Reverse Response of an Ion-Recognition Polyampholyte to Specific Ion Signals at Different pHs

Nobuo Hara,[†] Hidenori Ohashi,[‡] Taichi Ito,[‡] and Takeo Yamaguchi*[,†,‡]

Department of Chemical System Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan, and Chemical Resources Laboratory, Tokyo Institute of Technology, Nagatsuta 4259, Midori-ku, Yokohama 226-8503, Japan

Received August 27, 2008; Revised Manuscript Received October 24, 2008

ABSTRACT: We synthesized and characterized for the first time an ampholytic ion-recognition linear copolymer of [3-(methacryloylamino)propyl]trimethylammonium chloride (MAPTAC), acrylic acid (AA), and benzo[18]crown-6-acrylamide (BCAm). In this copolymer, the MAPTAC unit has a positive charge. The AA unit has a negative charge that depends on the pH. The crown receptor of the BCAm unit forms a complex with specific ions such as Ba^{2+} because of the high complex formation constant which behaved like a fixed positive charge. Thus, the copolymers behaved as an ion-recognition polyampholytes and shrank at a pH equal to the isoelectric point (IEP), which shifted to a higher pH when the BCAm complexed with a cation. At that time, the BCAm also became hydrophilic with water of hydration accompanied by the cation. As a result of the combination of these two effects, we found that the reverse behaviors of swelling and shrinking occurred at different pHs in response to the same ion signal.

Introduction

Biopolymers such as protein, DNAs, and RNAs are known to have various intramolecular interactions, such as electrostatic, hydrophilic, and hydrophobic interactions, as well as hydrogen bonds. These interactions are considered to be among the important factors in determining the structures and functions of biopolymers. Biopolymers also show many functions in response to molecular signals. In the case of proteins, phosphorylation/dephosphorylation usually changes the polymer's function. In the case of DNAs, polymer function is mainly controlled by methylation.

Some synthetic molecular-signal-responsive polymers and hydrogels have also been reported, insprired by the functions of biopolymers. A lectin-loaded cross-linked polymer network of *N*-isopropylacrylamide (NIPAM) showed distinct swelling behavior in response to different saccharides.[1] A temperature-sensitive hydrogel copolymerized via molecular imprinting showed a volume change in response to specific molecules.[2] An antigen−antibody semi-IPN hydrogel showed reverse swelling behavior in a buffer solution in response to a specific antigen.[3] These previous researches utilized the change in cross-linking density or hydration condition induced by molecular signals but did not utilize the electrostatic interaction.

Recently, there has been much interest in polyampholytes because they have many similarities to biopolymers such as proteins.[4] The polymer chain of polyampholytes contains both cationic and anionic groups, and the balance of positively and negatively charged groups can be controlled by changing the monomer content in the feed solution.[5,6] The balance of positively and negatively charged groups also changes when these charged groups are sensitive to the pH of the solution. Synthetic polyampholytes have an isoelectric point (IEP) at a specific pH, where the polymer chain is electroneutral and shrinks.[7] The synthetic polyampholytes also show the antipolyelectrolyte effect, in which the polymer chain is soluble at the IEP because of the electric shielding of the fixed charges due to a high salt concentration.[8] However, this electrostatic interaction has not been controlled by molecular signals.

Many synthetic host compounds such as crown ethers[9] and cryptand complexes[10,11] have been designed and analyzed in the field of supramolecular chemistry.[10] Benzo[18]crown-6-acrylamide (BCAm), one of the molecular recognition compounds, has a crown ether receptor and traps specific ions such as K^+ and Ba^{2+}.[12] The copolymer of NIPAM and BCAm was synthesized, and the shift in the lower-critical-solution temperature was observed when the BCAm captured specific ions.[13] Recently, we hypothesized on the basis of our previous researches that captured ions behaved like fixed positive charges when the BCAm formed a complex with a specific ion because of the osmotic pressure generated by the Donnan exclusion-like effect under a specific ion concentration gradient.[14] In addition, we found that the complex of a BCAm and a specific ion retains about 70−80 water molecules and makes the polymer chain more hydrophilic.[15]

In this research, we synthesized a linear copolymer of MAPTAC, AA, and BCAm (Figure 1). Its phase-separation behavior in response to pH, ion species, and salt concentration was investigated. The effect of the composition of the copolymers was also studied. MAPTAC has a stable quaternary ammonium base, amide bond, and propyl group, while AA has a pH-sensitive carboxylic acid group.[16] The molecular structure of poly-MAPTAC-*co*-AA-*co*-BCAm contains both positively and negatively charged groups and well-balanced molecular interactions, such as electrostatic, hydrophilic, and hydrophobic interactions, as well as hydrogen bonds. In addition, complex formation between BCAm and ions has the above-mentioned unique physicochemical effects, which are expected to trigger unique phase-separation phenomena of the copolymer.

Experimental Section

Materials. [3-(Methacryloylamino)propyl]trimethylammonium chloride (MAPTAC, 50 wt % aqueous solution) was purchased from Aldrich Co., Ltd.; inhibitor was removed using an adsorption column before polymerization. Acrylic acid was purchased from Wako Chemical Co., Ltd., and purified by distillation. BCAm was synthesized according to reported procedures.[12] 2,2′-Azobis(2-methylpropionamidine) dihydrochloride (V-50) was purchased from Wako Chemical Co., Ltd., and used as an initiator. Standard aqueous

* Corresponding author: Tel +81-45-924-5254; Fax +81-45-924-5253; e-mail yamag@res.titech.ac.jp.
† The University of Tokyo.
‡ Tokyo Institute of Technology.

