Molecular Motions and Viscoelasticity of Amorphous Polymers near T_g

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ABSTRACT: Rotational correlation times τ_c for rubrene and tetracene are reported near and below T_g in three polymers: polyisobutylene, polystyrene, and Bisphenol A polysulfone. A photobleaching method was used to obtain τ_c values from 10^{-1} to 10^3 s. In each polymer matrix, the orientation autocorrelation function for tetracene (the smaller probe) decays more rapidly and less exponentially than the correlation function for rubrene. τ_c for a given probe at the T_gs of the matrices varies more than 3 decades. For the three polymers studied, probe rotation times at T_g showed a systematic decrease with increasing matrix T_g. Viscoelastic relaxation times characteristic of the Rouse modes of the matrix polymers are closely related to probe rotation times and also not constant at T_g. Thus T_g is not an isolocal mobility state for molecular motions on a fixed length scale. On the other hand, the viscoelastic relaxation time associated with the glassy modulus is almost constant at T_g. These results suggest that the characteristic length scale for motions associated with the relaxation of the glassy modulus varies significantly for the three polymers studied. Trends in the KWW β values which describe probe reorientation support this interpretation.

Introduction

Dynamics in glass-forming materials are characterized by a broad range of relaxation times and a strong temperature dependence, particularly near the glass transition temperature T_g. These qualitative features are shared by many types of glass-forming materials, including small inorganic and organic molecules, as well as polymers. In addition to these features, the glass transition in high molecular weight polymers has a unique feature associated with it, the transition from glassy-like to rubbery-like behavior.

It is clear that the glass transition observed in the laboratory is kinetic in nature. T_g, which can be defined by the change of the temperature dependence of volume or heat capacity as the sample is cooled at a constant rate, strongly depends on the cooling rate. The most widely accepted explanation for the glass transition is that at T_g some characteristic relaxation time of the system becomes longer than the experimental time scale. Naturally one might expect that a particular kind of molecular motion might occur at the same rate at T_g in all polymers. One idea that was discussed long ago was that the viscosity η is constant at T_g.[1] However, it is clear that this *isoviscous state* concept cannot be correct for polymers. Viscosity shows a strong molecular weight dependence, typically M_w^{3-4} for high molecular weight polymers, while T_g is essentially independent of molecular weight in this regime.[2] Thus, the molecular motions responsible for the glass transition do not involve the entire chain but must be some sort of local motion.[3]

The dynamics of amorphous polymers on length scales long compared to the repeat unit are well described by theories based on the bead–spring model.[4] For example, the viscoelastic relaxation spectrum in the glass-to-rubber transition zone agrees well[5] with Rouse theory.[6] Molecular motions which occur in this time regime are the same for all amorphous linear polymers; sometimes these motions are referred to as Rouse modes. In contrast, more localized molecular motions depend on the structure of the repeat unit. As a result, viscoelastic relaxation spectra differ for various polymers near the glassy zone.[5]

The complexity of polymer motions near T_g is exemplified by the breakdown of thermorheological simplicity. Plazek found that the recoverable compliance in the softening zone and the viscosity show somewhat different temperature dependences.[7] Similar behavior has been subsequently reported by other researchers.[8,9] Inoue et al. showed that the viscoelastic relaxation spectrum in the glass transition zone can be separated into two components (denoted by R and G) with different temperature dependences.[10,11] The R component is responsible for rubberlike viscoelasticity. This component is well described by the Rouse theory in the transition zone and supports the stress in the rubbery and terminal flow zone. The G component is responsible for relaxation from the high glassy modulus. The frequency dependence of the G component of many polymers is very similar to that of the glassy modulus of low molecular weight glass formers like dibutyl phthalate. The existence of R and G components with different temperature dependences means that the molecular motions involved in large-scale chain motion (Rouse modes) and those involved in the relaxation of the glassy modulus are fundamentally different. This may be related to the different temperature dependences observed for the normal mode and the segmental mode in dielectric measurements.[12–14]

One possible interpretation of the glass transition in polymers is that some particular Rouse mode relaxes at the same rate in all polymers at their T_gs. This essentially corresponds to an *isomonomeric friction state* because the monomeric friction coefficient is the dominant factor determining the temperature dependence of the Rouse modes. Note that here and throughout this paper we use the term *monomeric friction coefficient* in the specific manner that it is used in ref 5; the monomeric friction is the friction experienced by a large section of a chain expressed on a per repeat unit basis. Often the Rouse theory has been used to extract this quantity from experimental measurements. Not all authors use this term in this manner.

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In an early summary, Ferry indicated that monomeric friction coefficients are not constant at T_g but vary by more than 4 decades.[5] The large variation in these data may be partially due to experimental difficulties such as inaccuracies in the determination of T_g and possible contamination by impurities. Plazek et al. showed later that four vinyl polymers included in Ferry's analysis have essentially the same local molecular mobility at T_g.[15] The monomeric friction coefficients for these four polymers are also almost identical at T_g. Although one might infer from Plazek's work that the monomeric friction coefficients for all polymers are equal at their T_gs, the results presented here indicate that this is unlikely.

In this study we report the reorientation times of two probes (rubrene and tetracene) in three polymers (polystyrene, polyisobutylene, and Bisphenol A polysulfone) in the vicinity of T_g. T_g for these polymers ranges from 205 to 459 K. Probe reorientation was measured in the time window from 10^{-2} to 10^{4} s with a recently developed photobleaching method.[16,17] The photobleaching technique is unique in being able to measure single-particle correlation times at very long times and very low probe concentrations. At probe concentrations in the range of 10 ppm, there is no plasticization of the host and no concern about interactions among the probe molecules. Results from the photobleaching technique can be combined with more conventional methods to observe rotation times in the range of 10^{-10} to 10^{4} s.[18,19] Studies on a low molecular weight glass former show that the temperature dependence of probe rotation times agrees well with that of the viscosity over this wide time window.[17,20] On the other hand, probe dynamics in polymers might be expected to be more complex, since the glass transition of polymers involves different kinds of molecular motions which show different temperature dependences as described above.

Probe methods do not observe chain motion directly and this feature sometimes is a disadvantage. On the other hand, an advantage of the probe method is that one can introduce a reference length scale (the probe size) for the comparison of dynamics in various polymeric systems. A comparison of our results with viscoelastic measurements supports our interpretation of the probe rotation studies.

