Exploring the Origin of Negative Viscosity Change in Polymer Solutions

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ABSTRACT: We have studied a model polymer solution based on 1,4-polybutadienes (PBD) to explore the origin of negative intrinsic viscosity in polymer solutions where the polymer has typically a lower glass transition temperature than that of the solvent. Viscoelastic measurements are carried out to show that the PBD solutions possess smaller viscosity than that of the solvent at low temperatures. DSC analysis shows that the incorporation of the 1,4-PBD into a butadiene-based solvent of higher glass transition temperature depresses the solution glass transition temperature below that of the solvent. By designing a reference system with the same glass transition characteristics as the solution, we recover the positive effect of the polymer hydrodynamic contribution to the solution viscosity, suggesting that the conventional molecular theories for polymer solutions can be phenomenologically remedied by incorporating the polymer plasticization effect.

I. Introduction

Polymer dynamics play an important role in processing and design of polymeric materials. A theoretical description of viscoelastic properties requires basic knowledge of the friction interactions between chain segments and a continuum medium in the case of solutions and between the various segments in the case of polymer melts and blends. Conventional molecular-like theories[1,2] for *dilute* polymer solutions obtain an Einstein-like expression for the solution viscosity $[(\eta - \eta_s)/c\eta_s]|_{c\to 0} = [\eta]$, where η_s is the solvent viscosity, and the intrinsic viscosity $[\eta]$ depends only on the hydrodynamic volume of a single chain. This classical result has been suggested to be in error[3] when certain polymer solutions are found to show negative viscosity change (NVC), $\eta < \eta_s$ or $[\eta] < 0$, especially when η is measured at high frequencies in oscillatory shear. The common explanation is that the solvent dynamics become affected by the incorporation of polymer. The molecular mechanism for how this coupling process occurs has been under active investigation.

Extensive experimental studies[3−12] have been performed to explore the physical origin of NVC. It is found that incorporation of polymer may either speed up or slow down the solvent rotational relaxation described by relaxation time $\tau_s(c,T)$, where c is the polymer concentration. In other words, the ratio $\tau_s(c,T)/\tau_{s0}$ can be either smaller or larger than unity (see Figure 1 of ref 3), where τ_{s0} is the solvent relaxation time in absence of the polymer. Systematic efforts have been directed toward understanding questions such as why this ratio increases with c in one solution and decreases in another, how τ_s/τ_{s0} depends on the temperature T, and what connection the observed modification of the solvent dynamics has with the NVC. In particular, it has been suggested[3,5] that the polymer influence on the solvent dynamics can be accounted for in terms of an effective local viscosity $\eta_e = \eta_s[\tau_s(c,T)/\tau_{s0}]$, where η_s is the viscosity of the pure solvent.

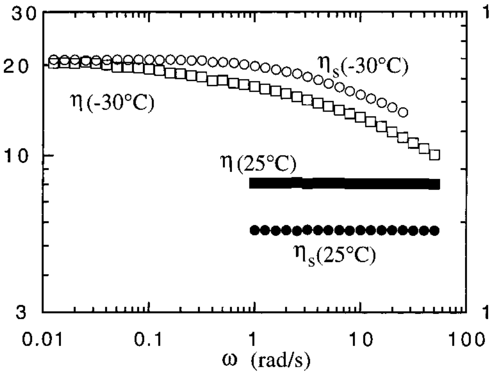

Figure 1. Comparison of the 2.6% solution viscosity η (PBD1) with the solvent (oBD2) viscosity η_s or η_{20} at 25 °C (left axis) and −30 °C (right axis), respectively, as a function of frequency ω in oscillatory shear.

