**Effect of Solvent Selectivity on Chain Exchange Kinetics in Block Copolymer Micelles**

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**ABSTRACT:** The effect of solvent selectivity on the chain exchange kinetics for two poly(styrene-alt-ethylene-propylene) block copolymer micelles (SEP 26–70 and SEP 42–64, where the number denotes the molecular weight of each block in kg/mol) is investigated in pure squalane and in binary mixed solvents of squalane and 1-phenyldodecane, using time-resolved small-angle neutron scattering (TR-SANS). The exchange rate accelerates by 5 orders of magnitude for both micelles when adding only 25 vol % 1-phenyldodecane to squalane, compared to micelles in pure squalane. This acceleration is attributed to two factors: faster relaxation dynamics of the core blocks as more solvent penetrates into the core, serving as a plasticizer, combined with a reduced energy barrier for chain expulsion due to the lower Flory–Huggins interaction parameter $\chi$ between the core block and the solvent. By fitting the TR-SANS data to an established theoretical model, the enthalpic penalty of chain expulsion is determined for SEP micelles in mixed solvents. These results are quantified by a $\chi$-dependent function derived from Flory–Huggins theory, where $\chi$ values between the polystyrene (PS) core block and binary mixed solvents are estimated by a combination of static light scattering and cloud point measurements with PS homopolymers. This work quantifies the role of $\chi$ in chain exchange kinetics of block copolymer micelles.

**INTRODUCTION**

Self-assembled block copolymer (BCP) micelles in selective solvents offer useful solution properties. They are widely used in a variety of applications, including nanolithography, drug delivery, and viscosity modification. The solvent quality is an important factor for both thermodynamics and dynamics of BCP micelles, which can be tuned by either changing the composition of binary solvent mixtures or altering the temperature.

In terms of thermodynamic properties, scaling models predict the aggregation number of chains within a micelle ($N_{agg}$) to be proportional to the interfacial tension ($\gamma$) between the core block and solvent for crew-cut micelles, which have relatively longer core than corona block lengths (i.e., $N_{core} \gg N_{corona}$). For hairy micelles (i.e., $N_{core} \ll N_{corona}$), a scaling of $N_{agg} \sim \gamma^{1/3}$ was proposed. Quintana and co-workers studied the structures and thermodynamic properties of micelles formed by poly(styrene)-b-poly(ethylene-alt-propylene) (PS-PEP or SEP) diblock copolymers in various solvent mixtures. The authors reported lower aggregation numbers, smaller micelle sizes, lower critical micelle temperatures (CMT), and higher critical micelle concentrations (CMC) in less selective solvents, reflecting lower interfacial tension between the core block and solvent. Alternatively, changing the temperature is another way to adjust the solvent quality. Bang et al. showed a decrease in $N_{agg}$ and core radius ($R_{core}$) of poly(styrene)-b-poly(isoprene) (PS-PI) micelles in tetradecane and an increase of solvent fraction in the micelle core, when the temperature was elevated toward the CMT.

Recently, Choi et al. systematically investigated a series of PS-PEP diblock copolymers in pure squalane and binary solvent mixtures of squalane and 1-phenyldodecane, where 1-phenyldodecane is a less selective solvent than squalane. In good agreement with observations by Quintana et al. and Bang et al., the authors observed a smaller aggregation number, lower CMT, and higher solvent fraction in the core upon increasing the volume fraction of 1-phenyldodecane in binary solvent mixtures.

The solvent quality also plays a critical role in the equilibrium dynamics of BCP micelles. Single-chain exchange is believed to be the dominant mechanism for BCP micelles near equilibrium. Both theory and experiment have shown a strong dependence of chain exchange kinetics on solvent selectivity. The scaling theory by Halperin and Alexander attributes the activation energy ($E_a$) of chain expulsion to the additional surface of a collapsed core block, i.e., $\gamma N_{core}^{2/3} a^2$ where $\gamma$ reflects the effect of solvent selectivity. $N_{core}$ is the number of core block repeat units, and $a$ is the size of one repeat unit. Following this theoretical prediction, Lund and co-workers showed an acceleration in chain exchange kinetics of BCP micelles in mixed solvents of squalane and 1-phenyldodecane.
exchange kinetics of poly(ethylene-alt-propylene)-b-poly-(ethylene oxide) (PEP-PEO) micelles by reducing the interfacial tension between the PEP core block and solvent, adding more N,N-dimethylformamide into water, and/or increasing temperature. Based on kinetic studies of dilute SEP diblock copolymer micelles in squalane, Choi and co-workers established a quantitative model (eq 4) to account for the dramatic influence of the core block length, dispersity of core block length, and solvent selectivity. This model attributes $E_c$ to the unfavorable core block monomer–solvent interactions captured by $kT N_{core}$, where $\chi$ is the Flory–Huggins interaction parameter between the core block and solvent. Dissipative particle dynamics (DPD) simulations by Li and Dormidontova examined the effect of solvent selectivity by adjusting the pairwise repulsive interaction parameters, leading to the same form for $E_c \sim \chi N_{core}$ as proposed by Choi et al.