10.1021/ma801936t CCC: $40.75
Published on Web 01/30/2009

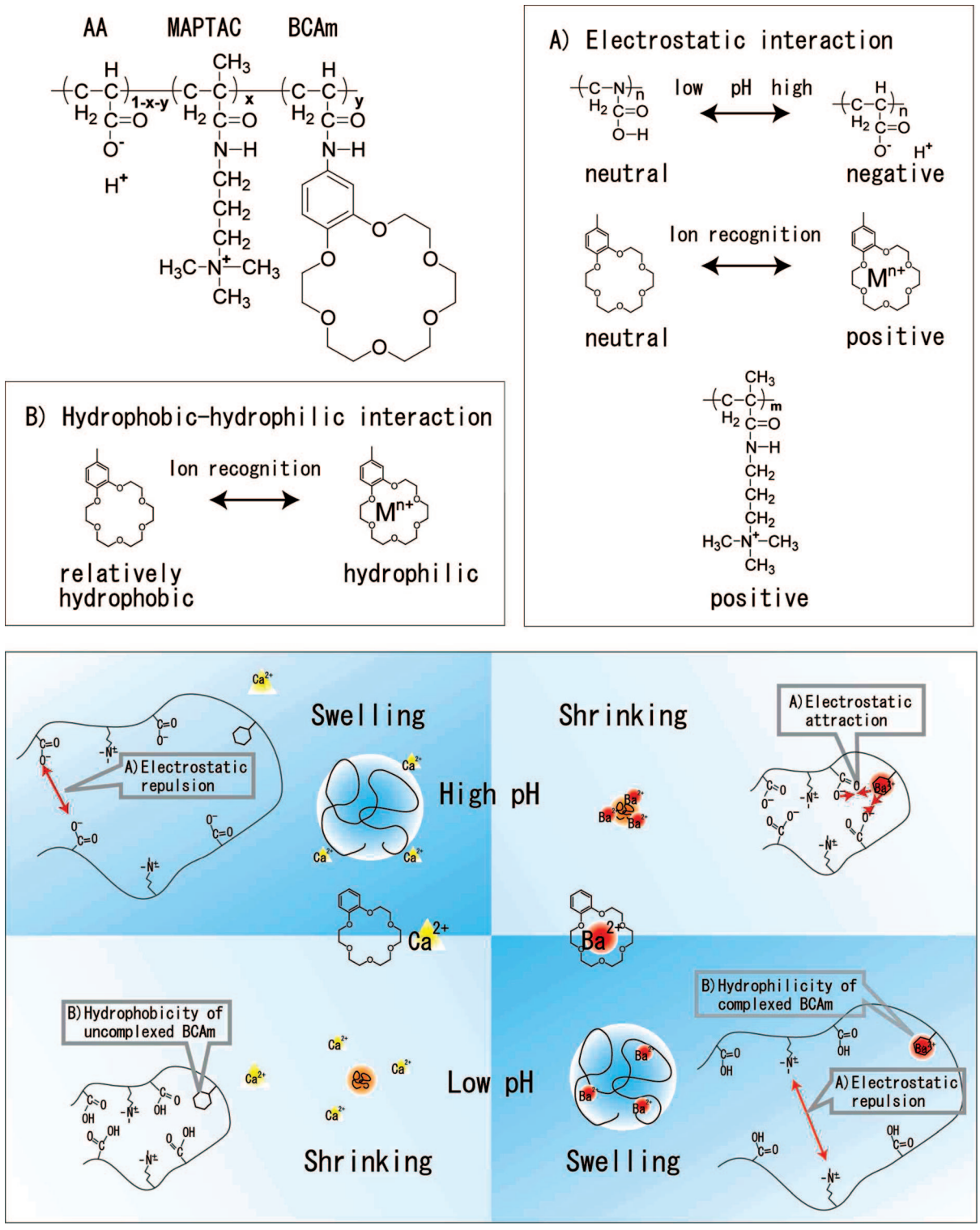

Figure 1. Chemical structure, intramolecular interactions, and concept of molecular-recognition response of poly-MAPTAC-*co*-AA-*co*-BCAm.

solutions of hydrochloric acid and sodium hydroxide were purchased from Wako Chemical Co., Ltd., and used for IEP measurements and turbidimetric titrations.

Preparation of the Linear Copolymer. Poly-MAPTAC-*co*-AA-*co*-BCAm was synthesized by free-radical copolymerization. The molar copolymerization ratios were controlled according to Table 1. Aqueous solutions of MAPTAC, AA, and BCAm were prepared from degassed RO water. The ratio of initiator was fixed at 0.5 mol % for all monomers, and the weight percentage of monomers was fixed at 15 wt %. The aqueous solution was kept at 50 °C for 48 h under N_2 after initiating polymerization by visible light for 12 min. The copolymer was dissolved in RO water, purified by dialysis—using a dialysis membrane for which the molecular weight cutoff was about 12 000—and dried under vacuum. Chloride ions contained in the aqueous monomer solution of MAPTAC were also removed by dialysis after polymerization.

