

Thermodynamic study on phase transitions of poly(benzyl methacrylate) in ionic liquid solvents*

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Abstract: The lower critical solution temperature (LCST) phase behavior of poly(benzyl methacrylate) (PBnMA) in room-temperature ionic liquids (ILs) was studied by considering the effect of the chemical structure of ILs on the phase separation temperature (T_c). It was found that the LCST behavior of PBnMA was observed in ILs containing [NTf₂]⁻ anions and PF₆⁻ anions. T_c changed significantly with a small change in the chemical structures of the cations. High-sensitivity differential scanning calorimetry (DSC) was successfully performed for studying the LCST phase separation of PBnMA in two different imidazolium-based ILs. Endothermic peaks corresponding to the phase separation of PBnMA from the ILs were clearly observed at ca. 100 °C in the DSC thermograms. It was experimentally verified for the first time that the negative enthalpy and entropy change of mixing of PBnMA in ILs caused the LCST phase separations. The absolute values of the thermodynamic parameters for the phase transition of PBnMA in ILs obtained in this study were much lower than those reported in previous studies for aqueous polymer solutions that exhibit LCST phase behavior, such as poly(*N*-isopropylarylamide) and poly(vinyl methyl ether). Small changes in the thermodynamic parameters resulted in a large change in the phase separation temperature even by small changes in the chemical structure of the ILs and polymers. The microscopic desolvation process detected from the DSC measurements was inferred to have occurred before the macroscopic phase separation detected from turbidity measurements. The dependence of the endothermic peak temperatures on the DSC scan rate was observed even at slow scan rates. These results indicate that the phase separation of PBnMA from ILs is characterized by extremely slow kinetics.

Keywords: high-sensitivity DSC; ionic liquids; lower critical solution temperature; phase transition; poly(benzyl methacrylate).

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INTRODUCTION

Ionic liquids (ILs) are of great interest as a promising new class of solvents owing to their unique properties such as non-flammability, negligible volatility, high ionic conductivity, and a wide electrochemical window [1]. We have been interested in macromolecules in ILs from the viewpoint of materials science; our previous papers were the first to report certain mixtures of polymers and ILs that showed phase transitions with changing temperature [2,3]. In particular, poly(benzyl methacrylate) (PBnMA) and related copolymers exhibit lower critical solution temperature (LCST) phase separation in ILs [2b], typically in 1-ethyl-3-methylimidazolium bis(trifluoromethane sulfonyl)imide [C₂mim][NTf₂]; this behavior of PBnMA is similar to the phase behavior of poly(*N*-isopropylacrylamide) (PNIPAm) in aqueous solutions [4]. The phase behaviors of ILs with organic solvents have also been explored; such mixtures are expected to find application in separation and extraction processes [5]. Rebelo et al. were the first to report the LCST phase behavior of mixtures of aromatic compounds and ILs [6]. These authors also noted the formation of a liquid clathrate between an aromatic compound and an IL due to cation- π interaction [7]. In contrast, the upper critical solution temperature (UCST) phase transitions of PNIPAm in an IL have also been found [2a] and have attracted considerable interest because the phase behavior of PNIPAm in an IL is completely different from that of PNIPAm in aqueous solutions. Lodge et al. successfully demonstrated the synthesis of a thermoprocessable gel with high ionic conductivity via the self-assembly of triblock copolymers; they employed the UCST phase transitions of PNIPAm in an IL [8]. Information on the phase transition of polymers and their gels in ILs can be used for preparing smart materials with a wide usable temperature range since this reversible phenomenon can be observed even in an open atmosphere as solvent evaporation does not occur. However, the characterization of such phase transitions of polymers in ILs is elementary.

The LCST phase transition of a polymer is a relatively rare phenomenon in media other than water since it is accompanied by a negative enthalpy change (ΔH_{mix}) and a negative entropy change (ΔS_{mix}) upon mixing with the solvent. The LCST phase separation occurs when the entropy contribution ($\Delta S_{\text{mix}}T$) to the Gibbs energy change (ΔG_{mix}) exceeds ΔH_{mix} . In the case of aqueous polymer solutions, hydrophobic hydration is considered to play an important role in decreasing both enthalpy and entropy of the solutions with mixing. When a hydrophobic group is introduced in water, water molecules form a clathrate-like ordered structure around the hydrophobic group, leading to a decrease in the mixing entropy. PNIPAm consists of hydrophilic acrylamide groups and hydrophobic isopropyl groups [4]. Similarly, PBnMA in [C₂mim][NTf₂] consists of solvophilic methacrylate groups and solvophobic benzyl groups; this feature motivated us to study the phase behavior of a PBnMA/IL system. Consequently, we observed LCST phase transition in the PBnMA/IL system. Further investigation of the phase behavior of random copolymers of styrene and methyl methacrylate [P(St-*r*-MMA)], consisting of functional groups similar to PBnMA, confirmed that certain P(St-*r*-MMA)s also exhibited LCST phase separation in [C₂mim][NTf₂] [2c]. This result clearly indicates the importance of the coexistence of both structure-forming aromatic groups and solvophilic methacrylate groups in the polymer structure for LCST phase separation to occur. More recently, we reported LCST phase separations for a polyether, poly(ethyl glycidyl ether) (PEGE), in ILs [2d]. ¹H NMR spectroscopic measurements of a PEGE/[C₂mim][NTf₂] binary system revealed that hydrogen bonds between the protons of [C₂mim] cations and the oxygen atoms of PEGE play a crucial role in decreasing the entropy of the solution [2d], which appears to be different from the factors affecting the mixing entropy of the PBnMA/IL system. The experimental results of LCST phase behavior of polymers in water and in ILs indicate that “structure-forming liquids”, into which both the liquids are classified, are essential for such phase behavior.

