

Translation-Rotation Paradox for Diffusion in Glass-Forming Polymers: The Role of the Temperature Dependence of the Relaxation Time Distribution

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Comparisons are made of the translational and rotational diffusion of small-molecule probes in a polymer near its glass transition temperature, T_g . In the rubbery state, $1.1T_g > T > T_g$, translational diffusion is much less temperature dependent than rotational reorientation; in a “quenched” glass, translation and rotation have similar temperature dependencies. This is explained to be a consequence of the fact that in the rubbery state near T_g the breadth of the polymer relaxation distribution is strongly temperature dependent, while in the quenched glass it is temperature invariant. [S0031-9007(97)03501-1]

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There have been reports [1–10] of behavior, called the translation-rotation paradox for diffusion [3,4], where two effects have been noted in low-molecular-weight and polymeric glass formers. The first relates to the temperature dependencies of the (probe or self-)translational diffusion coefficient, D , and the rotational diffusion coefficient, the latter being proportional to the temperature dependence of the inverse average rotational relaxation time, $\langle\tau\rangle^{-1}$, or, equivalently, the product of temperature and inverse shear viscosity, $T\eta^{-1}$ (T is often not included, given the strong temperature dependence of η^{-1}). As a glass former is cooled from far above the glass transition temperature, T_g , the temperature dependencies of D and rotational diffusion are identical; however, at $T_g < T < T_c$, where $T_c \approx 1.2T_g$, the temperature dependence of D is smaller than that of $\langle\tau\rangle^{-1}$ or η^{-1} . For example, Fujara *et al.* [1] noted in NMR studies of orthoterphenyl that $D \sim \eta^{-1}$ for $T > T_c$ but that $D \sim \eta^{-0.75}$ for $T < T_c$. Similar effects are found in probe studies in rubbery polymers [6,7,9], with the reduction in the temperature dependence of D relative to $\langle\tau\rangle^{-1}$ or η^{-1} being a function of probe size. Thus, for $T_g < T < T_c$ there is an apparent violation of Stokes-Einstein-Debye scaling for which $D \sim \langle\tau\rangle^{-1} \sim T\eta^{-1}$. The second related effect is that, during an average rotational relaxation time, a calculation of an average probe translational displacement, $(6D\langle\tau\rangle)^{1/2}$, suggests that near T_g probes translate as much as 2 orders of magnitude or more [2,6,10] than their molecular dimensions during an average rotational relaxation time. In other words, for $T_g < T < T_c$, there is an apparent “enhancement” of translation relative to rotation.

It has been argued [7–10] that these effects are due to spatial heterogeneity and that the apparent enhancement of translation and the different temperature dependencies of D and $\langle\tau\rangle$ are due to differences in which translation and rotation studies average the heterogeneous dynamics. The correlation between the breadth of the rotational relaxation distribution, a measure of heterogeneity, and enhancement of translational motion support this [10].

Here we report the first measurement of probe rotational and translational dynamics in a “quenched” glassy polymer and compare it to the measurement in the rubbery state for $T < 1.1T_g$. By obtaining distributions of rotational relaxation times via second harmonic generation (SHG), we show that, from T_g to $1.1T_g$, rotational dynamics are thermorheologically complex, i.e., there is a strong temperature dependence of the breadth of the rotational relaxation distribution. For temperatures accessed in the quenched glassy state, rotational dynamics are thermorheologically simple, i.e., there is little or no temperature dependence of the breadth of the rotational relaxation distribution. These results show that, while an apparent enhancement in translation relative to rotation may be explained by the probes sensing a distribution of relaxation times, consistent with the existence of local spatial heterogeneity, the different temperature dependencies of rotation and translation require that the breadth of the relaxation time distribution or the extent of local spatial heterogeneity be temperature dependent [9].

