Supporting Information

for

Chain Exchange Kinetics in Diblock Copolymer Micelles in Ionic Liquids: The Role of χ

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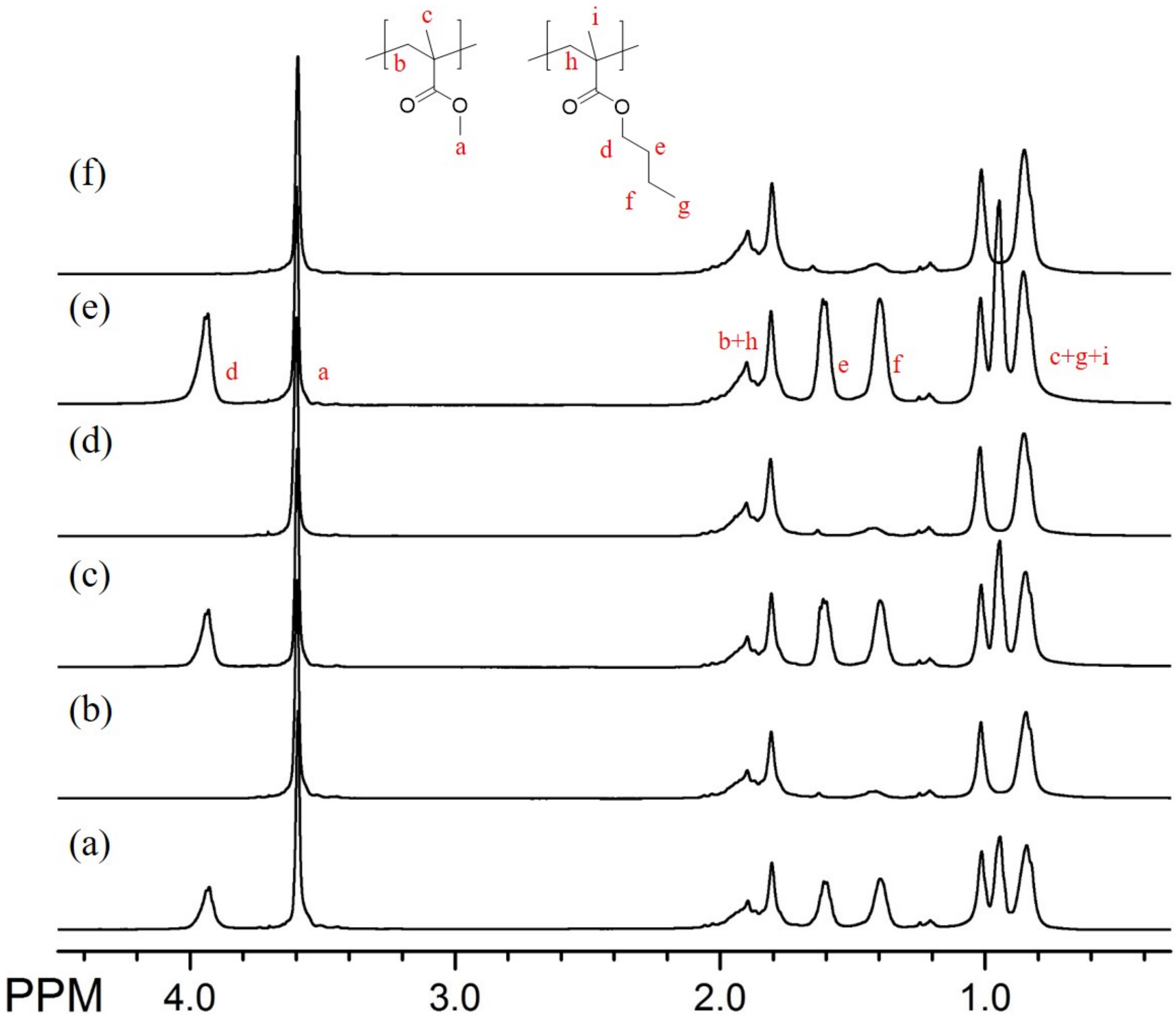

Figure S1. [1]H-NMR spectroscopy of PMMA-*b*-(*d*)PnBMA copolymers in $CDCl_3$: (a) PMMA-*b*-PnBMA (25-24); (b) PMMA-*b*-*d*PnBMA (25-25); (c) PMMA-*b*-PnBMA (25-35); (d) PMMA-*b*-*d*PnBMA (25-38); (e) PMMA-*b*-PnBMA (25-53); (f) PMMA-*b*-*d*PnBMA (25-54).

