

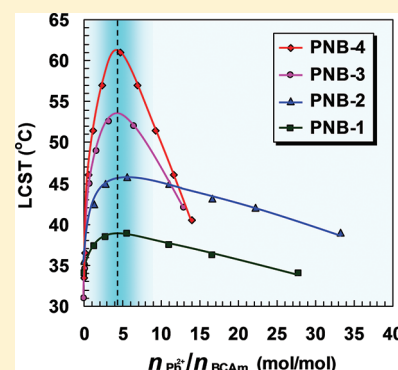
# Comprehensive Effects of Metal Ions on Responsive Characteristics of P(NIPAM-co-B18C6Am)

Bao Zhang, Xiao-Jie Ju,\* Rui Xie, Zhuang Liu, Shuo-Wei Pi, and Liang-Yin Chu\*

School of Chemical Engineering, Sichuan University, Chengdu, Sichuan 610065, P. R. China

**S** Supporting Information

**ABSTRACT:** Comprehensive investigations of the effects of species and concentrations of metal ions on the ion-responsive behaviors of poly(*N*-isopropylacrylamide-co-benzo-18-crown-6-acrylamide) (P(NIPAM-co-B18C6Am)) are systematically carried out with a series of P(NIPAM-co-B18C6Am) linear copolymers and cross-linked hydrogels containing different crown ether contents. The results show that when the B18C6Am receptors form stable B18C6Am/ $M^{n+}$  host-guest complexes with special ions ( $M^{n+}$ ), such as  $K^+$ ,  $Sr^{2+}$ ,  $Ba^{2+}$ ,  $Hg^{2+}$ , and  $Pb^{2+}$ , the LCST of P(NIPAM-co-B18C6Am) increases due to the repulsion among charged B18C6Am/ $M^{n+}$  complex groups and the enhancement of hydrophilicity, and the order of the shift degree of LCST of P(NIPAM-co-B18C6Am) is  $Pb^{2+} > Ba^{2+} > Sr^{2+} > Hg^{2+} > K^+$ . With increasing the content of pendent crown ether groups, the LCST shift degree increases first and then stays unchanged when the B18C6Am content is higher than 20 mol %. Remarkably, it is found for the first time that there exists an optimal ion-responsive concentration for the P(NIPAM-co-B18C6Am) linear copolymer and cross-linked hydrogel in response to special metal ions, at which concentration the P(NIPAM-co-B18C6Am) exhibits the most significant ion-responsivity either in the form of linear copolymers or cross-linked hydrogels. With an increase of the content of crown ether groups, the value of corresponding optimal ion-responsive concentration increases. Interestingly, there exists an optimal molar ratio of metal ion to crown ether for the P(NIPAM-co-B18C6Am) copolymer in response to  $Pb^{2+}$ , which is around 4.5 (mol/mol). If the ion concentration is too high, the ion-responsive behaviors of P(NIPAM-co-B18C6Am) may even become surprisingly unobvious. Therefore, to achieve satisfactory ion-responsive characteristics of P(NIPAM-co-B18C6Am)-based materials, both the operation temperature and the ion concentration should be optimized for the specific ion species. The results in this study provide valuable guidance for designing and applying P(NIPAM-co-B18C6Am)-based ion-responsive materials in various applications.



## INTRODUCTION

Metal ions play important roles in life activities. Many metal ions, such as  $K^+$ ,  $Na^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$ , and  $Cr^{3+}$ , are essential components of metabolism and cofactors for a variety of biological processes, including oxidative phosphorylation, gene regulation, and free-radical homeostasis.<sup>1–5</sup> Deficiency states of these metal ions with clinical abnormalities have been identified, whereas these essential elements can also cause toxic effects at high doses.<sup>6</sup> Moreover, heavy metal ions, one of the most serious environmental pollutants, are becoming a severe public health problem.<sup>7</sup> Some heavy metal ions, such as  $Pb^{2+}$ ,  $Ba^{2+}$ ,  $Hg^{2+}$ , and  $Cd^{2+}$ , have serious toxicity to the living organisms even in low concentrations.<sup>8–14</sup> So, the detection of ion species and ion concentration would be crucial to our life. Until now, many analytical methods have been developed for the detection of metal ions, for example, inductively coupled plasma optical emission spectrometry analysis,<sup>15,16</sup> flame atomic absorption spectrometry,<sup>17,18</sup> electrothermal atomic absorption spectrophotometry,<sup>19,20</sup> fluorescent chemosensors,<sup>21,22</sup> and so on. However, these detection methods are usually sophisticated and need professional equipment. Thus, researchers are still

seeking simpler and easier analytical methods for the detection of metal ions.

Recently, a series of ion-recognizable smart materials composed of the poly(*N*-isopropylacrylamide-co-benzo-18-crown-6-acrylamide) (P(NIPAM-co-B18C6Am)) copolymer, which exhibit both thermoresponsive and ion-recognition properties, have been developed, such as linear-grafted gating membranes,<sup>23–30</sup> hydrogels,<sup>31,32</sup> microspheres,<sup>33</sup> and microcapsules.<sup>34,35</sup> PNIPAM, a popular thermosensitive polymer, exhibits a lower critical solution temperature (LCST) due to the presence of both hydrophilic amide groups and hydrophobic isopropyl groups in its side chains.<sup>36</sup> B18C6Am, with a crown ether cavity, has remarkable properties of selectively recognizing specific metal ions and forming stable “host-guest” complexes.<sup>37,38</sup> So, in the P(NIPAM-co-B18C6Am) copolymer, the two units of monomers have different roles, i.e., NIPAM unit acts as an actuator and B18C6Am unit is used as an ion-signal sensing receptor. When the crown ether receptors

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capture specific metal ions ( $M^{n+}$ ), the LCST of the copolymer could shift to a higher temperature due to the repulsion among charged B18C6Am/ $M^{n+}$  complex groups and the enhancement of hydrophilicity of the copolymer. In other words, the P(NIPAM-*co*-B18C6Am) copolymer could change from shrunk state to swollen state at a constant temperature between the two LCSTs in response to specific metal ions.<sup>39,40</sup> Although a lot of investigations on the ion-responsive characteristics of P(NIPAM-*co*-B18C6Am)-based materials have been reported previously,<sup>39,40</sup> the species and concentration of the investigated metal ions are still limited, especially for the heavy metal ions.

