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Difference in Lower Critical Solution Temperature Behavior between Random Copolymers and a Homopolymer Having Solvatophilic and Solvatophobic Structures in an Ionic Liquid[†]

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The solubility and phase behavior of poly(benzyl methacrylate) (PBzMA) and poly(styrene-*co*-methyl methacrylate) (P(St-*co*-MMA)) in a hydrophobic ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethane sulfone)imide ([C$_2$mim][NTf$_2$]), have been explored as a function of temperature. Although both polymers have solvatophobic phenyl groups and solvatophilic methacrylate groups in the structure, their distribution on the polymer chains is quite different. In PBzMA, both structures are incorporated in each monomer unit, whereas in P(St-*co*-MMA)s the distribution is statistically determined by the monomer reactivity ratio of St and MMA. Both polymer solutions in [C$_2$mim][NTf$_2$] become turbid with an increase in temperature (lower critical solution temperature (LCST) behavior). The turbidity change occurs sharply at 100 °C for PBzMA, whereas it is sluggish for P(St-*co*-MMA)s. The LCST-type phase-separation temperature for P(St-*co*-MMA)s decreases with an increase of the St composition. The sluggish phase separation for P(St-*co*-MMA)s has been explained in terms of the presence of the MMA sequences along the polymer chain, which inhibits the St aggregation to a certain extent. The dynamic light scattering (DLS) measurements for PBzMA reveal that the hydrodynamic radius of PBzMA suddenly changes at 100 °C; below this temperature, no aggregation is observed. This result strongly implies that the coil-to-collapse transition is of the first-order type. It has been demonstrated that the LCST-type phase separation of the polymers in an ionic liquid is greatly affected by the distribution of the solvatophilic and solvatophobic groups on the polymer chains.

Introduction

Ionic liquids (ILs) are comprised entirely of ions, and they exist as liquid at ambient temperature.[1−4] ILs have attracted considerable attention because of their unique properties such as nonvolatility, nonflammability, and thermal and chemical stability. Recent fundamental studies on ILs have focused not only on the physicochemical properties of ILs themselves[5−7] but also on their mixtures with other solvents.[8−13] Extensive studies on the IL mixtures with either water or alcohols have been conducted in order to use them in the separation of processes. For example, Brennecke and co-workers[8a,b] claimed that the upper critical solution temperature (UCST) of ILs and alcohol mixtures was strongly affected by their chemical structures, particularly, the alkyl chain length of alcohol and imidazolium cations and the hydrogen-bonding ability. Therefore, the importance of van der Waals dispersion interaction between the alkyl chains of cations and alcohol, in addition to Coulombic force, was suggested. Wasserscheid and co-workers[8d] have given great importance to the performance of organic liquid phase-separable catalytic reactions using an IL medium. Rebelo, Seddon, and co-workers have reported the LCST (lower critical solution temperature)-type phase separation of IL solutions.[10] They found experimental results on the unique liquid-phase

diagrams of closed-loop-type one-phase region coexisting with UCST-type phase separation and of "hourglass"-type phase separation for the quasi-binary mixtures of chlorinated organic solvents and imidazolium-type ILs.[10a]

On the other hand, ILs in polymer systems have also attracted much attention.[14] Syntheses of polymers in ILs have been a subject of interest.[15] ILs have also been used as solvents for polymers with a view to enhancing the ion transport dynamics of the polymer electrolyte materials.[16] Our group has been concerned with this study,[17] paying special attention to the electrochemically task-specific properties.[18−20] Research on the solubility and phase behavior of a polymer solution in ILs appears to be another challenging field[21] in terms of enriching our knowledge of polymer solution chemistry and fabricating future materials by using the phase transition of polymers and ILs. Recently, Lodge and co-workers demonstrated the formation of supramolecular assembly of block copolymers in the IL solutions.[22] A small-angle neutron scattering study by Triolo and co-workers clearly revealed that 1-butyl-3-methylimidazolium tetrafluoroborate ([C$_4$mim][BF$_4$]) behaved as a good solvent for deuterated poly(ethylene oxide).[23] We have also reported the phase behavior of polymers and polymer gels in ILs.[24] Poly(*N*-isopropylacrylamide) (PNIPAm), which undergoes LCST-type phase separation in aqueous solutions with a change in the temperature, demonstrates a completely opposite phase behavior (UCST-type phase separation) in 1-ethyl-3-methylimidazolium bis(trifluoromethane sulfone)imide ([C$_2$mim][NTf$_2$]).[24a] Most recently, it has been found that poly(benzyl methacrylate)
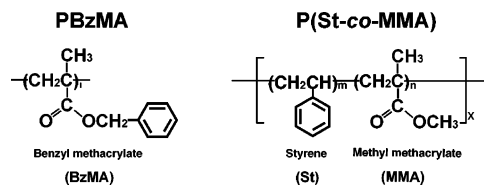
LCST Behavior of Random Copolymers and a Homopolymer

