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The Anion Binding Affinity Determines the Strength of Anion Specificities of Thermosensitive Polymers

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Electronic supplementary information

Abstract In this work, we demonstrate that the strength of anion specificities of thermosensitive polymers is determined by the affinity of direct anion binding to the polymers. We have prepared a series of thermosensitive statistical copolymers with distinct thermoresponsive behaviors. The anions can specifically interact with the different types of thermosensitive polymers in very different strengths. A similar strength of specific anion effects on thermoresponsive behaviors can be observed at very different salt concentrations for the different types of thermosensitive polymers. A stronger anion binding to the thermosensitive polymers gives rise to a more obvious anion specificity and vice versa. The work presented here opens up opportunities for the application of ion binding affinity to modulate the strength of ion specificities of thermosensitive polymers.

Keywords Specific ion effect; Polyzwitterion; Ion-polymer interaction; Thermosensitivity; Ion-pairing

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Ion specificities are ubiquitous in various systems including biology,[1−3] colloids,[4−6] and polymers.[7−14] Since the Czech scientist Franz Hofmeister firstly discovered these ion-specific effects more than 100 years ago, the ion specificities have been extensively investigated by the experimentalists and theoreticians in a wide range of fields.[15−25] In general, the ion specificities of polymers in aqueous solutions can be observed only at high salt concentrations (typically above 0.1 mol/L), where the long-range nonspecific electrostatic interactions are effectively screened due to the small Debye length, and the properties of the polymer systems are dominated by the short-range ion-specific interactions.[13,26,27] However, a few previous studies have demonstrated that the specific ion effects on polymers can also be observed at low salt concentrations (typically around millimolar salt concentrations).[28−30] The reason why a similar strength of ion specificities can be observed at very different salt concentrations for different polymer systems remains elusive.

For instance, the obvious specific ion effects on neutral polymers are usually observed at the salt concentrations higher than ~100 mmol/L, whereas the ion specificities of charged polymers can be obviously observed at the salt concentrations as low as ~0.1−1 mmol/L.[13,26,28−33] We hypothesize that the strength of ion specificities of polymers is closely related to the affinity of direct ion binding to the polymers. Specifically, a higher ion binding affinity leads more ions to bind to the polymers at a certain ion concentration, such that the different types of ions can be more effectively distinguished and a stronger ion specificity of the polymers is resulted. It is well-known that the neutral poly(*N*-isopropylacrylamide) (PNIPAM) and the charged poly(sulfobetaine methacrylate) (PSBMA) exhibit the lower critical solution temperature (LCST) and the upper critical solution temperature (UCST) behaviors in aqueous solutions, respectively (Fig. S1 in the electronic supplementary information, ESI).[26,34−37] To test the above hypothesis, we have prepared a series of statistical copolymers of poly(sulfobetaine methacrylate-*co*-*N*-isopropylacrylamide) (P(SBMA-*co*-NIPAM)) with either the UCST or the LCST behavior (Fig. 1 and Table S1 in ESI), where the anions exhibit a much stronger binding to the positively charged quaternary ammonium groups of the SBMA units (K_a') than that to the partially positively charged amide groups of the NIPAM units (K_a) according to our previous study.[38] In this work, our aim is to clarify the reason why a similar strength of anion specificities can be observed at very different salt concentrations for different types of thermosensitive polymers.

Fig. 2(a) shows the salt concentration (C_{salt}) dependence of cloud point temperature (T_{cp}) of the PNIPAM aqueous solutions in the presence of different types of anions with the Na^+ as the common cation. The specific anion effects on the thermoresponsive behavior of PNIPAM observed in Fig. 2(a) are

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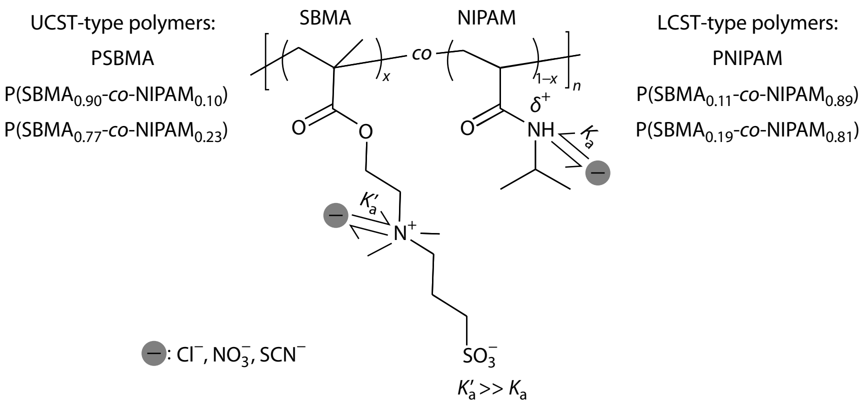

Fig. 1 Schematic illustration of the direct interactions between P(SBMA-*co*-NIPAM) and anions.

