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Thermoresponsive polycations

Vikram Baddam and Heikki Tenhu *

Aqueous solutions of polyelectrolytes are known to be complex; however, when the charged polymer carries a simple counterion such as sodium or chloride it is usually soluble in water. By modifying the hydrophobic/hydrophilic balance of the polymer structure with substituents in the charged repeating unit or by changing the counterion, the solubility and thermal behavior of the polymer can be varied. Recent interest in polymeric ionic liquids has moved much of the focus towards asymmetric systems where the polymer may bind a bulky, often hydrophobic, counterion. Polyelectrolytes with hydrophobic substituents and/or counterions are often thermoresponsive and, interestingly, by refining the structure, it is possible to change the LCST behavior into UCST, and even the coexistence of both LCST and UCST is possible. In this review, we summarize recent progress made on investigating the thermoresponsive behavior of polycations and cationic copolymers in aqueous and non-aqueous solvents. The main emphases are on tuning the solution properties of polycations with alkyl substituents, counterions, and copolymer structures.

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1. Introduction

Polyelectrolyte solutions have been extensively studied for years, and many theoretical and experimental investigations have been conducted to understand the conformations of polyelectrolyte chains in solution.[1–5] Compared to the solutions of non-charged polymers, polyelectrolyte solutions are complicated because of several variable interactions.[6] So far, discussions on polyelectrolytes have mainly concentrated on the polymer chain conformation and its dependence on simple counterions, such as Na^+, Cl^-, *etc.*[7–12] The chain conformation is dictated by coulombic interactions and added salts determine the functionality of a polyelectrolyte and play a crucial role when employing the polyelectrolyte for its applications.[13–22]

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The importance of counterions on the properties of polyelectrolytes has only recently been realized. Counterions affect the solubilities of the charged chains and can make them stimuli-responsive in aqueous or non-aqueous solvents. The solubility of a permanently charged polymer is not prominently affected by pH but this may change when using hydrophobic counterions.[23–28] Ionic interactions can be modulated by an external stimulus like temperature, and this is how a polyelectrolyte may become thermoresponsive in aqueous or non-aqueous systems.

Thermoresponsive polymers that undergo phase separation either below the upper critical solution temperature (UCST) or above the lower critical solution temperature (LCST) are well documented in the literature.[29–34] The phase separation mechanism of nonionic LCST polymers is mainly based on intra- or intermolecular hydrophobic interactions, which change when the hydration layer around the polymer breaks down upon heating.[29,35] The UCST behavior is due to intra- and intermolecular H-bonding or electrostatic interactions.[30,36–39] The thermoresponsive behavior of polyelectrolytes is different from that of non-charged polymers, as the phase separation process depends on three body interactions, including polymer–polymer, polymer–water, and strong polymer–counterion interactions. The behavior of a non-ionic polymer is mainly due to the polymer–polymer and polymer–water interactions. In non-ionic systems, one can manipulate the phase transition behavior by adding hydrophilic or hydrophobic units to the main polymer chain or to the repeating units. Zhao *et al.* proposed the thermodynamic mapping of thermo-responsive polymer systems based on various interactions and polymer chain architectures.[40]

A few reviews already discussed some polyelectrolytes that exhibited thermoresponsive behavior in aqueous or non-aqueous systems,[36,41,42] however, structural variation of polycations and copolymer architectures was not reported in detail. In the present short review, we first discuss certain non-ionic, zwitterionic and anionic thermoresponsive polymers and their phase separation mechanisms. Recently, interest in thermo-responsive polycation systems has noticeably increased[43–46] and the main focus of the present review is on novel studies of cationic polymers. The main aim of the review is to summarize observations concerning how detailed chemical structures of the cationic structural units and the type of counterion affect the phase separation processes in aqueous or non-aqueous polycation systems.

2. Thermoresponsive polymers

2.1. Nonionic polymers

Polymers that phase separate upon heating or cooling are already well-known.[33,34,47–49] In a LCST system, polymers are miscible with a solvent below a certain temperature, but phase separation occurs above it. Poly(*N*-isopropylacrylamide) (PNIPAM) is the most studied polymer, and phase separation takes place above the LCST (about 32 °C), or simply T_{cL}, see Fig. 1. The phase separation of such non-ionic systems is

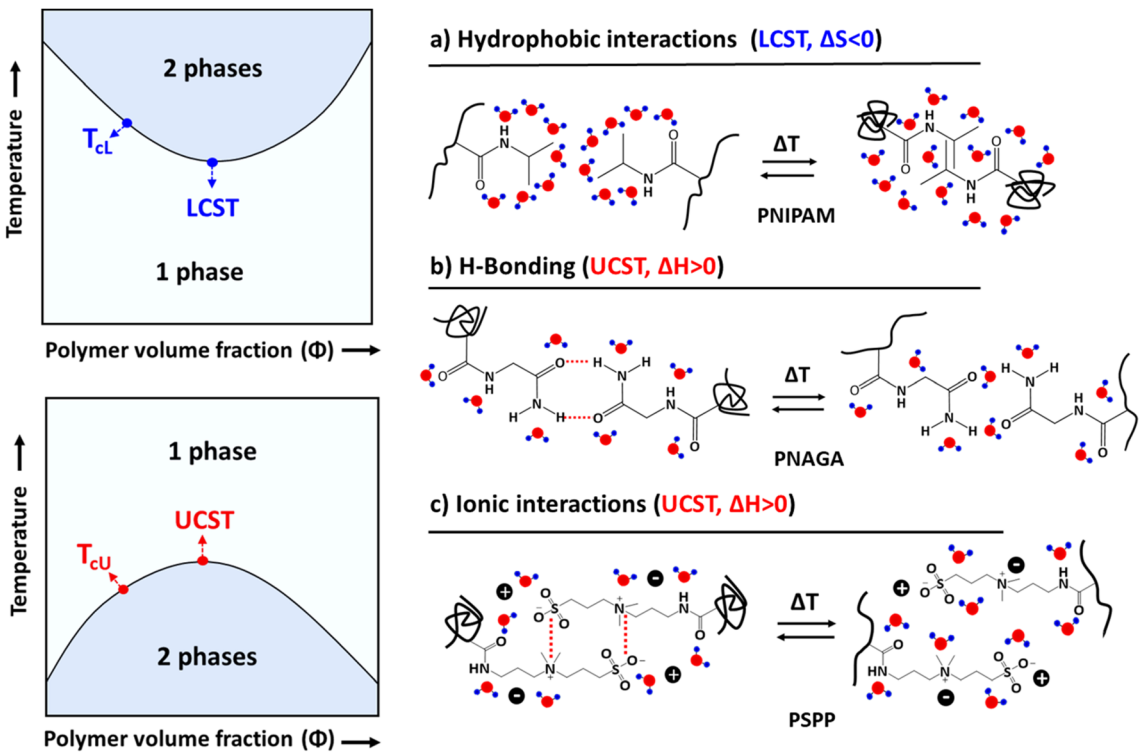

Fig. 1 Phase diagrams of thermoresponsive polymer solutions with LCST or UCST. Types of interactions involved in different polymer phase separation processes: (a) hydrophobic interactions in PNIPAM, (b) H-bonding interactions in PNAGA, and (c) ionic interactions in PSPP.

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mainly dependent on the negative entropy of mixing ($\Delta S_m < 0$ when $T <$ LCST) due to the polymer–solvent interactions. As the water cages surrounding the repeating units are disrupted by heating, the polymer chains start to aggregate above the cloud point temperature.

UCST polymers behave oppositely. Polymers are soluble above certain critical temperatures (T_{cU}), but phase separate below that. Poly(*N*-acryloyl glycinamide) (PNAGA) is an example of a nonionic polymer that shows the UCST-type phase transition in aqueous solutions. The polymers dissolve above the UCST because of the positive enthalpy of mixing ($\Delta H_m > 0$).[31] The UCST-type phase separation can be observed in several hydrogen-bonding polymers, such as polymethacrylamide, acrylamide-, ureido-, and imidazole-based polymers.[37,39,40,50–54] When the polymer chain carries both H-bond donors and acceptors, inter- and intra-chain H-bonds build up. Solubilizing such a polymer requires the disruption of the H-bonds by thermal energy, and this is the origin of the UCST behavior in nonionic polymer systems. Electrostatic interactions trigger similar processes in the case of oppositely charged polyelectrolytes.[55,56]

2.2. Polyzwitterions and polyanions

Polyzwitterions and polyampholytes exhibit UCST or LCST-type phase transitions in aqueous or non-aqueous systems due to intra- and intermolecular electrostatic interactions and dipole–dipole interactions between oppositely charged ionic groups.[30,44,57–62] Sulfobetaine-based zwitterionic polymers undergo UCST-type phase transitions in aqueous solutions. The behavior depends on the molar mass of the polymer, salt, and polymer concentrations. A few studies have been conducted to elucidate the effects of the molecular structure of polysulfobetaines, such as **S1**, on their thermoresponsive behavior.[56,63] Hildebrand *et al.* studied polysulfobetaines in which the anionic and cationic charges were separated with various different spacers. They observed that polymers where the spacers were substituted with hydroxyl groups underwent phase separation at lower temperatures compared to the polymers with alkyl spacers (**S2** and **S3** in Fig. 2).[56] The cloud point temperatures can be tuned with alkyl substituents in the sulfobetaine repeating units. It has been observed that with sulfobetaines with long or bulky alkyl spacers, the solubilities of the polymers increase in water (**S4** and **S5**). This is because the steric hindrance of larger alkyl groups decreases the electrostatic interactions between the ionic groups.[64]

Wang *et al.* studied polysulfobetaines **S6** by changing the length of one of the alkyl substituents of the quaternary nitrogen.[64] Polymers with methyl substituents undergo UCST-type phase separation in water, whereas those with ethyl, propyl, or butyl substituents are soluble. Interestingly, polymers with long alkyl substituents (pentyl or hexyl) undergo LCST phase transitions upon heating (Fig. 2A and B). By increasing the alkyl length to *n*-heptyl, polymers become totally insoluble in water.[64] This intriguing solution behavior is due to the increase in the entropic penalty (ordering of water molecules) as well as weakening of the electrostatic interactions between zwitterionic groups by introducing hydrophobic units.

Few thermoresponsive polyanions in aqueous systems have been reported.[19,41] For instance, anionic styrene sulfonate (PSS) and 3-sulfopropyl methacrylate polymers (PMPS) undergo LCST-type phase transitions in aqueous solutions, see Fig. 3. The phase separation of these polymers is mainly due to hydration changes around the anionic repeating units and the hydrophobic balance of the counterions. Upon heating, polymers form random aggregates that are surrounded by cationic counterions.[41,65,66]

In the case of PMPS, the polymer does not phase separate when using $[P_{4444}]^+$ as a counter ion.[66–69] However, by changing the alkyl substituent from butyl to hexyl in the tetraalkylphosphonium ions ($[P_{4444}]^+$ to $[P_{4446}]^+$), the polymers undergo LCST-type phase separation upon heating. The cloud point T_{cL} shifts to lower temperatures with the addition of more hydrophobic $[P_{4448}]^+$ ions with *n*-octyl substituents.[68] For styrene-based poly styrene sulfonate tetrabutylphosphonium, PSS $[P_{4444}]$, LCST-type phase separation can be induced using the same $[P_{4444}]^+$ counter ions and T_{cL} can be tuned with counterions, the monomer SS$[P_{4444}]$, and polymer concentrations (see Fig. 3).[67,70] When increasing the polymer, counterion, or monomer concentration, the T_{cL} shifts to lower temperatures (Fig. 3A, C and D). Alternatively, with the addition of simple salts like KBr, the cloud point shifts to higher temperatures, or the LCST-type phase transitions disappear at high salt concentrations (see Fig. 3B). The phase separation processes of the same PSS systems were studied using gemini-cationic counterions.[71,72] In these cases, the phase transitions of the solutions are sensitive to the counterion and polymer concentrations, similar to the monocationic PSS $[P_{4444}]$ systems.

Zhang *et al.* conducted in-depth studies on the phase separation of PSS.[72] They observed that the polymers underwent liquid–liquid phase separation upon heating. This was reasoned to be the effect of polymer dynamic crosslinking by the gemini counterions. Based on variable-temperature ^{1}H NMR and two-dimensional correlation analysis, the authors concluded that dehydration of anionic chains mainly served as the driving force for phase separation in the PSS aqueous solution. The polymerized anion tends to form aggregated cores with dications distributed around the globules at the end of the transition process. The LCST-type phase transitions were also observed in covalently cross-linked gels of PSS and acrylate-based sulfonate polymers.[73] The cloud points of the gels decrease with increasing crosslinker concentration. The behavior of the gels differed from that reported for linear polymers. The endotherms measured calorimetrically upon heating were very broad.[73]

Aside from polysulfonates, a few carboxylic polyanions that show LCST or UCST-type phase transitions have been reported.[38,74,75] Polyanions made of borate ($-B^-$–) and sulfonylimide ($-SO_2N^{(-)}SO_2-$) have been studied as single-ion conducting polymers.[76] However, to the best of our knowledge, there have been no studies on the thermoresponsive behavior of such polyanions.

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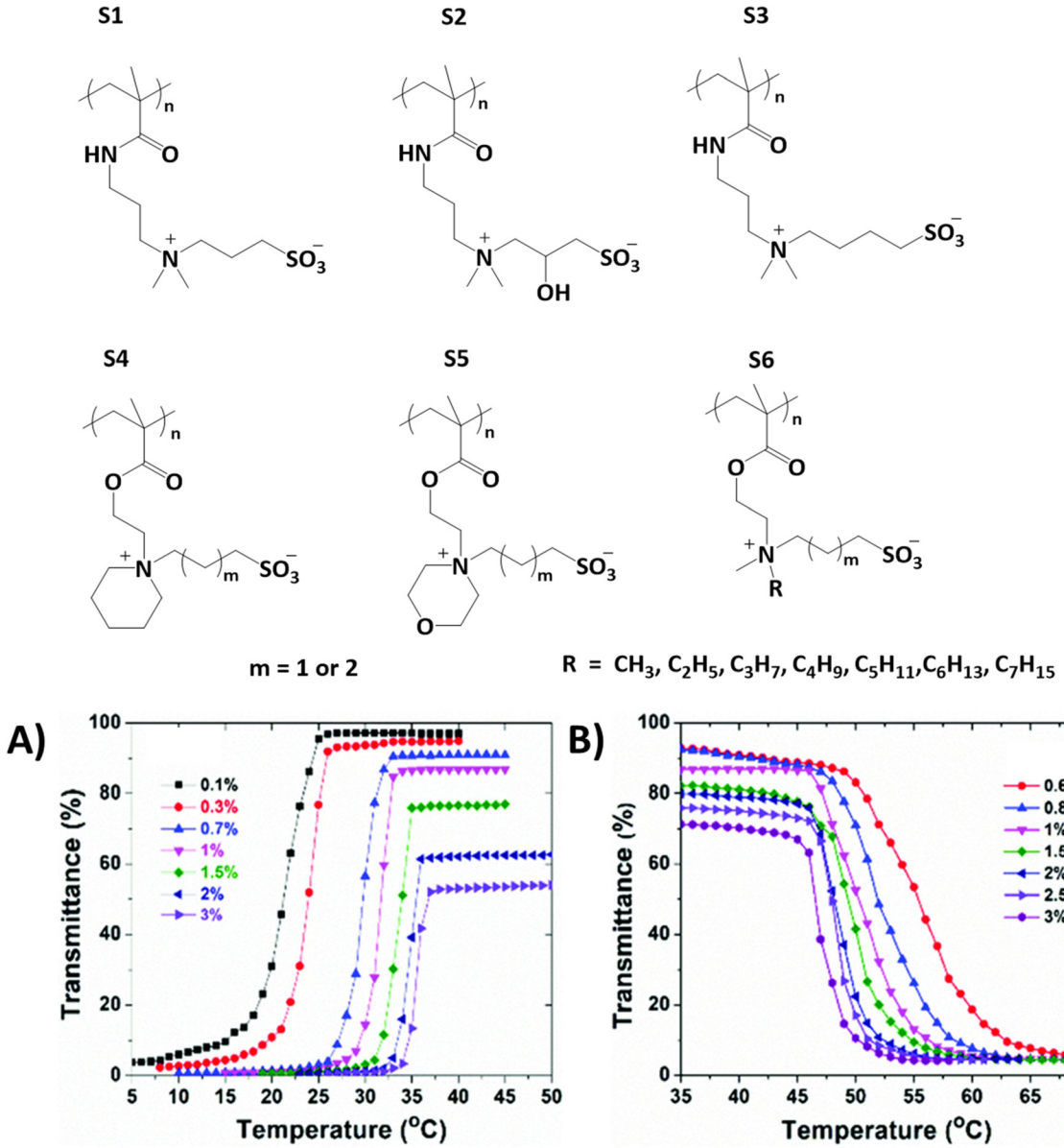

Fig. 2 Series of zwitterionic polysulfobetaines. (A) Transmittance data collected upon cooling **S6** with methyl substituents; (B) collected upon heating **S6** with a *n*-pentyl substituent at various polymer concentrations. Reproduced from ref. 64. Copyright 2018 Royal Society of Chemistry.

Thermoresponsive polyelectrolytes or poly(ionic liquid)s have only recently gained attention, and polycation systems are presently being explored much more intensely than polyanions. This could be owing to the larger structural variances of polymerizable cationic ionic liquids or ionomers than the anionic ones. This gives us a good reason to discuss the polycations separately.

3. Thermoresponsive behavior of polycations

The solution properties of polycations change significantly if simple ions (Cl^-, Br^-, *etc.*) are replaced with bulkier counterions. The change is especially noticeable for fluorinated counterions, such as tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-), trifluoromethanesulfonate (OTf^-), and bis(trifluoromethylsulfonyl)amide (NTf_2^-). Polycations can undergo phase separation by modulating the coulombic interactions between the cationic repeating units and the counterions with temperature. Several polycations have been reported to show phase separation in aqueous or non-aqueous solutions either above the cloud point temperature (T_{cL}) upon heating (LCST-type) or below the cloud point temperature (T_{cU}) upon cooling (UCST-type). However, the type of phase separation process mainly depends on the hydrophilic–hydrophobic balance of cationic repeating units and of the counterions.

