LCST-type liquid–liquid phase separation behaviour of poly(ethylene oxide) derivatives in an ionic liquid†

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We present a new series of polymer–ionic liquid solutions exhibiting LCST-type liquid–liquid phase separation behaviour, and reveal their phase behaviour and intermolecular interactions based on phase diagrams and NMR analysis.

Ionic liquids (ILs) have attracted considerable attention due to their high chemical and thermal stabilities, negligible vapor pressure, wide liquid temperature ranges and tunable chemical structures; they are thus frequently called 'designer solvents'.[1] These remarkable properties have led to the use of ILs as solvents for chemical reactions or functional materials.[2] Recently, certain IL-containing binary systems have been found to exhibit a liquid–liquid phase separation phenomenon with a critical temperature: upper critical solution temperature (UCST) and/or lower critical solution temperature (LCST).[3,4] It is expected that IL-containing binary mixtures that exhibit a thermoresponsive phase behaviour will find applications in efficient chemical extraction, separation and so on.

In polymer solutions, it is well known that poly(*N*-isopropylacrylamide) (PNIPAAm) and its derivatives exhibit an LCST-type phase separation behaviour in aqueous solution, and various thermoresponsive soft materials (gels and block copolymers) have been proposed.[5] Recently, our research group has also reported polymer–IL solution systems that exhibit a critical solution temperature: UCST-type phase separation behaviour for PNIPAAm–1-ethyl-3-methylimidazolium bis(trifluoromethane sulfonyl)amide ([C_2mim][NTf_2]) solution[6] and LCST-type phase behaviour for poly(benzyl methacrylate)–[C_2mim][NTf_2] solution.[7] A more detailed study is required to understand these polymer–IL composite systems; however, it is difficult to show their complete phase diagrams due to their low miscibility in a high-concentration solution. Poly(ethylene oxide) (PEO) is a more well-studied polymer, and its phase behaviour when dissolved in imidazolium ILs has been investigated by a molecular dynamics simulation[8] and a small-angle neutron scattering measurement;[9] these investigations suggest that imidazolium-type ILs act as good solvents for PEO. In this study, we report the LCST-type phase separation behaviour of liquid-phase PEO derivatives, poly(ethyl glycidyl ether) (PEGE) and [C_2mim][NTf_2] binary solutions, and their phase behaviour has been studied on the basis of their phase diagrams and intermolecular interactions.

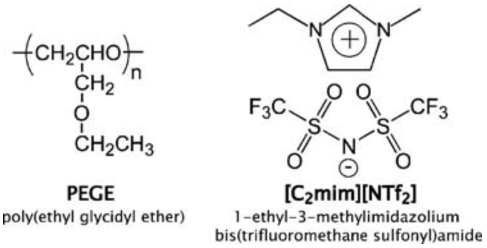

Fig. 1 Chemical structures of PEGE (left) and [C_2mim][NTf_2] (right).

PEGE (Fig. 1) was synthesized by the ring-opening anionic polymerization of the corresponding epoxide, as described in the literature.[10,11] In this study, four types of PEGE with different molecular weights were prepared (Table 1). [C_2mim][NTf_2] (Fig. 1) was synthesized according to the general procedure.[12] PEGEs and [C_2mim][NTf_2] were dried *in vacuo* (<1 mmHg) at 80 °C for 48 h. Their water contents were so low that there was no influence of contaminated water (PEGE: [H_2O]<125 ppm, [C_2mim][NTf_2]: [H_2O]<18 ppm). PEGE–[C_2mim][NTf_2] solutions were prepared by directly mixing them in a glove box, and highly viscous solutions were thoroughly mixed by a vortex mixer or a planetary mixer.

