Viscoelastic Properties of Amorphous Polymers. 7. Changes of the Anomalous Behavior of Low Molecular Weight Polystyrene with the Addition of a Diluent

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ABSTRACT: Torsional shear measurements of the recoverable creep compliance of a 54.7% solution of a narrow molecular weight distribution polystyrene of low molecular weight, 4000, in tri-*m*-tolyl phosphate are reported as a function of temperature, near and above the glass temperature. Time−temperature superposition of the experimental data is found to be impossible. In fact the steady-state recoverable compliance, J_s, decreases with decreasing temperature as in undiluted low molecular weight polystyrene and other polymers. However, compared with the recoverable compliance data obtained previously in an undiluted polystyrene sample with a comparable molecular weight of 3400, J_s is a significantly weaker function of temperature. Furthermore, the large difference between the temperature dependences of the local segmental retardation time τ^*_α and ηJ_s observed in the bulk polymer is significantly reduced when the polymer is diluted by TCP. As a consequence, the separation between log τ^*_α and log(ηJ_s), is drastically reduced. These changes of the viscoelastic anomalies of low molecular weight polystyrene when diluted by a lower T_g solvent are shown to be consistent with the predictions of the coupling model.

I. Introduction

In several earlier papers, some of which were published in this series, we have addressed several general kinds of viscoelastic behavior of polymers.[1−5] In high molecular weight entangled polymers these viscoelastic phenomena include (1) the time scale shift factor, $a_{T,\alpha}$, of the local segmental motion having a stronger temperature dependence than that, $a_{T,\mathrm{w}}$, of the terminal dispersion,[6−12] and (2) the glass−rubber softening dispersion is thermorheologically complex [5,13−15] caused by $a_{T,\alpha}$ having a stronger temperature dependence than that, $a_{T,\mathrm{R}}$, of the Rouse modes generalized for undiluted polymers.[16,17] In high molecular weight entangled polymers the steady-state recoverable compliance, J_s (previously denoted by J_e^0), is temperature independent and $a_{T,\mathrm{w}}$ is experimentally identical to the temperature shift factor, $a_{T,\eta}$, of the viscosity.[17]

In low molecular weight unentangled polymers, the Rouse retardation time τ_R defined by the product, ηJ_s, has a much weaker temperature dependence than $a_{T,a}$ of the local segmental motions. Consequently, as temperature is decreased to approach the glass temperature, T_g, the shorter time scale of the local segmental motions tend to encroach upon the longer time scale of the Rouse modes. There is a concomitant decrease of J_s and a more dramatic decrease in J_s is found in polymers with lower molecular weights.[2−5,11,18−21] One may object to the use of the Rouse model generalized for undiluted polymers[17] to describe the viscoelastic response of low molecular weight polymers because of limited number of Kuhn step lengths. However, experimentally it is found that J_s obtained at temperatures sufficiently high above the glass temperature is remarkably well described by the modified Rouse model prediction: $J_s = 0.40(M/\rho RT)$, where M is the molecular weight and ρ the density, down to the low molecular weights of polystyrene samples considered in the present work as well as in an earlier work.[20] This remarkable success of the modified Rouse model in its parameterless prediction of J_s down to the low molecular weights of our present interest and the absence of a better description lead us to continue to use Rouse modes when referring to the contribution to viscoelastic response of low molecular weight polymers other than the local segmental motions. These interesting viscoelastic properties that were discovered quite a while ago and reproduced in different polymers and in various laboratories should be considered, by any standard, the important issues for theoretical treatment. However, possibly due to the lack of explanation by extant theories of polymer viscoelasticity for a long time and research in the field moving on to address other problems, these anomalous viscoelastic properties have been largely ignored. A consequence has been the general practice of most workers to assume thermorheological simplicity and to report a single average temperature dependence when two or three are present. Some investigations have not observed present complexities due to the self-imposed restriction to the use of standard 2.54 cm diameter rheometer plattens, which limit the incursion into the glass−rubber dispersion. At this time, the only available explanations of these anomalous viscoelastic properties of undiluted polymer we know of[2−5,9,19] have been based on the coupling model.[22−25] We encourage others who prefer different theoretical approaches to address the same problems. We are still seeking to relate molecular structural features with the departures from thermorheological simplicity.

