# Cationic Poly(ionic liquid) with Tunable Lower Critical Solution Temperature-Type Phase Transition

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Ⓢ Supporting Information

ABSTRACT: A cationic polyelectrolyte based on the styrenic ionic liquid tributyl-4-vinylbenzylphosphonium pentanesulfonate was found to undergo a lower critical solution temperature (LCST)-type phase transition in aqueous solutions. This phase transition occurs in a wide temperature range in terms of polymer concentration as well as type and concentration of externally added salts. Anion exchange and salting out effects are responsible for the flexible phase transition temperature.
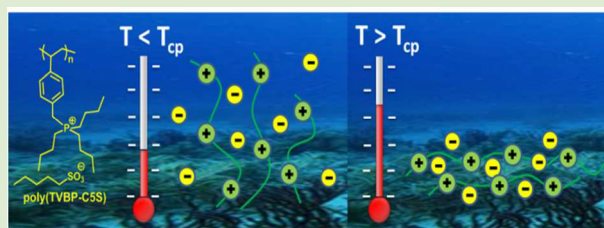
Polymers with lower critical solution temperature (LCST)-type phase transition behavior are a unique class of thermally responsive soft matter, which are of great interest in fundamental research and materials design.[1−8] Compared to other external environmental parameters, such as pH, electric field, humidity, or pressure, the reversible structural transition by means of temperature is practically easy to conduct and to control. There are several well-studied LCST-type polymers in aqueous solution including poly(N-isopropylacrylamide), poly-(2-oxazoline)s, poly(oligo(ethylene glycol) methacrylate), poly-(2-(dimethylamino)ethyl methacrylate), etc.[9−16] These polymers are exclusively neutral or weakly charged when dissolved in aqueous solution.

Strong polyelectrolytes with LCST-type phase transition were comparably much less studied. Ritter et al. reported that poly[1-butyl-3-vinylimidazolium bis(trifluoromethanesulfonyl)-imide] shows a pseudo-LCST effect in aqueous solution, however assisted by the presence of cyclodextrin.[17] The cyclodextrin complexes the large hydrophobic anion at low temperature, solubilizes the polymer, and slips off at elevated temperatures. Aoshima et al. demonstrated that poly(vinyl ether)s with imidazolium or pyridinium salt pendants undergo LCST-type phase separation though in organic media.[18] Polymers with an imidazolium tetrafluoroborate ion pair in the pendant group exhibited an upper critical solution temperature (UCST)-type phase separation in aqueous solution.

Ohno et al. first observed the LCST-type phase transition of a strong anionic polyelectrolyte, poly(4-tetrabutylphosphonium styrene sulfonate) in aqueous solution.[19] In their research, several tetraalkylphosphonium styrene sulfonate-based ionic liquids (ILs) with temperature-dependent water miscibility were initially synthesized and investigated. Free radical polymerization of these ILs through the anion unit led to polymerized ionic liquids or poly(ionic liquid)s (PILs), one of which showed LCST-type phase transition in water. Very recently, poly(tributylhexylphosphonium 3-sulfopropyl meth-

acrylate) was found to show the same effect,[20] the phase transition temperature varying in a wide range. Also, some PILs copolymerized with thermoresponsive polymers, like PNIPAM and PPO, were studied.[21,22] Our group further demonstrated the potential of such a PIL as "smart" polymeric stabilizers to control and design the exfoliation and deposition events of reduced graphene layers at a specific temperature in water.[23]

In this communication, we present a cationic PIL (Scheme 1) with a LCST-type phase transition in aqueous solution. Its

Scheme 1. Chemical Structures and Synthetic Route to a Series of Cationic PILs Bearing a Phosphonium Sulfonate Ion Pair in Each Monomer Unit (Bu = n-butyl)
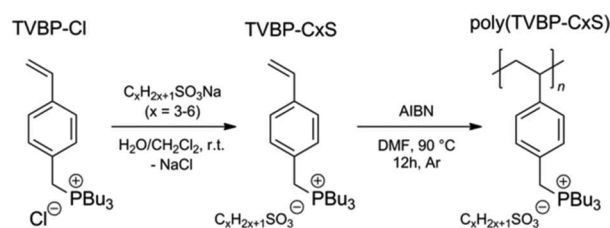
tunable phase transition behavior in aqueous solution in terms of polymer concentration and foreign salts was studied. The anion exchange and salting out effects are suggested to control their solution behavior in the presence of salts. This finding enriches the toolbox of thermoresponsive polymers by introducing a strong polyelectrolyte candidate with permanent cationic charge, therefore broadening the design scope of smart materials.

