Colloid Polym Sci (2008) 286:1425–1434
DOI 10.1007/s00396-008-1913-z

ORIGINAL CONTRIBUTION

Potentiometric titration behavior of poly(acrylic acid) within a cross-linked polymer network having amide groups

Mika Furukawa · Raymond S. Farinato ·
Etsuo Kokufuta

Received: 4 July 2008 / Revised: 17 July 2008 / Accepted: 28 July 2008 / Published online: 21 August 2008

Abstract This study aimed to investigate the effect of COOH group distribution within a polymer network having amide groups, with which the COOH could form hydrogen bonds. We employed here two polyelectrolyte gels composed of *N*-isopropylacrylamide (NIPA) networks, either copolymerized with acrylic acid (AA) or within which poly(acrylic acid) (PAA) was entrapped. Both gels (AA–NIPA ~ 1:4 mol/mol) were prepared by aqueous red-ox polymerization with *N*,*N*'-methylenebisacrylamide as the cross-linker. Finely divided gels in NaCl solutions (0.025 and 0.1 M) were titrated with NaOH and back-titrated with HCl at 25 °C. The results of the copolymer gel (CG) agreed well with those of a linear copolymer and a nanoscale gel which had a similar AA content to CG. However, marked differences were observed in the titration behaviors of the AA-copolymerized and PAA-entrapped gels, mainly due to the hydrogen bonding between the entrapped PAA chain and its surrounding NIPA network.

Keywords Poly(*N*-isopropylacrylamide)-based polyelectrolyte gels · Gel-entrapped poly(acrylic acid) · Potentiometric titration · Interpolymer complex · Hydrogen bonding

Introduction

Polycarboxylic acids like poly(acrylic acid) (PAA) form interpolymer complexes in acidic aqueous solutions with such polymers as poly(*N*-isopropylacrylamide) (PNIPA) [1–5] and poly(ethylene oxide) (PEO) [2–8]. It is generally believed that hydrogen bonding, e.g., between PAA (a Brønsted "polyacid" (BPa) acting as a proton donor) and PEO (a Brønsted "polybase" (BPb) acting as a proton acceptor), plays an important role in this complex formation. A similar mechanism may be hypothesized in the case of a polymer network (gel) of cross-linked BPb chains, within which linear BPa chains are entrapped. In such a situation, the formation of hydrogen bonds could result in a "contractile" force causing the gel to shrink [9, 10–12]. Addition of base (e.g., NaOH) that would break these hydrogen bonds would thereby lead to a reswelling of the gel due to both elimination of the contractile force and generation of additional ionic repulsion. In most previous studies [1–8], complex formation by hydrogen bonding has been examined using a set of water-soluble, linear BPa and BPb chains. A few studies have also dealt with complexation of nanogel or microgel particles with a linear BPa [13]. We now extend studies of this kind to complexation between macroscopic gels and an entrapped linear polymer chain.

Extensive studies of hydrogen bonding interactions that take place in "bulk" gel systems with entrapped BPa or BPb chains would be of significance to basic and applied sciences. For example, in biological systems, there are many tissues composed of linear macromolecules or

M. Furukawa
Graduate School of Life and Environmental Sciences,
University of Tsukuba,
Tsukuba, Ibaraki 305-8572, Japan

R. S. Farinato
Kemira Water Solutions, Inc.,
1937 W. Main St.,
Stamford, CT 06904, USA

E. Kokufuta (✉)
Graduate School of Life and Environmental Sciences and Institute
of Applied Biochemistry, University of Tsukuba,
Tsukuba, Ibaraki 305-8572, Japan
e-mail: kokufuta@sakura.cc.tsukuba.ac.jp

globular proteins, which are entrapped within a gel-like matrix [14]; thus, research of this sort could provide a key for understanding the nature of biochemical interactions. These studies can also provide the basis for developing models to aid in the construction of polymer-based materials that undergo size changes due to hydrogen bonding. However, few attempts have been made to study complex formation due to hydrogen bonding between an entrapped polymer and a surrounding polymer network. The reason for this seems to be the lack of good experimental methods. For example, IR spectroscopy is useful for detecting hydrogen bonds between functional groups (e.g., >C=O, –OH, and –NH–) bound to a linear or cross-linked polymer [13, 15], but not between such groups bound to an entrapped polymer and its surrounding network, since there is a strong presence of other hydrogen bonds that form among network-bound functional groups.

