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Experimental determination of the cooperative length scale of a glass-forming liquid near the glass transition temperature

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Photon correlation spectroscopy and dielectric relaxation are used to examine the molecular reorientation relaxation dynamics of a fragile glass-forming liquid Aroclor (a mixture of polychlorinated biphenyls), modified by the addition of low- and high-molecular-weight polyisoprene and polybutadiene as a function of temperature and polymer solute concentration. Concentration fluctuation contributes a temperature-dependent broadening of the relaxation spectrum of Aroclor. The rate of change of the Aroclor relaxation spectrum with temperature is more pronounced when the polymers added are of low molecular weight and exhibits a steplike decrease in the neighborhood of some characteristic molecular weight. The radius of gyration of the polymer with this characteristic molecular weight is about 15 Å, which determines the cooperative length scale *L(T)* of Aroclor to be approximately 30 Å near and above the glass transition temperature. [S1063-651X(98)01811-X]

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INTRODUCTION

The glass transition and molecular dynamics of relaxation of supercooled liquids continue to be the subject of intensive research for over the past few decades. A variety of experimental techniques have been applied to gain insight into the physics of glass-forming systems. The problem of the glass transition in bulk glass-formers is difficult to solve because of the presence of several complicating factors. First and foremost is the many-body nature of the dynamics (sometimes loosely referred to as *cooperativity* [1,2]), which makes it difficult to be accurately described, particularly over a large time range from microscopic times less than a picosecond to macroscopic times of the order of 10^5 s. Some models [1,2] expect that the cooperative effects from the many-body molecular dynamics, henceforth referred to as ''cooperativity,'' are responsible at least partly for the nonexponentiality [1,2], dynamically heterogeneous nature [3–6], and slowing down of relaxation rate with decreasing temperature according to the Vogel-Fulcher-Tammann-Hesse relation [1,2]. It is generally believed that cooperativity plays an important role in the relaxation mechanism of glass-forming systems; however, the concept remains ill defined and varies from author to author. Sometimes, some authors used the word ''cooperativity'' in an intuitive sense. Generally speaking, the many-body aspects of the molecular dynamics of relaxation in many glass-formers implies that the motion of the basic molecular units has to be cooperative, meaning that some units move first before the others take their turn. Thus cooperative motions slow down the independent motions of the basic units, engender dynamic heterogeneity [3–6] in their movements, and lead to a non-exponential time dependence of the correlation function of macroscopic variables. More specifically, in some models, such as that proposed by Adam and Gibbs [7], cooperativity means that the rearranging movement of a molecule is possible only if a certain number of neighboring molecules are also moved. In spite of the connection made by many models and simulations to cooperativity, there are theories of the glass transition such as the mode coupling theory [8] that do not rely on the idea of cooperative rearrangements.

Some theoretical models proposed to describe the dynamic behavior of a supercooled liquid have explicitly introduced the concept of molecules rearranging themselves cooperatively within regions of a characteristic size that increases with decreasing temperature. Among these models is the work of Adam and Gibbs [7], which considered configurational entropy and introduced the cooperatively rearranging regions (CRRs), defined as the smallest regions that can experience a transition to a new configuration without requiring a simultaneous change outside its boundary. Adam and Gibbs [7] had assumed the size of the CRRs to be inversely proportional to the configurational entropy per molecule. A consequence of such a relationship and the Adam and Gibbs theory, the size of the CRRs that is a measure of cooperativity grows steadily as the temperature is lowered. The idea of the existence of a characteristic length scale of cooperativity that exhibits a temperature dependence quite different from that of the static structural correlation length has been very attractive. The concept of length scale of cooperativity, defined as the cube root of the CRR volume, is not the same as the concept of correlation length since the latter is usually defined by the density-density correlation at a given time. Assuming, however, that the local rearranging mobility is controlled by the local density, then we could have some coupling between local density fluctuations and cooperativity.

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Up until now, there exist only indirect methods to determine such a length scale experimentally. Donth and coworkers [9–11] suggested from an analysis of experimental data by theoretical model the existence of a length scale of the order of a few nanometers for polymers. On the experimental front, Jackson and McKenna [12] examined the dependence of the glass transition temperature on system size by differential scanning calorimetry and reported a decrease of the glass transition temperature (T_g) with the size of the sample. Arndt *et al.* [13] employed dielectric spectroscopy to study the effect of confinement on the molecular dynamics of low-molecular-weight supercooled liquids and gave an estimate of the length scale of cooperativity to be greater than 7 nm in the vicinity of the calorimetric glass transition. Streck, Mel'nichenko, and Richert [14] investigated the effect of confinement on the molecular dynamics of a supercooled liquid (2-methyltetrahydrofurane) by solvation dynamics spectroscopy and concluded that the length scale is close to 30 Å at T_g.