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SCHEME 1: Chemical Structure of Poly(benzyl methacrylate) (PBzMA) and Poly(styrene-*co*-methyl methacrylate) (P(St-*co*-MMA))

(PBzMA) and its gels exhibit LCST-type phase behavior in ILs.[24b] The studies of the behavior of polymers in ILs are only at the early stage, although they are rich in chemistry as demonstrated above.

In this paper, we report the difference in LCST behavior in an IL between random copolymers and a homopolymer having solvatophilic and solvatophobic structures. Methacrylate and phenyl groups are found to be solvatophilic and solvatophobic, respectively, to a hydrophobic IL, $[C_2mim][NTf_2]$.[17c,21a,24b] Therefore, the random copolymers, consisting of styrene (St) and methyl methacrylate (MMA) (P(St-*co*-MMA)s), and PBzMA have amphiphilicity toward $[C_2mim][NTf_2]$, where P(St-*co*-MMA)s have statistical sequence of the solvatophilic and solvatophobic structures along the polymer chains and PBzMA has both structures in the same repeating unit (Scheme 1). It would be interesting to know the difference in the solubility and phase behavior between these two series of polymers in $[C_2mim][NTf_2]$. In this study, the solubility and phase behavior of PBzMA and P(St-*co*-MMA)s in $[C_2mim][NTf_2]$ have been explored as a function of temperature.

Experimental Section

Preparation and Characterization of Materials. $[C_2mim]$-$[NTf_2]$ was prepared and characterized according to the procedure reported earlier. [6b,18b,25] PBzMA was purchased from Across. On the basis of gel permeation chromatography (GPC) using tetrahydrofuran (THF) as the carrier solvent and Tosoh columns calibrated by PSt standards, the number average molecular weight (M_n) and the polydispersity index (M_w/M_n, where M_w is the weight average molecular weight) were found to be 28.3 kDa and 2.76, respectively. Copolymerization of St with MMA was carried out according to the following procedure. St and MMA maintaining the appropriate molar ratios were dissolved in benzene, where the total monomer concentration was fixed at 2 M. The monomer solution was deaerated by purging N_2 for 20 min. Radical polymerization was carried out by heating for 12 h in the presence of 1 mol % 2,2′-azobis-(isobutyronitrile) as the initiator. The products were purified by the reprecipitation method three times using toluene as a good solvent and hexane as a poor solvent. The obtained precipitates were collected and dried under reduced pressure. All the copolymers were characterized by ^{1}H NMR, and the copolymer compositions were calculated by elemental analysis, as shown in the Supporting Information (SI). The M_n and M_w/M_n values of the copolymers determined by GPC are also shown in SI. Polymer−IL solutions were prepared using THF as the cosolvent, followed by evaporation.

Turbidity and Solubility Measurements for Polymers in IL. A drop of the polymer/$[C_2mim][NTf_2]$ solutions (3 wt %) was placed onto a concave glass slide and covered with a cover glass. The glass slide was set onto a hot stage (Imoto), enabling the temperatures to be controlled up to 400 °C. An Ocean Optics USB 2000 fiber optic spectrometer was used with a tungsten halogen lamp (Ocean Optics, Inc. LS-1) as a light source. The

temperature was changed in steps of 0.2 °C, and the transmittance of the polymer/$[C_2mim][NTf_2]$ solutions was monitored at 500 nm after waiting for 4 min to observe the turbidity of the solution. Almost no hysteresis in the transmittance was observed at this rate. The solubility of P(St-*co*-MMA)s (3 wt %) in $[C_2mim][NTf_2]$ was also judged by the naked eye.

Refractive Index Measurements. The refractive index of $[C_2mim][NTf_2]$ was measured using an Abbe refractometer NAR-1T attached with a thermostatic bath that allows the temperature to be controlled between 10 and 50 °C. To estimate the refractive indices above 50 °C, the analytical curve was estimated by using the refractive indices in the temperature range 10−50 °C, and those above 50 °C were calculated by extrapolation of the curve.