Potentiometric titration has been commonly employed in previous studies [1–8, 13] to examine complexation in an aqueous solution containing both BPa and BPb macromolecules. We have demonstrated that potentiometric titration is useable for dispersions of not only polyelectrolyte nanogels (hydrodynamic radius ~ 55 nm at pH 3.7 and at 25 °C) but also macroscopic bulk gels having irregular sizes and shapes ranging from 1 to 2 mm in a swollen state [16]. Thus, potentiometric titration should be a promising method for the present purpose. Using this approach, we have looked at complex formation in a system in which PAA is entrapped within a network of cross-linked PNIPA chains. Special attention has been paid to the kinetics of these titrations, i.e., the rate of attaining acid–base equilibrium. We also focused on how to obtain reliable data from which the formation of hydrogen bonds between PAA chains and the NIPA network can be investigated. It has been found that titration data are very consistent with the formation of a complex by hydrogen bonding between monomer units of PAA and PNIPA, even when the former substance was entrapped into a polymer network of the latter substance. This paper reports an examination of hydrogen bonding within a polymer-entrapped gel using forward titration with NaOH and back titration with HCl of the entrapped polyacid.

Experimental

Materials and gel preparation We used two gel samples, polymer-entrapped gel (EG) and copolymer gel (CG), both of which are chemically composed of acrylic acid (AA), *N*-isopropylacrylamide (NIPA), and *N*,*N*'-methylene-bisacrylamide (MBA) as a cross-linker. The CG sample was prepared by red-ox polymerization of an aqueous solution containing NIPA ($F_w \sim 113$ g/mol; 0.516 mol/l), AA ($F_w \sim 72$ g/mol; 0.138 mol/l), and MBA ($F_w \sim 154$ g/mol; 9.09×10^{-3} mol/l), which was initiated by adding ammonium persulfate (0.04 g per 100 ml of pre-gel solution) and *N*,*N*,*N*',*N*'-tetramethylethylenediamine (2.5 ml per 100 ml of pre-gel solution). To prepare EG, prepolymerized PAA ($M_w \sim 4.5 \times 10^5$ g/mol) was used instead of AA monomer. The molar concentrations of monomer units were the same for both CG and EG. More gel preparation details are described in our previous paper [9].

Finely divided samples of each gel, having irregular sizes and shapes, were obtained by pushing the gel rod through a 1-mm mesh screen. These gel pieces were purified by repeated swelling and deswelling performed in cold and hot water, respectively. Recall that NIPA gels exhibit a reversible temperature-induced shrinkage at elevated temperature (~32 °C). The purification was considered complete when total organic carbon analysis showed that there was no detectable organic carbon in the washings. Purified gels were dispersed in 1 mM HCl to completely convert them to the acid form, lyophilized, and then dried at 50 °C for 3 days under reduced pressure.

In addition to the EG and CG samples, a copolymer and nanogel composed of NIPA and AA were used as control samples; both of which had been prepared in our previous study [16]. Several characteristics of all the samples used are shown in Table 1.

Potentiometric titration Titrations of rehydrated fine dispersions of the gels as well as of nanogel suspensions and copolymer solutions were performed with 0.1 N NaOH at 25 °C under nitrogen. Back titrations with 0.1 N HCl were also performed on the EG and CG samples to examine any titration hysteresis. All the samples for the titration had their ionic strength adjusted to 0.025 or 0.1 M with NaCl. Triply distilled carbonate-free water was used as the solvent.

Several modifications were made to a TOA model AUT-501 titration apparatus to allow the following operations to

Table 1 Properties of samples

Sample	Carboxyl content		Reference
	mmol g^{-1} of dry mass	AA–NIPA (mole/mole)[a]	
EG	1.91	0.250	This work
CG	1.87	0.244	This work
Copolymer nanogel[b]	2.75	0.387	[16]
Copolymer[c]	2.79	0.395	[16]

[a] Calculated from moles of COOH in 1 g of dry mass by assuming that the weight of MBA (cross-linker) is negligibly small.

[b] Hydrodynamic radius $\langle R_h \rangle = 55 \pm 2$ nm in salt free at pH 3.70±0.03 and at 25 °C.

[c] Weight average molar mass $M_w \sim 9 \times 10^4$ g/mol.

be made with the aid of a computer: (1) an accurate volume (0.05 ml) of titrant can be automatically added when a pH remains constant for 30 min within the range of ±0.01 unit (measuring limit), the condition of which was determined from careful preliminary experiments; (2) error due to drift of electrode potential with time is avoided by using the same pair of pH electrodes, one for continuously measuring the solution pH and the other for confirming the measured values by periodic calibration (at least at half-day intervals) using two standard solutions (phthalate buffer for pH 4.01, citrate–phosphate buffer for pH 6.86); and (3) all the data can be recorded by the computer for later analysis.

