All-atom molecular dynamics simulation of solvent diffusion in unentangled polystyrene film

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Supporting Information

Removing of the dissolved polystyrene (PS) chains in the dilute solution systems.

Throughout the longer simulations, especially at temperatures below Tg, we observed instances where several PS chains dissolved into a solvent, only to reabsorb over time, thus affecting the nature of the diffusion process. In response, we conducted additional simulations at 298 K where PS chains moving at least 20 Å from the interface and diffusing into the solvent were permanently excluded from the simulations. Through our investigation, we found that removing PS chains that had moved at least 10, 15, 20, or 25 Å from the interface had varying effects on the diffusion process. Removing chains at a distance of 10 or 15 Å had notable impacts on the dynamics of PS chains between the removed chain and the interface. However, removing chains at 25 Å allowed some PS chains to reabsorb onto the surface. We determined that removing chains at a distance of 20 Å from the interface effectively prevented reabsorption while minimizing disruption to the interface and diffusion behavior.
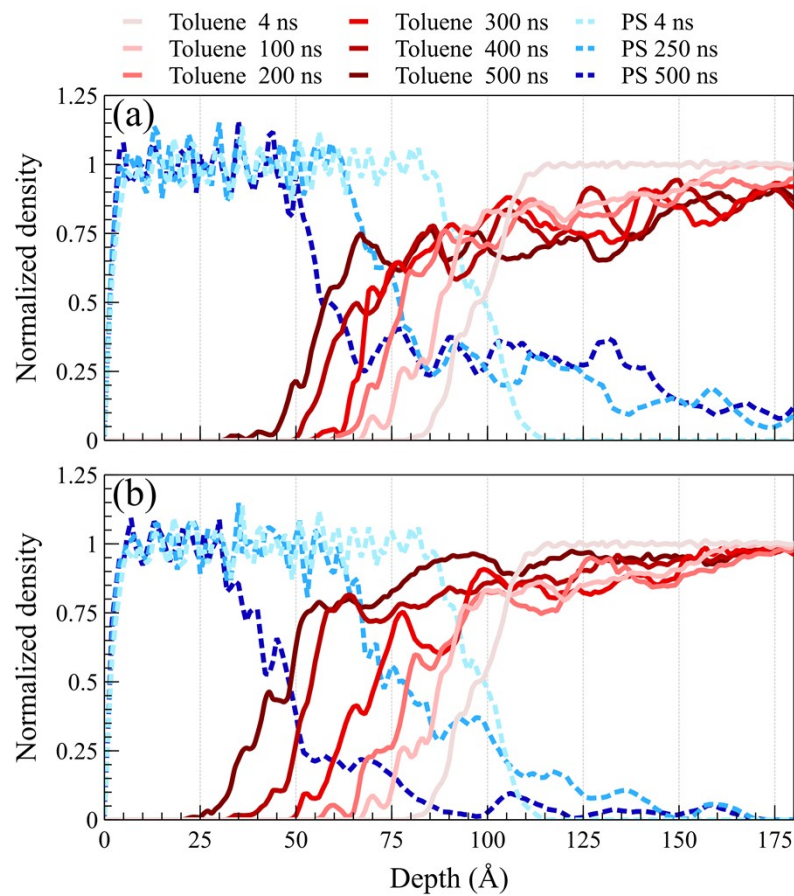
Figure S1 Normalized density profiles of toluene and PS for (a), concentrated solution and (b), dilute solution. Blue lines represent PS and red lines represent toluene.
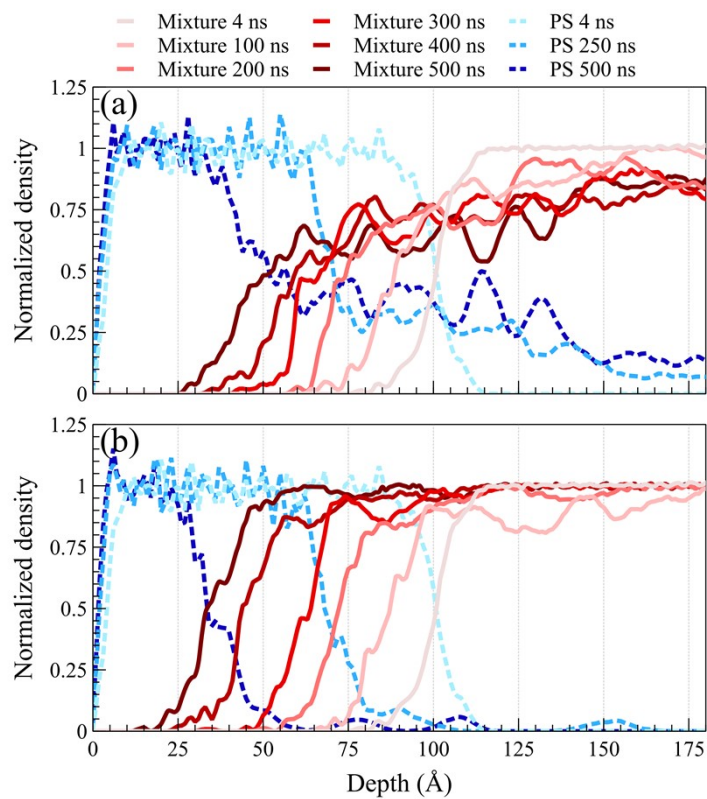
Figure S2 Normalized density profiles of the equimolar mixture of acetone and toluene and PS for (a), concentrated solution and (b), dilute solution. Blue lines represent PS and red lines represent the mixture.
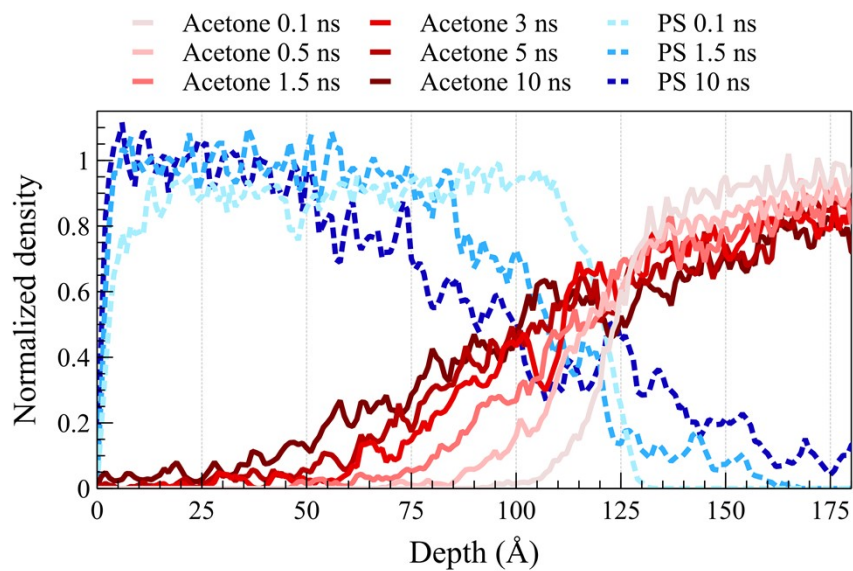

