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Motion of Single Terrylene Molecules in Confined Channels of Poly(butadiene)−Poly(ethylene oxide) Diblock Copolymer

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The motion of terrylene probe molecules in confined PB channels of an asymmetric PB−PEO diblock copolymer has been investigated by single molecule tracking. The one-dimensional diffusion coefficients were found to be significantly smaller and had a narrower distribution compared to two-dimensional diffusion coefficients in PB. The trajectories of some single molecules showed unusual behavior of directed motion where mean square displacement had a parabolic dependence on lag time. The likely origin of this behavior is discussed in terms of local variations in the PB channel width and the resulting change in the local density. The results show the effect of nonuniformities and heterogeneities in the channels on the motion of single molecules and demonstrate the sensitivity of single molecule tracking in characterizing self-assembled block copolymer morphologies.

An understanding of molecular motion in confined spaces is important both scientifically and technologically in areas such as molecular sieving, membrane separation, transport through biological membranes, and porous catalysts. Collective motion of molecules in ensembles under confinement has long been studied by nuclear magnetic resonance (NMR),[1,2] fluorescence correlation spectroscopy (FCS),[3−5] and neutron scattering[6] techniques. Single molecule tracking is an important alternative to these techniques because it does not rely on statistical averaging, and therefore allows for the observation of nonuniformities in motion over relatively large distances.[7,8] The recorded trajectories of the probe molecules do not only provide dynamical information about the molecular motion but also give information about the structure of the host material and probe−host interactions.[9] The technique has recently been applied to investigate a variety of systems including mesoporous materials,[8,10,11] defects in crystals,[12] biological membranes,[13] and phospholipid layers.[14−16] All of these probe−host systems share a common property: The probe molecules move in low density regions such as pores, defects, and interfaces.

Although the potential of block copolymers to form ordered morphologies by self-assembly has been exploited in various applications ranging from patterning/templating to membranes,[17,18] the movement of single probe molecules in these dense self-assembled channels has not yet been investigated. In this Letter, we describe the investigation of the motion of single probe molecules in confined channels of a microphase separated block copolymer and report on the observation of directed motion. The likely origin for this unusual behavior is discussed in terms of the local variations in the channel width and the sensitivity of the local density to the channel width. Diffusion coefficients in one-dimensional (1D) channels are also compared with those observed in two-dimensional (2D) PB layers formed by a symmetric PB−PEO diblock copolymer.

A high molecular weight asymmetric amphiphilic diblock copolymer, poly(butadiene)−poly(ethylene oxide) (PB_{593}−PEO_{3705}, subscripts denote the average number of monomers), was chosen as the host material. In the bulk, the hydrophobic and amorphous minor component PB (volume fraction, f_{PB} = 0.20) forms cylindrical channels in the matrix of the hydrophilic and crystalline major component PEO. A hydrophobic fluorescent probe molecule, terrylene (Figure 1a), was chosen such that it selectively went into the amorphous PB block due to the hydrophobic interactions. Single molecule tracking experiments were performed at room temperature (∼25 °C) which was above the glass transition temperature of the PB block (∼ −10 °C) and below the melting temperature of the PEO block (∼65 °C). This allowed the movement of the probe molecules in PB channels, while the crystalline PEO block provided the confinement barriers. PB−PEO films were spin coated on glass substrates from toluene solutions containing terrylene. The film thickness was between 50 and 60 nm.

The self-assembled morphology was achieved by annealing the films at 65 °C for several hours following spin coating. Figure 1b shows the atomic force microscopy (AFM) phase image of a film after 6 h of annealing. The dark lines in this image correspond to PB channels, while brighter lines indicate the crystalline PEO blocks. The period of the self-assembled morphology was determined to be 59 ± 1 nm corresponding to an average PB channel diameter of 28 nm in the bulk. The hydrophilic PEO block prefers to be in touch with the underlying glass substrate. As the presence of hydrophobic PB block at the air/film interface lowers the interfacial energy, the PB channels exposed at the top surface are seen to be wider than the expected bulk diameter, resulting in slightly wider channels. A film thickness of 50−60 nm may also allow a second layer of PB channels to be partially incorporated on top of the film, as drawn schematically in Figure 1a.