A natural question which arises is what will happen to these viscoelastic anomalies of a low molecular weight polymer after it has been diluted by a low T_g solvent? Will the viscoelastic anomalies remain? This creep and recovery study of a 54.7% low molecular weight polystyrene in *m*-tricresyl phosphate (*m*-TCP) is motivated by the desire to answer these questions. The experi-

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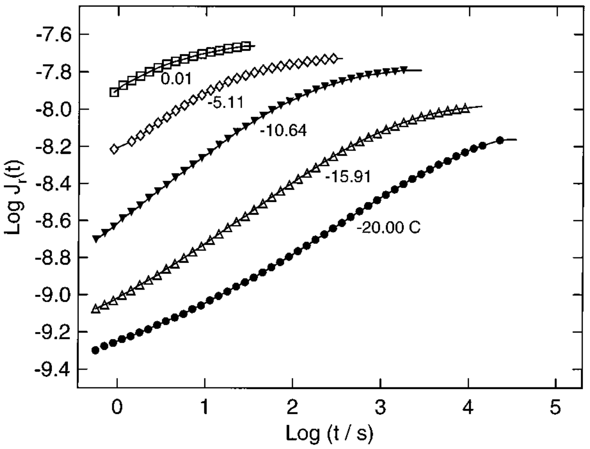

Figure 1. Plots of the logarithm of the recoverable compliance, $J_r(t)$, (cm^2/dyn) versus the logarithm of time t for a 54.7% solution of PS-4000 in *m*-TCP measured at the five temperatures indicated.

mental measurements and the results are reported in the following paragraphs. After that, we shall return to compare the data with theoretical ideas based on the coupling model, particularly with the predicted changes in the viscoelastic behavior of low molecular weight polymers when dissolved in a solvent with a lower T_g.

II. Experimental Section

The PS sample has a polydispersity index, M_w/M_n, of about 1.05 with a weight average molecular weight M_w = 4000 (Glasgow PS 4000). The preparation of the 54.7% polymer solution in tri-*m*-tolyl phosphate (more commonly called *m*-tricresyl phosphate, *m*-TCP) was described before.[26] Here concentration is expressed in terms of percent by weight. The shear creep compliance $J(t)$ and the recoverable compliance, $J_r(t) = J(t) - t/\eta$ where η is the zero shear viscosity, were determined by the torsional creep method using a magnetic-bearing creep apparatus as previously described.[13,20,26] The $J_r(t)$ curves which are measured *directly* (not obtained from the difference $J(t) - t/\eta$; see ref 20 for description) cover a time window of more than four decades at three of the five temperatures of measurement, 0.01, −5.11, −10.64, −15.91, and −20.00 °C, and are shown in Figure 1. Recoverable compliances are generally measured following steady-state creep, where the terminal velocity yields the viscosity. To avoid possible misunderstanding that our $J_r(t)$ curves were obtained from the difference $J(t) - t/\eta$, we cite from ref 20 the statement: "It is eminently clear that very little can be concluded about the form of the recoverable compliance from the total creep compliance curves. Subtraction of the viscous deformation, as indicated by didactic portrayals of creep to ascertain the recoverable contribution is not practical where $t/\eta > 0.8J(t)$."

Recoverable compliance points that are greater at longer recovery times which have been shown to be due to minuscule high molecular weight tails[20,27] are not displayed here. We have frequently encountered high recoverable compliances which are due to the presence of high molecular weight tails in samples; even when they are fractions of anionically polymerized narrow-distribution samples. These "high molecular weight tail" artifacts of the 54.7% polymer solution were removed from the $J_r(t)$ curves in Figures 1−4. The original long-time dispersions in the 3400 bulk polystyrene are still shown in Figure 4 as they were in the original publication.[20] In the 1971 publication[20] and in ref 27 evidence is given that very high molecular weight tails yield misleading high recoverable compliances at time beyond which a viscoelastic steady-state is achieved in samples with smaller tails. These tails cannot often be seen in gel permeation chromatography curves GPC (or SEC), but can be reduced by further fractionation. They, of course, vary from sample to sample with the same molecular weight.

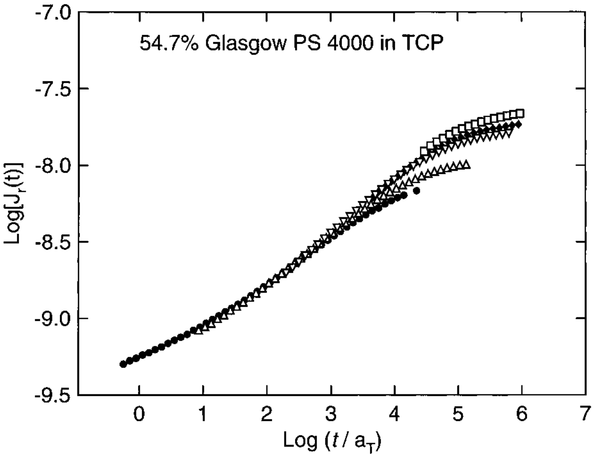

Figure 2. Plots of the recoverable compliance curves of Figure 1 against the logarithm of the reduced time, t/a_T (s). Temperature-dependent horizontal shift factors, a_T, relative to −20.0 °C, have been empirically determined to give the best superposition below the knee of the curves. Symbols used are the same as in Figure 1.