Conductometric titration Titration was performed with the same setup as used for the potentiometric titration, except that a conductivity meter (TOA model WM-50EG, DKK-TOA Co., Tokyo, Japan) equipped with a conductance cell (TOA model CT-57101B) was used instead of a pH meter and pH electrode. The CG and EG samples were dispersed into pure water, and their concentrations were adjusted to 20% of those used for the pH titration. The reason for the use of a diluted sample was to minimize any effect of gel volumes on the conductivity. As the titrant, 0.02 N NaOH was used, i.e., 20% of the concentration used for the pH titration.

Results and discussion

Experimentally, it is very difficult to measure the pH within the gel phase at each stage of the titration. We therefore employed fine dispersions of the gels and measured the pH of the surrounding media. This necessitates assuming that the acid–base equilibrium between the gel and external phase is completely attained at each stage of the titration. In order to directly confirm this assumption, however, we once again come up against the problem of measuring the pH within the gel phase. Our idea for circumventing this conundrum was to compare titration data for these finely divided CG gels with data for copolymers and nanogels of NIPA and AA having similar chemical compositions (see Table 1). The equilibrium process for copolymers and nanogels should be more rapid than for macroscopic gel particles. Thus, when there is good agreement among the titration curves for copolymer, nanogel, and CG [16] of the same nominal compositions, this would validate our procedure for macroscopic gels, at least with regards to the attainment of equilibrium.

Time dependence of pH changes during titration

First, we must examine how pH varies as a function of time after addition of an aliquot of titrant. Figure 1 shows typical examples of time-dependent titration curves for finely divided samples of CG and EG gels. Hash marks on the top of each graph indicate times at which 0.05 ml of titrant was added. There are several differences to be noted between the titration curves of EG and CG. At each step in the titration of EG with NaOH, the addition of an aliquot of titrant caused a rapid and large increase in pH, the value of which eventually became constant with time (see Fig. 1a). In the case of back titration of EG with HCl, the opposite response was observed, i.e., for each aliquot of titrant added, there was a rapid and large decrease in pH followed by an increase of pH to a constant value (Fig. 1b). Similar responses were observed in a 0.1-M NaCl solution containing PAA (sodium salt) and PNIPA (mole ratio of AA to NIPA ~ 1:4) when it was titrated with HCl (data not shown). In contrast to the EG or the PAA–PNIPA mixture, the CG sample showed more conventional titration curves both with NaOH and HCl. Features of these titration curves were the same as those of the corresponding copolymer and nanogel titration curves, except that the kinetics for the CG sample were slower. The corresponding observed characteristics of EG titration behavior will be discussed below in terms of the difference in hydrogen bonding interactions within EG and CG samples.

Other notable features in Fig. 1 are the slower rates of achieving acid–base equilibrium at the point near complete neutralization for PAA entrapped within a NIPA network (i.e., EG) and for AA copolymerized with NIPA in the CG network. This is, however, commonly observed, to greater or lesser degree, even in acid–base titration of low-molecular-weight compounds.

Raw titration curves

The next stage of data analysis required us to obtain the "raw" equilibrium titration curves from time-dependent titration curves. A pH(t) value that remained unchanged within ±0.01 for half an hour was regarded as an equilibrium pH value (pH_{eq}) at each titrant volume (see "Experimental" section). In this way, an equilibrium titration curve was obtained by plotting pH_{eq} against titrant volume. In Fig. 2, the case for EG is shown as an example. Titration with NaOH (see Fig. 2a), followed by back titration with HCl (see Fig. 2b), showed a clear endpoint as indicated by the differential curve ($\Delta pH/\Delta V$; $\Delta V =$ 0.05 ml). The NaOH volume (1.91±0.025 ml) at the endpoint in the forward titration agreed well with the HCl volume (1.93±0.025 ml) used between the two peaks of the differential curve in Fig. 2b. The amount (1.92 mmol/g) of PAA-bound COOH calculated from the titration data is close to that (1.98 mmol/g) calculated from the composition of the pre-gel solution used for the preparation. These results indicate that the COOH groups within the EG are