The objective of this study is to systematically investigate the comprehensive effects of species and concentrations of metal ions upon the ion-responsive characteristics of both P(NIPAM-*co*-B18C6Am) linear copolymers and P(NIPAM-*co*-B18C6Am) cross-linked hydrogels with different crown ether contents. Besides the well-known alkali metal ions  $Li^+$ ,  $Na^+$ ,  $K^+$ , and  $Cs^+$ , and the alkaline earth metal ions  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$ , and  $Ba^{2+}$ , heavy metal ions with serious toxicity to living organisms including  $Pb^{2+}$ ,  $Hg^{2+}$ ,  $Cr^{3+}$ , and  $Cd^{2+}$  are selected in this study to test the ion-responsive behaviors of the P(NIPAM-*co*-B18C6Am) copolymer. From the systematic results, some definitely new phenomena are found for the first time; e.g., an optimal ion-responsive concentration is found for the P(NIPAM-*co*-B18C6Am) linear copolymer and cross-linked hydrogel in response to special metal ions. That is, if the ion concentration increases too much, the ion-responsive property of P(NIPAM-*co*-B18C6Am) will be unexpectedly hindered to some extent. For the case of  $Pb^{2+}$ , the ion-responsive behavior of P(NIPAM-*co*-B18C6Am) could even become surprisingly unobvious when the ion concentration is too high. Interestingly, there exists an optimal molar ratio of metal ion to crown ether for the P(NIPAM-*co*-B18C6Am) copolymer in response to  $Pb^{2+}$ , which is around 4.5 (mol/mol). Therefore, the results in this study are valuable for designing and applying P(NIPAM-*co*-B18C6Am)-based ion-responsive materials in various applications.

## MATERIALS AND METHODS

**Materials.** NIPAM (kindly provided by Kohjin Co., Ltd., Japan) was purified by recrystallization with a hexane/acetone mixture (50/50, v/v). B18C6Am was synthesized according to reported procedures.<sup>41,42</sup> *N,N'*-Methylene-bis-acrylamide (MBA, Chengdu Kelong Chemicals, China) was used as a cross-linker. 2,2'-Azobis(isobutyronitrile) (AIBN, Shanghai Reagent Fourth Factory, China) was recrystallized with ethanol and used as initiator for synthesis of linear copolymers. 2,2'-Azobis(2-amidinopropane dihydrochloride) (V50, Qingdao Runxing Photoelectric Material Co., Ltd., China) was used as initiator for synthesis of cross-linked hydrogels. All other chemicals were of analytical grade and were used as received. Deionized water (18.2 M $\Omega$ , 25 °C) from a Milli-Q Plus water purification system (Millipore Co., USA) was used throughout the experiments.

**Preparation and Composition Characterization of P(NIPAM-*co*-B18C6Am) Linear Copolymers.** P(NIPAM-*co*-B18C6Am) linear copolymers were prepared by thermally initiated free-radical copolymerization of NIPAM and B18C6Am monomers using AIBN as initiator and tetrahydrofuran (THF) as solvent. The concentration of total monomer was 0.3 mol L<sup>-1</sup>, and the molar ratio of AIBN in the total monomer was 1 mol %. Nitrogen gas was bubbled into

the solution for 20 min to remove dissolved oxygen in the system. The conical flask was sealed immediately and then immersed into a constant-temperature water bath at 60 °C. The polymerization was carried out at 60 °C for 12 h under nitrogen atmosphere. After the polymerization was completed, the copolymers were purified three times by reprecipitation with anhydrous ether from THF and then dried under vacuum 40 °C for 24 h. The theoretical molar ratios of B18C6Am in the total monomer were 0 mol %, 5 mol %, 7.5 mol %, 15 mol %, and 25 mol %, and the corresponding prepared linear polymers were labeled as PN, PNB-1, PNB-2, PNB-3, and PNB-4, respectively.

The composition characterizations of obtained copolymers were characterized by Fourier transform infrared spectrometry (FT-IR, IR Prestige-21, Shimadzu Co., Japan) and nuclear magnetic resonance spectrometry (<sup>1</sup>H NMR, Bruker-400, Bruker Co., Germany). The molecular weight of the copolymer was determined by gel permeation chromatography (GPC, Waters-2410, Waters Co., USA).

**Preparation and Composition Characterization of P(NIPAM-*co*-B18C6Am) Hydrogels.** Cross-linked P(NIPAM-*co*-B18C6Am) hydrogels were prepared by thermally initiated free-radical cross-linking copolymerization of NIPAM and B18C6Am monomers in water using V50 as initiator and MBA as cross-linker. The molar ratios of MBA and V50 to the total monomer were 2 mol % and 0.5 mol %, respectively. The concentration of NIPAM was 1.0 mol L<sup>-1</sup>, the molar ratios of B18C6Am to NIPAM were 0 mol %, 7.5 mol %, and 15 mol %, and the corresponding prepared hydrogels were labeled as PN, PNB-7.5%, and PNB-15%, respectively. The polymerization was carried out at 70 °C for 8 h under nitrogen atmosphere. After the gelation was completed, the prepared hydrogels were purified by immersing the hydrogels in an excess of deionized water and replacing the water every 12 h to remove residual unreacted components. The washing process continued for 7 days. The purified P(NIPAM-*co*-B18C6Am) hydrogels were cut into thin discs (the thickness was about 2 mm) and then equilibrated in deionized water or salt solutions.

The obtained hydrogels were characterized by an FT-IR spectrometer (IR Prestige-21, Shimadzu Co., Japan).

**Comprehensive Investigation on the Effects of Metal Ions on the Responsive Characteristics of P(NIPAM-*co*-B18C6Am) Linear Copolymers.** The ion-recognition and thermoresponsive behaviors of P(NIPAM-*co*-B18C6Am) linear copolymers with different B18C6Am contents were comprehensively studied by evaluating their LCST values in different metal ion solutions with different concentrations. To minimize salting-out effects,<sup>43–45</sup> nitrate was chosen as the model salt. The concentrations of metal ions were in the range 0–200 mmol L<sup>-1</sup> (mM), and the concentrations of linear copolymers in metal ion solutions were all fixed at 0.5 wt %. The thermoresponsive behaviors were evaluated by measuring the transmittance of the copolymer solutions at 500 nm and at various desired ambient temperatures using an ultraviolet spectrophotometer (UV-1700, Shimadzu Co., Japan). The temperature of the solutions was controlled with a thermoregulator (TCC-240A, Shimadzu Co., Japan). The temperature at which the transmittance decreased to half of the initial value was taken as the LCST.

