

Tunable Lower Critical Solution Temperature of Poly(butyl acrylate) in Ionic Liquid Blends

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Abstract We describe the lower critical solution temperature (LCST)-type phase behavior of poly(butyl acrylate) (PBA) dissolved in hydrophobic 1-alkyl-3-methylimidazolium bis{(trifluoromethyl) sulfonyl}amide ionic liquids (ILs). The temperature-composition phase diagrams of these PBA/ILs systems are strongly asymmetric with the critical composition shifted to low concentrations of PBA. As the molecular weight increases from 5.0×10^3 to 2.0×10^4 , the critical temperature decreases by about 67 °C, and the critical composition shifts to a lower concentration. Furthermore, the LCST of PBA/ILs system increases as increasing the alkyl side chain length in the imidazolium cation. Using IL blends as solvents, the LCST of PBA can be tuned almost linearly over a wide range by varying the mixing ratio of two ionic liquids without modifying the chemical structure of the polymers.

Keywords PBA; ionic liquid; LCST; Thermo-responsive

Citation: Chen, L.; Huang, J.; Zhao, C.; Zhou, J. J.; Liu, M. J. Tunable lower critical solution temperature of poly(butyl acrylate) in ionic liquid blends. *Chinese J. Polym. Sci.* 2021, 39, 585–591.

INTRODUCTION

Ionic liquids (ILs) are a class of solvents that have drawn great attention during the past two decades due to their appealing physicochemical properties such as negligible vapor pressure, good chemical and thermal stability, wide liquid temperature ranges, and high ionic conductivity. ILs are known as “designer solvents” because of the ability to select the appropriate anion and cation to achieve the desired properties.^[1] The polymer/ILs composite system is a major research interest regarding ILs as the solvent, which has been widely investigated and show broad applications such as polymer electrolytes in lithium batteries and solar cells.^[2–4] In addition, the ionogels formed by crosslinking of polymer or self-assembly of block copolymer in ILs gradually received increasing attention in recent years due to their shapeable and leakage-free properties, which are favorable to wearable and portable devices.^[5,6] Their possible applications include membranes for fuel cells and gas separations, gels for solid-state electrolyte and thin-film transistors.^[7–10] Therefore, to optimize the practical application of polymer/ILs based materials, it is important to understand the miscibility and mixing mechanism of these two components.

In general, the miscibility of a polymer and a solvent often varies as temperature changes. The LCST-type phase behavior is known as the solubility of a polymer in solvent decreases as temperature increases such as poly(*N*-isopropylacrylamide) (PNIPAm) and poly(vinyl methyl ether) (PVME) in water and water/organic solvent mixture,^[11,12] while the upper critical solution temperature (UCST)-type phase behavior is known as the solubility of a polymer in solvent increases as temperature increases such as PNIPAm in ionic liquid.^[13] In polymer/ILs solution system, both LCST and UCST phase behaviors have been reported. The wide liquid range and low vapor pressure of ILs provide possibilities for the wide temperature range measurement of the cloud point (CP) of polymer/ILs solution. Ueki and Watanabe first reported the experimental observations of LCST-phase behavior for poly(benzyl methacrylate) in 1-alkyl-3-methylimidazolium bis{(trifluoromethyl) sulfonyl}amide ($[C_n\text{MIM}][\text{NTf}_2]$) ionic liquid, and the LCST can be controlled by copolymerization of poly(benzyl methacrylate) with solvatophobic (styrene) or solvatophilic (methyl methacrylate) comonomers.^[14,15] Besides, Ueki and Watanabe demonstrated the UCST phase behavior of PNIPAm in $[C_n\text{MIM}][\text{NTf}_2]$, whereas PNIPAm shows the LCST phase behavior in water.^[11,13] Then, the LCST-type phase behavior of poly(ethyl glycidyl ether) in $[C_n\text{MIM}][\text{NTf}_2]$ is also reported by Watanabe and co-workers.^[16] Later, the LCST-type phase behaviors of PEO/ $[C_n\text{MIM}][\text{BF}_4]$ solution and *Pn*BMA/ $[C_n\text{MIM}][\text{NTf}_2]$ solu-

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Received September 7, 2020; Accepted October 23, 2020; Published online November 26, 2020

tion were demonstrated by Lodge and co-workers.^[17–20] To date, various polymer/ILs systems have been reported to possess either LCST or UCST phase behavior.^[21,22] However, for the PBA/ILs system, there are different opinions on the solubility of PBA in $[C_2MIM][NTf_2]$ ILs.^[23,24] Consequently, a systematic and detailed study on the stimuli-responsive property of this promising PBA/ILs system is deserved.

Herein, we reported a LCST-type phase behavior solution comprising poly(butyl acrylate) and $[C_nMIM][NTf_2]$ ionic liquids. In this work, the LCST-type phase behavior of PBA/ $[C_2MIM][NTf_2]$ solution is systematically studied through a typical procedure. Increasing the molecular weight of PBA from 5.0×10^3 to 2.0×10^4 , the critical temperature decreases by 67 °C and the critical composition slightly shifts to a lower concentration. The LCST of PBA increases as the length of the alkyl chain in the imidazolium cation increases. By varying the mixing ratio of two structurally similar ILs in their blends, the LCST of polymer/ILs solution can be easily tuned in a wide temperature range without modifying the chemical structure of the polymers. Moreover, the LCST of PBA/ILs solution varies almost linearly with the weight fraction of ionic liquid in their blends, and the linear trend in CPs of PBA/ILs solution also provides a strategy to estimate the LCST of the PBA/ILs solution with CP beyond the limit of the instrument.