In contrast to the similarity in the phase behaviors of aqueous and IL solutions, there is a distinct difference between the LCST phase behavior in water and in ILs. Figure 1a shows the LCST phase separation temperatures (T_c 's) of aqueous solutions of PNIPAm, random copolymers of NIPAm with dimethyl acrylamide [P(NIPAm-*r*-DMAAm)], and random copolymers of NIPAm with butyl meth-

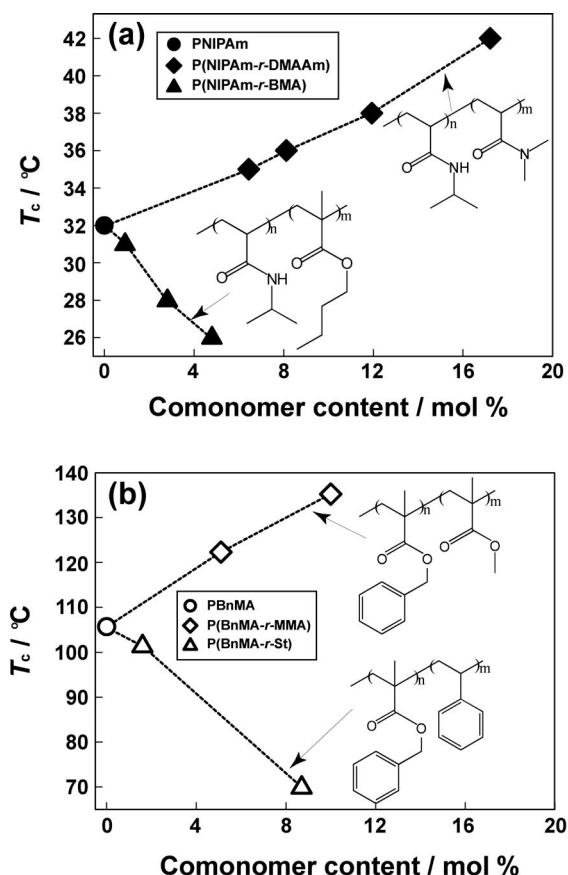


Fig. 1 (a) LCST phase separation temperature (T_c) for PNIPAm copolymers in water as a function of the comonomer content. Filled circle: PNIPAm; filled diamond: random copolymers P(NIPAm-*r*-DMAAm); filled triangle: random copolymers with P(NIPAm-*r*-BMA). All the data were obtained from ref. [9]. (b) T_c of PBnMA copolymers in $[C_2mim][NTf_2]$ as a function of the comonomer content. Open circle: PBnMA; open diamond: random copolymers with P(BnMA-*r*-MMA); open triangle: random copolymers with P(BnMA-*r*-St).

acrylate [P(NIPAm-*r*-BMA)] as a function of the comonomer content [9]. T_c increases with the amount of hydrophilic DMAAm, but decreases with an increase in the hydrophobic BMA comonomer content. As seen in Fig. 1a, T_c of PNIPAm increases and decreases by 5 °C when it is copolymerized with ca. 10 mol % of hydrophilic DMAAm and hydrophobic BMA, respectively. In sharp contrast, much larger T_c changes are observed in an IL when PBnMA is copolymerized with MMA, P(BnMA-*r*-MMA), or St, P(BnMA-*r*-St), as shown in Fig. 1b [2b]. PMMA and PSt are completely compatible and incompatible in $[C_2mim][NTf_2]$, respectively. Therefore, random copolymerization with MMA increases T_c of PBnMA, while copolymerization with St lowers T_c of PBnMA. The magnitude of the change reaches 30 °C when PBnMA is copolymerized with ca. 10 mol % of MMA or St. It is thus apparent that T_c of PBnMA and related polymers in ILs changes to a great extent for even a small change in the chemical structures of the polymers. The influence of the chemical structures of ILs on T_c should also be studied since ILs with the desired solvent property can be obtained by choosing the appropriate chemical structures of cations and anions and by selecting suitable combinations of ILs.