Figure S3 Normalized density profiles of acetone at 400 K are shown for concentrated solution system. Blue lines represent PS and red lines represent acetone at different times as shown by the figure legend above.

Table S1 Comparison of different methods for representing density fronts as a single point for Acetone dilute case. As shown in Figure 1, solvent density shows a sharp front at each timeframe, depicted as a red curve. We examined three methods to assign a single point as the front position in each timeframe; average, fixed-slope line, and spline. For the average method, the one-dimensional position was determined by computing the average value of the front data points. In the fixed-slope line method, lines were fitted to each front, sharing the same slope that minimized the fitting error. The center of each line was then adopted as the front position. In the spline method, a spline was fitted to each front, and the position of the spline center was employed as the front position. Subsequently, the resulting one-dimensional positions were fitted to two distinct motion behavior: $Z = vt$ and $Z = vt^n$. The performance of the average method was similar to or better than the more complicated methods, resulting in a smoother movement profile. A similar trend was observed for toluene and the mixture systems.

Method	Average	Fixed-slope line	Spline
Goodness of fit for $Z = vt$	$R^2 = 0.993$	$R^2 = 0.994$	$R^2 = 0.993$
Goodness of fit for $Z = vt^n$	$R^2 = 0.995$	$R^2 = 0.994$	$R^2 = 0.994$

Table S2 Fitted parameters and their 95% confidence bounds of the function $Z = vt^n$ describing the front position as a function of time for acetone, toluene, and the mixture cases.