The molecular dynamics of the structural relaxation responsible for the glass transition can be obtained in the form of density and orientation time correlation functions, respectively, by light scattering techniques, polarized and depolarized photon correlation spectroscopy (PCS), and dielectric relaxation (DR) spectroscopy. In this work we report PCS and DR results on the molecular dynamics of a glass-forming liquid Aroclor (polychlorinated biphenyl), containing various amounts of dissolved polyisoprene (PI) or polybutadiene (PB) at temperatures in the vicinity of T_g of the mixtures. We found that there are significant differences in the Aroclor reorientation relaxation spectrum and its change with temperature depending on whether the dissolved polymer is of low or high molecular weights (M_w). There is a nearly steplike crossover from the low-M_w property to the high-M_w property at some molecular weight M_c. This interesting effect was discovered from data taken by PCS. It would be of interest to see whether or not this effect is general and independent of the probe. Hence, subsequently we used dielectric relaxation spectroscopy to investigate the molecular dynamics of Aroclor and found qualitatively the same results. The origin of this sharp crossover is traced to enhanced polymer concentration fluctuation when the size of the polymer Gaussian coil matches the cooperative length scale of Aroclor. The radius of gyration of the polymer with molecular weight equal to M_c provides a direct experimental determination of the cooperative length scale of Aroclor near and above T_g.

EXPERIMENT

The solvent Aroclor is a mixture of polychlorinated biphenyls having a glass transition temperature equal to 229 K. Solutions of PI (M_w=1000, 2200, 4000, 8000, 20 000, and 43 000) in Aroclor and 1,4-PB (M_w=1000, 2500, and 100 000) in Aroclor were filtered in a cylindrical light scattering cell and finally the samples were sealed under vacuum. It is well known from the literature [15–17] that polymers including polyisoprene, polybutadiene, and polystyrene are dissolved in Aroclor to form homogeneous solutions without microphase separation in the large polymer concentration range studied in this work.

Depolarized dynamic light scattering measurements were made using the technique and apparatus described earlier equipped with an Ar^+ laser (Spectra Physics) emitting vertically polarized light with wavelength at 488 nm and an ALV-5000 full digital correlator. The scattered light passed through a Glan-Thompson polarizer with an extinction better than 10^{-7}. Measurements of the complex dielectric function have been made with a Novocontrol BDC-S system composed of a frequency response analyzer (Solartron Schlumberger FRA 1260) and a broadband dielectric converter with an active sample cell. The latter contains six reference capacitors in the range 25–1000 pF. Measurements were made in the frequency range 10^{-2}–10^{6} Hz using a combination of three capacitors in the active sample cell. The samples were confined between two 20-mm-diam gold-plated stainless-steel plates separated by 100 μm. The sample cell was placed in the cryostat. The sample temperature was controlled between 210 and 273 K and measured with a PT100 sensor in the lower plate of the sample capacitor with an accuracy of ±0.1 K.

RESULTS

The dynamic light scattering experimental correlation functions were treated in the homodyne limit. The measured intensity autocorrelation function $G(q,t)$ is related to the desired normalized field correlation function $g(q,t)$ by

$$G(q,t)=A[1+f|\alpha g(q,t)|^2]. \tag{1}$$

Here $q=(4\pi n/\lambda)\sin(\theta/2)$ is the scattering vector, n is the refractive index of the bulk polymer, θ is the scattering angle, λ is the laser wavelength, f is the instrumental factor calculated by means of a standard, α is the fraction of the total scattered intensity associated with orientation fluctuations with correlation times longer than 10^{-6} s, and A is the base line. Analyses have been performed for the $g(q,t)$ correlation functions by using the Kohlrausch-Williams-Watts (KWW) function