Our results indicate that the rotation time of a given probe is not the same in the three polymer matrices at the matrix T_gs. We find more than 3 orders of magnitude variation in the rotation times at T_g. Thus T_g is not an isolocal mobility state for our probes. Similarly, viscoelastic relaxation times characteristic of the Rouse modes of the three polymers are not identical at T_g, and a good correspondence is observed between the Rouse modes and probe reorientation. This result suggests that Rouse modes do not play a significant role in determining T_g. On the other hand, the viscoelastic relaxation time associated with the glassy modulus is found to be fairly constant at T_g. The difference between the correlation time for probe rotation and the relaxation time for the glassy modulus can be interpreted in terms of different characteristic length scales for the glass transition in different polymer matrices.

Experimental Section

Materials. The polymers and probes used in this study are shown in Figure 1. Rubrene and tetracene were purchased from Aldrich (98 and 99%, respectively) and used without further purification. Polyisobutylene (PIB) and polystyrene (PS) were purchased from Polysciences, Inc. The PS was reported to have M_w = 50 000 and M_w/M_n = 1.06. The PIB had a broad molecular weight distribution with a reported M_η = 85 000; it was purified by benzene–methanol precipitation prior to use. Bisphenol A polysulfone (PSF, M_w = 30 000) was a gift from Idemitsu Kosan Co. NMR measurements indicate that these polymers contain no detectable impurities.

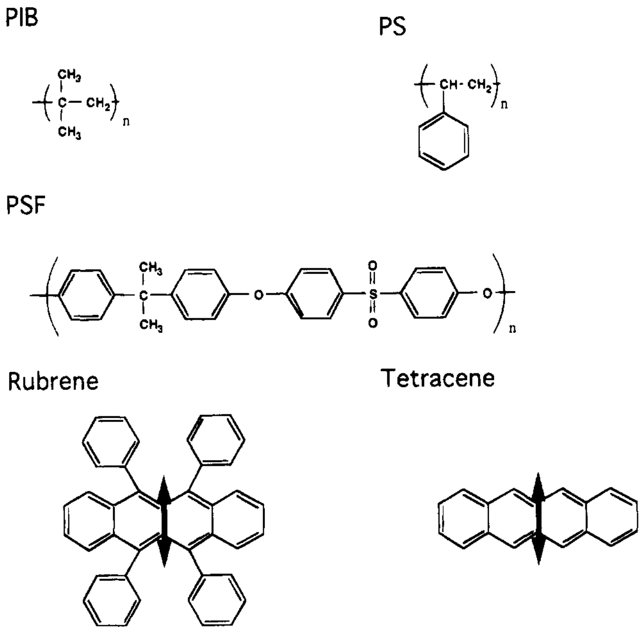

Figure 1. Molecular structures of probe molecules and polymers. The transition dipoles of the probes are indicated.

Samples for rotational diffusion measurements were prepared as follows. For PIB samples, the polymer and the probe were dissolved in chloroform and then filtered (0.5 μm pore size). This solution was cast on a glass plate in a desiccator and dried under vacuum at 373 K for about 1 week. The PIB samples were sandwiched between two prisms for the optical experiments. PS samples were prepared by freeze-drying a dilute solution of polymer and probe in benzene. The powder obtained was molded into a 2 mm thick disk at about 403 K. PSF samples were first cast from dichloromethane solution into a 0.1 mm thick film. The film was then dried at 463 K for one night and molded into a 1 mm thick disk. The optical densities of chromophores in the final samples were 0.1–0.2 (rubrene at 488 nm, tetracene at 456 nm). This corresponds to probe concentrations of 10–100 ppm. DSC measurements showed no T_g change due to the presence of the probes or any residual solvent.

DSC Measurements. Sample T_gs were determined using a Perkin-Elmer DSC-7. For measurements above room temperature, In and Zn were used for temperature calibration. In and Hg were used for calibration when liquid nitrogen was used as a coolant. In order to provide a consistent thermal history, all samples were first held for 2 min at $T_g + 30$ K and then cooled to $T_g - 60$ K with a cooling rate 10/K min. After being held at this temperature for 2 min, the samples were reheated at 10 K/min. T_g was determined from this heating run using the middle point convention.

Strictly speaking, the DSC method described above determines the fictive temperature, not T_g.[21] This is because the thermal signature of the transition is recorded upon heating from a nonequilibrium state. The temperature program used above determines a quantity sometimes denoted $T_{f,g}$ which approximates the true T_g which would be observed in a cooling experiment.[21]

Photobleaching Technique. A photobleaching technique recently developed in our laboratory was used to measure ultraslow reorientation times near and below T_g. Since details of this technique and the experimental apparatus are described elsewhere,[17] only a brief description is given here. An orientationally anisotropic probe population is created by selective photobleaching with a high-intensity polarized writing beam. The created anisotropy decays through rotational diffusion.

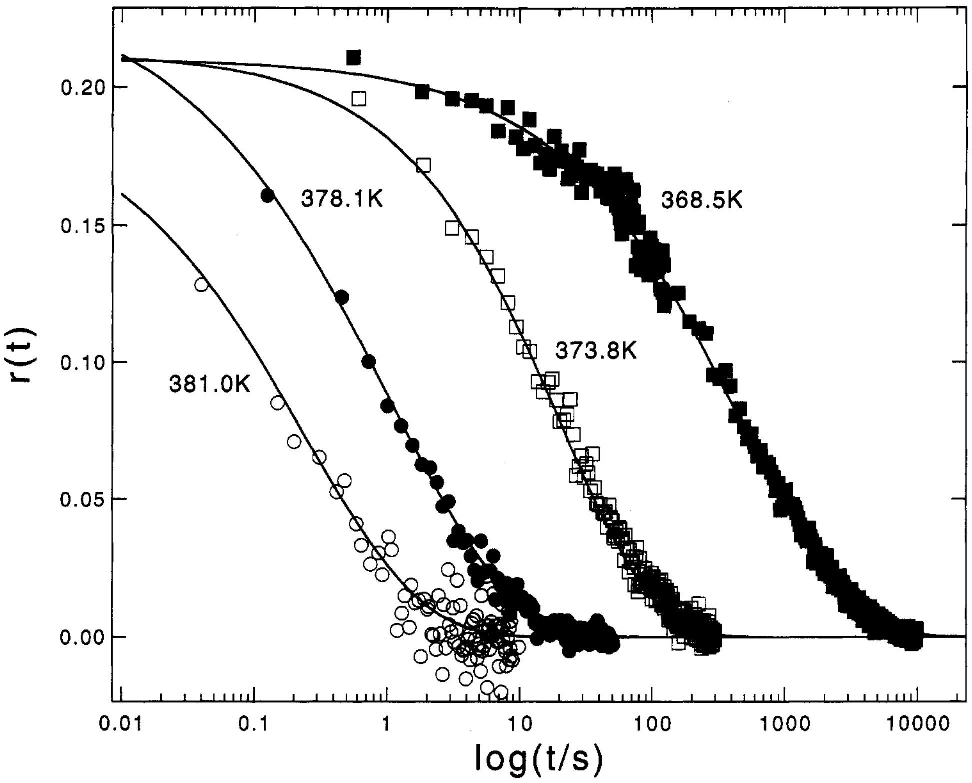

Figure 2. Anisotropy functions for the rotation of rubrene in polystyrene at various temperatures above and below the DSC T_g. Solid lines are least square fits to the KWW equation.

