

Dynamics of aroclor and its modification by dissolved polystyrene

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Dynamic mechanical spectroscopy, dielectric spectroscopy, and viscosity measurements were carried out on Aroclor 1254 (PCB54), a chlorinated biphenyl. The temperature dependences of both the dielectric relaxation times and the viscosity depart from a single Vogel–Fulcher behavior, at a temperature, T_B , equal to 294 K. The ratio of this characteristic temperature to T_g ($= 246$ K) is close to that found previously for other Aroclors, having different chlorine levels. The shapes of the dielectric and mechanical relaxation functions were equivalent, yielding a value for the Kohlrausch stretch exponent equal to 0.625 at T_g . However, the relaxation times for the dielectric modulus were substantially larger than the viscosity and mechanical relaxation times. The respective temperature dependences of the viscosity and the dielectric relaxation times, although similar, deviated from the Debye–Stokes relation with decreasing temperature. The temperature associated with this deviation is somewhat higher than T_B , and coincides with the temperature at which the relaxation function approaches Debye behavior. These phenomena all reflect the alleviation at high temperature of intermolecular constraints on the dynamics. The addition of high molecular weight polystyrene (PS-90k) to the PCB54 had an almost negligible effect on the dielectric relaxation times, notwithstanding that the polystyrene's glass temperature is 130 degrees higher than T_g for PCB54. The PS-90k exerted a more significant effect on the mechanical relaxation times of the PCB54. However, the modification of the Aroclor dynamics is still orders of magnitude less than the effect of the dissolved PS-90k on the relaxation times of an oligomeric PS (PS-o). This low molecular weight PS has a T_g identical to that of the PCB54. The dramatic difference between the effect of added polymer on the dynamics of Aroclor versus PS-o can be ascribed to differences in their capacity for intermolecular coupling with the PS-90k solute. © 2002 American Institute of Physics. [DOI: 10.1063/1.1497637]

INTRODUCTION

There has been long-standing interest in modifying the dynamics of small molecules by the addition of polymers.^{1–3} Both the sign and the magnitude of the change in the solvent's viscosity and relaxation times reflect changes in the motion of solvent molecules residing in the vicinity of dissolved polymer chains.

The qualitative nature of these changes can generally be predicted from the relative glass temperatures, T_g , of the components. To wit, the addition of higher T_g polymer slows down the dynamics, while a lower T_g component would have the opposite effect. Interestingly, when the glass temperatures of the components are close, anomalies have been observed.^{4–8} For example, the addition of *higher* T_g polyvinylethylene (PVE) has been shown to *speed up* the relaxation of Aroclors (polychlorinated biphenyls).^{9,10} In this system, the anomaly can be ascribed to the positive changes in excess volume of mixing.¹⁰ Although mixtures of Aroclor and PVE exhibit a single glass transition temperature, and only one segmental relaxation dispersion in light scattering,⁹ dynamic mechanical and dielectric spectra,¹¹ ¹³C nuclear

magnetic resonance (NMR) results demonstrated that the motions of the components occur at very different time scales.¹² Moreover, while affirming the existence of the anomaly of faster motion of Aroclor upon addition of higher T_g PVE, the NMR results showed that the dynamics of the PVE speed up as well.

In this paper we report dielectric and mechanical spectroscopy measurements of the effect of high molecular weight polystyrene (PS) on the relaxation of two lower T_g materials, an Aroclor and oligomeric PS. These components are miscible in all proportions; nevertheless, the relaxation properties of the mixtures are not predictable from the respective glass temperatures of the neat components.

EXPERIMENT

The polychlorinated biphenyl was Monsanto's Aroclor 1254 (PCB54, obtained from J. Schrag of the University of Wisconsin), which has 54% by weight chlorine. Aroclors are mixtures of polychlorinated biphenyls having different chlorine content. The presence of various homologs suppresses crystallization which, along with their minimal volatility, make them ideal glass-formers for experimental studies.

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TABLE I. Effect of polymer on solvent dynamics.