Characterization. The synthesized linear copolymers were characterized by FT-IR, elemental analysis, and UV−vis spectroscopy. The FT-IR spectrum of the linear copolymer was measured using the KBr disk technique with an MGNA 550 (Nicolet). Elemental analysis was performed on a 2400II (Perkin-Elmer). The UV−vis spectrum of the linear copolymer was measured using a U-3310 (Hitachi). The absorption intensities in the UV−vis spectrum were measured using an aqueous solution of copolymers.

Table 1. Molar Compositions of the Monomer Solutions and Copolymers, with MAPTAC, AA, and BCAm Content as 100 mol %[a]

composition of monomer solutions				copolymerization ratio		
[mol %]	MAPTAC	AA	BCAm	MAPTAC	AA	BCAm
(a)	100			100		
(b)	38	62		39	61	
(c)	24	76		25	75	
(d)	18	82		18	82	
(e)	14	43	43	12	39	49
	(24)	(76)	(76)	(23)	(77)	(96)
(f)	12	57	30	9	65	26
	(18)	(82)	(42)	(12)	(88)	(35)

[a] Compositions with MAPTAC and AA content as 100 mol % are shown in parentheses.

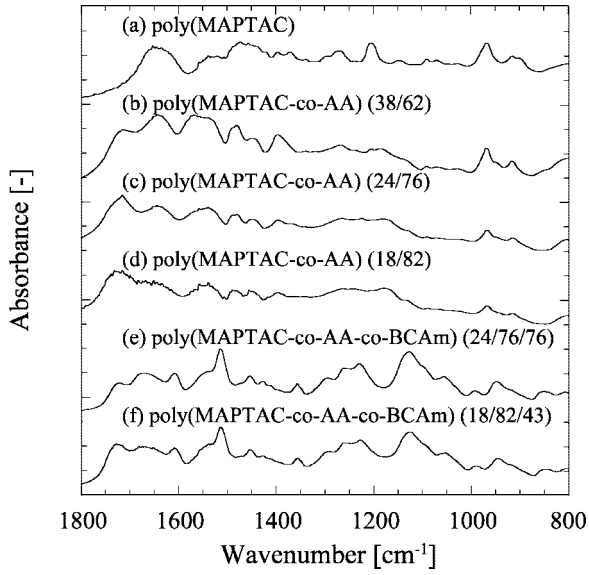

Figure 2. FT-IR spectra of poly(MAPTAC), poly(MAPTAC-*co*-AA), and poly(MAPTAC-*co*-AA-*co*-BCAm).

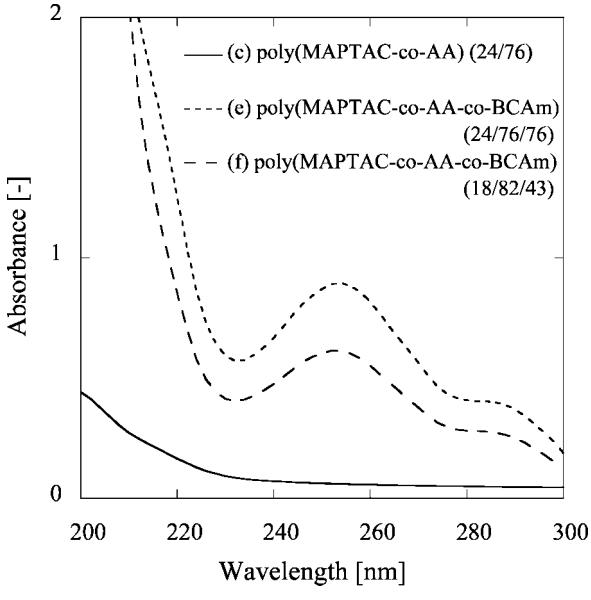

Figure 3. UV spectra of poly(MAPTAC-*co*-AA) and poly(MAPTAC-*co*-AA-*co*-BCAm).

Turbidimetric Measurement. Copolymer solutions change turbidity when copolymer chains shrink, and this behavior was measured spectrophotometrically as the optical density at 650 nm. Turbidimetric titration of the linear copolymer solution was performed in 0.2 wt % copolymer concentration at 25 °C. The pH was first changed to about pH 2 by adding 0.01 M HCl aqueous solution, and it was then changed to pH 12 by adding 0.01 M NaOH aqueous solution in 10 μL aliquots. Each time, the pH was measured using a pH meter HM21P (TOD-DKK), and the optical density was measured. Measurements were carried out a few minutes after titration to obtain a stable optical density value. The turbidimetric titration of the linear copolymer solution was also carried out with various concentrations of $CaCl_2$, $SrCl_2$, and $BaCl_2$. Turbidity changes were also measured by adding 0.1 M aqueous solution of $CaCl_2$, $SrCl_2$, and $BaCl_2$ in 10 μL aliquots in both acid and base conditions and by alternately adding 0.1 M aqueous solution of $BaCl_2$ and [18]crown-6.