In this paper, the phase behaviors of PBnMA in different ILs are presented in detail. On the basis of the result, a thermodynamic study of the LCST phase behavior of PBnMA in an IL solvent is carried out. Although many studies have reported the thermodynamic properties of the LCST phase behavior

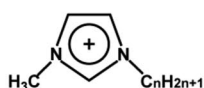
of aqueous polymer solutions [10–12], no study has reported the thermodynamic properties of polymer/IL solutions. Differential scanning calorimetry (DSC) is a useful and powerful tool for determining the basic thermodynamic properties and phase behavior of polymer solutions. The use of a custom-made DSC [13] allows us to determine the thermodynamic properties of the LCST phase behavior of PBnMA in ILs. We present the first experimental evidence for negative ΔH_{mix} and negative ΔS_{mix} of mixing of PBnMA when it is mixed in ILs. Further, the extremely slow kinetics of the phase change of PBnMA in an IL is discussed; such a discussion is possible because the DSC is designed to scan temperatures at an extremely slow rate.

EXPERIMENTAL

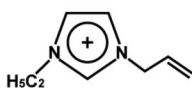
Synthesis and characterization of materials

The chemical structure and abbreviation of the ILs investigated in this study are shown in Scheme 1. $[\text{C}_n\text{mim}][\text{NTf}_2]$ ($n = 1, 2, 4, 6, 8$), $[\text{C}_n\text{mim}]\text{PF}_6$ ($n = 4, 6, 8$), $[\text{C}_4\text{mim}]\text{BF}_4$, $[\text{C}_4\text{mim}][\text{TfO}]$, $[\text{C}_4\text{mim}][(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}]$, $[\text{C}_4\text{py}][\text{NTf}_2]$, $[\text{bmpro}][\text{NTf}_2]$, $[\text{btma}][\text{NTf}_2]$, $[\text{C}_2\text{mim}][\text{DCA}]$, and

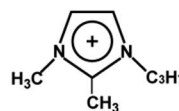
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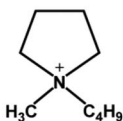
1-alkyl-3-methylimidazolium

[C_nmim]

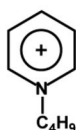
1-allyl-3-ethylimidazolium

[aeim]

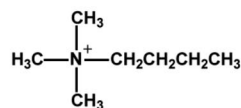
1,2-dimethyl-3-propylmethylimidazolium

[C₂dmim]

butylmethylpyrrolidinium

[bmpro]

1-butyl-pyridinium

[C₄py]

butyltrimethylammonium

[btma]

<Anion>

[NTf₂]

bis(trifluoromethanesulfonyl)imide

PF₆

hexafluorophosphate

[TfO]triflate
(trifluoromethanesulfonate)**BF₄**

tetrafluoroborate

CF₃COO

trifluoroacetate

N(SO₂C₂F₅)

bis(pentafluoroethanesulfonyl)imide

[DCA]

dicyanamide

SCN

thiocyanate

Scheme 1 Cation and anion structures of the ILs used in this study.

[C₂mim]SCN were synthesized and characterized by following a previously reported procedure [14,15]. [C_{*n*}mim][TfO] (*n* = 2, 6, 8) was purchased from Aldrich Fulka, and [C₂aem][NTf₂] was purchased from TCI. All the ILs were dried under high vacuum at 100 °C for 48 h. They were finally stored in an argon atmosphere glovebox (VAC, [O₂] < 1 ppm, [H₂O] < 1 ppm). PBnMA was purchased from Acros Organics. By means of gel permeation chromatography using tetrahydrofuran (THF) as the carrier solvent and Tosoh columns calibrated using 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) of the polymer were found to be 28.3 kDa and 2.76, respectively. PBnMA was dissolved in each IL used in this study. The polymer/IL solutions were prepared using THF as a cosolvent, and subsequently THF was evaporated. The final polymer concentration in the solution was 3 wt % for turbidity measurements and 5 wt % for DSC. The turbidity measurements for the polymer solutions were performed by employing a previously reported procedure [2b,c].

High-sensitivity differential scanning calorimetry

We use a custom-made high-sensitivity DSC of the heat-flux type. It is specifically constructed for the experiment by enhancing the sensitivity of the conventional DSC [13]. Thermoelectric modules are used for the heat-flux sensor (the Zeebeck effect) and heat pumps (the Peltier effect), and the system adopted for temperature regulation is a kind of predictive controller instead of a PID controller. In this system, the amount of current supplied to the Peltier elements to generate or remove heat is predicted both from the difference between the actual sample temperature and the set temperature and from the temperature history up to the beginning of temperature regulation.

The calorimeter can measure heat flows as small as 1×10^2 nW with a baseline fluctuation within 50 nW. This baseline stability, which corresponds to the sensitivity of the calorimeter, is about 50–60 times higher than that of commercially available calorimeters [13]. This apparatus is also designed to scan as slowly as 0.01 mK s⁻¹, if necessary; such a scanning rate enables us to follow an extremely slow thermal process. As the relaxation time of the apparatus is estimated to be about 2 s [12], the dynamics of thermal processes with relaxation times exceeding 2 s can be determined. Measurements can be made in either direction, i.e., during heating or cooling, by changing the direction of the current in the thermoelectric modules.