Changes in the anisotropy, $r(t)$, are monitored with a low-intensity reading beam whose polarization is modulated between parallel and perpendicular to the writing polarization. $r(t)$ is related to the autocorrelation function of the absorption dipole **u** of the probe:

$$r(t) = {}^2/_5\langle P_2[\mathbf{u}(0)\cdot\mathbf{u}(t)]\rangle \tag{1}$$

Here P_2 is the second Legendre polynomial and the brackets represent an ensemble average. The orientation of the absorption dipole in rubrene and tetracene is indicated in Figure 1.

The photobleaching method is limited in the measurement of fast rotational diffusion by the time required to create an anisotropic orientational distribution of probes. For the writing beam power used in this study (<0.3 W/mm^2), this writing time is from 1 ms to 10 s, depending on the probe molecule.

A home-built cryogenic Dewar held the samples during measurement. Temperature was controlled within 0.01 K using a Lake Shore Model 330 temperature controller. The platinum RTD used was calibrated within ±0.06 K against standards supplied by Lake Shore and traceable to a NIST standard. A flow cell sample holder was also used for PS and PSF measurements. The temperature of the circulating fluid was controlled within 0.03 K by a VWR Model 1136 heating circulator. The data obtained using the cryogenic Dewar and the flow cell sample holder agree within experimental error. The absolute accuracy of the reported temperatures is 0.2 K.

Possible effects which can cause systematic errors in the photobleaching results are local heating, bleaching too deeply, probe concentrations which are too high, and residual photobleaching.[17] The results reported here were obtained under conditions where these effects are negligible.

Correlation Time. The orientation autocorrelation function CF(t) can be obtained from the anisotropy $r(t)$ by

$$\mathrm{CF}(t) = r(t)/r(0) \tag{2}$$

A model-independent average correlation time τ_c can be defined as

$$\tau_c = \int_0^\infty \mathrm{CF}(t)\,\mathrm{d}t \tag{3}$$

The data can be approximately fit with the Kohlrausch–Williams–Watts (KWW) function:

$$\mathrm{CF}(t) = \exp\{-(t/\tau)^\beta\} \tag{4}$$

Within this approximation, τ_c is given by

$$\tau_c = (\tau/\beta)\Gamma(1/\beta) \tag{5}$$

where Γ is the gamma function. The KWW function is an extremely flexible two-parameter function and is used for this reason.

Results and Discussion

Correlation Function Shape. Figure 2 shows examples of the anisotropy decay function, $r(t)$, measured with the photobleaching technique for rubrene in polystyrene. With decreasing temperature, the correlation function shifts to long times. As shown by the continuous curves in the figure, fits to the KWW equation are reasonably good at each temperature. The β and $r(0)$ values obtained from the fits do not depend on temperature in the temperature region studied. Qualitatively similar results were obtained for the other polymer/probe combinations. $r(0)$ and β values are summarized in Tables 1 and 2.

Effect of Physical Ageing. As indicated in Figure 2, measurement temperatures for rubrene rotation span the DSC T_g for PS (375 K). We believe that the data obtained below T_g represent dynamics in the *equilibrium* melt for all of our samples. It is well known that the dynamics of a polymer below T_g can be affected by the thermal history of the sample. To eliminate this effect and ensure that our results represent the equilibrium state, samples were kept at constant temperature and measurements repeated until τ_c no longer depended upon ageing time. Figure 3 shows two examples of ageing experiments. In each case the sample was quenched from 388 K to the indicated temperature within 30 s and then held isothermally. At first τ_c increases as the elapsed time, τ_e, after the quench

Table 1. Rubrene Reorientation

polymer	T_g/K	$r(0)$	β	$\log(\tau_C(T_g))$	C_1	C_2/K	$f_g/B \times 10^2$	$\alpha_f/B \times 10^4$
PIB	205	0.18 ± 0.07	0.860 ± 0.15	3.9[a]	13.0	57.2	3.35	5.86
PS	375	0.20 ± 0.06	0.61 ± 0.05	1.0	13.8	54.9	3.15	5.74
PSF	459	0.19 ± 0.06	0.44 ± 0.07	0.5	12.8	47.8	3.40	7.12

[a] Extrapolation with WLF equation.

Table 2. Tetracene Reorientation

polymer	T_g/K	$r(0)$	β	$\log(\tau_C(T_g))$	C_1	C_2/K	$f_g/B \times 10^2$	$\alpha_f/B \times 10^4$
PIB	205	0.14 ± 0.05	0.60 ± 0.12	2.2	13.3	54.3	3.26	6.01
PS	375	0.08 ± 0.06	0.35 ± 0.10	0.2	24.3	85.3	1.79	2.04
PSF	459	0.12 ± 0.06	0.33 ± 0.09	−1.4[a]				

[a] Extrapolation with WLF equation for rubrene.