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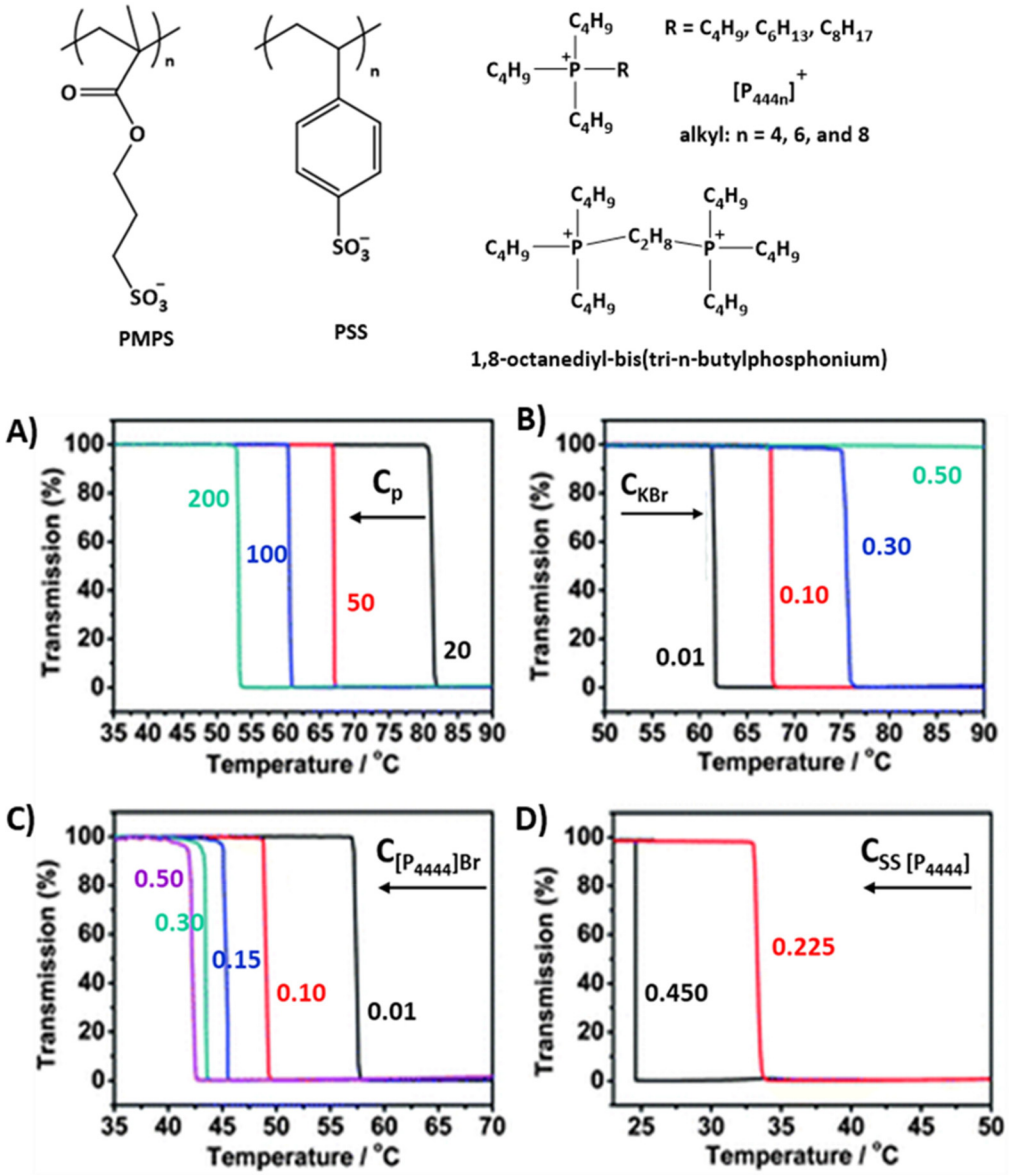

Fig. 3 Strong polyanions that show LCST-type phase transitions with corresponding hydrophobic counterions. (A) Transmittance curves of PSS [P_{4444}] solutions with various polymer concentrations (C_p), (B) PSS [P_{4444}] (100 g L^{-1}) in aqueous KBr solutions (0.01–0.5 M), (C) PSS [P_{4444}] (100 g L^{-1}) in [P_{4444}]Br (0.01–0.5 M) aqueous solutions, (D) PSS [P_{4444}] (100 g L^{-1}) in SS [P_{4444}] aqueous solutions. Reproduced from ref. 67. Copyright 2012 Royal Society of Chemistry.

Interesting research has already been conducted on the phase separation of polycations with hydrophobic counterions. For example, aqueous solutions of the cationic poly(allylammonium chloride) (PAAC) phase separate when introducing hydrophobic counterions like *p*-ethylbenzenesulfonate (EBS^-) ions.[24] This phenomenon was also investigated for solutions of the styrene-based polycation poly((vinylbenzyl)trimethylammonium chloride) (PVBTMAC) with hydrophobic fluorescent ions such as pyrene sulfonate (PSA^-). Excimer emission of PSA^- ions in the presence of PVBTMAC confirmed the formation of hydrophobic domains.[25] Analogous to nonionic polymers, polycations may phase separate from aqueous solutions when introducing a cosolvent. The strong polycation poly(methacryl oxyethyl trimethylammonium) (PMOTA) with its methanesulfonate counterion undergoes a reversible coil-to-globule transition upon increasing the acetone content in aqueous polymer solutions. It was concluded that the free energy of the system, determined by coulombic interactions and strong ion pairing, led to intra- and intermolecular associations when the dielectric constant of the solution was lowered with the addition of acetone.[77,78] Throughout the following discussion on responsive polycations, we refer to numbering given in Scheme 1.

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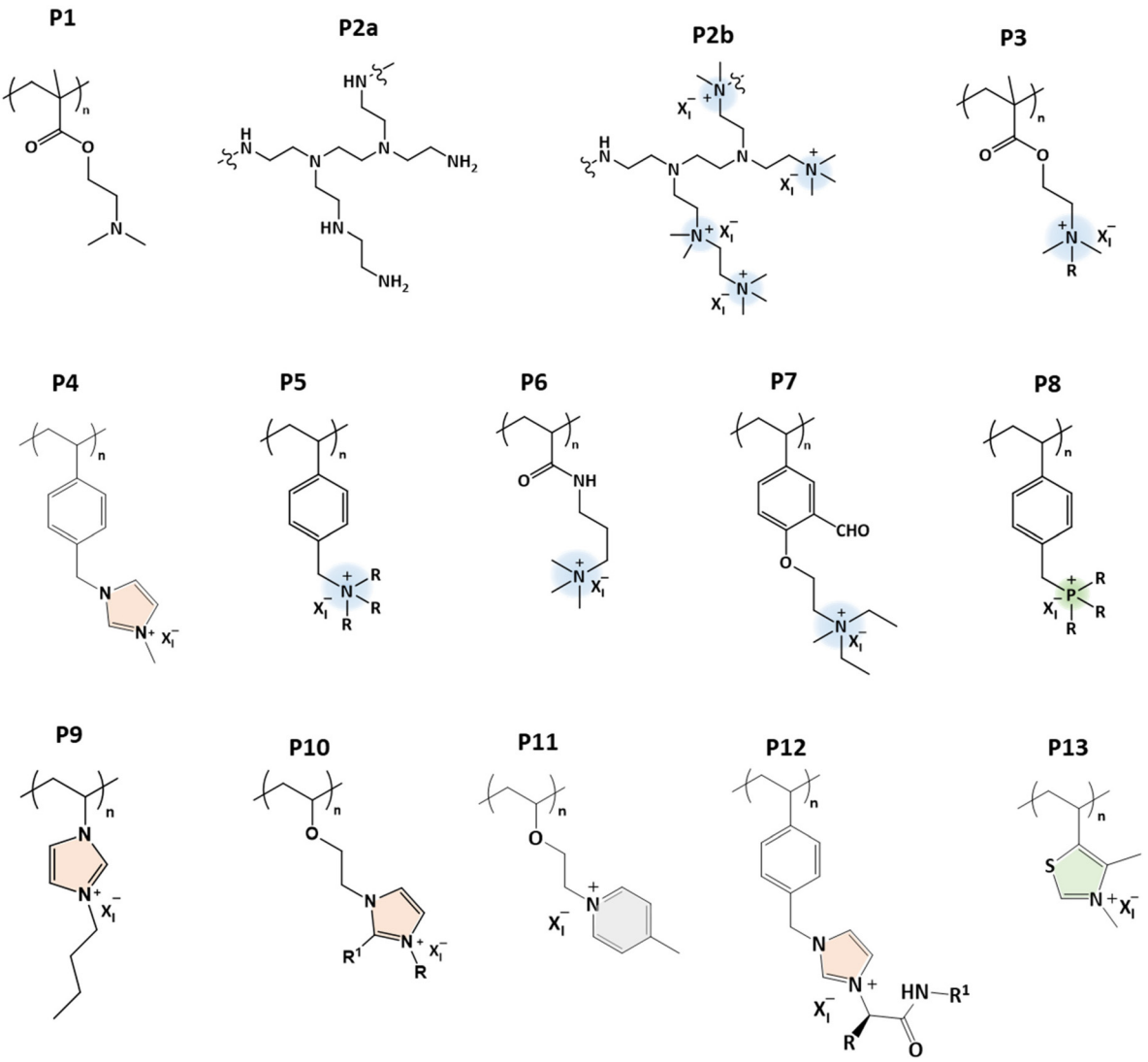

Scheme 1 Vinyl-based thermoresponsive polycations.

Poly(*N*,*N*-dimethylaminoethyl methacrylate) (PDMAEMA; **P1**) is a weak polycation and besides its pH responsiveness, it can show LCST in aqueous solutions. Both UCST and LCST behaviors may be observed by adjusting the pH of PDMAEMA solutions when using either mono- or multivalent counterions.[79–81] Other tertiary amine polymers have been reported to show thermoresponsive behavior in aqueous solutions. Pang *et al.* recently reviewed the thermoresponsive behavior of tertiary amine functionalized poly((meth)acrylamide)s, poly((meth)acrylates), poly(styrenes), poly(vinyl alcohols), and poly(ethylene oxides).[82]

3.1. UCST transition

Strong polycations with UCST-type phase transitions have been studied much more than those with a LCST. Noh *et al.* studied the thermoresponsive behavior of the branched polyethylene imine (PEI) and methylated PEI, MPEI (**P2**).[83] They observed the UCST-type phase transition for PEI in aqueous solutions with simple ions like Cl^-, Br^-, and I^-. When the ionic interactions between the counterion and PEI are strong enough to overcome the water–ion interaction, conditions are created that lead to the UCST behavior. However, this behavior was only observed under extreme pH conditions. In the latter case, it was observed that the hydrophobicity of the counterion of methylated PEI was an important parameter to induce the UCST transition. When I^- or BF_4^- were used as counterions, MPEI underwent phase separation, whereas with Br^- and Cl^- MPEI was soluble over the temperature range 0–100 °C. The behavior also depended on the molar mass of the polymers: higher T_{cU} values were recorded for a high molar mass polymer compared to the short one.[83] Such properties were also observed for PDMAEMA under certain pH conditions. When using hydrophobic counterions like bistrifluoromethane sulfonylimide (NTf_2^-), PDMAEMA undergoes an UCST-type phase transition in aqueous solutions.[81]

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Strongly charged PMOTA (**P3**) with different alkyl substituents and BF_4^- as a counterion displays an UCST-type transition.[84] However, the same polymer with an iodide counterion (PMOTAI) is water-soluble at any temperature. The addition of the hydrophobic counterion NTf_2^- to an aqueous solution of PMOTA leads to complete phase separation due to strong ion pairing.[85] In the presence of NaCl or changing the counterions to less hydrophobic trifluoromethanesulfonate (OTf^-) ions, an UCST-type phase transition can be induced. Similarly, a styrene-based polycation with imidazolium pendants (**P4**) also undergoes an UCST-type transition and the reported cloud point temperatures are higher than those for **P3** under the same conditions. A low amount of triflate counterions is needed to make **P4** thermoresponsive due to the hydrophobic phenyl units. For both polymers, a sufficient ionic strength (NaCl) is required to observe the cloud/clearing point when using the NTf_2^- counterions. The cloud points can be tuned over a wide temperature window by changing the ionic strength of solutions. In the case of **P3**, the maximum T_{cU} was observed at around 500 mM in both LiOTf and KOTf aqueous solutions (Fig. 4A).[85] The same styrene-based imidazolium polycation **P4** with BF_4^- counterions was reported to show an UCST-type phase transition in methanol/water (80/20) mixtures. The T_{cU} strongly depends on the molar mass and concentration of the polymer. T_{cU} increased from 14 to 21.4 °C when the DP of **P4** increased from 36 to 107. In addition, the T_{cU} can be tuned to lower temperatures with increasing water content in solvent mixtures.[86]

Styrene-based quaternary ammonium polycations (**P5a**) carrying either OTf^- or Cl^- as counterions are well soluble in water, however, they become thermoresponsive with an UCST-type phase transition upon the addition of a small amount of triflate ions. In the presence of 0.1 M of LiOTf, the polycations with a low molar mass (DP = 24) undergo phase separation below 35 °C. However, with increasing molar mass of **P5a**, the T_{cU} shifts to higher temperatures (DP = 61, T_{cU} = 51 °C) when the LiOTf concentration remains constant. The other two acrylamide-based polycations poly(3-(acrylamido)propyl)trimethylammonium chloride (PAMPTMAC; **P6**) or methacrylate-based **P3** do not phase separate at any temperature under similar conditions (DP = 24, 1 g L^{-1} and LiOTf = 0.1 M).[87]

Recently, the influence of alkyl substituents on the phase separation of styrene-based polycations was investigated in several salt solutions.[88] The polycation with ethyl substituents, **P5b**, undergoes an UCST-type phase transition in the presence of the counterions SCN^-, OTf^-, and NTf2$^-$ (Fig. 4B). As in the case of **P3**, when NTf_2^- was the counterion, a secondary salt, NaCl (0.5 M), was needed to induce the UCST-type behavior. Interestingly, at certain NTf_2^- concentrations, **P5b** phase separation may take place in two steps. At room temperature **P5b** forms particles. Upon heating, the transmittance decreases (LCST-type transition), but solutions become clear again upon further heating above T_{cU} (UCST-type transition). On the other hand, only UCST-type phase transitions were observed upon cooling. The T_{cU} can be tuned with other counterions (OTf^-, SCN^-) without using NaCl (Fig. 4B). The UCST-type phase transition was also observed in the presence of NO_3^-, however, a high amount of salt (2.4 M of $NaNO_3$) was needed when compared to the hydrophobic ions. It was concluded that the minimum concentration of salt inducing the salting-out effect decreased in the following order: $NaNO_3$ > NaSCN > LiOTf > $LiNTf_2$ with 500 mM NaCl. **P5c** with *n*-propyl substituents exhibits UCST-type phase transitions in NaH_2PO_4 solutions. Similar to **P5b**, the polymer undergoes stepwise phase separation (LCST and UCST-type) in NaSCN or $NaNO_3$ solutions, and the process can be reversible upon cooling at certain $NaNO_3$ salt concentrations. In addition, the same polymer undergoes a LCST-phase transition in concentrated salt solutions (3.5 M NaCl). Polymers with longer *n*-alkyl substituents show the LCST-type transition in various salt solutions (this is discussed in the next section). The switching of the phase separation behavior from UCST to LCST-type was mainly attributed to changes in the hydrophobic–hydrophilic balance of the cationic structures. Short alkyl chain polycations are well soluble in water but become insoluble when using hydrophobic counterions. Additionally, due to hydration changes

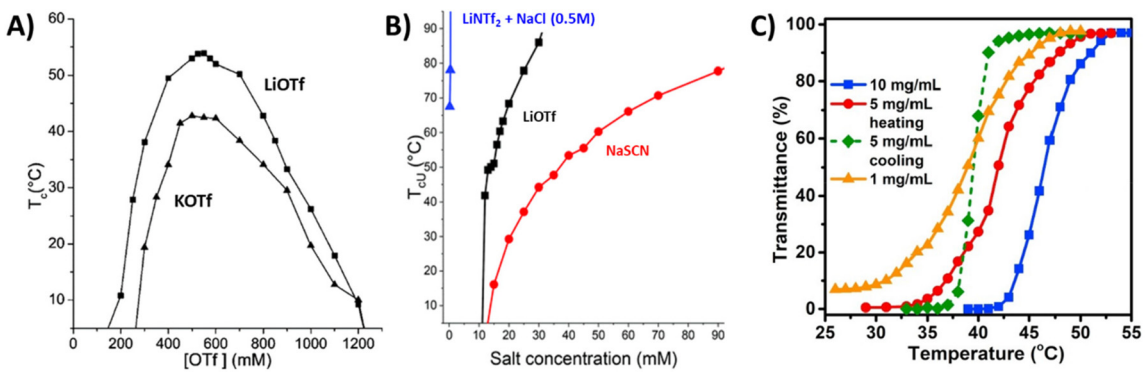

Fig. 4 (A) T_{cU} values of PMOTAI (**P3**) solution (1 mg mL^{-1}) as a function of the concentration of OTf ions with either LiOTf or KOTf. Adapted from ref. 85. Copyright 2014 American Chemical Society. (B) The T_{cU} points for **P5b** in various salt solutions. Reproduced from ref. 88. Copyright 2020 Royal Society of Chemistry. (C) Transmittance curves for aqueous **P7** solutions at different polymer concentrations. Reproduced from ref. 89. Copyright 2019 with permission from Elsevier.

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around the long alkyl substituents, the polymers become insoluble at elevated temperatures. The polymer–water interactions are overruled by polymer–ion interactions.[88]

The UCST-type phase transitions can also be observed for other styrene-based polycations **P7**, which contain reactive aldehyde groups (Fig. 4C).[89] In the presence of BF_4^- counterions, the T_{cU} increases with increasing polymer concentration. The phase behavior can be tuned *via* the post-modification of aldehyde substituents on the aromatic groups. With the formation of oxime, the cloud point shifts to lower temperatures. These polymers with a secondary amine as a weak cationic group undergo the LCST-type phase transition in water/alcohol mixtures.