Dynamic Light Scattering. DLS measurements were carried out using a DLS/ SLS-5000 compact goniometer (ALV, Langen, Germany) coupled with an ALV photon correlator. A 22-mW He−Ne laser (Uniphase Co. Ltd., U.S.A.) was used as the light source. The wavelength of the light in vacuum is $\lambda = 632.8$ nm. Although the laser power was relatively weak, the output photon-count rate was enhanced about 50 times as compared to the conventional pinhole system used in our laboratory. This was achieved by employing a set of static and dynamic enhancers (devices to enhance the photon counting rate) and a high quantum efficient avalanche photodiode detection system. The time correlation function, $g^{(2)}(\tau)$, is obtained by taking time correlation of the scattering intensity, where τ is the decay time. The characteristic decay time distribution function $G(\Gamma^{-1})$ was obtained from $g^{(2)}(\tau)$ using an inverse Laplace transform program (a constrained regularization program, CONTIN, provided by ALV).[26] Here, Γ is the decay rate. The scattering angle range was 90°. The observation temperature was varied from 30 to 100 °C with a precision of ± 0.1 °C. In this temperature range, polymer−IL solutions used for the DLS measurements remained light-scattering transparent, indicating that the multiple scattering did not occur. At above 100 °C, the DLS measurements were not carried out because the solutions became opaque and strong multiple scattering was observed.

Results and Discussion

Turbidity and Solubility Change of Polymers in $[C_2mim]$-$[NTf_2]$ with Temperature. A PMMA solution (3 wt %) in $[C_2mim][NTf_2]$ remained transparent independent of temperature (30−300 °C). On the other hand, PSt was phase-separated from $[C_2mim][NTf_2]$ and did not completely dissolve in it (3 wt %). Figure 1 shows the change in the turbidity (transmittance at 500 nm) of PBzMA and P(St-*co*-MMA) solutions (3 wt %) in $[C_2mim][NTf_2]$, where 100% transmittance indicates that the solution is transparent and the decrease indicates that the solution becomes turbid because of phase separation. It is interesting to note that both PBzMA and P(St-*co*-MMA) solutions become turbid with an increase in temperature (LCST-type phase separation). It has been reported that certain aromatic solvent (benzene, toluene, α-methylstyrene, xylene)/IL binary systems undergo LCST-type phase separation.[9,10] When solutes having phenyl groups are polymers (PSt), the dissolution of the solutes in $[C_2mim][NTf_2]$ became less favorable compared with the monomeric solutes and PSt did not dissolve in it. By introducing the solvatophilic methacrylate structure into the polymers, PBzMA and P(St-*co*-MMA)s appear to dissolve in $[C_2mim]$-$[NTf_2]$ and to exhibit the LCST-type phase separation at elevated temperatures.

As can be seen from Figure 1, the temperature at which a P(St-*co*-MMA) solution starts to become turbid shifts to lower
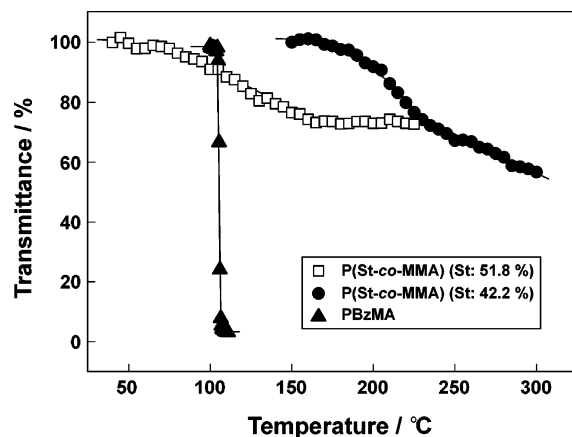
Figure 1. Temperature dependence of transmittance at 500 nm for polymer/[C$_2$mim][NTf$_2$] solutions (3 wt %). Black triangle: PBzMA (M_n = 28.3 kDa, M_w/M_n = 2.76); white square: P(St-*co*-MMA) (St composition: 51.8%, M_n = 27.1 kDa, M_w/M_n = 1.57); black circle: P(St-*co*-MMA) (St composition: 42.2%, M_n = 23.9 kDa, M_w/M_n = 2.61).
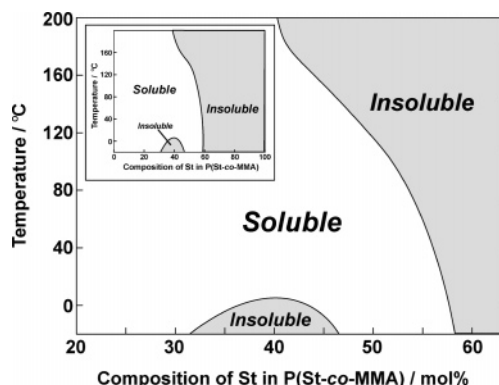