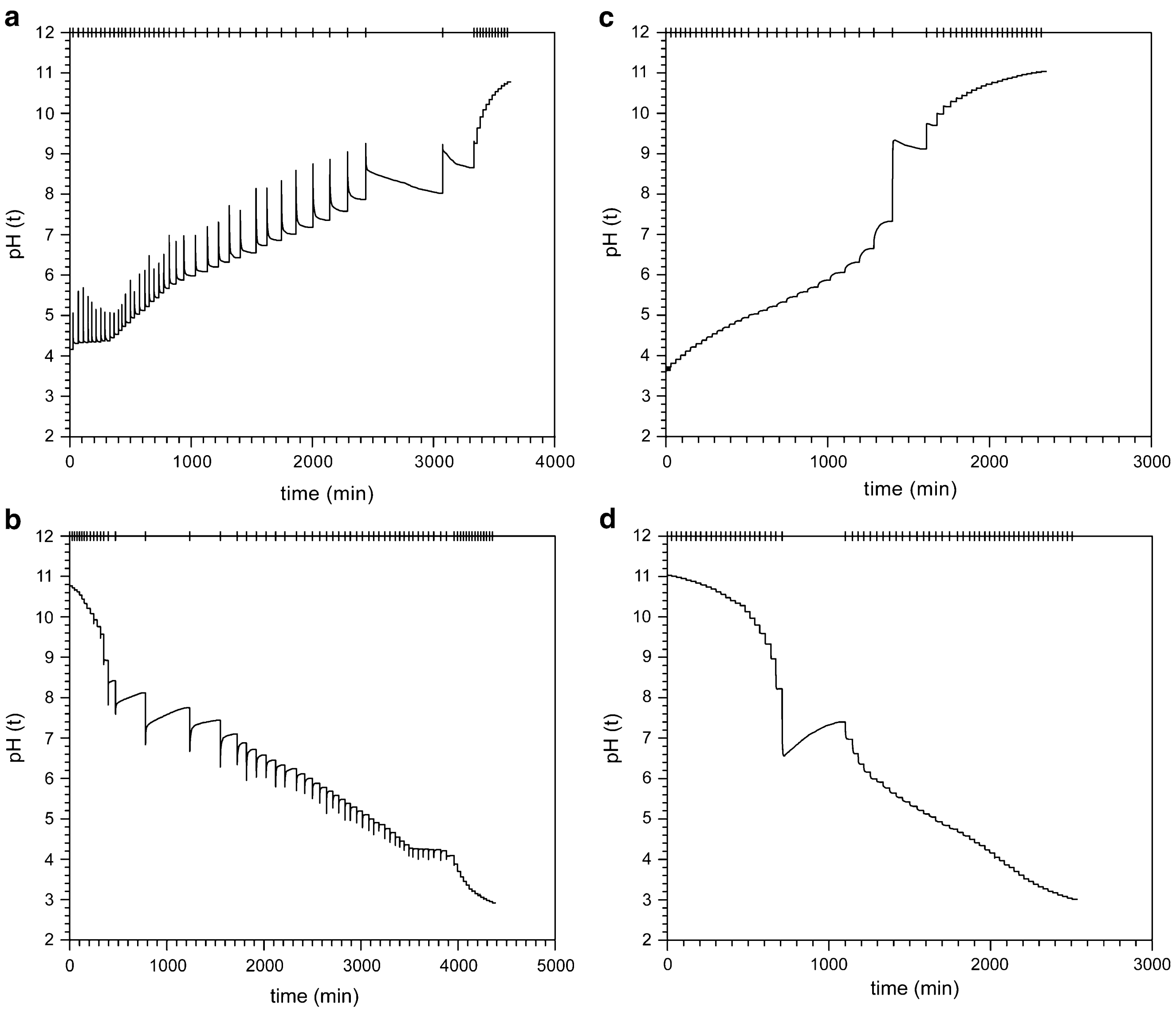

Fig. 1 Examples of pH change versus time during potentiometric titrations of EG with NaOH (**a**) and with HCl (**b**) as well as of CG with NaOH (**c**) and with HCl (**d**). *Hash marks* on the *top* of each *graph* show the time at which 0.05 ml of titrant was added. The sample concentration (C_p in moles of COOH per liter) was adjusted to 3.70±0.15 mmol/l based on the carboxyl content shown in Table 1. Titration conditions were: 25 °C, sample size=50 ml, and ionic strength=0.1 (NaCl)

titratable, as we have concluded in our previous study [16] performed with three random copolymer systems composed of AA and NIPA, i.e., a liner copolymer, nanogel, and bulk gel.