Biswas *et al.* studied the thermoresponsive behavior of styrene-based phosphonium polycations (**P8a**), which carry hydrophobic tri-phenyl substituents.[91] The polycation exhibited the UCST-type phase transition in aqueous solutions in the presence of the sodium salts NaBr or NaCl (Fig. 5). The cloud point temperature T_{cU} was dependent on the polymer molar mass, concentration, and the size of the counterions. The phase transition could be induced with a small amount of NaBr, whereas in the case of Cl^- ions 450 mM of NaCl was needed (Fig. 5C). T_{cU} increased with increasing salt concentration. Large anions with high polarizability interact strongly with the larger number of cationic phosphonium groups. Thus, polymers became insoluble below 100 °C in the presence of I^-, SCN^-, and CN^- ions. A co-nonsolvency effect was observed for **P8a**; T_{cU} decreased linearly with increasing fractions of MeOH in the water–MeOH mixtures (polymer M_n = 40 kDa, 0.5 wt% with 550 mM NaCl) (Fig. 5D). A similar decrease in T_{cU} with increasing volume percent of DMF and DMSO was observed in the mixed solvent systems. The same

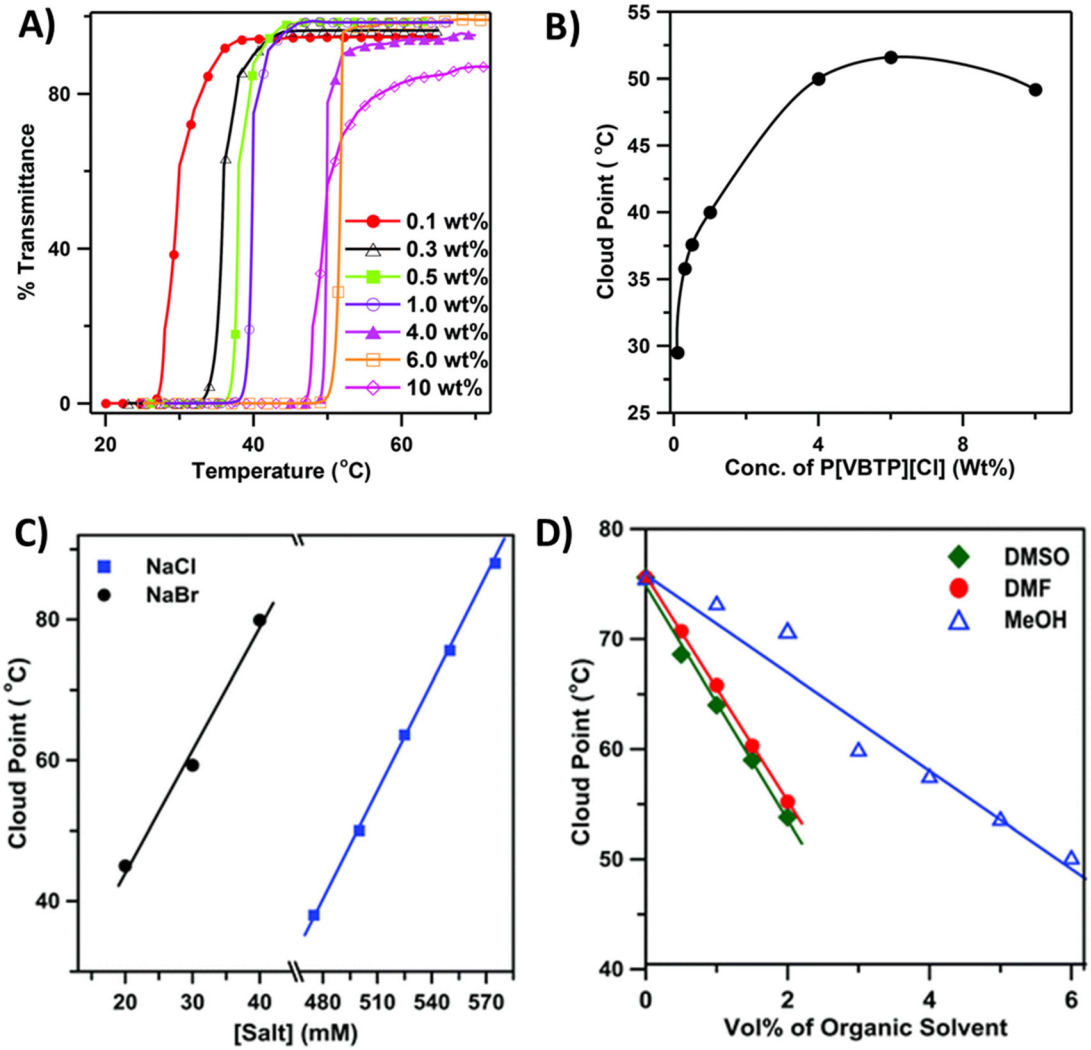

Fig. 5 (A) Transmittance cooling curves of aqueous solutions of **P8a** containing 475 mM NaCl and (B) corresponding phase diagram. (C) Plot of T_{cp} values as a function of NaCl and NaBr concentration for 0.5 wt% aqueous **P8a** (M_n = 40 kDa) solution. (D) Effect of organic cosolvent composition on the T_{cp} values of **P8a** (M_n = 40 kDa, 0.5 wt%) in a water–organic solvent binary mixture containing 550 mM NaCl. Reproduced from ref. 90. Copyright 2016 Royal Society of Chemistry.

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research group also reported imidazolium-based polycation **P9**, which showed the UCST-type phase transition in aqueous NaI solutions.[92]

Imidazolium-based polycations with ether backbones **P10** were reported to exhibit UCST-type transitions in aqueous solutions.[93,94] The polycations with BF_4^- counterions undergo UCST-type transitions when less hydrophobic substituents (Me = **P10a** or Me_2 = **P10b**) are present on the imidazolium rings. If the alkyl substituents are long like *n*-butyl (**P10c**) or *n*-pentyl (**P10d**), the polymer solubility may change, and UCST-type phase transitions are possible in methanol or ethanol depending on the counterion (BF_4^- or NTf_2^-).[93]

3.2. LCST transition

So far, we have discussed the UCST-type phase separation process of polycations driven by strong polymer–counterion interactions. Interestingly, the phase separation process can be changed to LCST by changing the alkyl chain substituents and the charged moieties to more hydrophobic ones. Ritter *et al.* studied the LCST-type phase separation of imidazolium-based polycations **P9** with NTf_2^- counterions in aqueous cyclodextrin (CD) solutions.[95] The polycations undergo the LCST-type phase transition in aqueous solutions when ionic interactions between the bulky counterions and butyl imidazolium repeating units are weakened by CDs (Fig. 6). The behavior is similar to nonionic LCST polymer systems; however, in the case of **P9**, it is due to entropy driven decomplexation of the anions and CDs at higher temperatures. In the presence of CDs at $T <$ LCST, the polymers are well soluble in water as the NTf_2^- ions are bound to the host–guest complexes with CDs. The phase transition temperatures T_{cL} increase significantly with increasing CD concentrations as higher energies are needed to break the host–guest complexes.

Yuan *et al.* studied cationic poly(tributyl-4-vinylbenzylphosphonium) (PVBTBP) bearing alkyl sulfonate counterion **P8b**.[43] Similar to polyanions **PSS [P_{4444}]**, this polymer shows a LCST-type phase transition in aqueous solutions. The phase transition behavior in either trialkyl ammonium or phosphonium-based polycation systems is similar to the aforementioned polyanion systems.[96,97] The phase separation temperatures of the polymers are strongly dependent on the salt and polymer concentrations, as well as on the length of the alkyl chain substituents both on the counterions and on the cationic repeating units. Polycation **P8b** bearing *n*-pentylsulfonate counterions ($C5S^-$) undergoes a LCST-type phase separation in pure water (T_{cL} = 45 °C, polymer concentration 3 wt%).[43] The cloud point temperature increases with the addition of NaCl, and decreases when sodium sulfonate salts (NaC*n*S) with different alkyl chain lengths are introduced (0.02 M in all cases). As shown in Fig. 7A, the shift in the cloud point temperature follows the hydrophilicity order of anions, $Cl^- > C3S^- > C4S^- > C5S^- > C6S^-$. Addition of NaCl leads to a continuous increase of the T_{cL}, which is ~44 °C in pure water and 87 °C in 0.5 M NaCl, see Fig. 7B. When NaC5S was added, the T_{cL} decreased sharply down to below 20 °C at 0.07 M. In the case of NaC3S, a constant T_{cL} ~ 40 °C was observed over a low salt concen-

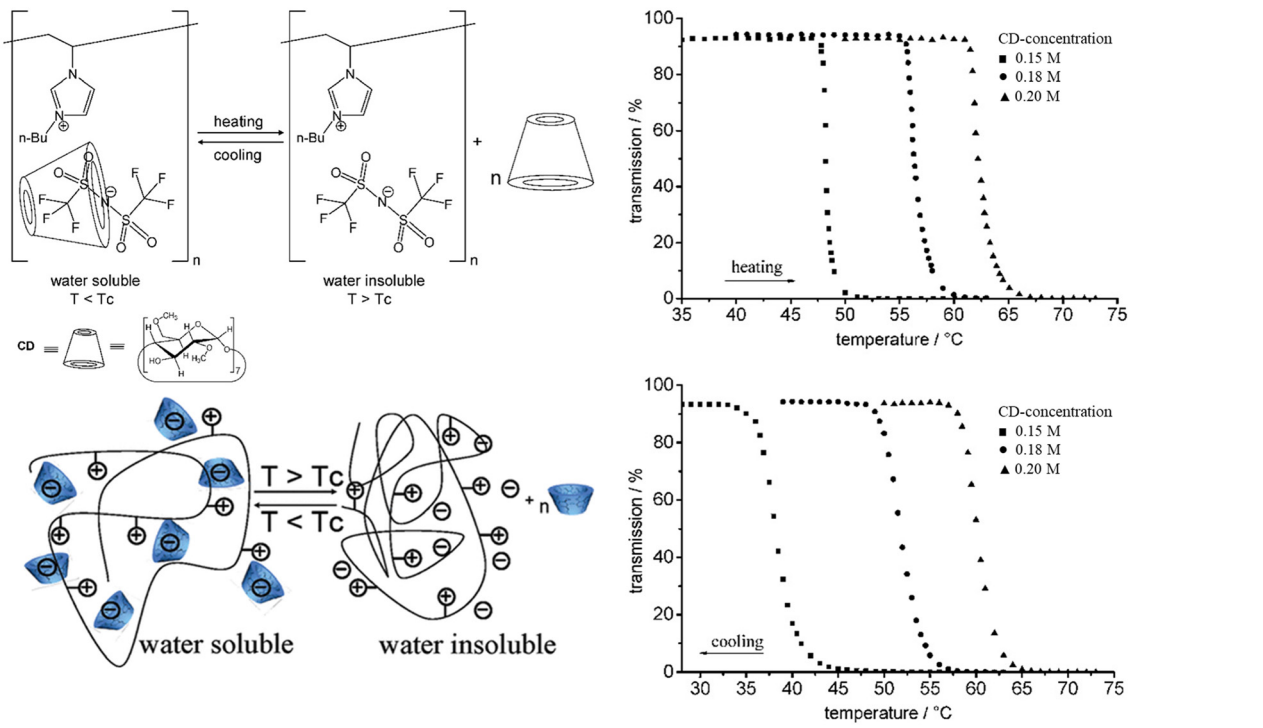

Fig. 6 Pseudo-LCST behavior of **P9**. Transmittance curves for aqueous **P9** solutions at different CD concentrations. Reproduced from ref. 95. Copyright 2008 American Chemical Society.

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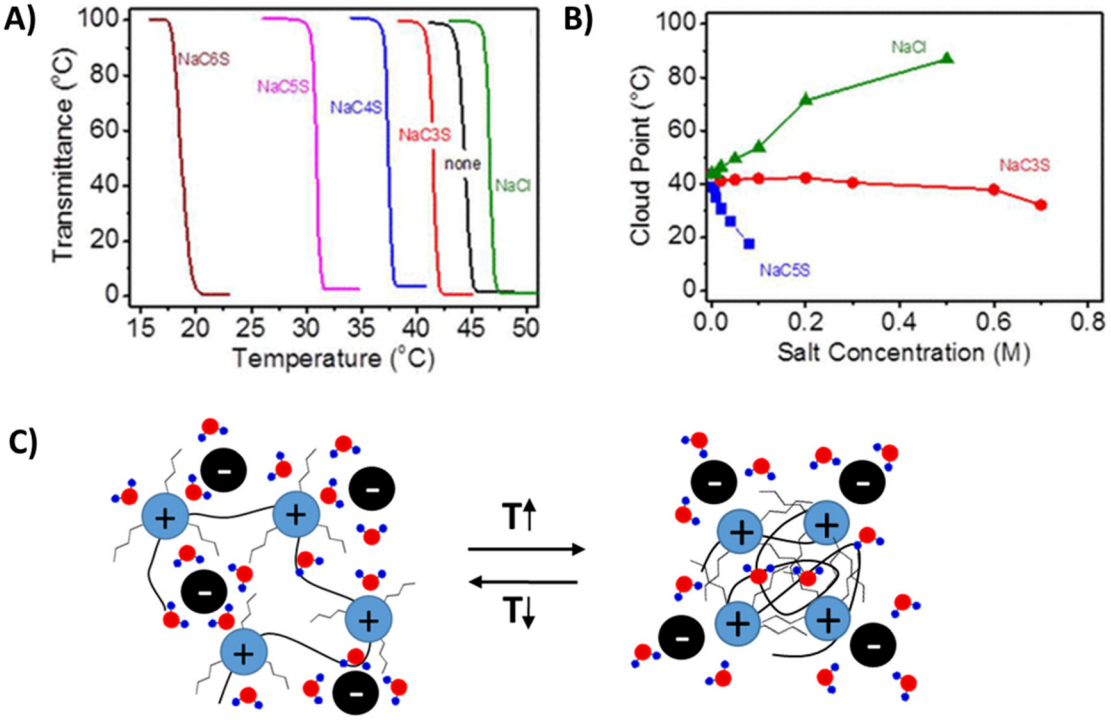

Fig. 7 (A) Turbidity curves of 3 wt% aqueous solution of **P5e** in the presence of sodium salts (0.02 M). (B) Plot of the cloud point temperature versus salt concentration. Reprinted from ref. 43. Copyright 2013 American Chemical Society. (C) Cartoon representation of the LCST-type phase separation mechanism of polycations.

tration range (0.002 to 0.6 M), indicating that an anion exchange process was taking place. However, above 0.6 M, similar behavior was observed to that in the case of NaC5S. Ohno *et al.* reported different cloud point temperatures for similar polymer systems bearing phosphonium or ammonium cationic groups. Ammonium-based polycations (**P5e**) phase separate above 65 °C, whereas phosphonium ones (**P8b**) do it at 45 °C when the cation is substituted with *n*-pentyl units.[98] The cloud point shifts to lower temperature in the case of hexyl substituents (**P5f**) and the hydrophobic polycations form particles in aqueous solutions at room temperature. In the case of **P5d**, the LCST-type phase separation can be induced by anion exchange from Cl^- to $C6S^-$ and the T_{cL} shifts to lower temperature with increasing polymer concentration (Fig. 7c).[99]

More recently, Karjalainen *et al.* studied styrene-based systems in various aqueous salt solutions.[88] The polycations **P5d** and **P5e** underwent LCST-type phase transitions. With increasing NaC5S concentration, the cloud point of **P5d** shifted first to lower temperatures and then started to increase. The behavior was similar when NaCl (0.25 M) was introduced as a secondary salt to screen the main ionic interactions. The LCST-type phase separation can also be induced using high concentrations of NaCl; the T_{cL} shifts to lower temperatures upon increasing the salt concentration from 1 to 3 M. Interestingly, using other sodium salts like $NaNO_3$, Na_2HPO_4, Na_2SO_4, and Na_2CO_3, LCST-type phase separation can be induced in **P5d** and **P5e** with or without NaCl as a secondary salt. However, a high amount of salt is needed compared to NaCnS systems.

Charged polymers are often observed to phase separate from organic solvents with increasing temperature. Reasons behind these observations are very different from what is known to take place in water. The main driving force is the balance of polymer–solvent and polymer–polymer interactions, which depend on the dielectric constant of the solvent.[78] Organic solutions are briefly discussed here because this also opens a view to develop systems where charged polymers are dissolved in mixed solvents.

Polycations with vinyl ether backbones and imidazolium or pyridinium salt pendants show LCST-type phase separation in various organic solvents.[94] Polycation **P10c** with butyl imidazolium units is insoluble in nonpolar solvents (hexane and ethyl acetate) but soluble in polar solvents, such as water and methanol. However, it undergoes a LCST-type phase separation in chloroform when the counterion is chloride. Phase separation was observed for pyridinium polycations **P11** in chloroform/methanol mixtures with a low methanol content [chloroform/methanol 97/3 (w/w)]. The T_{cL} is dependent on the polymer molar mass and concentration. In addition, the polymer solubility can be changed by changing the alkyl substituents or counterions. When two methyl or one *n*-pentyl substituents were bound to the imidazolium ring, the polycation with the SbF_6^- counterion underwent a LCST-type phase transition in acetone or THF solutions. Such behavior was mainly due to the counter-anion-mediated weakening of inter-

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actions between the polymer pendants and the solvent upon heating.

Styrene-based polycations with chiral cationic imidazolium units (**P12**) also undergo the LCST-type phase transition in $CHCl_3$.[99] The cloud point temperature increased with changing the substituent in the imidazolium ring from butyl to phenyl. In contrast, when the substituent in the imidazole ring was changed from (L)-valine to (L)-phenylalanine, the transition temperature decreased from 48.5 to 12.5 °C. Furthermore, T_{cL} decreases when counterions are changed from Cl^- to NTf_2^- ions.