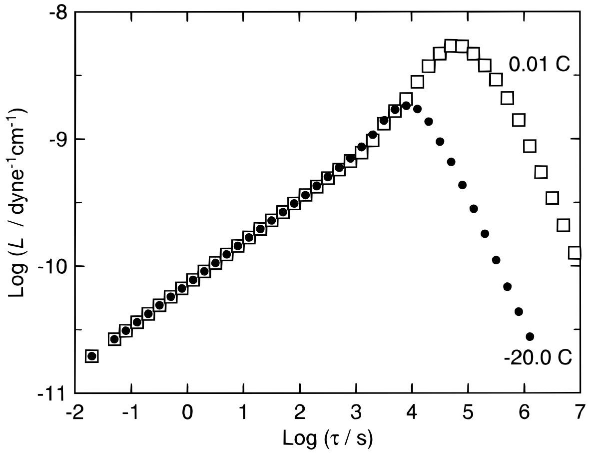

Figure 3. Logarithmic plot of the retardation spectrum $L(\tau/a_T)$ at two temperatures, 0.01 and −20.0 °C, for the 54.7% solution of PS-4000 in *m*-TCP. The reference temperature is −20.0 °C.

III. Failure of the Time−Temperature Superposition

The logarithmic $J_r(t)$ plots at the various temperatures could not be successfully superposed by a simple translation along the log*t* axis because of there is a marked decrease of the steady-state recoverable compliance J_s defined by

$$J_s = \lim_{t\to\infty} J_r(t) \qquad (1)$$

as the temperature of measurement decreases toward T_g. Nevertheless, the short time portions of the isothermal $J_r(t)$ curves can be superposed. The reduced plot of $J_r(t/a_T)$ as a function of the reduced time t/a_T can be seen in Figure 2, where log a_T is the translation required along the log*t* axis to partially superpose the data of the reference temperature T_0 (selected as −20.0 °C). The values of log a_T listed in Table 1 can be represented well by the Vogel−Fulcher−Tamman−Hesse (VFTH) equation

$$\log a_T = -16.27 + \frac{846}{T - (-72.0C)} \qquad (2)$$

The measured values of η at a number of temperatures

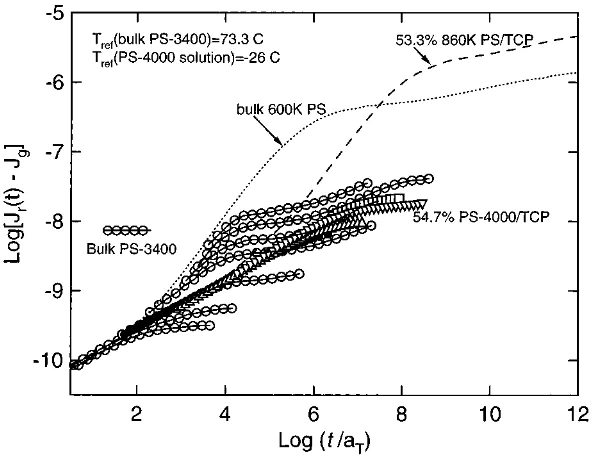

Figure 4. Logarithmic plot of $J_r(t/a_T) - J_g$ as a function of reduced time: (a) for the bulk PS with $M = 3400$ at seven temperatures, 100.6, 94.3, 89.9, 84.3, 79.8, 75.0, and 70 °C (open circles); (b) for the bulk PS with $M = 600\,000$ (dotted curve); (c) for the 54.7% solution of PS-4000 in *m*-TCP at five temperatures (other symbols as used in Figures 1 and 2); (d) for the 53.3% solution of PS with $M = 860\,000$ (dashed curve). The reference temperatures for the four samples are given in the text.

Table 1. The Shift Factor a_T and the Measured Values of η of a Solution of 54.7% PS-4000 in TCP

temp (°C)	log a_T	log (η/poise)
9.96		5.87
5.04	−5.29	6.55
0.01	−4.52	7.25
−5.11	−3.60	8.11
−10.64	−2.55	9.20
−15.82		10.44
−15.91	−1.18	
−20.00	0.00	11.60

are listed in Table 1. The temperature dependence of η can be represented well by the VFTH equation

$$\log \eta = -5.16 + \frac{963}{T - (-77.5\mathrm{C})} \qquad (3)$$

The difference between the temperature dependences given by eqs 2 and 3 is real. The retardation spectrum $L(t/a_T)$ defined by the expression

$$J_r(t/a_T) = J_g + \int_{-\infty}^{\infty} L(\tau/a_T)(1 - e^{-t/\tau})\, d(\ln \tau) \qquad (4)$$

was calculated from the measured $J_r(t)$ for two temperatures $T = 0.01$ and -20.0 °C by a numerical iteration procedure described previously.[26] The value of J_g determined at the reference temperature T_o was 2.68×10^{-10} cm^2/dyn. The calculated $L(t/a_T)$'s are shown in Figure 3 and they exhibit once again[3,18−21] the breakdown of time−temperature superposition through the change in shape of the peak. On decreasing the temperature, there is an erosion of the $L(\tau/a_T)$ peak apparently only on the long retardation time side. This behavior of $L(\tau/a_T)$ and the concomitant strong temperature dependence of J_s have been seen before in undiluted low molecular weight PS[20,21] and other polymers.[2−5,11,18,19]

