miscible with PVPh (single phase over the entire blend composition range) at ambient temperature (Figure 2) and the upper limits of miscibility were determined for these two blends. We predict that about 10% of styrene must be incorporated into PVPh to render it miscible with PiPMA, while as much as 50% is necessary for the corresponding PtBMA blend. A typical diagram depicting the limits of miscibility for the latter blend at 25 °C is shown in Figure 4. We intend to experimentally test these predictions in the near future.

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Registry No. PVPh, 24979-70-2; PEMA, 9003-42-3; PS, 9003-53-6; PMMA, 9011-14-7; PPMA, 25609-74-9; PBMA, 9003-63-8; PiPMA, 26655-94-7; PtBMA, 25189-00-8; (ST)(VPh) (copolymer), 24979-74-6.

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Diffusion of Camphorquinone in Oriented Polycarbonate Films

Viscoelastic properties of polymers are affected by externally applied perturbations. The external perturbation, such as stretching, induces a preferred orientation of polymer chain segments along the deformation axis. Conventional techniques (such as radioactive tracer and pulsed gradient NMR, etc.) for measuring the translational diffusion coefficient are limited to about 10^{-10} cm^2/s. Diffusion of small molecules embedded in solid-state polymers in the vicinity of the glass transition temperature (T_g) occurs at a smaller rate, in the order of 10^{-13}–10^{-15} cm^2/s, depending on the size of the diffusants. As a result, very little systematic study of small-molecule transport in polymers has been carried out. By use of the technique of laser-induced holographic grating relaxation (LIHGR), it has been possible to investigate the diffusion coefficient as small as 10^{-15} cm^2/s.[1-3] Although the small molecules are not covalently bonded to the polymer chain, it is found that the diffusion coefficient of the probing dye molecules dissolved in the amorphous solid-state polymer is determined by the relaxation dynamics of the polymer chain.[1,2] It is thus anticipated that orientation of the polymer chain by stretching will also impose a pronounced effect on the diffusion coefficient of the probing molecules. The study of the anisotropic diffusion behavior of the probe molecules in the polymer solid is difficult by using the conventional technique.

In this communication, we report the first quantitative measurement of the diffusion behavior of camphorquinone in stretched polycarbonate films using the LIHGR technique.

Experimental Section. Polycarbonate (PC) film samples were prepared by dissolving the PC resin (purchased from Aldrich Chemical Co., M_w = 20 000–25 000, polydisperse) and camphorquinone (CQ, 0.5% by weight relative to PC) in CH_2Cl_2 and then filtering the solution to remove dust. The filtered solution was casted on a Teflon plate to produce a film about 0.3–0.4 mm thick. The film was then uniaxially stretched in a silicone oil bath at a temperature slightly above T_g (≈148 °C) at 153 °C with a manually operated puller. The drawn films were then quenched to room temperature. In addition to the unstretched film, five specimens with percent elongation equal to 50, 70, 95, 123, and 150 were also prepared for the LIHGR measurement.

The holographic grating is induced by crossing two equal-intensity coherent beams derived from an argon ion laser radiation. The laser wavelength is 488.0 nm, and the crossing angle θ is 14.6°, corresponding to a grid spacing of 1.92 μm. The film was mounted in a rotatory stage; the long axis of the film can be accurately rotated with respect to the laser beams (see Figure 1). The temperature of the films was controlled in an oven set at 118 ± 0.1 °C.

Results and Discussion. Shown in Figure 2 is the effective diffusion coefficient [$D(\alpha)$] of camphorquinone in stretched PC having a percent elongation equal to 123% at 118 °C as a function of the orientation angle α. Only the transverse motion with respect to the grating contributes to the diffraction intensity. At $\alpha = 0°$ the optical experiment samples only molecules diffusing along the direction of stretch ($D_\parallel$). On the other hand, at $\alpha = 90°$, it samples those diffusing along the direction perpendicular to stretch ($D_\perp$). The effective diffusion coefficient observed at angle α is found to be related to $D_\parallel$ and $D_\perp$ by the equation: $D(\alpha) = D_\parallel \cos^2 \alpha + D_\perp \sin^2 \alpha$. This angular dependence is consistent with the fact that the diffusion coefficient is proportional to $\langle |\mathbf{r}|^2 \rangle$; stretching the film

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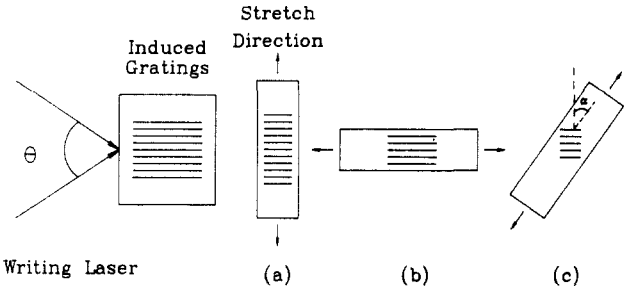

Figure 1. Orientation of the PC films with respect to the laser beams for the LIHGR measurement.