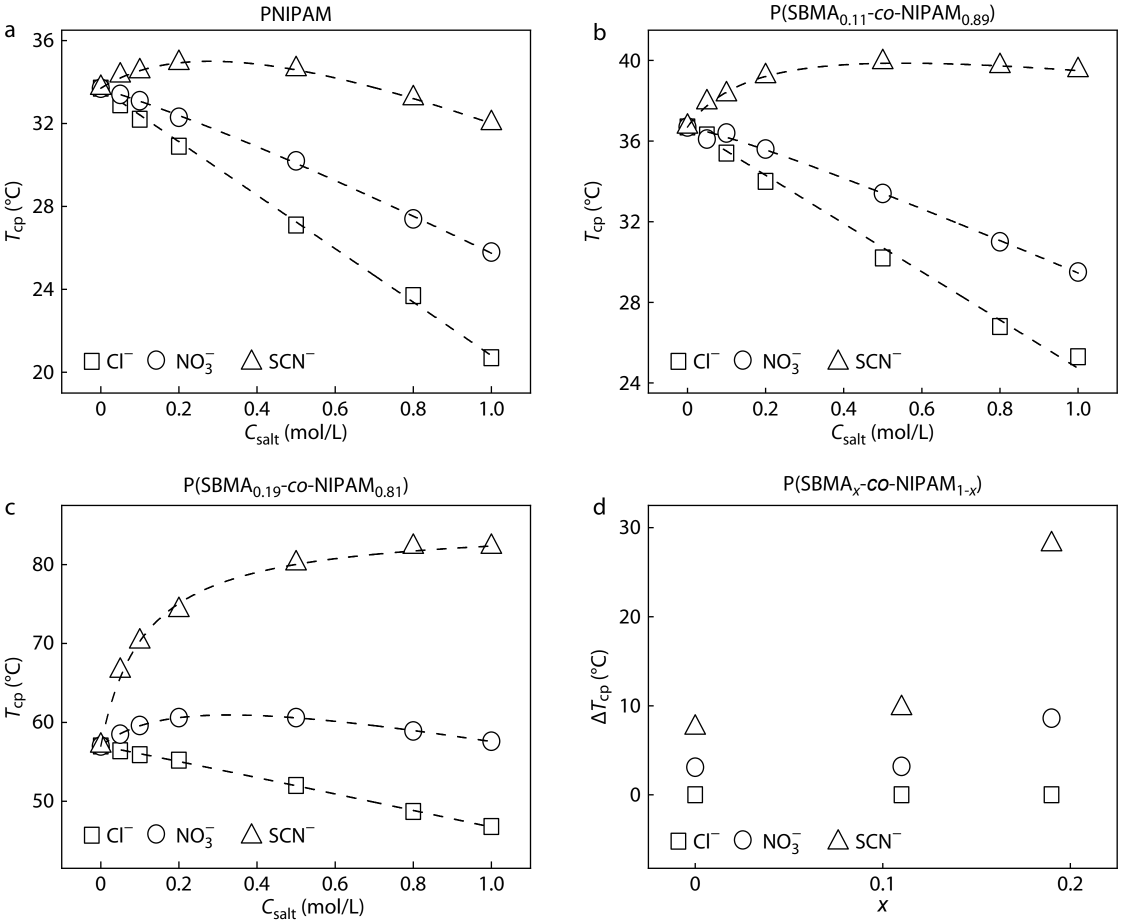

Fig. 2 (a–c) C_{salt} dependence of T_{cp} of the LCST-type polymers in the presence of different types of anions with Na^+ as the common cation, where the polymer concentration is fixed at 10.0 mg/mL in the aqueous solutions. (a) PNIPAM, (b) P(SBMA$_{0.11}$-*co*-NIPAM$_{0.89}$), and (c) P(SBMA$_{0.19}$-*co*-NIPAM$_{0.81}$). The dashed lines in panels (a), (b), and (c) are the curve fits to the experimental data with Eq. (1). (d) ΔT_{cp} between the anions as a function of x at a salt concentration of 0.5 mol/L, where the values of ΔT_{cp} are obtained using the value of T_{cp} for Cl⁻ as the reference for the same type of polymer.

