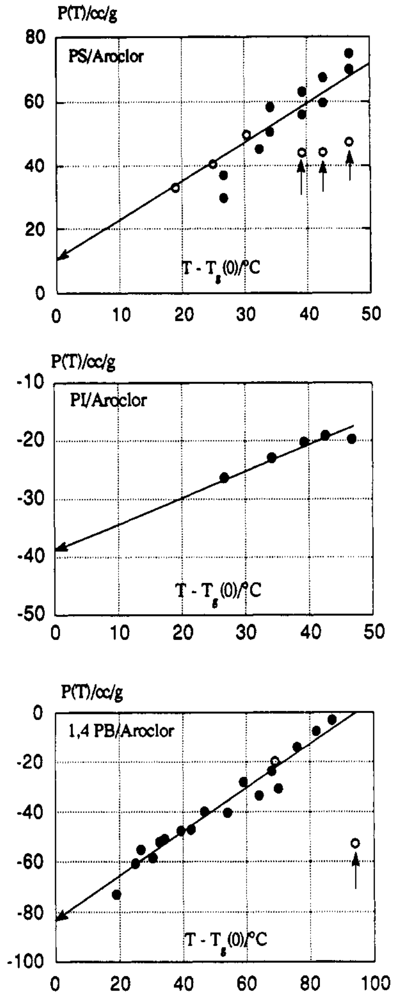

Figure 1. Temperature dependence of $P(T)$ for polystyrene (PS), polyisoprene (PI), and 1,4-polybutadiene (1,4-PB) in Aroclor 1248. Data points: PS, filled circles from refs 1 and 6 (OEB) and unfilled circles from ref 3 (DRS) and ref 9 (FRS); PI, from ref 6 (OEB); 1,4-PB, filled circles from ref 1 (OEB) and ref 8 (^{13}C NMR) and unfilled circles from ref 7 (DRS, PCS).

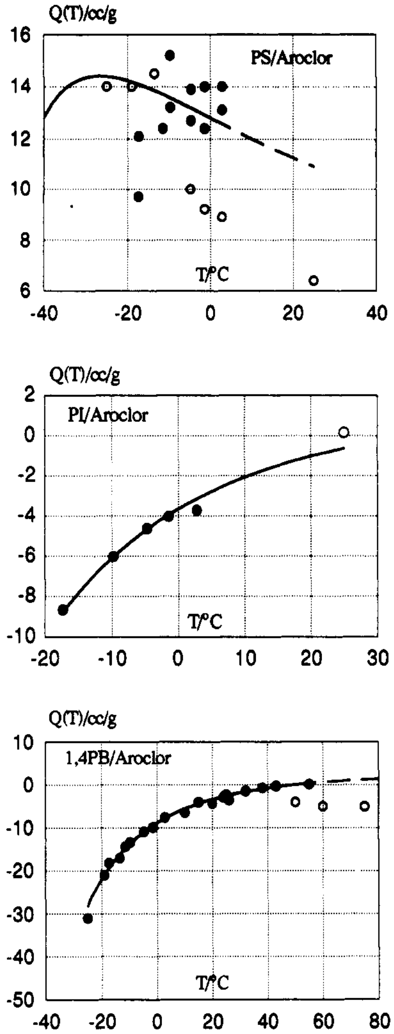

Figure 2. Comparison between calculated and measured $Q(T)$ for PS, PI, and 1,4-PB in Aroclor 1248. The data point symbols have the same meanings as in Figure 1. The unfilled circles for PS and PI at the highest temperatures are added from ref 2 (PFG-NMR).

legitimate to deduce from this finding that the α values of the respective polymers in bulk appear below $\alpha(0)$. This is because we have no guarantee that eq 15 truncated at the term linear in c may be extended to the bulk polymer.