**Comprehensive Investigation on Effects of  $Pb^{2+}$  Ion on the Responsive Characteristics of P(NIPAM-*co*-B18C6Am) Hydrogels.** The  $Pb^{2+}$ -responsive behaviors of P(NIPAM-*co*-B18C6Am) hydrogels with different crown ether

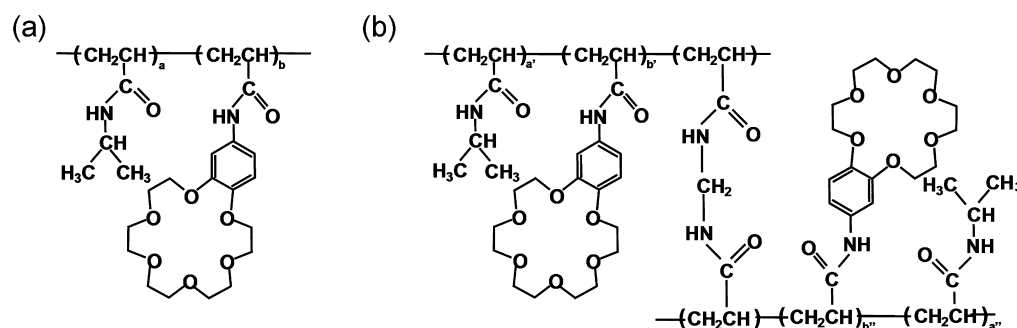


Figure 1. Chemical structures of the P(NIPAM-co-B18C6Am) linear copolymer (a) and cross-linked hydrogel (b).

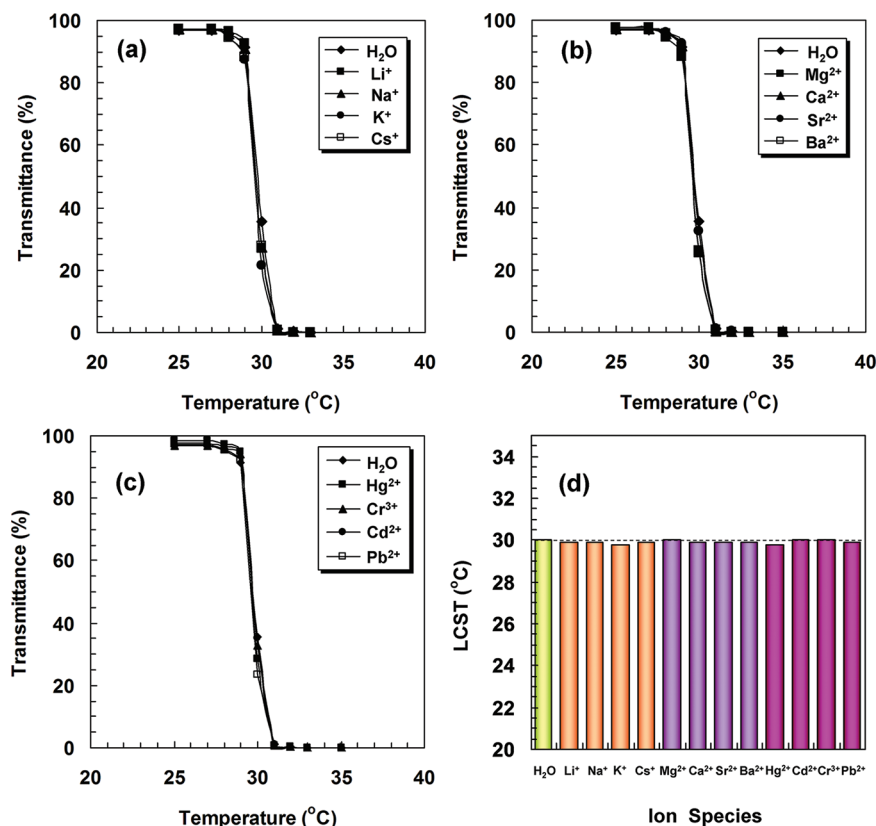


Figure 2. Temperature-dependent transmittance change of PNIPAM polymer solution containing different metal ions (a–c), and the effect of metal ions on the LCST of PNIPAM polymer (d). The concentrations of metal ions were all controlled to 20 mM.

contents were studied by evaluating the volume-phase transitions in Pb<sup>2+</sup> solutions at various ambient temperatures in the range from 20 to 55 °C. The Pb<sup>2+</sup> concentrations were all fixed at 20 mM.

## RESULTS AND DISCUSSION

**Composition Characterizations of P(NIPAM-co-B18C6Am) Linear Copolymers and Cross-Linked Hydrogels.** The chemical structure of the P(NIPAM-co-B18C6Am) linear copolymer is schematically illustrated in Figure 1a. The FT-IR spectra of B18C6Am monomer, NIPAM monomer, and P(NIPAM-co-B18C6Am) linear copolymers with different B18C6Am contents are illustrated in Figure S1 in the Supporting Information, which confirms the successful synthesis of P(NIPAM-co-B18C6Am) linear copolymers.

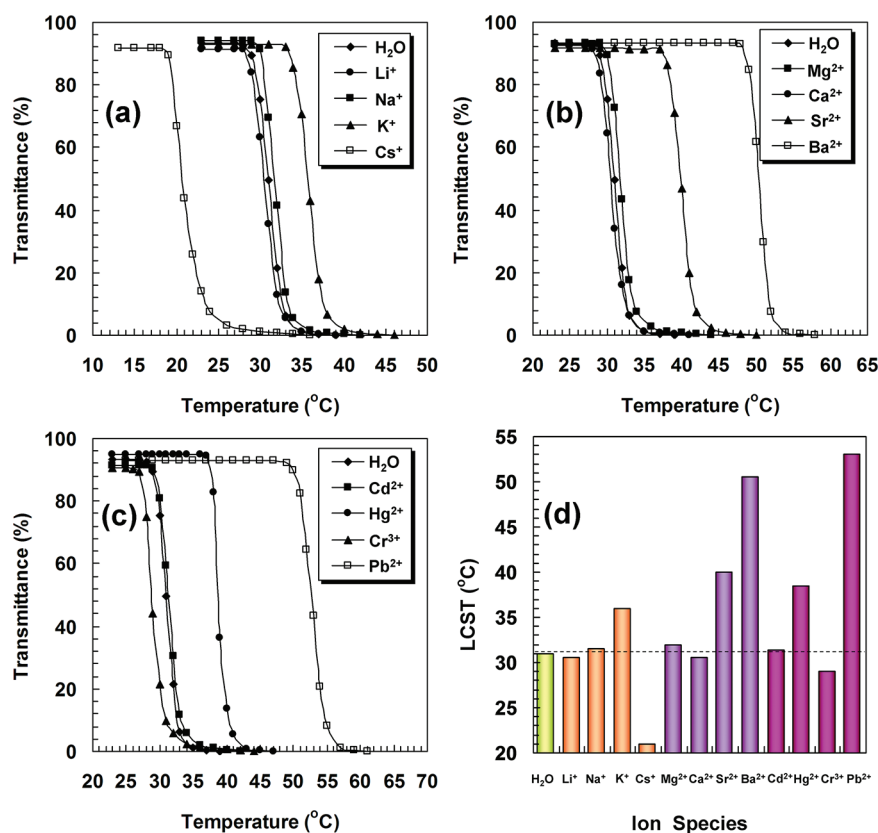
The actual content of the B18C6Am units in the copolymer ( $C_n$ ) is accounted according to the results of <sup>1</sup>H NMR spectra illustrated in Figure S2 in the Supporting Information. The  $C_n$

values of PNB-1, PNB-2, PNB-3, and PNB-4 copolymers are 5.9 mol %, 10.3 mol %, 21.0 mol %, and 35.6 mol %, respectively.