EXPERIMENTAL

General Materials

All of the following chemical reagents were used as received from Sigma-Aldrich: butyl acrylate (BA), ethyleneglycol dimethacrylate (EGDMA, crosslinker), diethoxyacetophenone (DEOP, photo-initiator), ethyl 2-bromoisobutyrate (EIBB), and tris[2-(dimethylamino)ethyl]amine (Me_6TREN). Copper chloride (CuCl) was acquired from Alfa. 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_2MIM][NTf_2]$, >99%) and 1-propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_3MIM][NTf_2]$, >99%) were purchased from Lanzhou Yulu Fine Chemical Co., Ltd. Ethanol (AR), toluene and acetone (AR) were

supplied by Beijing Chemical Works. Deionized water was obtained *via* Milli-Q. All photo images in the current work were taken by the photo camera (Canon 60D).

Synthesis of PBA Homopolymers

n-Butyl acrylate is purified using a basic alumina column. The PBA homopolymers are synthesized *via* atom transfer radical polymerization (ATRP) according to the literature.^[25] Toluene is added to a flask, and the solution is stirred and bubbled using dry nitrogen for more than 1 h. Finally, EIBB (initiator), Me_6TREN (ligand), CuCl (catalyst) and BA (monomer) are added to the system under nitrogen with the molar ratio of EIBB/ Me_6TREN /CuCl/BA fixed at 1/1/1/*n*. The polymerization reaction is carried out at 80 °C for 12 h. The as-prepared PBA is purified by precipitation using cold methanol. The characterizations of the homopolymers are given in Fig. S1 and Table S1 (in the electronic supplementary information, ESI).

Preparation of Polymer/ILs Solutions

For low concentration (<40 wt%), the PBA can directly be dissolved in ionic liquid by predetermined ratio. For high concentration (>40 wt%), a cosolvent method is utilized to prepare polymer/IL solution, since the ILs have essentially no vapor pressure. PBA and ILs are first mixed with the assistance of ethanol. The ethanol is then slowly evaporated in an oven (80 °C) under vacuum for at least 48 h to remove the residual ethanol. For PBA/ionic liquid blend system, a 2 wt% PBA-20 is used. Ionic liquid mixtures are made by combining $[C_2MIM][NTf_2]$ and $[C_3MIM][NTf_2]$ in a predetermined ratio.

Cloud Point Measurements

The cloud point of PBA/ILs is determined by optical transmittance measurements at 658 nm at a heating rate of roughly 0.3 °C/min using dynamic light scattering (Anton Paar, Litesizer™ 500). We define the CP values of PBA/ILs solution as the temperatures at which the transmittance drops to 80%.

RESULTS AND DISCUSSION

Images in Fig. 1(a) show the basic LCST phase behavior of PBA/

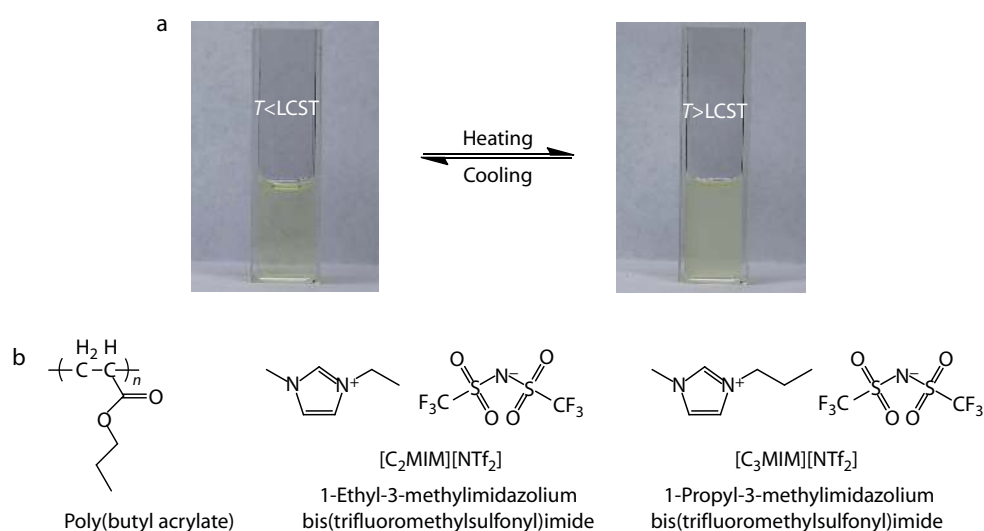


Fig. 1 LCST phase behavior of PBA in ionic liquid. (a) Photographs of PBA/ILs solution (5k, $[C_2MIM][NTf_2]$, 2 wt%) at temperatures below and above the LCST (32 °C). (b) Structural formula of PBA and the ILs used in this work.