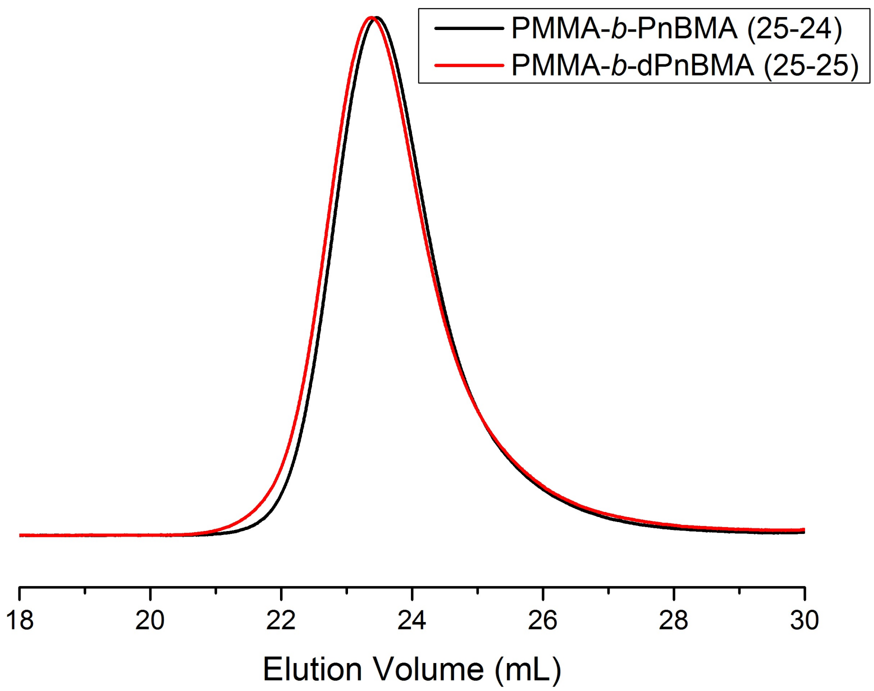

Figure S2. Normalized SEC traces (refractive index detector) of PMMA-*b*-PnBMA (25-24) and PMMA-*b*-*d*PnBMA (25-25). THF was used as an eluent at a flow rate of 1.0 mL/min.

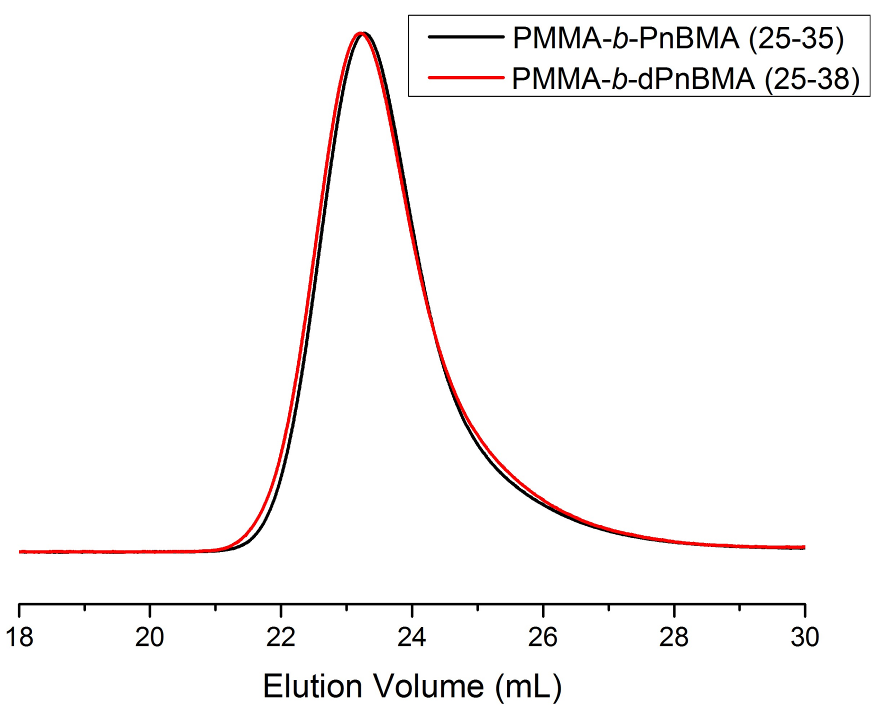

Figure S3. Normalized SEC traces (refractive index detector) of PMMA-*b*-PnBMA (25-35) and PMMA-*b*-*d*PnBMA (25-38). THF was used as an eluent at a flow rate of 1.0 mL/min.