Results and Discussion

Characterization of Copolymers. Figure 2 shows the FT-IR spectra of the copolymers. Copolymerization of MAPTAC, AA, and BCAm was determined by FT-IR measurements. The peaks are 1650 cm^{-1} from the amide bond of MAPTAC, 1720 cm^{-1} from the carboxyl group of AA, and 1133 cm^{-1} from the ether group of BCAm. Figure 3 shows the UV spectra of copolymers of BCAm, which had an absorbance peak at 255 nm. The copolymerization ratio of BCAm was estimated from the following proportional relationship between the absorbance at 255 nm and concentration of poly-BCAm:

$$C_{\mathrm{BCAm}} = 1.21 \times 10^{-4} a \ \mathrm{mol/L} \quad (1)$$

where a is the absorbance at 255 nm and C_{BCAm} is the concentration of poly-BCAm.[17] The copolymerization ratio of MAPTAC to AA was determined by the weight ratio of carbon and nitrogen atoms obtained from elemental analysis. The total molar copolymerization ratios MAPTAC:AA:BCAm determined from these measurements are shown in Table 1. These molar copolymerization ratios are in close agreement with those used in the synthesis. The molar copolymerization ratios are shown for MAPTAC, AA, and BCAm content as 100 mol %.

pH Dependence of Poly(MAPTAC), Poly(MAPTAC-*co*-AA), and Poly(MAPTAC-*co*-AA-*co*-BCAm). In general, a polyampholyte shrinks at a pH equal to the IEP, where the positive and negative charges balance and the solution of linear copolymer becomes turbid.[5,18] The monomer of MAPTAC is a chloride ion salt, and poly(MAPTAC) acts as a positive charge whose amount is not affected by pH (Figure 1). AA is a weak acid, and it acts as a negative charge whose magnitude is affected by the degree of dissociation. Thus, the balance of positive and negative charges changes depending on the pH of the solution. The amount of negative charge is low because of the low degree of dissociation of AA at pHs below the IEP, while negative and positive charges balance when the pH equals the IEP, and negative charges exceed positive charges at pHs above the IEP. Since the dissotiation degree α of weak acid relates to pH by the following equation

$$\mathrm{pH} = \mathrm{p}K_{\mathrm{a}} + \log\left(\frac{\alpha}{1-\alpha}\right) \quad (2)$$

the pH of the IEP where the ratio of the positive and the negative charges inside the linear polymer balance can be estimated. Using $\mathrm{p}K_{\mathrm{a}} = 4.25$ previously reported for poly(acrylic acid),[19] the pH of the IEP was calculated as 4.5, 3.9, 3.7, 3.9, and 3.7 for copolymer (b), (c), (d), (e), and (f) respectively, for (e) and (f) without considering the effect of the copolymerized BCAm.

Figure 4 shows the pH dependencies for the turbidimetric titrations of the 0.2 wt % aqueous copolymer solutions of poly(MAPTAC), poly(MAPTAC-*co*-AA), and poly(MAPTAC-*co*-AA-*co*-BCAm). The absorbance of the aqueous polymer solution of (a) poly(MAPTAC) is low over the entire pH range. This is because poly(MAPTAC) contains only positive charges

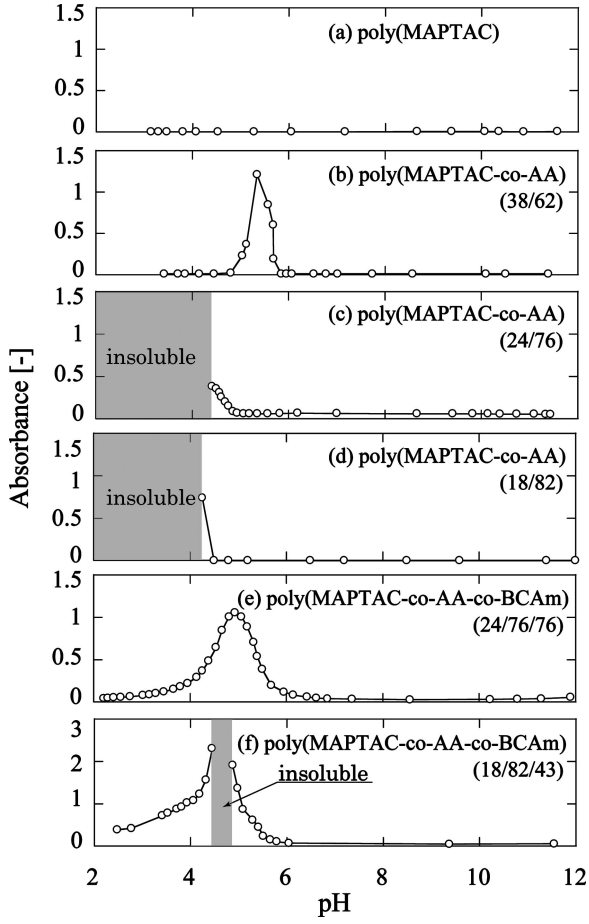

Figure 4. pH dependence of poly(MAPTAC-*co*-AA) and poly(MAPTAC-*co*-AA-*co*-BCAm).