ILs solution at temperatures below and above the LCST, respectively. As shown in Fig. 1(a), the solution is transparent below the LCST, indicating a single-phase solution, while a decrease in transmittance is observed at temperature above the LCST, suggesting that the solution undergoes liquid-liquid phase separation. Through this strategy, the LCST of various PBA/ILs solutions can be determined. The structural formula of PBA and the ILs used in this work are given in Fig. 1(b). In this work, PBA-5 and PBA-20 (the numbers indicate the molecular weight in kg/mol) with different molecular weights are prepared by atom transfer radical polymerization (Fig. S1 and Table S1 in ESI).

To quantitatively identify the LCST of PBA/ILs solution, the cloud points of PBA/ILs are determined by optical transmittance measurements at 658 nm at a heating rate of roughly 0.3 °C/min using dynamic light scattering. The transmittance of 100% indicates a single-phase solution, and a decrease in transmittance suggests that the solution undergoes liquid-liquid phase separation. When dissolving 5 wt% PBA-20 in [C₃MIM][NTf₂] at room temperature, a clear and transparent solution with ~100% transmittance is obtained. When temperature increases above the LCST, the solution becomes cloudy, and the transmittance quickly decreases to almost zero. We define the LCST as the temperature at which the transmittance drops to less than 80%. In Fig. 2, different weight fractions of PBA-20 in [C₃MIM][NTf₂] are investigated. The LCSTs of 0.5 wt%, 1 wt%, 2 wt%, 5 wt%, 10 wt%, 20 wt%, 30 wt%, 40 wt%, 50 wt% of PBA-20 in [C₃MIM][NTf₂] are determined as 78, 67, 58, 53, 53, 59, 63, 70, and 80 °C, respectively. Further increasing the temperature above the LCST, the cloudy solution gradually separates into two phases. In the stable biphasic liquid mixture, the upper phase is PBA-rich solution and the lower phase is [C₃MIM][NTf₂]-rich solution, since the density of polymer is lower than that of the ionic liquid. Furthermore, this phase transition behavior of PBA/ILs system is completely reversible. The liquid-liquid phase separation of PBA-20 in [C₃MIM][NTf₂] ionic liquids and corresponding particle size distribution during the phase separation are characterized and given as shown in Figs. S2 and S3 (in ESI).

Similar LCST-type phase behavior is also observed for PBA-5 in [C₃MIM][NTf₂]. The CPs of 0.5 wt%, 1 wt%, 2 wt%, 5 wt%, 10 wt%, 20 wt%, 30 wt%, 40 wt% and 50 wt% of PBA-5 in [C₃MIM][NTf₂] are identified as 148, 137, 129, 123.5, 120, 126, 131.5, 138.5 and 147.5 °C, respectively. Based on the data determined by the transmittance measurements, the temperature-composition phase diagrams for PBA-5 and PBA-20 in [C₃MIM][NTf₂] are shown in Fig. 3. Both curves are convex downward, and the critical temperatures (T_c) are determined to be roughly 53 and 120 °C with the critical compositions (w_c) of 5 wt%–10 wt% (between 5 wt% and 10 wt%) and 10 wt% for PBA-20 and PBA-5, respectively. Dash lines in Fig. 3 show the critical compositions for PBA-20 and PBA-5. The T_c decreases by 67 °C and w_c shifts to lower concentration as the molecular weight increases from 5.0×10^3 to 2.0×10^4 . This phenomenon is commonly observed in other polymer solutions and blends that exhibit LCST-type phase behavior.^[16,17,26] However, compared to other typical polymer solutions with LCSTs, the molecular weight dependence of T_c in the PBA/[C₃MIM][NTf₂] system is relatively strong. Moreover, un-

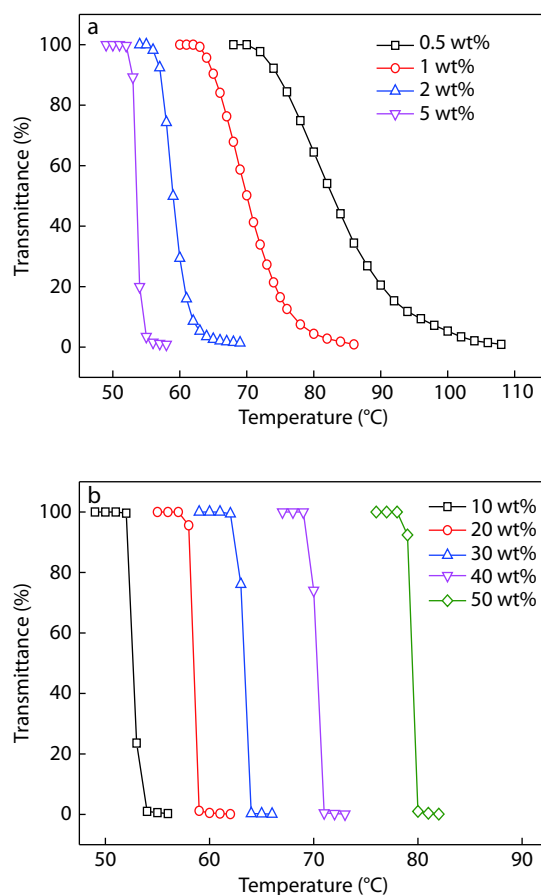


Fig. 2 Cloud point measurement of PBA-20/IL solution ([C₃MIM][NTf₂]). (a) Temperature dependence of transmittance at 658 nm for low PBA-20 concentration measured at a heating rate of ~0.3 °C/min. (b) Temperature dependence of transmittance at 658 nm for high PBA-20 concentration measured at a heating rate of ~0.3 °C/min.