Solute (T_g)	Solvent (T_g)	c (g/ml)	$\partial \ln \xi / \partial c$	
			$\tau(M'')$	$\tau(G'')$
PS-90k (374.4)	PCB54 (246)	0.13	1.1	9.8
PS-90k (374.4)	PS-o (244.0)	0.10	...	91

PCB54 is primarily pentachlorobiphenyl, having a glass temperature, $T_g = 246$ K, as measured by DSC at 10 deg/min.

Two polystyrenes were used, having respective molecular weights of 590 g/mol (obtained from Polymer Scientific) and 90 000 g/mol (Johnson Matthey). The former is an oligomer, having just six monomer units per chain, with a polydispersity of 1.07. We refer to these samples respectively as PS-o and PS-90k. PS-o has a calorimetric glass temperature, 244.0 K, almost equal to that of PCB54. The T_g of PS-90k is much higher, =374.4 K.¹³

A blend of the PCB54 with the high molecular weight PS was prepared by first dissolving the PS-90k in cyclohexane, prior to addition to the Aroclor. To remove the solvent, this solution was kept in vacuum at 40 °C for a few days to achieve constant weight. A blend of the two PS was also prepared, again using cyclohexane to facilitate mixing. The concentration of these mixtures, c , expressed as grams of PS-90k per ml of solvent, are given in Table I.

Dielectric measurements were carried out over 13 decades of frequency (10^{-4} – 10^9 Hz), using an IMASS time domain dielectric analyzer, a HP4284A LCR meter and a HP4291A impedance analyzer.

Viscosities were obtained with a Bohlin VOR rheometer, using a parallel plate geometry. To enable measurements over 10 decades of viscosity, two plate diameters (2.5 and 4.0 cm diam) in combination with two torsion bars (11 and 299 g-cm) were utilized. Both dynamic and steady state viscosities were measured, with no differences between the data. Dynamic mechanical measurements in the vicinity of the glass transition were obtained using a second Bohlin VOR, equipped with electronic transducer. A parallel-plate geometry was employed, with sample radius and gap of 6.4 and 1.5 mm, respectively. The frequency range of the mechanical measurements was from 10^{-4} to about 2 Hz. Temperature variation for both rheometers was less than ± 0.1 deg.

RESULTS

Neat aroclor

The most probable relaxation time is defined from the frequency of the maxima in the dielectric loss peaks, $\tau = 1/2 \pi f_{\max}$. Figure 1 displays these τ for neat PCB54 over the measured range of temperatures. Defining a dynamic glass temperature as the temperature at which τ equals 100 s, we obtain $T_g = 245.7$ K. This is less than 0.5 K higher than the calorimetric T_g . It is usual practice to describe temperature dependences using the Vogel–Fulcher (VF) equation¹⁴