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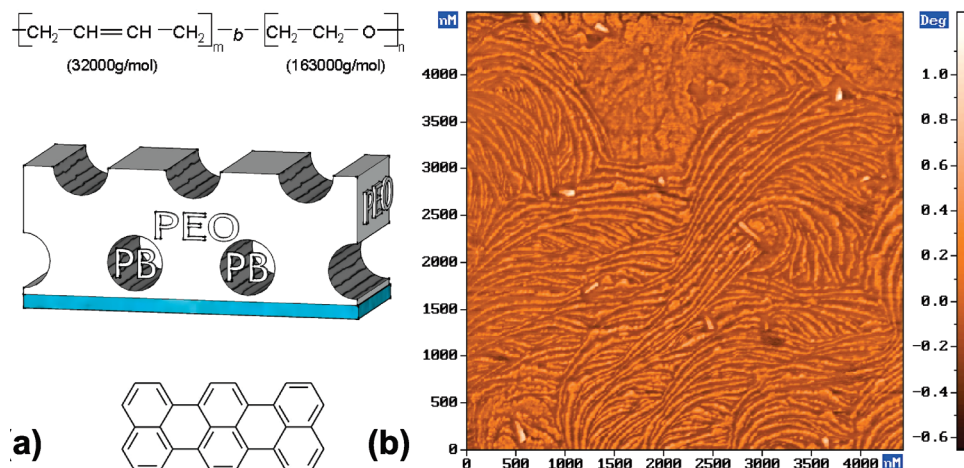Letters

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Figure 1. (a) Chemical structure of the PB−PEO diblock copolymer (top), illustration of the self-assembled bulk morphology (center), and the chemical structure of terrylene (bottom). (b) AFM phase image of the terrylene-doped PB−PEO diblock copolymer thin film after 6 h of annealing.
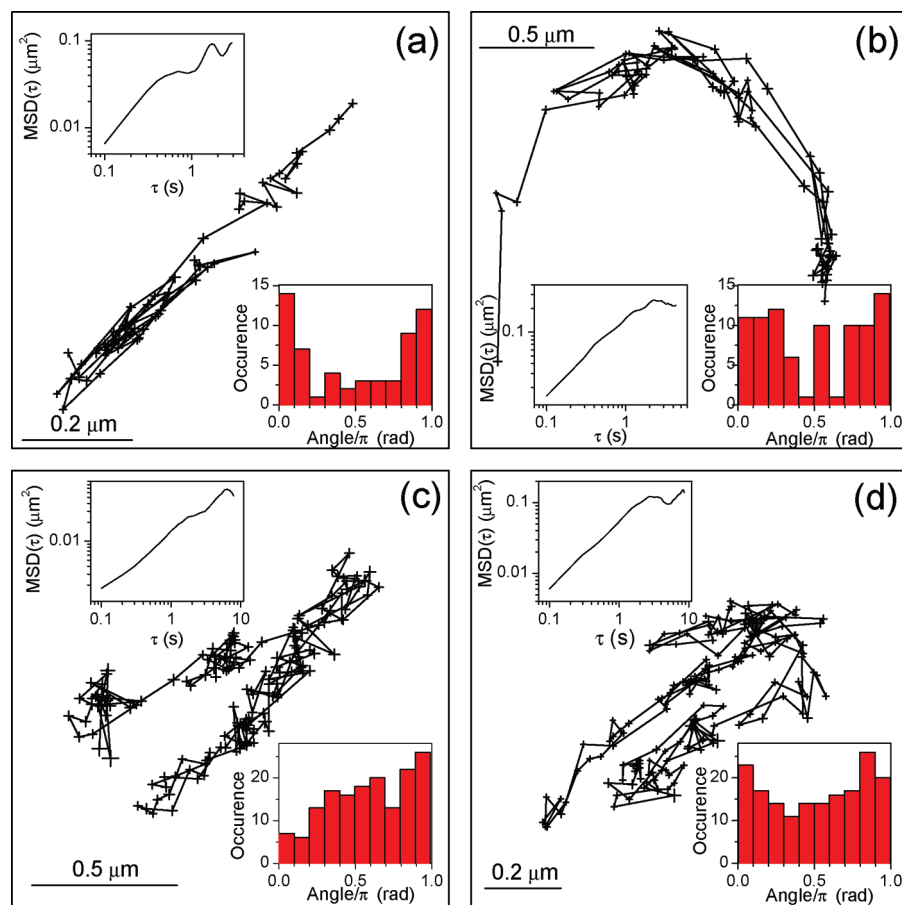

Figure 2. Trajectories followed by four different single molecules. Error bars indicate the localization accuracies at each step. Insets show the corresponding log−log plots of mean square displacements as a function of lag time and angle histograms.