IV. Comparison of the Viscoelastic Anomaly in Diluted and Undiluted Polymers

Since the anomalous strong temperature dependence of J_s and L in the solution of PS in TCP was found in both diluted and undiluted PS, it is natural for us to compare them quantitatively. Of particular interest is the comparison with the data of a bulk polymer with nearly the same molecular weight as the PS diluted by TCP. For this reason, we have chosen to reexamine the data of the PS sample (PC-11) with 3400 molecular weight reported in Reference 20 and J_g was determined to be 9.55×10^{-11} cm^2/dyn. Recently we have shown[28] that the local segmental (α) contribution of PS to $J_r(t)$ can be represented by the equation[29,30]

$$J_\alpha(t) = J_g + (J_{s\alpha} - J_g)[1 - \exp(-t/\tau_\alpha)^{1-n_\alpha}] \qquad (5)$$

where $1 - n_\alpha \approx 0.36$, τ_α is the retardation time, and $J_{s\alpha} - J_g \approx 2.6 \times 10^{-10}$ cm^2/dyn, where $J_{s\alpha}$ is the steady state compliance contributed by the local segmental motions. We have found that it fits the experimental data well (see for example Figures 4 and 7 in ref 3). The stretched exponential form is also consistent with that proposed by the coupling model. Using this expression to fit the local segmental contribution to the measured $J_r(t)$ of PC-11 at $T = 70$ °C, τ_α(70 °C) is determined to be 2.5×10^3 s. The shift factor determined before, $\log a_T = -13.46 + 389/(T - 41.1)$ with the reference temperature $T_o = 70$ °C, enables us to find that τ_α is equal to 10^2 s at $T = 73.3$ °C. Here we shall use 73.3 °C as our reference temperature because we shall compare the viscoelastic response of different polystyrene polymers at their respective T_g's which are uniformly defined by $\tau_\alpha(T_g) = 10^2$ s. In Figure 4 the reduced $J_r(t/a_T) - J_g$ of PC-11 are shown at seven temperatures, 100.6, 94.3, 89.9, 84.3, 79.8, 75.0, and 70 °C, in descending order as open circles. For clarity, data points belonging to the same temperature are strung together by a solid curve. We have included for comparison the data of $J_r(t/a_T) - J_g$ of an undiluted high molecular weight (6.0×10^5) PS sample A-19 (dotted curve) in Figure 4. The A-19 data has been shifted horizontally to superpose the PC-11 data[20] on the short reduced time or low compliance portion.

The T_g of the 54.7% PS-4000 in TCP corresponding to polymer motion is significantly lower than that of the bulk polymer. The reduced $J_r(t/a_T)$ shown in Figure 2 has to be shifted horizontally by an additional 2.16 decades to longer times in order that the short time portion of $J_r(t/a_T) - J_g$ superposes onto the curve for PC-11 as shown (points represented by the other symbols which are the same as those used in Figure 1) in Figure 4. The additional shift of 2.16 decades means the reduced data of the 54.7% PS-4000 in TCP in Figure 4 has now a reference temperature of −26.0 °C. Superposition of the short time (low $J_r(t/a_T) - J_g$) portion of the undiluted and diluted data means that their retardation times of the local segmental motion are about the same, i.e. ≈ 10^2 s. This result indicates also that T_g of the 54.7% PS-4000 in TCP is −26.0 °C according to the definition stated above. Again, we include the data of $J_r(t/a_T) - J_g$ of a 53.3% high molecular weight (8.6×10^5) PS sample PC-6A (dashed curve) in Figure 4. The PC-6A solution data has been shifted horizontally to superpose the 54.7% PS-4000 in TCP data on the short time or low compliance range.

The calculated $L(\tau/a_T)$'s of all four polymer systems corresponding to the reduced data shown in Figure 4 are displayed in Figure 5. The relation between the viscoelastic responses of the low and the high molecular weight polymers in either the undiluted or the diluted state is made particularly clear by comparing their $L(\tau/a_T)$'s. In each case, as the molecular weight of the

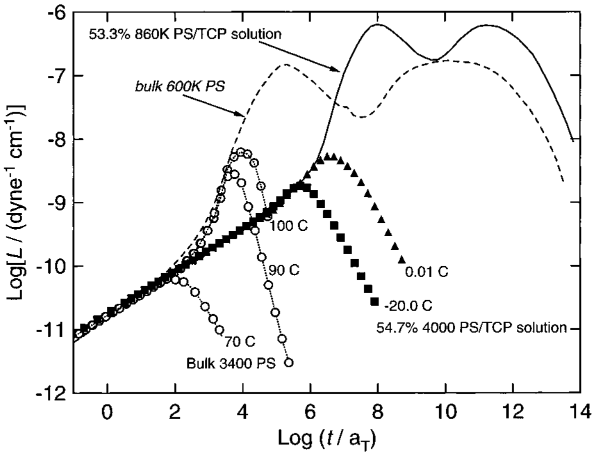

Figure 5. Logarithmic plot of the retardation spectra $L(\tau/a_T)$ for the four samples (a−d) appearing in Figure 4.