Figure 1 shows structures of the polymer, polyisobutylmethacrylate (PIBMA), and probes, disperse red 1 and 4-(dimethylamino)-4'-nitrostilbene (DANS). Probes were chosen based on their ability to be used in SHG and fluorescence nonradiative energy transfer (NRET)

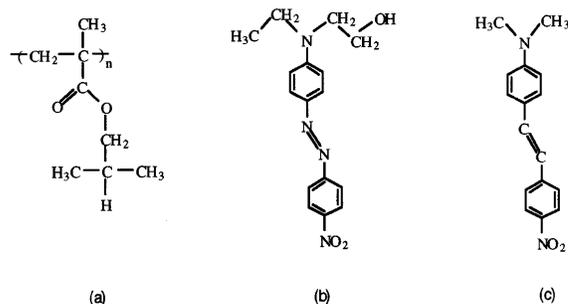


FIG. 1. Polymer and probes used in this study: (a) polyisobutylmethacrylate (PIBMA), (b) disperse red 1, (c) 4-(dimethylamino)-4'-nitrostilbene (DANS).

studies for measuring rotational and translational dynamics, respectively.

For SHG, PIBMA films containing 0.96 mol% disperse red 1 or 1.6 mol% DANS were spin coated onto quartz substrates patterned with planar chrome electrodes. Samples were poled above T_g [11] using a 30 kV/cm dc field until a steady-state SHG intensity was reached and then quenched, if necessary, to the measurement temperature. The temporal decay in SHG intensity from 20 s onward was measured by switching off the depolarizing field while the decay from 5 μ s to 2 s was measured using a variable time delay for switching off the poling field with respect to the laser pulse. For NRET, a “sandwich” geometry was used in which a film containing a copolymer with a covalently attached NRET donor species (99.88 mol% isobutylmethacrylate and 0.12 mol% pyrene-labeled monomer) is layered on top of a film doped with a NRET acceptor (0.21 mol% disperse red 1 or 0.26 mol% DANS). The sandwich was annealed at the measurement temperature, and the decrease in donor fluorescence due to acceptor diffusion was measured. For glassy-state measurement, samples were annealed briefly above T_g [11] and quenched to the measurement temperature. SHG and NRET studies in the glassy state were done over similar time frames, resulting in similar small degrees of physical aging during measurement [12]. See Refs. [6] and [13] for full descriptions of experiments.

The square root of SHG intensity is proportional to $\chi_{NO}^{(2)}$, the orientation component of the second-order macroscopic susceptibility normalized to 1 at zero time, when the poling field resulting in probe orientation is removed, yielding a relaxation to a random orientation. For low-poling fields, $\chi_{NO}^{(2)}(t) \sim \langle \cos \theta \rangle$, where θ is the angle between the probe dipole moment and the poling field vector. $\chi_{NO}^{(2)}$ decays are fit to the Kohlrausch-Williams-Watts (KWW) equation [14]:

$$\chi_{NO}^{(2)}(t) = \exp[-(t/\tau)^\beta], \quad (1)$$

where τ is the characteristic relaxation time and $0 < \beta < 1$. Figure 2 shows fits of Eq. (1) to SHG data. The average rotational reorientation relaxation time is determined from

$$\langle \tau \rangle = \int_0^\infty \exp\left[-\left(\frac{t}{\tau}\right)^\beta\right] dt = \frac{\tau \Gamma(1/\beta)}{\beta}, \quad (2)$$

where Γ is the gamma function.

