Penetrant Diffusion in a Solid Ordered Triblock Copolymer

Marcus Giotto, Guoxing Lin, Alana Canfield, and Alan A. Jones*

Carlson School of Chemistry and Biochemistry, Clark University, Worcester, Massachusetts 01610

Received August 22, 2005
Revised Manuscript Received October 13, 2005

Pulse field gradient (PFG) NMR measurements of diffusion in heterogeneous solid polymer systems provide a measure of the structure influencing translational motion.[1] The influence of structure leads to a dependence of the apparent diffusion constant on the time over which diffusion is observed. The effects of structural heterogeneity have been observed for penetrant diffusion in random copolymers,[2−4] polymer blends,[5] nanocomposites,[6,7] and dispersed oil drops in polymers.[8] The structure is not regular or well-defined in these systems so observing diffusion in a strongly segregated block copolymer with a well-defined morphology would be informative. The effect of morphology on diffusion in block copolymers has been considered before,[9] but NMR allows for the diffusion to be viewed directly over a range of length scales. Diffusion in solutions of block copolymers has been examined by PFG NMR;[10,11] however, the case for consideration here is the solid where the morphology of a cast film is retained and only swollen with a selective penetrant. The system selected for study is a SEBS triblock polymer: poly(styrene)-*block*-poly(ethene-*co*-but-1-ene)-*block*-poly(styrene) with a molecular weight of 49K and styrene end blocks of 16K. With a styrene content of 66 wt %, a morphology consisting of hexagonally packed rubbery ethylene butylene (EB) rods in a glassy polystyrene (PS) matrix is expected.[12−14] The penetrant selected for this study is 2,2,4-trimethylpentane (TMP) which has a low solubility in PS and a high solubility in EB rubber. The measured solubility in polystyrene is 2.85 and 227 wt % in the SEBS triblock under study, which implies a solubility of 625 wt % in the EB rubber. The diffusion of TMP is expected to be of the order of 10^{-7} cm^2 s^{-1} in the EB rubber[15] and 10^{-14} cm^2 s^{-1} in glassy PS.[16] The combination of the solubility and diffusion differences ensures that the conductive phase will be the EB rubber and the surrounding PS will act as a barrier. Although cylinders are the expected morphology, similar PFG NMR results are expected for lamella as well. The large solubility and diffusivity difference between the two domains is an ideal circumstance for observing the influence of morphological structure on the translational motion of a penetrant.

A SEBS film was prepared by casting from a 5 wt % solution of the triblock in toluene. The solution was evaporated from a Mylar sheet leaving a film with a thickness of about 100 μm. The film was then cut into disks and placed in an 8 mm NMR tube which was sealed after adding 20 wt % TMP. PFG measurements were made on a Varian Inova 400 MHz wide-bore NMR spectrometer in an 8 mm direct detection probe with high gradient capability (1000 G/cm) from Doty Scientific. Glass spacers were used in the NMR tube to center the sample of the correct size in the region of the radio frequency and gradient coils. Using proton NMR, the apparent diffusion constant of the penetrant, D, was measured as a function of the time Δ over which self-diffusion occurs in the stimulated echo pulse sequence. Measurements were made at 26 °C. Only the initial decay of echo amplitude was monitored, typically to a level of about 50% of the original amplitude. A system of conducting cylinders surrounded by a barrier phase will show diffraction behavior if echo amplitude is significantly decreased.[17] Diffusion in an apparently porous system can be characterized by focusing on the initial decay[18] which is the strategy pursued here. At a given time, Δ, the gradient amplitude g was varied from 0 to up to 800 G/cm. The time, Δ, ranged from 4 ms to 1 s. A fixed value of 1 ms was used for δ, the length of the gradient pulses, for a given determination of the apparent diffusion constant. The apparent diffusion constant at a given value of Δ is calculated from the slope of a plot of the logarithm of the echo amplitude vs g^2. The apparent diffusion constant for the TMP in the SEBS film is shown in Figure 1 where it is plotted as a function of the average root-mean-square displacement $\langle r\rangle^{1/2}$ of a TMP molecule. The root-mean-square displacement is calculated from the equation

$$\langle r^2\rangle^{1/2} = 6D_{\mathrm{app}}\Delta \qquad (1)$$

It corresponds to the average distance a TMP molecule diffuses in a time Δ assuming an isotropic medium. In the experiment, diffusion is observed in the direction parallel to the magnetic field, and the medium is a sum over all orientations of the EB domains relative to the field. At short times the medium is anisotropic, but at longer times diffusion will average over the structure. This average is roughly achieved since D_{app} approaches a plateau at large values of $\langle r^2\rangle^{1/2}$. This same general behavior is observed for TMP in other SEBS samples and at a variety of concentrations of TMP in the 10−25 wt % range.