However, there is a limitation to this simple relation when considering the scenario near the CMT. At $T_{CMT}$, there should be no energy barrier for chain expulsion, i.e., $E_c \approx 0$. However, the solvent quality is approximately at the theta condition for the core block at $T_{CMT}$, i.e., $\chi \approx 0$, taking the solvent volume as the reference volume. To address this issue, Ma and Lodge proposed an elaborate $\chi$-dependent function $f(\chi)$ to replace $\chi$, so that the adapted expression is $E_c \sim f(\chi) N_{core}$. The authors incorporated this modified function within Choi’s model and successfully interpreted the time-resolved small-angle neutron scattering (TR-SANS) data of poly(n-butyl methacrylate)-b-poly(methyl methacrylate) (PnBMA-PMMa) micelles in solvent mixtures of the ionic liquids 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([BMIM][TFSI]) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TFSI]), which are lower critical micelle temperature (LCMT) systems.

This work aims to test the universality of this $\chi$-dependent function with SEP micelles in binary mixed solvents of squalane and 1-phenyldodecane. In contrast to the previously studied PnBMA-PMMa/ionic liquid, this system has an upper critical micellization temperature (UCMT). We quantify the consequence of varying the solvent composition and temperature on the rate of chain exchange using TR-SANS, independent approaches, static light scattering (SLS) and cloud point measurements, have been adopted for direct measurements of $\chi$ between the core block and the solvent as a function of solvent composition and temperature.

### EXPERIMENTAL SECTION

#### Materials

Two polystyrene (PS) homopolymers were synthesized by anionic polymerization. The molecular weight and molecular weight distribution of one PS with $M_w = 1.3 \text{ kg/mol}$ were characterized by matrix-assisted laser desorption/ionization mass spectroscopy (MALDI-MS), and those of the other PS ($M_w = 23 \text{ kg/mol}$) were characterized by size exclusion chromatography equipped with a refractive index detector and a multiangle light scattering detector (SEC-MALS), as shown in Figure S1. Two pairs of SEP and core block-deuterated dSEP diblock copolymer were reproduced from the previous work. They were synthesized by sequential anionic polymerization of PS-PI and (dPS)-PII, followed by selective precipitation of the PI block using a Ni/Al catalyst under 400 psi deuterium $D_2$ (purchased from Cambridge Isotope Laboratories Inc.). The average repeat unit of PEP is $C_5D_2H_7$ after the deuteration reaction, where $D_2$ is a result of $D_2$ saturation and a small amount of H/D exchange. Perdeuterated styrene monomer ($C_6D_8$) was purchased from Polymer Source Inc., while protonated styrene and isoprene monomer were from Sigma-Aldrich Inc. SEC-MALS and proton nuclear magnetic resonance spectroscopy ($^1$H-NMR) were performed to determine the molecular weight and molecular weight distribution, which are summarized in Table 1. The number in the name of each polymer refers to the molecular weight, e.g., SEP 26–70 indicates $M_w \approx 26$ and 70 kg/mol for the PS and PEP blocks, respectively.

#### Table 1. Polymer Characteristics

<table>
<thead>
<tr>
<th>polymers</th>
<th>$M_w/\text{PS}$ (kg/mol)</th>
<th>$M_w/\text{PEP}$ (kg/mol)</th>
<th>$M_w/\text{SEP}$ (kg/mol)</th>
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<td></td>
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<tr>
<td>PS 23</td>
<td>23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SEP 26–70</td>
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<td>70</td>
<td>1.04</td>
</tr>
<tr>
<td>dSEP 29–71</td>
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<td>71</td>
<td>1.10</td>
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</tr>
<tr>
<td>dSEP 47–67</td>
<td>47</td>
<td>67</td>
<td>1.10</td>
</tr>
</tbody>
</table>

*Note: Characteristics of SEP and dSEP diblocks were reproduced from refs 20 and 30.*