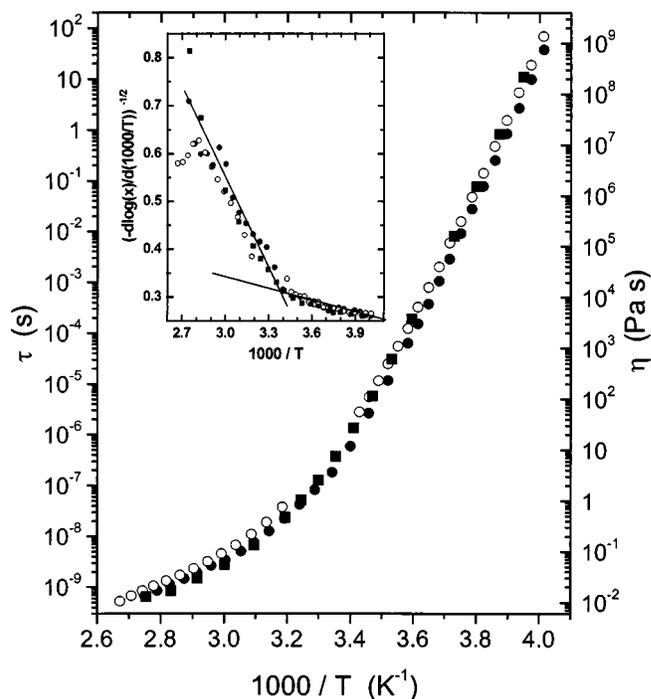


FIG. 1. Dielectric relaxation times ($=1/2 \pi f_{\max}$) (●) and viscosities (■) measured for neat PCB54, along with the dielectric τ for a blend with PS-90k ($c=0.13$ g/ml; ○). The range of the respective ordinate scales is the same, to demonstrate the near equivalence of the respective temperature dependences. The inset shows the Stickel function for these data, where x represents relaxation time or viscosity and the solids lines indicate the two regimes of VF behavior.

$$\log \tau = A + \frac{DT_0}{T - T_0}, \quad (1)$$

where T_0 is the Vogel temperature and A and D are constants. Equation (1) describes the present data over about eight decades of τ , however, deviations from a single VF description occur.

This deviation can be assessed from plots of the derivative function.¹⁵ In the inset to Fig. 1, we plot the quantity $[-d \log(\tau)/d(1000/T)]^{-1/2}$ versus $1000/T$ (“Stickel plot”¹⁶), whereby a VF dependence gives a straight line (with zero slope for Arrhenius behavior). It is evident that the low temperature data for PCB54 conform to one VF relation; beyond $T_B \sim 294$ K, the data deviate to a second VF relation.¹⁷ Previous results for Aroclors having different chlorine contents and glass temperatures showed that the ratio T_B/T_g was constant, equal to 1.17.¹⁸ This is equivalent within experimental error to the value herein for PCB54, $T_B/T_g = 1.19$ (using the glass temperature determined from the dielectric relaxation times).

The viscosity, η , of the PCB54 was measured over the same temperature range as the dielectric measurements. These data are included in Fig. 1. The temperature dependence of η is nearly equivalent to that of dielectric relaxation times; consequently, the viscosity data yield the same value of $T_B = 294$ K (Fig. 1 inset). A viscosity relaxation time can be obtained from the Maxwell relation, $\eta = G_\infty \times \tau_\eta$, in which G_∞ is the glassy modulus. G_∞ varies somewhat with both temperature and frequency, equaling ~ 1.2 GPa at 240

K, which is 4 degrees below T_g . (This corresponds to the beginning of the glassy plateau in the mechanical spectrum, and thus somewhat underestimates G_∞ .) Using this value of G_∞ in the Maxwell relation yields τ_η which are as much as a factor of 50 smaller than the dielectric τ in Fig. 1.

This difference in relaxation times suggests that the relevant length scales for dielectric relaxation and viscosity are different. The polarity of the Aroclor derives from the pendant chlorines, which subtend the entire molecule. Strong constraints on reorientational motions are expected to give rise to long relaxation times. On the other hand, the anisotropic shape of the biphenyl structure facilitates the translational motions underlying the viscosity, whereby the τ_η are relatively smaller. Hence, the observed differences between the dielectric and viscosity relaxation times are plausible.

The respective temperature dependences of the relaxation times and viscosities are related according to the Debye–Stokes equation¹⁹

$$\tau = \frac{V\eta}{kT}, \quad (2)$$

in which k is the Boltzmann constant and V an effective volume. We assess conformance to this equation from a double logarithmic plot of η versus τ (Fig. 2). An apparent proportionality between these quantities is observed over the entire temperature range. In the upper inset to Fig. 2, we plot the ratio $\eta/T\tau$ on a linear ordinate scale, where a (small) difference in temperature dependences becomes apparent as temperature is lowered. This change transpires substantially away from the temperature, T_B , associated with the change in dynamics. In the lower inset to Fig. 2, we show the full width at half maximum (FWHM) of the dielectric loss peak. It is noteworthy that the relaxation is close to a Debye process (i.e., exponential decay) in the vicinity of the temperature at which Eq. (2) becomes valid.