When a polymer is incorporated into a solvent to make a solution, it produces two effects on the measured solution viscosity η: (a) the well-known Einstein-like polymer hydrodynamic contribution, which is positive, and (b) polymer *plasticization* or *deplasticization* of the solvent. It is plausible to think that the deplasticization effect may occur when the polymer's glass transition temperature, $T_g{}^p$, is much higher than $T_g{}^s$ of the solvent. This deplasticization may produce a positive contribution to η and may account for the nonvanishing intrinsic viscosity at high frequencies, i.e., $[\eta]_\infty > 0$. The plasticization effect is possible when $T_g{}^p$ is considerably lower than $T_g{}^s$. This plasticization is expected to adversely affect the solution viscosity, i.e., to produce a negative contribution to η. When the polymer plasticization effect overcomes the polymer hydrodynamic effect, we expect a negative intrinsic viscosity (NIV) or $[\eta] < 0$ to occur.

Many theoretical attempts have been made to "rescue" the original bead−spring model (BSM) of Rouse and Zimm. These include introduction of internal viscosity[13−15] to account for $[\eta]_\infty > 0$ at high frequencies and new modifications[16−18] that can produce $[\eta] < 0$. It appears that the polymer plasticization and deplasticization effects on the solvent are not accounted for in these theoretical studies. On the other hand, a simple revision of the BMS may be sufficient to offer an adequate description of polymer solution rheology. This would merely involve replacing[3] the solvent η_s with an effective local viscosity η_e in the formalism.

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Table 1. Characteristics of PBD and Oligomeric BD

	M_w	M_n	vinyl (%)	T_g (°C)
PBD1	64 000	59 000	10	−91.6
PBD2	119 000	108 000	10	−91.4
oBD1		1500	25	−89.2
oBD2		1000	45	−51.4

In this work we carry out simple experiments to identify the principal cause for the observed NIV. Using 1,4-polybutadiene (PBD) solutions involving a solvent with a significantly higher glass transition temperature, we show that $(\eta - \eta_s) < 0$ arises predominantly from the solution having a lower glass transition temperature than that of the solvent, which is evidence that the polymer plasticization occurs. The DSC characterization of the glass transition behavior of the PBD solutions allows us to subtract the *polymer plasticization* effect from the overall polymer influence on the solution viscosity and to recover an approximate quantification of the polymer hydrodynamic contribution. Specifically, lowering of the solvent glass transition temperature T_g^s by 1,4-PBD can be approximately accounted for using a reference (mixed) solvent containing plasticizing oligomeric 1,4-butadiene. As a good approximation, viscosity of the reference solvent can be used to mimic the effective local viscosity η_e experienced by the polymer chains. Therefore, this protocol of constructing reference solvent introduces a second method to access the value of η_e through independent experiment. Indeed, the 1,4-PBD solutions are found to always have a higher viscosity than η_e even at high frequencies at various concentrations and temperatures. In other words, the solution viscosity has the modified form: $\eta = \eta_e\{1 + [\eta]_h c + O(c^2)\}$, where the true intrinsic viscosity $[\eta]_h$ has only to do with the polymer hydrodynamic contribution and does not turn negative.

II. Experimental Section

A. Materials. Our present study is based on two 1,4-polybutadienes (PBD1 and PBD2) of different M_w provided by Dr. Adel Halasa at Goodyear. An oligomeric butadiene (oBD2 from Aldrich) of high vinyl content is selected as the solvent of higher T_g^s. A second oligomeric 1,4-butadiene (oBD1 from Aldrich) is employed to simulate the plasticization effect of PBD1 and PBD2 on oBD2. Table 1 contains the basic information about these four materials. It is clearly seen that oBD1 has its glass transition temperature quite close to those of PBD1 and PBD2, and oBD2 has a significantly higher glass transition temperature.

All the solutions are prepared by directly dissolving 1,4-PBD in oBD2 without using any organic solvent. The solution concentration is measured in terms of the polymer weight fraction ϕ. The mixture is stirred thoroughly under room temperature for about 7−10 days until the mixture becomes homogeneous. At all temperatures and concentrations, the solutions look transparent and clear before, during, and after measurements.