The thiazolium-based polycation (**P13**) with PF_6^- counterions was reported to exhibit a LCST-type phase transition in acetone.[100] The T_{cL} shifts to lower temperatures with increasing polymer concentration (Fig. 8A). In addition, T_{cL} can be tuned by external salts ($LiBF_4$, $LiNTf_2$, and KPF_6) as well as with cosolvents (THF, DMF, or DCM) (Fig. 8C and D). In the presence of bulky counterions, the cloud point shifted from 37 °C (pure acetone) to a higher temperature of 45 °C with 0.01 M of $LiNTf_2$. In contrast, a gradual decrease in T_{cL} down to 30 °C and 23 °C was observed in the presence of PF_6^- and BF_4^- ions (Fig. 8C). Alternatively, the addition of 2–6 wt% of DMF (a good solvent for the polymer) resulted in a high shift in T_{cL} to 49 °C or even beyond the investigated temperature range. In addition to the increased solvent quality, hydrogen bonding between the C2 proton of the thiazolium ring and solvent molecules may affect the polymer behavior in the presence of DMF. Therefore, the cloud point shifted toward higher temperatures. Opposite behavior was observed for the same system when mixing the polymer solution with a poor solvent, such as THF or DCM. With the addition of THF or DCM, the cloud point temperature decreased gradually, similarly to the case of adding bulky counterions (Fig. 8D).

Based on the above observations, it is possible to draw conclusions on the structural characteristics of cationic moieties, as well as counterions, which are crucial in designing thermoresponsive polycations. With short alkyl substituents, most polycations show UCST-type phase transitions in the presence of counterions that bring hydrophobicity to the polymers. Polycations or counterions with long alkyl chain substituents undergo LCST-type phase transitions, similarly to the polyanions discussed earlier. Polycations and the types of their phase transitions in aqueous or non-aqueous solutions are summarized in Table 1.

3.3. UCST or LCST of cationic polypeptides

Synthetic polypeptides are structurally more complicated than vinyl polymers. They mimic natural peptides with excellent biocompatibility and unique secondary structures (*e.g.*, α-helix and β-sheet) and are widely used for biological or biomedical applications.[101] A few nonionic synthetic polypeptides that show UCST behavior under physiologically relevant conditions

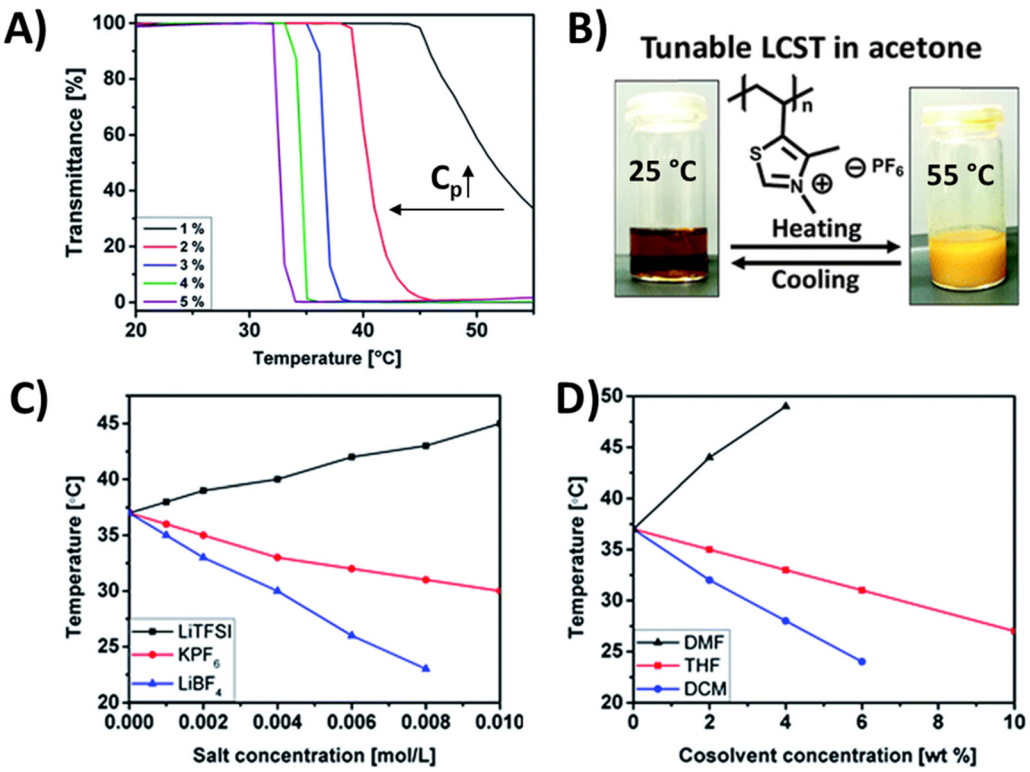

Fig. 8 (A) Turbidity curves for acetone solutions of **P13** measured at various polymer concentrations. (B) Photographs of a 3 wt% **P13** solution in acetone below the T_c (left) and above the T_c (right). T_{cL} measured for 3 wt% **P13** solutions in acetone: (C) at different concentrations of external salts; (D) at different concentrations of cosolvents. Reproduced from ref. 100 with permission from the Royal Society of Chemistry, copyright 2016.

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Table 1 List of thermoresponsive vinyl-based cationic homopolymers with various counterions and alkyl substituents

Polycation	Compound number	R	R^1	X_I	X_T	Type of transition
PDMAEMA	**P1**	—	—	—	$[Co(CN)_6]^{3-}$ $[Fe(CN)_6]^{4-}$ $[Cr(CN)_6]^{3-}$ NTf_2^-	LCST or UCST
PEI	**P2a**	—		—	Cl^-, Br^-, I^-	UCST
M-PEI	**P2b**	—		Cl^-, Br^-, I^-	Cl^-, Br^-, I^-	
PMOTA	**P3a**	Methyl		Cl^-, Br^-, I^-, BF_4^-	BF_4^-, OTf^-, NTf_2^-	UCST
	P3b	Ethyl		Br^-	BF_4^-	
	P3b	*n*-Butyl		Br^-	BF_4^-	
PVBMIm	**P4**	—		Cl^-, BF_4^-	BF_4^-, OTf^-, NTf_2^-	UCST
PVBTAA	**P5a**	Methyl		Cl^-, OTf^-	OTf^-	UCST
	P5b	Methyl		Cl^-	$H_2PO_4^-$, SO_4^{-2}, Cl^-, NO_3^-, SCN^-, OTf^-, NTf_2^-	UCST or LCST
	P5c	*n*-Propyl		Cl^-	$H_2PO_4^-$, Cl^-, NO_3^-, SCN^-	UCST or LCST
	P5d	*n*-Butyl		Cl^-	$H_2PO_4^-$, CO_3^-, SO_4^{-2}, Cl^-, NO_3^-, SCN^-, OTf^-, NTf_2^-, *n*-$C_4H_9SO_3^-$, *n*-$C_5H_{11}SO_3^-$, *n*-$C_6H_{13}SO_3^-$, *n*-$C_{12}H_{25}SO_3^-$	LCST
	P5e	*n*-Pentyl		Cl^-	$H_2PO_4^-$, CO_3^-, SO_4^{-2}, Cl^-, *n*-$C_4H_9SO_3^-$, *n*-$C_5H_{11}SO_3^-$	LCST
	P5f	*n*-Hexyl		*n*-$C_4H_9SO_3^-$		LCST
PAMPTMAC	**P6**	—	—	Cl^-	OTf^-, NTf_2^-	UCST
PDEVB	**P7**	—	—	I^-, BF_4^-	BF_4^-	UCST
PVBTAP	**P8a**	Phenyl		Cl^-	Cl^-, Br^-	UCST
	P8b	*n*-Butyl	—	Cl^-, *n*-$C_3H_7SO_3^-$, *n*-$C_4H_9SO_3^-$, *n*-$C_5H_{11}SO_3^-$, *n*-$C_6H_{13}SO_3^-$		LCST
	P8c	*n*-Pentyl	—	Cl^-	*n*-$C_4H_9SO_3^-$	LCST
PVBuIm	**P9**	—	—	Br^-, NTf_2^-	I^-, NTf_2^-	UCST or LCST
PVEIm	**P10a**	Methyl	H	Cl^-	BF_4^-	UCST
	P10b	Methyl	Methyl	Cl^-	BF_4^-, NTf_2^-, SBF_6^-	
	P10c	*n*-Butyl	H	Cl^-	Cl^-, BF_4^-, NTf_2^-	LCST
	P10d	*n*-Pentyl	H	Cl^-	Cl^-, BF_4^-, NTf_2^-, SBF_6^-	
PVEPy	**P11**	—	—	Cl^-		LCST
PVBVIm	**P12a**	Val	Phenyl	Cl^-	Cl^-, NTf_2^-	LCST
	P12b	Val	*n*-Butyl	Cl^-	Cl^-	LCST
PVBPIm	**P12c**	Phe	Phenyl	Cl^-	Cl^-	LCST
PMVTh	**P13**	—	—	PF_6^-	PF_6^-, BF_4^-, NTf_2^-	LCST

X_I^- = initial counterion from synthesis, X_T^- = counterion added to induce thermoresponsive behavior.

have been reported in the literature, and in this section we discuss some cationic derivatives of those.[64,65] The compound numbers refer to Scheme 2.

Tang's group synthesized several polyglutamate derivatives with cationic pendants. Helical L-glutamate polypeptides bearing various imidazolium or pyridinium side groups (**P14**, **P17**) are thermoresponsive in aqueous solutions in the presence of I^- or BF_4^- counterions.[102] This behavior is very dependent on the alkyl substituents of the cationic groups and counterion. Polycation **P14b** goes through an UCST-type phase transition in NaI or $NaBF_4$ aqueous solutions, whereas **P14a** with methyl substituents is well soluble. Interestingly, **P14b** with BF_4^- counterions can undergo a LCST-type transition in acetone, and with I^- ions an UCST transition in methanol or ethanol. The effect of salt concentrations was studied on **P15**, another type of imidazolium-based polypeptide with *n*-alkyl spacers.[103] With increasing the $NaBF_4$ or NaI concentration, T_{cU} shifts to higher temperatures, whereas the opposite trend is observed with the addition of NaCl.[67] Polypeptide **P16** with thioether spacer units exhibits UCST behavior when using I^- or BF_4^- ions.[104]

Similar observations have been made for pyridinium-based polycations, with either *n*-alkyl or benzyl linkers between the cationic group and the backbone.[105,106] Polymers **P17a** and **b** with either 2-methyl or 4-methyl pyridinium groups are insoluble in water. However, the polymers undergo UCST-type phase transitions below 30 °C in the case of 3-methyl pyridinium.[105] In polymers with aromatic spacers, **P18**, the solution behavior is independent of the position of methyl substituents. Polymers exhibit UCST-type phase behavior in water in the presence of BF_4^- ions.[106] The cloud point temperatures T_{cU} were tuned by either changing the polymer or salt concentration. Tang's group also synthesized more complex di-cationic polypeptides containing cationic *n*-butyl imidazolium pendants (**P19**) or ammonium pendants with sulfonium linkages (**P20**). These dicationic polymers underwent UCST-type

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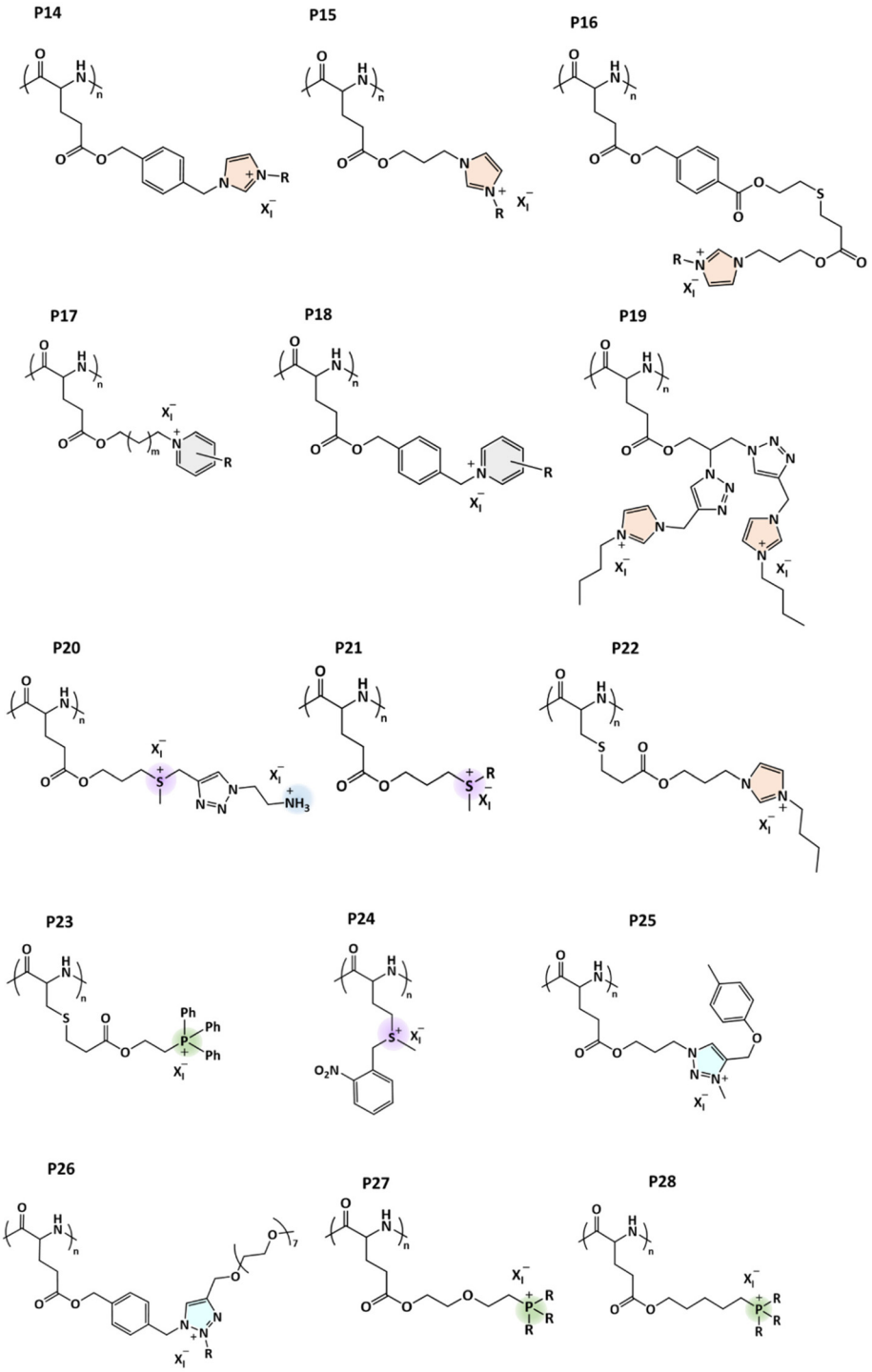

Scheme 2 Thermoresponsive cationic polypeptides.

phase transitions in aqueous BF_4^- solutions. The T_{cU} of the polymers can be adjusted through varying the polymer or $NaBF_4$ concentrations. The cloud point shifts to a lower temperature in the presence of halides (Cl or I). Due to the amine groups in **P20**, the cloud points can be changed by altering the pH as well.[107] Alternatively, cationic sulfonium polypeptides **P21** undergo UCST-type phase transitions in methanol or ethanol when different alkyl substituents are present. The T_{cU} can be tuned by changing the counterions.[107]

A few cationic poly(L-cysteines) have been reported to be thermoresponsive in aqueous solutions in the presence of hydrophobic counterions (I^-, SCN^-, BF_4^- and ClO_4^-).[108] Imidazolium-based poly(L-cysteine) **P22** with a BF_4^- counterion has a T_{cU} in aqueous solutions similar to that of polyglutamic

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P15. Due to the higher number of intermolecular H-bonds, a higher T_{cU} was observed for **P22** than for **P15**. More recently, Anas *et al.* investigated the solution properties of triphenyl phosphonium-based poly(L-cysteine)s (**P23**) in several aqueous salt solutions, see Fig. 9. In the presence of hydrophobic counterions, polymers phase separate with added salt. The

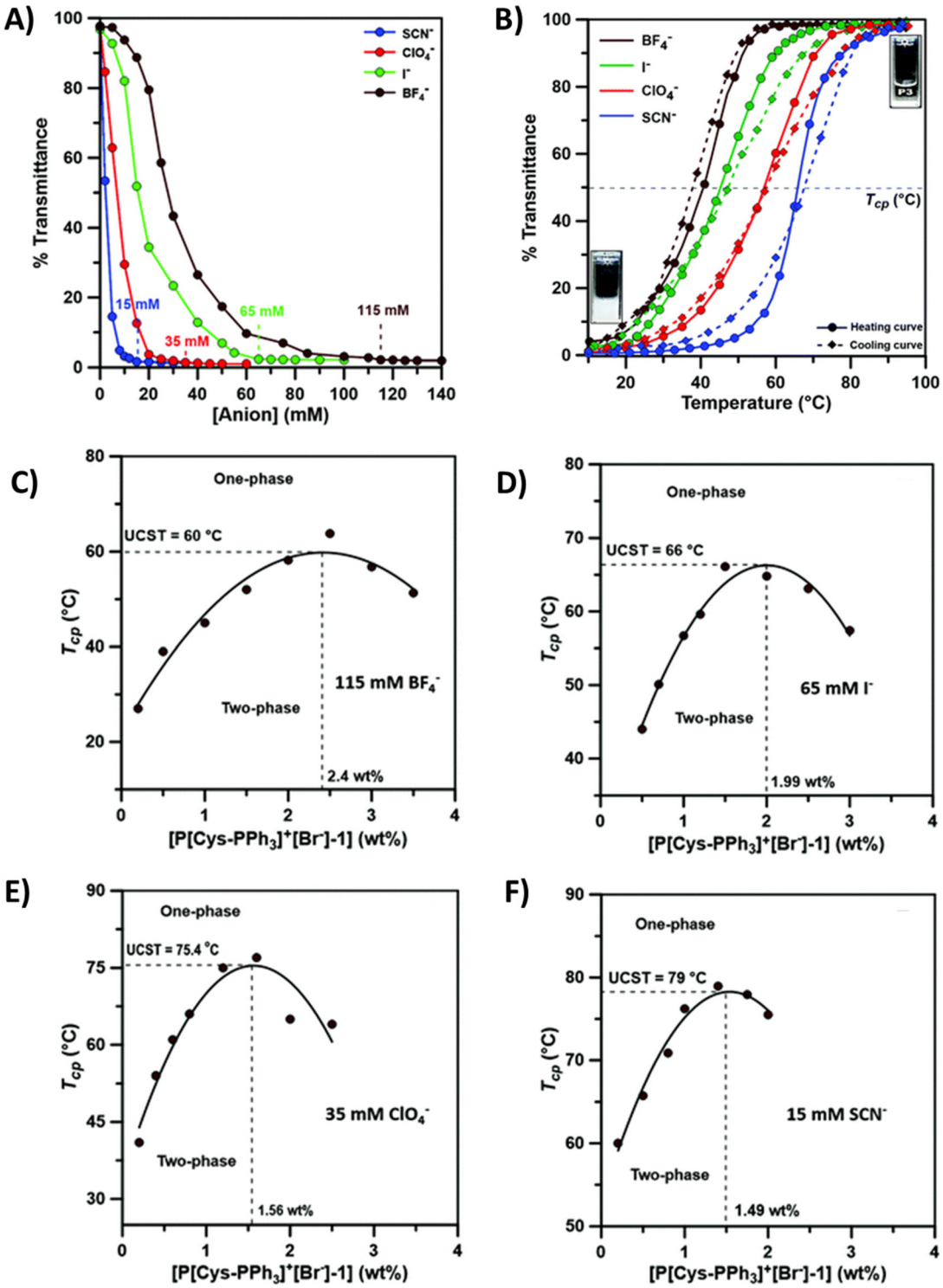

Fig. 9 (A) Turbidity curves of 0.5 wt% aqueous P[Cys-PPh_3]$^+$[Br^-] (**P23**) solutions with varying concentrations of different chaotropic anions (SCN^-, ClO_4^-, I^- and BF_4^-). (B) Turbidity curves of an aqueous **P23** solution (0.5 wt%) in the presence of minimum concentrations of different chaotropic anions (BF_4^-, I^-, ClO_4^- and SCN^-). UCST-type phase diagram of **P23** of varying polymer concentrations in the presence of 115 mM of BF_4^- (C), 65 mM of I^- (D), 35 mM of ClO_4^- (E) and 15 mM of SCN^- (F) in water. Reproduced from ref. 108 with permission from the Royal Society of Chemistry, copyright 2021.