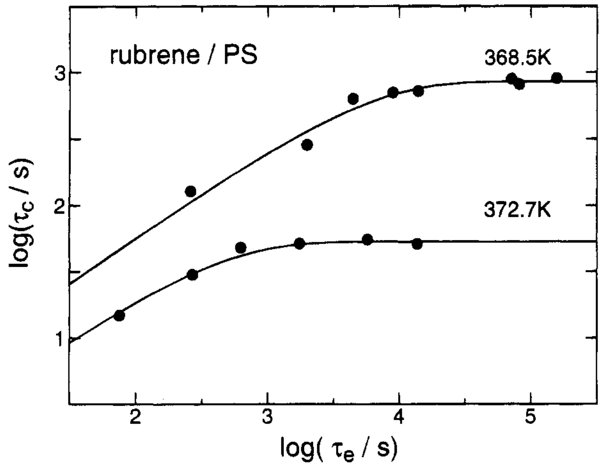

Figure 3. Time evolution of the correlation time for rubrene in polystyrene after a fast temperature drop from 385 K to the indicated temperatures. Thermal equilibration time is less than 30 s. The lines are drawn to guide the eye.

increases; eventually, τ_c levels off at its equilibrium value. The long-time value of τ_c obtained in this way is in excellent agreement with extrapolation of values from above T_g. A more detailed discussion of physical ageing will be published separately.[22]

Polystyrene. Figure 4 shows rotational correlation times for rubrene and tetracene in bulk polystyrene as a function of inverse temperature. The temperature range for rubrene in PS is 384 K (111 °C) to 368 K (95 °C) and includes the DSC T_g = 375 K (102 °C); all data for tetracene were obtained below T_g. Naturally, τ_c increases with decreasing temperature, and the larger probe (rubrene) rotates more slowly than the smaller probe (tetracene). As described above, the β value in the KWW equation did not depend on temperature in the studied temperature range. In addition, Figure 4 indicates that there is no discontinuity or drastic change in temperature dependence of probe rotation times around the DSC T_g. This result is expected as our data were obtained from well-aged equilibrium samples. A change in the temperature dependence of rotational motion around T_g has been observed for quenched samples.[23] Similar discontinuities have been observed for the translational diffusion of probes in a number of polymers,[24] dielectric relaxation spectroscopy of poly(vinyl acetate),[25] and thermally stimulated discharge measurements in polysulfone.[26] Preliminary results for tetracene rotation in PS were published previously;[18] the temperatures reported in this earlier work are inaccurate due to thermal gradients which have been largely eliminated in our current apparatus.

The temperature dependence of τ_c for rubrene in Figure 4 cannot be described by an Arrhenius equation.

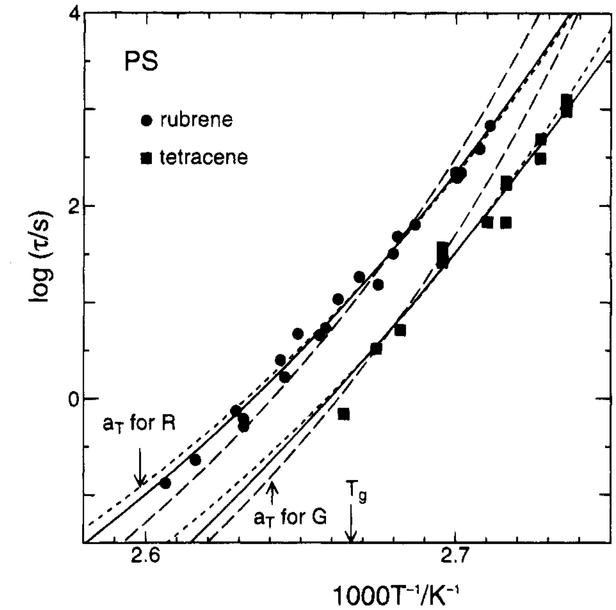

Figure 4. Arrhenius plot of rotation times for rubrene and tetracene in polystyrene. Solid lines indicate WLF fits to the rotation data. Dashed lines represent a_T for the R (- - -) and G (— — —) viscoelastic functions.

The solid lines in the figure indicate the best fits for each probe to the WLF equation.[27]

$$\log(\tau_c(T)/\tau_c(T_g)) = -C_1(T - T_g)/(C_2 + T - T_g) \quad (6)$$

Here, $\tau_c(T_g)$ represents the value of τ_c at T_g. The parameters from these fits are summarized in Tables 1 and 2. Owing to the limited temperature range, the reported values of C_1 and C_2 are not very accurate.

It is interesting to compare the temperature dependence of probe reorientation with the temperature dependence of the bulk mechanical properties of polystyrene. Some correspondence is expected since the local motions which allow the probes to reorient are ultimately responsible for many features of the linear viscoelasticity of polymers. As described in the Introduction, recent studies have shown that the viscosity and the relaxation of the glassy modulus can have different temperature dependences in amorphous polymers. Inoue et al. used viscoelastic and birefringence measurements to separate the relaxation spectrum in the glass transition zone into R and G components by using a modified stress-optical rule.[10] The temperature dependence of each component can be described by a WLF equation. For the case of PS, a_T for the R component agrees reasonably well with a_T reported by Plazek[7] for the viscosity; similar agreement is observed between a_T's for the G component and the recoverable compliance.[28]

Table 3. Viscoelastic Properties

		R component					G component				
polymer	T_g/K	$\log(\tau_R(T_g))$	C_1	C_2/K	$f_g/B \times 10^2$	$\alpha_f/B \times 10^4$	$\log(\tau_G(T_g))$	C_1	C_2/K	$f_g/B \times 10^2$	$\alpha_f/B_x \times 10^4$
PIB[a]	205	3.3[d]	14.3	72.5	3.04	4.19	0.1	13.7	64.8	3.18	4.91
PS[b]	375	1.4	12.0	49.9	3.62	7.25	0.1	12.0	41.6	3.61	8.68
PSF[c]	459	0.7[d]	15.1	49.0	2.88	5.87	0.0	15.8	43.7	2.76	6.31

[a] Reference 32. [b] Reference 25. [c] Reference 36. [d] Extrapolation with WLF equation.

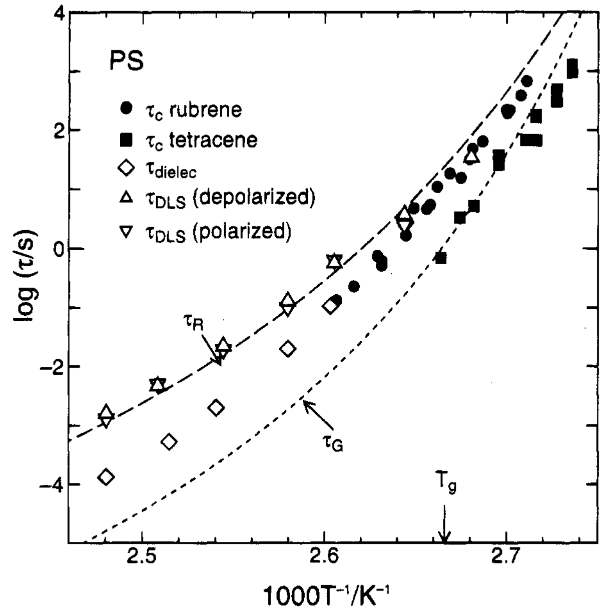

Figure 5. Comparison of various relaxation times in polystyrene. See text for discussion.