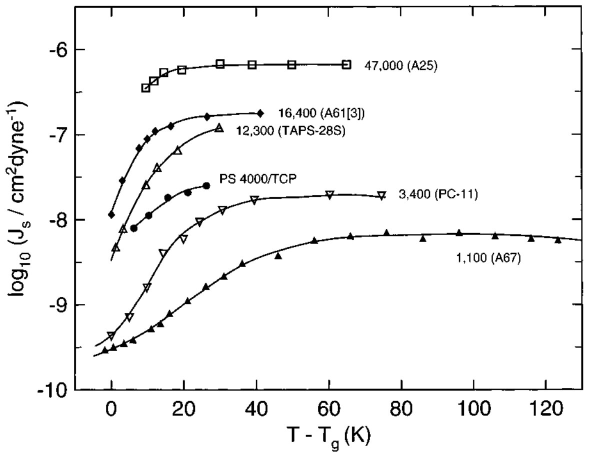

Figure 6. Semilogarithmic plots of the equilibrium recoverable compliance, J_s, as a function of the temperature, $T - T_g$, for five undiluted polystyrenes with molecular weights as indicated, and for the 54.7% solution of PS-4000 in *m*-TCP (filled circles).

polymer is decreased the Rouse modes of longer wavelengths and retardation times no longer make their appearance. Such a behavior is expected from the molecular weight dependence of the Rouse model for undiluted polymer and concentrated polymer solutions.[17] However, the dramatic depletion of long retardation modes in the retardation spectrum (equivalent to a marked decreased of J_s in Figure 4) as temperature is decreased toward T_g in low molecular weight polymers is an anomalous viscoelastic behavior not easily explained. This anomaly is found in both the undiluted PC-11 and the 54.7% PS-4000 in TCP. It should be noted that the effect is drastically reduced when the polymer is diluted. This comparison can be seen in a plot of $J_s(T)$ against the reduced temperature $T - T_g$ of the 54.7% PS-4000 in TCP and the PC-11. It is clear from this plot (Figure 6) that the decrease of $J_s(T)$ as a function of $T - T_g$ is much reduced when the polymer is diluted by TCP. We have plotted in Figure 6 $J_s(T)$ versus $T - T_g$ of other undiluted PS with different molecular weights. The rate of decrease of $\log J_s(T)$ with decreasing $T - T_g$ in the 54.7% PS-4000/TCP solution is significantly reduced compared with the undiluted PC-11 which has nearly the same molecular weight. It is smaller than in all of the undiluted PS's with molecular weights $M \leq 1.64 \times 10^4$, and appears to be comparable to that for a much high molecular weight polymer with $M = 4.7 \times 10^4$. We extrapolate the smooth T-dependence of $J_s(T)$ of the 54.7% PS-4000/TCP solution to $T = T_g$ and obtain a rough estimate of $J_s(T_g) = 10^{-8.37}$ cm^2/dyn. Figure 7 shows that this value for the solution (open circle) is about an order of magnitude larger than that expected from the dependence of $J_s(T_g)$ of undiluted polymers on the molecular weight (smooth curve drawn through the data represented by solid circles). Thus, we conclude from the data that the magnitude of the anomalous decrease of $J_s(T)$ of low molecular weight PS is drastically reduced when the polymer is diluted.

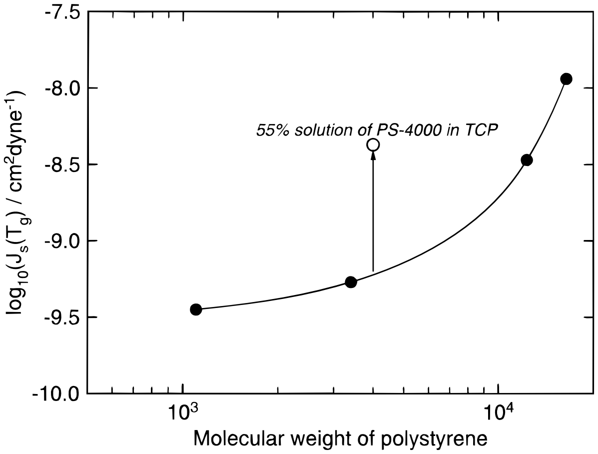

Figure 7. Logarithmic plot of the steady-state recoverable compliance at T_g, $J_s(T_g)$, as a function of molecular weight of polystyrene. Filled circles are for undiluted polymer and the lone open circle is for the 54.7% solution of PS-4000 in *m*-TCP. The vertical arrow indicates the change after the polymer has been diluted by addition of the solvent.