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minimum amount of anions required to induce UCST-type phase separation decreases in the order BF_4^- > I^- > ClO_4^- > SCN^- as shown in Fig. 9A and B. Next, T_{cU} values were measured upon changing the polymer concentration and keeping the salt concentration constant. The maximum T_{cU} varied from 60 to 79 °C depending on the counterion, see Fig. 9C, D, E, and F.[109]

A counterion-induced UCST was also observed for water soluble methionine pendant polypetides.[109] Polymer **P24** phase separates in the presence of Br^-, SO_4^{2-}, I^-, ClO_4^- and SCN^- ions. T_{cU} points are very dependent on the type of counterion. T_{cU} values collected for 1 wt% polymer solutions of different ionic strengths were 35 °C (300 mM of Br^-), 33 °C (200 mM of I^-), 40 °C (100 mM of ClO_4^-) and 49 °C (50 mM of SCN^-).

Polypeptides with 3-methyl-1,2,3-triazolium iodide linkages (**P25**) exhibit reversible UCST-type phase behaviors in both methanol and ethanol/water binary solvent mixtures.[110] The phase transition of polypeptides completely changes when ethylene glycol oligomer side chains are bound to the triazolium cationic units.[111] Xu *et al.* synthesized poly(4-methylbenzyl-L-glutamate) bearing Y-shaped triazolium cationic units with oligoethylene glycol and alkyl (such as 1-butyl, 1-hexyl, and 1-dodecyl) side chains (**P26a–c**). These triazolium-based polypeptides undergo LCST-type phase transitions in aqueous solutions, similar to their non-charged precursors (*i.e.*, before quaternization) with ethylene glycol oligomer side chains (Fig. 10). The clouding behavior of the polymers is significantly dependent on the DP of the polypeptide chain and the length of the alkyl substituents on the triazolium units (Fig. 10A and B). The cloud point decreases with increasing concentration of the polymer or $NaBF_4$ (Fig. 10C and D).[111]

Water-soluble homopolypeptides with tributylphosphonium cationic units connected *via* ether linkages (**P27**) were able to show dual thermoresponsive behavior in aqueous solutions.[112] The phase separation of **P27a** is similar to that of the above discussed styrene-based cationic polymers (**P5c**, **P5d**). In the presence of I^- counterions, the polymer undergoes stepwise phase segregation (T_{cL} and T_{cU}; T_{cL} < T_{cU}) in aqueous solutions (Fig. 11). The phase behavior is further

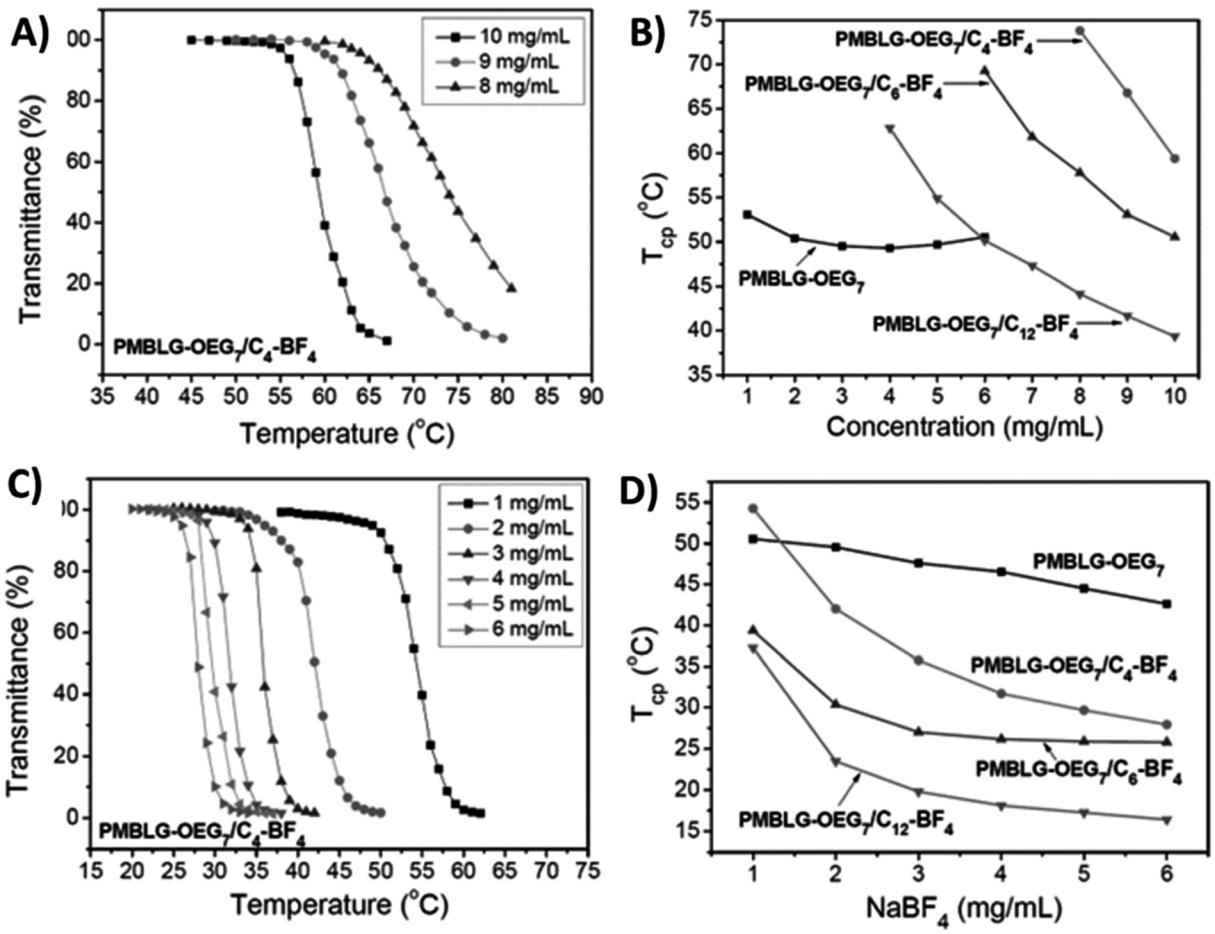

Fig. 10 (A) Transmittance curves of PMBLG-OEG_7/C_4-BF_4 (**P26a**) at different polymer concentrations in DI H_2O. (B) Plots of T_{cp} versus concentrations in DI H_2O for **P26** with different alkyl substituents. (C) Transmittance curves of PMBLG-OEG_7/C_4-BF_4 (**P26a**) at different $NaBF_4$ concentrations in aqueous solutions. (D) Plots of T_{cp} versus $NaBF_4$ in aqueous solutions of **P26** with different alkyl substituents. Reproduced from ref. 111 with permission from the Royal Society of Chemistry, copyright 2016.

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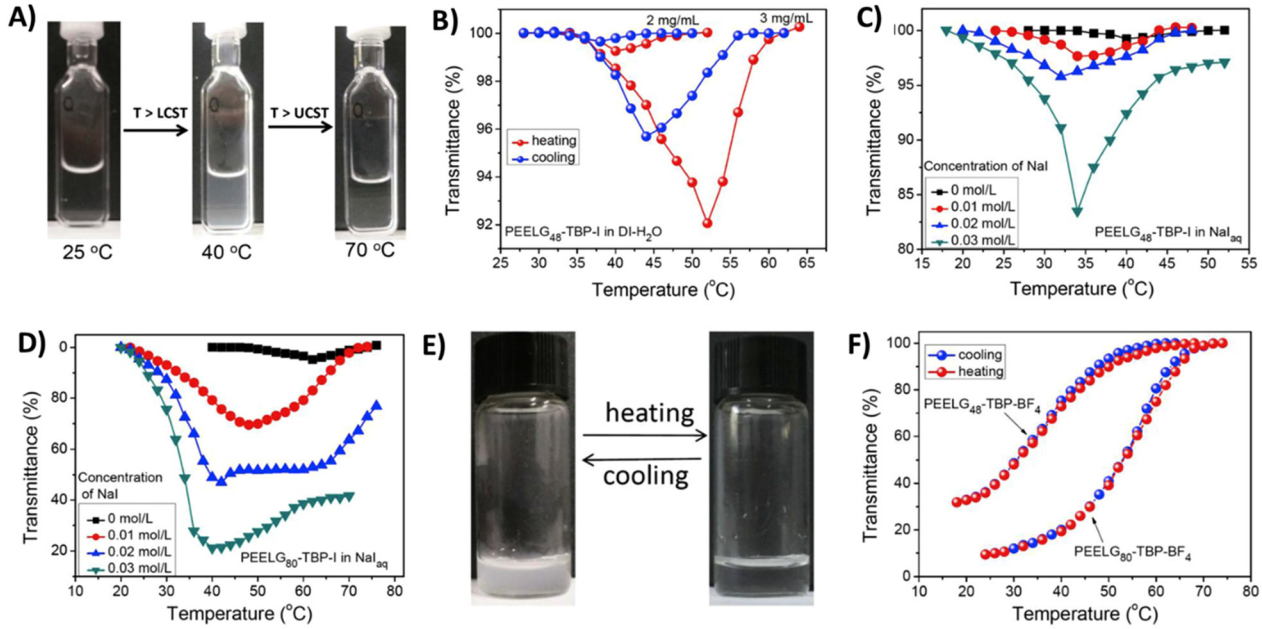

Fig. 11 (A) Optical images of **P27a** (DP = 80, X = I^-) in aqueous NaI solutions (0.02 mol L^{-1}) at different temperatures to demonstrate the LCST < UCST behavior. Plots of transmittance at λ = 500 nm versus temperature for (B) **P27a** (DP = 48, X = I^-) in deionized (DI) H_2O with different polymer concentrations in heating/cooling cycles. (C) **P27a** (DP = 48, X = I^-) and (D) **P27a** (DP = 80, X = I^-) in DI H_2O and NaI_{aq} at different salt concentrations (polymer concentration = 2 mg mL^{-1}). (E) Optical images of **P27a** (DP = 80, X = BF_4^-) in DI H_2O at different temperatures (polymer concentration = 3 mg mL^{-1}). (F) Plots of transmittance at λ = 500 nm versus temperature for **P27a** (DP = 48 or 80, X = BF_4^-) in DI H_2O in a cooling/heating cycle (polymer concentration = 3 mg mL^{-1}). Reprinted from ref. 113. Copyright 2017 with permission from Elsevier.

affected by the molar mass of the polymer and salt concentration. Using more hydrophobic BF_4^- counterions, the phase behavior changes to only UCST-type transitions or polymers may even become insoluble. Similar polypeptides, containing 1-butylimidazole or 3-methylpyridine cationic pendants, are completely soluble in water or PBS over the temperature range 0–100 °C.[112] On the other hand, polymers **P27b** and **P28** with poor water solubility show UCST-type phase transitions in PBS in the presence of I^- or BF_4^- counterions. The T_{cU} can be readily changed from 20 to 90 °C by adjusting the polymer concentration.

Overall, the hydrophilic–hydrophobic balance of the polymer structures is crucial in designing thermoresponsive polypeptides. The counterion-induced UCST phase separation can be changed to LCST by introducing short hydrophilic ethylene glycol moieties like DEG or OEG. In this case, the cationic polypeptides either undergo a single LCST-type transition or both UCST and LCST transitions, see Table 2.

4. Thermoresponsive cationic copolymers

4.1. Random copolymers

It has been shown that in nonionic LCST copolymer systems, the cloud point temperatures can be shifted either to lower or higher temperature ranges by adding hydrophobic or hydrophilic repeating units. Correspondingly, in UCST copolymers, the cloud point shifts to a higher temperature when the number of hydrophobic repeating units increases. The thermoresponsive behavior of such copolymers has been thoroughly discussed in the literature.[31,40] The phase separation process for copolymers made of opposite thermoresponsive units is often complex. The polymers can either undergo phase separation with dual transitions (T_{cL} and T_{cU}) or become completely soluble with no thermoresponsive behavior.

Several copolymers comprising nonionic and cationic repeating units have been reported to show UCST or LCST-type phase transitions in aqueous solutions. The polymers discussed in this section are shown in Scheme 3 and Table 3. Homopolymers of 2-hydroxyethyl methacrylate (PHEMA) undergo LCST-type phase transitions in aqueous solutions.[114] However, the solution behavior changes in HEMA copolymers containing either weak cationic DMAEMA units or strong cationic ones such as MOTAC or [3-(methacryloylamido)propyl]trimethylammonium chloride (MAPTAC). Copolymers with strong charges (**P29** and **30**) undergo both LCST and UCST-type transitions in water. The double phase transitions of these polymers are strongly dependent on the NaCl concentration and also vary with the polymer concentration, copolymer composition, or pH.[115] On the other hand, a series of HEMA copolymers **P31a–b** with phosphonium-based (vinylbenzyl)triphenylphosphonium chloride (VBTPPC) cationic units form turbid dispersions in the presence of Cl^- ions. These turbid dispersions undergo UCST-type phase transitions upon heating as the cationic units become soluble in aqueous

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Table 2 Summary of thermoresponsive cationic polypeptides

Polycation	Compound number	R	X_I^-	X_T^-	Type of transition
PMBLG-Im	**P14a**	Methyl	Cl^-	Cl^-, I^-, BF_4^-	LCST or UCST
PPLG-Im	**P14b**	*n*-Butyl	Cl^-	Cl^-, I^-, BF_4^-	UCST
PMBLG-S-Im	**P15**	*n*-Butyl	Cl^-	Cl^-, I^-, BF_4^-	UCST
PPLG-Py	**P16**	*n*-Butyl	Cl^-	Cl^-, I^-, BF_4^-	UCST
PHLG-Py	**P17a**	2-Methyl	Cl^-	Cl^-, I^-, BF_4^-	UCST
PMBLG-Py	**P17b**	4-Methyl	Cl^-	Cl^-, I^-, BF_4^-	UCST
PPLG-Im_2	**P18**	H, 2-, 3- or 4-methyl	Cl^-	BF_4^-	UCST
PPLG-MSEA	**P19**	—	Br^-	I^-, BF_4^-	UCST
PPLG-MS	**P20**	—	Cl^-	BF_4^-	UCST
PPLC-Im	**P21a**	Methyl	Br^-	I^-, BF_4^-	UCST
PCys-PPh_3	**P21b**	*n*-Butyl	Br^-	Br^-, I^-	UCST
PMetNB	**P21c**	Propargyl	Br^-	Br^-, I^-	UCST
PPLG-TAz	**P22**	—	BF_4^-	Cl^-, I^-, BF_4^-	UCST
PMBLG-OEG_7/C_n	**P23**	—	Br^-	I^-, SCN^-, ClO_4^-,BF_4^-	UCST
PEELG-PBu3	**P24**	—	Br^-	Br^-, SO_4^{-2} I^-, ClO_4^-, SCN^-	UCST
PEELG-PPh3	**P25**	—	I^-	I^-	UCST
PPLG-PBu3	**P26a**	*n*-Butyl	Br^-	Br^-, BF_4^-	LCST
PMBLG-Im	**P26b**	*n*-Hexyl	Br^-	Br^-, BF_4^-	
PPLG-Im	**P26c**	Dodecyl	Br^-	Br^-, BF_4^-	
PMBLG-S-Im	**P27a**	*n*-Butyl	Cl^-	I^-, BF_4^-	LCST and UCST
PPLG-Py	**P27b**	Phenyl	Cl^-	I^-, BF_4^-	UCST
PHLG-Py	**P28**	*n*-Butyl	Cl^-	I^-, BF_4^-	UCST

X_I^- = initial counterion from synthesis, X_T^- = added counterions.

salt solutions (Fig. 12A). The cloud points shift to higher temperatures with increasing VBTPAC content in the copolymer composition.

