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Time-Resolved Optical Study of the Rotational Mobility of Small Probe Molecules in Bulk Polyisoprene

The local dynamical processes that contribute to fundamentally and practically important properties of polymeric materials have been studied both experimentally and theoretically.[1] Because polymer chain dynamics occur over a wide range of time scales, it is important to have access to a correspondingly wide dynamic range in which to monitor these processes. In this communication, we report on time-resolved optical experiments that indirectly probe polymer dynamics occurring on a well-defined molecular length scale. A transient grating technique has been used to investigate the rotational dynamics of anthracene and 9,10-dimethylanthracene (DMA) in bulk polyisoprene. The temporal evolution of the orientation correlation function for these chromophores has been measured over a dynamic range encompassing 7 decades (100 ps to 1 ms). In this study, the probe molecule is present at a vanishingly low concentration (<0.01%) so that the physical properties of the host material remain unaltered. In this initial report, we focus on the dynamical properties of the matrix polymer. Our major conclusion is that the temperature dependence of the rotational mobility of small probes is well described by the temperature dependence of the steady-shear viscosity from T_g + 120 °C to T_g + 20 °C. We observe no evidence that these probes are sensitive to any sub-T_g processes in polyisoprene. In a future publication we will provide a full description of these experiments, including a detailed analysis of the mechanism for probe reorientation.[2]

Experimental Section. The bulk polyisoprene samples were prepared as previously described.[3] The polyisoprene (Polysciences) used in these experiments had $M_w = 34\,000$ and $M_w/M_n = 1.04$ with a microstructure of 68% cis-1,4, 25% trans-1,4, and 7% vinyl-3,4. The glass transition temperature was determined to be −69 ± 2 °C by DSC. The chromophore concentrations were $\approx 5 \times 10^{-4}$ M, low enough to ensure that excitation transfer effects are negligible.

Two different transient grating experiments were used in this study. In each case, a short optical pulse initiated the experiment by exciting the singlet origin transition (380 nm for anthracene, 400 nm for DMA). A singlet excited state transition at 590 nm was used to probe dynamics from 50 ps to 10 ns. This technique has been described in detail elsewhere.[4] In order to access dynamics occurring on longer time scales (10 ns to 1.5 ms), two synchronously operated Q-switched/mode-locked Nd:YAG laser systems were used. The first laser system produced the excitation pulse, while the second laser system produced a probe pulse at 430 nm corresponding to a long-lived triplet absorption of anthracene. Because of the low triplet quantum yield of DMA, only the single laser transient grating experiment could be utilized to investigate its mobility in this matrix.

Results and Discussion. Figures 1 and 2 show results from the singlet and triplet transient grating experiments on a bulk polyisoprene sample containing a very low concentration of anthracene. Note the different time scales for the two measurements. The experimental observable is the time-dependent anisotropy function $r(t)$, which describes the rotational motion of the probe in terms of an orientation correlation function. The insets to Figures 1 and 2 depict the relative orientations of the excitation and probe transition moments used in each experiment. Their relative orientations are approximately parallel when probing the singlet absorption and approximately orthogonal when probing the triplet absorption. The negative anisotropy values in Figure 2 arise from the initial anticorrelation of excitation and probe transition moments.

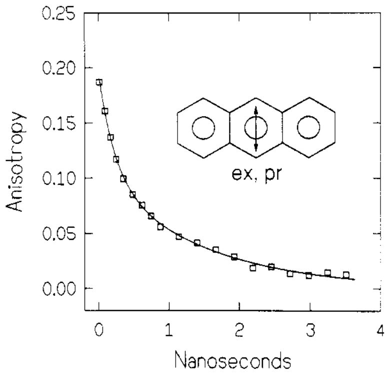

Figure 1. Time-dependent anisotropy for anthracene in bulk polyisoprene at 40 °C. The inset depicts the approximate relative positions of the excitation (ex) and probe (pr) transition moments used in this singlet transient grating experiment. The squares are the experimental anisotropies, and the line represents a fit to the anisotropic rotational diffusion model.

