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Solvent-Facilitated Homopolymer Sorption in Swollen Block Copolymer Matrices

Joy E. Stevens,[†] Wiriya Thongruang,[‡] Nikunj P. Patel,[†] Steven D. Smith,[§] and Richard J. Spontak*,[†]

Department of Chemical Engineering, North Carolina State University,
Raleigh, North Carolina 27695; Faculty of Engineering, Prince of Songkhla University,
Songkhla 90112, Thailand; and Corporate Research Division, The Procter & Gamble Company,
Cincinnati, Ohio 45239

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ABSTRACT: Homopolymer sorption in microphase-ordered block copolymers can provide insight into the factors governing transport of chain molecules in dense nanostructured environments, as well as yield novel nonequilibrium materials. Here, we examine the sorption of homopolymer B (hB) in ABA triblock copolymers swollen in a B-selective solvent. Gravimetric analysis reveals that the solubility of hB (S_{hB}) varies linearly with solution concentration (C) and that $(\partial S_{hB}/\partial C)_T$ depends on the molecular weight of the B midblock (M_B). These data also show that the effective diffusion coefficient of hB is $\sim 10^{-8}$ cm^2/s, independent of M_B.

Introduction

Molecular diffusion in confined heterogeneous media constitutes an active and important field of research in response to the ongoing emergence of nanostructured materials[1] and the use of multifunctional polymeric materials in separations-based technologies.[2] The design of novel organic−inorganic hybrid materials has, for instance, required new and surprising mechanistic paradigms to explain the unexpected permeation of small-molecule penetrants.[3] While hybrid nanocomposites afford tremendous versatility and promise in this endeavor, their development can be hampered by problems associated with uniform dispersion and long-term stability. In contrast, some soft materials, such as block and graft copolymers, possess an inherent nanostructure that arises from the enthalpically or entropically driven spontaneous ordering of the chemically dissimilar monomer sequences.[4,5] Previous studies of microphase-separated block copolymers for use as gas separation membranes have demonstrated that material characteristics such as phase connectivity and long-range nanostructural alignment, which can be collectively grouped under morphology, impact the effective diffusion coefficient (D_{eff}) of the penetrant species.[6−9] Phase mixing[9,10] and specific chemical interactions between diffusing molecules and copolymer moieties[11] can likewise strongly influence the diffusive process by which small molecules migrate through microphase-separated block copolymer matrices.

Recent efforts have also sought to use nanostructured block copolymers for liquid separation technologies.[12] The efficacy of copolymers possessing hydrophilic blocks designed to confront contemporary challenges facing water purification, for example, likewise depends on molecular architecture and block surface energy, since the copolymers undergo solvent-induced swelling and surface reconstruction.[13,14] In this vein, molecular transport in nanostructured block copolymers can be further extended to include homopolymer molecules. Using low-molecular-weight homopolymer molecules as tracer species for this purpose has elucidated the roles of morphology, copolymer architecture, and defects on the mechanism of polymer diffusion in dense,[15,16] as well as solvent-swollen,[17] heterogeneous media. Incorporation of a parent homopolymer into an ordered block copolymer furthermore constitutes an established and facile means by which to modify, in controllable fashion, the morphologies[18,19] and properties[20] of nanostructured copolymers. While such modification commonly relies on codissolution of the homopolymer and copolymer in a relatively neutral solvent, another strategy to imbibe homopolymer B (hB) molecules into microphase-ordered ABA triblock copolymers employs a nonequilibrium diffusive approach[21] in which the copolymer is swollen in a hB-rich solution composed of a B-selective solvent. In this work, we examine the diffusion and solubility of low-molecular-weight hB in a series of selectively swollen ABA triblock copolymers differing in midblock molecular weight and, hence, composition.