The photographs of the LCST-type phase separation behaviour for a PEGE–[C_2mim][NTf_2] binary solution are shown in Fig. 2. At room temperature, PEGE and [C_2mim][NTf_2] were completely miscible, and a clear solution was obtained (Fig. 2 left). When the temperature was increased, the solution became turbid at a certain temperature (cloud point) (Fig. 2 middle), and it gradually separated into two liquid–liquid phases (Fig. 2 right). In this stable biphasic mixture, the upper and lower phases comprised a PEGE-rich phase and a [C_2mim][NTf_2]-rich

Table 1 Characterization of PEGE

Polyether	Units, *n*	$M_n{}^a$/g mol^{-1}	$M_w/M_n{}^b$
$PEGE_{37}$	37	3800	1.15
$PEGE_{79}$	79	8100	1.19
$PEGE_{97}$	97	10 000	1.26
$PEGE_{216}$	216	22 000	1.75

[a] The number average molecular weight (M_n) of PEGE was determined by the ratio of ^{1}H NMR integral intensities. [b] The polydispersity index (M_w/M_n) was determined by size exclusion chromatography (SEC) measurements.

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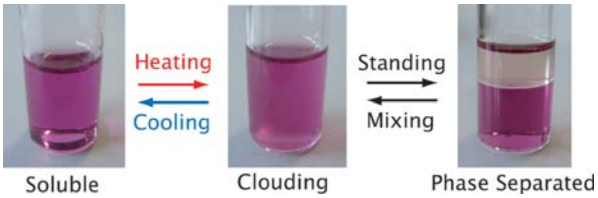

Fig. 2 Photographs of LCST-type phase separation behaviour of a PEGE–[C_2mim][NTf_2] binary system. The color is due to a dye dissolved in the ionic liquid.

phase, respectively, because of their different densities (PEGE: $d \approx 1.0$ g mL^{-1}, [C_2mim][NTf_2]: $d \approx 1.5$ g mL^{-1}). This mixing–demixing phenomenon occurred reversibly depending on the temperature change in a manner similar to the classical liquid–liquid phase separation behaviour of aqueous polymer solutions.[13]

In order to examine what occurs during the demixing process at temperatures close to the clouding temperature, we attempted to directly observe the phase transition by using an optical microscopic. A glass slide with a hole for a sample solution was used for a mount; the sample droplet was observed by using a digital microscope equipped with a hot stage to control the temperature. The optical microscopy photographs of a 5 wt% (concentration of PEGE) PEGE$_{79}$–[C_2mim][NTf_2] solution at 90–105 °C are shown in Fig. 3. Microscopic droplets suddenly appeared from the bulk homogeneous solution above the cloud point, and these droplets became larger at a higher temperature with coalescence, while nothing was observed below the cloud point. Thus, it was found that the light scattering of microscopic droplets resulted in the visual clouding of the macroscopic solution. When the weight fraction of PEGE was increased, the ratio of the emerging droplets also increased (data not shown), indicating that the droplets mainly comprised PEGE (PEGE-rich phase). Therefore, the microscopic droplets were formed by the aggregation of the PEGE chain with increasing temperature. In fact, small-angle X-ray scattering (SAXS) and static light scattering (SLS) measurements of a dilute PEGE$_{79}$–[C_2mim][NTf_2] solution revealed the size of the polymer particles: PEGE chains were dissolved in [C_2mim][NTf_2] with a random coil conformation at a temperature sufficiently lower than the cloud point ($R_g \approx 1.4$ nm at 30 °C); on the other hand, large aggregated particles were detected in the vicinity of the cloud point ($R_g \approx 300$ nm at 90 °C). Such a phenomenon, wherein droplets of a polymer-rich phase appear from the bulk solution as mentioned above, is analogous to the phase separation event well known as coacervation in aqueous media.[13]