Squalane (sql) was used as a highly selective solvent for the PEP blocks, so that the PS blocks aggregate into the core while PEP blocks form the swollen corona. 1-Phenyldodecane (phd), on the other hand, is relatively less selective, capable of dissolving SEP diblocks as free chains. Binary solvent mixtures were prepared by mixing squalane with various volume fractions of 1-phenyldodecane, which were calculated using densities of squalane (0.810 g/mL) and 1-phenyldodecane (0.856 g/mL) at room temperature, assuming no volume change on mixing. Deuterated 1-phenyldodecane (C$_8$D$_{13}$O)$_2$ and deuterated squalane (C$_{30}$D$_{62}$O)$_2$ used in neutron scattering experiments were purchased from CDN Isotopes Inc., while regular solvents were from Sigma-Aldrich Inc.

#### Micelle Solution Preparation

Dilute micelle solutions (0.5 and 1 vol %) were prepared using a co-solvent procedure. The polymer was dissolved in squalane with a similar amount of dichloromethane (Sigma-Aldrich Inc.) as co-solvent. After the polymer was completely dissolved, the solution was filtered through 0.2 $\mu$m hydrophobic PTFE filters to remove dust. The micelle solution was then evaporated at room temperature for 2 days until a constant weight was achieved. Micelles formed as the dichloromethane were then degassed under vacuum for 5 min to remove air bubbles and residual dichloromethane. Finally, micelle solutions were annealed at 160 °C for 1 h to equilibrate and then allowed to cool back to room temperature.

#### Cloud Point Measurements

The cloud point measurements were performed on a home-built optical transmission apparatus, which consists of a helium–neon laser with wavelength $\lambda = 633 \text{ nm}$, a sample heating stage, and a photodiode detector. Various volume fractions of 1.3 kg/mol PS were mixed with squalane in a glass ampule, which was then flame-sealed under vacuum. The sample was heated to 180 °C or a higher temperature, held for 30 min to completely dissolve, i.e., as a one-phase solution, and followed by a subsequent cooling at a rate of 1 °C/min. As shown in Figure 5a, the transmittance showed a sudden decrease when the solution underwent phase separation. The cloud point was defined as the temperature at which the transmittance dropped to 80% of the initial transmittance of the one-phase solution.

#### Static Light Scattering (SLS)

SLS was performed to determine the second virial coefficient $A_2$ of PS in pure squalane and in binary solvent mixtures of squalane and 1-phenyldodecane. A series of dilute PS samples ($M_w = 23 \text{ kg/mol}$, $M_w/\text{SEP}=1.03$, in Table 1) were used for measurement, with various concentrations (10–50 mg/mL) prepared in binary mixed solvents and sealed in LS glass tubes. The refractive indices of the solvent and the refractive index increment (dn/dc) values for the
Time-Resolved Small-Angle Neutron Scattering. TR-SANS experiments were conducted on the CG-2 SANS beamline in the High Flux Isotope Reactor (HFIR), Oak Ridge National Laboratory. We used a wavelength of 4.75 Å with the spread of $\Delta \lambda/\lambda = 0.13$ and a sample-to-detector distance of 10 m to access a q range of 0.007–0.1 Å$^{-1}$. Micelle solutions were loaded into 1 mm quartz banjo cells and fixed in a sample block for heating and cooling. Each scattering experiment takes 5 min. The evolution of excess scattering intensity is proportional to the change of contrast between the micelle cores and solvent: $I(q) - I(\infty) \sim (\rho_{\text{core}}(q) - \rho_{\text{solute}}(q))^2$, where $I(q)$ is the instantaneous intensity at time $I(\infty)$ is the intensity at infinite time ($t = \infty$).

A contrast matching strategy is employed for the solvent used in TR-SANS experiments, such that the scattering density of the solvent matches that of completely mixed micelle cores. $\rho_{\text{solvent}} = \rho_{\text{mix}}(t = \infty) = (\rho_{\text{ps}} + \rho_{\text{dps}})/2 = 3.93 \times 10^{13} \text{cm}^{-2}$, using the values listed in Table 2.

Isotopic solvent mixtures of h-(1-phenyldodecane), d-(1-phenyl-72 12 dodecane) h-squalane, and d-squalane were prepared using the calculated volume fractions, as listed in Table 2.