similar to those reported in the previous studies.[7,26] For example, T_{cp} decreases with increasing salt concentrations for Cl^- and NO_3^-, whereas it initially increases and then decreases with increasing salt concentration for SCN^-. The specific anion effects on T_{cp} of PNIPAM can be well understood on the basis of the model proposed by Cremer *et al.* consisting of three kinds of interactions between anions, PNIPAM, and water molecules.[26] The specific anion effects on T_{cp} of P(SBMA$_{0.11}$-*co*-NIPAM$_{0.89}$) and P(SBMA$_{0.19}$-*co*-NIPAM$_{0.81}$) are shown in Figs. 2(b) and 2(c). It is evident that the specific anion effects on T_{cp} are amplified with increasing salt concentration from 0 mol/L to 1.0 mol/L for all the LCST-type polymers.

As the molar fraction of SBMA (x) increases, the value of T_{cp} increases for the same type of anion at the same salt concentration due to the enhanced polymer hydrophilicity by incorporating more SBMA units into the polymers. For the same type of anion, the salt concentration dependence of salting-in and salting-out effects are respectively strengthened and weakened with increasing x for the LCST-type polymers. This is because the solubility of PSBMA is enhanced with increasing salt concentration[39] and a higher x would give rise to a more obvious increase in solubility of the LCST-type polymers with increasing salt concentration.

More importantly, the specific anion effects on T_{cp} of the LCST-type polymers can be amplified by increasing x, as reflected by the difference in T_{cp} (ΔT_{cp}) between the anions, which is amplified with an increase in x at 0.5 mol/L (Fig. 2d). Similar amplifications of ΔT_{cp} between the anions for the LCST-type polymers with increasing x are also observed at other salt concentrations (Fig. S2 in ESI). What concerns us is why the strength of anion specificities of the LCST-type polymers is enhanced with increasing x. According to the previous studies,[26,38,40,41] the direct anion-NIPAM interaction is dominated by the interaction between anions and the partially positively charged amide group, whereas the direct anion-SBMA interaction is dominated by the interaction between anions and the positively charged quaternary ammonium group. Therefore, it is reasonable to expect that the amplification of the specific anion effects on T_{cp} of the LCST-type polymers with increasing x should be closely related to the difference in strength between these two types of anion-polymer interactions. We will come back to this point later.

In Figs. 3(a)–3(c), the specific anion effects on T_{cp} of the UCST-type polymers can be observed around millimolar salt concentrations, where the anion specificities are amplified with increasing salt concentration from 0 mmol/L to 10.0 mmol/L. On the other hand, the strength of the specific anion effects on T_{cp} of the UCST-type polymers is only slightly influenced by x at the low salt concentrations (Fig. 3d and Fig. S3 in ESI), but is enhanced with increasing x at the relatively high salt concentrations (Fig. S3 in ESI). Again, the amplification of anion specificities of the UCST-type polymers with increasing x should be closely correlated with the difference in strength between anion-SBMA and anion-NIPAM interac-