B. Instruments. Viscosities of the solutions are measured with a dynamic mechanical spectrometer (Rheometrics RMS-800). The RMS-800 is equipped with a 200−2000 g cm dual range, force rebalance transducer. Oscillatory shear measurements are carried out in the parallel-plate geometry with 25 mm diameter disks. The experimental temperature ranges from 40 to −30 °C. At every temperature, the sample is allowed to equilibrate for about 10−20 min in the RMS-800 at the preset temperature before measurement. The temperature fluctuation during the measurement is about ±0.1−0.3 °C. The experimental uncertainty due to the temperature fluctuation can be minimized by repeating the rheological measurements.

A modulated DSC (DSC 2920 from TA instruments) is employed to characterize the glass transition behavior of the two PBD, two oBD, and their mixtures. Before each measurement, the baseline is checked to ensure the quality of the results. All measurements are carried out at a heating rate of 10 °C/min.

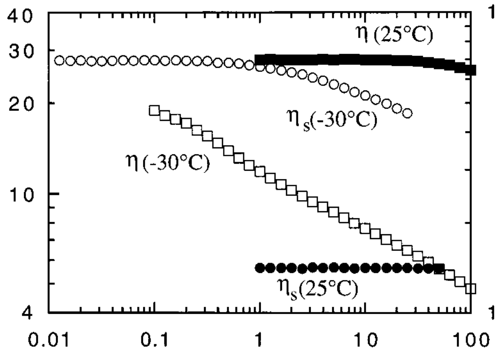

Figure 2. Comparison of the 10% solution viscosity η (PBD1) with η_s at 25 °C (left axis) and −30 °C (right axis), respectively, as a function of the oscillation frequency ω.

III. Results

We first carry out oscillatory-shear measurements of a 2.6% solution made of PBD1 and oBD2 at two temperatures and obtain the absolute values of the complex viscosity η^*. For notational simplicity, we write $|Q^*|$ as Q here and below, where Q represents either η, η_s, or η_e. In all the figures to follow, the viscosity has the unit of Pa s, and its value at a low temperature is presented on the right-hand-side vertical scale with its value at a high temperature on the left-hand-side scale. Figure 1 shows that the relationship between the solution with $\phi = 0.026$ and solvent viscosities, η and η_s, where the full symbols should be read using the scale on the left-hand-side and the open symbols on the right-hand-side scale. Here η_s is the viscosity of the pure oBD2 and therefore can also be equivalently denoted as η_{20}. At low temperatures such as −30 °C, the Rouse melt relaxation time of oBD is sufficiently long relative to the experimental time window, and shear thinning occurs as shown by the open circles. At 25 °C, η is about 50% higher than η_s, indicating that this 2.6% PBD1 solution is essentially dilute. At −30 °C, η becomes smaller than η_s even in the zero-frequency Newtonian limit. The shear thinning behavior of the solution at higher frequencies drives η even lower than η_s. The same kind of phenomenon has been reported many times in the past for other solutions including ones based on 1,4-polybutadiene.[4−9] A common origin is expected for this “anomalous” phenomenon. Below we explore the dominant cause for $\eta - \eta_s < 0$.

It is important to recognize from Figure 1 that the temperature is an important variable. In other words, $\eta - \eta_s < 0$ does not occur unless the experimental temperature is sufficiently low. A similar phenomenon is observed for the 10% solution ($\phi = 0.1$) as shown in Figure 2. Here we see the phenomenon amplified at the higher concentration. Besides the polymer plasticization effect, shear thinning reduces the polymer hydrodynamic contribution and drives η even lower than η_s at high frequencies at −30 °C although η is nearly 10 times η_s at 25 °C. The negative viscosity change is also seen for a third solution at a concentration of only 1.5% of PBD2: Figure 3 indicates that the polymer plasticization is present to cause $\eta < \eta_s$ whenever it overcomes the positive polymer hydrodynamic condition. To the lowest order in concentration c, both polymer plasticiza-

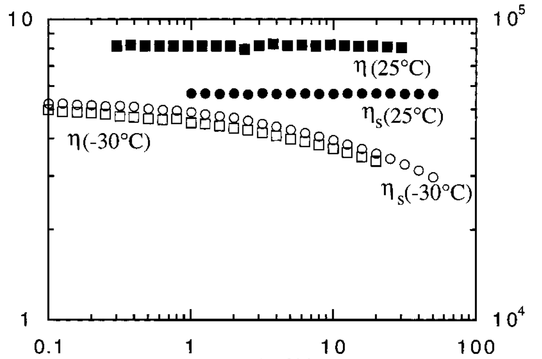

Figure 3. Comparison of the 1.5% solution viscosity η (PBD2) with η_s at 25 °C (left axis) and −30 °C (right axis), respectively, as a function of the oscillation frequency ω.