When the same VBTPPC cationic units were copolymerized with NIPAM, the polymers (**32a** and **32b**) with low ionic contents underwent LCST-phase transitions (Fig. 12B). This behavior is mainly attributed to NIPAM, and the T_{cL} shifts to higher temperatures with an increase in the cationic units and decreases with an increase in NaCl. Copolymers with a high content of ionic units (19.3 and 34.5%) do not phase separate in pure water. However, copolymer **P32c** with 19.3% cations exhibits a LCST-type phase transition in the presence of NaCl (69 mM Cl^- ions). In the case of copolymer **P32d** with 34.5% cationic units, the polymers underwent both UCST and LCST-type phase transitions ($T_{cL} < T_{cU}$) in aqueous solutions in the presence of 160 mM of Cl^- ions. The insolubility window can be tuned with varying salt and polymer concentrations (Fig. 12C & D). In addition, the copolymers of VBTPPC and styrene (**P33a–c**) or methyl methacrylate (**P34a–c**) undergo UCST phase transitions in aqueous or methanol solutions when external halide ions are introduced.

Jana *et al.* studied copolymers consisting of oligo(2-ethyl-2-oxazoline)acrylate (OEtOxA) and cationic ionic liquid units VBTPPC or 1-vinyl-3-butylimidazolium bromide (VBuIm-Br).[117] The copolymers (**P35**) with VBTPPC show solution properties and thermoresponsive behavior similar to the NIPAM case and the cloud point can easily be tuned by adjusting the copolymer composition and the ionic strength. The OEtOxA copolymers containing a low amount of cationic segments showed LCST-type phase transitions in aqueous salt solutions. Both LCST and UCST-type transitions occur when the content of ionic repeating units is 73 wt% (**P35e**, see Fig. 13A).[117] The copolymer with much higher ionic PVBTPPC content shows only a UCST-type transition in the presence of 500 mM Cl^- ions, as do the PVBTPPC homopolymers. In the copolymers with imidazolium-based cationic units, **P36**, similar phase behavior was observed in aqueous solutions with I^- ions. Polymer **P36a** with an ionic content of 64 wt% undergoes both LCST and UCST phase separation. T_{cL} decreases with increasing polymer concentration, whereas the T_{cU} shifts to higher temperatures (Fig. 13B). In copolymers with a high content of ionic units, **P36b and c**, the LCST-type phase transition disappears over a certain I^- ion concentration range due to the hydrophobic nature of the cationic moieties.

Random copolymer **P37** comprising oligo(ethylene glycol) methacrylate (OEGMA) and imidazolium-based cationic units shows a LCST-type phase transition in the presence of SCN^-, BF_4^-, PF_6^- or NTf_2^- counterions (Fig. 14A).[118] The cloud point temperatures of these copolymers depend on the type of anion. The T_{cL} shifts to high temperatures and stable aggregates form as the hydrophilicity of the anions increases. However, the phase separation process takes place in a single step, as in the case of homopolymers of OEGMA. Recently, amphiphilic random co(ter)polymers **P38** bearing poly(ethylene glycol) (PEG), a quaternary ammonium cation and dodecyl groups were reported to exhibit LCST-type phase transitions in aqueous salt solutions.[120] The cloud point temperature depended on the ratio of PEG and cation units, salt concentration, and salt species. In solutions of copolymers containing equal amounts of ethylene glycol and cationic units, T_{cL} dramatically changes from 97 °C to 53 °C depending on the salt species in the following order: T_{cL} = 97 °C (CH_3COONa), 79 °C (NaCl), 70 °C (NaI), 68 °C ($NaNO_3$), and 53 °C (Na_2SO_4). Soll *et al.* prepared thermoresponsive copolymers comprising imi-

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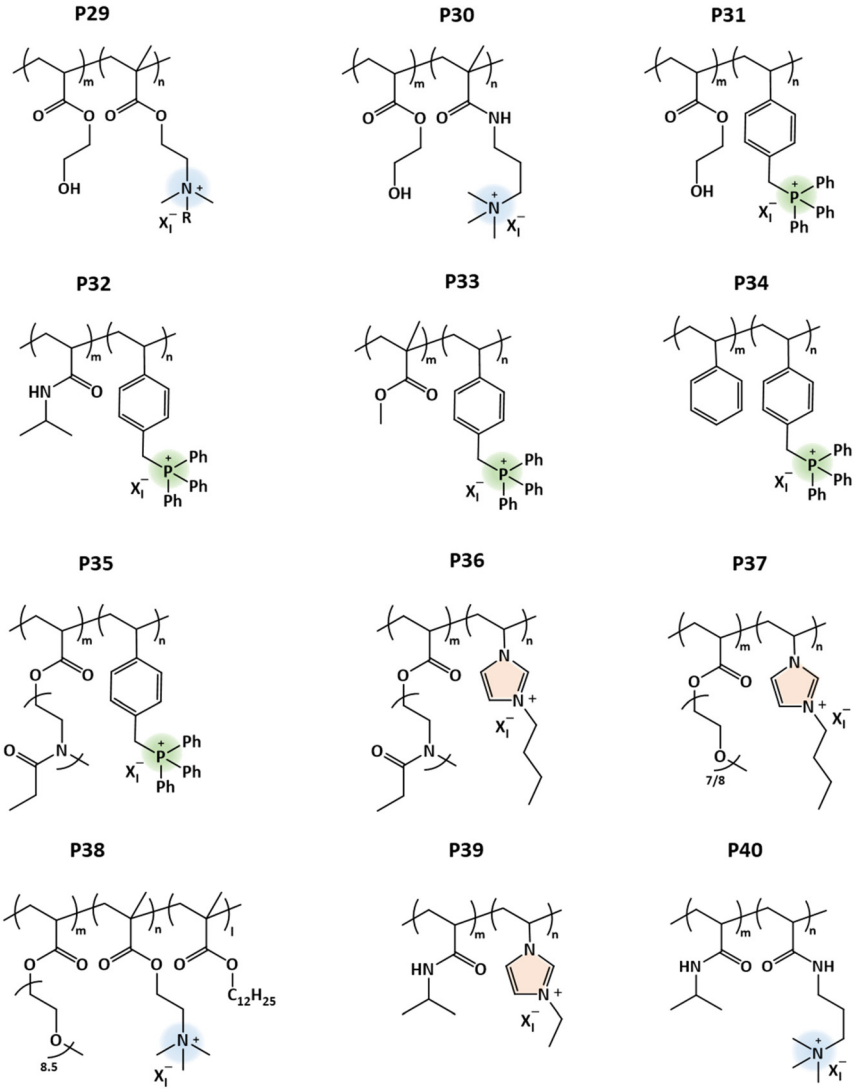

Scheme 3 Thermoresponsive random copolymers.

dazolium-based 1-vinyl-3-ethylimidazolium bromide (VEIm-Br) cations and NIPAM **P39**. The thermoresponsiveness of the copolymers is mainly attributed to the NIPAM behavior. The phase transitions change with the polymer compositions and added salts, see Fig. 14B and C.[119] Either by increasing the salt concentration or decreasing the ionic content in the copolymers, the cloud point T_{cL} shifts to lower temperatures. At high ionic contents, copolymers form stable aggregates upon phase separation, but it may also be that the thermoresponsiveness totally vanishes. Random copolymers of NIPAM and AMPTMAC, **P40**, exhibit LCST, UCST, or both phase transitions ($T_{cL} < T_{cU}$) in the presence of NTf_2^- ions. These double phase transitions mainly occur when the copolymers consist of equal amounts of NIPAM and AMPTAMC units (**P40d**). The copolymers experience a LCST-type separation with a lower amount of AMPTMAC (**P40a**). Only an UCST-type separation was observed for copolymers with a high AMPTMAC content (**P40e**).[121]

4.2. Block copolymers

The thermoresponsive behavior of polymers can be tuned with the copolymer architecture. Block copolymers undergoing phase separation in water when heated have been well reported in the literature. Due to the block architecture, the hydrophilic block copolymers can form self-assembled core–shell nanoparticles when one of the blocks phase separates above T_{cL} or below T_{cU} and the other block remains soluble. In such cases, the copolymers can be used to encapsulate and release poorly water-soluble active substances in a controlled way. Copolymers made of two thermoresponsive blocks are of special interest because, as the temperature changes, the copolymers can build up inverse micelles (LCST > UCST or LCST < UCST). If both blocks lose their solubility upon heating, the phase separation of the polymers may take place stepwise ($LCST_1$ > $LCST_2$ or $UCST_2$ > $UCST_1$). Finally, in the case of amphiphilic block copolymers, phase separation may lead to

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Table 3 List of thermoresponsive random copolymers

Polymer	Compound number	m	n	l	X_l^-	Type of transition
P(MOETAC-*co*-HEMA)	**P29a**	93	7	—	Cl^-	LCST and UCST
	P29b	92	8	—	Cl^-	
	P29c	86	14	—	Cl^-	
P(MPTMAC-*co*-HEMA)	**P30a**	96	4	—	Cl^-	LCST and UCST
	P30b	93	7	—	Cl^-	
	P30c	91	9	—	Cl^-	
P(VBTPP-*co*-HEMA)	**P31**	89.5	10.5	—	Cl^-	UCST
		80	20	—	Cl^-	
		71.4	28.6	—	Cl^-	
P(VBTPP-*co*-NIPAM)	**P32a**	98.9	1.1	—	Cl^-	LCST
	P32b	98	2	—	Cl^-	
	P32c	80.7	19.3	—	Cl^-	
	P32d	65.5	34.5	—	Cl^-	LCST and UCST
P(VBTPP-*co*-MMA)	**P33a**	90	10	—	Cl^-, I^-	UCST
	P33b	82	18	—	Cl^-, I^-	
	P33c	4	96	—	Cl^-	
P(VBTPP-*co*-St)	**P34a**	78	22	—	Cl^-	UCST
	P34b	35.6	64.4	—	Cl^-	
	P34c	9.7	90.3	—	Cl^-	
P(VBTPP-*co*-OEtOxA)	**P35a**	25	2	—	Cl^-	LCST
	P35b	25	4	—	Cl^-	
	P35c	25	11	—	Cl^-	
	P35d	25	25	—	Cl^-, I^-	
	P35e	10	42	—	Cl^-	LCST and UCST
	P35f	10	46	—	Cl^-	UCST
P(VBuIm-*co*-OEtOxA)	**P36a**	20	40	—	Br^-	LCST and UCST
	P36b	20	75	—	Br^-	UCST
	P36c	3	60	—	Br^-	
P(VBuIm-*co*-OEGMA)	**P37**	—	—	—	SCN^-, BF_4^-, PF_6^-, NTf_2^-	LCST
P(PEGMA-*co*-MOTAI-*co*-DMA)	**P38a**	32	99	65	Cl^-, I^-, NO_3^-,	LCST
	P38b	42	92	43	Cl^-, I^-, NO_3^-, SO_4^{-2}, CH_3COO^-	
	P38c	59	94	30	Cl^-, I^-, NO_3^-,	
	P38d	68	98	21	Cl^-, I^-, NO_3^-,	
P(VEIm-*co*-NIPAM)	**P39**	—	—	—	Br^-	LCST
P(AMPTAC-*co*-NIPAM)	**P40a**	83	7	—	NTf_2^- + Cl^-	LCST
	P40b	71	15	—	NTf_2^- + Cl^-	
	P40c	65	23	—	NTf_2^- + Cl^-	
	P40d	43	37	—	NTf_2^- + Cl^-	LCST and UCST
	P40e	27	50	—	NTf_2^- + Cl^-	UCST

m, n, and l indicate the DPs of different repeating units. m refers to the non-ionic monomer, n to the cationic monomer. l is for dodecylmethacrylate (**P38**).

nanoparticles with a multitude of morphologies, depending on the mutual lengths of the blocks and the T_{cL} of the responsive block.

4.2.1. PNIPAM as a thermoresponsive block. We next look at block copolymers and start with those that combine cationic and non-charged responsive blocks (see Scheme 4 and Table 4). It is natural to begin with polymers with PNIPAM blocks. Several reports have been published on polymers where the other block was an imidazolium-based polycation.[122–125] Texter *et al.* demonstrated the formation of core–shell particles of cationic diblock copolymers of NIPAM (**P41**).[124] In addition to thermal collapse in pure water, block copolymers underwent inverse micellization in aqueous KBr solutions. In this case, while the poly(ionic liquid) block was condensed, the colloidal stability appeared to be provided by a corona of PNIPAM. Similar observations were also made by Yuan *et al.* with hydrophilic block copolymers **P42a** containing PNIPAM and cationic poly(VEIm-Br) blocks (Fig. 15A). Particles with poly(ionic liquid) cores underwent phase separation above the LCST of PNIPAM.[126] Wang *et al.* explored solutions of similar block copolymers **P42b** but used poly(VBuIm-Br) **P9** as the hydrophobic PIL blocks.[123] In this case, micelles consisting of a relatively hydrophobic core of PIL and a hydrophilic shell of PNIPAM formed in water at room temperature. At elevated temperatures, PNIPAM phase separated and larger aggregates built up. The occurrence of the phase transition depends on the ionic content or the copolymer architecture. Random copolymers made with the same IL and NIPAM units as in block copolymer **P42b** do not show phase separation in water.

Luo *et al.* studied a series of block copolymers **P43a–f** comprised of PNIPAM and styrene-based poly(vinylbenzyl)methylimidazolium (PVBMIm) with BF_4^- counterions.[127] As shown in Fig. 15B, copolymers with long cationic blocks are soluble at all temperatures. However, upon decreasing the DP of PIL or increasing the NIPAM content, the polymer undergoes a LCST-type phase transition and the sizes of the aggregates vary with the block ratios. We investigated a similar system where the

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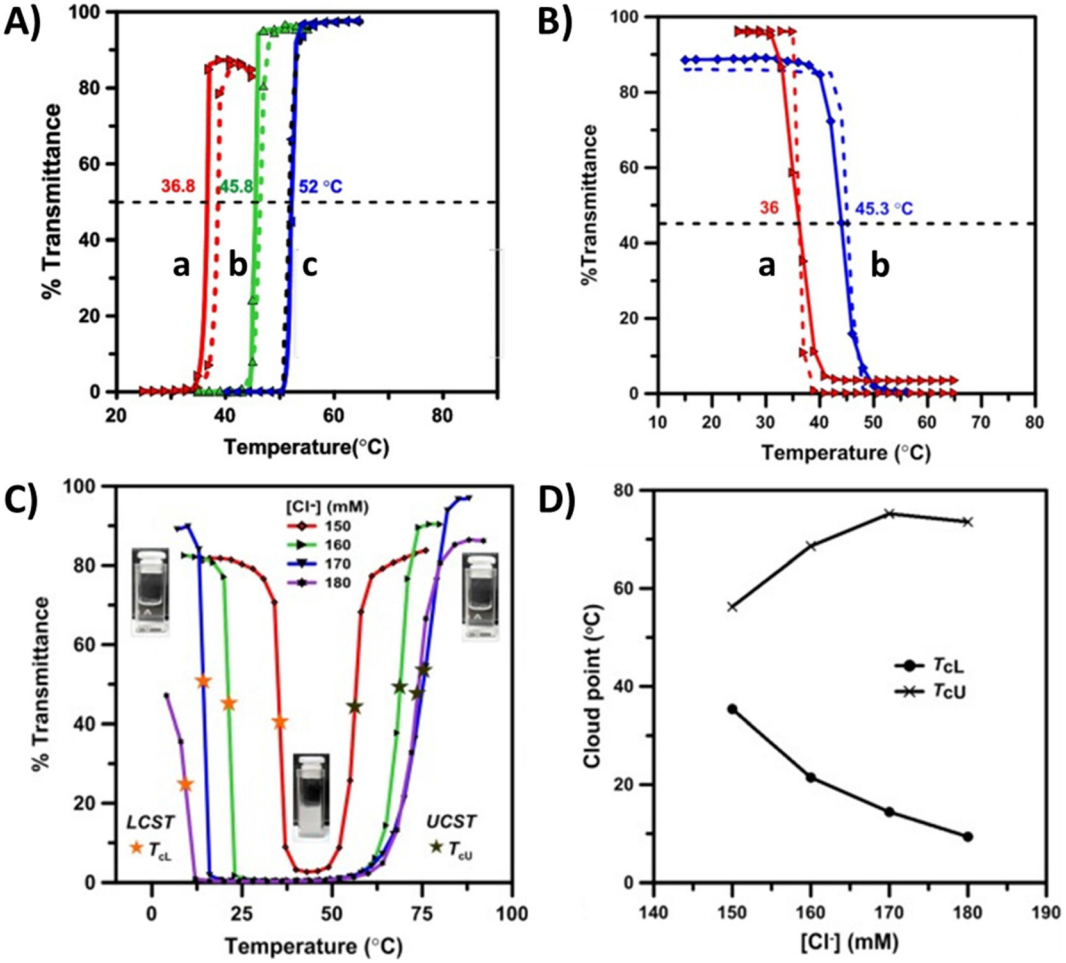

Fig. 12 (A) Turbidity curves for aqueous copolymer solutions of **P31** (1 wt%) with various Cl^- ion contents: (a) **P31a**, Cl^- = 10 mM; (b) **P31b**, Cl^- = 25 mM; (c) **P31c**, Cl^- = 75 mM. (B) Turbidity curves of 1 wt% aqueous solutions of **P32a** (a) and **P32b** (b) with various PNIPAM contents. (C) Turbidity curves of aqueous **P32c** solutions (0.25 wt%) at different Cl^- ion concentrations. (D) T_{cL} and T_{cU} points of **P32d** (0.25 wt%) as a function of [Cl^-] ions measured from the heating curves shown in (C). Reproduced from ref. 116. Copyright 2020, with permission from Elsevier.

imidazolium-based polycation was chain extended with NIPAM with different DPs (**P44**).[129] The copolymer micelles with longer PNIPAM blocks underwent a LCST-type thermal transition and large aggregates were observed by DLS at elevated temperatures. The phase separation behavior of NIPAM block copolymers was also evaluated by changing the substituents on the vinyl imidazolium PIL segments. Block copolymer **P45** with hydrophilic 1-(2-ethoxyethyl)-3-vinylimidazolium bromide (EtOEVI-Br) IL segments was soluble in water at low temperature, and formed micelles upon phase separation of PNIPAM blocks above T_{cL}. By changing the IL segments to hydrophobic 1-(3-phenylpropyl)-3-vinylimidazolium bromide (PVI-Br) units, the polymers showed poor solubility in water. In the case of copolymer **P46**, the block copolymers form micelles with PIL cores at room temperature, which phase separate upon heating as NIPAM chains collapse above the LCST (Fig. 15C).