The diffusion is tortuous in nature with fast diffusion observed at short times or equivalently small distances. Not that the diffusion constants at short length scales are in the range of 10^{-7} cm^2 s^{-1}, as would be expected for a rubbery matrix. This fast diffusion occurs inside the EB phase. As the TMP contacts the PS at the walls of the EB domain, D_{app} decreases. The EB phase swollen by the penetrant has a diameter or thickness in the range of tens of nanometers but a length in the range of microns. The latter is determined by the grain size,[19] a second morphological characteristic that can affect diffusion in a block copolymer. Together these two distances determine the length scale for the initial contact with the PS which acts as a barrier. The initial contacts with polystyrene will occur on the length scale of the diameter or thickness that is in the tens of nanometers range. This length scale is too short for observation with gradients in the range of 1000 g/cm. However, the average length scale is in the micron range since it is determined by the grain size[19] of EB domains, and cast films of block copolymers of this type commonly have grain boundaries[19] between domains where the orientation of the EB phase changes. At the

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* Corresponding author. E-mail: ajones@clarku.edu.

10.1021/ma0518454 CCC: $30.25

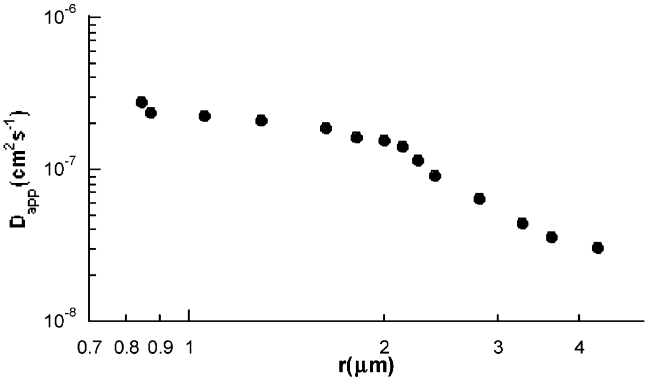

Figure 1. Apparent diffusion constant of TMP vs distance determined by pulse field gradient diffusion. The system is 20 wt % TMP in a SEBS membrane consisting of 64% styrene end blocks.

grain boundary, the EB in one domain may not be well connected to the EB in the next domain though earlier investigations based on gas permeability showed this not to be a major factor.[9] Various types of dislocations have been observed and described for the block copolymer morphology at a grain boundary.[19] In general, though, there could be a narrowing of the connections between cylinders or lamella at the boundary if not an outright disconnection. In any of these cases, diffusion will be impeded, leading to a drop in the apparent diffusion constant. There is a distribution of grain sizes with all orientations relative to the gradient field in any real sample so the drop is spread out over a range of sizes. In our case the major drop occurs between about 2 and 5 μm and corresponds to an order of magnitude decrease in D_{app}.

Effective medium theory predicts the diffusion constant for a sample composed of all orientations to be one-third the value inside a conductive cylinder.[20] The order of magnitude drop observed in this system indicates restrictions to transport at the interface of grain boundaries beyond that produced by considering the sample as a composite of all orientations. Given the observed order of magnitude drop in D_{app}, grain boundaries and grain boundary morphology play an important role in potential applications of block copolymers as membranes. The morphology controlled by relative block molecular weights in the triblock copolymer only partially determines transport in an actual membrane. Block copolymers are used as templates for designing conductive phases in such applications as fuel cells,[21] and while the block copolymer morphology provides one level of control, the effects of grain boundaries must be considered as well. PFG NMR can directly assess the effects of grain boundaries.

Acknowledgment. This work was supported by the Army Research Office, Grant DAAD19-03-1-0087. The authors thank Drs. Donald Rivin and Nathan S. Schneider for solubility measurements of TMP in PS and the triblock copolymer.

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MA0518454