Figure 4 compares the temperature dependence of τ_c for rubrene and tetracene in PS with a_T for the viscoelastic R and G components.[28] The WLF parameters for these two components are given in Table 3. A precise comparison is difficult because of the limited temperature range and the scatter of the τ_c data. The temperature dependence of τ_c is slightly different from both the R and G components, but it seems close to the R component. This is consistent with probe rotation measurements in PS across a much wider temperature range reported by Blackburn et al.[18] They found that τ_c for 9,10-bis(phenylethynyl)anthracene (BPEA) in the range of 10^{-10}–10^3 s has very nearly the same temperature dependence as η. Since BPEA is intermediate in size between tetracene and rubrene, we expect that the rotation of these two probes also shows the same temperature dependence as the R component and η.

In Figure 5, we compare correlation times for the rotation of rubrene and tetracene in PS to literature data for characteristic relaxation times in PS obtained by other techniques.[29-31] Here, τ_{DLS} is a mean correlation time of the correlation function of the scattered light measured by dynamic light scattering; τ_{DLS} is calculated using eq 3. We define τ_{dielec} as $1/\omega_{max}$, where ω_{max} is the angular frequency at which ϵ'' shows a maximum. τ_G and τ_R are defined similarly from the maxima of E_G'' and E_R'', respectively; E_G'' and E_R'' describe the contributions of the G and R components to the imaginary part of the complex Young's modulus. τ_G is the characteristic relaxation time of the glassy modulus. τ_R represents the short-time end of the relaxation spectrum of the R component. Since the frequency dependence of the R component in the glass transition zone agrees well with the Rouse theory,[10] we will interpret τ_R in the context of this theory as τ_N, the relaxation time of the fastest mode of a Rouse chain with $N + 1$ submolecules. *Although this is clearly a significant assumption*, it is supported by the comparison between τ_R and probe rotation times below. Regardless of whether this assumption is correct, we emphasize that the experimental definition of τ_R is unambiguous.

Before comparing the data shown in Figure 5, it should be noted that absolute correlation times or relaxation rates obtained by different experimental methods can vary even if the underlying molecular motion is the same. For example, the frequency of maximum loss obtained from G'' and J'' can differ by more than 1 decade.[32] Moreover, since the depicted τ values are average values for wide distributions of relaxation times, they depend on the averaging method which in turn often depends on the experimental techniques. In addition, sample differences may cause T_g shifts of a few degrees.

The main features of Figure 5 are summarized as follows: (1) τ_c for rubrene is similar to τ_{dielec}, τ_R, and τ_{DLS} in the studied temperature region, while τ_c for tetracene is close to τ_G. (2) The temperature dependences of τ_c for rubrene and tetracene are close to those of τ_{DLS} and τ_R. The latter point is more clearly seen in Figure 4. (3) The absolute values of τ_R and τ_c are reasonably consistent with the assumption discussed above that τ_R is equal to the fastest Rouse relaxation time. Under this assumption, τ_R represents the P_1 autocorrelation time of the end-to-end vector of a Rouse submolecule whose molecular weight is estimated to be M = 940 g/mol.[33] Since the molecular weights of rubrene and tetracene are 533 and 228 g/mol, respectively, we would expect that their rotational correlation times should be somewhat faster than τ_R.

Polyisobutylene. Figure 6 shows an Arrhenius plot of rotation times for rubrene and tetracene in polyisobutylene. Qualitatively, the results are similar to those for PS shown in Figure 4. However, although the measured correlation times cover almost the same range, all measurements on PIB were performed above the DSC T_g. Thus τ_c values for rubrene and tetracene are larger at T_g in PIB than in PS. The solid lines in the figure are best fits to the WLF equation; parameters are given in Tables 1 and 2.

For PIB, the difference in temperature dependence between η and the recoverable compliance has been found to be negligibly small.[34] This result is consistent with the rheooptical measurement which demonstrates that τ_R and τ_G show the same temperature dependence.[35] Open circles and squares in Figure 6 indicate τ_R and τ_G, respectively. In the case of PIB, τ_G is much smaller than τ_R. This is due to the unusual frequency dependence of PIB's G component. The temperature dependence of τ_R and τ_G in the studied temperature region can be described by the WLF equation with parameters given in Table 3. These parameters are in accord with other data in the literature.[36]

The temperature dependence of τ_c for rubrene in PIB agrees well with that of the viscoelasticity. Preliminary comparison of τ_c far above T_g using time-correlated single photon counting supports this result.[22] τ_c for

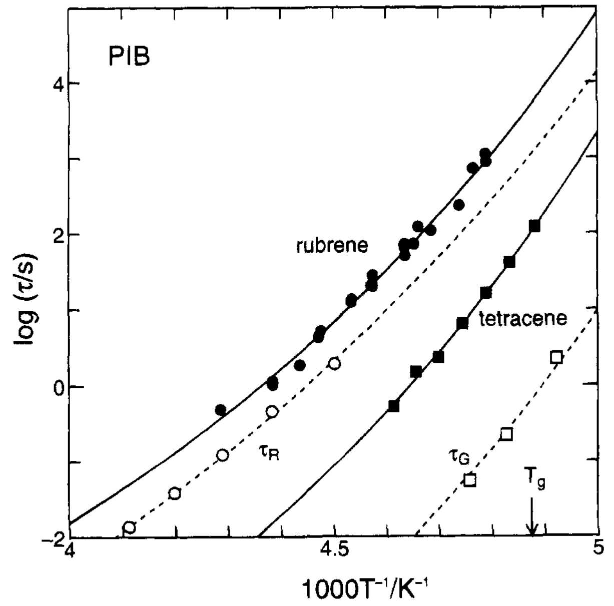

Figure 6. Arrhenius plot of rotation times for rubrene and tetracene in polyisobutylene. Also shown are viscoelastic relaxation times for the R and G components. Solid lines indicate fits to the WLF equation.

tetracene may have a slightly stronger temperature dependence than that for rubrene. The ratio of τ_c for rubrene to τ_R is about 8 in PIB, while it is less than 1/2 in PS (Figure 4). The larger ratio in PIB can be attributed to the smaller submolecule size of PIB[35] (estimated as 250 g/mol) if τ_R is assumed to equal the fastest Rouse relaxation time.