Figure 2. Solubility diagram for P(St-*co*-MMA)s (3 wt %) in [C$_2$-mim][NTf$_2$]. The gray region indicates that the solution is turbid, whereas the white region indicates the solution is transparent (soluble).
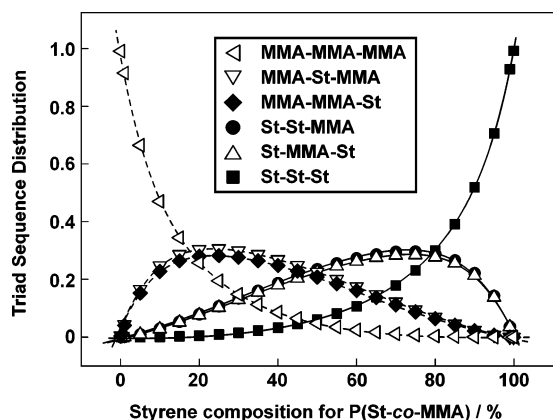

Figure 3. Triad sequence distribution for P(St-*co*-MMA)s as a function of the St composition.

temperature with an increase of the St composition. Figure 2 shows the solubility diagram for P(St-*co*-MMA)s, determined by the naked eye, as a function of the St composition. The copolymers with higher St composition than 0.6 do not dissolve in [C$_2$mim][NTf$_2$] in the temperature range shown in Figure 2. In the composition range from about 40 to 60 mol %, the LCST behavior is seen and the phase separation temperature becomes lower with an increase of the St composition, consistent with the results in Figure 1. The copolymers with the St composition lower than about 30 mol % are soluble independent of the
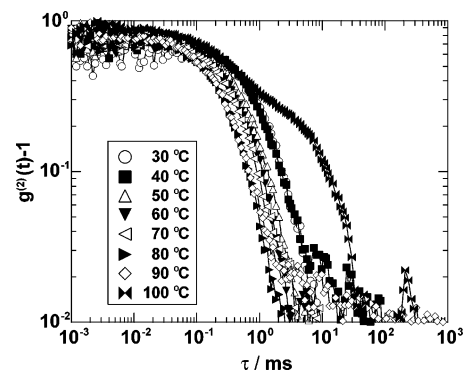

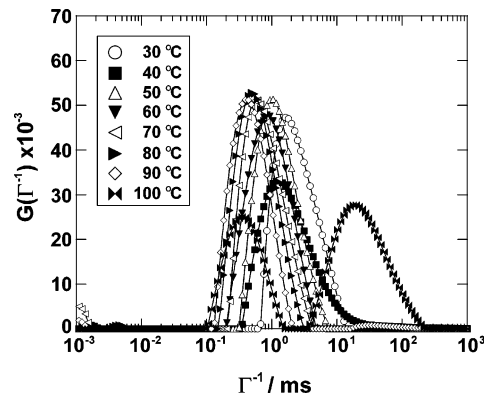**Figure 4.** Temperature dependency of $g^{(2)}(\tau)$ for PBzMA (3 wt %) in [C$_2$mim][NTf$_2$].

Figure 5. Temperature dependency of $G(\Gamma^{-1})$ for PBzMA (3 wt %) in [C$_2$mim][NTf$_2$].

temperature, as seen for PMMA. Interestingly, the P(St-*co*-MMA)s with the St composition of about 32−45 mol % exhibit a UCST-type behavior. Consequently, the copolymers with the 42.2 and 45.6 mol % St compositions exhibit both LCST- and UCST-type solubility behaviors.

