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Observations of Shear-Induced Molecular Orientation in a Polymer Melt Using Fluorescence Anisotropy Measurements

Introduction. Fluorescence anisotropy measurements have been employed by many authors to explore both molecular relaxation times and molecular orientation. Dynamic depolarization measurements of solutions of polymers tagged with fluorophores have been used to explore molecular relaxation models.[1-4] Steady-state anisotropy measurements have yielded orientation functions for highly extended polymers and cross-linked rubber.[5-8]

In this investigation, we have measured fluorescence anisotropy using steady-state illumination as a function of applied shear loading. We consider the anisotropy r

$$r = \frac{I_{zz} - I_{zx}}{I_{zz} + 2I_{zx}} \qquad (1)$$

where I_{zz} is the intensity of the fluorescence when both polarizer and analyzer are orientated in the z direction, and I_{zx} is the fluorescence intensity when the polarizer and analyzer are oriented in the z and x directions, respectively. In general, anisotropy will depend on molecular orientation, fluorescence decay time τ, and the rotational relaxation of the probe τ_r. Theoretical models of anisotropy that take into account these quantities have been carried out by several authors.[6,9-12] In all of the published work, uniaxial orientation was assumed, a situation applicable to extensional strain, liquid crystals, and fibers. The symmetry of uniaxial orientation does not apply in the case of shear flow, but published work provides a framework for extending the models. The objective is to calculate the time-dependent anisotropy decay, $r(t)$, of a photoselected ensemble of dye molecules. Under steady-state shear flow, anisotropy decay is governed by the Smoluchowski equation, i.e., rotational diffusion in the presence of a spatial orientation potential $U(\theta,\phi)$, where θ is the angle between the absorption dipole of the chromophore and the direction of flow (laboratory z direction) and ϕ is the azimuthal angle measured from the x axis and the laboratory y axis points in the direction of the excitation light beam.

For shear flow, anisotropy will be a function of orientation factors of θ and ϕ. For example, at $t = 0$, we have calculated

$$r(0) = \frac{A\langle\cos^4\theta\rangle + A\langle\cos^4\theta\cos^2\phi\rangle - A\langle\cos^2\theta\cos^2\phi\rangle}{A\langle\cos^4\theta\rangle - 2A\langle\cos^4\theta\cos^2\phi\rangle + 3B\langle\cos^2\theta\rangle + 2A\langle\cos^2\theta\cos^2\phi\rangle} \qquad (2)$$

Here, $A = (3\cos^2\delta - 1)/2$, $B = (1 - \cos^2\delta)/2$, and δ is the angle between the absorption and emission dipoles. When $\tau/\tau_r \ll 1$, eq 2 holds for all time.[5,12] But, when $\tau \approx \tau_r$, depolarization due to rotational relaxation of the probe occurs and anisotropy will decay from its initial value given by eq 2. The details of the calculation of $r(t)$ describing rotational diffusion in the potential field of an applied shear stress will be the subject of a future publication.

Our primary objective was to use fluorescence anisotropy measurements to monitor shear-induced molecular orientation in polymer systems. To do this, we optically instrumented a cone and plate rheometer and we synthesized a polymeric fluorescent probe molecule consisting of anthracene-tagged polybutadiene (PB) for which anthracene is positioned in the center of the main polymer chain (see Figure 1). Tagged PB has the potential to participate in the entanglement network of a host polymer matrix and thereby orient with the matrix under applied shear stress. Below, we present measurements of anisotropy of tagged PB, doped into a PB matrix, as a function of shear stress over a range of shear rates for which the matrix PB is non-Newtonian. Similar experiments, performed in extension on cross-linked polyisoprene, demonstrated agreement between orientation determined from fluorescence anisotropy and birefringence measurements.[7] To our knowledge, no previous measurements of fluorescence anisotropy of a polymer undergoing shear flow have been published.