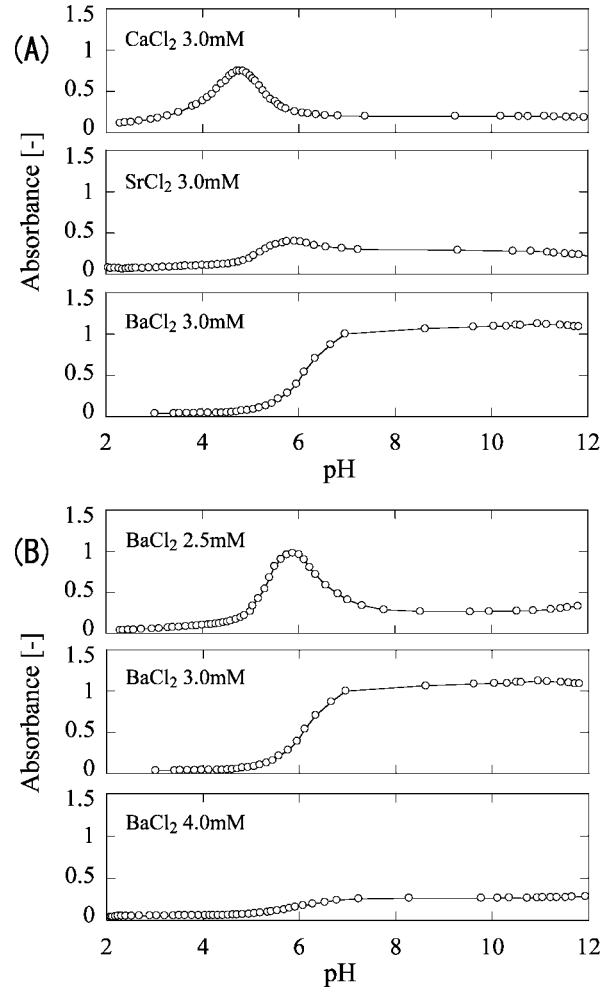

Figure 5. pH dependence of the copolymer used in Figure 4e, poly(MAPTAC-*co*-AA-*co*-BCAm) (24/76/76), with salt. (A) Different ion species of $CaCl_2$, $SrCl_2$, and $BaCl_2$. (B) Concentration dependence of $BaCl_2$.

inside the polymer chain and is always swollen by electrostatic repulsion. The absorbance of copolymers of poly(MAPTAC-*co*-AA) varied according to the pH of the solution. A 0.2 wt % aqueous solution of copolymer (b) turned turbid at about pH 5.4; copolymers (c) and (d) turned turbid and resulted in precipitation below pH 4.4 and 4.2, respectively. Copolymers (e) and (f) have the same ratio of MAPTAC to AA as copolymers (c) and (d) and contain BCAm with 43 and 30 mol %, respectively. The 0.2 wt % aqueous solution of copolymer (e) turned turbid at about pH 5.0; copolymer (f) turned turbid and resulted in precipitation at about pH 4.6. However, these values of pH were higher than the pH of the IEP estimated by the calculation; their trends were almost the same according to the monomer compositions. Therefore, behavior as a polyampholyte was confirmed for the aqueous solution of both poly(MAPTAC-*co*-AA) and poly(MAPTAC-*co*-AA-*co*-BCAm). Their differences are expected to be due to the different value of pK_a from the reported value with different component of the copolymerization.

Thus, a solution of copolymer (b) turned turbid when the pH equaled the IEP. Solutions of copolymers (c) and (d) turned turbid and resulted in precipitation because the copolymer of high AA content could reach the IEP with low degree of dissociation and also because of the hydrogen bond between dissociated AA[20] and the relatively hydrophobic uncomplexed BCAm. The pH of the IEP of copolymers (e) and (f) were measured to be about 0.5 higher than those of copolymers (c) and (d). Copolymers (e) and (f) were more soluble than (c) and (d), probably because the difference of the value of pK_a and the ratio of hydrogen bonds was decreased by copolymerization with BCAm.

The concentration of the Na^+ ion after turbidimetric titration was about 10 mM. The peak of the turbidity of the IEP was observed at the same pH reproducibly by multicycle measurement of the titration; however, the peak height slightly decreased because of the increase of the concentration of the added salt, which is called the anti-polyelectrolyte effect.

Different Ion Species Changed the IEP Shift. The result for copolymer (e) will be explained after the next two sections. Figure 5A shows the pH dependence for the turbidimetric titrations of 0.2 wt % aqueous polymer solution of poly(MAPTAC-*co*-AA-*co*-BCAm) in the presence of various salts. The concentration of the salts $CaCl_2$, $SrCl_2$, and $BaCl_2$ was controlled to 3.0 mM at the beginning of the titration. BCAm forms complexes with various ions, and the complex formation constants increase in the order Ca^{2+}, Sr^{2+}, Ba^{2+}.[21] The balance of charges inside the polymer chain is also estimated from the complex formation constant K and eq 2 by considering the complexed divalent ions into positive charges. Using log K = 1.1 and 1.6 for Sr^{2+} and Ba^{2+}, respectively, which were previously reported for poly-NIPAM-*co*-BCAm,[17] the pH of the IEP shifted higher by 0.1 and 0.5 in the presence of 3.0 mM ions.

An aqueous solution of copolymer in the presence of 3.0 mM Ca^{2+} ions turned turbid at about pH 4.9. The pH at the IEP did not shift from that of the same titration without Ca^{2+} ions because the complex formation constant of BCAm and Ca^{2+} ion is low, and the positive charges were not introduced inside

the polymer chain. The copolymer also became soluble, and the absorbance decreased because of the anti-polyelectrolyte effect in the presence of $CaCl_2$ salt. An aqueous solution of the copolymer in the presence of 3.0 mM Sr^{2+} ions turned turbid at about pH 5.9. The pH at the IEP shifted by about 1.0 compared with that of the same titration without Sr^{2+} ions. This was because BCAm and Sr^{2+} ions formed complexes and positive charges were introduced inside the copolymer chain. The solution of the copolymer also became soluble, and the absorbance decreased because of the hydrophilic change of complexed BCAm and the antipolyelectrolyte effect. An aqueous solution of copolymer in the presence of 3.0 mM Ba^{2+} ion turned turbid at a pH of about 6.0. This is because the complex formation constant of BCAm and Ba^{2+} ion is high. The total positive charges of MAPTAC and those introduced inside the copolymer chains are in balance with the negative charges of dissociated AA, and the polymer chain remained at the IEP in the higher pH range. Although the observed shift range of the pH is wider than the calculated values, their trends are well consistent with the order of the complex formation constant. Their differences are expected to be due to the difference of the values of complex formation constant, which are widely different according to the copolymerization systems and other effects such as hydrophilic change of complexed BCAm.