Dielectric data on PIB in the literature are limited to high temperatures.[37] If the same temperature dependence is assumed for the dielectric data as observed for viscoelasticity, τ_{dielec} at T_g is about 10 times larger than τ_G. However, it is difficult to interpret even this extrapolated result since the dielectric signal in PIB is believed to arise from a chemical impurity.[32]

Polysulfone. The rotation times of rubrene and tetracene in polysulfone are shown in Figure 7. All data for tetracene were measured below T_g. Ageing data which are not shown here indicate that the displayed values are equilibrium values. The solid line running through the rubrene data indicates a fit to the WLF equation. Because tetracene data were obtained in only a narrow temperature range, we could not determine WLF parameters for tetracene. The solid line shown for tetracene uses WLF parameters for rubrene. Open circles and squares indicate τ_R and τ_G, respectively.[38] WLF parameters for viscoelastic properties are given in Table 3. Other viscoelastic data are very limited, and viscosity data for PSF near its glass transition temperature are not available to our knowledge. Reported values of $\omega_{\max}$ of $E''(\omega)$ and their activation energy are in accord with the G component.[39] τ_{dielec} data[40] are indicated by diamonds.

The temperature dependence of τ_c is close to that of τ_R, and τ_c values for rubrene are almost equal to τ_R. Since the submolecule size of PSF is estimated as 580 g/mol,[38] this agreement in absolute relaxation times supports the assumption that τ_R equals the fastest Rouse relaxation time. τ_c for tetracene in PSF is smaller than τ_G below T_g. τ_{dielec} is about 3 times larger than τ_c of rubrene and also larger than τ_R. The temperature dependence of τ_{dielec} seems to agree with that of the G component.

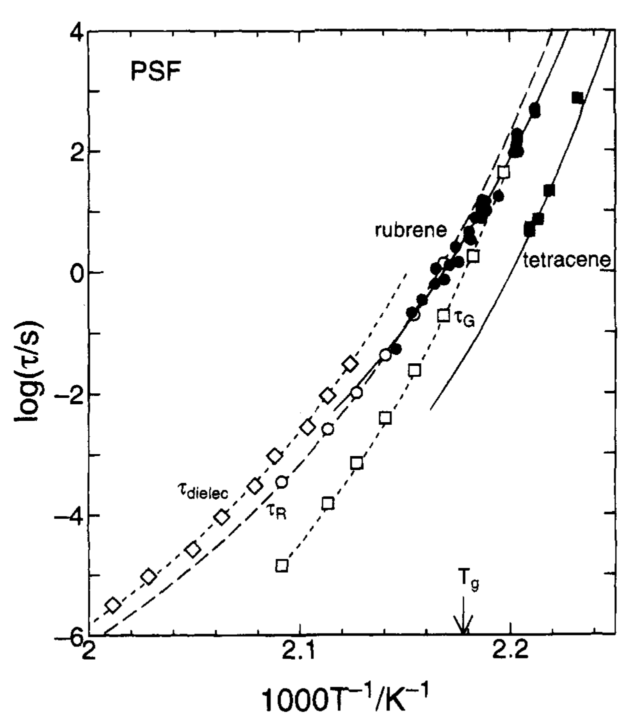

Figure 7. Arrhenius plot of rotation times for rubrene and tetracene in polysulfone. Dielectric and viscoelastic relaxation times are also indicated.

Comparison of Probe Motion in Different Polymers. Correlation Times at T_g. It has long been appreciated that the glass transition observed in the laboratory is a kinetic phenomenon. As the system is cooled through T_g, some characteristic relaxation time of the system becomes long compared to the time scale of the experimental method. In a DSC measurement, the average enthalpy relaxation time $\langle\tau_H\rangle$ at T_g becomes long compared to a time scale determined by the heating rate. A simple model of this process predicts that $\langle\tau_H\rangle$ will be nearly constant at T_g in different materials if the same heating rate is used to determine T_g.[41] Dr. J. M. O'Reilly performed a more sophisticated analysis[42] of our DSC traces for the three polymers using the Tool–Narayanaswamy formalism. The average enthalpy relaxation times estimated at the DSC T_gs are 31, 101, and 24 s, respectively, for PIB, PS, and PSF. Thus $\langle\tau_H\rangle$ at T_g can be regarded as essentially constant for these polymers.[43] We now turn our attention to the behavior of τ_c at T_g.

τ_c at T_g for rubrene and tetracene in the three polymer matrices is plotted against the matrix T_g in the lower part of Figure 8. Preliminary results for poly(methyl acrylate) (PMA, T_g = 288 K) are included.[44] The bars for τ_c in the figure are not errors but indicate the full width at half-maximum of the relaxation time distribution; these were calculated using the β values in Tables 1 and 2.[45]

Figure 8 clearly shows that $\tau_c(T_g)$ for each probe is not constant but varies more than 3 decades depending upon the polymer matrix. This difference corresponds to a temperature shift of 15 K (see Figure 10). Thus the variation of $\tau_c(T_g)$ cannot be attributed to the experimental error in temperature or T_g measurements. Therefore we can conclude that T_g *is not an isolocal mobility state for rigid probes* even though the enthalpy relaxation time is constant.

Viscoelastic Relaxation Times at T_g. The characteristic relaxation times of viscoelasticity, τ_R and τ_G, evaluated at T_g are plotted against T_g in Figure 9.

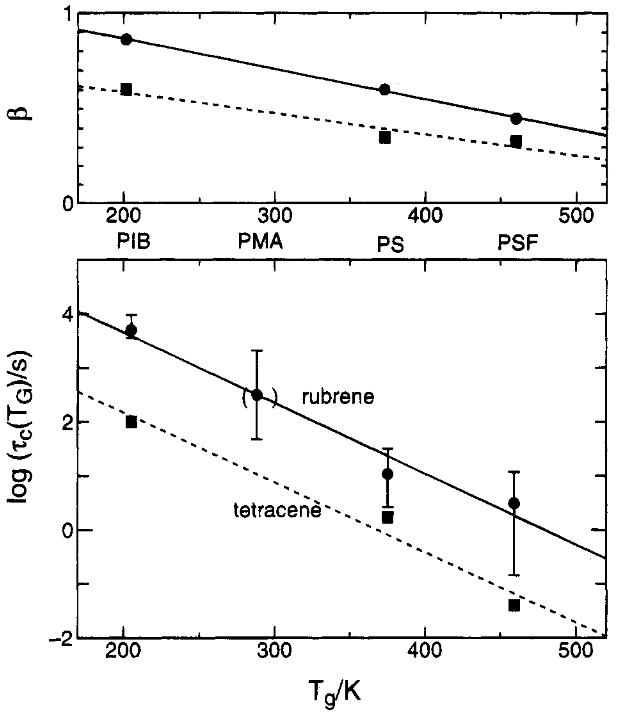

Figure 8. Lower panel: the rotation times of tetracene and rubrene at the matrix T_g plotted as a function of T_g. Upper panel: KWW β parameters which characterize the rotation of these probes at T_g. T_g is determined by DSC measurement.