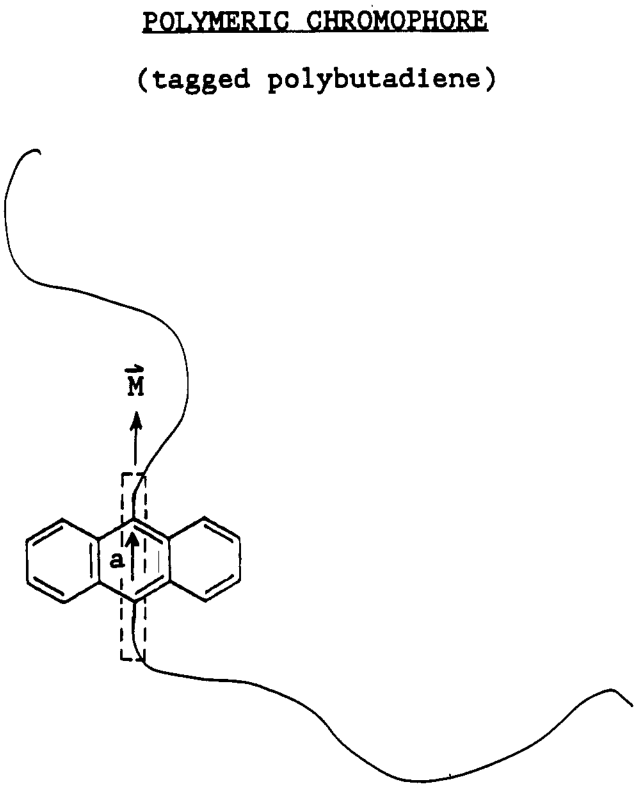

Figure 1. Representation of the tagged polybutadiene probe molecule. The absorption dipole a is coincident with the local direction **M** of the polymer main chain. The strings represent the main chain of polybutadiene.

Experimental Procedure. Materials. The matrix polymer material was 420 000 molecular weight PB, 36% cis, 55% trans, and 9% vinyl, which was obtained from Scientific Polymer Products.[13] Specimens were prepared by mixing the tagged PB and the host matrix PB in a common solvent, cyclohexane, and subsequently evaporating off the cyclohexane. Concentration of the anthracene-tagged PB was 0.1% by weight of matrix PB. Cetane plasticizer was added at 5 and 50% by weight of matrix PB plus plasticizer for the two specimens studied. A control specimen, free anthracene doped into PB plasticized at 10%, was also prepared.

The tagged PB probe molecule was derived from bifunctional anthracene, which was covalently bonded by ester linkages to PB chains so that the fluorescent anthracene resides at a central position on the polymer main chain as depicted in Figure 1. The starting materials were dicarboxyl-terminated PB, molecular weight = 16 000, and 9,10-anthracenedicarboxaldehyde. The anthracenedicarboxaldehyde was converted to anthracenedimethanol and subsequently covalently bonded to the dicarboxyl-terminated PB via an esterification reaction. Gel permeation chromatography data show that the tagged PB has a molecular weight of 30 000, which is approximately

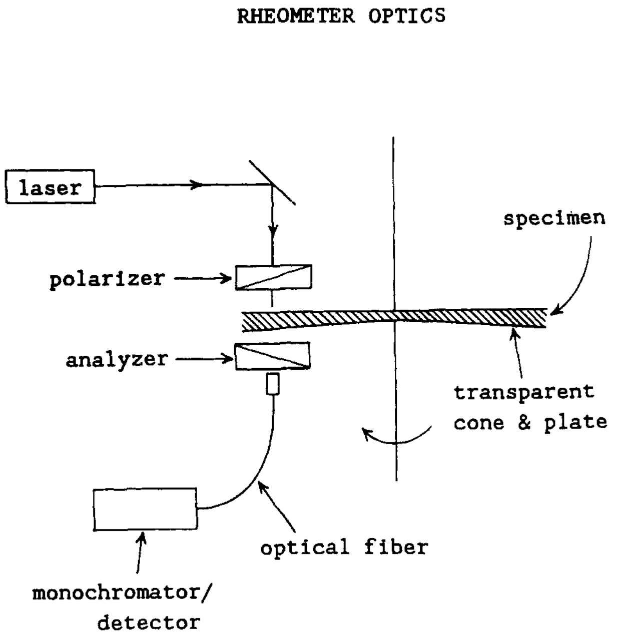

Figure 2. Abbreviated sketch of the experimental arrangement.