Figure 5B shows the pH dependence for the turbidimetric titrations of 0.2 wt % of aqueous polymer solution of poly(MAPTAC-*co*-AA-*co*-BCAm) in the presence of various concentrations of $BaCl_2$, namely 2.5, 3.0, and 4.0 mM. An aqueous solution of the copolymer in the presence of 2.5 mM Ba^{2+} ion turned turbid at about pH 5.9 by complexation of BCAm and Ba^{2+} ions. An aqueous solution of the copolymer in the presence of 4.0 mM Ba^{2+} ions became slightly turbid above a pH of about 6.0. The number of total positive charges on MAPTAC and those introduced inside the copolymer chains exceeds the number of negative charges on the dissociated AA. The polymer chain did not reach the IEP, and the solution turned slightly turbid. The anti-polyelectrolyte effect with high salt concentration and hydrophilic change of complexed BCAm were also reasons for the low absorbance.

From these results, positive charges were introduced into the polymer chain by complex formation of BCAm and cations depending on the complex formation constant and the concentration of the cation. The behaviors of swelling and shrinking of polymer chains and the amount of positive charge inside the polymer chains were controlled by the species and the concentration of the ion.

Ion Recognition Changed by an Anti-polyelectroyte Effect. Figure 6A shows the turbidimetric measurements of 0.2 wt % aqueous copolymer solutions upon gradually adding 0.1 M solutions of various salts at pH 5.0, where the copolymer was at the IEP without salt. The polymer initially shrank at the IEP and gradually changed to swelling by the addition of salt solution. The absorbance decreased in the order of Ba^{2+}, Sr^{2+}, Ca^{2+}, which is the order of the complex formation constants. This is because of the IEP shift to higher pH by complex formation of BCAm and the cation, and there is also the influence of the anti-polyelectrolyte effect.

Figure 6B shows the turbidimetric measurements of 0.2 wt % copolymer solution upon gradually adding 0.1 M solution of various salts at pH 11.6. The copolymer was initially swollen and gradually changed to shrinking by the addition of salt solution. The absorbance increased in the order Ba^{2+}, Sr^{2+}, Ca^{2+}, which is the order of the complex formation constants. The carboxylic groups of AA are all dissociated at pH 11.6, and negative charges are initially in excess. Positive charges are introduced into the copolymer chain by complex formation between BCAm and the cation. The polymer chain started to shrink at the point where the positive charges balanced the negative charges. When the number of positive charges exceeded the number of negative charges, the polymer chain started swelling again. We also deduce from these results that the number of positive charges inside the polymer chain was controlled by the species and the concentration of ions, and the antipolyelectrolyte effect crucially affected the behavior.

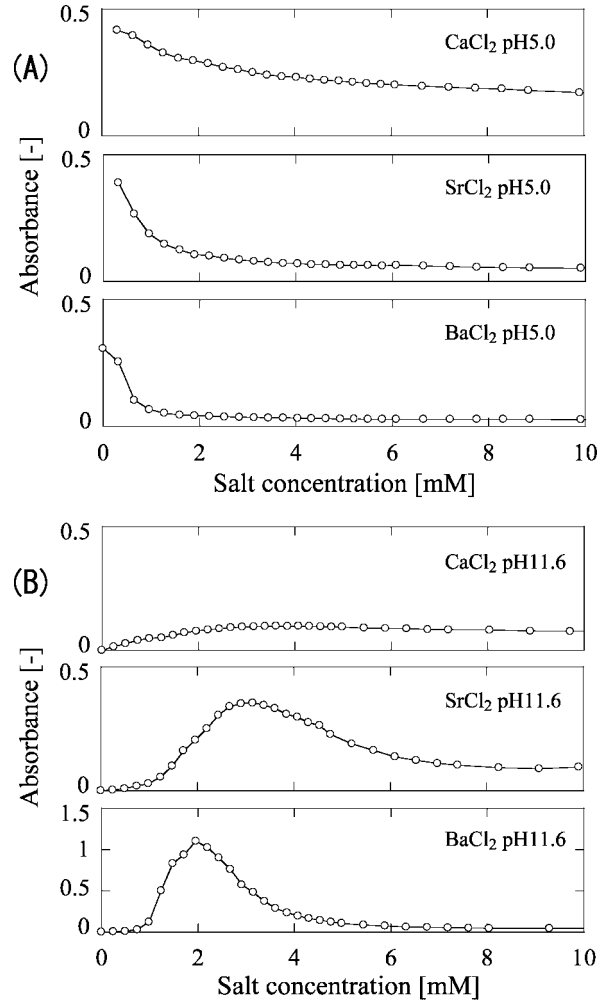

Figure 6. Salt concentration dependence of the copolymer (e) (poly-MAPTAC-*co*-AA-*co*-BCAm) (24/76/76). (A) Different ion species of $CaCl_2$, $SrCl_2$, and $BaCl_2$. (B) Concentration dependence of $CaCl_2$, $SrCl_2$, and $BaCl_2$.

