Macromolecules **1985**, *18*, 587–589

if not dramatic, differences in the nature of the dependence of the size change on solution temperature and polymer molecular weight for these two similar linear, flexible polymers. As seen here, this substitution reduced the rate of sub-Θ chain shrinkage and prevented chain collapse. In an earlier study of the behavior of PαMS in toluene,[39] this substitution promoted chain swelling in good solvent, thereby shifting the molecular weight threshold for the Gaussian-to-excluded volume transition from about 10^7 for polystyrene downward to about 10^5 for PαMS.

In conclusion, the observed differences in behavior between PαMS and polystyrene are most easily explained as being due to substituted methyl group steric hindrance effects and indicate the desirability of extending current theoretical treatments of polymer size behavior, e.g., sub-Θ chain shrinkage and collapse, to include such details.

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Registry No. PαMS (homopolymer), 25014-31-7.

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Diffusion of Dye Molecules in Polymers above and below the Glass Transition Temperature Studied by the Holographic Grating Technique

Studies of the diffusion of dye molecules in polymers are important in technological applications. They also provide important information about the effect of the chain relaxation of polymers on the diffusional process. Existing in the literature are data of diffusion of small molecules (such as Ar, CH_4, and hydrocarbons) in polymer glasses.[1] The diffusion coefficients of these small molecules in polymers at temperatures above T_g were measured by radioactive tracer or NMR techniques.[2] The diffusion coefficients obtained are greater than 10^{-10} cm^2/s and upon traversing the glass transition temperature,[1] a change of the apparent activation energy E_A was found in many cases. In all cases, the E_A values determined for the dissolved molecules were far below the corresponding values of the "glass process" governing segmental chain mobility of the polymer in this temperature region. Diluent diffusion above T_g could be combined with some of the scarce data[3] below T_g within the framework of a free volume theory.[4] The holographic grating technique[5-7] provides access to the measurement of very small diffusion coefficients expected for larger molecules dissolved in polymeric glasses. In the present communication, we present the first results obtained in polycarbonate glasses. To our knowledge, this is also the first report which applies the holographic grating technique to the study of the dye diffusion process in the polymer glass.

Poly(bisphenol A carbonate) (PC) with $M_w = 35\,000$ was obtained from the Bayer Co. Our samples, which contained about 0.5 wt % of the dye, were prepared by precipitation from a dichloromethane solution into petroleum ether. The residue was dried under vacuum for 1 day at 50 °C and an additional 2 days at ~160 °C, where sintering to a dense regulus was avoided. The dried sample was pressed into pellets for the diffusion measurements performed as described elsewhere.[6,7] Using DSC with a heating rate of 10 K min^{-1}, we determined T_g = 150 °C. No effect in T_g could be found on dissolving the dye in PC; neither could the melting peak below 300 °C be detected, suggesting the fact that the sample is amorphous. Poly-

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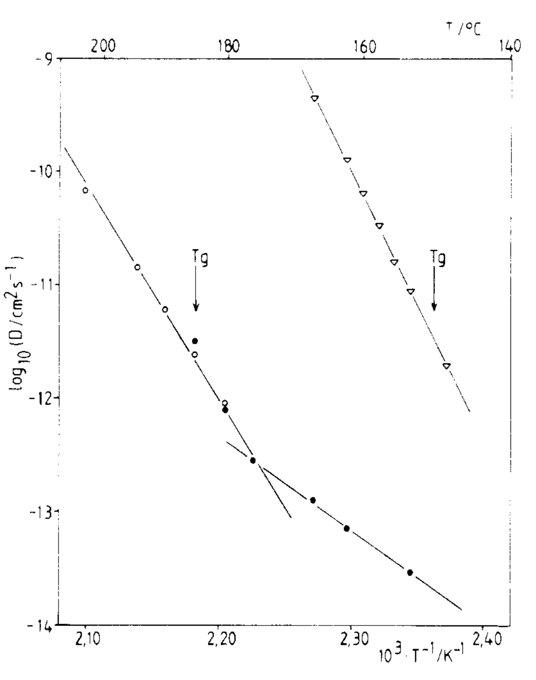
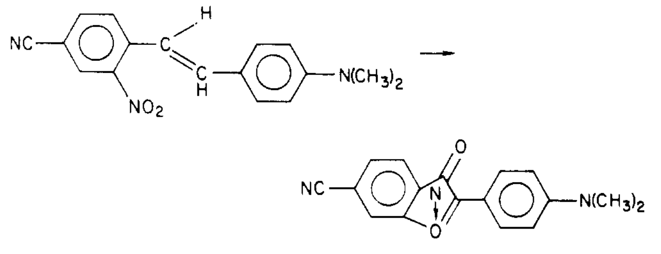


Figure 1. Dye diffusion coefficients (see text) in PC (▽) and TMPC (○, ●): open symbols, measurements at $\lambda = 458$ nm and $d > 2$ μm; full circles, measurements at $\lambda = 488$ nm and $d = 0.345$ μm.