A series of tributyl-4-vinylbenzylphosphonium-based IL monomers containing an alkanesulfonate anion with different

chain length from propyl to hexyl (Scheme 1) were synthesized from a commercially available monomer salt tributyl-4-vinyl-benzyl phosphonium chloride. The IL monomers are termed TVBP-CxS, where x is the carbon number of alkyl sulfonate. The melting points of all compounds, as measured by differential scanning calorimetry (DSC), were below 100 °C, thus matching the definition criteria of ILs. These ILs were intentionally chosen because the ion pair of phosphonium sulfonate has been observed to exhibit reversible interactions with water molecules at different temperatures in several ILs and anionic PILs, as mentioned above. In our system, we chose the styrenic phosphonium cation which allows for the preparation of cationic PILs.

^{1}H NMR spectroscopy was employed to confirm the chemical structure of these new IL monomers and corresponding PILs.[24−28] Figure 1 displays the ^{1}H NMR spectra of
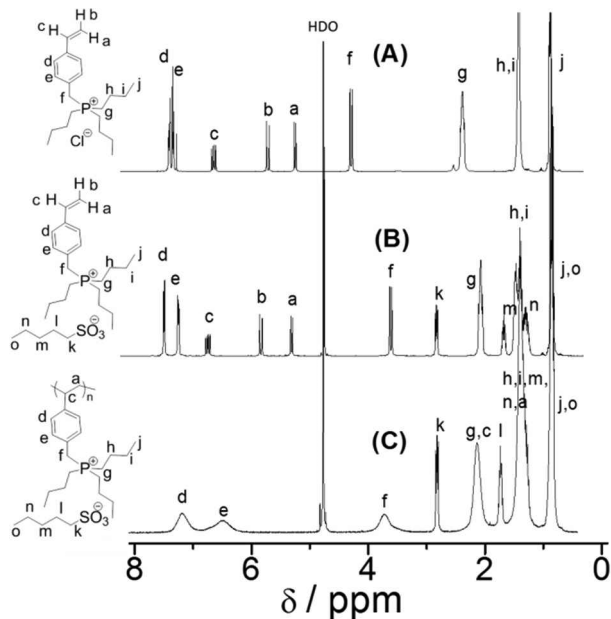

Figure 1. ^{1}H NMR (400.1 MHz, D$_2$O) spectra of (A) tributyl-4-vinylbenzylphosphonium chloride, (B) TVBP-C5S, and (C) poly-(TVBP-C5S).

tributyl-4-vinylbenzylphosphonium chloride, TVBP-C5S, and its PIL poly(TVBP-C5S) (weight-average molecular weight, M_w = 58.0 kg mol^{-1}, dispersity, M_w/M_n = 1.8, by analytical ultracentrifugation (AUC), see Supporting Information), which, as will be discussed later, is the only LCST-type cationic PIL in this series in the liquid water temperature range. (See Supporting Information for ^{1}H NMR spectra of other IL monomers and PILs.) Figure 1A shows the monomer salt with chloride anion. The phenyl protons show a combined signal at 7.4 ppm. The well-resolved signals at 6.6, 5.7, and 5.3 ppm are attributed to the three vinyl protons. The benzylic CH$_2$ next to the phosphonium cation appears at 4.3 ppm. The protons in the butyl chains are observed at high field at 2.4, 1.4, and 0.9 ppm. After the exchange of the chloride anion by pentanesulfonate, new signals at 2.8, 2.1, 1.7, and 1.3 ppm can be attributed to the four CH$_2$ sets of protons in the pentyl chain, while the CH$_3$ protons overlap with the methyl protons in the cations at 0.9 ppm. The cation exchange also splits the phenyl protons into two sets at 7.5 and 7.3 ppm and shifts the benzylic CH$_2$ protons to a higher field at 3.7 ppm. The vinyl

protons stay intact. The integral ratio of the CH$_2$ protons (g in Figure 1) in butyl chains to the phenyl protons (d in Figure 1) is measured to be 3.0, identical to the expected value, confirming the quantitative anion exchange. Following the polymerization, the vinyl protons vanished completely, and the newly formed backbone protons overlapped with the pentyl protons at 2.1 and 1.3 ppm.