$$\alpha g(q,t)=A_f\exp[-(t/\tau_f)^{\beta,f}]. \tag{2}$$

The parameters A_f, τ, and β give, respectively, the contrast, relaxation time, and shape parameter of the relaxation process. Depolarized dynamic light scattering measurements were recorded in the temperature range 218–257 K. Typical depolarized intensity-intensity correlation functions for a scattering angle of 90° are shown in Fig. 1 for a 13% PB(2500)/Aroclor(1248) solution at four temperatures. The errors of the measurement are smaller than the size of the symbols. The depolarized scattering intensity arises from fluctuations in the anisotropic part of the polarizability tensor. Due to the large difference between the optical anisotropy of Aroclor and that of an isolated PI or PB chain the depolarized intensity-intensity correlation function is determined primarily by the Aroclor solvent dynamics. The shape parameter β here is considerably smaller than the corresponding quantity of pure Aroclor because concentration fluctuations in the mixture with polymer contribute significantly, in addition to cooperative dynamics, to the measured dispersion now characterized by β. The fit of the data to the KWW function gave a temperature-dependent distribution

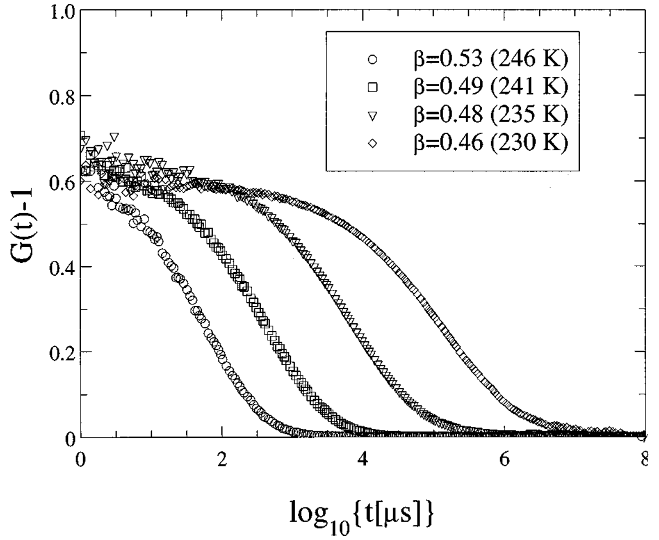

FIG. 1. Depolarized experimental correlation functions for a 13% low-molecular-weight ($M_w = 2500$) PB/Aroclor mixture at different temperatures.

parameter β. The dielectric relaxation data show similar properties. Typical dielectric loss curves for the 13% PI(8000)/Aroclor solution are shown in Fig. 2 at six temperatures originating from the Aroclor primary reorientation relaxation. The errors of the measurement are smaller than the size of the symbols used. The observed dielectric spectra originate from the motion of the Aroclor molecules that have the largest dipole moment among molecules of the mixtures. The spectra were well represented by a single Havriliak-Negami function over a broad temperature range, which, after a half-sided cosine transformation into the time domain, were fitted to the KWW stretched exponential and from which the shape parameter β was extracted (see Fig. 3). As found previously in several polymer and polymer/solvent systems [18–20], both dynamic light scattering and dielectric spectroscopy give β's that compare well within experimental error.

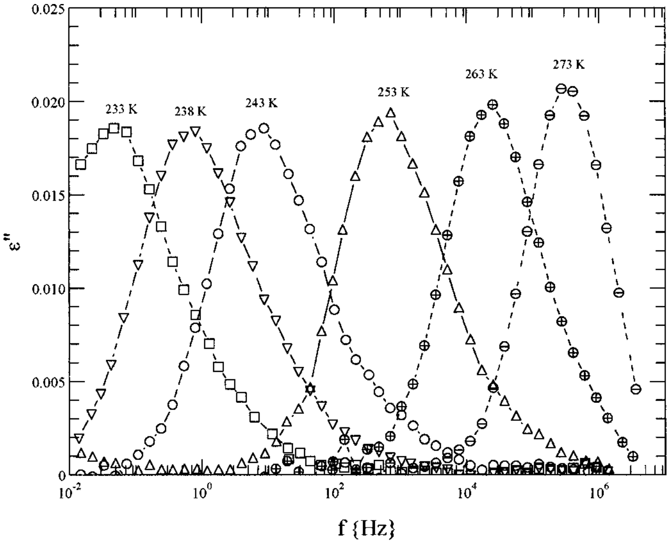

FIG. 2. Frequency and temperature dependence of the dielectric loss for 13% PI(8000)/Aroclor solution corresponding to the Aroclor primary α relaxation.