Table 2. Volume Fraction of Each Component in the Contrast Matching Solvent

<table>
<thead>
<tr>
<th>Solvent</th>
<th>h-phd</th>
<th>d-phd</th>
<th>h-sql</th>
<th>d-sql</th>
</tr>
</thead>
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<tr>
<td>50/50 vol % phd/sql</td>
<td>45 vol %</td>
<td>5 vol %</td>
<td>0</td>
<td>50 vol %</td>
</tr>
<tr>
<td>25/75 vol % phd/sql</td>
<td>25 vol %</td>
<td>0</td>
<td>19 vol %</td>
<td>56 vol %</td>
</tr>
<tr>
<td>0/100 vol % phd/sql</td>
<td>0</td>
<td>0</td>
<td>42 vol %</td>
<td>58 vol %</td>
</tr>
</tbody>
</table>

### RESULTS AND DISCUSSION

Micelle Chain Exchange Kinetics. TR-SANS experiments were performed to probe the chain exchange kinetics of SEP block copolymer micelles in various solvent mixtures. Figure 1a shows a representative plot of time-dependent scattering intensities of 1 vol % SEP 26–70 micelles in the mixed solvent 25/75 vol % phd/sql at 58 °C. The intensity of a postmixed specimen (red curve) was measured at room temperature where no chain exchange occurs, so it represents the initial state with unmixed cores, i.e., $I(\infty) = I_{\text{postmixed}}$. It shows the highest intensity because of the largest contrast between micelle cores and solvent. After the system was heated to the target temperature, 58 °C, for example, micelles underwent chain exchange. Thus, the contrast between partially mixed cores and solvent decreases, leading to a decrease in scattering intensity with time, as shown in Figure 1a. The premixed micelle solution represents the state of complete chain exchange, i.e., $I(\infty) = I_{\text{premixed}}$, since the protonated and deuterated polymer chains were molecularly mixed in the micelle preparation step. Under the contrast matching condition for fully mixed cores, the intensity of the premixed specimen matches that of the solvent except in the low q regime ($<0.015 \text{ Å}^{-1}$), where there is a small contribution from the corona scattering. This well-matched contrast between the core and solvent indicates that the composition of solvent molecules in the core is close to that of the macroscopic solvent mixture, due to the fact that 1-phenyldodecane and squalane are both poor solvents ($\chi_{\text{PS-phd}} = 0.74$ and $\chi_{\text{PS-sql}} = 1.67$, see below), leading to a low degree of overall solvation.

A normalized relaxation function, $R(t)$, is defined to quantify the rate of chain exchange.
It is displayed in Figure 3. We note that the shift factors of temperature of 70 °C were switched from 125 to 70 °C converted from the reported values because the reference temperature was almost frozen. The empirical shift factors used in the tTS method are 64 micelles, respectively. The main reason is that the reference chain exchange is prohibitively large in pure squalane, i.e., 10^10 times faster than in pure squalane. The same trend was observed for SEP 26 micelles in various binary mixed solvents at a reference temperature of 70 °C, where the volume fraction of squalane in binary mixed solvents varied from 50 to 100%. Data of SEP micelles in pure squalane were adapted from ref 30.

The time–temperature superposition (tTS) method is employed to construct R(t) master curves with a reference temperature of 70 °C, as shown in Figure 2. The chain exchange rate increases significantly for both SEP micelle systems with reducing solvent selectivity by mixing squalane with a higher volume fraction of 1-phenyldodecane. For instance, SEP 42–64 micelles exchange chains about 10^5 times faster in 50 vol % squalane than in 75 vol % squalane and, furthermore, 10^9 times faster than in pure squalane. The same trend was observed for SEP 26–70 micelles. The timescale of chain exchange is prohibitively large in pure squalane, i.e., 10^5 and 10^9 min at R(t) = 0.5 for SEP 26–70 and SEP 42–64 micelles, respectively. The main reason is that the reference temperature 70 °C is close to the glass transition temperature (T_g) of the PS block in the micelle core, where the PS chains are almost frozen.

The empirical shift factors used in the tTS method are displayed in Figure 3. We note that the shift factors of previously studied micelle systems in pure squalane have been converted from the reported values because the reference temperature was switched from 125 to 70 °C. Since the T_g of the PS block in the core is about 70 °C for micelles in pure squalane, the previous empirical trend line should still work but needs shifting to the reference temperature 70 °C, i.e., log(a_T) = -0.0936 × (T - 70 °C). The data of binary mixed solvents at multiple temperatures are displayed in Figure S6 in the Supporting Information and were empirically shifted to overlap with those obtained at 70 °C, e.g., data of SEP 26–70 in the 25/75 vol % phd/sq solvent, which were collected at 68 °C.