The weight average molecular weights of linear copolymers ( $\bar{M}_w$ ) are in the range 2900–4900 determined by GPC data (Figure S3 in the Supporting Information).

The chemical structure of the P(NIPAM-co-B18C6Am) cross-linked hydrogel is illustrated in Figure 1b. The FT-IR spectra of P(NIPAM-co-B18C6Am) cross-linked hydrogels are shown in Figure S4 in the Supporting Information, which confirms the successful fabrication of P(NIPAM-co-B18C6Am) hydrogels.

**Effects of Metal Ions on the Responsive Characteristics of P(NIPAM-co-B18C6Am) Linear Copolymers.** The temperature-dependent transmittance changes of PN and PNB-3 linear polymer solutions containing different metal ions are shown in Figures 2a–c and 3a–c, respectively. The concentrations of metal ions are all controlled to 20 mM. It



**Figure 3.** Temperature-dependent transmittance change of PNB-3 copolymer solution containing different metal ions (a–c), and the effect of metal ions on the LCST of PNB-3 copolymer (d). The concentrations of metal ions were all controlled to 20 mM.

can be seen that all polymer solutions undergo a rapid transmittance change when the ambient temperature varies across a corresponding temperature region. The temperature at which the transmittance decreases to half of the initial value is taken as the LCST. The influences of metal ions on the LCST values of PN and PNB-3 linear polymers are shown in Figures 2d and 3d, respectively.

As seen in Figure 2, the temperature-dependent transmittance changes of PN linear polymer in various metal ion solutions are almost the same as that in deionized water. That is to say, PNIPAM linear polymer without B18C6Am receptors has no ion-responsive actions, so the LCST of PNIPAM linear polymer remains almost constant in deionized water and all nitrate solutions.

Similarly, the transmittance change curve of PNB-3 linear copolymer in Li<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cd<sup>2+</sup>, or Cr<sup>3+</sup> solution has no obvious difference compared with that in deionized water. In contrast, the LCST of PNB-3 linear copolymer in K<sup>+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>, Hg<sup>2+</sup>, or Pb<sup>2+</sup> solution shifts to a higher temperature and turns to a lower temperature in Cs<sup>+</sup> solution. The order of the extent of the positive LCST shift from large to small is Pb<sup>2+</sup> > Ba<sup>2+</sup> > Sr<sup>2+</sup> > Hg<sup>2+</sup> > K<sup>+</sup>. The LCST increases about 5 °C in K<sup>+</sup> solution (LCST ≈ 36 °C), 7 °C in Hg<sup>2+</sup> solution (LCST ≈ 38 °C), 9 °C in Sr<sup>2+</sup> solution (LCST ≈ 40 °C), 19 °C in Ba<sup>2+</sup> solution (LCST ≈ 50 °C), and 22 °C in Pb<sup>2+</sup> (LCST ≈ 53 °C), while it decreases about 10 °C in Cs<sup>+</sup> solution (LCST ≈ 21 °C). Such distinct changes of the phase-transition temperature result from the formation of crown-ether/metal-ion complexes.

The formation and stability of the crown-ether/metal-ion complexes is dominated by the size/shape fitting or matching between the host and guest molecules. The B18C6Am

receptors in the linear copolymer could selectively capture specific metal ions whose size fits the cavity size of crown ether well and bound with the cavity tightly and effectively, and form stable host–guest complexes.<sup>25</sup> The sizes of K<sup>+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>, Hg<sup>2+</sup>, and Pb<sup>2+</sup> could match the cavity of 18-crown-ether and form a stable 1:1 crown-ether/metal-ion complex. The positive LCST shift of the P(NIPAM-*co*-B18C6Am) copolymer results from the repulsion among charged complex groups and the enhancement of hydrophilicity of the copolymer when the specific metal ions are captured by the cavities of crown ethers. The order of the complexes' stability constant (log *K*) of benzo-18-crown-6 with metal ions in water is Pb<sup>2+</sup> > Ba<sup>2+</sup> > Sr<sup>2+</sup> > K<sup>+</sup>, as listed in Table 1. This order shows a good correlation with the order of the positive LCST shift. On the other hand, although Cs<sup>+</sup> is too large to fit into the crown ether cavity of B18C6Am, it could form a stable 2:1 complex with the crown ethers.<sup>42,46</sup> Two crown ether cavities from adjacent polymer chains form a 2:1 “sandwich” complex with one Cs<sup>+</sup>; such complexation could cause PNB-3 linear copolymer chains to contract.<sup>42,46</sup> Therefore, the LCST of the P(NIPAM-*co*-B18C6Am) copolymer shifts to a lower temperature when Cs<sup>+</sup> ions are added in the solution.

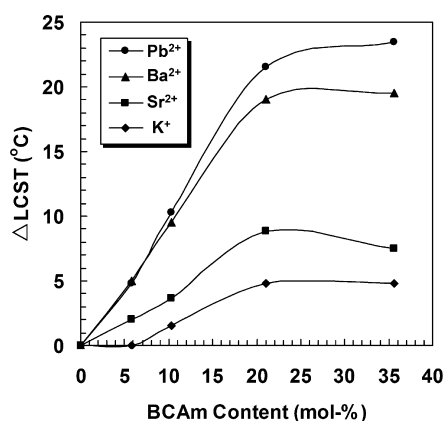
The value of ΔLCST, which is the difference of the LCST values of the P(NIPAM-*co*-B18C6Am) linear copolymer in the absence and presence of metal ions, depends on the amount of pendent crown ether groups, as shown in Figure 4. When the content of crown ether groups in the linear copolymer is low, the increase of LCST is low. With increasing the content of pendent crown ether groups, the ΔLCST increases simply first and stays unchanged when the crown ether content is more than 20 mol %. It can also be found that the order of the extent



**Table 1.** Ionic Radii and Formation Constants ( $\log K$ ) of Complexes of Benzo-18-crown-6 with Metal Ions in Water at 25 °C

metal ion	ionic radius <sup>a</sup> (Å)	$\log K^{b-d}$ (mol <sup>-1</sup> dm <sup>3</sup> )
Li <sup>+</sup>	0.76	
Na <sup>+</sup>	1.02	1.38
K <sup>+</sup>	1.38	1.74
Cs <sup>+</sup>	1.67	0.88
Mg <sup>2+</sup>	0.72	
Ca <sup>2+</sup>	1	0.5
Sr <sup>2+</sup>	1.18	2.41
Ba <sup>2+</sup>	1.35	2.90
Pb <sup>2+</sup>	1.19	3.19
Hg <sup>2+</sup>	1.19	
Cr <sup>3+</sup>		
Cd <sup>2+</sup>	0.95	

<sup>a</sup>Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr., Sect. B* **1969**, *25*, 925–946. <sup>b</sup>Takeda, Y.; Kohno, R.; Kudo, Y.; Fukada, N. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 999–1003. <sup>c</sup>Izatt, R. M.; Pawlak, K.; Bradshaw, J. S. *Chem. Rev.* **1991**, *91*, 1721–2085. <sup>d</sup> $K = [ML^{n+}]/[M^{n+}][L]$ , in which  $M^{n+}$  and L are metal ion and benzo-18-crown-6, respectively.