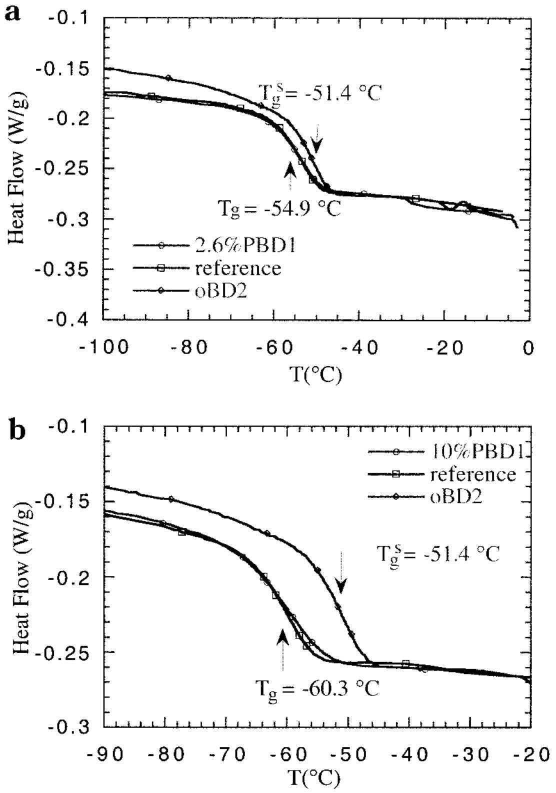

Figure 4. (a) Glass transition characteristics of 2.6% solution, its reference system (3.1%), and the pure oBD2, where T_g stands for the average glass transition temperature of both solution and the reference system. (b) The glass transition characteristics of 10% solution, its reference system (12%), and the pure oBD2.

tion and hydrodynamic contribution increases in absolute magnitude linearly with c. The former increases strongly with lowering temperature whereas the latter is relatively independent of temperature, making the negative viscosity change (NVC) possible to see at low temperatures.

In search for a phenomenological indication of NVC, we examine the glass transition characteristics of the solution and the corresponding solvent. Figure 4a shows that the 2.6% PBD1 solution has a depressed glass transition temperature $T_g(\phi)$ ($<T_g^s$) relative to that of the pure solvent (oBD2). Thus, at any given experimental temperature, the solution stays further above its $T_g(\phi)$ than the solvent does from its T_g^s. This polymer plasticization is stronger at a lower temperature and increases with the polymer concentration. As a result, the solvent actually has a higher viscosity η_s ($>\eta$) than the solution at −30 °C, as shown in Figures 1−3.

Table 2. $T_g(\phi)$ of Polymer Solutions and Reference Systems

	2.6% PBD1		10% PBD1		oBD2
samples	soln	ref	soln	ref	
ϕ (wt % of PBD or oBD1)	2.6	3.1	10	12	0
T_g (°C)	−54.9		−60.3		−51.4

To separate the contribution of the plasticization from the hydrodynamic contribution to the solution viscosity η, it is desirable to have the plasticization accounted for separately. This can be done by constructing a reference medium that has similar glass transition behavior to that of the solution. oBD1 listed in Table 1 has a glass transition temperature close to that of PBD1 and a molecular weight too low to give any hydrodynamic contribution. The plasticization effect occurring in the PBD solution can be simulated by adding oBD1 to oBD2. Figure 4a shows that a reference system made of 3.1% oBD1 and 96.9% oBD2 has glass transition characteristics identical to those of the 2.6% PBD1 solution. To the first approximation, we may think that the dynamic environment experienced by the PBD1 chains can be represented by this reference system. In other words, the polymer hydrodynamic contribution to the solution viscosity η can be evaluated with respect to the viscosity η_e of the reference system.