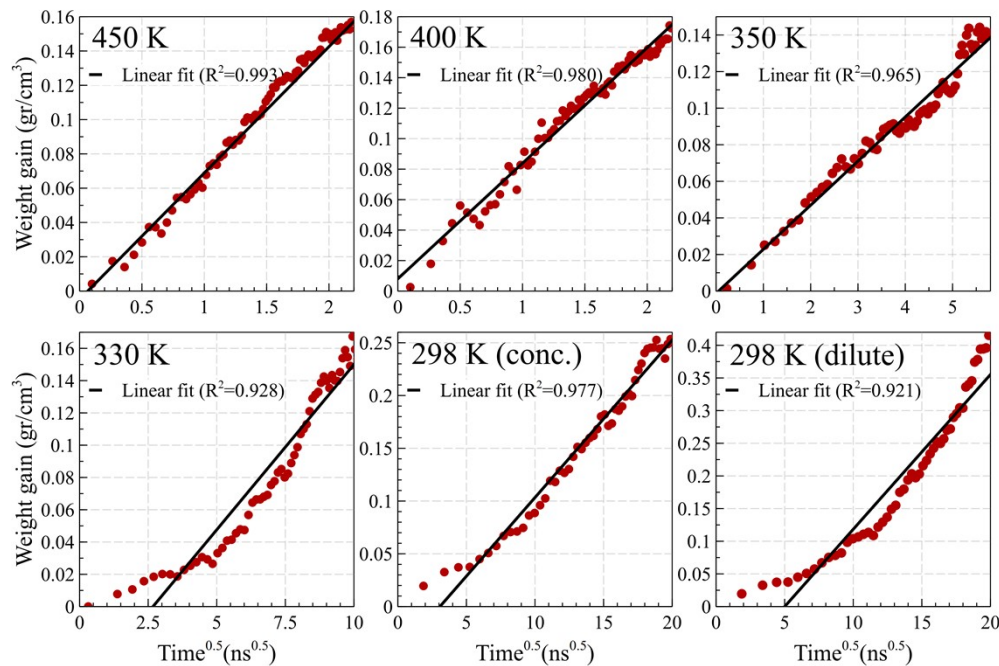| Solvent	v	n	Goodness of fit (R^2)
Acetone concentrated	0.2493 ± 0.0508	0.8647 ± 0.0348	0.9778
Acetone dilute	0.0883 ± 0.0105	1.0686 ± 0.0201	0.9951
Toluene concentrated	0.2024 ± 0.0304	0.8551 ± 0.0257	0.9868
Toluene dilute	0.0474 ± 0.0099	1.1309 ± 0.0355	0.9863
Mixture concentrated	0.3704 ± 0.0449	0.8004 ± 0.0208	0.9901
Mixture dilute	0.1533 ± 0.0166	0.9774 ± 0.0184	0.9949

Figure S4 Weight gain of the polymer film at different temperatures when exposed to the equimolar mixture of acetone and toluene, normalized by the volume of the polymer film. Fickian diffusion of the solvent into PS is evident at elevated temperatures of 450 K and 400 K at figures (a) and (b), confirmed by the linear change in weight gain when plotted against the square root of time. Approaching the glass transition temperature of PS changes the diffusion regime and consequently, weight gain fails to change linearly against the square root of time.
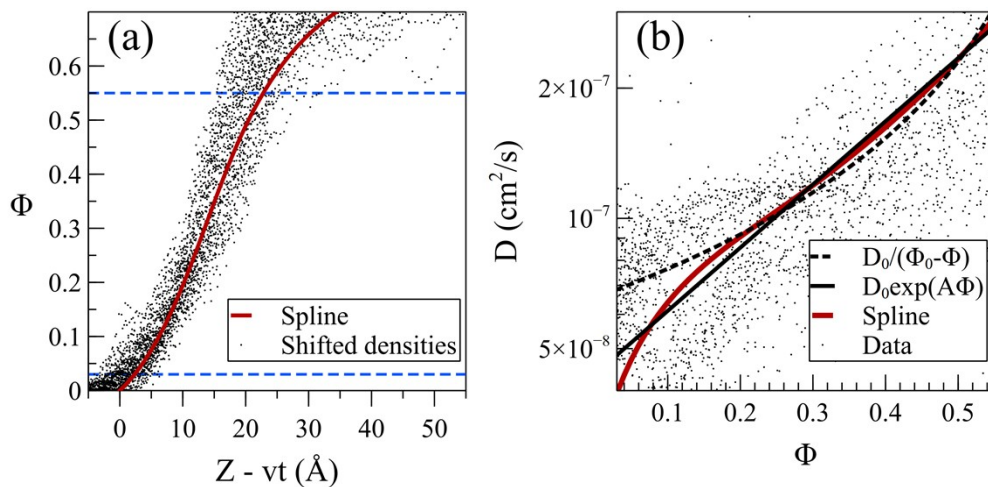