(*o*-tetramethylbisphenol A carbonate) (TMPC) with $M_w = 100\,000$ was obtained from Bayer as a fine powder. It was mixed with a dye solution in acetone, which is a nonsolvent of TMPC. The sample was also dried for 1 day at 50 °C but subsequently kept under vacuum for 3 days at 180 °C. From DSC, we obtained $T_g = 203$ °C for pure TMPC and 185 °C for the sample that contained 1% of the dye and a small amount of acetone. No indication of crystalline melting was found below 300 °C.

The photoreaction of the orange dye leads to a colorless intermediate which reacts thermally to the blue main product:[8,9]



The thermal step is sufficiently rapid at temperatures $T \geq 150$ °C, where the diffusion coefficients shown in Figure 1 could unambiguously be determined by assuming that the decay constant of the forced Rayleigh scattering[5,6] is given solely by $\tau^{-1} = 8\pi^2 D/d^2$, where $d = \lambda/(2 \sin(\theta/2))$ is the grid spacing of the holographic grating. Slight deviation from the exponential decay was found for the measurements with TMPC (see Figure 2). This is probably caused by secondary products which diffuse more slowly. A complete analysis is difficult at this time since the contribution of the reactants to the changes of the absorbance and of the index of refraction are unknown. Thus the D values given in Figure 1 should be considered as a weighted average of the diffusivities of the orange (reactants) and blue (products) dyes shown above which are, however, of comparable magnitude. In PC, the decay of the scattering intensity at lower temperatures down to 130 °C can also be found. However, no quantitative analysis of the experimental results at these temperatures was possible because of the interference of the thermal reaction step, which becomes slow below 150 °C. The separation of the slow thermal step can be carried out by more extensive studies of the decay curves with different grid spacings.

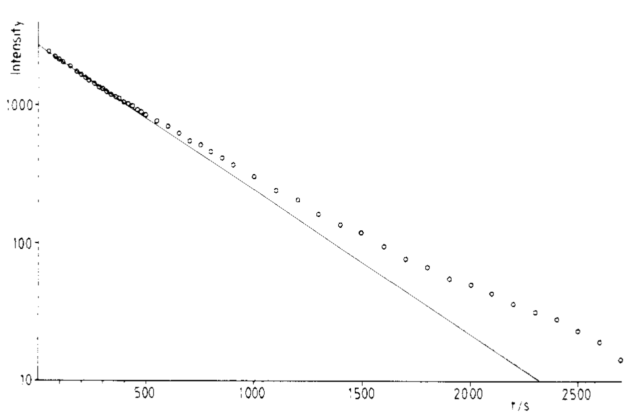


Figure 2. Intensity of forced Rayleigh scattering determined in TMPC at 150 °C (see Figure 1). The background intensity ($t \rightarrow \infty$) has been subtracted from the data shown in the figure.

The apparent activation energy $E_A = 452$ kJ mol^{-1} determined from the Arrhenius plot of the PC data shown in Figure 1 is smaller than the corresponding value of 610 kJ mol^{-1} obtained from dielectric relaxation measurements in PC.[10] In TMPC, we find $E_A = 361$ kJ mol^{-1} above T_g and 158 kJ mol^{-1} below T_g. It is interesting to note that the slope change occurs at 10 K below the T_g value determined from DSC. This may be due to the relatively large DSC heating rate of 10 K min^{-1}. However, it is also possible that the additional "free volume" introduced by the dye molecule in TMPC causes an increase in segmental mobility which "freezes" at a lower temperature. It should also be noted that the dye diffusion coefficients determined at the DSC glass transition temperatures of PC and TMPC, respectively, are equal within the accuracy of the T_g determination. This is in agreement with the assumption of a "universal" amount of free volume present at T_g. Furthre studies of the temperature dependence of D for diffusant dyes of varying size should provide important information upon cooperative segment mobility below T_g. A project dealing with the diffusion of dye molecules in a polymer matrix is under way.

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Morphology of Block Polymers near a Free Surface

The microphase transition and morphology of block polymers have been the subject of extensive studies in recent years.[1-11] These studies have been concerned with the morphology of the microdomains in solutions[8,10,11] and solids[1-7,9] as a function of molecular parameters (such as molecular weight and chemical composition), polymer concentration, and temperature and also with microphase transitions (i.e., formation and dissolution of the microdomains) caused by changing temperature[7-9,12] and concentration.[8,10,11] Except for a few studies,[13,14] most of this work has been devoted to study the structure of block polymers in bulk but not near a free surface or interfaces with other materials.