The sample was transferred into an aluminum vessel and hermetically sealed in a globe box under a dry N₂ atmosphere. The weights of the polymer/IL solutions used as samples in these measurements were typically 18 to 20 mg (the weight of PBnMA in the solutions was ca. 1 mg). The standard heating or cooling rate during the DSC measurements was 4 mK s⁻¹. In order to study the heating or cooling rate dependencies, the rate was varied from 0.5 to 4 mK s⁻¹.

RESULTS AND DISCUSSION

Effect of chemical structure of ILs on phase behavior of PBnMA

The solubility of PBnMA in 13 different ILs in the temperature range between 25 and 240 °C is examined in order to determine the effect of the chemical structure of the ILs on the phase behavior of PBnMA. The upper temperature limit is determined from the decomposition temperature of PBnMA, which is obtained to be around 250 °C from thermogravimetry. [C_{*n*}mim][TfO] (*n* = 2, 4, 6, 8), [C₄mim]BF₄, [C₈mim]BF₄, [C₄mim][(C₂F₅SO₂)₂N], [btma][NTf₂], [C₄mim]PF₆, [C₂mim][DCA], and [C₂mim]SCN are incompatible with PBnMA. In contrast, [C₈mim][NTf₂] and [C₄py][NTf₂] are completely compatible in the above-mentioned temperature range. Certain solutions of PBnMA in ILs with either [NTf₂] or PF₆ anions exhibit LCST phase separation. Figure 2 shows the relationship between *T_c* of 3 wt % PBnMA in each IL and the chemical structure of the cations. For ILs with [C_{*n*}mim] cations, *T_c* of PBnMA monotonically increases with the length of the alkyl chain attached to the imidazolium

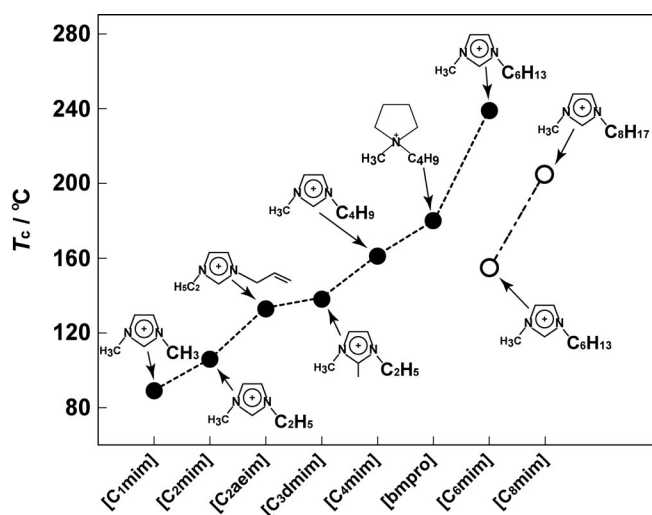


Fig. 2 Relationship between LCST phase separation temperature (T_c) of PBnMA and chemical structure of IL cations. Filled and open circles indicate ILs with $[\text{NTf}_2]$ anions and PF_6 anions, respectively.

cation. The T_c 's of PBnMA in $[\text{C}_1\text{mim}][\text{NTf}_2]$, $[\text{C}_2\text{mim}][\text{NTf}_2]$, $[\text{C}_4\text{mim}][\text{NTf}_2]$, and $[\text{C}_6\text{mim}][\text{NTf}_2]$ are determined to be 89, 105, 161, and 239 °C, respectively. A similar effect of the alkyl chain length on the compatibility of alcohol/IL mixtures has been reported by Brennecke and coworkers, although the effect was observed in UCST systems [5]. T_c of PBnMA/ $[\text{C}_3\text{dmim}][\text{NTf}_2]$ is between that of $[\text{C}_2\text{mim}][\text{NTf}_2]$ and that of $[\text{C}_4\text{mim}][\text{NTf}_2]$. This implies that the LCST phase behavior is not strongly affected by the hydrogen-bond-donating ability of the cations. This behavior is completely different from the LCST phase behavior of PEGE in an IL [2d], which is strongly dependent on the hydrogen-bond-donating ability of the cations. It is interesting to note that $[\text{bmpro}][\text{NTf}_2]$, whose cation is not aromatic, also exhibits LCST phase separation, thus indicating that the planarity or aromaticity of the cations does not affect the ability of ILs to form structures around the benzyl groups. It is clear from these results that T_c 's of PBnMA in ILs change significantly not only as a result of small changes in the polymer structure, as mentioned in the introduction, but also due to small changes in the IL structures. The following DSC studies reveal why such a large T_c change occurs in PBnMA/IL systems.