The water miscibility of the as-synthesized IL monomers and PILs in aqueous solution at a weight fraction of 5 wt % was tested by turbidity measurements (UV−vis, λ = 670 nm). TVBP-C3S was found to be completely soluble up to 100 °C, while TVBP-C6S was only slightly soluble. The corresponding PILs show the same behaviors. In contrast, TVBP-C4S and TVBP-C5S are soluble in water yet become immiscible above 31 and 53 °C, respectively (Supporting Information). When polymerized, the formed poly(TVBP-C4S) is soluble in water throughout the entire liquid water range, while poly(TVBP-C5S) undergoes an LCST-type phase transition. This transition is dependent on the polymer concentration. Figure 2A shows
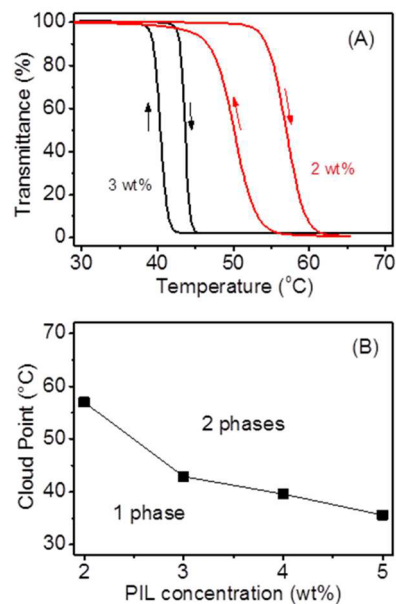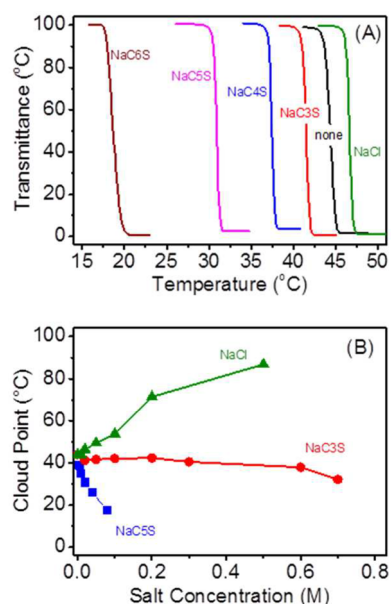

Figure 2. (A) Turbidity curves of poly(TVBP-C5S) at 2 wt % and 3 wt % in water. (B) Plot of the cloud point temperature vs polymer concentration.

the turbidity curves of poly(TVBP-C5S) in aqueous solution at a concentration of 2 wt % and 3 wt % from 30 to 70 °C. At 3 wt %, rather sharp transitions (despite the broad molecular weight distribution of the polymer) in both the heating and the cooling curves and narrow hysteresis (Δ = 4.3 °C) were detected. At 2 wt %, the phase transition becomes comparably broader in both heating and cooling cycles. Meanwhile, the hysteresis loop expands (Δ = 7.1 °C) considerably. At 4 wt % and 5 wt %, macroscopic phase separation takes place in the heating loop severely such that the precipitate was incompletely dissolved in the cooling cycle, causing broad hysteresis. It should be noted that the heating−cooling cycle is fully reversible. The cloud point temperature, T_{cp}, defined as the temperature of 80% transmittance in the heating run, was measured for poly(TVBP-C5S) at 2 wt % to 5 wt % and found to decrease from 57 to 32 °C (Figure 2B). No clouding was observed at 1 wt % or below.

Foreign salts added to an aqueous polyelectrolyte solution will increase the ionic strength, which in turn leads to the

screening of the electrostatic interactions between ionized groups, thus reducing the polyelectrolyte effects, such as stretched chain conformation, high viscosity, etc.[29−33] For thermoresponsive polyelectrolytes, ionic strength is a useful tool to adjust their cloud point in aqueous solution. For instance, we reported that an anionic PIL, poly(4-tetrabutyl-phosphonium styrene sulfonate), could vary its T_{cp} by addition of potassium bromide or tetrabutylphosphonium bromide. Ohno et al. also demonstrated that the T_{cp} of another anionic PIL, poly(tributylhexylphosphonium 3-sulfopropyl methacry-late), in aqueous solution decreased upon addition of a buffer containing KH_2PO_4/K_2HPO_4.[20] Yet the intrinsic correlation between the salt type and the phase transition change is not understood.

Figure 3A shows the turbidity curves of the poly(TVBP-C5S) solution (3 wt %) in the presence of six sodium salts at a

Figure 3. (A) Turbidity curves of poly(TVP-C5S) at 3 wt % in aqueous solution in the presence of 0.02 M salt of different types. (B) Plot of the cloud point temperature vs salt concentration.

final concentration of 0.02 M. When salt is introduced to the aqueous solution of poly(TVBP-C5S), two effects can be readily observed. First, the partial anion exchange between C5S and the foreign anion makes the polymer either more hydrophilic or more hydrophobic, which in turn amplifies or disrupts the polymer−water interactions. Second, the common salting out effect will cause collapse and precipitation of the polyelectrolyte out of the solution.

Considering the structure feature, the hydrophilicity of the anions decreases in the sequence of $Cl^- > C_3S^- > C_4S^- > C_5S^- > C_6S^-$. Therefore, at the same salt concentration, the T_{cp} follows exactly the same trend in Figure 3A. A difference is yet noticed between NaCl and $NaCxS$, as the former increases the T_{cp} and the latter impacts oppositely. This reveals that by addition of NaCl the anion exchange effect is far stronger, while the salting out effect dominates the polymer solution behavior in the case of adding $NaCxS$.