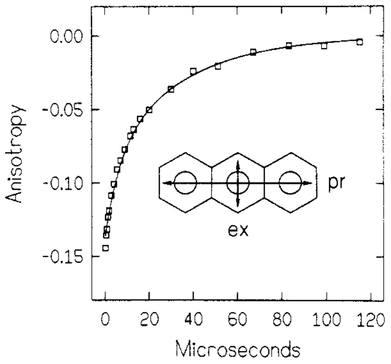

Figure 2. Time-dependent anisotropy for anthracene in bulk polyisoprene at −40 °C. The inset depicts the approximate relative positions of the excitation (ex) and probe (pr) transition moments used in this triplet transient grating experiment. The line through the data is a fit to the anisotropic rotational diffusion model.

The anisotropy data in Figures 1 and 2 could not be fit by a single exponential. The solid lines running through the data represent fits to the anisotropic rotational diffusion model.[5] Because of the high symmetry of the anthracene chromophore, this model, which generally consists of a sum of five exponentials, reduces to a biexponential form. At temperatures between −20 and −45 °C, the shape of $r(t)$ remained essentially constant. The mechanism responsible for the orientational relaxation in this temperature range is rotational diffusion about the long axis of the anthracene molecule. At higher temperatures, the shape of $r(t)$ is temperature dependent. This indicates that the ratios of the diffusion constants for different molecular axes are changing with temperature. For DMA, we also observed that the anisotropy decays were nonexponential and changed shape with temperature. This is consistent with previous work on DMA in other matrix materials.[6,7] The $r(0)$ values in Figures 1 and 2 do not correspond to their limiting values of 0.4 and −0.2 due to overlapping vibronic transitions.[8] We will present a full account of our analysis of the anisotropy decays in a future publication.[2]

The rotational correlation time, τ_c, was used to characterize the temperature dependence of the probe rotational mobility. τ_c is defined as the integral of the best fit correlation function and allows a model-independent characterization of the anisotropy decays. Figure 3 illustrates the temperature dependence of τ_c for anthracene and DMA in bulk polyisoprene from 54 °C (T_g + 123 °C)

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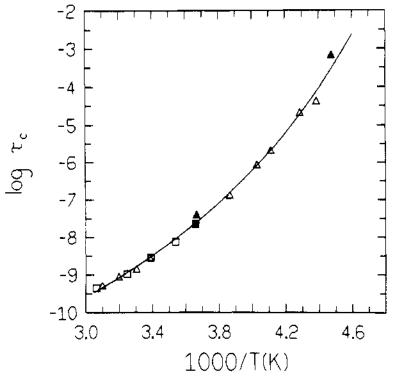

Figure 3. Temperature dependence of the rotational correlation time τ_c (in seconds) for anthracene (△) and DMA (□) in bulk polyisoprene. The darkened symbols represent correlation times extracted from constrained fits when the accessible time window was insufficient to observe the complete anisotropy decay. The line represents the temperature dependence of η/T for a bulk polyisoprene sample having a similar microstructure and molecular weight. This line has been vertically shifted to coincide with log τ_c over the temperature range studied. Correlation times shorter than 30 ns were measured using the singlet transition, while longer times were measured with the triplet transition.

to −49 °C (T_g + 20 °C). The solid line represents the temperature dependence of the steady-shear viscosity (actually η/T) of a bulk polyisoprene sample with a similar microstructure and molecular weight.[9] The viscosity curve has been vertically shifted to coincide with log τ_c over the temperatures investigated. The temperature dependence of τ_c is non-Arrhenius over this temperature range and is in excellent agreement with the temperature dependence of η/T. This agreement indicates that the bulk viscosity has the same temperature dependence as the effective local viscosity that the probe experiences ($\tau_c \propto \eta/T$ according to the Debye–Stokes–Einstein equation). Since the local polymer dynamics responsible for the rotational mobility of the probe molecules occur on length scales that are on the order of the size of these probes (6–10 Å), these chromophores are sensitive to dynamics on the scale of a few monomer units. Hence, these results provide further evidence that local dynamics on this small length scale are intimately linked to the main glass transition. This conclusion is consistent with previous time-resolved optical studies of the dynamics of anthracene-labeled polymer chains in bulk elastomers. Transient grating experiments performed by Hyde et al.[3] and time-resolved fluorescence anisotropy decay measurements carried out by Viovy et al.[10] measured the temperature dependence of labeled chain motion in bulk polyisoprene and polybutadiene at temperatures well above T_g. The temperature dependence of the local dynamics in both of these polymer systems was found to be in reasonable accord with that predicted by the WLF equations for these materials over the temperature ranges investigated.