The stronger plasticization effect in the 10% PBD1 solution can also be accounted for using oBD1 as shown in Figure 4b, where the reference system of 12% oBD1 and 88% oBD2 exhibits the same glass transition characteristics, both having a glass transition temperature $T_g(\phi)$ considerably lower than T_g^s. The finite breadth of the transition may indicate that there are more than one type of segment in each sample whose glass transition temperatures may range as broadly as the transition width indicates. Table 2 summarizes the T_g values for the solutions and the *corresponding* reference systems. The overlapping of the DSC curves ensures that the reference systems possesses the same glass transition characteristics as those of the corresponding polymer solutions, although this does not guarantee that both the reference and solution possess the same amount of free volume, nor does this ensure that the two samples have identical local dynamics. Nevertheless, the DSC data provide a simple way to account for the plasticization effect.

Since the reference system has a lower $T_g(\phi)$ than T_g^s of the pure solvent, their viscosities do not change with temperature as rapidly as η_s does. Figure 5 shows a comparison between η_s and the viscosity η_e of the reference systems at 25 (full symbols) and −30 °C (open symbols), respectively. The plasticization effect increases with lowering temperature and with concentration of the lower T_g component, as expected. At a lower temperature, η_e of the reference system is more significantly below η_s.

IV. Free Volume Theory for Component Dynamics in Polymer Mixtures

In this section, we would like to discuss a simple free volume theory that can be used to provide a practical means of accounting for the polymer plasticization and deplasticization effects in solutions where the solvent is a melt of short Rouse chains. Suppose the polymer and the solvent are denoted as species 1 and 2, respec-

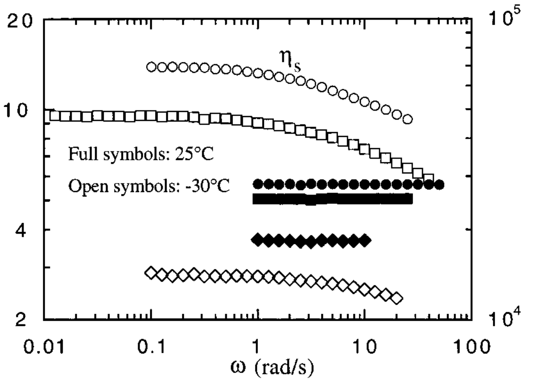

Figure 5. Comparison of the viscosity η_e of the two reference systems, 3.1% (squares) and 12% (diamonds), with the solvent viscosity η_s (circles) at 25 °C (full symbols, left axis) and −30 °C (open symbols, right axis), respectively, as a function of the oscillation frequency ω.

tively. A reference system of viscosity η_e can be constructed using oligomeric form of species 1 and species 2. In our current experimental example, it is the mixture of oBD1 and oBD2. Such a system can be regarded as a molecular mixture of two Rouse melts whose Rouse friction coefficients are ζ_{10} and ζ_{20}, respectively, in their pure states. Assuming the friction coefficients are modified from ζ_{10} and ζ_{20} to $\zeta_1(\phi,T)$ and $\zeta_2(\phi,T)$, respectively, in the reference mixture, we can approximate its viscosity η_e as

$$\eta_e = \phi\eta_1 + (1 - \phi)\eta_2 \tag{2}$$

where the Rouse melt viscosities η_1 and η_2 are proportional to ζ_1 and ζ_2, respectively.