DSC measurements for LCST phase separation of PBnMA dissolved in $[\text{C}_1\text{mim}][\text{NTf}_2]$ and $[\text{C}_2\text{mim}][\text{NTf}_2]$

Figure 3 shows typical DSC traces of pure $[\text{C}_2\text{mim}][\text{NTf}_2]$ and $[\text{C}_2\text{mim}][\text{NTf}_2]$ in which 5 wt % PBnMA is dissolved. The heating rate is 2 mK s^{-1} in the case of both these traces. In the temperature range 25–130 °C, no significant peaks are observed in the DSC thermogram for the IL without the polymer (Fig. 3a). In contrast, upon heating, an endothermic peak (demixing process) is observed around the phase separation temperature of PBnMA in $[\text{C}_2\text{mim}][\text{NTf}_2]$ (Fig. 3b) [2b]. The appearance of a single endothermic peak that can be attributed to the polymer solution clearly indicates that the phase separation of PBnMA in an IL occurs at this temperature. Since the endothermic peak appears during an extremely slow heating (demixing) process, an increase in the enthalpy and entropy occurs at the phase separation temperature, where ΔG_{demix} is considered to be zero. Conversely, during the reverse process (mixing process), negative ΔH_{mix} and ΔS_{mix} accompany the mixing of PBnMA in $[\text{C}_2\text{mim}][\text{NTf}_2]$.

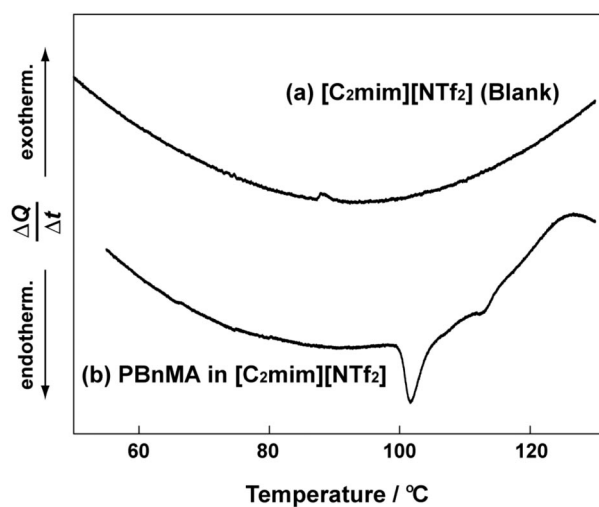


Fig. 3 Typical DSC curves at a heating rate of 2 mK s^{-1} for (a) pure $[\text{C}_2\text{mim}][\text{NTf}_2]$ (blank) and (b) $[\text{C}_2\text{mim}][\text{NTf}_2]$ in which 5 wt % PBnMA is dissolved.

Figure 4 shows the DSC thermograms of 5 wt % PBnMA in $[\text{C}_1\text{mim}][\text{NTf}_2]$ and in $[\text{C}_2\text{mim}][\text{NTf}_2]$ obtained at a heating rate of 4 mK s^{-1} . As in the case of PBnMA in $[\text{C}_2\text{mim}][\text{NTf}_2]$, the PBnMA/ $[\text{C}_1\text{mim}][\text{NTf}_2]$ solution also exhibits an endothermic peak around the phase separation temperature that is determined from turbidity measurements, as discussed in our previous report [2b]. Table 1 summarizes the thermodynamic data obtained from the DSC measurements; all the data for the polymer in ILs are averaged over at least two measurements. T_{min} for each thermogram is defined as the temperature at which an endothermic peak reaches a minimum. ΔH is estimated from the area under the endothermic peak of the DSC thermogram, and it is normalized by the weight of the polymer in the sample solutions. ΔS can be calculated from the expression for the Gibbs free energy of demixing by assuming ΔG to be zero. As shown in the table, the absolute values of ΔH and ΔS for PBnMA in $[\text{C}_1\text{mim}][\text{NTf}_2]$ are higher than those for PBnMA in $[\text{C}_2\text{mim}][\text{NTf}_2]$. However, thermodynamic data are available for only two IL solutions in this study because of the limitation of higher temperature control in the DSC apparatus used in this study. The decrease in ΔH between the $[\text{C}_1\text{mim}][\text{NTf}_2]$ and $[\text{C}_2\text{mim}][\text{NTf}_2]$ solvents suggests that ILs that possess imidazolium cations with a short alkyl chain contribute to a more exothermic mixing of PBnMA. This enthalpy stabilization during mixing gives rise to the negative ΔS_{mix} for both the solutions, that is, it leads to structure-forming solvation. Certain mixtures of aromatic compounds and imidazolium-based ILs exhibit LCST phase separation (vide supra) [6]. The entropy loss of mixing is attributed to the formation of liquid clathrates via associative interactions such as the cation- π interactions between the IL cations and the aromatic compounds; these interactions weaken the packing interaction between cations and anions to a degree sufficient to form localized cage structures. Rogers et al. have reported that the ratio of the aromatic compound to IL in liquid clathrates increases with the *N*-substituted alkyl chain length of imidazolium cations, while the anionic structure of the IL remains unchanged [7a]. This implies that ILs with short alkyl chains result in the formation of thermodynamically stable solvation cages through attractive interactions with the aromatic groups, as seen in the case of PBnMA in ILs.