The T_g of the core block in binary mixed solvents will decrease with the increase of the solvent fraction in the core region when the solvent selectivity is reduced. The values of the reduced core T_g are estimated by the Fox equation

$\frac{1}{T_g^{\text{red}} g, PS} = \frac{1}{T_g^{\text{red}} g, PS} + \frac{w_1}{T_g^{\text{red}} g, squalane} + \frac{w_2}{T_g^{\text{red}} g, phd}$

where T_g^{red} is the glass transition temperature of the core block in a wet core with weight fractions w_1 and w_2 of squalane (sql) and 1-phenyldodecane (phd), respectively. T_g^{red} ≈ 343 K (70 66 °C) represents the glass transition temperature of a dry core as

**Figure 1.** (a) Representative TR-SANS intensity evolution traces at 58 °C and (b) R(t) traces of the 1 vol % SEP 26–70 micelles in the 25/75 vol % phd/sql solvent at different temperatures.

**Figure 2.** R(t) master curves and theoretical model fits for 1 vol % SEP micelles in various binary mixed solvents at a reference temperature of 70 °C.
reported by Lai et al. 41 This value is lower than $T_g$ of bulk PS due to the small size of the PS domains in the spherical micelles (≤11 nm) and because the PS core block repeat units located at the interface are plasticized by the solvent. Solvent glass transition temperatures $T_g$ of squalane and 1-phenyldodecane are estimated to be 89, 3, % phd/sql binary solvent. In this case, the weight fractions of squalane and 1-phenyldodecane. For example, 13 vol % phd/sql binary solvent in the core reported by Choi et al. (which was more than 130 °C). Here, we note that no residual solvent was detected in the core of SEP micelles in squalane at 70 °C by Choi et al. (see above) using the volume fraction of binary mixed solvent in the core reported by Choi et al. and the trend line as a function of temperature at a reference temperature of 70 °C, 42 °C, 43 °C, and 8 wt % in the core region, respectively. The glass transition temperatures of PS, squalane, and 1-phenyldodecane are estimated to be 89, 3, and 8 wt % phd/sql binary solvent.

Figure 3. Shift factors $\log(a_T)$ and the trend line as a function of temperature at a reference temperature of 70 °C, open circles for SEP 42–64, and filled diamonds for SEP 26–70 in binary mixed solvents, together with the shift factors and the fitted trend line from our previous studies: $\log(a_T) = -0.0936 \times (T - 70 °C)$. 42

As noted in Table 3, the TR-SANS experimental temperatures were designed for appropriate timescales from several minutes to hours, to capture the evolution of scattering intensities by SANS. These temperatures are at least 12 °C higher than the glass transition temperature of the core block, so that the core blocks are able to relax. On the other hand, they are more than 50 °C lower than the critical micelle temperature where the rate of chain exchange would be very fast.

To describe the TR-SANS data quantitatively, a theoretical model (eq 4) has been established by previous studies on diblock micelles. 43,44 This model makes the following assumptions: (i) single-chain exchange is the dominant mechanism near equilibrium; (ii) chain expulsion is the rate-limiting step; (iii) the motion of core blocks follows Rouse dynamics when buried in the micelle cores; and (iv) the activation energy $E_a$ of chain expulsion is a result of the enthalpy penalty from unfavorable interactions between the core blocks and corona/solvent matrix and the entropy gain from the relief of corona chain stretching upon expulsion.

$$R(t) = \int P(N) \exp \left[ -\frac{6\pi^2 kT}{N_{core}^2 k_b T} \right] dN_{core}$$

(4)

$$P(N) = \frac{z^{+1} N_{core}^{+1}}{\Gamma(z + 1)} \exp \left( -\frac{z N_{core}}{N_a} \right)$$

(5)

Here, $N_{core}$ is the degree of polymerization of the core blocks and $P(N_{core})$ is a Schulz–Zimm distribution function that accounts for dispersity of the core blocks, given by eq 5, where $z = [N_a/N_n - 1]^{-1}$, $\Gamma$ is the $\gamma$ function, and $N_a/N_n$ represents the dispersity. Considering the small mismatch in the