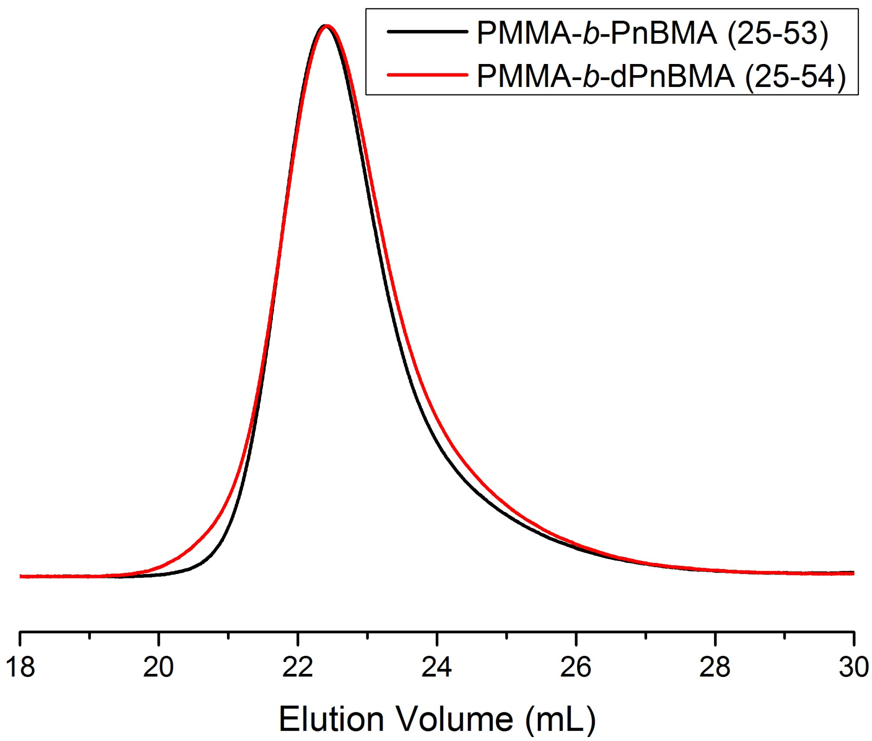

Figure S4. Normalized SEC traces (refractive index detector) of PMMA-*b*-PnBMA (25-53) and PMMA-*b*-*d*PnBMA (25-54). THF was used as an eluent at a flow rate of 1.0 mL/min.

Determination of monomeric friction coefficient for PnBMA.

According to the Rouse model, the monomeric friction coefficient (ζ) can be estimated by

$$\zeta = \frac{36 M_0 \eta_0}{\rho N_A N b^2} \tag{S1}$$

in which M_0, η_0, ρ, N_A, N and b are the molar mass of the monomer, zero-shear viscosity of an unentangled polymer, density, Avogadro number, degree of polymerization, and the statistical segment length, respectively.[1] For PnBMA, M_0 = 142 g/mol, ρ = 1.07 g/cm^3 and b = 6.1 Å. Therefore, by measuring the zero-shear viscosity of PnBMA at different temperatures, we are able to calculate the monomeric friction coefficient at these temperatures, and thereby obtain a WLF-type relationship for ζ and temperature. The WLF equation is given below:

$$\log(\zeta / \zeta_{\mathrm{ref}}) = -\frac{C_1(T - T_{\mathrm{ref}})}{C_2 + (T - T_{\mathrm{ref}})} \tag{S2}$$

We conducted the dynamic viscosity measurement on a 45 kg/mol PnBMA homopolymer, using an ARES rheometer. As can be seen from Figure S5a, the G' and G'' indicate that there is at most weak entanglement in this sample, therefore, PnBMA has a Rouse-like rheological behavior even at this molecular weight. In Figure

S5b, the zero-shear viscosity, η_0, was obtained by extrapolating these dynamic viscosity data to $\omega = 0$; then ζ at 90, 100, 110, 120 and 150 °C was calculated on the basis of eq. S1 (the result is given in Table S1). We select 110 °C (383K) as the reference temperature (T_{ref}), and fit $\log(\zeta/\zeta_{ref})$ to eq. S2. The fitting gives $C_1 = 10.1$ and $C_2 = 191$ ºC (Figure S5c).

In the study of chain exchange kinetics, we are interested in ζ at 65 °C. With the C_1 and C_2 obtained from fitting, $\zeta(65°C) = 7.1\times10^{-4}$ N-s/m, which has the same magnitude as the value reported by Ferry, *et al.*[1, 2, 3]