A free volume theory can be developed to depict the friction factors ζ_1 and ζ_2 or η_1 and η_2. Suppose the free volume fractions of pure species 1 and 2 are given by $f_{10}(T)$ and $f_{20}(T)$, respectively. Upon mixing, the free volume fractions can be written as

$$f_1 = f_{10}(T) + (1 - \phi)q(T) \tag{3a}$$

$$f_2 = f_{20}(T) + \phi p(T) \tag{3b}$$

where $q(T)$ and $p(T)$ are only functions of temperature. Here we postulate that the mutual influence is proportional to the corresponding weight fraction. Assume the friction factors take the Doolittle form, $\zeta_i = A\exp(B/f_i)$ where A and B are constants and the subscript "i" takes one of four symbols:1, 2, 10, and 20. It is straightforward to show that

$$\ln(\zeta_1/\zeta_{10}) = (B/f_{10})\left[\frac{-q(1 - \phi)}{f_{10} + q(1 - \phi)}\right] \tag{4a}$$

$$\ln(\zeta_2/\zeta_{20}) = (B/f_{20})\left[\frac{-p\phi}{f_{20} + p\phi}\right] \tag{4b}$$

Inserting eqs 4a and 4b into eq 2 allows us to depict the composition and temperature dependence of η_e. In the limit of $\phi \to 0$,

$$\eta_e \cong \eta_2 = \eta_{20}\exp[A'\phi/(1 + B'\phi)] \tag{5}$$

where η_{20} is the viscosity of the pure species 2, $A'(T) = -p(T)B/[f_{20}(T)]^2$ and $B'(T) = p(T)/f_{20}(T)$. This formulation is more general than that given by Fujita.[19,20] Furthermore, eq 5 provides a more detailed expression than the simple exponential function of ϕ indicated by the experimental data in refs 3 and 5.

If $T_{g1} < T_{g2}$ and they are sufficiently apart, the mixture typically has a glass transition temperature $T_g(\phi)$ satisfying $T_{g1} < T_g(\phi) < T_{g2}$, as determined by DSC as shown in Figure 4a,b. This usually implies that the species 2 undergoes the glass transition at a temperature below T_{g2}. According to eq 3b, this means $p(T) > 0$. Thus, a simple DSC measurement would us allow to predict the sign of A' in eq 5 and the magnitude of η_e relative to η_{20} of the pure solvent. In particular, we expect, on the basis of the DSC data in Figure 4a,b, that $\eta_e < \eta_{20} = \eta_s$ at all temperatures. This is fully supported by the rheological data in Figure 5.

V. Data Analyses

Figure 5 indicates that the effect of plasticization increases with the concentration of the low-T_g component and with lowering temperature. We can express this behavior of η_e as a function of temperature and concentration to the first order in c

$$\eta_e = \eta_s\{1 + [\eta]_{pl}c\} \tag{6}$$

where $[\eta]_{pl} = [(\eta_e - \eta_s)/c\eta_s]|_{c\to 0}$ is negative, representing to the first order the viscosity change due to the plasticization. Moreover, the absolute value of $[\eta]_{pl}$ increases sharply as the temperature is lowered. $[\eta]_{pl}$ was previously denoted as $[\eta_e]$ by Morris et al.[5] A comparison between eqs 5 and 6 with $\eta_s \equiv \eta_{20}$ shows that $[\eta]_{pl} \propto A'(T) = -p(T)B/[f_{20}(T)]^2$. When the coupling effect on free volume is neglected and the glass transition is taken as a state of iso-free-volume, it can be shown that $p(T) = \alpha_1(T - T_{g1}) - \alpha_2(T - T_{g2}) > 0$ for $T_{g1} < T_{g2}$. This form is equivalent to that given by Fujita.[20] It adequately describes the temperature dependence of the plasticization effect, i.e., that of η_e/η_s or $[\eta]_{pl}$.