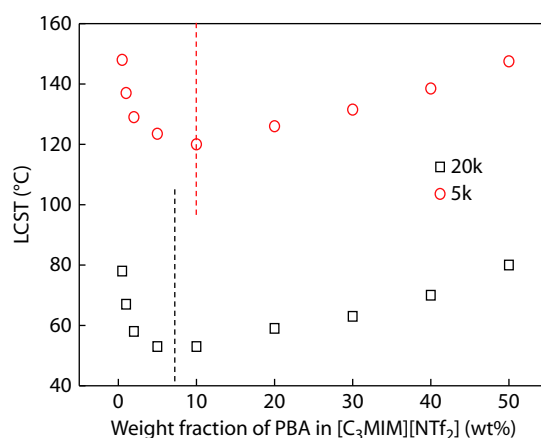


Fig. 3 Temperature-composition phase diagram for PBA-5 and PBA-20 in [C₃MIM][NTf₂]. As the molecular weight increases from 5.0×10^3 to 2.0×10^4 , the critical temperature decreases by about 67 °C, and the critical composition shifts to a lower concentration.

like the typical LCST phase diagram of polymer solutions, the PBA/[C₃MIM][NTf₂] phase diagram is asymmetric, with the critical composition shifted to a low concentration of PBA.

The LCST-type phase separation is a phenomenon where the mixing Gibbs free energy (ΔG_{mix}) changes from negative to positive with an increase in temperature. From a thermodynamic viewpoint, a negative enthalpy (ΔH_{mix}) and a negative entropy of mixing (ΔS_{mix}) are essential for LCST phase behavior.^[27] It can also be understood as the competition between interactions such as hydrogen bonding, Coulombic attractions, and solvation effects among the polymer segments and the solvent molecules. Pioneering work by Watanabe and co-workers showed that poly(benzyl methacrylate) exhibits LCST phase behavior in $[\text{C}_n\text{MIM}][\text{NTf}_2]$,^[14] the coexistence of structure-forming solvophobic groups and solvophilic groups in the polymer is necessary for the LCST-type phase behavior. They hypothesized that the negative ΔS_{mix} arises from the formation of ordered structures *via* cation- π interactions between the cations of IL and the aromatic groups in the polymer.^[28,29] Subsequent work by Lodge and co-workers showed that poly(*n*-butyl methacrylate) also exhibits LCST phase behavior in $[\text{C}_n\text{MIM}][\text{NTf}_2]$ ionic liquid.^[17] However, the ordered structures *via* cation- π interactions

between the cations and the aromatic groups do not exist in their system. They argued that the LCST-type phase behavior is attributed to the coexistence of solvophilic methacrylate groups and solvophobic *n*-butyl side chains; the oriented solvation by van der Waals interaction or hydrogen bonding (minor role) acts as driving force for the LCST phase behavior in their system. Similarly, in this work, the solvophilic acrylate groups and solvophobic *n*-butyl side chains are the key factor for the LCST phase behavior of PBA/ILs solution. The introduction of solvophobic *n*-butyl side chains in hydrophobic IL leads to the oriented solvation around the solvophobic *n*-butyl side chains, thus resulting in negative ΔS_{mix} . Consequently, the dissolution of polymer generates disadvantageous entropic contributions ($\Delta S_{\text{mix}}^\ddagger$) that overwhelm ΔH_{mix} to the free energy of mixing (ΔG_{mix}) as the temperature is increased, leading to phase separation.

We also investigate how IL structure affects the phase behavior of PBA. As shown in Figs. 4(a) and 4(b), the temperature dependence of transmittance at 658 nm for different PBA-5 concentrations in $[\text{C}_2\text{MIM}][\text{NTf}_2]$ is measured. The CPs