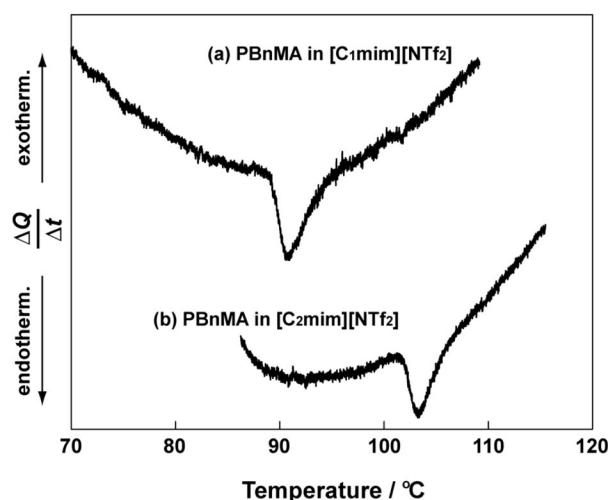


Fig. 4 DSC thermograms at a heating rate of 4 mK s^{-1} for (a) 5 wt % PBnMA dissolved in $[\text{C}_1\text{mim}][\text{NTf}_2]$ and (b) 5 wt % PBnMA dissolved in $[\text{C}_2\text{mim}][\text{NTf}_2]$.

Table 1 Thermodynamic properties of various polymer solutions with LCST phase behavior*.

Solvent	Polymer	M_w/kDa	M_n/kDa	M_w/M_n	$T_{\text{min}}^{\text{a}}/\text{°C}$	$\Delta H^{\text{b}}/\text{J g}^{-1}$ of polymer	$\Delta S^{\text{c}}/\text{J K}^{-1}\text{g}^{-1}$ of polymer
$[\text{C}_1\text{mim}][\text{NTf}_2]$	PBnMA	78.1	28.3	2.76	90.9	5.39	0.0150
$[\text{C}_2\text{mim}][\text{NTf}_2]$	PBnMA	78.1	28.3	2.76	103.5	4.28	0.0114
	PNIPAm	160	49	3.2	34.0	62.8	0.204
	PVME	70			36.4	67.0	0.217
Water	PPG	1			40.9	100.5	0.320
	HPC	100			48.4	20.9	0.0650

*Average thermodynamic parameters of the IL solutions were measured at a heating rate of 4 mK s^{-1} . All the data for aqueous polymer solutions were obtained from ref. [10]. Abbreviations of polymers are as follows. PBnMA: poly(benzyl methacrylate); PNIPAm: poly(*N*-isopropylacrylamide); PVME: poly(vinyl methyl ether); PPG: poly(propylene glycol); HPC: hydroxypropylcellulose.

^aTemperature (obtained from DSC) corresponding to endothermic peak minimum.

^bEnthalpy of demixing calculated from endothermic peak area (J g^{-1} of polymer).

^cEntropy of demixing calculated from ΔH and the expression for Gibbs free energy of demixing.

LCST phase separation of polymers in ILs and in water

Table 1 also shows previously reported thermodynamic parameters for the LCST phase separation of aqueous polymer solutions such as PNIPAm and poly(vinyl methyl ether) (PVME) in water [10]. The ΔH values of PBnMA in the ILs considered in this study are found to be much lower than those of PNIPAm in aqueous solutions [10]. However, there are a few examples exhibiting sufficiently low ΔH values under LCST phase separation, even in aqueous polymer solutions [12,16]. It is accepted that the LCST phase transition of such aqueous polymer solutions is associated with the hydrophobic solvation (vide supra), where the cooperative hydrogen bonding between water molecules is strong around hydrophobic groups; this strong bonding leads to a decrease in the enthalpy and entropy of mixing of the solutions. On the other hand, the main factors facilitating the dissolution of PBnMA in the ILs appear to

be relatively weak interactions such as cation- π interaction and van der Waals forces—induction and dispersion forces. We have reported that the LCST phase separation temperature of polymers in ILs is drastically changed as a result of even a small change in the structure of the polymer or the IL. As shown in Fig. 4, a difference of ca. 10 °C is observed in the phase separation temperatures of PBnMA dissolved in $[C_1\text{mim}][\text{NTf}_2]$ and in $[C_2\text{mim}][\text{NTf}_2]$, although the chemical structures of the two solvents differ by only one methylene unit in the *N*-substituent of the imidazolium cation. This phenomenon can be understood from the much smaller magnitudes of ΔH and ΔS for polymers in ILs as compared to those in aqueous solutions. Thus, a small change in the enthalpy and entropy of mixing resulting from structural changes in the polymers can lead to a large change in the phase separation temperature.