When the plasticization effect is present, i.e., when $T_g^{\,p} < T_g^{\,s}$ (or $T_{g1} < T_{g2}$ in the notion used above), the polymer chains should be viewed as surrounded by an effective solvent with viscosity η_e instead of η_s in formulating a molecular theory for polymer solution dynamics. Replacing η_s with η_e in the usual expression for the solution as first did by Morris et al.,[5] the polymer hydrodynamic contribution may be measured in terms of the ratio η/η_e. In other words, we have to the first order in c

$$\eta = \eta_e\{1 + [\eta]_h c\} \tag{7}$$

where by definition $[\eta]_h = [(\eta - \eta_e)/c\eta_e]|_{c\to 0}$. Because η_e contains about the same level of plasticization as η does, η is not expected to drop below η_e upon lowering the temperature. This is illustrated in Figure 6 for both 2.6% and 10% solutions at −30 °C. All the full symbols stay above the horizontal line, and all the open symbols drop below the line at −30 °C. This means that at such a low temperature the plasticization produces a negative contribution to η that overshadows the polymer hydrodynamic contribution represented by $[\eta]_h$ in (7).

Combining eqs 6 with 7, we obtain to the first order in the concentration c

$$\eta = \eta_s\{1 + ([\eta]_{pl} + [\eta]_h)c\} \equiv \eta_s + \delta\eta_{pl} + \delta\eta_h \tag{8}$$

where $\delta\eta_{pl} \equiv \eta_e - \eta_s < 0$ describes the plasticization

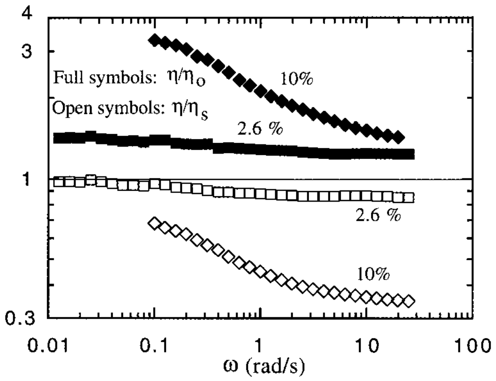

Figure 6. Viscosity ratios of 2.6% and 10% solutions at −30 °C.

effect and $\delta\eta_h \equiv \eta - \eta_e$ quantifies the hydrodynamic effect. When the plasticization effect overcomes the hydrodynamic contribution at a lower temperature, we may observe $\eta < \eta_s$ as shown in Figure 6. The same formalism as described in (6)−(8) has previously been phenomenologically suggested.[3]

The plasticization effect is weaker at higher temperatures. For example, we no longer have a negative viscosity change, i.e., $(\eta - \eta_s) > 0$ in the 2.6% solution at and above −20 °C. This temperature dependence is explicitly described in Figure 7 in terms of both $(\eta - \eta_s)/\eta_s$ and $(\eta - \eta_e)/\eta_e$. $(\eta - \eta_s)/\eta_s$ decreases strongly with temperature because η_s increases faster than η with lowering temperature. Since the reference system and the solution have nearly identical glass transition characteristics, we would expect $(\eta - \eta_e)/\eta_e$ to be essentially independent of temperature. This is apparently not the case as shown Figure 7. The factors responsible for the decrease of $(\eta - \eta_e)/\eta_e$ remains to be explored in the future.

VI. Discussion

When a polymer has a much lower glass transition temperature than that of a solvent, its incorporation into the solvent is expected to result in two competing factors: kinetic and hydrodynamic in nature. In other words, besides the usual hydrodynamic contribution to the solution viscosity, the polymer also plasticizes the solvent. The rivalry between these two effects determines the relationship between the solution η and the solvent viscosity η_s. The original bead−spring model (BSM) of Rouse−Zimm for polymer solution dynamics does not take into account the polymer influence on the solvent dynamics.[1,2] Thus, the temperature dependence of any dynamic quantities such as molecular relaxation times and viscosity has been regarded to be the same as that of the solvent up to the semidilute regime.[2] When the solvent has much faster dynamics than the segmental dynamics of the polymer chains, which is usually true for $T_g^s \ll T_g^p$, the overall solution dynamics is dictated by the fast solvent dynamics, and their temperature dependence is essentially that of the pure solvent. The polymer may have a small deplasticization effect on the solvent dynamics. At high concentrations, it is more convenient to describe the polymer dynamics in terms of those of the undiluted polymer. Fujita free volume theory[20] can be applied to depict the plasticization effect of the polymer by the solvent.[1]

When $T_g^s < T_g^p$, the solvent plasticization by the polymer chains can be significant and can speed up the solution dynamics relative to the pure solvent dynamics.