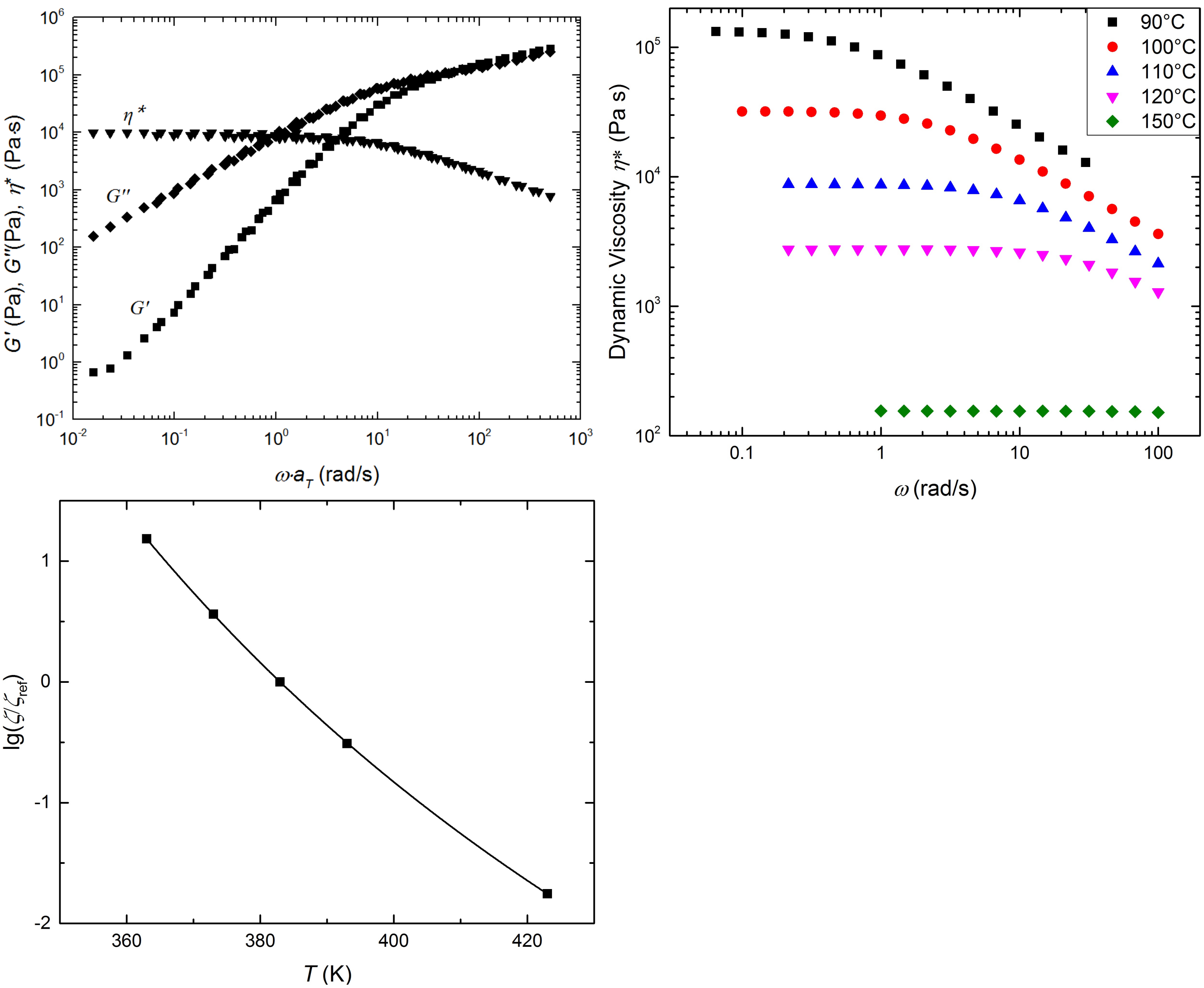

Figure S5. (a) Storage modulus (G'), loss modulus (G''), and dynamic viscosity (η^*) after time-temperature superposition, with $T_{ref} = 383$K. (b) Dynamic viscosity (η^*) of PnBMA (45K) as a function of frequency at various temperatures. (c) The monomeric friction coefficient (ζ) relative to the one at reference temperature (ζ_{ref}) for PnBMA as a function of temperature. $T_{ref} = 383$ K, and the solid line is the best fit to the WLF equation.

Table S1. Zero-shear viscosity and monomeric friction coefficient of PnBMA (45K) at different temperatures.

T (K)	η_0 (Pa-s)	ζ (N-s/m)	ζ/ζ_{ref}
363	1.33×10^{5}	8.4×10^{-6}	1.5×10^{1}
373	3.19×10^{4}	2.0×10^{-6}	3.6
383	8.74×10^{3}	5.5×10^{-7}	1
393	2.76×10^{3}	1.7×10^{-7}	3.1×10^{-1}
423	1.55×10^{2}	9.7×10^{-9}	1.8×10^{-2}

References

1. Ferry, J. D. *Viscoelastic Properties of Polymers (3rd Ed)*, Wiley: New York, 1980; pp 328-343.

2. Ferry, J. D.; Landel, R. F. Molecular Friction Coefficients in Polymers and Their Temperature Dependence. *Kolloid-Zeitschrift* **1956**, *148*, 1-6.

3. Meyer, H. H.; Mangin, P.-M. F.; Ferry, J. D. Dynamic Mechanical Properties of Poly(n-Butyl Methacrylate) Near Its Glass Transition Temperature. *J. Polym. Sci.: Part A* **1965**, *3*, 1785-1792.