The dynamic mechanical shear modulus was also measured for the PCB54, at several temperatures just above T_g . The range of these measurements was limited by the need to have the dispersion in the loss modulus, $G''(\omega)$, fall within the experimentally accessible frequency range. Nevertheless, it is interesting to compare the results to the dielectric data. To do this, we calculate the dielectric modulus, $M^*(\omega)$, which is equal to the reciprocal of the dielectric constant $\epsilon^*(\omega)$.

As seen in the representative results shown in Fig. 3, there is a very little difference between the shape of the two loss moduli, although the peak in the dielectric loss modulus, $M''(\omega)$, may be slightly broader. The loss modulus data were fit to the Laplace transform of the Kohlrausch function^{20,21}

$$G''(\omega) = \omega \int_0^\infty \exp(-(t/\tau_K)^\beta) \cos(\omega t) dt, \quad (3)$$

in which τ_K is the Kohlrausch relaxation time ($>\tau$ defined from the peak frequency) and β the stretch exponent. At T_g , we obtain $\beta=0.625$, which is comparable to the value reported for PCB48, an Aroclor having slightly lower chlorine content.¹¹

The dielectric spectra in Fig. 3 were shifted slightly in frequency to allow comparison to the mechanical loss

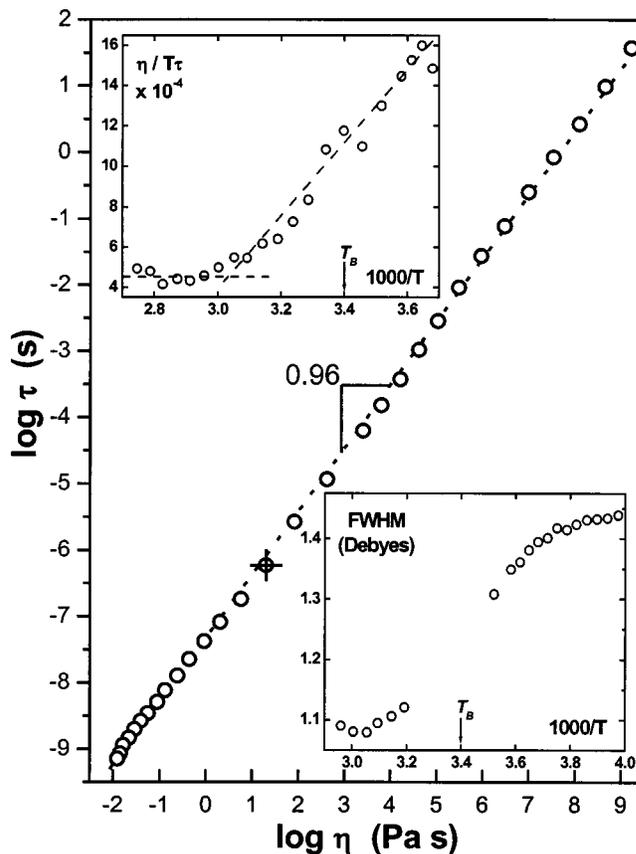


FIG. 2. The relationship between the viscosity and the dielectric relaxation times for PCB54. The power law slope is close to unity, which is the DSE prediction [Eq. (2)]. The cross denotes $T_B (= 294 \text{ K})$. The upper inset shows the ratio of the viscosity to the product of the dielectric relaxation time and temperature. The dashed lines are only to guide the eyes. In the lower inset are the widths at the half-intensity points of the peak, normalized by the FWHM of a Debye relaxation ($= 1.14$ decades). The gap falls in the range of frequencies over which the HP4284A and HP4291A instruments overlap; results are shown only for dielectric loss peaks which could be measured entirely with one spectrometer.

moduli. There is no reason to expect the orientational relaxation times probed dielectrically to be equal to the mechanical relaxation times, although for a small molecule such as PCB54, these τ should be similar. In Fig. 4 are displayed the τ measured mechanically. These are quite close to the values of τ_η calculated from the viscosity data. By comparing with the data in Fig. 1, it can be seen that the mechanical relaxation times are substantially smaller than the dielectric relaxation times. Even using the dielectric modulus, the corresponding τ are still a factor of eight larger than their mechanical counterparts.