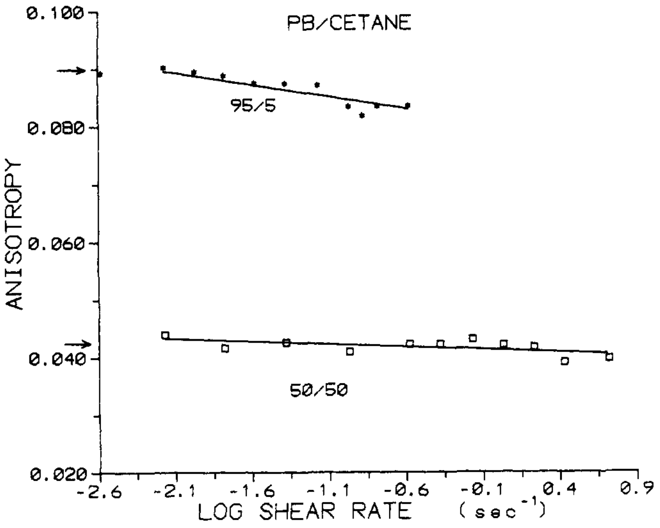

Figure 3. Anisotropy plotted vs shear rate for the 5 and 50% cetane-plasticized polybutadiene specimens, designated 95/5 and 50/50, respectively. Each specimen has been doped at 0.1% concentration by weight with the anthracene-tagged probe molecule. The arrows point to values of anisotropy at zero shear.

twice that of the starting PB, and its molecular weight distribution is somewhat broader. We concluded that there is one anthracene per polymer chain and that it is positioned in the center of the main chain as shown in Figure 1.

Instrumentation. Simultaneous measurements of shear rate, shear stress, and fluorescence anisotropy were obtained by combining a Weissenberg rheogoniometer with the anisotropy optics. An abbreviated sketch of the experimental arrangement is shown in Figure 2. The transparent cone and plate materials of the rheometer are quartz for the upper plate and poly(methyl methacrylate) for the bottom cone. The essential elements of the optics are the argon ion laser light source, the transparent cone and plate of the rheometer, a customized optical mount for mounting polarizer and analyzer at the rheometer, the optical fiber cable for collection and transmission of the fluorescence radiation, and the monochromator with photomultiplier detector. The 364-nm line is selected from the laser for excitation of anthracene. The beam is directed through a crystal polarizer and the quartz plate parallel with the velocity gradient in the sheared specimen and with polarization parallel to the tangential velocity of the rotating cone. I_{zz} and I_{zx} were obtained by the analyzer, which is oriented at 0 to 90° by a computer-driven solenoid. Here z is the direction of tangential velocity, x is in the radial direction of the cone and plate, and y is in the direction of the light beam. The reported anisotropy values, measured at 425 nm, are an average of 40 or more measurements, which had a standard deviation of 0.0015 or less. All measurements were made at 23 °C.

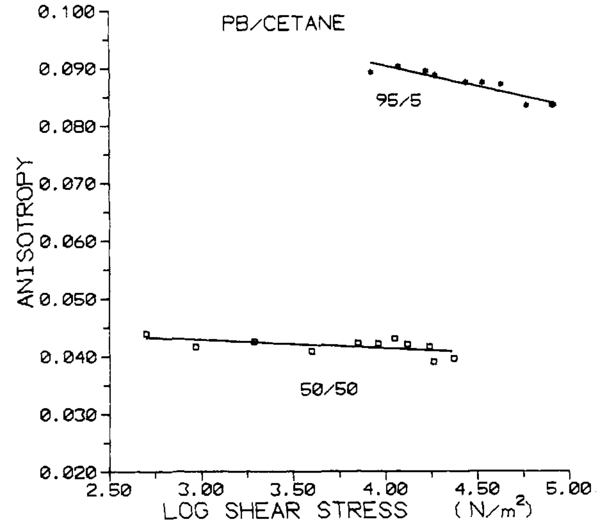

Figure 4. Anisotropy plotted vs shear stress for the 5 and 50% cetane-plasticized polybutadiene specimens, designated 95/5 and 50/50, respectively. Each specimen has been doped at 0.1% concentration by weight with the anthracene-tagged probe molecule.