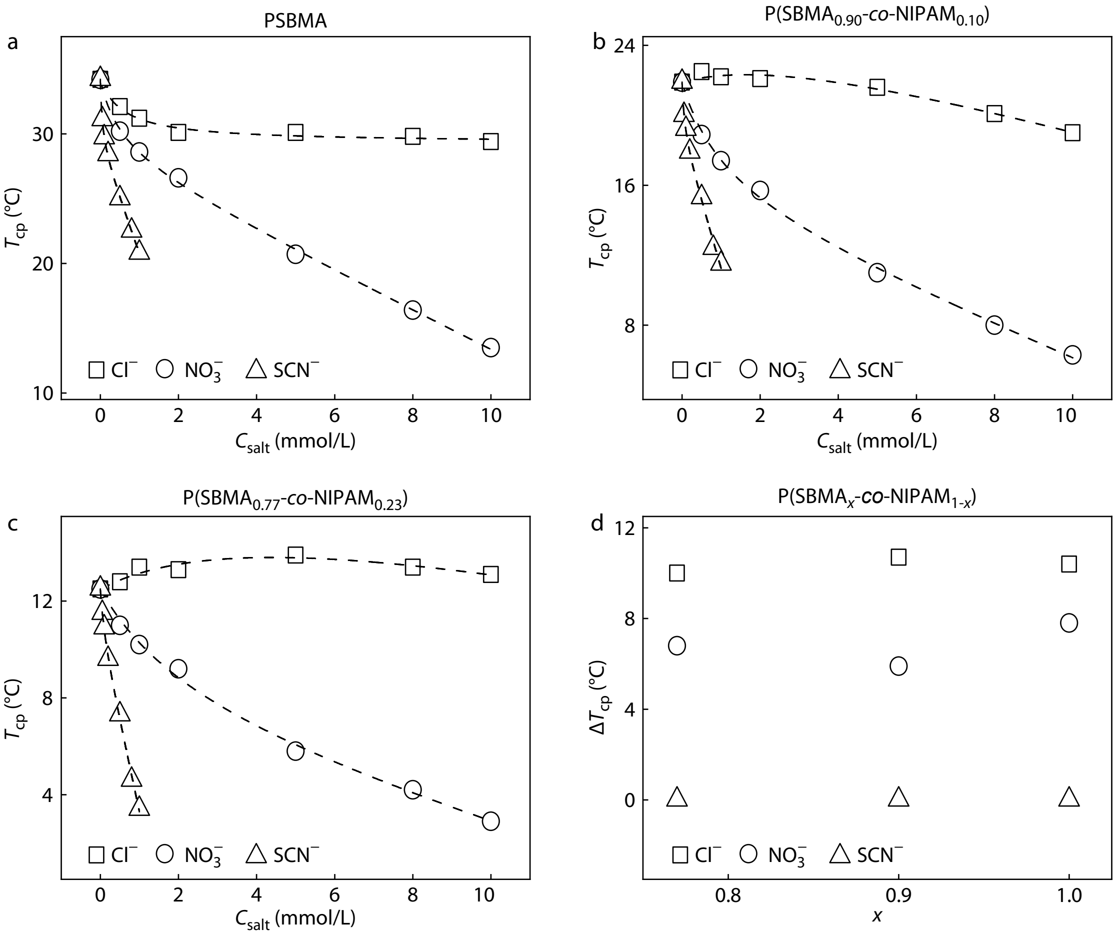

Fig. 3 (a–c) C_{salt} dependence of T_{cp} of the UCST-type polymers in the presence of different types of anions with Na^+ as the common cation, where the polymer concentration is fixed at 10.0 mg/mL in the aqueous solutions. (a) PSBMA, (b) P(SBMA$_{0.90}$-*co*-NIPAM$_{0.10}$), and (c) P(SBMA$_{0.77}$-*co*-NIPAM$_{0.23}$). The dashed lines in panels (a), (b), and (c) are the curve fits to the experimental data with Eq. (2). (d) ΔT_{cp} between the anions as a function of x at a salt concentration of 1.0 mmol/L, where the values of ΔT_{cp} are obtained using the value of T_{cp} for SCN⁻ as the reference for the same type of polymer.

tions. In Fig. 2(d), the strength of specific anion effects as reflected by the ΔT_{cp} is ~10 °C at 0.5 mol/L for PNIPAM and P($SBMA_{0.11}$-*co*-$NIPAM_{0.89}$). A similar strength of anion specificities is observed at 1.0 mmol/L for PSBMA, P($SBMA_{0.90}$-*co*-$NIPAM_{0.10}$), and P($SBMA_{0.77}$-*co*-$NIPAM_{0.23}$), as shown in Fig. 3(d). That is, a 500 times higher salt concentration is required for the former two LCST-type polymers to achieve a similar strength of anion specificities with that for the latter three UCST-type polymers.

To analyze the reason why a similar strength of anion specificities can be observed at very different salt concentrations for different types of thermosensitive polymers, Eqs. (1) and (2) are respectively employed to model the salt concentration dependence of T_{cp} for the LCST- and UCST-type polymers (Figs. 2 and 3), where T_0 is the T_{cp} of the polymer solutions in the absence of salt, and [M] is the molar concentration of the salts. The constant c is correlated with the salting-out effect for the LCST-type polymers and the constant c' is related to the salting-in effect for the UCST-type polymers. K_a and K_a' are the anion binding constants for the LCST- and UCST-type polymers, respectively. B_{max} (B_{max}') represents the maximum increase (decrease) in T_{cp} for the LCST (UCST)-type polymers caused by the direct anion binding.[26,42] The fitting parameters are listed in Table 1, Tables S2 and S3 (in ESI).

$$T = T_0 + c[\mathrm{M}] + \frac{B_{max}K_a[\mathrm{M}]}{1 + K_a[\mathrm{M}]} \tag{1}$$

$$T = T_0 - c'[\mathrm{M}] - \frac{B_{max}'K_a'[\mathrm{M}]}{1 + K_a'[\mathrm{M}]} \tag{2}$$

Table 1 The binding constants (K_a and K_a') obtained from the fitting of experimental data using Eq. (1) or Eq. (2).