Nevertheless, over the range of our measurements, the temperature dependences of the respective τ are the same. This is expected given the equivalence of the dielectric and viscosity data in Fig. 1. These results are consistent with the established correlation of the temperature dependence of structural relaxation times with the breadth of the relaxation function.^{22–26}

Mixtures with polystyrene

It is well-established that addition of polymer can modify the solvent dynamics, as has been shown previously

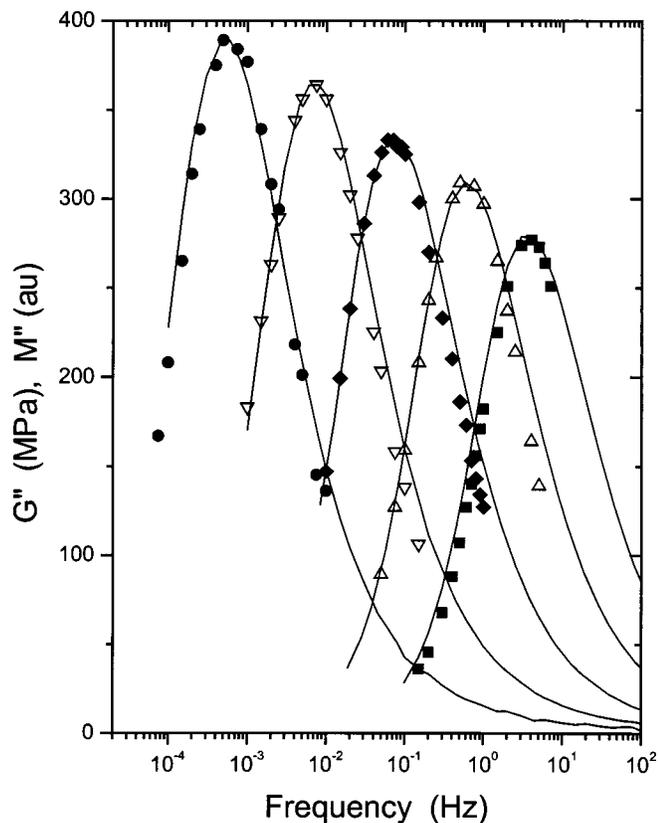


FIG. 3. Comparison of the mechanical loss modulus (symbols) with the imaginary part of the dielectric modulus, M'' (solid lines), for the neat PCB54. The temperatures for the G'' spectra are 240 K (●), 244 K (△), 248 K (◆), 252 K (▽), and 256 K (■). The dielectric spectra having peak frequencies closest to that of the G'' spectra were chosen for the comparison. They were shifted slightly in frequency and vertically scaled to coincide with the loss modulus at the peak maxima.

for PS/PCB48 solutions.¹⁻³ Herein, we obtained both dielectric and mechanical spectra on PCB54 with added polystyrene. The dielectric strength of the PCB54 was measured to be 2.7 ± 0.15 over the range of measurement temperatures. This is ~ 60 -fold larger than the dielectric strength of polystyrene. Consequently, dielectric loss spectra on mixtures of Aroclor and PS will reflect predominantly the dynamics of the former.

Included in Fig. 1 are the dielectric relaxation times for a solution of PCB54 with PS-90k ($c = 0.13$ g/cc). It can be seen that there is almost no difference between these and τ for the neat PCB54. That is, the addition of polymer having a 130 degrees higher T_g has a negligible effect on the dynamics of the PCB54. As expected from this near-equivalence of the relaxation times of the neat Aroclor and its mixture, T_B is also unchanged by addition of the PS-90k (inset to Fig. 1).