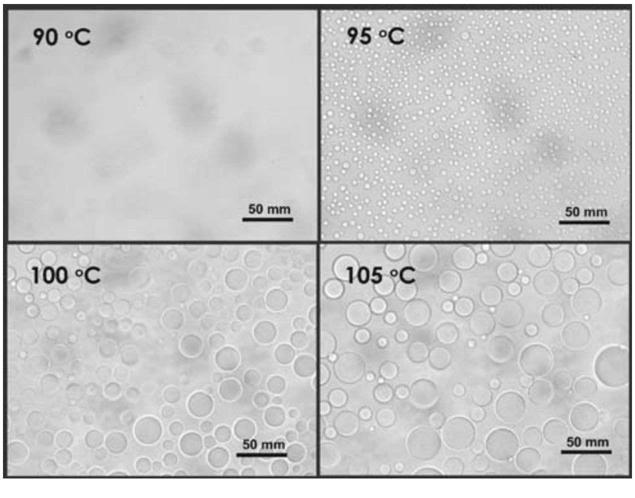

Fig. 3 Optical microscopy observation images for 5 wt% PEGE$_{79}$–[C_2mim][NTf_2] solution at 90–105 °C.

Phase diagrams provide important information that helps in the understanding of binary mixing systems. In the PEGE–[C_2mim][NTf_2] binary system, phase separation phenomena can be observed in the temperature range 65–105 °C, and liquid–liquid binary mixtures allow us to easily and accurately determine the cloud points over the entire composition. In the next step, concentration–temperature phase diagrams for four different molecular weight PEGEs and [C_2mim][NTf_2] binary systems were represented by plotting the cloud points that were observed by a visual detection method (heating rate <0.05 °C min^{-1}) (Fig. 4). All the coexistence curves were convex downward, and the LCST (T_c) for the PEGE$_{216}$–[C_2mim][NTf_2] solution was determined to be 67 °C with a critical concentration (w_c) of 4 wt% PEGE. It was found that w_c was shifted to a concentrated composition of PEGE and T_c increased with a decrease in the molecular weight of the four types of PEGE. Such a trend can be commonly observed in other aqueous polymer solutions that exhibit an LCST-type phase behaviour.[14] Therefore, it was demonstrated that PEGE–[C_2mim][NTf_2] binary systems exhibit an LCST-type phase behaviour. To the best of our knowledge, this is the first example of polymer–IL binary mixtures that exhibit a liquid–liquid LCST-type phase behaviour.

We attempt to understand why PEGE–[C_2mim][NTf_2] binary systems exhibit an LCST-type phase behaviour. Here, we discuss this phenomenon from the viewpoint of

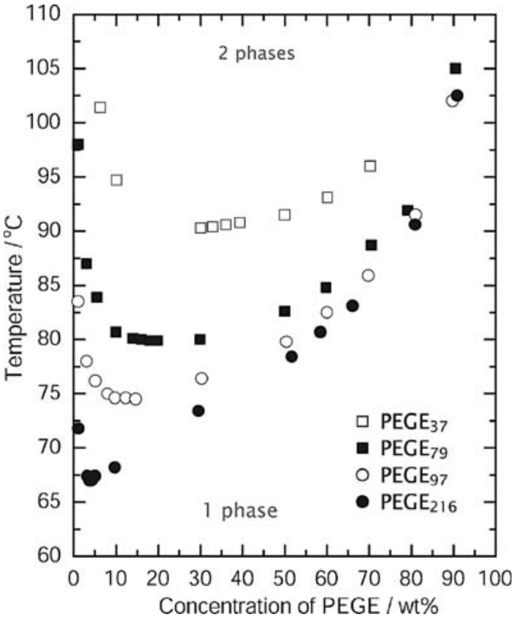

Fig. 4 Phase diagrams for different molecular weight PEGEs and [C_2mim][NTf_2] binary systems.