The trajectories of the single molecules in annealed PB−PEO films not only confirmed the presence of one-dimensional channels in the plane of the film but also provided additional information about the heterogeneities and defects. Figure 2 shows four typical trajectories of single molecules in motion. The insets in each graph show the mean square displacements, MSD(τ), as a function of lag time (τ), and the distribution of the angle between two consecutive steps in the trajectory. All trajectories indicate the motion of the molecules in one-dimensional channels. The average width of the trajectories remains around 25−60 nm, while the molecules travel a contour

length of 0.5−3.0 μm. The distribution of angles between two consecutive steps in almost linear trajectories, such as Figure 2a, is peaked at 0 and π rad, indicating the dominance of forward and backward steps in motion and confirming the one-dimensional nature of the trajectories. The trajectory in Figure 2b is an example of a curved single PB channel similar to those seen in the AFM picture of Figure 1b. Large variations were observed in step lengths at different parts of a given trajectory. These can be attributed to the presence of physical heterogeneities in the single channels such as variable channel diameter and local curvature, although the chemical heterogeneities in
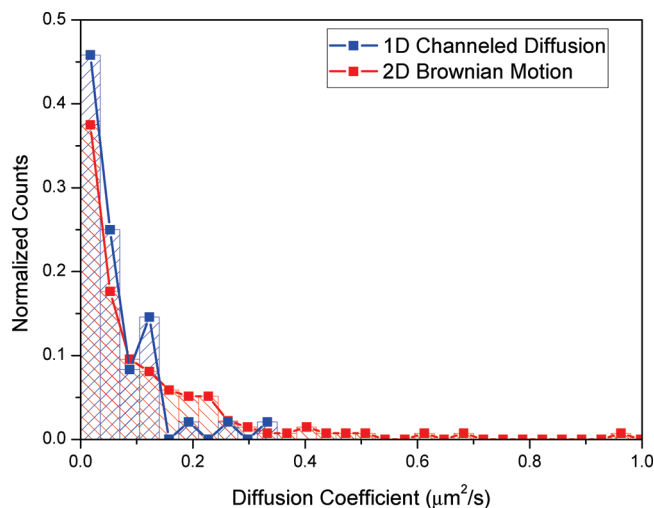
Figure 3. Normalized histograms of diffusion coefficients of single terrylene molecules in one-dimensional PB channels and two-dimensional PB layers. Diffusion coefficients were determined by fitting the $MSD(\tau)$ vs τ curves obtained using single molecule trajectories to $MSD(\tau) = 2D\tau$ in 1D and $MSD(\tau) = 4D\tau$ in 2D.
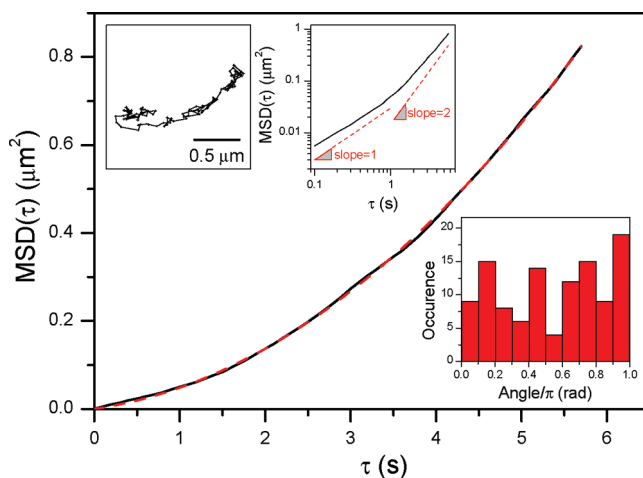

Figure 4. Mean square displacement of a single molecule exhibiting directed motion. The dashed line shows the parabolic best fit curve. Insets show the trajectory followed by the molecule (upper left), the log−log plot of $MSD(\tau)$ vs τ indicating the slope change from 1 to 2 (upper right), and the corresponding angle histogram (lower). Dashed curves in the upper right inset are guides for the eye indicating slopes 1 and 2.