Triplet transient grating experiments performed at −70 °C ($\approx T_g$) reveal that $r(t)$ is time independent over the experimental time window (out to 1.5 ms). Hence, the anthracene probe is not sensitive to any sub-T_g transitions in this polymer system. This is not altogether surprising since dynamic mechanical measurements have shown at most a weak β transition in *cis*-polyisoprene.[11]

Our principal conclusion that the motion of small probe molecules in polyisoprene is sensitive only to the α transition is at variance with recent results by Queslel et al.[12] These investigators used steady-state fluorescence depolarization to study the rotational motion of DMA and larger probes in polyisoprene and other elastomers. For DMA in a predominantely *cis*-polyisoprene elastomer, they observed that the rotational mobility of the probe had a substantially weaker temperature dependence than predicted by the WLF equation for this material. The mobilities of the larger probes showed a stronger temperature dependence than DMA, but even this temperature dependence was weaker than that given by the WLF equation. The authors concluded that the mobility of DMA (because of its small size) was influenced by motions associated with sub-T_g transitions. In contrast, our time-resolved results for DMA and anthracene (a slightly smaller molecule) in polyisoprene show that the rotational motion of these probes has the same temperature dependence as the WLF equation (from viscosity measurements). The difference between our work and that of ref 12 lies in the temperature dependence of the probe mobility, since the temperature dependences of the WLF equations used in this paper and in ref 12 are essentially the same. We will not speculate extensively on the reasons for these differences. We note that the measurements reported here cover much wider temperature and time ranges than the results from ref 12 and that our experiments measured the entire time dependence of the anisotropy decays. As a result, the interpretation of our results does not depend on the assumption of an exponentially decaying anisotropy function which was made in ref 12. As mentioned earlier, our results are inconsistent with this assumption.

The preliminary results presented here indicate that time-resolved optical studies of probe rotation are a potentially useful technique to investigate dynamics in polymers melts near and above T_g. The optical method is sufficiently sensitive that only very small quantities of the probe molecule are required. Consequently, the dynamics of the host can be directly observed without having to extrapolate to infinite dilution in probe concentration. The wide dynamic range available with this technique facilitates a comprehensive view of the dynamics of these complex systems. Future work will examine probe mobility in polymers with more pronounced sub-T_g transitions and in simple glass-forming systems. We are also developing experimental techniques which will allow us to extend these studies to temperatures below T_g.

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Registry No. DMA, 781-43-1; anthracene, 120-12-7; polyisoprene, 9003-31-0.