In this report we present the morphology of the microdomains of an AB diblock polymer formed as a consequence of liquid–liquid microphase separation of the constituent polymer A and B at or near the air surface in contrast to the morphology in bulk. The morphology at the surface will be dramatically affected by the surface free energy (an additional physical factor which does not affect the morphology in bulk) and therefore be different from the morphology in bulk. It may be unnecessary to say that studies of the surface morphology of block polymers are of academic and practical importance in connection with biomedical science and applications such as in thromboresistance[15] and cell separation.[16]

A polystyrene–polyisoprene diblock polymer designated HY-12 was synthesized by living anionic polymerization at −78 °C using *sec*-butyllithium as the initiator and tetrahydrofuran as the solvent. The number-average molecular weight of the block polymer determined by osmometry was 5.24×10^5 and the weight fraction of the polystyrene component determined by elemental analysis was 52%. The film used in this study was prepared by casting a ca. 10 wt % solution of the block polymer in toluene in a petri dish and evaporating the solvent very gradually at 30 °C for a few days. After further drying under vacuum for several days, a film of 0.35-mm thickness was obtained. Test specimens 1 cm × 1 mm were cut from the film and stained overnight with osmium tetraoxide vapor. This process was necessary before embedding the specimens. Otherwise, the block polymer film would have been swollen by epoxy resin during the embedding process and the original structure would have been destroyed. The effectiveness of the structural fixation by osmium tetraoxide to prevent the swelling by epoxy resin was rigorously examined. Then the test specimens were embedded in epoxy resin.

Special care was taken to distinguish the two sample surfaces, i.e., the surfaces which contact air and glass. For this purpose, the solidified epoxy resin blocks A were trimmed into small blocks B composed of B_1 (solidified epoxy resin) and B_2 (block polymer specimen) in the way shown in Figure 1. The morphology of the specimen at a free surface can be studied by examining the morphology at and near the interface between B_1 and B_2. Other surfaces of the block B are nothing other than those of bulk epoxy resin and bulk specimen. In this way the free surface of the specimen can be definitely distinguished from the interface with the glass.

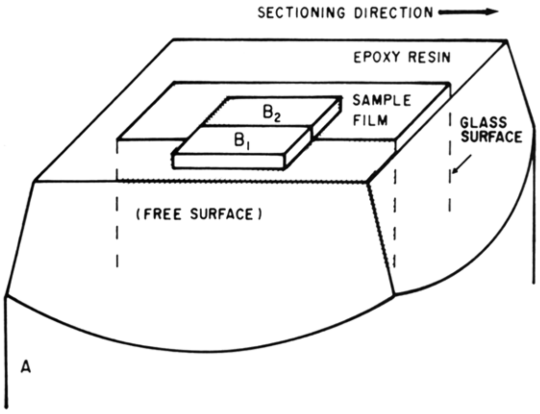

Figure 1. Schematic diagram representing the trimming method of specimen embedded in epoxy resin blocks.

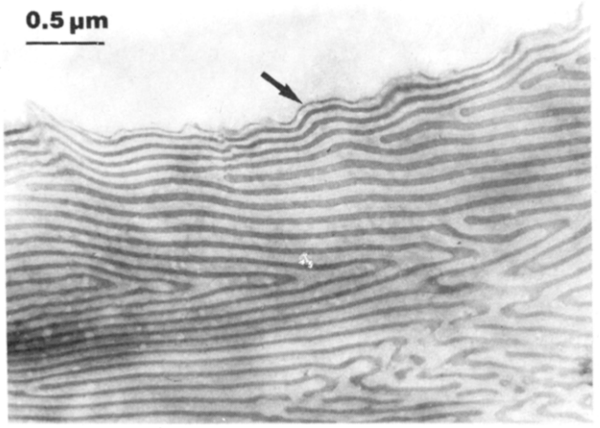

Figure 2. Electron micrograph showing a typical microdomain structure at the free surface of the HY-12 film. The lamellae are parallel to the surface. The arrow indicates the free surface.

Ultrathin sections sliced normal to the film surface and of ca. 50-nm thickness were obtained from the trimmed blocks B using an LKB 4800A ultrotome. Transmission electron micrographs of the ultrathin sections were obtained with a Hitachi H-600S electron microscope. The free surface of the block polymer film was easily distinguished in the micrographs, because the thin sections are attached by the structureless epoxy resin. In this way one can investigate the morphology of the microdomains as a function of depth from the free surface in the plane normal to the film surface.

Figure 2 shows a typical cross section of the HY-12 film at and near the free surface. The top bright part of the micrograph without structure corresponds to that of epoxy resin and the bottom part with periodic dark and bright microdomains corresponds to that of HY-12. The alternating lamellar structures of polyisoprene (dark domains) and polystyrene microphases (bright domains) are more or less aligned with their interfaces parallel to the free surface of the film. In this micrograph the free surface, i.e., the interface between the specimen and air, is observed between the dark, thin polyisoprene layer (which is indicated by an arrow) and epoxy resin. In general, lamellar

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