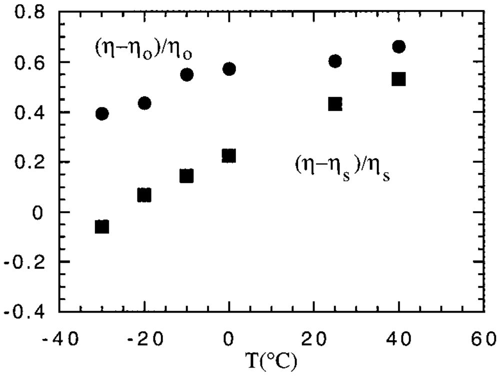

Figure 7. Viscosity increments relative to the pure solvent and the reference system for the 2.6% solution and its corresponding reference, as a function of temperature.

Using solvent viscosity η_s to depict the polymer hydrodynamic contribution in the BSM is no longer adequate. In particular, the polymer chains may experience a local medium viscosity η_e significantly lower than η_s due to their own plasticization. The leading order revision of the original BSM simply involves replacement of η_s with η_e. Such a modification is at the same phenomenological level as that on which the BSM of Rouse and Zimm is based. The modified BSM can be successfully applied to describe the solution dynamics only if some method can be constructed either experimentally or theoretically to measure or calculate η_e as a function of the concentration and temperature. In section III we have demonstrated an experimental protocol involving construction of a reference system whose glass transition temperature is identical to that of the solution. Approximately, the viscosity of this reference can be taken as η_e. A more sophisticated experimental determination of η_e has been put forward previously.[3] It remains to be shown whether the current measurement of η_e indeed mimics the local viscosity in the polymer solution. In section IV, we have also presented a generalized Fujita-type free volume theory for η_e. It provides a phenomenological account for η_e as a function of concentration ϕ and temperature T.

NMR and fluorescence relaxation measurements[8,12,21] have been carried out to directly examine the local segmental dynamics in search for the origin of negative viscosity change (NVC). For solutions exhibiting NVC, the solvent dynamics are found to be accelerated by incorporation of polymer and to have a stronger temperature dependence than that of the local polymer dynamics.[8,21] Since the NMR experiments[8,21] probe the spin−lattice relaxation within the length scale of the repeat unit where the solvent may not be regarded as a continuum, the conformational relaxation time $\tau_c \propto \eta_s^{\alpha} \exp(E_a/k_BT)$ has $\alpha = 0.4 < 1$, where E_a is the activation energy. Subsequent fluorescence relaxation measurements[12] obtained $\alpha = 0.83$ for a similar polymer solution. Thus, the dynamic information about polymer motion is not unique and varying when probed on different scales.

As elucidated in sections III and IV, the negative viscosity change (NVC) primarily arises from the polymer plasticization of the solvent, which echoes with an idea put forward previously by Lodge and co-workers.[3,5] Once this plasticization effect is accounted for, which can be done at the mean-field level, the Rouse−Zimm theory of polymer solution hydrodynamics is recovered.

VII. Conclusion

In the present study, we have explicitly demonstrated how polymer plasticization leads to the negative viscosity change in polybutadiene-based solutions. By eliminating the *negative* polymer plasticization contribution $\delta\eta_{\rm pl} = \eta_{\rm e} - \eta_{\rm s}$ using a reference system whose viscosity $\eta_{\rm e}$ approximately matches the local viscosity present in the corresponding polymer solution, we are able to estimate the actual polymer hydrodynamic contribution $\delta\eta_{\rm h} = \eta - \eta_{\rm e}$ to the solution viscosity η in eq 8 and show that $\delta\eta_{\rm h}$ stays positive throughout the frequency range in oscillatory shear at all temperatures. This idea[3,5] of identifying polymer plasticization of the solvent as the principal origin of NVC should be universal and apply to all experimental systems exhibiting a lower solution viscosity than that of the solvent.

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