Mori *et al.* synthesized linear and star block copolymers containing poly(VEIm-Br) cationic segments and poly (NIPAAm) as a thermoresponsive segment. Similar to the above discussed copolymers, the T_{cL} shifted to higher temperatures in both linear and star block copolymers when compared to homopolymers of NIPAM.[125,130] In the case of star polymers, the phase transitions occurred much more sharply in the **P47** stars (PNIPAM is the inner block) compared to other ones, **P48**, with PNIPAM as the outer block. The phase separation was reversible upon cooling and heating. Above T_{cL}, **P47** stars phase separated and formed large aggregates (D_h = 570 nm). The aggregates were stable at elevated temperatures of >40 °C. The micelles consisting of a relatively hydrophobic core of PNIPAM and a hydrophilic shell of poly(VEIm-Br) aggregated in solution. On the other hand, a constant increase in the hydrodynamic diameters of the aggregates was observed for the **P48** stars from 230 nm at 35 °C to 670 nm at 40 °C. Similar size increments were also observed for linear block copolymers.

Several responsive NIPAM copolymers containing amine based cationic blocks have been reported. In general, these polymers have been employed in studies on polyelectrolyte complexes.[131–135]

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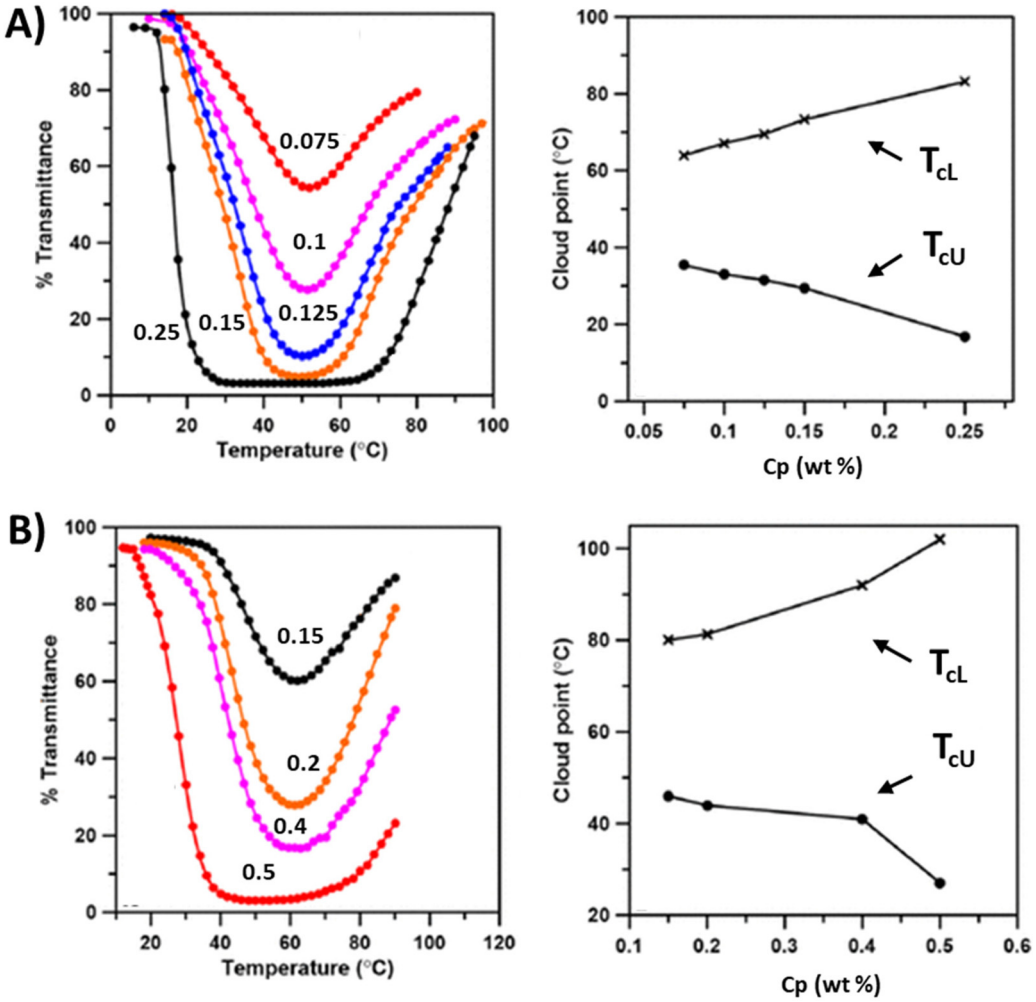

Fig. 13 (A) Turbidity heating curves for **P35e** in aqueous solutions at different polymer concentrations in the presence of 500 mM Cl^- ions and T_{cL} and T_{cU} points collected from heating curves (right). (B) Turbidity heating curves of aqueous **P36a** solutions at different polymer concentrations in the presence of 55 mM I^- ions and T_{cL} and T_{cU} points collected from heating curves (right). Polymer concentrations are indicated next to the transmittance curves. Adapted from ref. 117. Copyright 2018 American Chemical Society.

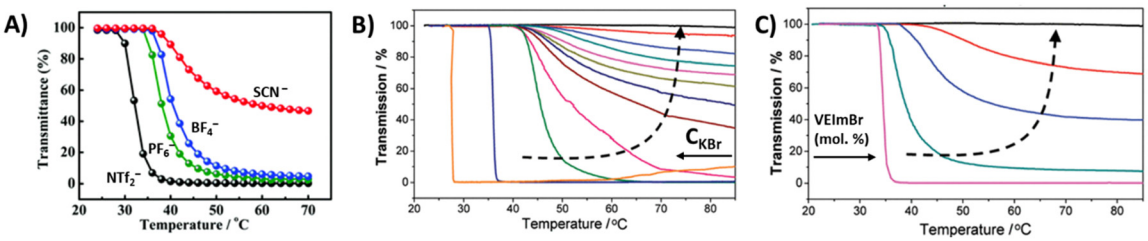

Fig. 14 (A) Transmittance heating curves collected for **P37** in various aqueous ionic solutions (0.1 wt%). Reproduced from ref. 118. Copyright 2017 Royal Society of Chemistry. (B) Turbidity curves of aqueous solutions (10 g L^{-1}) of **P39** with 7.6 mol% of VEIm-Br and different concentrations of KBr (from 0.001 to 1 M), C_{KBr} increasing in order from right to left. (C) Turbidity curves of aqueous solutions of **P39** with different VEIm-Br contents and a constant concentration of KBr (C_{KBr} = 0.015M), mol% increasing in order from left to right. Adapted from ref. 119. Copyright 2012 American Chemical Society.

4.2.2. Polycation as a thermoresponsive block. Several block copolymers consisting of a hydrophilic or hydrophobic nonionic block and a cationic thermoresponsive one have been reported. Much studied copolymers consisted of ethylene glycol units and weakly cationic DMAEMA. The block copolymers of DMAEMA containing either a poly(ethylene glycol) methyl ether (mPEG) or poly(di(ethylene glycol) methyl ether methacrylate) (PmDEGMA) block both undergo UCST and

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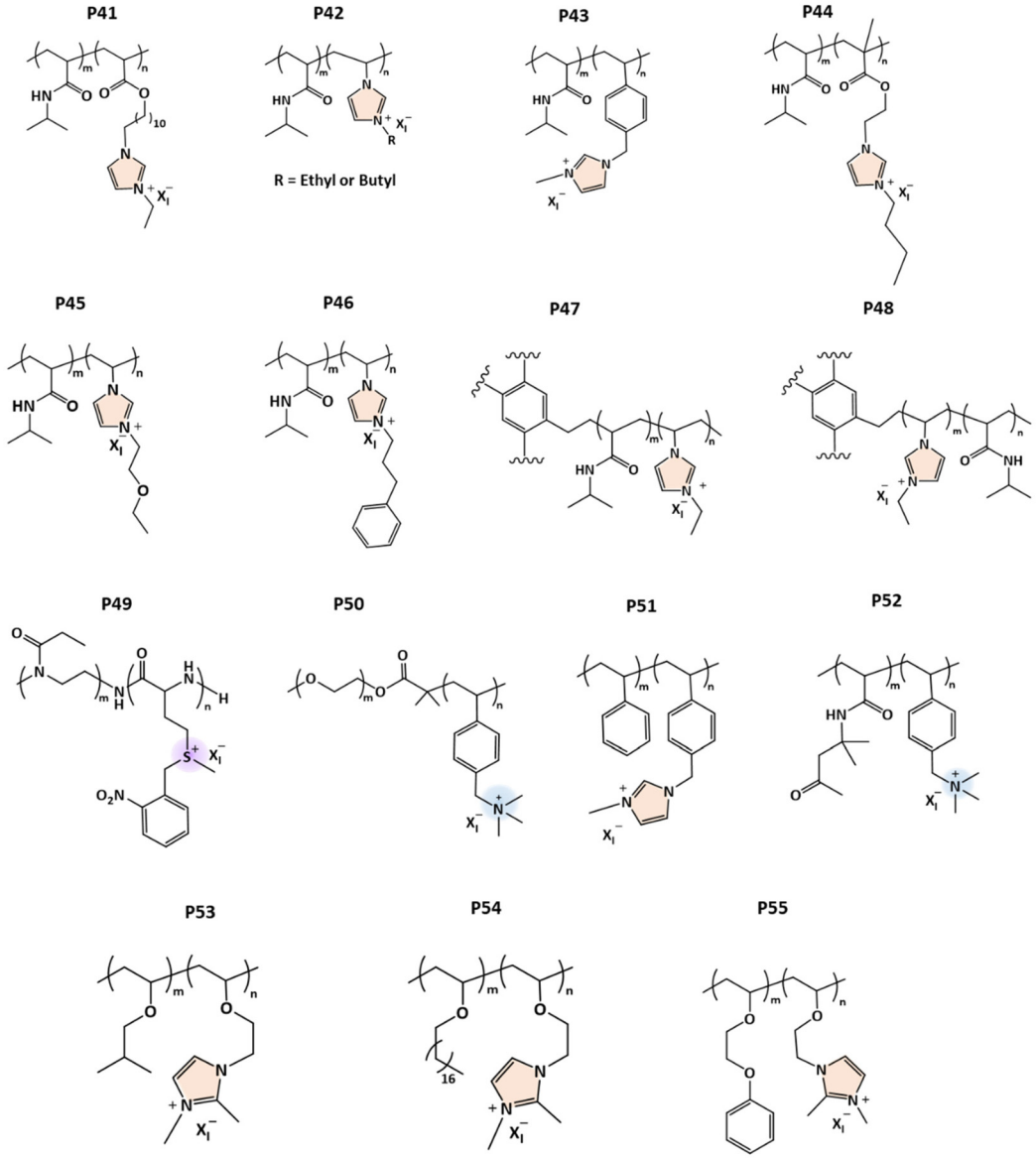

Scheme 4 Thermoresponsive block copolymers.

LCST-type transitions.[136,137] Zhang *et al.* reported that DMAEMA block copolymers of di- or tri- (ethylene glycol) methyl ether methacrylates, PmDEGMA or PmTEGMA, experienced triple responsive behavior (UCST < $LCST_1$ < $LCST_2$) in aqueous solutions. However, the phase behavior of the diblock copolymer PDMAEMA-*b*-poly(2-(2-methoxyethoxy)ethyl methacrylate) is dependent on the block composition and pH. In some cases, the thermoresponsive behavior may disappear with a high content of DMAEMA.[137] Micelles of a water soluble block copolymer, poly(ethylene oxide)-*b*-poly(2-vinyl pyridine), were reported to undergo an UCST phase transition under certain pH conditions when using divalent persulfate anions ($S_2O_8^{2-}$).[138]

A few diblock copolymers of strong polycations have been found to be thermoresponsive. Polypeptide block copolymers **P49** consisting of ethyl-oxazoline and methionine undergo UCST phase separation in aqueous I^-, ClO_4^- or SCN^- solutions similar to polymethionine. Polyethyl oxazolines, PEtOX, with DP greater than 100 are known to exhibit a LCST between 0 and 100 °C. However, in the methionine case, the PEtOX block was short and had no influence on the phase separation process. Zhao *et al.* recently reported self-assembled polypeptide structures of triblock copolymers bearing sulfonium and triphenylphosphonium iodide in aqueous solutions. These single-chain nanoparticles show UCST-type thermoresponsive properties in aqueous or PBS solutions.[139]

Recently, we studied the phase separation of diblock copolymers **P50** comprising PEG and styrene-based polycations with OTf^- counterions.[140,141] The block copolymers are well soluble in water, but phase separate upon the addition of LiOTf.

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Table 4 List of thermoresponsive block copolymers

Block copolymer	Compound number	*m*	*n*	X_1^-	Type of transition
PNIPAM-*b*-PEImA	**P41**	—	—	Br^-	LCST
PNIPAM-*b*-PVEIm	**P42a**	60	38	Br^-	LCST
PNIPAM-*b*-PVBuIm	**P42b**	50	17	Br^-	LCST
PNIPAM-*b*-PVBMIm	**P43a**	239	18	BF_4^-	LCST
	P43b	231	37	BF_4^-	
	P43c	221	56	BF_4^-	
	P43d	226	76	BF_4^-	
	P43e	92	76	BF_4^-	
	P43f	364	76	BF_4^-	
PNIPAM-*b*-PBuImMA	**P44a**	59	24	BF_4^-	LCST
	P44b	88	24	BF_4^-	
PNIPAM-*b*-PEtOEVIm	**P45**	27	73	Br^-	LCST
PNIPAM-*b*-PPVIm	**P46**	91	9	Br^-	LCST
$[(PNIPAM\text{-}b\text{-}PVEIm)]_4$ (star)	**P47**	38	62	Br^-	LCST
$[(PVEIm\text{-}b\text{-}PNIPAM)]_4$ (star)	**P48**	64	36	Br^-	LCST
PEtOx-*b*-PMetNB	**P49**	—	—	I^-, ClO_4^-, SCN^-	UCST
PEG-*b*-PVBTMAC	**P50a**	93	62	OTf^-	UCST and LCST
	P50b	93	81	OTf^-	UCST and LCST
	P50c	93	172	OTf^-	UCST
	P50d	93	270	OTf^-	UCST
PS-*b*-PVBMIm	**P51**	—	—	BF_4^-	UCST
PDAAm-*b*-PVBTMAC	**P52**	—	—	OTf^-	UCST
PIBVE-*b*-PImVE	**P53**	—	—	Cl^-, BF_4^-	UCST
PODVE-*b*-PImVE	**P54**	—	—	Cl^-, BF_4^-	UCST
PPhOVE-*b*-PImVE	**P55**	—	—	Cl^-, BF_4^-	UCST

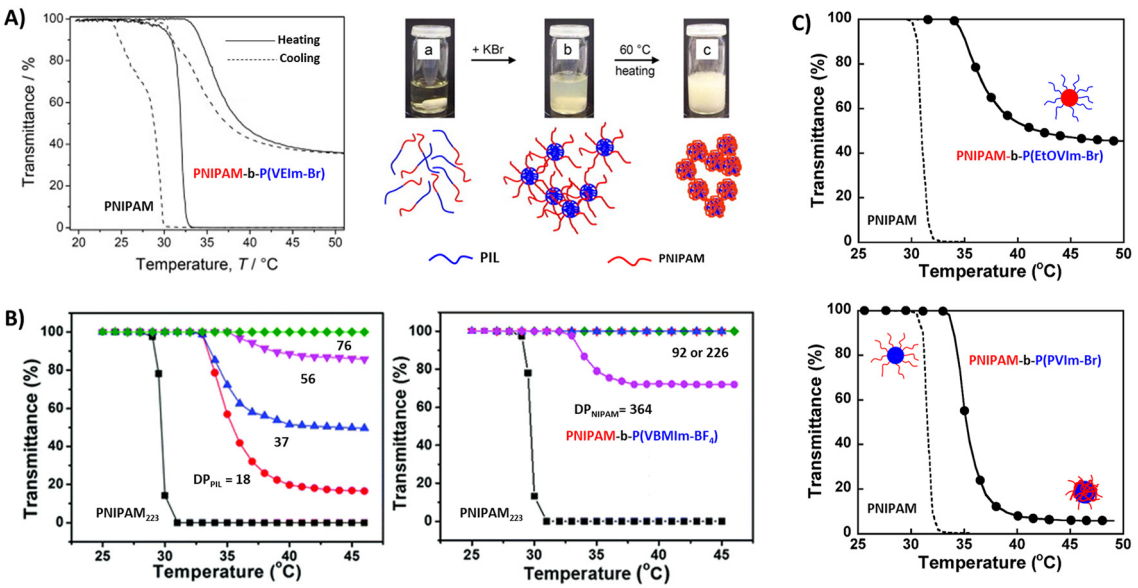

Fig. 15 (A) Temperature-dependent transmittance of PNIPAM and block copolymer **P42a** and photographs of the polymer solutions in pure water at 25 °C (a). (b) and (c) are in the presence of KBr at 25 °C and 60 °C. Reproduced from ref. 126. Copyright 2011 Elsevier. (B) Transmittance curves of aqueous **P43** solutions with various DPs of PIL blocks (left) and for copolymers with various DPs of PNIPAM blocks (right). Reproduced from ref. 127 with permission from the Royal Society of Chemistry. (C) Transmittance curves for block copolymers **P45** (top) and **P46** (bottom) in water. Reproduced from ref. 128. Copyright 2009 American Chemical Society.