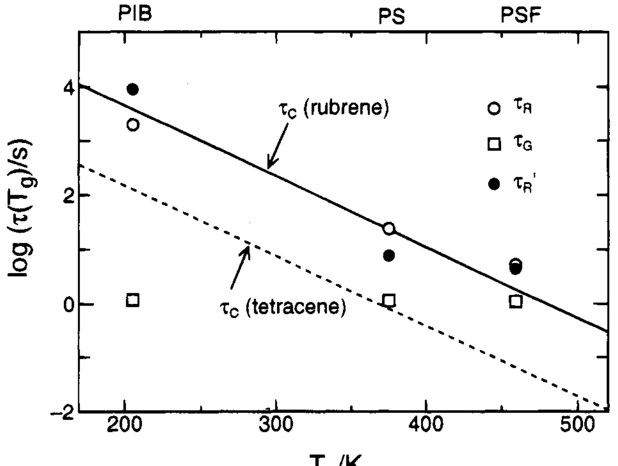

Figure 9. Viscoelastic relaxation times at T_g for the three polymer matrices. Filled circles represent the reduced relaxation time for the R component (see text). Solid and broken lines represent τ_c values at T_g for rubrene and tetracene, respectively. These lines are reproduced from Figure 8. The viscoelastic relaxation time for the R component is correlated with probe rotation. In contrast, the relaxation time for the G component is roughly constant at T_g for these polymers.

Figure 9 shows that τ_R is not constant at T_g. Moreover, the variation of $\tau_R(T_g)$ is very similar to $\tau_c(T_g)$. We suggest that the origin of the friction of probe rotational motion and the Rouse modes is the same, at least for the polymers studied; we return to this point below. On the other hand, Figure 9 shows that τ_G values for the three polymers are almost constant at T_g. Apparently, the G component has a strong correlation with the enthalpy relaxation. $\tau_G(T_g)$ is about 1 s; this is about 50 times smaller than $\langle\tau_H\rangle$.

The ratio $\tau_c(T_g)/\tau_G(T_g)$ for various polymers should provide some insight about the characteristic length scale of the motions responsible for the relaxation of the glassy modulus. τ_c for a given probe corresponds to molecular motion on a length scale defined by the probe size. If $\tau_c(T_g)/\tau_G(T_g)$ is near one, as is the case for rubrene in PSF, then the relaxation of the glassy modulus presumably has a characteristic length scale about the size of a rubrene molecule. For rubrene in PIB, this ratio is almost 10^4, indicating that the relaxation of the glassy modulus occurs on a length scale considerably smaller than rubrene. This speculation is supported by the variation of the KWW β parameter shown in the top part of Figure 8. The data indicate that large ratios of $\tau_c(T_g)/\tau_G(T_g)$ are correlated with large β values and thus narrower distributions of relaxation times. One would expect that a probe relaxing on the same length scale as those motions responsible for the relaxation of the glassy modulus would show β values similar to those seen in dielectric relaxation studies of polymers, i.e., values considerably less than one. On the other hand, a probe relaxing on a larger length scale can average over the spatial and temporal heterogeneities which may be responsible for smaller β values. This interpretation is supported by a recent study of probe rotation in *o*-terphenyl;[20] β values for probe rotation near T_g systematically increased with probe size. The same trend is also observed for rubrene and tetracene in the three polymers studied here.

The speculation of the previous paragraph leads to the conclusion that the motions responsible for the relaxation of the glassy modulus occur on a larger length scale in PSF than in PIB. This is physically appealing given the chemical structure of these polymers. When polymers with *p*-phenylene linkages in their backbones (e.g., PSF) undergo conformational transitions, one would expect rearrangements on larger length scales than would occur for polymers with only carbon–carbon single bonds in the backbone (e.g., PIB). Using other language, one could say that PSF has a larger local jumping unit than PIB. If local jumps occur at the same rate at T_g in these two materials, then one would expect shorter probe rotation times at T_g in PSF.

We do not expect all the systematic trends shown in Figures 8 and 9 to hold for all amorphous polymers. In contrast to the impression given by Figure 9, it is known that τ_R/τ_G can be quite different for two polymers with similar T_gs. For example, while τ_R/τ_G for PIB is more than 10^3, it is only about 10 for polyisoprene (T_g = 203 K).[46] Also, for polymers with similar structures and different T_gs, τ_R/τ_G has been observed to be almost constant.[38] This may be the reason why the four vinyl polymers studied by Plazek et al.[15] all showed similar retardation spectra at T_g. At present, we do not know how these variations in τ_R/τ_G would influence the relationship between $\tau_c(T_g)$ and the matrix T_g.

Role of Rouse Modes in Determining T_g. Figure 9 indicates that the variation of $\tau_R(T_g)$ is quite substantial. This by itself suggests that the Rouse modes are not responsible for the glass transition determined by enthalpy relaxation. This point can be further explored if we again make the assumption that the experimentally determined τ_R corresponds to the fastest Rouse relaxation time. With this assumption, we can reduce τ_R data for the three polymers to a submolecule molecular weight equal to that of rubrene (530 g/mol). This reduction is performed according to the Rouse theory by multiplying τ_R by the square of the submolecule molecular weight divided by 530 g/mol; the reduced τ_R is labeled τ_R' in Figure 9. τ_R' is quite similar to τ_R, and both are similar to $\tau_c(T_g)$. We pointed out above that

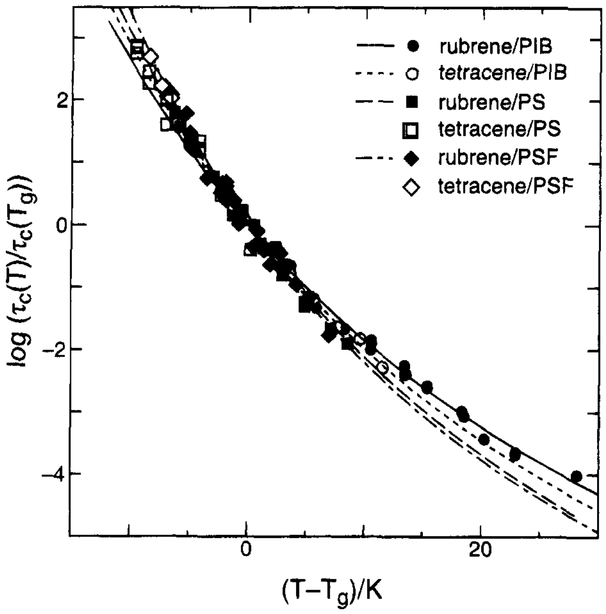

Figure 10. Comparison of the temperature dependence of rubrene and tetracene rotation in polyisobutylene, polystyrene, and polysulfone.

the temperature dependence of τ_c is close to that of τ_R (and thus τ_R') for each polymer. Thus, τ_c and τ_R' are strongly correlated with each other. This is exactly what is expected given our assumption that the experimentally determined τ_R corresponds to the fastest Rouse relaxation time; both τ_c and τ_R essentially monitor motion on a fixed length scale in the three polymers. In contrast, as discussed above, the motions responsible for τ_G apparently occur on larger length scales in PSF than in PIB.