A measure of the degree to which polymer solute modifies the dynamics is the change in the effective friction coefficient for the solvent, defined as $\xi = \tau(c, T) / \tau(0, T)$, where $c = 0$ refers to the neat solvent. For PS/PCB48 solutions studied by oscillatory electric birefringence, Morris *et al.*²⁷ reported a temperature-independent value of $\partial \ln \xi / \partial c = 13$ cc/g. This is very similar to the result obtained using light scattering.²⁸ From the dielectric data in Fig. 1, we cal-

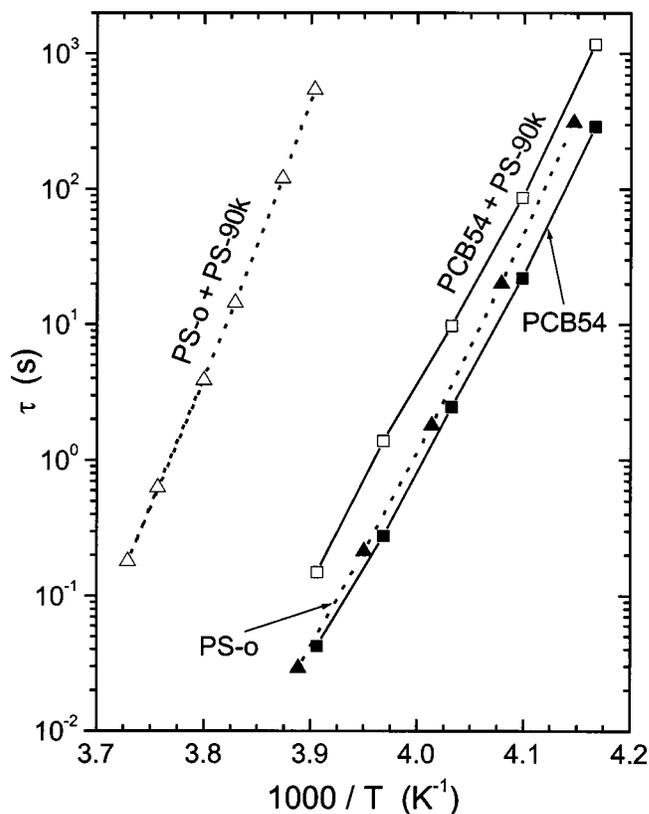


FIG. 4. Mechanical relaxation times for PCB54 neat (■) and mixed with PS-90k ($c = 0.13$; □) and for PS-o neat (▲) and mixed with PS-90k ($c = 0.10$; △).

culate a much smaller change in the dynamics for PCB54 with added PS-90k, $\partial \ln \xi / \partial c = 1.1 \pm 1$ cc/g.

The mechanical relaxation times for the mixture of PS-90k with PCB54 are shown in Fig. 4. Unlike the dielectric spectra, which reflect the polar Aroclor, we expect the PS components to contribute to the response measured mechanically. For the PS-90k in PCB54 solution, we obtain $\partial \ln \xi / \partial c = 9.8 \pm 1$ cc/g for the effect of solute on the mechanical relaxation times. This is an order of magnitude larger than the effect on the dielectric relaxation times, and roughly consistent with the results obtained by electric birefringence and light scattering.

Also included in Fig. 4 are results for a solution of the PS-90k dissolved in the oligomeric polystyrene. The latter has a T_g equivalent to that of PCB54, and as seen in the figure, the respective mechanical relaxation times for the neat fluids are quite close (within 40% of one another). Nevertheless, the addition of PS-90k to PS-o ($c = 0.10$ g/cc) effects a drastic change in the relaxation times (Fig. 4). The dynamics in the mixture are four orders of magnitude slower than in neat PS-o, making it difficult to obtain data over the same temperature range. We obtain a value of $\partial \ln \xi / \partial c = 91$ cc/g. The enormous difference in the effect of PS-90k on the dynamics of the respective liquids is summarized in Table I.