Experimental Section

A series of four poly(styrene-*b*-isoprene-*b*-styrene) (SIS) triblock copolymers possessing identical S end blocks of molecular weight (M_S) 30 000 was synthesized via living anionic polymerization in cyclohexane with *sec*-butyllithium as the initiator. The molecular weight of the I midblocks (M_I), ascertained from ^{1}H NMR and GPC, was varied to achieve the following I compositions (expressed as mass fractions): 0.40 ($M_I = 40\ 000$), 0.46 ($M_I = 51\ 000$), 0.55 ($M_I = 73\ 000$), and 0.60 ($M_I = 90\ 000$). These copolymers are designated as SIS40, SIS51, SIS73, and SIS90, respectively, and are described in more detail elsewhere.[20] Bulk films of the copolymers measuring about 1 mm thick were cast from 4% (w/v) solutions in reagent-grade toluene (Aldrich), dried over the course of 3 weeks, annealed under vacuum to remove residual solvent, and cut into 1 cm × 1 cm squares. A homopolyisoprene (hI) with a molecular weight of 7500 was also synthesized and dissolved in 20 mL of *n*-hexane (H, Fisher Scientific) to form solutions differing in concentration (C), expressed in % w/v, and stored in airtight flasks to avoid solvent evaporation. Each copolymer square was weighed on a gravimetric balance and then suspended in a solution of given C for either a predeter-

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[†] North Carolina State University.
[‡] Prince of Songkhla University.
[§] The Procter & Gamble Company.
* To whom correspondence should be addressed: e-mail rich_spontak@ncsu.edu.

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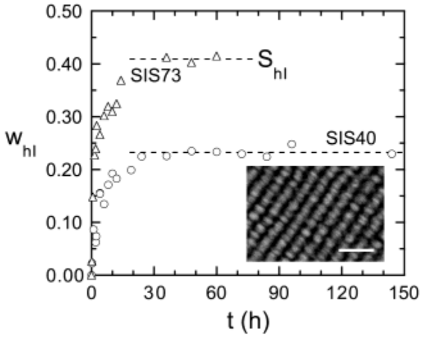

Figure 1. Homopolyisoprene mass fraction (w_{hI}) in two selectively swollen block copolymers, SIS40 (○) and SIS73 (△), presented as a function of the time (t) of exposure to a 5% w/v solution of hI in *n*-hexane. The dashed lines identify the hI solubility limit (S_{hI}) in each copolymer. The inset is a TEM image obtained from a lamellar SIS copolymer after long-term exposure to *n*-hexane, illustrating the solvent-induced change in copolymer morphology. The scale marker in the inset corresponds to 100 nm.

mined time interval to determine sorption kinetics or a period of 3 days to determine hI solubility. Solubility tests were repeated at least three times to determine the level of reproducibility. After a given immersion time, the squares were removed, washed with a detergent-containing aqueous solution, and rinsed with distilled water prior to drying under vacuum (for 2 days) and reweighing. Longer drying times under vacuum did not result in any further weight change. Residual solvent remaining in the PS microdomains after solvent removal was accounted for by performing complementary solubility tests in pure H, as described earlier.[21]

Results and Discussion

Homopolymer sorption kinetics for the SIS40 and SIS73 copolymers are provided in Figure 1, which displays homopolymer mass fraction (w_{hI}) as a function of exposure time (t) in 5% w/v hI/H solutions. Each measurement refers to a different specimen square in fresh solution. In both cases, w_{hI} is observed to increase sharply and then reach a limiting value, which differs in magnitude for the two copolymers. The limiting value realized after immersion times of at least 30 h denotes the solubility of hI in each copolymer (S_{hI}), as depicted in the figure. Although the SIS40, SIS51, and SIS73 copolymers initially possess lamellar morphologies, as discerned[20] from transmission electron microscopy (TEM), their morphologies evolve in the presence of H. This solvent, while selective for the I midblocks of the copolymers, is sufficiently soluble in the glassy S end blocks to plasticize the S lamellae. Swelling of the I midblocks, coupled with internal stress buildup in the S lamellae,[22] promotes chain rearrangement, void formation, and, ultimately, a morphological transition to a more complex, nonlamellar morphology[21] (see the inset provided in Figure 1). This morphology retains sufficient mechanical integrity to permit handling of the swollen films after exposure. In marked contrast, the neat SIS90 copolymer exhibits a hexagonally packed cylindrical morphology.[20] Upon even brief exposure to any of the hI/H solutions, the SIS90 films immediately fall apart. This observation is attributed to substantial matrix swelling and end block pullout from the plasticized cylinders, followed by failure of the microdomains to maintain a viable network. For this reason, no data are presented for the SIS90 copolymer series.