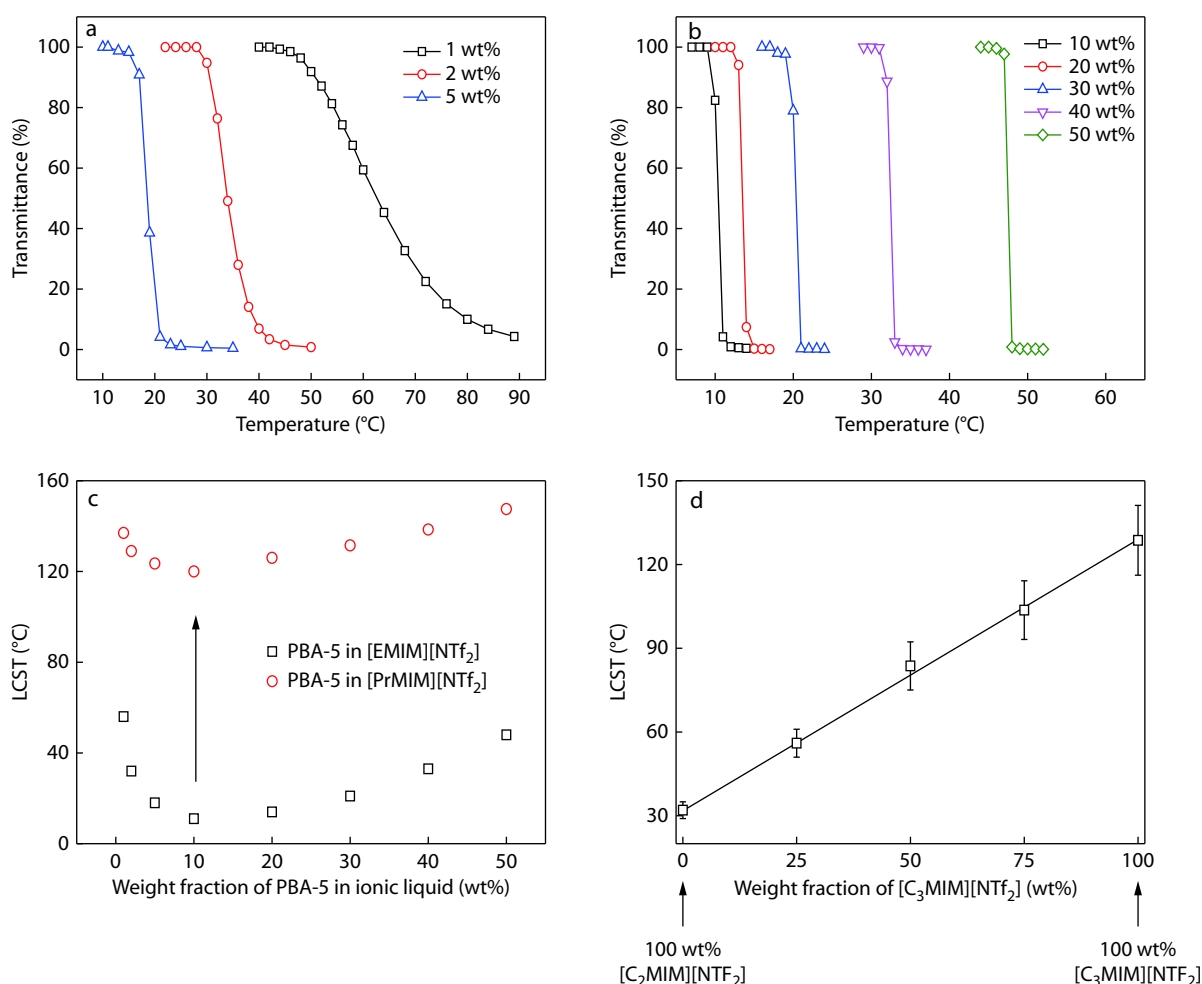


Fig. 4 LCST phase behavior of PBA-5 in different ILs and their blends. (a) Temperature dependence of transmittance at 658 nm for low PBA-5 concentration in $[\text{C}_2\text{MIM}][\text{NTf}_2]$ measured at a heating rate of ~ 0.3 $^{\circ}\text{C}/\text{min}$. (b) Temperature dependence of transmittance at 658 nm for high PBA-5 concentration in $[\text{C}_2\text{MIM}][\text{NTf}_2]$ measured at a heating rate of ~ 0.3 $^{\circ}\text{C}/\text{min}$. (c) Temperature-composition phase diagram for PBA-5 in $[\text{C}_2\text{MIM}][\text{NTf}_2]$ and $[\text{C}_3\text{MIM}][\text{NTf}_2]$. (d) The LCSTs as a function of the weight fraction of $[\text{C}_3\text{MIM}][\text{NTf}_2]$ in IL blends (2 wt% PBA-5).

of 1 wt%, 2 wt%, 5 wt%, 10 wt%, 20 wt%, 30 wt%, 40 wt% and 50 wt% of PBA-5 in $[\text{C}_2\text{MIM}][\text{NTf}_2]$ are identified as 56, 32, 18, 11, 14, 21, 33 and 48 °C, respectively. Based on the data determined by the transmittance measurements, the temperature-composition phase diagram for PBA-5 in ILs with different cation structures ($[\text{C}_2\text{MIM}]$ and $[\text{C}_3\text{MIM}]$) is achieved as shown in Fig. 4(c). We found that the length of the alkyl chain in the imidazolium cation has a significant influence on the miscibility of PBA in ionic liquid. At a certain concentration (2 wt%), the LCST of the PBA in $[\text{C}_2\text{MIM}][\text{NTf}_2]$ (32 °C) is about 97 °C lower than that in $[\text{C}_3\text{MIM}][\text{NTf}_2]$ (129 °C). Results indicate that a small increase in alkyl side chain length (C_2 to C_3) results in huge increase in the CP of the PBA/ILs solution. This result is consistent with the increase in CP with alkyl chain length in poly(benzyl methacrylate)/ $[\text{C}_n\text{MIM}][\text{NTf}_2]$ reported by Watanabe and co-workers, and (PnBMA)/ $[\text{C}_n\text{MIM}][\text{NTf}_2]$ and PEO/ $[\text{C}_n\text{MIM}][\text{BF}_4]$ reported by Lodge and co-workers. Watanabe and co-workers argued that this observation might be attributed to the microphase segregation.^[30] Simulations suggest that imidazolium-based ILs form segregated structures with polar ionic domains and nonpolar alkyl chain domains.^[31,32] Based on this theory, longer alkyl chain on the imidazolium cation may induce extended microphase segregation between the alkyl-chain group and the ionic channel formed by the imidazolium ring and counter anions, and the ordered dynamic domain structure (microphase segregation) lowers the entropy of ILs in return. Consequently, the loss of mixing entropy induced by the formation of ordered structure between polymer and ILs would be reduced, leading to an increase in the LCST. On the other hand, the increase in the alkyl chain length appears to induce an increase in the van der Waals interaction between the cations and alkyl main chain of PBA, lowering the mixing enthalpy and causing an increase in the LCST. In brief, the increase in LCST with the alkyl chain length of cation is a balance between the entropy and enthalpy changes upon mixing.