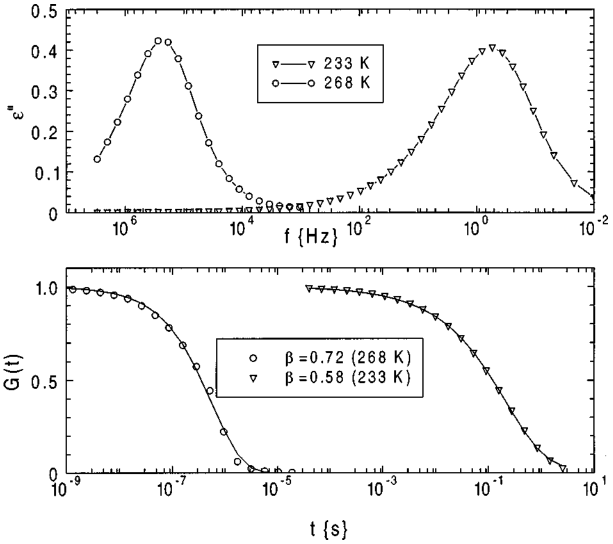

FIG. 3. Dielectric loss as a function of frequency for 25% PI(4000)/Aroclor solution showing the Aroclor primary relaxation for two temperatures in the upper part. Their counterparts in the time domain obtained by Fourier transformation are shown in the lower part. The solid curves in the lower part correspond to the fits of the normalized correlation functions to the KWW function with values of β indicated in the inset.

We found a pronounced temperature dependence of β for the low-molecular-weight PI and PB solutions in Aroclor by PCS and DR. In contrast, for the high-molecular-weight polymer solutions there is only a slight change in β with temperature. Typical results for solutions of PB and PI in Aroclor are shown, respectively, in Figs. 4 and 5. The temperature dependence of β from PCS experiments for PB/Aroclor solutions are plotted as a function of the reduced temperature T/T_{ref}, where T_{ref} is the temperature at which the measured Aroclor relaxation time in any of the PB/Aroclor solutions is equal to 1 s. Similarly, in Fig. 5 we have given the data of β from PCS and DR experiments for PI/Aroclor solutions in the same format. These plots of β versus T/T_{ref} provide objective comparisons between experimental data taken at different polymer concentrations and molecular weights. The interesting behavior found by PCS is confirmed by dielectric relaxation spectroscopy as illustrated by Fig. 5.

These results indicate that there is correlation between the rate of change in β with temperature and the size of the Gaussian coil of the polymer chain. The radius of gyration (R_g) changes almost by a factor of 10 from ~10 to 100 Å as one increases the molecular weight of PB from $M_w = 1000$ to 1×10^5. This suggests that the cause of the pronounced temperature dependence of β is the larger fluctuations in the modification of Aroclor reorientation dynamics by the added polymer when the size of the polymer R_g becomes comparable to or smaller than the cooperative length scale or the size of the cooperative rearranging regions. Figure 6 shows the R_g dependence of the slope $d\beta/dT$ for PI and 1,4-PB. It is evident that in the narrow range $1000 < M_w < 3000$ (or 10 Å$< R_g <$30 Å) the slope $d\beta/dT$ crosses over from its smaller high-molecular-weight value to the larger low-molecular-weight value.