**Figure 4.** Dependence of  $\Delta\text{LCST}$ , which is the difference of LCST values of P(NIPAM-*co*-B18C6Am) linear copolymers in the absence and presence of metal ions, on the content of crown ether groups in P(NIPAM-*co*-B18C6Am) linear copolymers. The concentrations of metal ions were all controlled to 20 mM.

of the positive LCST shift for the P(NIPAM-*co*-B18C6Am) linear copolymer is  $\text{Pb}^{2+} > \text{Ba}^{2+} > \text{Sr}^{2+} > \text{K}^{+}$ . These results also support the mechanism of the ion-responsive LCST shift via the pendent crown ether groups binding with special metal ions.

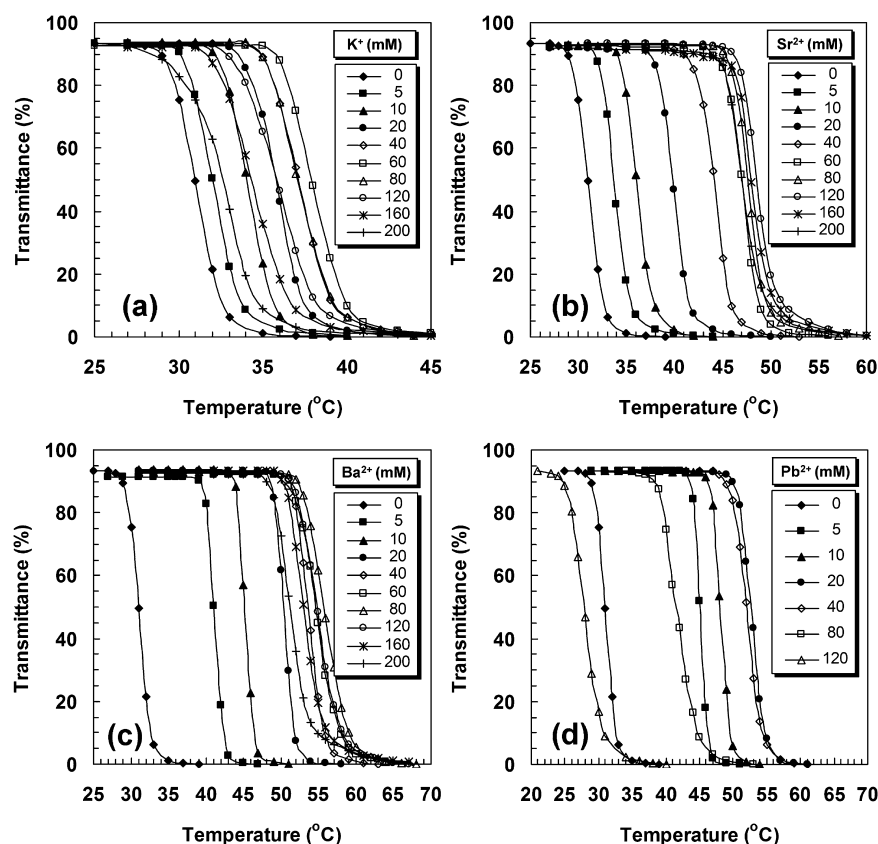
Figure 5 shows the temperature-dependent transmittance changes of PNB-3 linear copolymer in various ion solutions with different ion concentrations. The temperature-dependent transmittance change curves of PN, PNB-1, PNB-2, and PNB-4 polymers are, respectively, shown in Figures S5–S8 in the Supporting Information. The corresponding influences of metal ion species and concentrations on the LCST of PNB-1, PNB-2, PNB-3, and PNB-4 linear copolymers are shown in Figure 6. As a comparison, the corresponding influences of metal ion species and concentrations on the LCST of PNIPAM linear polymer are shown in Figure 7. With increasing the ion concentration, the LCST of all P(NIPAM-*co*-B18C6Am) linear copolymers increases first and then decreases surprisingly. For each ion species, there exists an optimal ion-responsive concentration for the P(NIPAM-*co*-B18C6Am) copolymer, at which point the

copolymer has the best ion-responsive property to the corresponding special metal ion. On the contrary, the LCST of PNIPAM linear polymer only decreases very slightly with increasing the ion concentration due to the slight salting-out effect.<sup>43–45</sup> The added salts would competitively bind with water molecules around PNIPAM-based polymer chains and cause the salting-out effect, which could make the LCST decrease to some extent. These different phenomena are mainly caused by the charge screening effects on the crown ether/metal-ion complexes. As mentioned above, because of the formation of 1:1 crown-ether/metal-ion complex, the P-(NIPAM-*co*-B18C6Am) linear copolymer has a higher LCST in specific ion solutions than that in deionized water. When the salt concentration is not so high, the LCST of P(NIPAM-*co*-B18C6Am) linear copolymer increases with increasing the metal ion concentration due to the increase of crown-ether/metal-ion complexes. However, when excess salts are added into the copolymer solution, excess ions could screen charges between crown-ether/metal-ion complexes, which would decrease electrostatic repulsion among the charged crown-ether/metal-ion complexes and finally result in a decrease of LCST in ion solutions with very high salt concentration.<sup>47</sup>

Figure 8 shows the influences of the content of crown ether groups on the optimal ion-responsive concentration for P(NIPAM-*co*-B18C6Am) linear copolymers. For each specific ion species, with the pendent crown ether groups increasing, the optimal ion-responsive concentration increases. The value of optimal ion-responsive concentration for the P(NIPAM-*co*-B18C6Am) linear copolymer with certain crown ether content is obviously different in aqueous solutions containing various metal ions due to the different effects of various ions on the phase transition of the P(NIPAM-*co*-B18C6Am) linear copolymer. The order of optimal ion-responsive concentration for P(NIPAM-*co*-B18C6Am) from large to small is  $\text{Sr}^{2+} > \text{Ba}^{2+} > \text{K}^{+} > \text{Pb}^{2+}$ , which indicates that  $\text{Pb}^{2+}$  is the most sensitive metal ion for P(NIPAM-*co*-B18C6Am) to respond to among the metal ions tested in this study.