Table 3. Characteristics of SEP Micelles in Binary Mixed Solvents

<table>
<thead>
<tr>
<th>micelle systems</th>
<th>$\bar{R}_h$</th>
<th>$\bar{N}_{agg}$</th>
<th>$\bar{R}_{core}$</th>
<th>$\bar{f}_{vol}$</th>
<th>$T_g^{ps}$</th>
<th>$T_{CMT}$</th>
<th>$T_{TR-SANS}$</th>
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<tr>
<td>SEP 42–64 micelles in</td>
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<tr>
<td>50/50 vol % phd/sql</td>
<td>34</td>
<td>53</td>
<td>10.1</td>
<td>±0.21</td>
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<td>39–49</td>
</tr>
<tr>
<td>25/75 vol % phd/sql</td>
<td>35</td>
<td>72</td>
<td>10.9</td>
<td>±0.13</td>
<td>37</td>
<td>180</td>
<td>87–97</td>
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<tr>
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<td>83</td>
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<td>±0</td>
<td>70</td>
<td>&gt;200</td>
<td>135–145</td>
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<tr>
<td>SEP 26–70 micelles in</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25/75 vol % phd/sql</td>
<td>35</td>
<td>62</td>
<td>8.8</td>
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<td>37</td>
<td>130</td>
<td>49–68</td>
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<tr>
<td>0/100 vol % phd/sql</td>
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<td>71</td>
<td>8.9</td>
<td>±0</td>
<td>70</td>
<td>200</td>
<td>100–115</td>
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</table>

$\bar{R}_h$ and $\bar{N}_{agg}$ are the micelle core radius, aggregation number of chains within a micelle, hydrodynamic radius, and volume fraction of solvent in the micelle core at 70 °C. The glass transition of the PS core block in the core estimated by the Fox equation. The critical micelle temperature determined by dynamic light scattering (DLS). The temperatures carried out in TR-SANS experiments. Note that $f_{vol}$, $N_{agg}$, $R_{core}$, $R_h$, and $T_{CMT}$ were reproduced from the previous work, except those of SEP 26–70 micelles in 25/75 vol % phd/sql, as shown in Figures S4 and S5.
Table 4. Parameters Used in the Model

<table>
<thead>
<tr>
<th>micelle systems</th>
<th>( \langle N_{\text{core}} \rangle )</th>
<th>( \zeta_T ) (70 °C) (N s/m)</th>
<th>( \zeta_{\text{corona}} )</th>
<th>( f(\chi)_{\text{fitted}} )</th>
<th>( N_c/N_{\text{n}}_{\text{fitted}} )</th>
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<tr>
<td>SEP 42–64 micelles in</td>
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<tr>
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<td>3.08 \times 10^{-8}</td>
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<td>2.34 \times 10^{-2}</td>
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<td>1.20 \times 10^{-3}</td>
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Table 5. Enthalpic Interactions between the Core Block and Solvent

<table>
<thead>
<tr>
<th>micelle systems</th>
<th>( \chi_{(v_1 = v_2)} )</th>
<th>( \chi_{(v_1 = v_3)} )</th>
<th>( a(\chi_{(v_1 = v_2)}/\chi_{(v_1 = v_3)}) )</th>
<th>( f(\chi) )</th>
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</thead>
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<tr>
<td>SEP 42–64 micelles in</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50/50 vol % phd/sql</td>
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<td>0.238</td>
<td>5.4</td>
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</tr>
<tr>
<td>SEP 26–70 micelles in</td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>25/75 vol % phd/sql</td>
<td>1.46</td>
<td>0.279</td>
<td>9.3</td>
<td>11.7</td>
</tr>
<tr>
<td>0/100 vol % phd/sql</td>
<td>1.67</td>
<td>0.320</td>
<td>15.5</td>
<td>15.0</td>
</tr>
</tbody>
</table>

Note that \( a = 0.58 \) gives best fit between \( a(\chi_{(v_1 = v_2)}/\chi_{(v_1 = v_3)}) \) and \( f(\chi) \), where \( v_1 = 463.5 \) cm/s and \( v_3 = 100 \) cm/s. Molar volumes of solvent and PS repeat unit, respectively.
with increasing temperature, indicating higher solubility of PS in the solvent, which is an upper critical solution temperature (UCST) system. On the other hand, $A_2$ is strongly dependent on the solvent composition as well, decreasing with the increasing volume fraction of squalane ($\phi_{sql}$).

\[
\chi' = \frac{1}{2} - \rho_p v_l A_2 (v_0 = v_l)
\]

\[
\chi = \frac{v_1}{v_1} \chi' (v_0 = v_2)
\]

Applying the Flory–Huggins theory for dilute polymer solutions, $\chi$ values were calculated from $A_2$ by eq 7 and then converted by eq 8 taking the molar volume of the PS repeat unit ($v_2 = 100 \text{ cm}^3/\text{mol}$) as the reference volume $v_0$, instead of the molar volume of the solvent $v_1$ in the traditional definition, where $\rho_p = 1.04 \text{ g/cm}^3$ is the density of PS. This is due to the use of the chemical degree of polymerization in the fitting model (eq 4) for TR-SANS data, i.e., $N_2 = N_{core}$ only if $v_0 = v_2$, where $N_2$ represents the volumetric degree of polymerization of the PS block. Moreover, the values of $\chi$ were determined in binary mixed solvents of low squalane volume fraction $\phi_{sql}$ (= 0, 5, 10, and 15 vol %), whereas TR-SANS experiments were performed in the other extreme, i.e., $\phi_{sql} = 50$, 75, and 100 vol %.