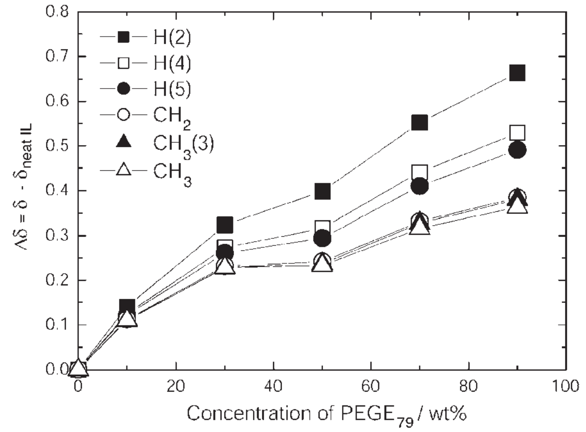

Fig. 5 Concentration dependence of $\Delta\delta$ on the PEGE$_{79}$–[C$_2$mim][NTf$_2$] binary system measured by a double NMR tube technique.

intermolecular interactions between PEGE and [C$_2$mim][NTf$_2$]. In order to exhibit an LCST-type phase behaviour, the occurrence of structure-forming solvation and a negative entropy change by mixing is essential. If the mixed molecules become more oriented by the molecular interactions, the mixing entropy should be decreased. Hydrogen bonding interactions are one of the most notable interactions that can be a driving force for the LCST-type phase behaviour;[4,5] furthermore, it has been reported that the protons of the imidazolium cation ring can act as proton donors and interact with anionic species[15] or proton accepting molecules[2] by hydrogen bonds. In order to confirm the intermolecular interactions, especially the hydrogen bonds, we conducted ^{1}H NMR spectroscopic measurements for the PEGE–[C$_2$mim][NTf$_2$] binary system using a double NMR tube technique.[15] The measurement samples were prepared by adding a PEGE$_{79}$–[C$_2$mim][NTf$_2$] solution and CDCl$_3$ containing TMS to the inner and outer tube, respectively, in a glove box, following which the sample tubes were sealed. When the PEGE content increased, the ^{1}H NMR signals of all the protons of the imidazolium cation in the PEGE–[C$_2$mim][NTf$_2$] solution shifted downfield as compared to those of neat [C$_2$mim][NTf$_2$]. Fig. 5 shows the change in the chemical shift of the protons that depends on the PEGE concentration. The downfield shift of all the protons in the imidazolium cation would be attributable to the decreased electron density of the protons derived from the interaction with PEGE.[12] Remarkably, $\Delta\delta$ for the protons at positions 2, 4 and 5 in the imidazolium cation ring were significantly larger than those of other protons. In contrast to the case of protons of the imidazolium cation, the ^{1}H NMR chemical shifts of the protons of PEGE were shifted upfield. These facts suggested that hydrogen bonds are formed between the protons of the imidazolium cation and the oxygen atoms of the PEGE chain. In particular, $\Delta\delta$ for the proton at position 2 of the imidazolium cation was larger than that of the other protons, indicating that this proton formed the strongest hydrogen bond.[12] Additionally, the effect of hydrogen bonds on the phase behaviour was further confirmed by the fact that PEGE was immiscible with 1-propyl-2,3-dimethylimidazolium bis(trifluoromethane sulfonyl)amide, where the proton at position 2 in the imidazolium cation is replaced by a methyl group. In the PEGE–[C$_2$mim][NTf$_2$] binary system, hydrogen bonding interactions between the [C$_2$mim] cation and the neighboring oxygen atoms in PEGE would yield solvation shells that induce a negative entropy change and give rise to the LCST-type phase behaviour.

In conclusion, this study presented a new series of PEGE–[C$_2$mim][NTf$_2$] binary systems that exhibit an LCST-type phase separation behaviour. Their phase separation behaviour was observed as a liquid–liquid segregation similar to the coacervation phenomenon. The hydrogen bonds between the protons of the [C$_2$mim] cation ring and the oxygen atoms of the PEGE chain appeared to be the primary driving force of the LCST-type phase behaviour. PEGE–[C$_2$mim][NTf$_2$] binary systems are expected to find IL-based applications (such as soft matter, intelligent gels, separation and extraction) as well as offering basic polymer solution chemistry.

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