Because  $\text{Pb}^{2+}$  is the most sensitive metal ion for P(NIPAM-*co*-B18C6Am) to respond to among the metal ions (Figures 6 and 8), the effect of the molar ratio of  $\text{Pb}^{2+}$  to crown ether on the LCST of the P(NIPAM-*co*-B18C6Am) linear copolymer is studied, and the results are shown in Figure 9. Interestingly, there exists an optimal molar ratio of metal ion to crown ether for the P(NIPAM-*co*-B18C6Am) copolymer in response to  $\text{Pb}^{2+}$ , which is all around 4.5 (mol/mol). That is to say, the optimal molar ratio is almost independent of the content of crown ether groups in the P(NIPAM-*co*-B18C6Am) copolymer.

**Effects of  $\text{Pb}^{2+}$  on the Responsive Characteristics of P(NIPAM-*co*-B18C6Am) Hydrogels.** The  $\text{Pb}^{2+}$ -recognition and thermoresponsive characteristics of P(NIPAM-*co*-B18C6Am) cross-linked hydrogels are studied by detecting the volume change of the hydrogel in deionized water and in  $\text{Pb}^{2+}$  aqueous solutions with different ion concentrations. Temperature-dependent volume change of cross-linked hydrogels with different B18C6Am contents in deionized water and in 20 mM  $\text{Pb}^{2+}$  aqueous solution are shown in Figure 10a–c, where  $V_T$  represents the volume of the hydrogel at certain test temperature  $T$  and  $V_{21}$  represents that at 21 °C. All hydrogels undergo volume shrinkage due to the phase transition of the polymer structure when the ambient temperatures change across a corresponding temperature region. The temperature, at which the value of  $V_T/V_{21}$  decreases to half of the total change



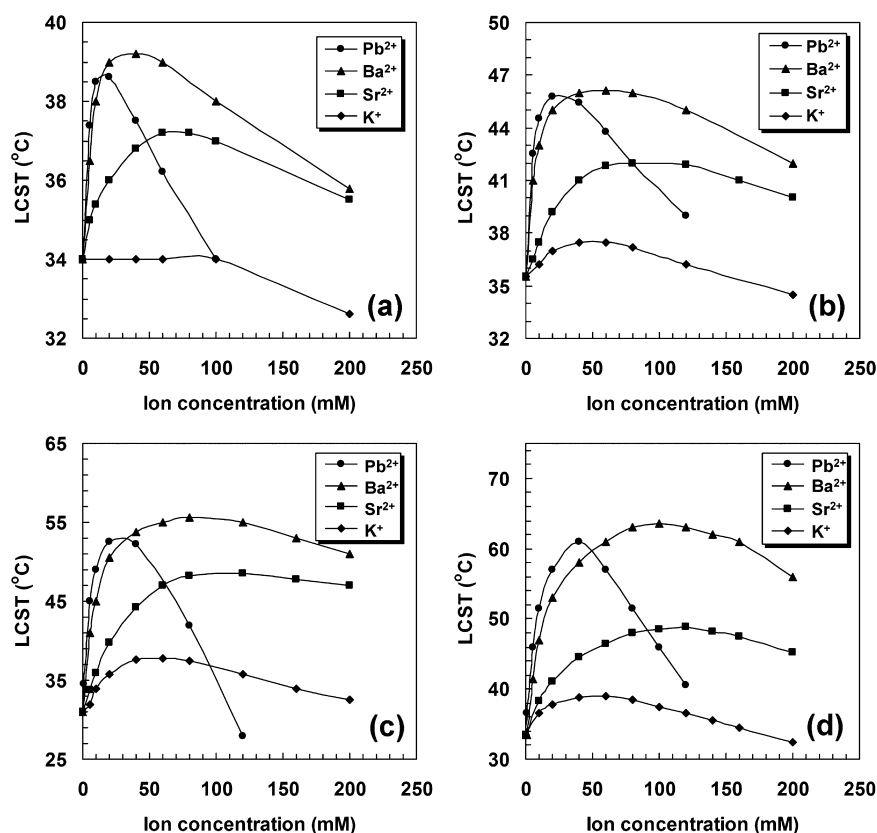
**Figure 5.** Temperature-dependent transmittance change of PNB-3 copolymer in different nitrate solutions with different ion concentrations. The molar ratio of crown ether unit in the copolymer is 21.0%.

value, is taken as the LCST of the cross-linked hydrogel. The comparison of the LCST values of hydrogels with different B18C6Am contents in deionized water and in  $\text{Pb}^{2+}$  aqueous solution is shown in Figure 10d. It can be seen that the volume change curves of cross-linked PNIPAM hydrogel in deionized water and in  $\text{Pb}^{2+}$  solution are almost coincident, and the LCST of PNIPAM hydrogel in  $\text{Pb}^{2+}$  solution does not have any significant change compared with that in deionized water. That is to say,  $\text{Pb}^{2+}$  scarcely affected the phase transition behavior of PNIPAM hydrogel. However, the LCST of the P(NIPAM-co-B18C6Am) cross-linked hydrogel in  $\text{Pb}^{2+}$  solution significantly shifts to a higher temperature compared with that in deionized water.

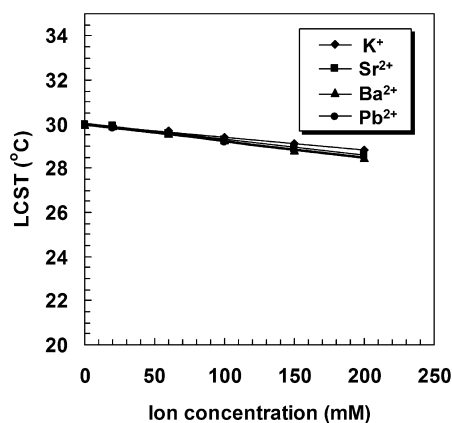
In 20 mM  $\text{Pb}^{2+}$  solution, the LCST of PNB-7.5% cross-linked hydrogel increases about 5 °C, and the LCST of PNB-15% cross-linked hydrogel shifts to 37.5 °C. These results are similar to the ion-recognition characteristics of the P(NIPAM-co-B18C6Am) linear copolymer, and also result from the formation of 1:1 B18C6Am/ $\text{Pb}^{2+}$  complexes.<sup>32</sup> The repulsion among the charged B18C6Am/ $\text{Pb}^{2+}$  complex groups and osmotic pressure within the hydrogel counteract the shrinkage of the hydrogel network with the increase of temperature, thereby resulting in the LCST changing to a higher temperature. Also, the degree of the LCST shift increases with an increase in the crown ether content.