V. Theoretical Interpretation

The dramatic decrease of $J_s(T)$ found in low molecular weight PS[20,21] and other polymers[2−5,11,18−20] with decreasing temperature has been a challenging viscoelastic anomaly for theory to explain. The experimental data of PS in solution reported here provides yet another startling effect that the decrease of $J_s(T)$ is drastically reduced when a diluent with lower T_g is introduced into the polymer. This additional effect should provide another impetus for researchers in the field of viscoelasticity to seek a theoretical interpretation of the general phenomena. We welcome others to explain the data on a theoretical basis. So far the only published theoretical explanation[2−4,19] is based on the coupling model.[22−25] Although the coupling model (CM) has not yet been given a rigorous theoretical foundation, recent works have pointed in the direction of chaos due to nonintegrable interactions between the relaxing elements.[23−25] Fortunately, the basic results of the coupling model have direct experimental support from quasielastic neutron scattering measurements in several polymers,[31,32] molecular dynamics simulation,[33] and high frequency conductivity measurements in glassy ionic conductors and glass-forming melts.[34−36]

At present the only explanation of the anomalous viscoelastic properties of undiluted polymer we know of has been offered by the coupling model.[5,19] This had been laid out in several papers published in this journal, and there is no need for any extensive review here. The crux of the explanation lies in the coupling model is description of the crowded local segmental motions (LSM),[2−4,9,19,23] which are responsible for the glass temperature. The dynamic constraints arising from intermolecular coupling and intermolecular interactions slow down the averaged relaxation rate of the LSM. The effective LSM relaxation time, τ^*_α, is determined by the coupling parameter, n_a, according to the equation

$$\tau^*_\alpha = [t_c^{-n_\alpha}\tau_{o\alpha}]^{1/(1-n_\alpha)} \tag{6}$$

Here t_c is the crossover time from independent relaxation, $\exp(-t/\tau_{o\alpha})$ for $t < t_c$, to an averaged slowed down relaxation, $\exp(-(t/\tau^*_\alpha)^{1-n_\alpha}$ for $t > t_c$. It is related to the quantity ω_c that appeared in earlier references by the identity $t_c \equiv (1 - n_\alpha)^{-1/n_\alpha}\omega_c^{-1}$. Recent quasielastic neutron scattering experiments in several polymers[31,32] have found t_c is temperature insensitive and has a value of about 2 ps. As explained before[2-5,11,18,19,23], $\tau_{o\alpha}$ and the Rouse relaxation times $\tau_{R,p}$ have the same underlying friction coefficient, $\zeta_o(T)$. Consequently, it follows from eq 6, the temperature shift factor $a_{T,\alpha}$ of the LSM has a stronger temperature dependence

$$a_{T,\alpha} \equiv \tau^*_\alpha(T)/\tau^*_\alpha(T_o) = [\zeta_o(T)/\zeta_o(T_o)]^{1/(1-n_\alpha)} \tag{7}$$

than that

$$a_{T,R} = \zeta_o(T)/\zeta_o(T_o) \tag{8}$$

of the Rouse modes. As mentioned before, one may object to the use of the Rouse model generalized for undiluted polymers[17] to describe the viscoelastic response of low molecular weight polymers when the chain has only a limited number of Kuhn step lengths. When a theory better than the Rouse model comes along its modes, in the context of the coupling model, must have also the friction coefficient, $\zeta_o(T)$, because of the absence of (entanglement) interaction in low molecular weight polymers. Thus, eq 8 will continues to hold when the Rouse model is eventually replaced by a more sophisticated model.

The larger the coupling parameter n_α, the larger is the exponent, $1/(1 - n_\alpha)$, appearing in eq 7 and stronger is the temperature dependence of $a_{T,\alpha}$ compared with $a_{T,R}$ (eq 8). Hence, the viscoelastic spectrum of a low molecular weight polymer is intrinsically thermorheologically complex. It can be easily shown from eq 6 that τ^*_α becomes longer (and its separation from the longer Rouse times shorter) with larger n_α, reflecting the fact that stronger dynamic constraints enhance the deceleration of the average relaxation rate which is proportional to $(\tau^*_\alpha)^{-1}$.

These properties of τ^*_α have been shown[2-4,19,23] to give rise to the marked decrease of J_s as temperature is lowered to approach T_g. Using polyisobutylene (PIB) which has[37,38] a smaller n_α than PS, we have demonstrated with experimental data obtained on samples having the same number of backbone carbon atoms that the anomalous decrease of J_s with temperature observed in PS is significantly reduced in PIB[2]. Weaker dynamic constraints and smaller attendant n_α result in a shorter τ^*_α and a less rapid temperature variation of $a_{T,\alpha}$, relative to the Rouse modes in the softening dispersion. Consequently, there is less encroachment of the LSM relaxation toward the Rouse relaxation time spectrum, $\tau_{R,p}$, (i.e. the separation between τ^*_α and $\tau_{R,p}$ is greater for PIB) and a smaller difference between the temperature dependences of $a_{T,\alpha}$ and the $a_{T,R}$ of the Rouse modes. From these results we have been able to explain how the anomalous decrease of J_s with temperature observed in PS is significantly reduced in PIB[2].