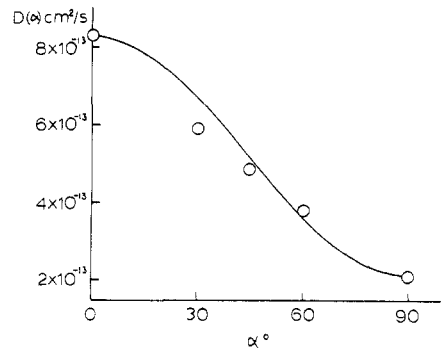

Figure 2. Effective diffusion coefficient, $D(\alpha)$, as a function of orientation angle α. The experimental data (O) are found to fit well to the equation $D(\alpha) = D_{\parallel} \cos^2 \alpha + D_{\perp} \sin^2 \alpha$ (curve).

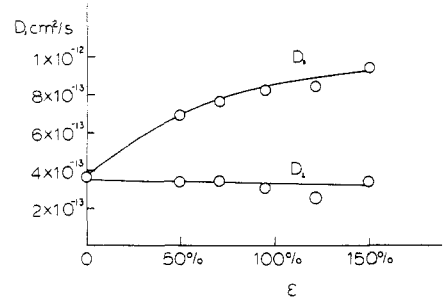

Figure 3. Diffusion coefficients $D_{\parallel}$ and $D_{\perp}$ plotted as a function of percent elongation.

causes the displacement vector to assume an angular dependence as $\mathbf{r} \cos \alpha + \mathbf{r} \sin \alpha$. Here $\mathbf{r}$ is the displacement vector of the diffusant. Comparisons of the measured with the calculated data are shown in Figure 2. The diffusion coefficient decreases by about a factor of 4 as α increases from 0 to 90°. Anisotropy in the diffusion coefficients increases as the drawing ratio is increased. Shown in Figure 3 are the diffusion coefficients $D_{\parallel}$ and $D_{\perp}$ plotted as a function of percent elongation. For the unstretched film $D_{\perp} = D_{\parallel} = 3.8 \times 10^{-13}$ cm²/s, which is equal to the diffusion coefficient of CQ measured in a PC pellate at the same temperature.[4] Up to 150% elongation, $D_{\perp}$ appears to be independent of stretch, whereas $D_{\parallel}$ increases steadily with increasing stretch. At 150% elongation, $D_{\parallel}$ increases nearly 3 times the unstretched value.

Early studies of the orientation effect on the transport properties of dye molecules in semicrystalline polymer fibers have shown that the diffusion coefficient along the direction of stretch first increases and then decreases with a further increase of the stretch ratio.[5] The effect has been interpreted as due to an increase in microvoids and channels or cracks induced by the stretch, in addition to polymer relaxation.[6] In amorphous polymers such as PC, stretching causes orientation of the chains along the direction of stretch; the oriented chains are expected to create an open channel and ease the molecular transport provided that the average channel width is wider than the size of the diffusants. Hence we expect that upon stretching the film, an increase in the diffusion coefficient occurs in the direction of stretch. On the other hand, within the present stretch range, as shown by Brillouin scattering[7] the chain orientation is not affected in the transverse direction for polymers subject to uniaxial stress; thus, we do not expect a strong effect on $D_{\perp}$ by stretching the film. Stretch-induced crystallization may complicate the interpretation. However, the stress-induced crystallization in amorphous PC film is negligible.[8] Neutron-scattering studies have been used to investigate the chain deformation of PMMA below T_g.[9] It would be interesting to carry out similar studies in PC and find out whether affine deformation is maintained on the scale of the diffusion length. Work along this direction is being planned.

We have shown in this work that the LIHGR technique can be used to study the anisotropic translational diffusion behavior of probing molecules in the oriented polymer film, when other measuring techniques are difficult for the study. In the polycarbonate film the diffusion coefficient of camphorquinone along the direction of stretch increases with stretch ratio, whereas the diffusion coefficient perpendicular to the direction of stretch remains nearly independent of stretch. The effect is interpreted as due to the orientation of the polymer chains. The LIHGR technique is anticipated to be applicable in the diffusion measurements for a variety of polymer films.

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Homo- and Copolymerization of Unprotected 2-(Hydroxymethyl)thiirane Initiated by Quaternary Ammonium Salts of Dithiocarboxylic Acids

Functionalization of polymers is an important purpose and copolymerization is one of the outstanding methods to reach it. Many functionalized polythiiranes have been synthesized.[1-6] Polythiiranes themselves are mainly obtained by the ring-opening polymerization of thiiranes.[7] We have previously described a new type of initiator for anionic thiiranes polymerization, namely, the crystallized, stable, quaternary ammonium salts of carbo(di)thioic

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