Results and Discussion. Figures 3 and 4 show anisotropy vs shear rate and shear stress for 5% and 50% plasticized specimens. Over the shear rate range investigated, these specimens displayed non-Newtonian behavior. Also shown in Figure 3 are the zero shear anisotropy values, 0.090 for the 5% plasticized specimen and 0.042 for the 50% plasticized specimen. If we assume random orientation for these specimens when under zero shear, then the difference in anisotropy can be attributed to different relaxation times τ_r. At random chromophore orientation, we have[6,10]

$$r_0 = \frac{2}{5}\,\frac{(3\cos^2\delta - 1)}{2}\,\frac{1}{(\tau/\tau_r + 1)} \tag{3}$$

where the term $(3\cos^2\delta - 1)/2 = 0.55$, as determined in a separate experiment.[14] If we use $\tau = 9.4$ ns,[3] then τ_r is estimated to be 6.50 and 2.24 ns for the 5% and 50% plasticized specimens, respectively. This short relaxation time is for the rotational motion of the chromophore absorption dipole and is a local relaxation involving only a few monomer units in the neighborhood of the anthracene fluorophore. Other experimental evidence of the local character of this relaxation is as follows: it is independent of molecular weight, and it has low activation energy, 2.8 kcal/mol.[14] Since the entanglement molecular weight is 2000 (37 monomer units) for PB,[15] we assume that the local relaxation time τ_r is independent of shear stress and is constant over the experimental range of shear stresses shown in Figure 4. We conclude that the observed shear-induced changes in r are due to orientation of the fluorophore attached to the polymer main chain and reflect chain segment orientation in its neighborhood. In addition to these data, we carried out a control experiment measuring anisotropy as a function of shear stress for free anthracene doped into 10% plasticized PB; anisotropy was observed to be independent of shear stress, indicating that attachment to the polymer chain is required.

In principle, anisotropy measurements yield three-dimensional information about $f(\theta,\phi)$, the distribution of chromophore absorption dipoles. This is indicated by the orientation factor terms in eq 2, which was derived for the geometry used in the experiment, i.e., an excitation light beam parallel with the velocity gradient. Flow birefringence studies of cone and plate rheometry, carried out for a light beam perpendicular and parallel to the velocity gradient, show that orientation is imposed on a polymer specimen both by shear stress τ_{yz} and normal stress differences $(\tau_{jj} - \tau_{ii})$.[16,17] Our ultimate objective is to calculate orientation factors $\langle \cos^4 \theta \rangle$, $\langle \cos^2 \theta \rangle$, and $\langle \cos^2 \phi \rangle$ from steady-state anisotropy measurements. This will be possible when the calculation of $r(t)$, depolarization due to rotational diffusion, is completed. Application of eq 2 is not appropriate here because we have determined that $\tau \approx \tau_r$.

The observation that r decreased with applied shear stress is opposite to that which has been observed for extensional stress.[7,18] The major difference between uniaxial extension and shear flow is the combination of orientation factors that contribute to the observed anisotropy. For extension, uniaxial symmetry can be invoked, thus eliminating ϕ dependence.[9,11,12] Equation 2 shows the manner in which orientation in the ϕ direction is expressed. Our experimental observations indicate that $f(\theta,\phi)$ develops from the imposed stress in such a way that the resultant combination of orientation factors causes r to decrease with shear stress.

We interpret the results for the 50% plasticized specimen in terms of the entanglement molecular weight, which increases from 2100 for the 5% plasticized specimen to 4000 for the 50% specimen. For the 30 000 molecular weight probe, this means a decrease from approximately 15 entanglements per chain when incorporated in the 5% plasticized material to approximately 8 per chain in the 50% plasticized specimen. The anisotropy data for the two specimens when compared at equivalent applied shear stress show that the ability of the probe molecule to follow the orientation of the matrix is severely diminished in the 50% plasticized material. We see in the data of Figure 4 that the slope of anisotropy vs shear stress is finite and negative at 5% and near zero at 50% plasticization.

This paper is a short summary of the results from a new experiment relating shear stress and fluorescence anisotropy. In future publications we will present results of ongoing experiments and from model calculations relating shear stress dependent anisotropy and orientation factors.

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