The LCSTs of PBA-5 in ionic liquid blends ($[\text{C}_2\text{MIM}][\text{NTf}_2]/[\text{C}_3\text{MIM}][\text{NTf}_2]$) with different mixing ratios are investigated. As shown in Fig. 4(d), in ionic liquid blends with different mixing ratios, PBA-5 shows reversible LCST phase behavior, and the CP value increases as the weight fraction of $[\text{C}_3\text{MIM}][\text{NTf}_2]$ increases. We plot the CPs of PBA-5 in IL blends as a function of the weight fraction of $[\text{C}_3\text{MIM}][\text{NTf}_2]$. The CPs increase almost linearly from 32 °C for PBA-5 (2 wt%) to 129 °C as the weight fraction of $[\text{C}_3\text{MIM}][\text{NTf}_2]$ increases. The results in Fig. 4(d) suggest that we can regulate the value of CP of PBA/ILs solution by tuning the mixing ratio of two ILs.

The linear trend of change in LCST is commonly observed in other polymer/ILs systems that exhibit a critical phase behavior, where the two ILs of ionic blends are structurally similar. For example, poly(benzyl methacrylate)/ $[\text{C}_n\text{MIM}][\text{NTf}_2]$, PEO/ $[\text{C}_n\text{MIM}][\text{BF}_4]$, PnBMA/ $[\text{C}_n\text{MIM}][\text{NTf}_2]$ and PNIPAm/ $[\text{C}_n\text{MIM}][\text{NTf}_2]$.^[13,14,17,18] However, the linear trend is not typical in polymer/molecular solvent systems such as PNIPAm in water/organic solvent mixtures. For example, Schild, Muthukumar, and Tirrell reported that the curves of CPs as a function of the weight fraction of organic solvent in water/organic solvent blends are convex downward.^[11] The CPs in their system de-

crease at first and then increases as the fraction of organic solvent increases in the blends. They also showed that the CP of poly(vinyl methyl ether) in water/methanol mixtures increases as the weight fraction of methanol increases, but the trend is not linear. They argued that upon mixing, the nature of water is affected in the blends; the organic solvents modify the water structure and the hydrogen bonding of water as the weight fraction of organic solvent increases. In contrast, the linear trend of LCST in current work and other polymer/ILs system suggest that the interactions between polymer and ILs do not change that much upon mixing two structurally similar ILs. Therefore, the situation of PBA/ $[\text{C}_n\text{MIM}][\text{NTf}_2]$ is much more close to an ideal random mixing process.

Further, to confirm the linear relationship between the CPs of PBA/ILs solution and weight fraction of certain ionic liquid in their blends, LCST phase behavior of PBA-20 in IL blends ($[\text{C}_2\text{MIM}][\text{NTf}_2]/[\text{C}_3\text{MIM}][\text{NTf}_2]$) with different mixing ratios are studied. Fig. 5(a) shows temperature dependence of transmittance at 658 nm for 2 wt% PBA-20 in $[\text{C}_2\text{MIM}][\text{NTf}_2]/$