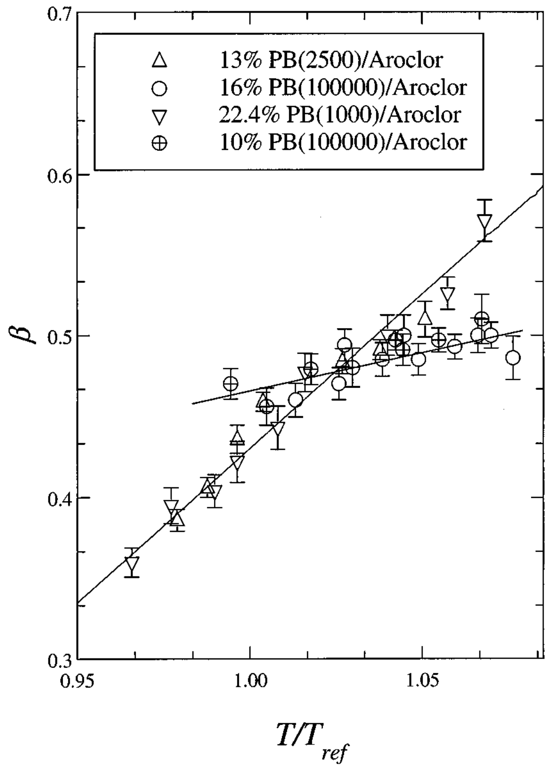

FIG. 4. Distribution parameter β from PCS experiments for four PB/Aroclor solutions as a function of the reduced temperature T/T_{ref}, where T_{ref} is the temperature at which the measured Aroclor relaxation time in any of the PB/Aroclor solutions is equal to 1 s. The solid line having steeper slope is the fit of β of the low M_w (2500) PB/Aroclor mixture to a linear function of T/T_{ref}. The other line shows the result of the fit of β of the high M_w (1×10^5) PB/Aroclor mixtures to a linear function of T/T_{ref}.

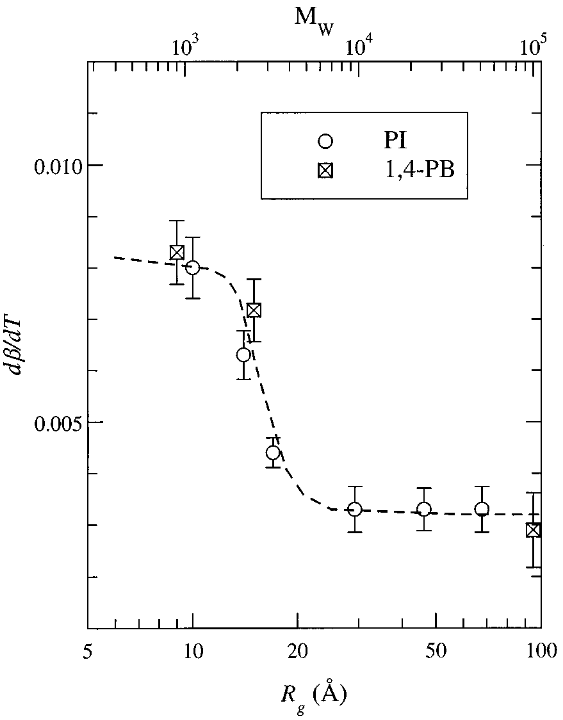

FIG. 6. Dependence of the slope $d\beta/dT$ on R_g for the PB/Aroclor and the PI/Aroclor solutions. The dashed curve indicates that the experimental data exhibit a steplike crossover from the low-molecular-weight regime to the high-molecular-weight regime at $R_g\sim15$ Å.

DISCUSSION

From previous works in solutions of polymers in Aroclor and other systems [18–24] it is well known that concentration fluctuations play an important role in determining the molecular dynamics of miscible binary mixtures. There is evidence of this effect in the polymer/Aroclor system from the data of Aroclor reorientation motion presented here and can be seen from the large dispersion width of the PCS field correlation functions and the dielectric loss curves. The dissolved polymer modifies the relaxation rate of the Aroclor [18–23] in the CRR and the change depends on the polymer concentration in the locality of the CRR. Polymer concentration fluctuation engenders different changes of relaxation rates in different cooperative rearranging regions. The large dispersion widths observed are due to the distribution of modified relaxation rates caused by polymer concentration fluctuations [18–23]. The extremes of polymer concentration fluctuation possible in a CRR of Aroclor are realized by the two opposite cases of an entire polymer coil being totally outside the CRR. Therefore, polymer concentration fluctuations sampled by the Aroclor CRRs depend not only on the averaged concentration of the polymer but also on the size of the polymer coils relative to the size of the CRR. One measure of the size of the polymer coil is its radius of gyration R_g, which for PB and PI in Aroclor, a good solvent, is related to the molecular weight by the expression $R_g \approx 0.3\sqrt{M_w}$. R_g is related to the end-to-end distance $\langle r\rangle$ by $R_g=\langle r\rangle/2$,26. At a fixed size of the CRRs given by the radius R the polymer concentration fluctuation in the CRR will be less for a higher-molecular-weight polymer with $R_g \gg R$ than for a low-molecular-weight polymer with $R_g \ll R$ at the same polymer concentration. This difference occurs because, in going from a lower to a higher-molecular-weight polymer at the same polymer weight concentration, the polymer con-