The LCST-type behavior in the PBzMA and P(St-*co*-MMA) solutions in [C$_2$mim][NTf$_2$] appears to be correlated with the presence of solvatophobic phenyl groups. One prerequisite for inducing an LCST-type phase separation is the structuring effect of the solution, which is responsible for decreasing the entropy of the solution. Aromatic solvents including benzene, toluene, and α-methylstyrene have been found to exhibit an LCST-type phase behavior in the imidazolium ILs.[9,10] It is also claimed that a clathrate phase formation was observed in the imidazolium-based IL−aromatic mixtures for the IL-rich phases.[11,12] It is considered that there exist associative interactions between the aromatic molecules and the salt ions, which separate the cation−anion packing interaction to a sufficient degree such that localized cage structures can be formed.[11,12] On the basis of these observations in the IL/solvent systems, it is speculated that the phenyl groups in PBzMA and P(St-*co*-MMA)s induce certain ordered structures when they are dissolved in [C$_2$mim]-[NTf$_2$]. With an increase of temperature the entropic effect causes desolvation (LCST behavior).

Figure 1 also indicates that the decrease in the transmittance with an increase in temperature is quite sharp for PBzMA, whereas it is sluggish for P(St-*co*-MMA)s. Since the measurements were conducted under the same rate of temperature change, this difference can be attributed to the difference in the aggregation kinetics between these polymers. Although both polymers have solvatophilic methacrylate and solvatophobic phenyl groups in their structures, their distributions on the polymer chains are quite different. In PBzMA both structures
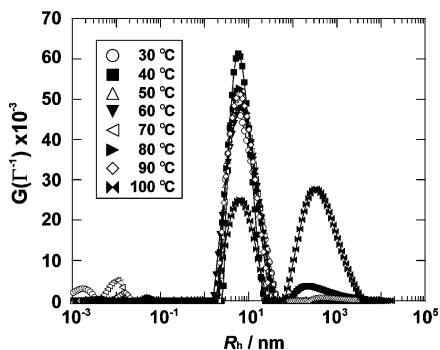
Figure 6. Distribution of the hydrodynamic radius (R_h) of PBzMA (3 wt %) in [C$_2$mim][NTf$_2$] at different temperatures.
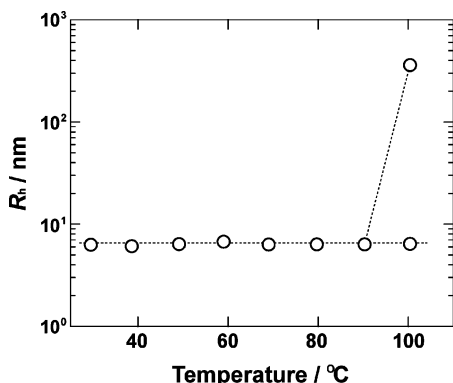

Figure 7. The hydrodynamic radius (R_h) of PBzMA (3 wt %) in [C$_2$-mim][NTf$_2$] as a function of temperature.

are incorporated in each monomer unit, whereas in P(St-*co*-MMA)s the distribution is statistically determined by the monomer reactivity ratio of St and MMA. Figure 3 shows the triad sequence distribution curve for P(St-*co*-MMA)s, calculated by Wall's method[27] based on the monomer reactivity ratio for the copolymerization (M$_1$ = St, M$_2$ = MMA: r_1 = 0.52, r_2 = 0.46). It can be seen that in P(St-*co*-MMA)s with the St compositions of 42.2 and 51.8 mol %, there exist about 5−10% MMA triads and about 20−30% MMA diads. With increasing temperature, the St units start to aggregate due to the desolvation from [C$_2$mim][NTf$_2$], but the MMA sequences can still be soluble at higher temperatures. In other words, the MMA sequences inhibit the St aggregation to a certain extent, resulting in a very sluggish turbidity change. We do not envisage the formation of structurally ordered entities, such as micelles, at the higher temperatures, because P(St-*co*-MMA)s are random copolymers from the monomers with similar monomer reactivity ratios and the MMA and St triad ratios are only 5−10% for the copolymers studied in Figure 1. In aqueous polymer solutions, the phase-separation temperature of PNIPAm is known to be controlled by the copolymerization; however, a loss of sharpness in the phase separation has been observed.[28] On the other hand, the desolvation of the phenyl groups in PBzMA from [C$_2$mim]-[NTf$_2$] leads to a cooperative aggregation of the polymer chains.