Ultra-slow kinetics of phase separation

Finally, the slow kinetics of the phase separation of PBnMA in an IL is discussed by comparing the data of thermodynamic phase separation obtained from the DSC measurements with those of macroscopic phase separation acquired from the turbidity measurements of the solutions. Figure 5 shows a DSC thermogram of PBnMA dissolved in $[C_2\text{mim}][\text{NTf}_2]$ (1 mK s⁻¹) along with the transmittance of the same polymer solution at 500 nm as a function of the temperature. For the turbidity measurements, the temperature is changed stepwise with increments of 0.2 °C, and the transmittance of the solution is recorded after 4 min in order to detect the macroscopic phase separation of the solution. Although the temperature variation is discontinuous during the turbidity measurements, the heating rate is assumed to correspond to ca. 0.83 mK s⁻¹, which is almost equal to the scan rate of the DSC measurements. It is interesting to note that the temperature corresponding to the endothermic peak resulting from the microscopic desolvation of PBnMA from the IL is observed to be lower than the temperature corresponding to the macroscopic phase separation by ca. 10 °C. Previous studies on aqueous polymer solutions have confirmed that the phase separation temperatures obtained from the endothermic peaks of DSC are in excellent agreement with those obtained from cloud point measurements [4,10,12] when the scan rates for both measurements are equal. This implies that microscopic and macroscopic phase separations occur simultaneously in the case of aqueous polymer solutions. In sharp contrast, in the case of PBnMA in an IL, the desolvation of the polymer from the IL occurs well before the macroscopic phase separation. One possible explanation for this phenomenon is that the rate of growth of polymer clusters, which is large enough to scatter 500-nm light, both in size and in terms of the number of clus-

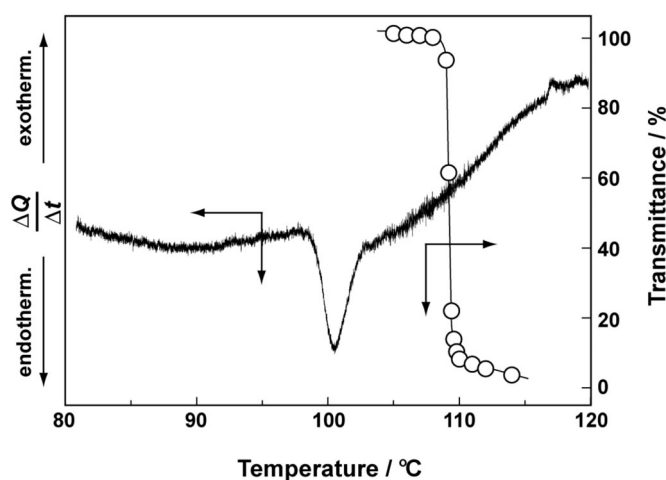


Fig. 5 DSC thermogram at a heating rate of 1 mK s⁻¹ for 5 wt % PBnMA dissolved in $[C_2\text{mim}][\text{NTf}_2]$ along with the transmittance at 500 nm as a function of the temperature for the same polymer solution.

ters is low in the IL due to the viscosity of the IL being much higher than that of water. In our previous investigation of PBnMA in $[C_2mim][NTf_2]$ using dynamic light-scattering measurements, large aggregates were observed in the solution when the temperature was close to the macroscopic phase separation temperature; however, the transparency of the polymer solution was constant [2c].

The unusually slow kinetics of the phase separation of PBnMA in an IL is also seen in Fig. 6. In general, in the case of the LCST phase separation of aqueous polymer solutions detected by DSC, it is considered that the temperatures corresponding to the endothermic peak minima are independent of the heating rate at rates less than or equal to 30 K h^{-1} (8.3 mK s^{-1}) [4]. A recent detailed report on the DSC measurements of the LCST phase behavior of PNIPAm and its derivative in aqueous solutions reveals that the endothermic peak temperature continues to decrease with the scan rate, even below 8.3 mK s^{-1} ; however, the change can be as small as $0.5\text{ }^\circ\text{C}$ [11c]. In contrast, the endothermic peak temperature for PBnMA in $[C_2mim][NTf_2]$ continues to strongly depend on the scan rate even when it is below 1 mK s^{-1} . The difference in the peak temperatures between the scan rates 4 mK s^{-1} ($104.0\text{ }^\circ\text{C}$) and 0.5 mK s^{-1} ($99.2\text{ }^\circ\text{C}$) is as high as $4.8\text{ }^\circ\text{C}$. This indicates that the heating rates are still sufficiently high for the polymer to undergo quasi-equilibrium phase transition and that the process of phase separation of PBnMA from $[C_2mim][NTf_2]$ has extremely slow kinetics. The endothermic peak temperatures are plotted as a function of the scan rates in Fig. 7. By extrapolating the plot to the scan rate of zero, we can obtain the quasi-equilibrium phase transition temperature as $98.9\text{ }^\circ\text{C}$. Due to the unusually slow dynamics of the phase separation of PBnMA from $[C_2mim][NTf_2]$, as mentioned above, it is unclear whether or not the extrapolation of the linear fit is appropriate for this system. We experimentally observe the phase separation of the same polymer solution after storing it at $95\text{ }^\circ\text{C}$ for 3 h. The transparency of the solution is unchanged when the solution is stored at $90\text{ }^\circ\text{C}$, even after 15 h. This observation provides corroborative evidence of the extremely slow kinetics of phase transitions.