We also performed salt-concentration-dependent turbidity measurements at the same polymer concentration for NaCl, NaC_3S, and NaC5S; results are displayed in Figure 3B. Addition of NaCl leads to a continuous increase of the T_{cp}

(∼44 °C → 87 °C at 0.5 M NaCl). Here, the anion exchange overcompensates the salting out effect. In the case of NaC3S, a constant $T_{cp} \sim 40$ °C was observed from 0.002 to 0.6 M. In this range, the anion exchange effect and the salting out effect seem to balance each other, whereas above 0.6 M the salting out effect takes the advantage and decreases the T_{cp}. When NaC5S was added, the anion exchange effect was intrinsically canceled, and C5S is the only anion in the system. The T_{cp} drops stepwise and more sharply by addition of NaC_5S. At 0.07 M of NaC5S, the T_{cp} is decreased down to below 20 °C.

A thermoresponsive polycation with tunable T_{cp} in aqueous solutions can be applied, for example, for nanoparticle stabilization and manipulation. Most noble metal nanoparticles, such as gold, silver, or platinum, are negatively charged in water. The cationic PIL can be absorbed tightly onto the nanoparticle surface via Coulombic interaction to render thermoresponsive function to nanoparticles.[34] As an example, shown in Figure 4,
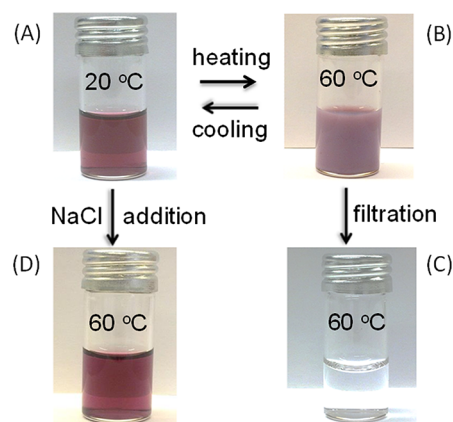
Figure 4. Photographs of poly(TVBP-C5S) stabilized gold nano-particles (A) at 20 °C, (B) at 60 °C, (C) after filtration at 60 °C, and (D) at 60 °C in the presence of 0.2 M NaCl. Polymer concentration is 3 wt % in all samples.

mixing a gold nanoparticle (10 nm, stabilized by citric acid) solution with poly(TVBP-C5S) at a final PIL concentration of 3 wt % yields a stable nanoparticle solution at room temperature. Upon heating, the solution becomes turbid due to the collapse and precipitation of the poly(TVBP-C5S)/nanoparticle hybrid. Filtration through a membrane filter (0.2 μm) at the same temperature yields a nanoparticle-free solution, as proven by UV−vis spectroscopy (Supporting Information). This might be considered as an alternative method to remove noble metal nanoparticles from aqueous solution, especially when they are rather small to be isolated by centrifugation. The average size of the Au particles after stabilization and the heating−cooling cycle remain unchanged, as evidenced by transmission electron microscopy (TEM; Supporting Information). In addition, if necessary the thermoresponsiveness of the hybrid solution can be readily abandoned by adding NaCl, as shown in Figure 4C. Thus, the thermoresponsiveness of the gold nanoparticles in aqueous solution can be rendered or canceled at will.

In conclusion, a strong cationic polyelectrolyte poly(tributyl-4-vinylbenzylphosphonium pentanesulfonate) was demonstra-ted to show a LCST-type phase transition in aqueous solution. The cloud point could be tuned in a wide temperature window in terms of polymer concentration and addition of salts. A detailed study on the monovalent salt addition process revealed

two parallel effects, the anion exchange and the salting out effect. The unique solution property of this cationic polyelectrolyte was applied as a smart stabilizer for nanomaterials to flexibly manipulate their solution state.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

(1) Experimental procedures for thermoresponsive IL monomers and PILs. (2) Melting points of TVBP-CxS (x = 3−6) measured by DSC. (3) ^{1}H NMR spectra of TVBP-CxS (x = 3∼6). (4) AUC sedimentation-velocity and -equilibrium data of poly(TVBP-C5S). (5) Turbidity curves of TVBP-C4S and TVBP-C5S at 5 wt % in water. (6) UV−vis spectra of poly(TVBP-C5S) and poly(TVBP-C5S)-Au nanoparticles in aqueous solution. (7) TEM images of poly(TVBP-C5S)-Au nanoparticles. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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■ NOTE ADDED AFTER ASAP PUBLICATION

This Letter posted ASAP on May 9, 2013. Figure 4 has been revised. The correct version posted on May 10, 2013.