Temperature Dependency of DLS for PBzMA in [C$_2$mim]-[NTf$_2$]. To understand the sharp phase separation dynamics of PBzMA (3 wt %) in [C$_2$mim][NTf$_2$], temperature-dependent DLS measurements were conducted. Figure 4 shows $g^{(2)}(\tau)$ for PBzMA. At 30 °C, a characteristic decay is observed at $\tau \approx 3$ ms. The decay shifts toward the lower τ-region with increasing temperature. However, a completely different behavior is observed at 100 °C. The results of the CONTIN analysis clearly reveal an interesting temperature variation of the dynamics of PBzMA in [C$_2$mim][NTf$_2$]. Figure 5 shows the results of the

CONTIN analysis of $g^{(2)}(\tau)$. Here, $G(\Gamma^{-1})$ is plotted as a function of the characteristic decay time Γ^{-1}. A single peak is observed in $G(\Gamma^{-1})$, and it shifts toward the lower τ-region with increasing temperature. However, it suddenly splits into two peaks at 100 °C, indicating a phase separation. It is interesting to note that the PBzMA/[C$_2$mim][NTf$_2$] mixture remained transparent at 100 °C for at least 30 min after the $G(\Gamma^{-1})$ peak with a higher τ (10^1−10^2 ms) had started to appear.

The diffusion coefficient (D) is obtained from the peak of $G(\Gamma^{-1})$ with $D = \Gamma/q^2$ or by analyzing $g^{(2)}(\tau)$ on the basis of the following equation:

$$D = -\lim_{\tau \to 0} \frac{d}{d\tau}[g^{(2)}(\tau) - 1] \tag{1}$$

where q is the momentum transfer given by

$$q = \frac{4\pi n}{\lambda}\sin\left(\frac{\theta}{2}\right) \tag{2}$$

where n is the refractive index of the solvent, and θ is the scattering angle. The hydrodynamic radius (R_h) of the polymer chains in a solution can be evaluated via the Stokes−Einstein equation, that is,

$$R_h = \frac{kT}{6\pi\eta D} \tag{3}$$

where k is the Boltzmann constant, and η is the solvent viscosity. Since both η and n are functions of temperature, these parameters should be evaluated in advance. The temperature dependence of the viscosity for [C$_2$mim][NTf$_2$] is in accordance with the VFT equation, as previously reported.[6a] The temperature dependence of n for [C$_2$mim][NTf$_2$] (Figure 1 in SI) can be expressed as follows:

$$n = 1.40 + 0.0318 \times \exp(-0.0189T[°C]) \tag{4}$$

By taking into account the data mentioned above, we evaluated the temperature variation of R_h for PBzMA in [C$_2$-mim][NTf$_2$], which is shown in Figures 6 and 7. Figure 6 shows the distribution of R_h of PBzMA in [C$_2$mim][NTf$_2$] at different temperatures. As shown in Figure 7, R_h is about 6.1 nm and remains unchanged irrespective of T up to 100 °C. However, large aggregates appear suddenly at 100 °C (Figures 6 and 7). The size of the aggregates is estimated to be 310 nm. In this system, macroscopic phase separation occurs without a gradual aggregation of each polymer. The weight fraction of the slower component, that is, the aggregate, is evaluated to be approximately 4.5 wt % using the method reported elsewhere.[29] As a result, we observed that a PBzMA/[C$_2$mim][NTf$_2$] single phase suddenly aggregated to form a turbid solution at a certain temperature, while R_h of PBzMA in [C$_2$mim][NTf$_2$] did not change with increasing temperature before the phase separation.

This type of temperature variation of R_h is consistent with the transmittance change with temperature for the PBzMA/[C$_2$-mim][NTf$_2$] solution, as shown in Figure 1. Moreover, we have already studied the equilibrium swelling ratio of the cross-linked PBzMA gel in [C$_2$mim][NTf$_2$] and have observed that this gel changes its volume in a discontinuous manner.[24b] These experimental observations would suggest that such phase changes could be expressed as a first-order phase transition. A discrete coil-to-collapse transition takes place at about 100 °C in the PBzMA/[C$_2$mim][NTf$_2$] system, resulting in a discrete change in the transmittance as well as the swelling ratio. In contrast, the sluggish aggregation for P(St-*co*-MMA) in [C$_2$-mim][NTf$_2$] with an increase in temperature suggests that the

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homogeneous phase of P(St-*co*-MMA)/[C₂mim][NTf₂] solutions does not change suddenly as observed in the PBzMA/[C₂mim]-[NTf₂] solution, even in a molecularly microscopic region.

Supporting Information Available: Characterization results of P(St-*co*-MMA), phase separation temperature of P(St-*co*-MMA) determined by the naked eye, and temperature dependence of refractive index of [C₂mim][NTf₂]. This material is available free of charge via the Internet at http://pubs.acs.org.

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