4770 *Macromolecules* **1997,** *30,* 4770−4771

Enhanced Translational Diffusion of 9,10-Bis(phenylethynyl)anthracene (BPEA) in Polystyrene

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Received December 27, 1996
Revised Manuscript Received May 9, 1997

Translational diffusion of small molecules in polymers has attracted attention for decades because of its technological importance.[1] Typically, the temperature dependences of the tracer diffusion coefficient, D_T, and the polymer viscosity, η, are interpreted in terms of coupling between probe and matrix motion according to free-volume theories.[1,2] However, this interpretation may need to be reevaluated for amorphous polymers[3−6] and a number of low molecular weight glass formers.[7−9] For some probes in these matrices, translational diffusion has a significantly weaker temperature dependence than η, while rotational motion has a temperature dependence which does not differ significantly from that of η. Free-volume theories provide little insight into these observations, only concluding that translational motion is partially decoupled from matrix motions while rotational motion is fully coupled.

Recently, Cicerone et al. reported translational diffusion measurements of tetracene and rubrene in polystyrene (PS) from $T_g - 10$ K to $T_g + 100$ K ($T_g = 373$ K) using a holographic fluorescence recovery after photobleaching (holographic FRAP) technique.[4] They reported that D_T has a considerably weaker temperature dependence than the rotational correlation times for the same probes. Thus, on average, probes translate farther and farther per rotational correlation time as T_g is approached from above, i.e., translational diffusion at T_g is enhanced. For tetracene in PS, the diffusion coefficient at T_g is *4 orders of magnitude* larger than would be expected on the basis of rotational correlation times and the assumption of a homogeneous matrix. Cicerone et al. suggested that *spatially heterogeneous dynamics* can account for this enhancement of translational motion in PS; i.e., they proposed that dynamics in some regions of the PS matrix are orders of magnitude faster than dynamics in regions perhaps 5−10 nm away. In such an environment, rotation and translation experiments average dynamics in very different ways. If the distribution of local relaxation times broadens as the temperature is lowered toward T_g, then translational motion will have a weaker temperature dependence than rotational motion. Cicerone et al. argued that the larger probe, rubrene, shows much less enhanced translation because it simultaneously experiences more than one region and hence experiences a more homogeneous environment. One possible model for diffusion in a matrix with spatially heterogeneous dynamics is presented in ref 10.

An alternate explanation for the dramatically enhanced translation of tetracene postulates that each tetracene molecule translates extremely anisotropically. Since tetracene has a uniform small cross section when viewed on end, one could imagine that tetracene translates much more efficiently in this direction.

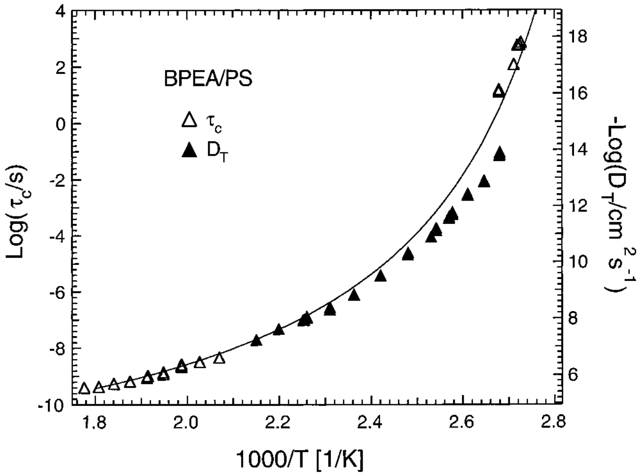

Figure 1. Translational diffusion coefficients (▲) and rotational correlation times (△) of BPEA in PS as a function of inverse temperature. The solid line shows the temperature dependence of η/T. Translational diffusion has a significantly weaker temperature dependence than rotation.

In order to distinguish between these possibilities, we have performed translational diffusion measurements on another probe in polystyrene, 9,10-bis(phenylethynyl)anthracene (BPEA). BPEA does not have a small uniform cross section (see Figure 2). Translational diffusion of BPEA should not be enhanced if anisotropic diffusion is the correct explanation. On the other hand, enhanced translation should be expected if spatially heterogeneous dynamics play an important role.

Results

We have measured translational diffusion coefficients of BPEA in PS from T_g to $T_g + 90$ K ($T_g = 373$ K) using the holographic FRAP technique. D_T values ranged from 10^{-8} to 10^{-14} cm^2/s. In Figure 1, we display these results with rotational correlation times τ_c for BPEA in PS.[3] The solid line shows the temperature dependence of η/T for PS.[11] D_T values for BPEA in PS clearly have a weaker temperature dependence than T/η, while τ_c roughly follows η/T. Thus, we observe that the translational motion of BPEA in PS is enhanced.