The temperature dependencies of $\langle \tau \rangle$, τ , and β for disperse red 1 are given in Table I. (Similar results are found for DANS.) $\langle \tau \rangle$ values demonstrate coupling of probe rotational dynamics to the cooperative segmental mobility or α -relaxation dynamics in PIBMA through several distinct signatures [13]: $\langle \tau \rangle$ at T_g is of the order of 100 s; the temperature dependence of $\langle \tau \rangle$ in the rubbery state fits well to a Williams-Landel-Ferry equation [15] with the parameters in agreement with those for the α relaxa-

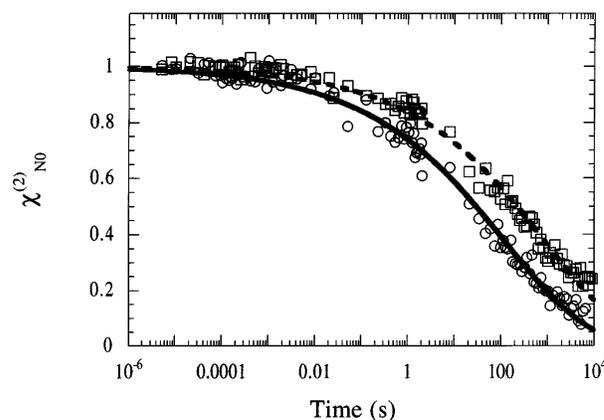


FIG. 2. $\chi_{NO}^{(2)}(t)$ for 1.6 mol% DANS in PIBMA at (□) $T_g = 23^\circ\text{C}$ and (○) $T_g = 13^\circ\text{C}$. Curves are fits to Eq. (1).

tion, and there is an apparent Arrhenius temperature dependence in the glassy state with an activation energy of roughly 200 kJ/mol.

Figure 3 shows typical NRET results from which D is determined. E is the energy transfer efficiency (fraction of excited-state donors returning to the ground state via NRET to acceptors). E is determined by monitoring donor fluorescence intensity, $I(t)$, with increasing diffusion time [6]:

$$E = [I(0) - I(t)]/I(0). \quad (3)$$

With appropriate experiments [6] and sufficiently short diffusion times, $E \sim (Dt)^{1/2}$, where t is the diffusion time. Figure 3 shows a strong temperature dependence of D . No physical aging effects resulting in a significant decrease in diffusion *during measurement* were apparent. Thus, D values at $T < T_g$ may be taken to be representative of a quenched glassy state.

The temperature dependencies of D and $\langle \tau \rangle^{-1}$ are shown in Fig. 4. There is quantitative agreement in the average rotational dynamics of the two probes (expected [13] when dynamics are coupled to the α relaxation) in the rubbery and glassy states and a quantitative difference in D , the latter is known to be a function of chromophore size [6]. As expected, above T_g the temperature dependencies of translational and rotational dynamics differ; each temperature dependence may be fit

TABLE I. Temperature dependence of β , τ , and $\langle \tau \rangle$ [see Eq. (1)] for 0.96 mol% disperse red 1 in PIBMA ($T_g = 53^\circ\text{C}$).

T ($^\circ\text{C}$)	β	τ (s)	$\langle \tau \rangle$ (s)
30	0.24	1700	50 000
40	0.24	120	4000
51	0.25	11	300
58	0.29	0.8	8
63	0.34	0.16	0.8
69	0.35	0.04	0.2
74	0.41	0.007	0.02
80	0.42	0.003	0.01

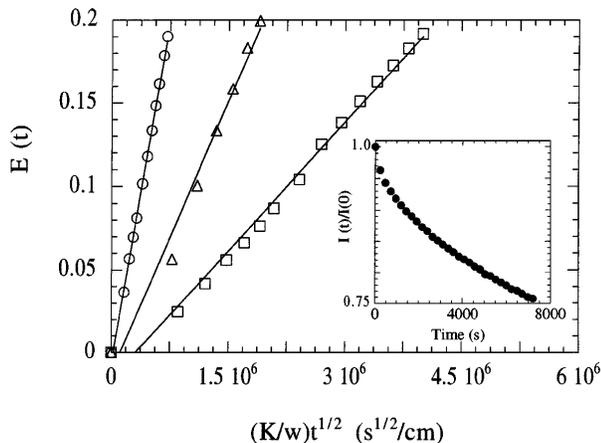


FIG. 3. Energy transfer efficiency as a function of $(K/w)t^{1/2}$ (w is donor film thickness, t is diffusion time, and K is a constant) for disperse red 1 in PIBMA at (\circ) $T_g + 8^\circ\text{C}$, (\triangle) $T_g - 2.6^\circ\text{C}$, and (\square) $T_g - 9^\circ\text{C}$. Slopes equal $D^{1/2}$ (see Ref. [6]). Inset: relative fluorescence intensity of pyrene functionality at 376 nm as a function of diffusion time for $T = T_g + 8^\circ\text{C}$.