References and Notes

(1) For example: Bullock, A. T.; Cameron, G. G.; Smith, P. M. *Eur. Polym. J.* **1975**, *11*, 617. Howarth, O. W. *J. Chem. Soc., Faraday Trans. 2* **1980**, *76*, 1219. Alig, I.; Steiber, F.; Wartewig, S.; Fytas, G. *Polymer* **1988**, *29*, 975. Skolnick, J.; Helfand, E. *J. Chem. Phys.* **1980**, *72*, 5489.
(2) Hyde, P. D.; Ediger, M. D. *J. Chem. Phys.*, to be published.
(3) Hyde, P. D.; Ediger, M. D.; Kitano, T.; Ito, K. *Macromolecules*, in press.
(4) Hyde, P. D.; Waldow, D. A.; Ediger, M. D.; Kitano, T.; Ito, K. *Macromolecules* **1986**, *19*, 2533.
(5) Chuang, T. J.; Eisenthal, K. B. *J. Chem. Phys.* **1972**, *57*, 5094.
(6) Viovy, J. L. *J. Phys. Chem.* **1985**, *89*, 5465.
(7) Labhart, H.; Pantke, E. R. *Chem. Phys. Lett.* **1973**, *23*, 482.
(8) Bree, A.; Katagiri, S.; Suart, S. R. *J. Chem. Phys.* **1966**, *44*, 1788.
(9) Nemoto, N.; Landry, M. R.; Noh, I.; Yu, H. *Polym. Commun.* **1984**, *15*, 141.
(10) Viovy, J. L.; Monnerie, L.; Merola, F. *Macromolecules* **1985**, *18*, 1130.

(11) Morgan, R. G.; Nielsen, L. E.; Buchdahl, R. *J. Appl. Phys.* 1971, *42*, 4653.
(12) Queslel, J. P.; Jarry, J. P.; Monnerie, L. *Polymer* 1986, *27*, 1228. (Note that Figures 5 and 6 have been interchanged in this reference.)

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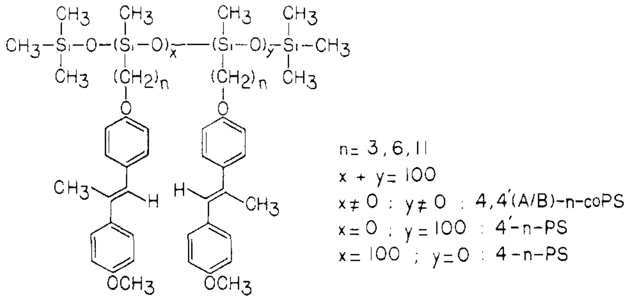
Transformation of a Monotropic Mesophase into an Enantiotropic Mesophase by Copolymerization of the Parent Polymers' Monomer Pair Containing Constitutional Isomeric Mesogenic Side Groups

In a series of publications from our laboratory,[1-3] we have suggested that copolymerization of monomer pairs containing mesogenic units which are constitutional isomers should depress the tendency toward side-chain crystallization of polymers containing long, flexible spacers and simultaneously provide qualitative information about the degree of decoupling. The previous experiments were performed with side groups based on 4-methoxy-4′-hydroxy-*trans*-α-methylstilbene (4-MHMS) and 4-hydroxy-4′-methoxy-*trans*-α-methylstilbene (4′-MHMS) constitutional isomers. However, all comonomer compositions were directly synthesized as mixtures of constitutional isomers by the monomethylation of 4,4′-dihydroxy-*trans*-α-methylstilbene.[1-3] Although the molar ratio between the two consitutional isomeric side groups was determined by spectroscopic methods, no information about the behavior of each of the two individual homopolymers based only on one individual constitutional isomer was available. Meanwhile we have synthesized and characterized the homopolymers based on 4-MHMS[4] and 4′-MHMS[5] individual isomers.

This paper describes the first quantitative results concerning the influence of copolymer composition on the phase transitions of thermotropic liquid-crystalline poly(methylsiloxanes) containing 4-MHMS (4-*n*-PS), 4′-MHMS (4′-*n*-PS), and different ratios between these two constitutional isomeric mesogenic side groups [4,4′(*A*/*B*)-*n*-coPS] attached to the polymer backbone through flexible spacers containing 3, 6, and 11 methylenic units (Scheme I). Ratio *A*/*B* refers to the molar ratio between 4-MHMS and 4′-MHMS constitutional isomeric side groups in the copolymer.

The synthesis and characterization of these homopolymers and copolymers were performed according to general procedures used in our laboratory.[3-6] Copolymers based on several different ratios between the two individually synthesized isomeric monomers[4,5] were synthesized. Phase transitions were assigned by a combination of differential scanning calorimetry (DSC) (20 °C/min) and thermal optical microscopy. DSC curves of all polymers were perfectly reproducible and independent of the heating or cooling scans that they were recorded from.