Figure 11 shows the effect of  $\text{Pb}^{2+}$  on the swelling/shrinking behaviors of cross-linked PNIPAM and P(NIPAM-co-B18C6Am) hydrogels, in which  $V_{\text{Pb}^{2+}}$  and  $V_{\text{H}_2\text{O}}$  are the volume of hydrogels in  $\text{Pb}^{2+}$  solution and that in deionized water, respectively. For P(NIPAM-co-B18C6Am) hydrogels, the

volume ratio value ( $V_{\text{Pb}^{2+}}/V_{\text{H}_2\text{O}}$ ) increases at first and then decreases with increasing the temperature. At a certain corresponding temperature ( $T$  °C), the value of  $V_{\text{Pb}^{2+}}/V_{\text{H}_2\text{O}}$  for both P(NIPAM-co-B18C6Am) hydrogels reaches a corresponding maximum value. Below  $T$  °C, the volume of the P(NIPAM-co-B18C6Am) hydrogel in deionized water decreases with the temperature increasing, whereas it keeps swelling in  $\text{Pb}^{2+}$  solution due to the repulsion among charged B18C6Am/ $\text{Pb}^{2+}$  complex groups and osmotic pressure within the hydrogel. When temperature increases above  $T$  °C, the value of  $V_{\text{Pb}^{2+}}/V_{\text{H}_2\text{O}}$  decreases as the P(NIPAM-co-B18C6Am) hydrogel in  $\text{Pb}^{2+}$  solution begins to shrink. The results indicate that the optimal operating temperature for  $\text{Pb}^{2+}$ -recognition application is around  $T$  °C, at which it has the most obvious isothermal volume change. The value of optimal operating temperature for  $\text{Pb}^{2+}$ -recognition of the P(NIPAM-co-B18C6Am) hydrogel with different crown ether content is different due to the different amounts of B18C6Am/ $\text{Pb}^{2+}$  complex groups. For PNIPAM hydrogel without B18C6Am receptors, the value of  $V_{\text{Pb}^{2+}}/V_{\text{H}_2\text{O}}$  decreases slightly around 30 °C caused by the salting-out effect of nitrate on PNIPAM hydrogel.<sup>43–45</sup> The effect of  $\text{Pb}^{2+}$  concentration on the swelling behavior of cross-linked PNIPAM hydrogel and P(NIPAM-co-B18C6Am) hydrogels with different B18C6Am at 35 °C is shown in Figure 12. With increasing the  $\text{Pb}^{2+}$  concentration, the  $V_{\text{Pb}^{2+}}/V_{\text{H}_2\text{O}}$  value of cross-linked P(NIPAM-co-B18C6Am) hydrogel also increases at first and then decreases. That is, there also exists an optimal  $\text{Pb}^{2+}$ -responsive concentration for the P(NIPAM-co-B18C6Am) hydrogel, at which the hydrogel has



**Figure 6.** Effects of the ion concentration on the LCST of P(NIPAM-*co*-B18C6Am) copolymer in different nitrate solutions. The copolymers are PNB-1 (a), PNB-2 (b), PNB-3 (c), and PNB-4 (d), respectively.

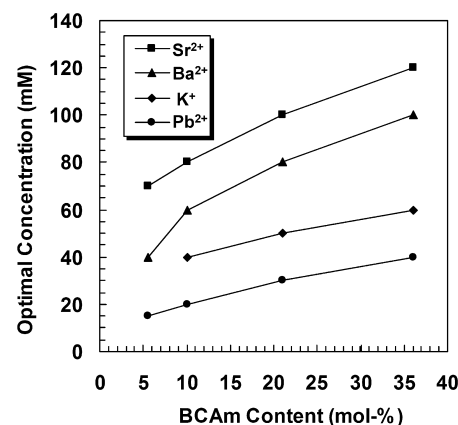


**Figure 7.** Effects of the ion concentration on the LCST of PNIPAM polymer in different nitrate solutions.

the largest  $\text{Pb}^{2+}$ -responsivity. The optimal  $\text{Pb}^{2+}$ -responsive concentration for PNB-15% hydrogel with larger B18C6Am content is higher than that of PNB-7.5% hydrogel, which is similar to the ion-recognition behaviors of the linear copolymer.

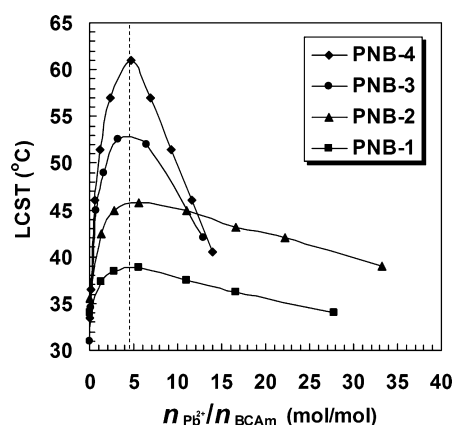
## CONCLUSIONS

Comprehensive effects of species and concentrations of metal ions upon the ion-responsive characteristics of both P(NIPAM-*co*-B18C6Am) linear copolymers and cross-linked hydrogels with different crown ether contents have been systematically investigated in this study. Alkali metal ions  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Cs}^+$ , alkaline earth metal ions  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$ , and heavy metal ions with serious toxicity to living organisms



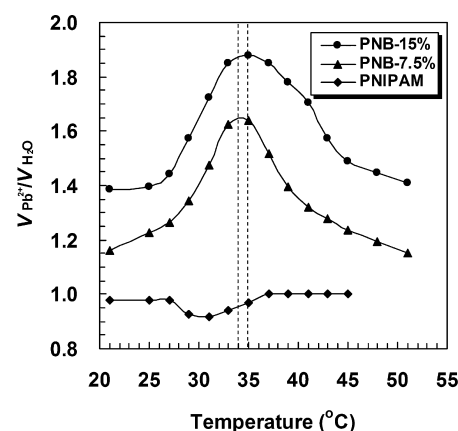
**Figure 8.** Dependence of optimal ion-responsive concentration for P(NIPAM-*co*-B18C6Am) linear copolymer on the content of crown ether groups in copolymers.

including  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Cd}^{2+}$  are selected to test the ion-responsive behaviors of P(NIPAM-*co*-B18C6Am) copolymers. The results show that when the B18C6Am receptors form stable B18C6Am/ $\text{M}^{n+}$  host-guest complexes with special ions ( $\text{M}^{n+}$ ), such as  $\text{K}^+$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Hg}^{2+}$ , and  $\text{Pb}^{2+}$ , the LCST of P(NIPAM-*co*-B18C6Am) increases due to the repulsion among charged B18C6Am/ $\text{M}^{n+}$  complex groups and the enhancement of hydrophilicity, and the order of the shift degree of LCST of P(NIPAM-*co*-B18C6Am) is  $\text{Pb}^{2+} > \text{Ba}^{2+} > \text{Sr}^{2+} > \text{Hg}^{2+} > \text{K}^+$ . With increasing the content of pendent crown ether groups, the LCST shift degree increases first and then stays unchanged when the B18C6Am content is higher than 20 mol %. The