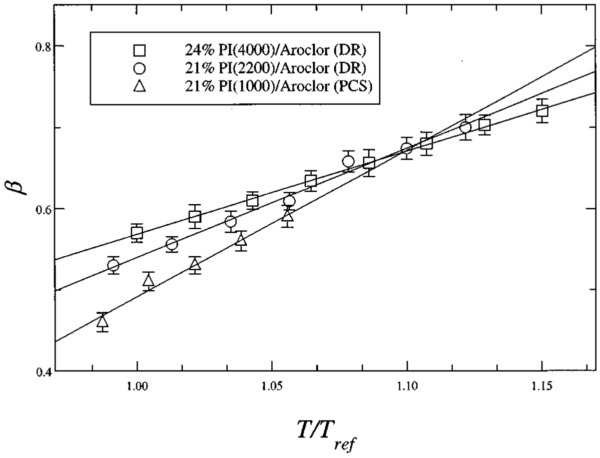

FIG. 5. Distribution parameter β from PCS and DR experiments for three PI/Aroclor solutions as a function of the reduced temperature T/T_{ref}, where T_{ref} is the temperature at which the measured Aroclor relaxation time in any of the PI/Aroclor solutions is equal to 1 s. The solid lines are the results of the linear fits of β against T/T_{ref} individually for the 21% PI(1000)/Aroclor mixture, 21% PI(2200)/Aroclor mixture, and 25% PI(4000)/Aroclor mixture.

centration fluctuations of the latter are effectively the same as those of the former after averaging over the larger R_g of the latter. Some of the concentration fluctuations present in the lower-molecular-weight polymer solution in Aroclor are effectively removed in the higher-molecular-weight polymer solution in Aroclor. Furthermore, since the overlap concentration c^* is proportional to $M^{3\nu-1}=M^{-4/5}$ (for ν=3/5), at a fixed concentration c above c^*, the polymer coils in an Aroclor solution of polymer with higher molecular weight will have more overlap, which tends to average out some of the polymer concentration fluctuation experienced by the Aroclor CRRs. From these two considerations, we conclude that the broadening of the dispersion of Aroclor relaxation by concentration fluctuation is expected to be more severe in solution of low-molecular-weight polymer than in solution of high-molecular-weight polymer. This property is in accord with the PCS and DR experimental data shown in Figs. 4 and 5, where the broadening is characterized by β. It is a general property of miscible blends [24–26] that the broadening of the dispersion of one component (i.e., Aroclor here) increases with decreasing temperature. Moreover, the sensitivity of the broadening to temperature variation increases with concentration fluctuation. Therefore, it is expected that Aroclor solutions of low-molecular-weight polymers have larger variation of the dispersion width than solutions of high-molecular-weight polymers. The experimental data summarized in Fig. 6 by the variation of $d\beta/dT$ with molecular weight or R_g of PI and 1,4-PB indicate that the observed behavior is consistent with the expectation.

The effect we observed is used as a method to determine the length scale of the modified Aroclor near the glass transition temperature T_g. This method is to carry out PCS and DR data of Aroclor solutions of PB and PI with a broad range of M_w's interpolating the low and high-molecular-weight regimes in the manner described here. Figure 6 shows that in the narrow range $1000<M_w<3000$ (or $10\,\text{Å}<R_g<30\,\text{Å}$) the slope $d\beta/dT$ crosses over from the smaller high-molecular-weight value to the larger low-molecular-weight value. From this rapid crossover behavior we can give an estimate that the radius of the CRR or the cooperative length scale is approximately equal to R_g at $M_w=3000$, which is ~15 Å.

CONCLUSIONS

The characteristics of the Aroclor reorientation motion seen by photon correlation and dielectric relaxation spectroscopies in Aroclor solutions of high-molecular-weight PI and PB are distinctively different from those in solutions of low-molecular-weight polymers. At constant polymer concentration, when the molecular weight of PI or PB is low, the photon correlation function shows a larger broadening of the dispersion of Aroclor relaxation and a more rapid change with temperature. We explain this property by the molecular-weight dependence of the concentration fluctuation of the dissolved polymer. When the size of the dissolved polymer coil is comparable to or smaller than the size of the Aroclor cooperative rearranging regions, the polymer concentration fluctuation is enhanced, resulting in a concomitant increase of broadening of the Aroclor reorientational relaxation spectrum. We have exploited this effect to determine the length scale of cooperativity near T_g to have a radius of ~15 Å.

ACKNOWLEDGMENT

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