As the results in Figure 1 reveal, the solubility of hI is considerably higher in SIS73 relative to that in SIS40. While this order agrees with intuitive expectation, it is not always observed. Figure 2a shows the dependence of S_{hI} on hI/H solution concentration (C) at ambient temperature for the SIS40, SIS51, and SIS73 copolymers. In the case of the first two copolymers, an increase in C promotes a monotonic increase in S_{hI}, which is expected on the basis of chemical potential differences and which is consistently higher in the SIS51 copolymer due to the greater volume of swellable I microdomains. Over the range of C explored, the variation of S_{hI} with respect to C appears nearly linear. This trend likewise applies to the $S_{\mathrm{hI}}(C)$ data for the SIS73 series with the exception that appreciable hI solubility is not achieved until sufficient driving force exists for the hI molecules to diffuse into the swollen copolymer matrix ($C > 1$% w/v). Such delayed homopolymer transport has been previously observed[21] in systems wherein the molecular weight of hI (M_{hI}) was systematically varied at constant M_{I}. At higher values of C, S_{hI} increases abruptly and eventually exceeds the values of S_{hI} attained by the other two copolymers. The variation of S_{hI} with regard to C under isothermal conditions, $(\partial S_{\mathrm{hI}}/\partial C)_T$, derived from the data displayed in Figure 2a is presented in Figure 2b as a function of M_{I}. Within experimental uncertainty, these results suggest the existence of a monotonically increasing linear relationship between $(\partial S_{\mathrm{hI}}/\partial C)_T$ and M_{I}, which confirms that hI solubility depends on C (a measure of the number of hI molecules available per unit volume) and M_{I} (a measure of the volume that, upon swelling in H, becomes available for hI uptake) at constant M_{S}. While it is not known whether such linearity is achieved with homopolymer/copolymer combinations differing in M_{hI} or chemical constitution, we have previously reported[21] that S_{hI} varies as $M_{\mathrm{hI}}{}^{-1/2}$ at constant M_{I} for related systems.

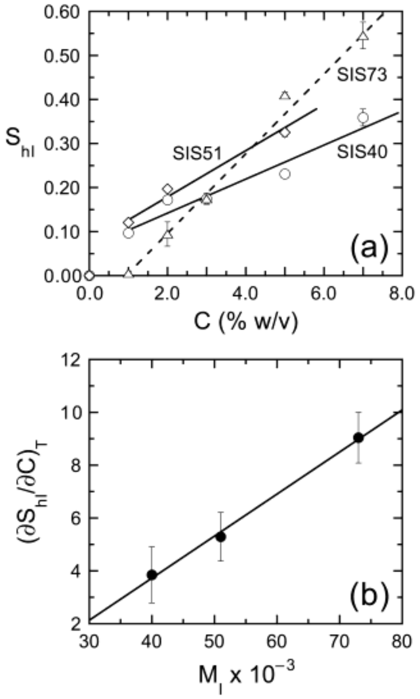

Figure 2. (a) Dependence of S_{hI} on hI/H solution concentration (C) in three different triblock copolymers: SIS40 (○), SIS51 (◇), and SIS73 (△). The solid and dashed lines are linear regressions to the data (exclusive of the $C = 0$ point at the origin). (b) Slopes of the curves in (a) displayed as a function of the molecular weight of the SIS copolymer midblock (M_{I}). The solid line is a linear regression to the data. The error bars in both figures identify the standard error in the data.