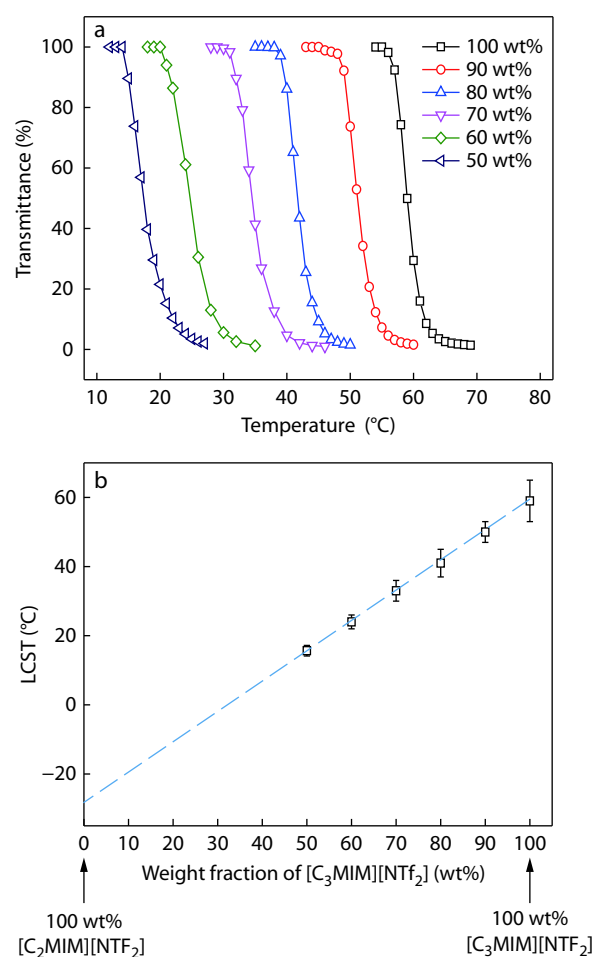


Fig. 5 LCST phase behavior of PBA-20 in IL blends. (a) Temperature dependence of transmittance at 658 nm for 2 wt% PBA-20 in $[\text{C}_2\text{MIM}][\text{NTf}_2]/[\text{C}_3\text{MIM}][\text{NTf}_2]$ blends. The weight fraction corresponds to $[\text{C}_3\text{MIM}][\text{NTf}_2]$. (b) The LCSTs as a function of the weight fraction of $[\text{C}_3\text{MIM}][\text{NTf}_2]$ in IL blends. The dash line is a linear fit to the data ($T_{\text{LCST}}(\text{PBA-20}) = 59 - 86 \times (1 - x)$, where x represents the weight fraction of the $[\text{C}_3\text{MIM}][\text{NTf}_2]$ in IL blends).

[C₃MIM][NTf₂] blends, the weight fraction in Fig. 5(a) corresponding to [C₃MIM][NTf₂]. The CPs of PBA-20 (2 wt%) in IL blends with 100%, 90%, 80%, 70%, 60% and 50% weight fraction of [C₃MIM][NTf₂] are identified as 59, 50, 41, 33, 24 and 16 °C, respectively. Plotting these data (Fig. 5b), we found that the CPs of the solution also decrease linearly from 59 °C for PBA-20 to 16 °C as the weight fraction of [C₃MIM][NTf₂] decreases. When the weight fraction of [C₃MIM][NTf₂] decreases to less than 40 wt% in IL blends, the CPs of solution is hard to be detected due to the lower limit of temperature control of the CP measurement instrument. However, through the linear relationship between CP of PBA/ILs solution and the weight fraction of ionic liquid in their blends, the CPs of the solution with lower weight fraction of [C₃MIM][NTf₂] are predictable. As shown in Fig. 5(b), dash line is a linear fit to the data, and the CP of PBA-20 in neat [C₂MIM][NTf₂] is predicted to be about −27 °C.

CONCLUSIONS

In this work, we reported the LCST-type phase behavior of PBA dissolved in hydrophobic 1-alkyl-3-methylimidazolium bis(trifluoromethyl) sulfonyl]amide ionic liquids. The temperature-composition phase diagrams of PBA/ILs systems are strongly asymmetric with the critical composition shifted to low concentrations of PBA. As the molecular weight increases from 5.0×10³ to 2.0×10⁴, the critical temperature decreases by about 67 °C. The length of the alkyl chain in the imidazolium cation has a significant influence on the miscibility of PBA in its corresponding ionic liquid. Besides, the LCSTs of PBA/ILs solution change linearly as changing the weight fraction of ionic liquid in their blends. These results not only suggest that the LCST of PBA/ILs solution can be easily tuned over a wide range of temperature by adjusting the mixing ratio of two ILs, but also provide a strategy to estimate the LCST of the solution with CP beyond the limit of the instrument. The wide temperature range adjustable LCST of PBA in ionic liquid is considered to have potential applications in the design of thermoresponsive materials such as thermoelectric electrolyte and ionic liquid gels.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <https://doi.org/10.1007/s10118-021-2522-2>.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Funds for Distinguished Young Scholar (No. 21725401), the National Key R&D Program of China (No. 2017YFA0207800), and the China Postdoctoral Science Foundation (No. 2019M650434).

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Electronic Supplementary Information

Tunable Lower Critical Solution Temperature of Poly(butyl acrylate) in Ionic Liquid Blends

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The characterization methods of PBA homopolymers: The molecular weight and molecular weight distribution (MWD) measurements of the PBA polymers were carried out by gel permeation chromatography (GPC) using a Waters 1515 Isocratic HPLC Pump and Waters 2414 Refractive Index Detector with tetrahydrofuran as the eluent at 35°C. Poly(methyl methacrylate) standards were used for calibration.

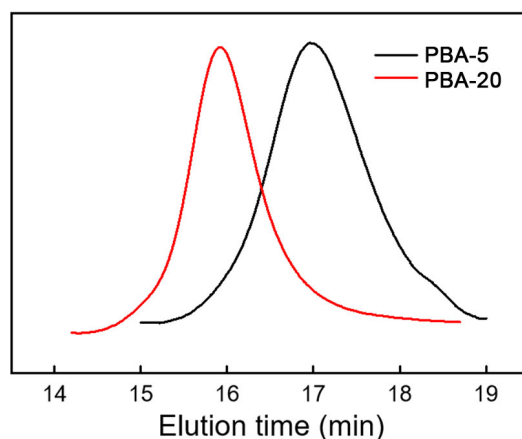


Fig. S1 GPC traces of the PBA homopolymers.