Figure S5 (a) shifting the density profiles, and the resulting master curve for toluene dilute solution. Horizontal dashed lines show the section of normalized density, Φ, with the acceptable uncertainty used to calculate diffusion coefficient, D. (b) Diffusion coefficient for toluene dilute solution based on its density profiles. Solid dots represent simulation data points while red curve shows diffusion coefficient values calculated from the master curve of shifted fronts. Dashed black line represents fitted model of $D_0/2(\Phi_0 - \Phi)$ with $D_0 = 0.46 \times 10^{-8} cm^2/s$ and $\Phi_0 = 0.70$. Solid black line is the best fit for $D_0 exp^{[20]}(A\Phi)$ with $D_0 = 0.44 \times 10^{-8} cm^2/s$ and $A = 3.36$.
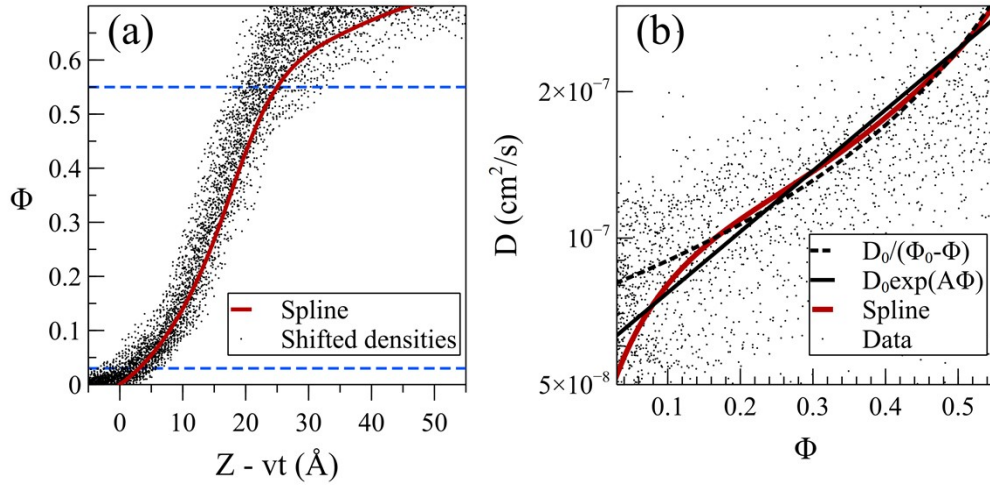
Figure S6 (a) shifting the density profiles, and the resulting master curve for the equimolar mixture of acetone and toluene dilute solution. Horizontal dashed lines show the section of normalized density, Φ, with the acceptable uncertainty used to calculate diffusion coefficient, D. (b) Diffusion coefficient for the mixture dilute solution based on its density profiles. Solid dots represent simulation data points while red curve shows diffusion coefficient values calculated from the master curve of shifted fronts. Dashed black line represents fitted model of $D_0/(\Phi_0 - \Phi)$ with $D_0 = 0.57 \times 10^{-7} \, cm^2/s$ and $\Phi_0 = 0.73$. Solid black line is the best fit for $D_0 exp(A\Phi)$ with $D_0 = 0.58 \times 10^{-7} \, cm^2/s$ and $A = 2.88$.

Derivation of diffusion coefficient of a solvent into the polymer bulk from Fick's nonlinear diffusion coefficient[1]:

$$\frac{\partial \Phi}{\partial t} = \frac{\partial}{\partial x}\left(D(\Phi)\frac{\partial \Phi}{\partial x}\right)$$

(S1)

$$\int_{x}^{\infty} \frac{\partial}{\partial t}\Phi(x',t)dx' = \left[D\frac{\partial \Phi}{\partial x}\right]_{x}^{\infty} = -D(\Phi)\frac{\partial}{\partial x}\Phi(x,t)$$

(S2)

$$D(\Phi) = -\frac{\int_{x}^{\infty} \frac{\partial}{\partial t}\Phi(x',t)dx'}{\frac{\partial}{\partial x}\Phi(x,t)}$$

(S3)

References:

1 J. Miao, M. Tsige and P. L. Taylor, *J. Chem. Phys.*, 2017, **147**, 044904.