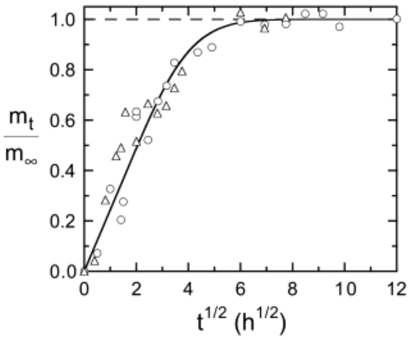

Figure 3. Gravimetric sorption data for the solvated SIS40 and SIS73 triblock copolymers recast into a format amenable to analysis (see text). The symbols are the same as those described in the caption of Figure 1, the solid line denotes the fit of the Balik[23] model (eq 1) to both data sets, and the dashed line identifies the solubility limit as $m_t \rightarrow m_\infty$.

To ascertain the value of the hI diffusion coefficient from the sorption data presented in Figure 1, we first reformat the data in a form amenable to analysis. This is achieved by plotting m_t/m_∞, where m_t denotes the mass uptake at time t and m_∞ identifies the mass uptake at the solubility limit, as a function of $t^{1/2}$. These reformatted data are shown for the SIS40 and SIS73 copolymer series in 5% w/v hI/H solution in Figure 3 and exhibit the shape that is characteristic of Fickian diffusion. While extraction of D_{eff} from sorption data can be achieved using a variety of different protocols (most of which only rely on the initial slope of the sorption curve),[12] we elect to use the Balik[23] model for fitting the entire sorption curve with a single expression that accounts for molecular diffusion at both long and short time scales. This expression can be written as

$$m_t/m_\infty = \phi(x)\, f(x) + [1 - \phi(x)]\, g(x) \tag{1}$$

where $x = D_{\mathrm{eff}}t/L^2$ and L is the thickness of the film. The short- and long-time contributions to eq 1 are given by

$$f(x) = 4(x/\pi)^{1/2} \tag{2a}$$

and

$$g(x) = 1 - (8/\pi^2)\mathrm{e}^{-\pi^2/x} \tag{2b}$$

respectively, and the weighting factor $\phi(x)$ is derived on the basis of the Fermi function, viz.

$$\phi(x) = (1 + \mathrm{e}^{(x-a)/b})^{-1} \tag{3}$$

Here, the parameters a and b are set[23] equal to 0.05326 and 0.001, respectively. The value of D_{eff} determined by fitting eq 1 to the data in Figure 3 is $(3.3 \pm 0.7) \times 10^{-8}$ cm^2/s irrespective of block copolymer, which indicates that hI diffusion occurs primarily through the swollen midblock matrix of each copolymer and is virtually unaffected by the presence of the S microdomains, despite their apparent spatial irregularity. The observation that D_{eff} does not vary at a solution concentration beyond any existing induction period (see, e.g., the solubility data for the SIS73 series in Figure 2a) is also consistent with the facts that (i) M_{hI} is constant and (ii) M_{I} is sufficiently large (well above the critical molecular weight of entanglement of hI) not to affect hI reptation. To put our diffusivity result in perspective, measured[15] values of D_{eff} for hI of comparable molecular weight in ordered block copolymers with alternating S (glassy) and I (rubbery) lamellae are typically much smaller in magnitude ($\sim 10^{-13}$ cm^2/s) than that reported here. Values of D_{eff} for hI of comparable molecular weight in toluene[24] and *n*-hexane,[25] on the other hand, tend to be on the order of 10^{-6} cm^2/s at ambient temperature.

Conclusions

This methodology of imbibing microphase-ordered triblock copolymers with a midblock-compatible homopolymer by diffusion from a homopolymer-rich midblock-selective solvent provides a viable means by which to (i) probe the factors governing sorption, namely, diffusion and solubility, and (ii) generate, in a reproducible manner, novel multicomponent materials. Through judicious choice of selective solvent as the homopolymer carrier, we expect that undesirable alteration of the existing microphase-ordered copolymer morphology could be significantly reduced, if not eliminated altogether, thereby permitting investigation of other (nonlamellar) morphologies. While the block copolymer/homopolymer blends and morphologies generated by this nonequilibrium route are currently of fundamental interest, it is conceivable that this methodology may also be exploited in (semi)continuous separation processes designed to remove macromolecules from solutions.

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