DISCUSSION AND CONCLUSIONS

The mechanical and dielectric loss moduli of neat PCB54 have essentially the same shape and, in accord with

the well-established correlation between time and temperature dependences,^{24,25} the corresponding relaxation times were found to have the same temperature dependence. Such results are different than found previously for Aroclor 1248, which has a lower chlorine content.¹¹ The dielectric relaxation times for PCB48 exhibited a weaker temperature dependence than τ measured mechanically.

For the neat PCB54, the magnitudes of the dielectric and mechanical relaxation times have the following order:

$$\tau(\epsilon'') > \tau(M'') \gg \tau(G'') \approx \tau_\eta.$$

This ranking is not unusual,^{11,29–31} although there are cases in which the dielectric and mechanical relaxation times are equivalent.³²

The temperature at which the dielectric relaxation times depart from a single VF dependence is the same as the value of this characteristic temperature determined from viscosity measurements. This implies a conformance of the relaxation times and viscosities to the Debye–Stokes relationship [Eq. (2)], although subtle deviations become apparent with decreasing temperature (Fig. 2). These occur at temperatures at which the peak breadth increases beyond that associated with a Debye (noncooperative) relaxation. Both phenomena reflect the development of intermolecular constraints, and the concomitant dynamic heterogeneity, with decreasing temperature.³³

The value of T_B determined dielectrically doesn't change with addition of PS-90k (Fig. 3). Invariance of T_B to the presence of dissolved polymer can be rationalized, considering this characteristic temperature to reflect the temperature at which intermolecular cooperativity becomes manifest (being entirely absent only at sufficiently high temperatures).³⁴ The structural relaxation times of PCB54 are virtually unchanged by addition of the PS, and likewise the characteristic temperature associated with the onset of strong intermolecular cooperativity should be unchanged.

As measured mechanically, the effect of PS-90k on the dynamics of the PS-o ($\partial \ln \xi / \partial c = 91$ cc/g) is an order of magnitude greater than its effect on PCB54 ($\partial \ln \xi / \partial c = 10.8$ cc/g), notwithstanding the equivalent glass temperatures of PS-o and PCB54. In terms of the glass temperature (defined as the temperature at which the mechanical relaxation time equals 100 s), the presence of PS-90k increases T_g by 16 and 2 degrees for PS-o and PCB54, respectively.

These results can be qualitatively explained by the consideration of the relative strength of the intermolecular cooperativity for the two solutions. The stretch exponents measured mechanically at T_g for the PCB54 is 0.62₅, which is substantially larger than the (molecular weight independent) value for polystyrene, $\beta = 0.46$.¹³ This means that the intermolecular constraints on local motion are stronger for PS than for the Aroclor.²⁶ When PS-90k is added to the oligomeric polystyrene, the strong intermolecular coupling is maintained. This contributes, in combination with the large friction coefficient of the high T_g PS-90k, to a large value of the relaxation time and the mixtures T_g .

However, the smaller, more symmetric Aroclor is not expected to strongly interact with the nonpolar PS; hence, constraints on local motion of the PCB54 are alleviated to