If one neglects the small difference in the flexibility of the three polymers and assumes that τ_R equals the fastest relaxation time of the Rouse chain, then τ_R is proportional to the Rouse submolecules' friction coefficient. One can then calculate that the monomeric friction coefficient at T_g is more than 1.5 decades larger for PIB than PSF. This further suggests that the Rouse modes are not responsible for T_g. This conclusion is not surprising given that Williams showed over 30 years ago that the Rouse model was not capable of accounting for the high modulus of glassy polymers.[47]

Comparison of the Temperature Dependence of τ_c. In Figure 10, τ_c for rubrene and tetracene in PIB, PS, and PSF are plotted against $T - T_g$. Here τ_c is reduced by $\tau_c(T_g)$. The lines in the figure are WLF curves for probe rotation (parameters in Tables 1 and 2).

The temperature dependence of τ_c in the three polymers is quite similar even though the absolute value of τ_c at T_g varies by more than 3 orders of magnitude. When the WLF equation was first introduced, it was thought that universal parameters might suffice in describing most polymer systems. Subsequent work has clearly shown that this is not the case.[48] However, this work has usually been based on the assumption of thermorheological simplicity; i.e., the different temperature dependences of the R and G components were not considered. A recent study shows that the temperature dependence of the G component is not universal.[49] On the other hand, a similar comparison for viscosity or the R component has not been performed. Unpublished data show that the R component shows much better similarity than the G component when $T - T_g$ is used as the reduced variable.[50] For the three polymers studied here, the small differences in temperature dependences of τ_c and the R component cause the τ_c values to superpose even better than the R component. It is unlikely that the temperature dependence of τ_c for probes is universal for all polymers.

Free Volume Theory. The reorientation times of rubrene and tetracene at T_g depend upon the polymer matrix, and for the three polymers studied, τ_c decreases with increasing T_g. In this section we will try to interpret these results using the concept of free volume. This concept has often been used to interpret the temperature dependence of viscoelastic properties of polymers[48] and translational diffusion data for small molecules in polymer systems.[51] The molecular interpretation of the effect of free volume on reorientational motion is less clear than for the case of translational motion. The effect of free volume on rotational motion might be expected to depend on probe shape, since perfect spherical particles would not need free volume to rotate. Conceivably, free volume might affect rotational diffusion about different molecular axes in different ways. In spite of these conceptual difficulties, it is worthwhile to attempt to use free volume theory since the results shown here indicate a strong correlation between probe rotation and viscoelasticity.

In free volume theory, the relaxation time can be related to the fractional free volume $f(T)$ by the Doolittle equation.[52]

$$\ln \tau = A + B/f(T) \qquad (7)$$

Here, A and B are constants. B for rotational motion may be different from that for viscoelasticity or diffusion of small molecules. If the probe rotation is determined only by free volume, we can assume that A and B for a given probe are independent of the polymer matrix. If we assume a linear temperature dependence for the free volume, we can derive a WLF equation for the temperature dependence for reorientational times. The following relationships are found between B and the parameters C_1 and C_2.

$$C_1 = B/2.303 f_g \qquad (8)$$

$$C_2 = f_g/\alpha_f \qquad (9)$$

Here, $f_g = f(T_g)$ is the fractional free volume at T_g and α_f is the thermal expansion coefficient of the free volume. Values of f_g/B and α_f/B for each probe/polymer system are summarized in Tables 1 and 2. The similar f_g/B values in the table are in accord with the similar temperature dependences for probe rotation shown in Figure 10. The smaller f_g/B value for tetracene in PS is due to inaccurate WLF parameters. Using eq 7, the f_g/B values can be used to predict $\tau_c(T_g)$. For rubrene, variation of f_g/B from 0.031 to 0.034 corresponds to a variation in $\tau_c(T_g)$ of a factor of only 17 and not the observed variation of more than 3 decades. In addition, the free volume predictions for $\tau_c(T_g)$ obtained in this way do not reproduce the trend shown in Figure 8. Therefore, the variation of $\tau_c(T_g)$ and the temperature dependence of τ_c cannot be explained consistently by eq 7. We conclude that probe rotation is not simply determined by free volume. Of course, the results in Figure 8 can be reproduced if A and B in eq 7 are allowed to vary for different polymers. Unfortunately, this approach has no predictive value.

Summary and Conclusions

In this paper, we have studied the rotational dynamics of two probe molecules in order to investigate molecular motions of three amorphous polymers near T_g. The results are summarized as follows: (1) The temperature dependence of the rotational correlation times of each probe in each polymer matrix tracks the temperature dependence of the viscoelastic functions, especially that of the Rouse modes. (2) τ_c for a given probe at the T_gs of the matrices varies more than 3 decades while the enthalpy relaxation time is essentially constant. Independent viscoelastic measurements can be interpreted to indicate that Rouse-type chain motions on the same length scale as the probes also vary by 3 decades at the DSC T_g. Thus T_g is not an isolocal mobility state for molecular motions on a fixed length scale. This result supports the viewpoint that Rouse modes are not responsible for the glass transition. (3) The viscoelastic relaxation time associated with the relaxation of glassy modulus is almost constant at T_g and seems to be well coupled with the enthalpy relaxation. The variation of τ_c at T_g can be interpreted in terms of a variation in the characteristic length scale of those motions responsible for relaxing the glassy modulus. The variation of the KWW β parameter supports this speculation. (4) For the three polymers studied, probe rotation times and the viscoelastic relaxation time associated with the Rouse modes showed a systematic decrease with increasing matrix T_g. It is unclear if this systematic trend will be observed in a broader series of polymers.

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