the channels cannot be ruled out. Figure 2c and d shows the presence of nearly parallel channels. The molecules move from one channel to a neighboring channel due to the presence of defects in the film. These defects correspond to the disordered regions where the channels intersect, as seen in Figure 1b. Once the molecule reaches the defect, it is temporarily trapped and moves randomly until it enters one of the intersecting channels. This random motion disrupts the minima observed in angle distribution for motion in well-defined channels (Figure 2a, lower inset) and results in a more uniform angle distribution. The 1D diffusion coefficients of the molecules were determined from the slope of $MSD(\tau)$ vs τ graphs using $MSD(\tau) = 2D\tau$.[7,9] For the molecules shown in Figure 2 and Figure S1 (Supporting Information), diffusion coefficients between 0.005 and 0.125 μm^2/s were measured. These values compare well to the diffusion coefficients of different dye molecules in various mesoporous systems.[19] Although they span a wide range of values because of the heterogeneities in the film, their distribution at large D values deviates significantly from that of 2D diffusion coefficients of terrylene molecules in PB, as shown in Figure 3.

2D diffusion coefficients were measured in very thin films (film thickness ∼27 nm) of poly(butadiene)−poly(ethylene oxide) diblock copolymer (PB_{593}−PEO_{989}, subscripts denote the average number of monomers) showing lamellar morphology in the bulk. In the film, PEO block is expected to be in touch with the underlying hydrophilic glass substrate and PB forms a two-dimensional layer on top of PEO at the air/film interface. The contact angle of water drops on the film surface was larger than 90°. The thickness of the PB layer is expected to be 13 nm on the basis of the volume fraction of PB ($f_{PB} = 0.49$). The normalized histograms of diffusion coefficients of 48 different terrylene molecules exhibiting 1D diffusion inside cylindrical channels of Figure 1b (PB_{593}−PEO_{3705}) and 136 different terrylene molecules exhibiting 2D diffusion in ∼13 nm thick top PB layers (PB_{593}−PEO_{989}) are compared in Figure 3. The average diffusion coefficients were determined as 0.061 and 0.112 μm^2/s for the 1D and 2D diffusion cases, respectively. For diffusion coefficients larger than 0.15 μm^2/s, a significant difference was observed. 2D diffusion coefficients were larger than those of 1D and spanned a range up to ∼1 μm^2/s, which is 3 times larger than the range of 1D coefficients.

In addition to one-dimensional normal single particle motion where $MSD(\tau)$ was proportional to lag time, directed single particle motion was also observed in the PB channels. Figure 4 shows the $MSD(\tau)$ vs τ graph of a molecule exhibiting directed motion together with its trajectory (upper left inset), and angle distribution (lower inset). $MSD(\tau)$ shows the characteristic parabolic dependence on lag time. The dashed line is a fit to the formula given by $MSD(\tau) = 2D\tau + (V\tau)^2$ with best fit parameters $D = 0.0138\ \mu m^2$/s and $V = 0.1432\ \mu m$/s.[7] The upper right inset shows the log−log plot of the same data, indicating the dominance of the normal diffusion at earlier lag times (slope of 1) and the directed motion at later lag times (slope of 2).

Results of the trajectory analyses performed on two other molecules undergoing directed motion are also shown in the Supporting Information (Figure S2). A frame-by-frame examination of the trajectories of directed motion shows that the molecules preferentially move in forward direction in longer steps or in consecutive steps, but the movement in the reverse direction is in shorter steps. Such motion can be explained by the nonuniformity of the PB channel widths because of the effect of film/substrate and air/film interfaces. With increasing channel width, the average mean free path of a single molecule increases and the local density in the channel decreases. Both contributions tend to direct the motion of probe molecules in the direction of increasing channel width. The movies in the Supporting Information show some trapped molecules doing random motion in narrow regions in the film. These molecules may have been trapped in wider parts of the channels where the channel width decreases in either direction. Our investigations to identify the contributions of other types of structural defects and chemical heterogeneities to single molecule motion have been continuing.

In summary, different types of behavior observed in tracking single molecules in dense PB channels confined by a crystalline PEO matrix highlight the sensitivity of the motion of single molecules to the nonuniformities and heterogeneities in the channels. The results demonstrate that the selective distribution of probe molecules in a certain block due to favorable interactions provides an opportunity to probe the morphology by tracking single molecules which may contribute to future efforts to achieve long-range order in self-assembled block copolymers. In addition, self-assembled block copolymers were

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shown to be model systems to study confined diffusion of single molecules in one and two dimensions.

Supporting Information Available: Description of sample preparation, experimental setup, and trajectory analysis; further experimental data on different molecules diffusing in parallel channels, demonstrating one-dimensional normal diffusion as well as directed motion; and movies of the trajectories followed by all of the molecules discussed in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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