	Anion identity	PNIPAM	P($SBMA_{0.11}$-*co*-$NIPAM_{0.89}$)	P($SBMA_{0.19}$-*co*-$NIPAM_{0.81}$)
K_a (L/mol)	Cl^-	~0	~0	1.6
	NO_3^-	0.9	2.4	3.9
	SCN^-	1.9	4.7	8.9
	Anion identity	PSBMA	P($SBMA_{0.90}$-*co*-$NIPAM_{0.10}$)	P($SBMA_{0.77}$-*co*-$NIPAM_{0.23}$)
K_a' (L/mol)	Cl^-	1659.2	235.4	190.3
	NO_3^-	1967.8	919.5	395.7
	SCN^-	19626.7	14768.2	7816.5

In Table 1, the K_a increases following the anion trend Cl^-<NO_3^-<SCN^- for the same LCST-type polymer. The direct anion binding to the LCST-type polymers is dominated by the interactions between the anions and the partially positively charged amide groups of NIPAM units. The anion specificity in terms of the values of K_a could be understood based on the theory of ionic dispersion forces, because the anionic polarizability is increased from Cl^- to SCN^- following the above anion trend. Furthermore, for the same kind of anion, the increasing K_a with increasing x for the LCST-type polymers indicates that a stronger anion binding is resulted as more SBMA units are incorporated into the polymers. For the UCST-type polymers, the direct anion binding to the polymers is dominated by the ion-pairing interactions between the anions and the positively charged quaternary ammonium groups of SBMA units. According to the law of matching water affinities,[43] the strength of the ion-pairing interactions as reflected by the K_a' value should increase following the anion trend Cl^-<NO_3^-<SCN^-, as the positively charged quaternary ammonium is a weakly hydrated group and the extent of hydration of the anions decreases following the anion trend Cl^->NO_3^->SCN^-.[30,44] This is what exactly observed for the UCST-type polymers. Moreover, for the same type of anion, the K_a' increases with increasing x for the UCST-type polymers, suggesting that the anion binding affinity is enhanced by incorporating more SBMA units into the polymers.

As shown in Figs. 2(d) and 3(d), the anion specificities of PNIPAM and P($SBMA_{0.11}$-*co*-$NIPAM_{0.89}$) have a similar strength with those for PSBMA, P($SBMA_{0.90}$-*co*-$NIPAM_{0.10}$), and P($SBMA_{0.77}$-*co*-$NIPAM_{0.23}$), but the anion specificities of the UCST-type polymers are observed at a salt concentration 500 times lower than those of the LCST-type polymers. If we have a close look at the Table 1, we can find that the K_a' for PSBMA is much larger than K_a for PNIPAM for the same kind of anion. As the interactions of the UCST- and LCST-type polymers with the anions are respectively dominated by the anion-SBMA and anion-NIPAM interactions, the K_a' values for all the UCST-type polymers are much larger than those of K_a values for PNIPAM and P($SBMA_{0.11}$-*co*-$NIPAM_{0.89}$) for the same kind of anion. Thus, in comparison with the LCST-type polymers, a similar strength of specific anion effects observed for the UCST-type polymers at a much lower salt concentration is attributed to the higher anion binding affinities for the latter polymers than the former ones.

In conclusion, a similar strength of anion specificities can be observed at very different salt concentrations for the LCST- and UCST-type polymers. The anion binding to the LCST-type polymers is dominated by the anion-NIPAM interaction, whereas the anion binding to the UCST-type polymers is dominated by the anion-SBMA interaction. As the latter interaction is much stronger than the former interaction, a similar strength of anion specificities can be observed at a much lower salt concentration for the UCST-type polymers, compared with that for the LCST-type polymers. Thus, our work demonstrates that the anion binding affinity determines the strength of specific anion effects on the thermosensitive polymers.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://doi.org/10.1007/s10118-021-2633-9.

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