It is mathematically convenient to extrapolate $\chi$ to high $\phi_{sql}$ solvents using a constant reference volume since $v_1$ varies with solvent composition. If a linear relationship is assumed with $v_1 = 288$ and 522 cm$^3$/mol for 1-phenyldodecane and squalane, respectively, $v_1 = 288 + 234\phi_{sql}$ cm$^3$/mol is estimated for binary mixed solvents. As summarized in Figure 4b, $\chi$ decreases with increasing temperature, following the empirical relation $\chi = A/T + B$. The slope of $\chi$ vs $1/T$ was observed to be a weak function of solvent composition in this relatively narrow composition range, while the intercept showed appreciable changes due to different excess entropy of mixing.

Considering the uncertainty in extrapolation of $\chi$ vs solvent composition, optical transmittance experiments were performed to measure cloud points of PS solutions in squalane, and, thus, to determine $\chi$ between PS and pure squalane. A lower-molecular-weight PS ($M_n = 1.3 \text{ kg/mol}$, $M_w/M_n = 1.1$) was used to obtain accessible cloud points. We, therefore, assume that any $M$ dependence of $\chi$ is less important than the dependence on solvent composition. Figure 5a displays the temperature-dependent transmittance of PS solutions. The cloud point was defined as the temperature at which the transmittance dropped to 80% of the transmittance of the one-phase solution. Figure 5b summarizes cloud points of PS solutions at different PS volume fractions ($\phi_{PS}$), ranging from

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**Figure 4.** (a) Second virial coefficient ($A_2$) for PS in binary mixed solvents as a function of temperature and composition and (b) calculated $\chi$ values from $A_2$, taking the PS repeat unit volume as the reference volume. The open circle is an extrapolation to 70 °C.

**Figure 5.** (a) Temperature-dependent transmittance of PS solutions in squalane at different PS volume fractions and (b) cloud points and the coexistence curve calculated by the Flory–Huggins theory with $\chi = 287/T - 0.517$. 

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Figure 6a displays χ between PS and binary mixed solvents as a function of composition at 70 °C and interpolated values at ϕ_{aq} = 50 and 75 vol % (red circles) and (b) enthalpy penalty of chain expulsion for SEP micelles in binary mixed solvents, comparing the fitted results from TR-SANS (f(χ)(N_{core})) and calculated values by the Flory–Huggins theory (a(χ − v_1/v_2)(N_{core})).

Figure 6a displays χ between PS and binary mixed solvents at 70 °C, where the data of ϕ_{aq} = 0, 5, 10, and 15 vol % were determined from A_{t} measurements in SLS, ϕ_{aq} = 100 vol % was determined by cloud point measurements, and ϕ_{aq} = 50 and 75 vol % were obtained from the linear fitting between χ and ϕ_{aq}. We assume that the molecular weight dependence of χ is negligible in the range of 26–42 kg/mol. Consistent with this, Hoarfrost and co-workers showed that χ between PnBMA and the ionic liquids [BMIM][TFSI] and [EMIM][TFSI] was almost constant when varying the molecular weight of PnBMA from 25 to 115 kg/mol.

\[
\Delta E/kT = a \left( \chi - \frac{v_1}{v_2} \right) N_{core} (v_0 = v_2)
\]

(Ma and Lodge derived the energy barrier of chain expulsion by the free energy difference (ΔE) between the core block within the micelle cores and in the solvent from the Flory–Huggins theory, as given by eq 9, where v_0 = v_2 and a is a constant. In their description, the micelle solution was treated as a two-phase system that is under equilibrium, with a polymer-rich phase within the micelle cores and a solvent-rich phase outside. For simplicity, the entropic contribution of the corona blocks was neglected in the derivation). Therefore, ΔE/purely represents the enthalpic penalty from unfavorable core block monomer–solvent contacts. Figure 6b shows the enthalpy penalty of chain expulsion for SEP micelles in binary mixed solvents. The fitted results from TR-SANS (i.e., f(χ)(N_{core})) agree with the calculated values within 4 kT difference, i.e., a(χ − v_2/v_1)(N_{core}), where a = 0.58, v_1 = 463.5 cm^3/mol and v_2 = 100 cm^3/mol were used in the calculation. The validation of this χ-related expression is independent of