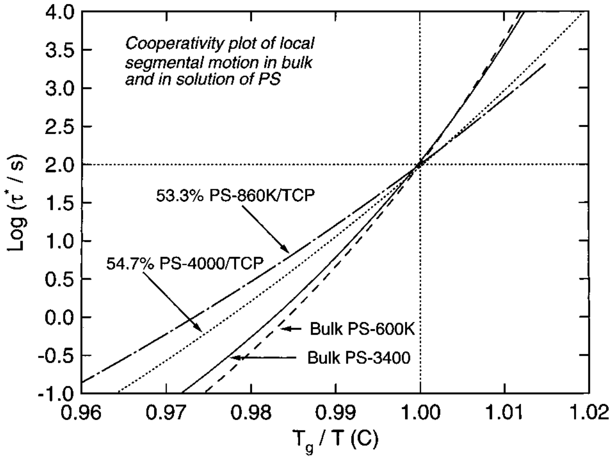

Figure 8. Semilogarithmic plot of the local segmental retardation time against normalized reciprocal temperature, T_g/T. Solid curve is for the undiluted PS with $M = 3400$. Dotted curve is for the 54.7% solution of PS-4000 in *m*-TCP. Dashed curve is for the undiluted PS with $M = 600\,000$. Dashed–dotted curve is for the 53.3% solution of PS with $M = 860\,000$.

Experimentally, weakening of the dynamic constraints imposed on the LSM of a polymer can also be accomplished by dissolving the polymer in a diluent that has a lower T_g. Fast reorientation and diffusional motions of the diluent molecules mitigate the dynamic constraints experienced by the remaining polymer in executing the LSM and consequently reduce n_α. An example of experimental evidence of the decrease of n_α with addition of diluent having a lower T_g can be found in the dielectric relaxation data of PVC dissolved in tetrahydrofuran.[39,40] An analysis of the dielectric data revealed that the width of the dielectric loss peak decreases with increase of diluent content, indicating a smaller n_a. Also, the temperature dependence of τ^*_α or its shift factor $a_{T,\alpha}$ becomes weaker as the diluent content is increased.[40] The second feature of the dielectric data is evident also from our viscoelastic data. In Figure 8, we compare the temperature dependence of log τ^*_α of bulk PC-11 (solid curve) and 54.7% PS-4000/TCP solution (dotted curve) by plotting against the normalized reciprocal temperature T_g/T. The T_g's of bulk PC-11 and the 54.7% PS-4000/TCP solution are 73.3 and −26.0C respectively. τ^*_α has the value of 10^2 s at these glass temperatures. In Figure 8 we have included the T_g-scaled temperature dependence of a 53.3% high molecular weight 8.6×10^5 PS sample (PC-6A) (dashed-dotted curve) and of a undiluted high molecular weight (6.0×10^5) PS sample A-19 (dashed curve). A weaker temperature dependence of τ^*_α results from the addition of about 45% TCP in PS for both the low and high molecular weight samples, as expected by the coupling model.[29,41] The relation of the T_g-scaled temperature dependences of the undiluted and diluted PS is like that between the undiluted PS and undiluted PIB.[29,41]

The Rouse retardation time τ_R defined by the product, ηJ_s, has a much weaker temperature dependence than $a_{T,\alpha}$ of the local segmental motion as predicted by eqs 7 and 8. In Figure 9 we have plotted these two retardation times of the 54.7% PS-4000/TCP solution (open and filled circles) together with four bulk PS samples A25, A61[3], PC11, and A67 with molecular weights equal to 4.7×10^4 (open and filled squares), 1.64×10^4 (open and filled diamonds), 3.4×10^3 (dashed curve and filled inverted triangles) and 1.1×10^3 (open and filled triangles), respectively. In all cases, τ^*_α has a stronger temperature dependence than ηJ_s. In Figure 9 we shift the logηJ_s data points of PS-4000/TCP (filled circles) uniformly vertically downward by 3.2 decades. The