by a modified Williams-Landel-Ferry equation [16,17]:

$$\log a_T = \frac{-\xi C_1 (T - T_g)}{C_2 + T - T_g}, \quad (4)$$

where $a_T = D(T_g)/D(T)$ or $\langle\tau(T)\rangle/\langle\tau(T_g)\rangle$, and ξ , ranging between 0 and 1, has been interpreted [17] as reflecting the degree of coupling of probe motion to the polymer cooperative segmental dynamics. For $\langle\tau\rangle$ values, $\xi = 1$ ($C_1 = 13$ and $C_2 = 58$ K for PIBMA); for D values, $\xi = 0.5$. In contrast, in a result unique to this study, *in the glassy state* there is substantial quantitative agreement in the temperature dependencies of probe translation and rotation. Both fit an Arrhenius expression with apparent activation energies of 200–230 kJ/mol. It is also clear that, while spatial heterogeneity is necessary for the translation-rotation paradox, heterogeneity alone is insufficient to explain the paradox completely, given that

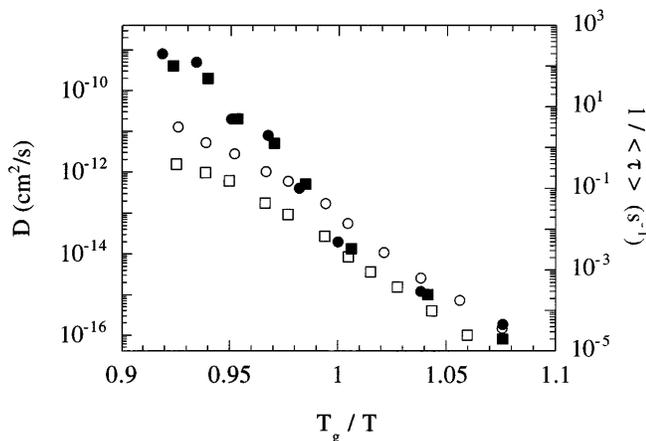


FIG. 4. Comparison of temperature dependencies of D [(\square) disperse red 1, (\circ) DANS] and $\langle\tau\rangle^{-1}$ [(\blacksquare) disperse red 1, (\bullet) DANS] in PIBMA.

a glass must have spatial heterogeneity (breadth of the relaxation time distribution) greater than or equal to that of a rubber or liquid. This is substantiated in Table I by the glassy systems having smaller β parameters, consistent with a broader relaxation distribution. Additionally, for DANS in PIBMA at $T_g/T = 1.038$, a calculation of the translational displacement during the average reorientation time $[(6D\langle\tau\rangle)^{1/2}]$ yields a value of 72 nm, roughly 70 times the length of a DANS molecule and similar to previous measures of enhanced translation.

Using τ and β values from Table I, it is possible to quantify more fully the temperature dependence of the rotational relaxation time distribution and its role in explaining the translation-rotation paradox. Figure 5 shows results from an algorithm [18] developed by Dhinojwala *et al.* [19] for interpreting SHG decays. There is a dramatic broadening in the distribution upon cooling toward T_g , indicative of thermorheological complexity, in agreement with α -relaxation dynamics in rubbery polymers [20] and other glass formers [21] near T_g . However, for the temperatures accessed in the glassy state, the breadth of the relaxation distribution is temperature invariant, and the distribution merely shifts to longer times with decreasing temperature [22].