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Table S1. Molecular characteristics of PBA homopolymers.

PBA homopolymers	DP	M_n (kg/mol)	M_w (kg/mol)	PDI
PBA-5	40	5.2	6.3	1.21
PBA-20	162	20.3	22.1	1.09

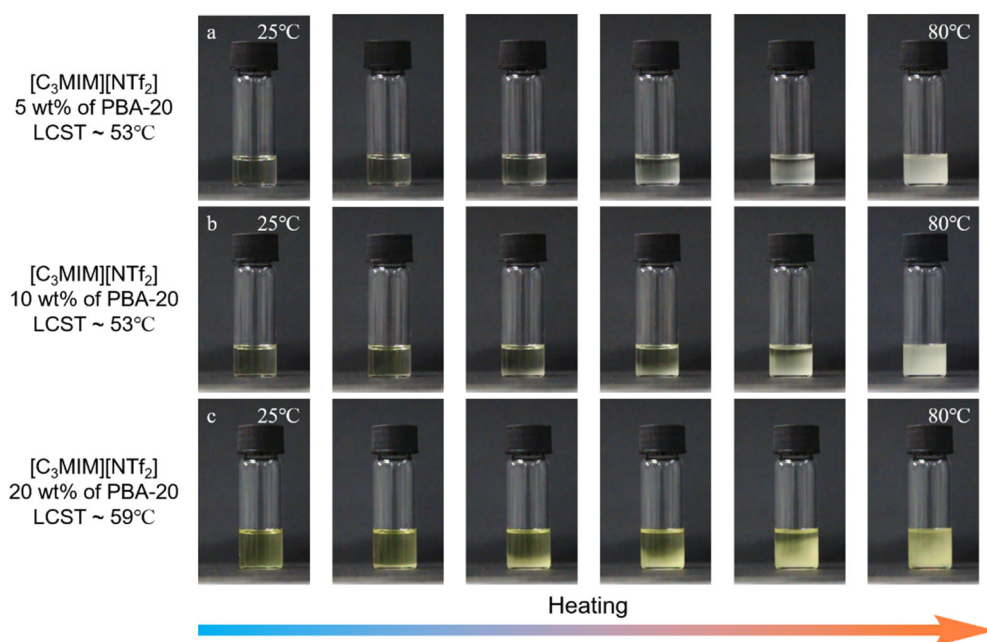


Fig. S2 Liquid-liquid phase separation of PBA-20 in $[C_3MIM][NTf_2]$ solution with the increase of temperature. a) 5 wt% of PBA-20. b) 10 wt% of PBA-20. c) 20 wt% of PBA-20.

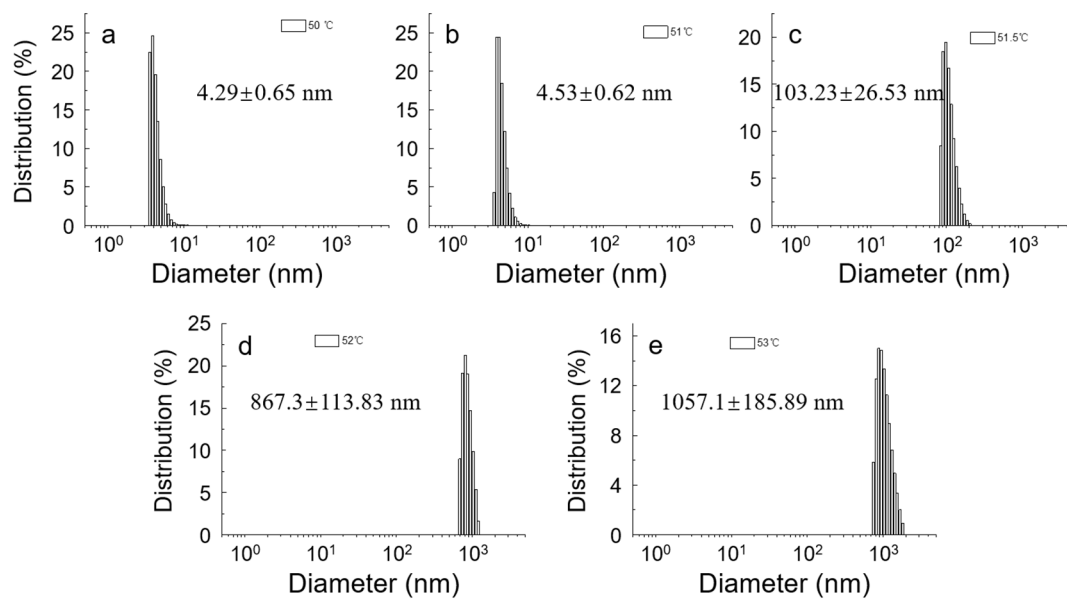


Fig. S3 Particle size distribution of PBA-20(5%) in $[C_3MIM][NTf_2]$ ionic liquids at different temperatures.