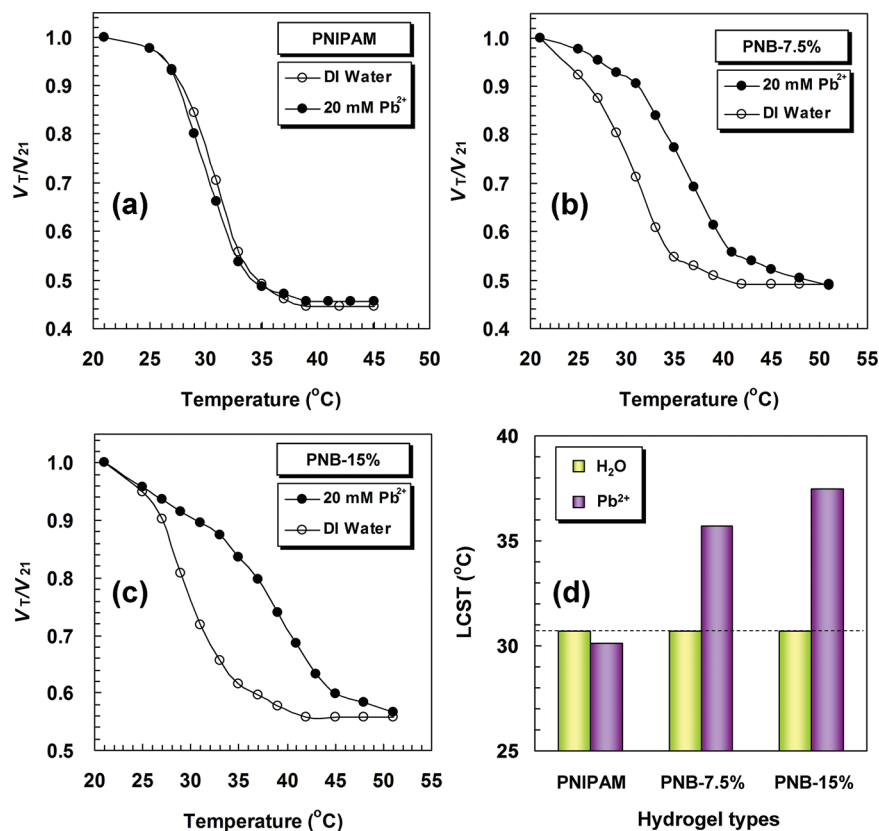
**Figure 9.** Dependence of the LCST values of P(NIPAM-*co*-B18C6Am) linear copolymers on the molar ratio of  $\text{Pb}^{2+}$  to crown ether groups in the copolymer.

experimental results remarkably show some definitely new phenomena for the first time. For example, an optimal ion-responsive concentration is found for the P(NIPAM-*co*-B18C6Am) linear copolymer and cross-linked hydrogel in response to special metal ions. If the ion concentration increases too much, the ion-responsive property of P(NIPAM-*co*-B18C6Am) will be unexpectedly hindered to some extent due to the charge screening effect. For the case of  $\text{Pb}^{2+}$ , the ion-responsive behavior of P(NIPAM-*co*-B18C6Am) could even become surprisingly unobvious when the ion concentration is too high. With an increase of the



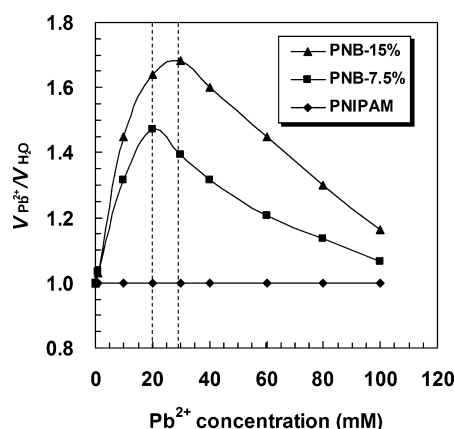
**Figure 11.** Temperature dependence of the volume ratio of cross-linked hydrogels with different contents of B18C6Am in 20 mM  $\text{Pb}^{2+}$  solution to that in deionized water.  $V_{\text{Pb}^{2+}}/V_{\text{H}_2\text{O}}$  is the volume ratio of the hydrogel disc in 20 mM  $\text{Pb}^{2+}$  solution to that in deionized water.

content of crown ether groups, the value of corresponding optimal ion-responsive concentration increases. Interestingly, there exists an optimal molar ratio of metal ion to crown ether for the P(NIPAM-*co*-B18C6Am) copolymer in response to  $\text{Pb}^{2+}$ , and this optimal molar ratio is almost independent of the content of crown ether groups in the P(NIPAM-*co*-B18C6Am) copolymer. Therefore, to achieve satisfactory ion-responsive characteristics of P(NIPAM-*co*-B18C6Am)-based materials, both the operation temperature and the ion concentration



**Figure 10.** Temperature dependence of volume changes of cross-linked hydrogels in deionized water and  $\text{Pb}^{2+}$  solution, where  $V_T/V_{21}$  is the ratio of volume of the hydrogel disc at temperature  $T$  to that at 21 °C (a–c). Comparison of the LCST values of cross-linked hydrogels with different contents of B18C6Am in deionized water and in  $\text{Pb}^{2+}$  solution with  $\text{Pb}^{2+}$  concentration being 20 mM (d).





**Figure 12.** Ion-concentration dependence of the volume ratio of cross-linked hydrogels with different contents of B18C6Am in  $Pb^{2+}$  solution to that in deionized water at 35 °C, where  $V_{Pb^{2+}}/V_{H_2O}$  is the volume ratio of the hydrogel disc in  $Pb^{2+}$  solution to that in deionized water.

should be optimized for the specific ion species. The results in this study provide valuable guidance for designing and applying P(NIPAM-co-B18C6Am)-based ion-responsive materials in various applications such as ion detectors, sensors, and actuators.

## ■ ASSOCIATED CONTENT

### Supporting Information

Results of FT-IR spectra of P(NIPAM-co-B18C6Am) linear copolymers and cross-linked hydrogels,  $^1H$  NMR spectra and GPC spectra of P(NIPAM-co-B18C6Am) linear copolymers with different molar ratios of the monomers, and the temperature-dependent transmittance changes of PNB-1, PNB-2, and PNB-4 copolymers in different nitrate solutions with different ion concentrations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [chuly@scu.edu.cn](mailto:chuly@scu.edu.cn) (L.-Y.C.); [juxiaojie@scu.edu.cn](mailto:juxiaojie@scu.edu.cn) (X.-J.J.). Phone and fax: +86 28 8546 0682.

### Notes

The authors declare no competing financial interest.

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