An important implication of this is that in the glassy state the temperature dependencies of the shortest and longest relaxation time regimes are equivalent, while in the rubbery state the temperature dependence of the shortest relaxation time regime is much less than that of the longest relaxation time regime. With a relaxation time distribution covering many orders of magnitude, $\langle\tau\rangle$ reflects only the long-side portion of the distribution. In contrast, D does not reflect $\langle\tau\rangle$ but instead can be related to a summation over all probes of the ratio of the square of a diffusive jump length to the relaxation time during which each jump is made, i.e., D reflects $\langle\tau^{-1}\rangle$ rather than $\langle\tau\rangle^{-1}$ in this temperature region [2]. Only when the relaxation is represented by a single relaxation time or

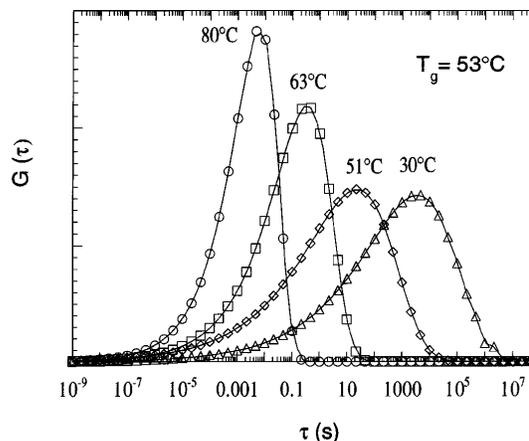


FIG. 5. Discrete relaxation time distributions calculated using KWW parameters listed in Table I for disperse red 1 in PIBMA. Curves are drawn to guide the eye.

the breadth of the relaxation distribution is temperature invariant will $\langle\tau^{-1}\rangle$ and $\langle\tau\rangle^{-1}$ have equivalent temperature dependencies [23]. These data are the first to provide evidence for the equivalence in a quenched glass of the temperature dependencies of $\langle\tau^{-1}\rangle$, $\langle\tau\rangle^{-1}$, and D .

Problems in exactly quantifying $\langle\tau^{-1}\rangle$ are due to the divergence of $\langle\tau^{-1}\rangle$ when Eq. (1) is the relaxation function [24]. One may attempt to estimate $\langle\tau^{-1}\rangle$ from the relaxation distribution [25],

$$\langle\tau^{-1}\rangle = \int_0^\infty \frac{G(\tau)}{\tau^2} d\tau = \sum_{i=1}^\infty \frac{G(\tau_i)}{\tau_i}. \quad (5)$$

To make an accurate estimate, accurate values for $G(\tau)$ are needed over many orders of magnitude in time, especially at the shortest times, well below the μs range where finite (very small) relaxation is present. (Small differences in $G(\tau)$ at very short times may account for the difference in D for DANS and disperse red 1 seen in Fig. 4.) This requires obtaining data with great accuracy on time scales less than a μs , not feasible with our current equipment. While this is an issue for future work, several points clearly result from this study. First, the lesser temperature dependence of D as compared to rotational dynamics in the liquid state very near T_g , known as the translation-rotation paradox for diffusion, can be associated with the strong temperature dependence of the breadth of the relaxation time distribution, i.e., thermorheological complexity, and is not merely a consequence of spatial heterogeneity. This is evident given that below T_g , where relaxation is thermorheologically simple and the system is more homogeneous than above T_g , D and $\langle\tau\rangle^{-1}$ exhibit similar temperature dependencies. Second, the enhancement of translation relative to rotation is a consequence of the breadth of the relaxation time distribution and should be observed at any temperature (not only for $T_g < T < T_c$) where the rotational relaxation distribution is sufficiently broad that $\langle\tau\rangle^{-1}$ and $\langle\tau^{-1}\rangle$ differ greatly, even if $\langle\tau^{-1}\rangle$ cannot be calculated with exactness.

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