The solid curves in Figure 2 show the $Q(T)$ (i.e., $[\eta_e]$) vs T relations calculated from eqs 20 and 21 with the above parameter values. For PI and 1,4-PB they fit the plotted data points fairly correctly, but for PS the agreement is limited to the temperature range below $T < 0$ °C. In fact, though not appearing here, the DRS values of $Q(T)$ for PS fall below 2 cm^3/g at T above 80 °C,[3] while the PS curve in Figure 2 stays as high as about 8 cm^3/g at 80 °C. At present, no reasonable explanation can be given for this marked disagreement. Interestingly, the PS curve shows a rather broad maximum at about −25 °C. This behavior seems to have something to do with the conclusion of Morris et al.[1] that $Q(T)$ for PS was independent of temperature in the range of their experiment (−17.3 to +25 °C). The curve for 1,4-PB predicts $Q(T)$ to change sign from negative to positive at about 60 °C, 100 °C above $T_g(0)$. The validity of this prediction is subtle because the free volume concept tends to fail as T approaches $T_g(0) + 100$ °C.[11]

Remarks

The above discussion has focused on the solvent dynamics affected by the presence of polymers. The more traditional problem is the mobility of a chain segment controlled by its surrounding solvent molecules. In Fujita's free volume theory, the relevant relation for this problem is

$$m_p(T,c) \sim [m_s(T,c)]^{1/B} \tag{24}$$

which is derived by eliminating f from eqs 11 and 12. With the Einstein–Stokes relation $m_s(T,0) \sim 1/\eta_s(T,0)$, eq 24 gives

$$\tau_p(T,0) = K[\eta_s(T,0)]^{1/B} \tag{25}$$

where τ_p denotes the rotational relaxation time of a chain segment (inversely proportional to m_p) and K is a constant that depends on the system. Substitution of the B value obtained above for PI leads to

$$\tau_p(T,0) = K[\eta_s(T,0)]^{0.75} \tag{26}$$

Using ^{13}C NMR to measure the correlation time τ_c of the C–H bond attached to the PI chain backbone in organic solvents covering a factor of 70 in viscosity, Glowinkowski et al.[12] found the correlation expressed by

$$\tau_c = C[\eta_s(T,0)]^{0.41} \tag{27}$$

where C is independent of solvent identity. Equation 26 does not conform to this finding in two respects. First, the exponents to $\eta_s(T,0)$ in eqs 26 and 27 are markedly different. Second, K should depend on solvent species, but C does not. More recently, it has been shown[6] that eq 27 held for 1,4-PB, too, but not for PS and 1,2-PB, for which the exponent to $\eta_s(T,0)$ was unity. Furthermore, Gisser and Ediger[8] found a value of 0.3 for the exponent from a similar NMR study on 1,4-PB in Aroclor.

Free volume theories of polymer solutions proposed so far tacitly restrict their objects to the motions of solvent and chain segment whose time scales are of similar order. The correlation time τ_c appearing above is associated with reorientation of a local C–H bond. Probably, such motion is much faster than the rotation of the solvent as a whole. If so, it seems that the above conflict between eq 26 and 27 is beyond the scope of current free volume theories.

Glowinkowski et al.[12] attempted to interpret eq 27 in terms of the Grote–Hynes theory[13] of chemical reactions, but no clear-cut explanation for this relation is as yet known.

The filled and unfilled data points in Figures 1 and 2 refer to translational and rotational motion, respectively. Thus, in Figure 2, the filled points indicate Q_D and the unfilled ones Q_τ. The marked difference between them observed for the PS/Aroclor 1248 system may be taken as evidence that the solvent molecule undergoes different polymer effects in its translation and rotation.[14] In the framework of Fujita's free volume theory, it may indicate that the parameter B differs for these modes of molecular motion.

Finally, the following remark may be in order. In the formulation presented above, the rule of thumb that the glass transition occurs at an isofractional free volume state has been invoked. However, Frick et al.[15] have recently reported a marked deviation from it for polystyrene in toluene.

Acknowledgment. I am much indebted to Professor T. P. Lodge of the Department of Chemistry, University of Minnesota, who gave me valuable comments as well as the numerical data for $Q(T)$ used for the present analysis.

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