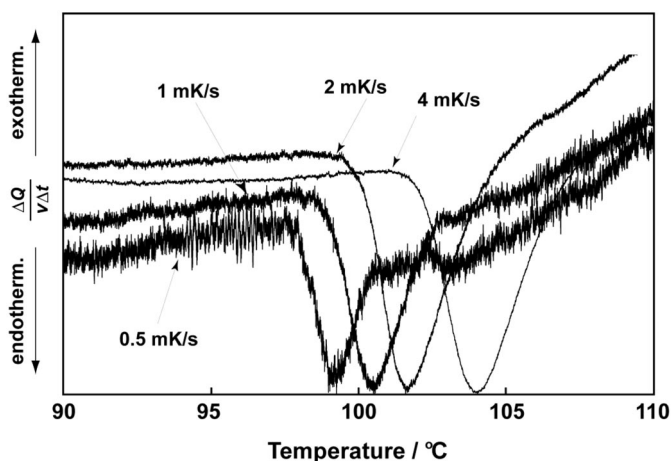


Fig. 6 DSC thermograms for 5 wt % PBnMA dissolved in $[C_2mim][NTf_2]$ at different heating rates (0.5, 1, 2, 4 mK s^{-1}). The values of the vertical axis are divided by the heating rate (v) to normalize the rate differences.

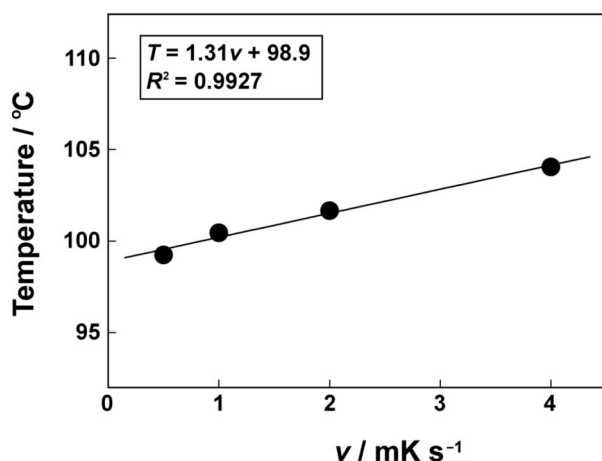


Fig. 7 Dependence of endothermic peak temperatures on the heating rate (v) for 5 wt % PBnMA dissolved in $[\text{C}_2\text{mim}][\text{NTf}_2]$.

CONCLUSION

The solubility of PBnMA in 13 different ILs in the temperature range between 25 and 240 °C was examined in order to understand the effect of the chemical structure of the ILs on the solubility. The LCST phase behavior of PBnMA was observed not only in ILs with $[\text{NTf}_2]$ anions but also in those with PF_6 anions. T_c was significantly changed by changing the chemical structures of the cations. DSC was successfully employed to study the LCST phase transitions of PBnMA dissolved in $[\text{C}_1\text{mim}][\text{NTf}_2]$ and in $[\text{C}_2\text{mim}][\text{NTf}_2]$. Endothermic peaks could clearly be observed at around 100 °C in the DSC thermograms; this temperature corresponded to the temperature of the phase separation of PBnMA from ILs. It was experimentally verified for the first time that LCST phase separations are caused by negative enthalpy change and entropy change of mixing of PBnMA in ILs. The phase separation temperature of PBnMA in $[\text{C}_1\text{mim}][\text{NTf}_2]$ was lower than that of PBnMA in $[\text{C}_2\text{mim}][\text{NTf}_2]$ by ca. 10 °C, which was in agreement with the phase separation temperatures determined from turbidity measurements [2b]. The absolute values of the thermodynamic parameters for the phase transition of PBnMA in ILs obtained in this study were much lower than those reported in previous studies for aqueous polymer solutions that exhibit LCST phase behavior. Small changes in the thermodynamic parameters resulted in a large change in the phase separation temperature even by small changes in the chemical structure of the ILs and polymers. In addition, the difference between the phase separation temperatures determined from the DSC and turbidity measurements indicated that the microscopic desolvation process occurred prior to the macroscopic phase separation. The endothermic DSC peaks may correspond to the “pre-aggregation” process, whereas in the aqueous polymer solutions, the microscopic and macroscopic phase separations occur simultaneously. The dependence of the endothermic peak temperatures on the DSC scan rate also confirmed that the phase separation proceeded with extremely slow kinetics.

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