0.04 to 0.8. The black line was the coexistence curve calculated by the Flory–Huggins theory, with two adjustable parameters in χ, assuming χ = A/T + B. Here, the reference volume is v_0 = 100 cm^3/mol, and N_1 = 5.2 and N_2 = 12.5 are volumetric degrees of polymerization for squalane and 1.3 kg/mol PS, respectively. As shown in Figure 5b, χ = 287/T − 0.517 gives the best fit. Therefore, χ = 0.32 between PS and squalane at 70 °C, with v_0 = v_1 = 100 cm^3/mol, i.e., χ = 1.67 if converted with v_0 = v_1 = 522 cm^3/mol. This large quantity suggests the strong incompatibility between PS core blocks and the solvent, driving the segregation of PS blocks into micelle cores.

The validation of this χ-related expression is independent of the molecular characteristics for the two SEP block copolymers with (N_{core}) that differ by a factor of 1.6, for which the exchange rate differs by a factor of 3–4 orders of magnitude.

A relatively large difference in fitted vs calculated values (5.4 vs 9.6) arises for the 50/50 vol % phd/sql micelle system in Table 5. This discrepancy is attributed to the two strict assumptions in the derivation of eq 9, that the solvent fraction in the core is close to zero and that polymer fraction in the solvent is negligible. They are reasonable assumptions for SEP micelles in pure squalane, where the micelle core is dry and the CMC is estimated to be as low as 10^{-6} g/mL. However, about 21 vol % solvent remains within the cores for 50 vol % squalane, as shown in Table 3. More solvent will penetrate into the core if χ between the core block and solvent is further reduced. Similarly, the significant drop in the CMT of SEP micelles reflects an increase of CMC in less selective solvents. Therefore, it is risky to neglect the polymer concentration in the solvent for SEP 42–64 micelles in 50/50 vol % phd/sql, which potentially causing the deviation from the theory. In this case, where χ is not large enough, a more complicated χ-dependent function is probably needed to account for the offset.

**Summary.** The chain exchange kinetics of SEP block copolymer micelles was investigated in pure squalane and in binary solvent mixtures of squalane and 1-phenylododecane by TR-SANS. The solvent composition significantly influences the kinetics of chain exchange between micelles, where 5 orders of magnitude faster kinetics were observed when mixing squalane with only 25 vol % 1-phenylododecane. This acceleration in the kinetics is attributed to two primary factors: (i) faster motion of core blocks in the core as more solvent penetrates into the core, serving as a plasticizer and (ii) reduced energy barrier of chain expulsion due to the higher solubility between the core block and solvent. By fitting the TR-SANS data to a theoretical model, the enthalpic penalty of chain expulsion was determined for SEP micelles in various binary mixed solvents, reflecting the change of the Flory–Huggins interaction parameter χ between the core block and solvent. Previously, Ma and Lodge proposed a χ-dependent function for this energy barrier in a strong segregated micelle system based on the Flory–Huggins theory. With a direct measurement of χ between the PS core block and solvent from second virial coefficients by SLS and from cloud point measurements by

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optical transmittance, the theoretically predicted values of activation energy compare favorably with the experimental results obtained from TR-SANS. In summary, this work quantifies the role of $\chi$ in the kinetics of chain exchange for a UCMT micelle system. The successful interpretation of chain exchange kinetics in both PnBMA-FMA/ionic liquids and SEP/hydrocarbon solvents points toward the possible universality of this $\chi$-dependent function for the activation energy. This potentially provides insights in selecting an appropriate solvent for the design of micelles.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.9b01877.

(i) MALDI-MS of 1.3 kg/mol PS and SEC trace of 23 kg/mol PS; (ii) refractive indices of binary mixed solvents as function of temperature and solvent composition, and dilute PS solutions at various polymer concentrations at 60 °C; (iii) refractive indices vs concentration of dilute PS solutions in 1-phenyl-dodecane at 23 and 60 °C, and Zimm plot of PS in 1-phenyldecane at 23 °C; (iv) temperature dependence of the LS detector counts and the hydrodynamic radius of 0.5 vol % SEP 26–70 polymer in the 25/75 vol % 1-phenyldecane/squalane mixed solvent upon heating and cooling; and (v) SAXS patterns of 1 vol % SEP 26–70 micelles in the 25/75 vol % phenyldodecane/squalane solvent at multiple temperatures (PDF)

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**