Interestingly, block copolymers with short cationic blocks, **P50a**, undergo stepwise phase separation with both UCST and LCST-type transitions (Fig. 16). Upon cooling, the clear polymer solutions become very turbid below T_{cU}. With further cooling, the dispersions slightly clear up below T_{cL} (Fig. 16A). The phase separation process is strongly dependent on the LiOTf concentration and the length of the cationic block. The insolubility window (intermediate phase) becomes wider with increasing the LiOTf concentration up to 400 mM and T_{cU} increases (Fig. 16B) when the cationic block is short (DP 62).

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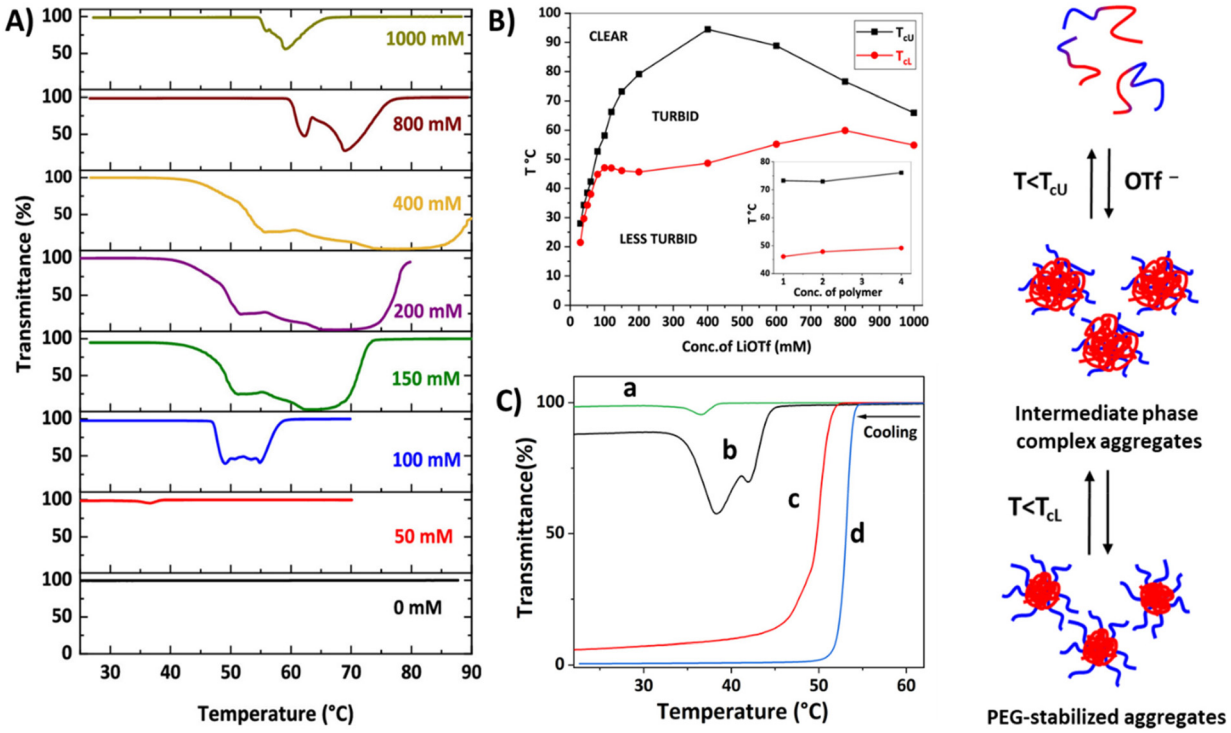

Fig. 16 (A) Transmittance cooling curves for **P50a** solutions (PVBTMAC DP = 62) and (B) T_{cU} and T_{cL} at different LiOTf concentrations (inset, T_{cU} and T_{cL} at different polymer concentrations). (C) Transmittance cooling curves for **P50** in aqueous triflate solutions (50 mM LiOTf). PVBTMAC DP (*a* = 62, *b* = 81, *c* = 172 and *d* = 270). Illustration of PEG-polycation phase separation in aqueous triflate solutions. Reproduced from ref. 141. Copyright 2018 American Chemical Society.

At high salt concentrations, T_{cU} decreases and narrow insolubility regions with more than one transmittance minimum are observed. The polymer concentration (inset in Fig. 16B) and end group have no effect on the phase separation process. The phase separation process was different in the block copolymer when the length of the cationic block increased to DP 81 (**P50b**); both LCST and UCST-type transitions were observed at certain salt concentrations (from 50 to 80 mM). No clearing transition was observed for the polymer solutions with 100 mM or higher LiOTf concentrations.[140] Only single UCST-type transitions were observed for block copolymers (**P50c** and **P50d**) with long cationic blocks (DP = 172 and 270) at any LiOTf concentration.[141]

Overall, the length of the polycation block turned out to have a critical effect on the thermal behavior of the polymers, as clearly shown in Fig. 16C. The transmittance curves in this figure were measured in aqueous 50 mM LiOTf. With short cationic blocks, the polymers underwent stepwise phase separation. First, the cationic blocks experienced an UCST-type transition below T_{cU}. Large complex aggregates built up and, therefore, the transmittance dropped. Upon further cooling, PEG-stabilized particles were formed below the clearing temperatures T_{cL}. As the number of cationic units increased, the phase separation of the polymers took place in a single step. ^{1}H NMR spectra suggested that ion-mediated interactions between PEG and cationic blocks led to such complex phase behavior. In the intermediate phase, some of the PEG units were buried in the cationic cores; therefore, no steric stabilization was possible in the high molar mass polymers. The behavior of the long cationic block polymers resembled that of the homopolymers and indicated the formation of unstable aggregates stabilized by electric charges.

Thermoresponsive polycations were also used to construct amphiphilic particles *via in situ* self-assembly methods. The particles consisted of hydrophobic or solvophobic cores, with the cationic blocks acting as thermoresponsive stabilizer blocks. Zhang *et al.* prepared diblock copolymer particles (**P51**) containing VBMIm-BF_4 and styrene blocks in methanol/water (85/15 v/v) mixtures.[86] The bluish dispersions obtained at 70 °C turned to opalescent gel-like solids upon cooling to room temperature. This is due to the UCST-type behavior of cationic blocks in water/MeOH mixtures. We reported amphiphilic diblock copolymers containing cationic VBTMAC and diacetone acrylamide (DAAM) units. Under dilute conditions, the particles constructed of block copolymers **P52** underwent an UCST-type transition in the presence of OTf^- ions (Fig. 17A).[142] The phase separation was dependent on the ratio of cationic units and OTf ions; the particle phase separation took place in two steps at a certain triflate concentration.

Recently, we prepared **P52** particles with various cationic block lengths in aqueous triflate solutions (Fig. 17).[87] When strong polyelectrolytes are used as particle stabilizers, the morphology of the particles is limited to only spheres. This is due to the strong electrostatic repulsion in the corona, which inhi-

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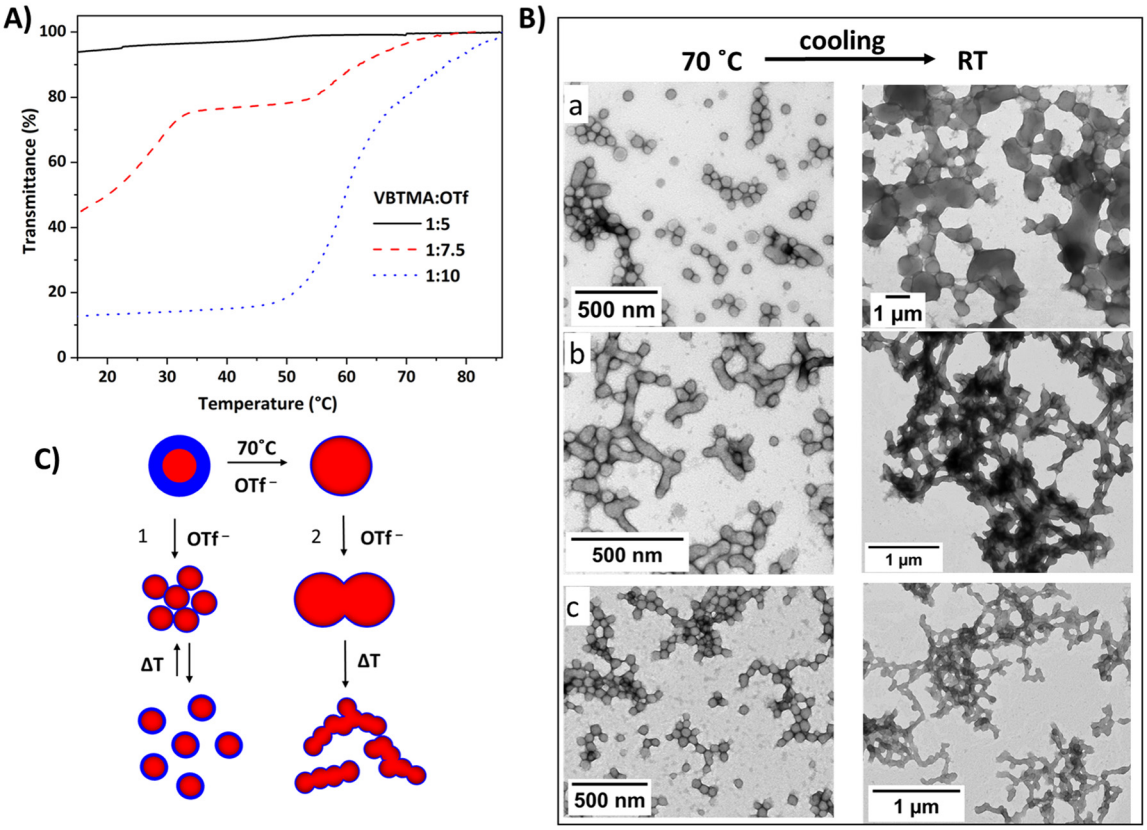

Fig. 17 (A) Normalized transmittance cooling curves for spherical nanoparticles of **P52** (0.1 w/w%) in aqueous triflate solutions with different cation/anion ratios. Reproduced from ref. 142. Copyright 2021 American Chemical Society. (B) TEM micrographs of **P52** particles obtained in aqueous triflate solutions using cationic stabilizers with different block lengths (at 70 °C and RT). DP of PVBTMAC is (a) 24, (b) 50 and (c) 61. Reproduced from ref. 87 Copyright 2022 Royal Society of Chemistry. (C) Schematic view of OTf induced temperature response of particles; case 1: UCST phase separation in dilute conditions; case 2: morphological changes in PISA upon cooling.

bits fusion of the particles. In the presence of OTf^- ions, the diblock copolymers formed fused particles or vesicles due to the strong ionic interactions between the triflate and polycation stabilizers, promoting the high packing efficiency. Particles formed at 70 °C under *in situ* conditions underwent phase separation and formed gel-like solids upon cooling to room temperature (Fig. 17C). However, a reversible phase transition was not observed upon heating.

Aoshima *et al.* extensively studied vinyl ether block copolymers that underwent sol–gel transitions upon changing the solution temperature. Recently, they prepared block copolymers **P53** consisting of dimethylimidazolium tetrafluoroborate-containing vinyl ether ([Me_2Im][BF_4]) and isobutyl vinyl ether (IBVE).[143] An aqueous solution of this diblock copolymer, **P53** (m = 400 units), showed UCST-type thermosensitive physical gelation behavior under dilute conditions. The opaque solutions of the diblock copolymer became viscous gels upon heating to 25 °C (see Fig. 18A). The sol–gel transition is likely due to the tight packing of the micelles at higher temperature and the viscoelastic behavior of the aqueous gels follows typical physical gel behavior. From DLS measurements, larger diameters were recorded above the gelation temperature for **P53** aqueous solutions (Fig. 18B). At high temperature, the micelle corona chains are extended because of the electrostatic repulsion and hydration of the [Me_2Im][BF_4] segments. Therefore, the micelles approach each other with spatial limitation in water, which leads to physical gelation through tight packing of the micelles. Smaller diameters (60 nm at 10 °C) were recorded for the precursor polymer consisting of oxyethylenic moieties, IBVE-*b*-(2-ethoxyethyl vinyl ether) ($IBVE_{50}$-$EOVE_{400}$). An almost horizontal plateau in the storage modulus (G') over a wide range of frequencies was observed for 1 wt% **P53** solution at 55 °C (Fig. 18C). The gelation behavior depends on polymer concentration, counter anions, and the polycation block length (table in Fig. 18). The 0.7 wt% aqueous solution of diblock copolymer **P53** (m = 400 units) gelated at 60 °C, while in the 1 wt% solution gelation took place at 25 °C. The 1 wt% solution of copolymer **P53** with a long cationic block (m = 800 units) gelates at 0 °C. The gelation concentration of the copolymer with the Cl^- counter anion was lower than that with BF_4^-, while the copolymer with PF_6^- did not gel at all.

Later, solution properties and the sol–gel transition of the block copolymers were investigated by changing the chemical composition of the hydrophobic block and of the alkyl substituents on cationic units, as well as the counterions.[144] Gelation was

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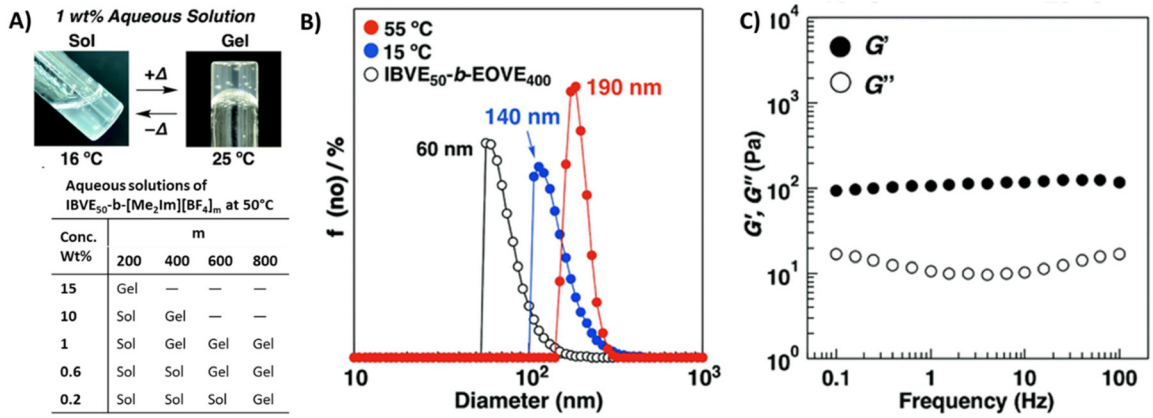

Conc. Wt%	m 200	400	600	800
15	Gel	—	—	—
10	Sol	Gel	—	—
1	Sol	Gel	Gel	Gel
0.6	Sol	Sol	Gel	Gel
0.2	Sol	Sol	Sol	Gel

Fig. 18 (A) Photographs of thermosensitive physical gelation behavior of **P53** (m = 400; sol: 16 °C, gel: 25 °C). (B) DLS size distributions collected for 0.01 wt% aqueous solutions of **P53** (m = 400) at 55 °C (red) and 15 °C (blue) and precursor copolymer ($IBVE_{50}$-$EOVE_{400}$) of **P53** at 10 °C (open symbols). (C) Frequency dependence of dynamic moduli, storage modulus G' (●) and loss modulus G'' (○) measured at 55 °C for **P53** (m = 400) 1 wt% aqueous solution. Reproduced from ref. 143. Copyright 2018 Royal Society of Chemistry.

observed only for polymers with Cl^- and BF_4^-, whereas with hydrophobic counterions like SbF_6^-, PF_6^-, or NTf_2^- the polymers were insoluble in water. The solubility and gelation behavior of the amphiphilic diblock copolymers were dependent on the structures of the imidazolium ionic segments. The gelation temperature increased with increasing the lengths of the alkyl substituents. The sol–gel behavior of the diblock copolymers was tuned by the alkyl side chains in the hydrophobic blocks. The block copolymers with hydrophobic segments with octadecyl vinyl ether (**P54**) or 2-phenoxyethyl vinyl ether (**P55**) underwent UCST-type thermosensitive sol–gel transitions upon heating, similar to the copolymers with IBVE segments.

5. Summary and future prospects

The review discusses progress made on thermoresponsive polymers, with a special focus on polycations. Solution properties of polycations have been studied for years. However, the importance of counterions for creating stimuli-responsive polymers in aqueous or non-aqueous systems has been recently realized. We briefly discussed thermoresponsive polycations and cationic random and block copolymers, as well as polymer particles.

When designing cationic LCST and UCST polymers, one needs to consider (1) the balance between electrostatic and hydrophobic interactions (LCST), and (2) ionic interactions between the polymer chains and counter ions *plus* the hydrophobicity of the polymer or counter ion (UCST).

Polycations, which are well soluble in water, undergo phase separation at a critical temperature (T_{cL}) upon heating when the alkyl substituents of the charged units are sufficiently hydrophobic. Alternatively, by using hydrophobic counterions, the phase separation process of water-soluble polycations can be reversed. In the presence of hydrophobic counterions, polycations either become totally water insoluble or undergo UCST-type phase transitions. The phase behavior of the polymers can be tuned from single to double phase transitions by changing the alkyl substituents or copolymerizing with nonionic monomers. Compared to nonionic systems, polyelectrolytes that show LCST-type phase transitions are less documented in the literature. However, several cationic copolymers with NIPAM or other thermoresponsive repeating units undergo LCST or UCST-type phase transitions. A few cationic copolymers show both LCST and UCST type transitions.

Besides their interesting tunable solution properties, thermoresponsive polycations may find interesting applications such as in hydrogels taking up/releasing water and in waste water treatment by a forward osmosis process.[145,146] In addition, applying the counterion strategies to polyelectrolyte brushes, films, or cationic biopolymers would be of fundamental interest in creating smart polymer systems. To generalize the conclusions drawn so far, it would be beneficial to take a closer look at polyanions. Several biopolymers (such as many polysaccharides and DNA) are anionic and it would certainly be beneficial to better understand the solution properties of such systems.

Author contributions

VB collected the data and wrote the manuscript together with HT.

Conflicts of interest

There are no conflicts to declare.

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