The product $D_T\tau_c$ is another way to examine the enhanced translation of BPEA in PS (see Figure 2). Data for tetracene and rubrene in PS are also plotted.[4,12] The straight dashed line at the bottom of the figure is the hydrodynamic prediction[7] from the Stokes−Einstein[13] (SE) and Debye−Stokes−Einstein[14] (DSE) equations. If the data fell on that line, probes would translate about 0.5 diameters/rotational correlation time. Near T_g, we observe that translational diffusion of BPEA in PS is enhanced by more than 2 orders of magnitude relative to rotation. This observation supports the idea that spatially heterogeneous dynamics are responsible for the enhancement of translational diffusion of probe molecules in polystyrene. This explanation also predicts that the nonexponential rotational correlation functions observed for probes in polymer matrices result from spatially heterogeneous dynamics.[4,9] If this is the correct explanation, a correlation should exist between enhanced translation and nonexponential rotational relaxation. To test this correlation, we plot $D_T\tau_c$ versus the KWW β parameter at T_g in Figure 3. We also included the data for two other polymer systems.[5,15]

Figure 3 shows a strong correlation between the $D_T\tau_c$ and the KWW β parameter in all three matrices. A correlation between enhanced translation and nonexponential rotation also exists for probes in low molecular weight glass formers.[7,9] Probe molecules whose rota-

S0024-9297(96)01907-9 CCC: $14.00

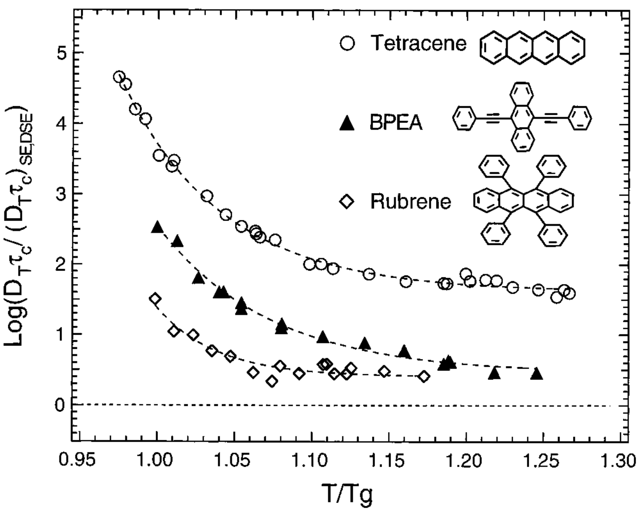

Figure 2. $D_T\tau_c$ for tetracene (○), BPEA (▲), and rubrene (◇) in PS plotted versus temperature. As the temperature is lowered toward T_g, translational diffusion is enhanced. BPEA τ_c values for construction of the ordinate were obtained by fitting the WLF equation to the τ_c data shown in Figure 1. τ_c values near T_g for tetracene and rubrene have been reported.[12] High-temperature τ_c values for these probes were estimated using the WLF equation for BPEA.

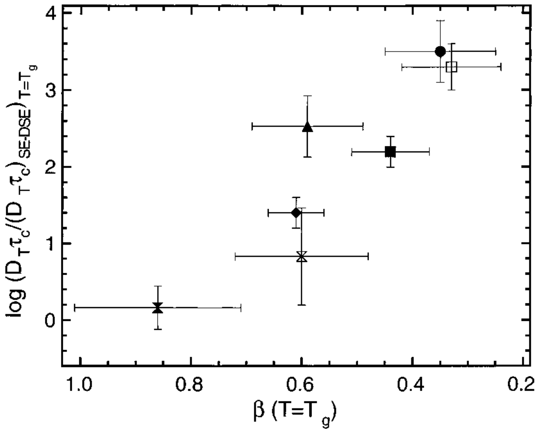

Figure 3. Correlation of enhanced translation ($D_T\tau_c$) with the KWW β parameter for probe rotation at T_g: tetracene/PS (●); BPEA/PS (▲); rubrene/PS (◆); tetracene/PSF[5] (□); rubrene/PSF[5] (■); tetracene/PIB[15] (vertical open bow tie); rubrene/PIB[15] (vertical solid bow tie). This correlation is expected if the dynamics in these systems are spatially heterogeneous.

tional correlation functions decay nearly exponentially ($\beta \approx 1$) exhibit very little enhanced translational diffusion. Larger probes tend to behave this way, since they average over the heterogeneity of the host matrix. On the other hand, small probe molecules experience a heterogeneous matrix and thus have nonexponential orientation correlation functions ($\beta < 1$) and significantly enhanced translational diffusion.

Summary

We performed translational diffusion measurements on BPEA in polystyrene in order to distinguish between two possible explanations for the pronounced enhancement of probe translational diffusion in polystyrene. Translational diffusion of BPEA in polystyrene is enhanced by 2.5 decades at T_g, consistent with the hypothesis that segmental dynamics in polystyrene near T_g are spatially heterogeneous. According to this explanation, the observed enhancement should be related to probe size, not probe shape. Very recent work by Sillescu and co-workers supports this aspect of our results.[16] Since current free-volume explanations of probe diffusion implicitly assume that the system is spatially homogeneous, we suggest these approaches may need to be modified to account for these results.

Acknowledgment. We thank Forrest Blackburn for helpful discussions and Maurice Leutenegger for preparing samples. Acknowledgment is made to the National Science Foundation (DMR-9424472) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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MA961907D