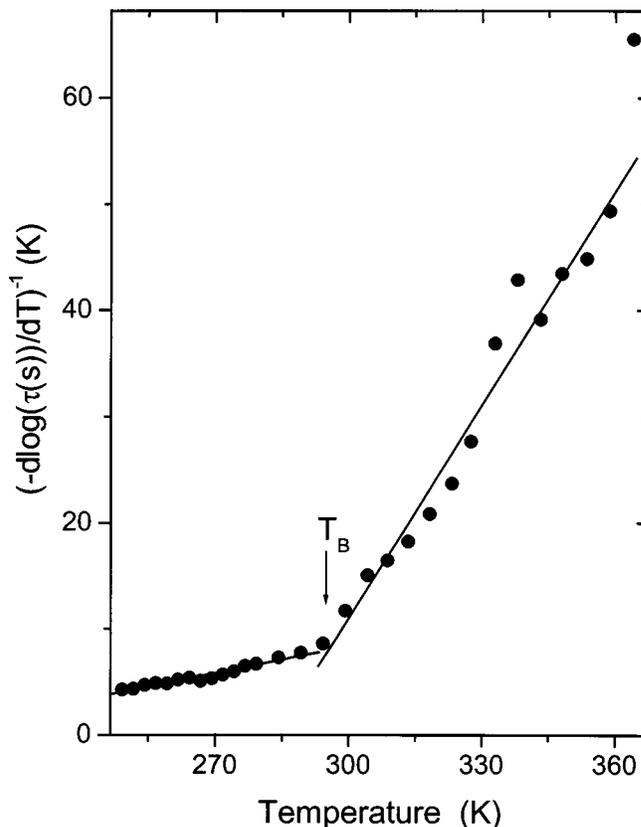


FIG. 5. The quantity $-(\partial \log \tau / \partial T)^{-1}$ vs temperature for the dielectric relaxation times of the neat PCB54, demonstrating that the determination of the characteristic temperature is independent of the functional form assumed for $\tau(T)$. The straight lines are the respective best-fits of Eq. (4) to the low temperature data ($T_c = 201$ K and $\gamma = 11.84$), and to the measurements above T_B ($T_c = 283.6$ K and $\gamma = 1.49$).

some extent by addition of the PS-90k. The (small) increase in relaxation time of the PCB54 upon addition of PS-90k is due only to the larger local friction from the higher T_g solute. For mixtures whose components are much closer in T_g than herein, these arguments can be quantified^{35–37} using a relationship for the coupling model.^{38,39} However, for the present materials this requires an overly long extrapolation of the relaxation times of the PS-90k.

Finally, there remains the interesting difference in the relaxation behavior measured by dielectric versus by mechanical spectroscopy. Not only are the dynamics slower as probed dielectrically, but moreover, the addition of the high T_g PS has an order of magnitude smaller effect on $\tau(M'')$ than on $\tau(G'')$. We believe the differing influences of temperature and diluent on these relaxation times are related to the different response of intra- and intermolecular motions to external variables. Such results are seen, for example, in simulations in which temperature and pressure are varied.⁴⁰ This divergence in properties as probed by different methods is just one of many phenomena that makes structural relaxation a challenging and unsolved problem in condensed matter physics. Development of a complete, quantitative theory of the glass transition requires consideration of anomalous experimental results, such as those described herein.

In response to a comment by the reviewer, we point out that although T_B was deduced herein from a Stickel plot,¹⁶

our determination of the characteristic temperature associated with a change in dynamics does not rely on the use of Eq. (1) to describe $\tau(T)$. For example, both idealized mode-coupling theory⁴¹ and a scaling-law model⁴² predict power law behavior

$$\tau(T) \propto (T - T_c)^{-\gamma}, \quad (4)$$

where γ is a constant. According to mode-coupling theory, the critical temperature lies above the glass temperature, whereas for the scaling-law analysis, $T_c < T_g$. Recently, Richert⁴³ concluded that such power laws give poorer fits to dielectric relaxation times than the Vogel–Fulcher equation. Nevertheless, in Fig. 5 we plot, as suggested by Eq. (4), the quantity $-(\partial \log \tau / \partial T)^{-1}$ for the dielectric relaxation times of PCB54. While Eq. (4) is not capable of describing $\tau(T)$ over the entire measured range, this derivative does linearize the data separately for temperatures above and below T_B . Moreover, the value, $T_B = 294$ K, is unchanged from that obtained in Fig. 1.

ACKNOWLEDGMENT

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¹⁷For the peak breadths measured herein, the most probable relaxation times plotted in Fig. 1 are about 20% larger at T_g than the average relaxation time, τ_{avr} . These become progressively closer with increasing temperature (since the breadth decreases), and thus the temperature dependence of τ_{avr} is somewhat weaker than that of τ . However, the Stickel plot and thus the determination of T_B is insensitive to the particular definition of relaxation time used. This was demonstrated in reference 15 for salol, which has an even more temperature-dependent peak breadth than the PCB54.

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