There is another expected effect of adding divalent ions, which dissociated carboxylic groups can be cross-linked by divalent ions above the pH of the IEP. It is understood mainly by electrostatic interaction on their charge size ratio measured in terms of ionic radii.[22] Thus, the interaction of added divalent ions decreases in the order of Ca^{2+}, Sr^{2+}, and Ba^{2+}. This interaction is expected to exist in the copolymer chain when divalent ion is added into the solution. However, from the Figure 6B, the copolymer chain shrank more in the order of high complex forming constant with BCAm, not in the order of the strength of the cross-link of the divalent ion. From this result, the effect of complex forming of BCAm with Ba^{2+} is thought to be stronger than the effect of the cross-link of the divalent ion. Therefore, we speculate that the effect of the cross-link by divalent ions is not obvious because the electrostatic interaction between the dissociated AA and the complexed BCAm is thought to be dominant in this copolymer system.

Reverse Response of Poly(MAPTAC-*co*-AA-*co*-BCAm) to Specific Ions at Different pHs. Parts A and B of Figure 7 show the alternate salt addition of $BaCl_2$ and [18]crown-6 to

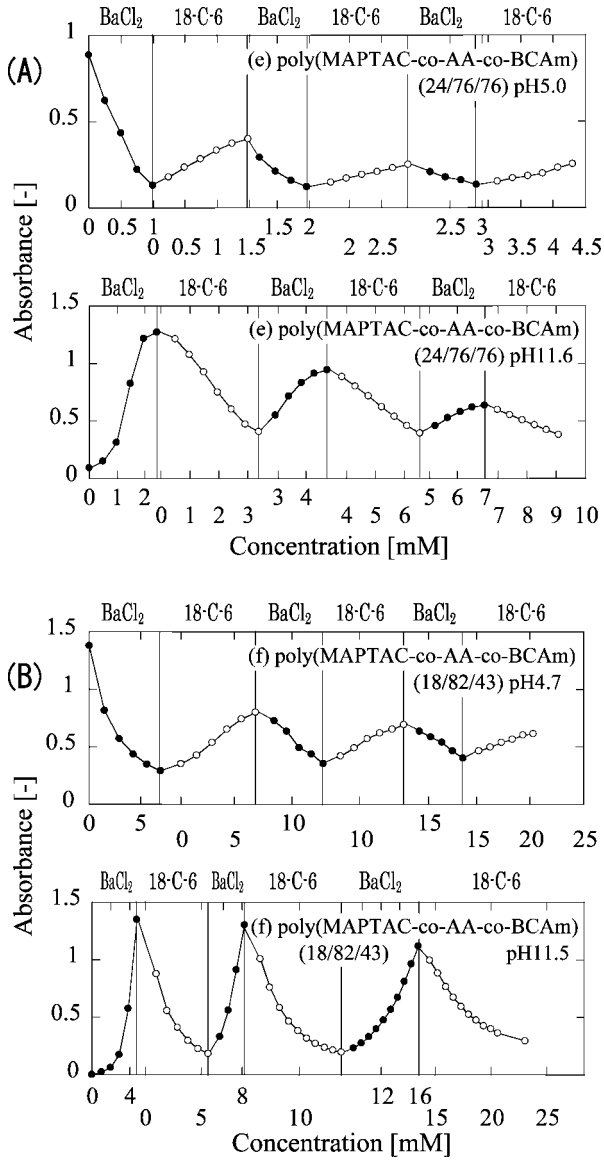

Figure 7. Turbidity change of the aqueous solutions of copolymers (e) and (f) by alternately adding $BaCl_2$ and [18]crown-6 aqueous solutions.

0.2 wt % aqueous copolymer solutions of (e) and (f), respectively. Turbidity was measured both at the IEPs and higher pHs of alkaline conditions. [18]Crown-6 can remove Ba^{2+} ions from the polymer chain because the complex formation constant of [18]crown-6 is higher than that of BCAm. Therefore, Ba^{2+} ions can be alternately introduced into the polymer chain by adding a 0.1 M aqueous solution of Ba^{2+} and [18]crown-6.

In this measurement, the behavior of swelling and shrinking was observed for both copolymers (e) and (f). The copolymer initially shrank when the pH was at the IEP and then changed to swelling by adding Ba^{2+} ions. The copolymer began shrinking again by adding [18]crown-6, and this behavior was observed alternately. The copolymer initially swelled in alkaline conditions then changed to shrinking by adding Ba^{2+} ions. The copolymer changed to swelling again by adding [18]crown-6, and this behavior was also observed alternately. The absorbance of the copolymer solution in the shrinking condition gradually decreased because of the anti-polyelectrolyte effect caused by the increase in the concentration of salt and [18]crown-6. The response of the absorbance change to salt concentration of copolymer (e) was more sensitive than for copolymer (f). This is because copolymer (e) has a higher molar composition of BCAm than copolymer (f).

Thus, we demonstrated the alternate swelling and shrinking behavior of an aqueous solution of poly(MAPTAC-*co*-AA-*co*-BCAm) by alternately adding a 0.1 M aqueous solution of Ba^{2+} and [18]crown-6. The behaviors of swelling and shrinking in response to the same ion addition were completely opposite under acidic and alkaline conditions.