Scheme I
Poly(methylsiloxanes) and Copoly(methylsiloxanes) Containing 4-MHMS- and 4′-MHMS-Based Mesogenic Side Groups and Different Spacer Lengths



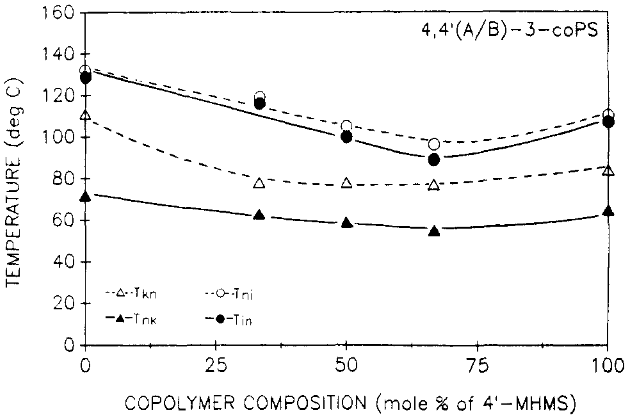


Figure 1. Dependence between (Δ, Tkn) crystalline–nematic, (▲, Tnk) nematic–crystalline, (O, Tni) nematic–isotropic, and (●, Tin) isotropic–nematic transition temperatures and the 4,4′-(*A*/*B*)-3-coPS copolymer composition.

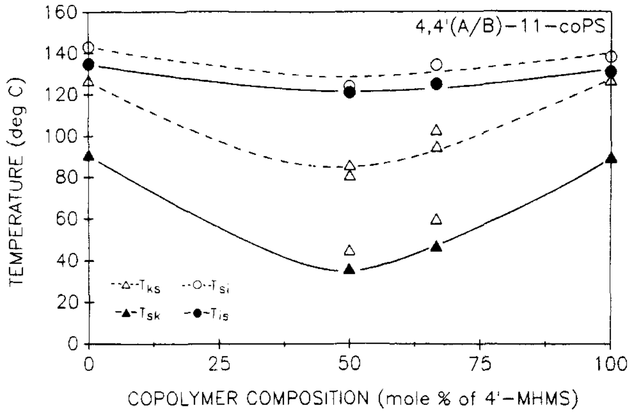


Figure 2. Dependence between (Δ, Tks) crystalline–smectic (▲, Tsk) smectic–crystalline, (O, Tsi) smectic–isotropic, and (●, Tis) isotropic–smectic transition temperatures and the 4,4′(*A*/*B*)-11-coPS copolymer composition.

Figure 1 presents the phase diagram of the copolymer system 4,4′(*A*/*B*)-3-coPS. Both homopolymers exhibit an enantiotropic nematic mesophase and side-chain crystallization.[4,5] The use of different ratios of these two constitutional isomeric side groups in the structure of 4,4′-(*A*/*B*)-3-coPS depresses to approximately equal extent both the nematic–isotropic and the crystalline–nematic (as well as their revers) phase transition temperatures. The enthalpy changes associated with the mesomorphic–isotropic and the reverse phase transitions of the homopolymers 4′-*n*-PS are equal to those of 4-*n*-PS (n = 3, 6, 11) and within experimental error are equal to those of their copolymers. For polymers with $n = 3$, $\Delta H_{\rm in} = 0.10$ kcal/mru, for polymers with $n = 6$, $\Delta H_{\rm in} = 0.09$ kcal/mru, and for polymers with $n = 11$, $\Delta H_{\rm is} = 0.75$ kcal/mru.

Figure 2 presents the phase diagram of the copolymer system 4,4′(*A*/*B*)-11-coPS. Both 4-11-PS and 4′-11-PS present an enantiotropic smectic mesophase and side-chain crystallization.[4,5] The resulting copolymers exhibit a strongly depressed crystalline melting transition temperature and a slightly lowered smectic–isotropic transition

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