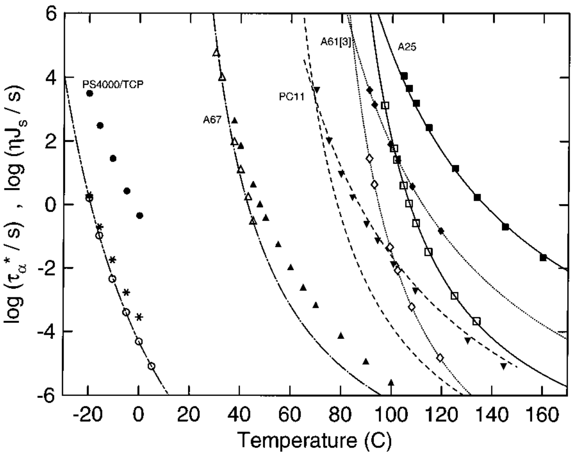

Figure 9. Semilogarithmic plots of the local segmental relaxation times, τ^*_α, and the terminal characteristic time, ηJ_s, for four undiluted low molecular weight polystyrene samples, A25, A61[3], PC11, and A67 with $M = 47\ 000$ (squares), 16 400 (diamonds), 3400 (inverted triangles), and 1100 (triangles), respectively. Open symbols are for τ^*_α and the corresponding filled symbol are for ηJ_s of the same sample. The dashed line for logτ^*_α for PC11 could not be measured but were deduced from the molecular weight dependence of τ^*_α (see Reference 20). The data of the 54.7% solution of PS-4000 in *m*-TCP are also shown by the filled and open circles for τ^*_α and ηJ_s, respectively. Points indicated by asterisks are obtained by shifting the ηJ_s data points of the 54.7% solution of PS-4000 in *m*-TCP uniformly vertically downward by 3.2 decades.

results (points represented by an asterisk) when compared with that of PC-11 indicate that the large difference between the temperature dependences of τ^*_α and ηJ_s observed in the bulk polymer is significantly reduced when the polymer is diluted by TCP. The behavior is consistent with eqs 7 and 8 with a smaller n_α when diluent is added to the polymer.

Since τ^*_α has a stronger temperature dependence than ηJ_s, the shorter time scale of the local segmental motion tends to encroach the longer time scale of the Rouse modes as temperature is decreased to approach the glass temperature, T_g. The degree of encroachment, measured by the separation, log R_τ, between logτ^*_α and logηJ_s, of bulk PS increases with decreasing molecular weight. However, on diluting the PS-4000 with 45.3% TCP the encroachment is drastically reduced when compared with that seen in PC-11 which has about the same molecular weight. This large reduction of the size of the viscoelastic anomaly due to the dilution of the polymer is made clear in Figure 10 by plotting the log $R_t(T_g)$ of the solution where the separation is shown to be three decades greater than that seen in the undiluted polymer. This large difference of log $R_\tau(T_g)$ between the undiluted polymer and its solution is a consequence of eqs 6–8 and again the fact that n_α decreases when the polymer is diluted.

Thus the coupling model predictions based on the difference of the coupling constants agree with the experimental observations.

VI. Conclusion

The experimental creep compliance data of a 54.7% polystyrene (with molecular weight = 4000) solution in TCP reported here shows that the anomalous viscoelastic properties (i.e. thermorheological complexity and marked decrease of J_s with decreasing temperature) found earlier in an undiluted polymer of comparable molecular weight is to a large extent diminished. This dramatic change of viscoelastic response of a low molecular weight polymer with dilution provides another important clue to the origin of the anomalous viscoelastic response. In our opinion, an understanding of the viscoelastic properties of polymer is incomplete without resolving the problem of what causes the observed anomalous viscoelastic response of the low molecular weight polymers. We encourage others to investigate this dramatic effect theoretically. Meanwhile, we find that the coupling model continues to provide a satisfactory interim explanation of the observed behavior in both undiluted and diluted polymers. In the framework of the coupling model, the addition of a low T_g diluent to PS mitigates the dynamic intermolecular constraints and decreases the coupling parameter, n_α, of the PS local segmental motion from its value of the neat polymer. The decrease in n_α leads to an immediate explanation of the dramatic suppression of the anomalous decrease in J_s with decreasing temperature when PS is diluted by tricresyl phosphate. Bulk polyisobutylene (PIB) has a smaller n_α than bulk PS[38,41] and this viscoelastic anomaly is much reduced[1,2] in PIB than in PS. Our experimental data presented in this paper indicate that a solution of PS behaves like PIB as far as this viscoelastic anomaly is concerned. This coincidence is no accident according to the coupling model because the two systems have coupling parameters that are smaller than bulk PS, and it is n_a which to a great extent controls the viscoelastic response of a polymer.

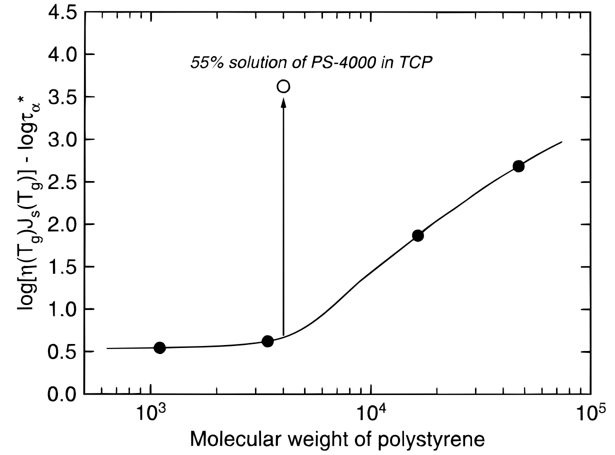

Figure 10. Logarithmic plot of the difference between logτ^*_α and logηJ_s of the undiluted polystyrene (filled circles) and the 54.7% solution of PS-4000 in *m*-TCP (open circle) against the molecular weight of the polymer.

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