Conclusions

We synthesized and characterized for the first time an ion-recognition polyampholyte. The copolymers of poly(MAPTAC-*co*-AA-*co*-BCAm) showed the behavior of polyampholytes and shrank when the pH equaled the IEP, which was shifted by the ion signal recognized by BCAm, which can form a complex with specific ions depending on the complex formation constant and the concentration of the ions. The intramolecular interactions, mainly electrostatic interactions, were controlled by ion recognition of BCAm and the pH of the solution, which led to the swelling and shrinking behaviors of the copolymer in response to both pH and ion recognition. We found that the reverse behaviors of swelling and shrinking occurred at a different pHs in response to the same ion signal. These phenomena are complicated and interesting, especially in terms of similarity to biopolymers, which respond to the same signal in different ways depending on changes in the external environment such as pH and temperature. The concept of macromolecular design in the present research is expected to be utilized in fields such as separation technology, biomaterials, and drug-delivery systems in the future.

References and Notes

(1) Kokufata, E.; Zhang, Y. Q.; Tanaka, T. *Nature (London)* **1991**, *351* (6324), 302–304.
(2) (a) Wulff, G. *Angew. Chem., Int. Ed.* **1995**, *34* (17), 1812–1832. (b) Watanabe, M.; Akahoshi, T.; Tabata, Y.; Nakayama, D. *J. Am. Chem. Soc.* **1998**, *120* (22), 5577–5578.
(3) (a) Miyata, T.; Asami, N.; Uragami, T. *Macromolecules* **1999**, *32* (6), 2082–2084. (b) Miyata, T.; Asami, N.; Uragami, T. *Nature (London)* **1999**, *399* (6738), 766–769.
(4) Kudaibergenov, S. E. *Polyampholytes: Synthesis, Characterization, and Application*; Kluwer Academic/Plenum Press: New York, 2002; p 220.
(5) Kudaibergenov, S. E.; Sigitov, V. B. *Langmuir* **1999**, *15* (12), 4230–4235.
(6) Mccormick, C. L.; Salazar, L. C. *Macromolecules* **1992**, *25* (7), 1896–1900.
(7) (a) Baker, J. P.; Stephens, D. R.; Blanch, H. W.; Prausnitz, J. M. *Macromolecules* **1992**, *25* (7), 1955–1958. (b) Skouri, M.; Munch, J. P.; Candau, S. J.; Neyret, S.; Candau, F. *Macromolecules* **1994**, *27* (1), 69–76.
(8) (a) Corpart, J. M.; Candau, F. *Macromolecules* **1993**, *26* (6), 1333–1343. (b) Patrickios, C. S.; Sharma, L. R.; Armes, S. P.; Billingham, N. C. *Langmuir* **1999**, *15* (5), 1613–1620.
(9) (a) Higgins, S. J. *Chem. Soc. Rev.* **1997**, *26* (4), 247–257. (b) Cacciapaglia, R.; Mandolini, L. *Chem. Soc. Rev.* **1993**, *22* (4), 221–231. (c) Olsher, U.; Izatt, R. M.; Bradshaw, J. S.; Dalley, N. K. *Chem. Rev.* **1991**, *91* (2), 137–164.
(10) Schneider, H. J.; Yatsimirsky, A. K. *Chem. Soc. Rev.* **2008**, *37* (2), 263–277.
(11) Lincoln, S. F. *Coord. Chem. Rev.* **1997**, *166*, 255–289.
(12) (a) Ungaro, R.; Haj, B. E.; Smid, J. *J. Am. Chem. Soc.* **1976**, *98* (17), 5198–5202. (b) Yagi, K.; Ruiz, J. A.; Sanchez, M. C. *Makromol. Chem., Rapid Commun.* **1980**, *1* (4), 263–268.
(13) (a) Irie, M. *Adv. Polym. Sci.* **1993**, *110*, 49–65. (b) Irie, M.; Misumi, Y.; Tanaka, T. *Polymer* **1993**, *34* (21), 4531–4535.
(14) Ito, T.; Yamaguchi, T. *J. Am. Chem. Soc.* **2004**, *126* (20), 6202–6203.
(15) Ito, T.; Nishikawa, M.; Yamaguchi, T. Manuscript in preparation.
(16) (a) Annaka, M.; Tanaka, T. *Nature (London)* **1992**, *355* (6359), 430–432. (b) Shibayama, M.; Tanaka, T. *Adv. Polym. Sci.* **1993**, *109*, 1–62. (c) Hirokawa, Y.; Tanaka, T.; Sato, E. *Macromolecules* **1985**, *18* (12), 2782–2784.

(17) Ito, T.; Sato, Y.; Yamaguchi, T.; Nakao, S. *Macromolecules* **2004**, *37* (9), 3407–3414.
(18) Kudaibergenov, S. E.; Didukh, A. G.; Zhumadilova, G. T.; Koizhaiganova, R. B.; Bimendina, L. A.; Noh, J. G.; Geckeler, K. E. *Macromol. Symp.* **2004**, *207*, 153–171.
(19) Ende, M. T. A.; Peppas, N. A. *J. Appl. Polym. Sci.* **1996**, *59* (4), 673–685.
(20) Karino, T.; Masui, N.; Hiramatsu, M.; Yamaguchi, J.; Kurita, K.; Naito, S. *Polymer* **2002**, *43* (26), 7467–7475.
(21) Izatt, R. M.; Bradshaw, J. S.; Nielsen, S. A.; Lamb, J. D.; Christensen, J. J. *Chem. Rev.* **1985**, *85* (4), 271–339.
(22) Rotello, V. E. *Nanoparticles Building Blocks for Nanotechnology*; Kluwer Academic/Plenum Publishers: New York, 2004; pp 225−250.

MA801936T