Comparison of titration curves

Now, we may compare the titration curves of EG with those of the other samples. Figure 3 shows plots of pH (=pH_{eq}) versus the degree of neutralization (α_n) for all the samples obtained at ionic strengths of 0.025 and 0.1 M. Note that an ionic strength of 0.025 M is enough to avoid any substantial change of ionic strength due to back titration by virtue of the generation of NaCl :$\sim$ COONa + HCl $\rightarrow$ $\sim$ COOH + NaCl. Plots for CG at ionic strength=0.025 M were little different from the coplotted data for the nanogel and copolymer [16], even though these later data were obtained in the absence of any added NaCl (ionic strength≈ 0; see Fig. 3a). Agreement among the titration data for these three samples was also observed at ionic strength= 0.1 M. These observations substantiate the suitability of our titration method.

Now looking at the results for the PAA-entrapped gel (EG), we find that the EG titration showed different features compared to the copolymer and copolymer gel results. The main differences were: (1) for $\alpha_n<0.25$, there is very little increase of pH, which starts out at a level greater than that of the copolymer and its gels; (2) a linear increase

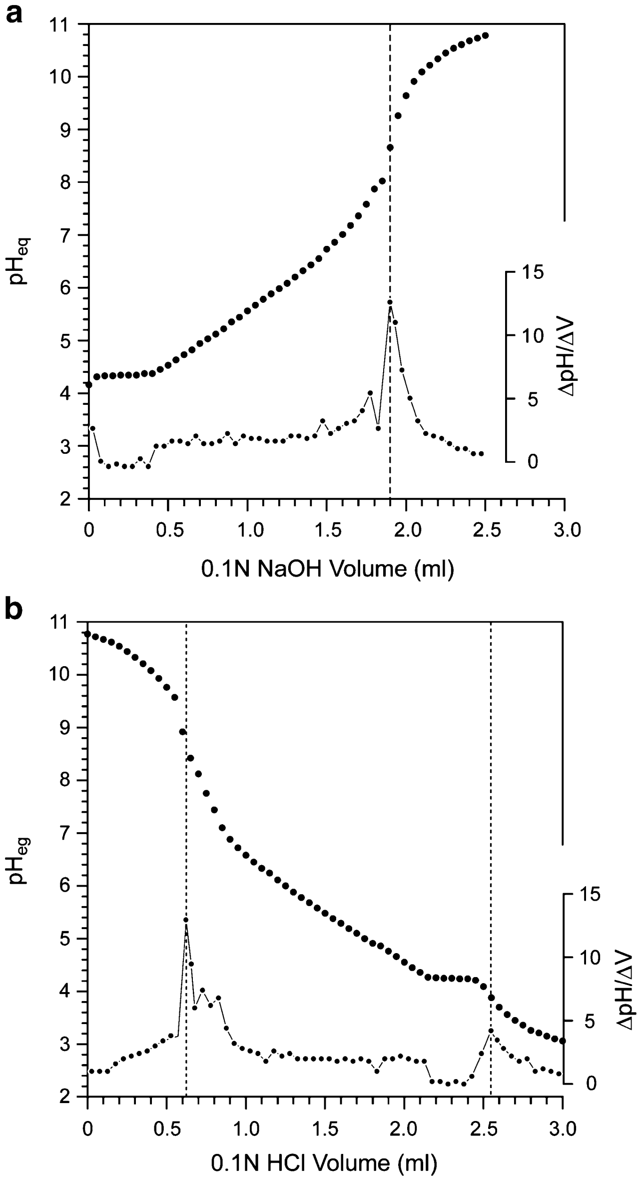

Fig. 2 Examples for endpoint determination in the titration of EG with NaOH (**a**) as well as with HCl (**b**). Equilibrium pH (pH$_{eq}$) in graphs **a** and **b** was obtained from Fig. 1a and b, respectively

of pH for α_n from 0.25 to 0.8; and (3) a slight effect of ionic strength, in which the pH decreases slightly with increasing the ionic strength. In addition, (4) there is generally no hysteresis between the forward titration with NaOH and the back titration with HCl. Although some disagreements between titrations with NaOH and HCl were observed at $\alpha_n<0.9$, this seemed to be due to very slow equilibration kinetics and also to a rapid pH change around the endpoint. Errors of this sort are difficult to avoid in potentiometric titrations of polyelectrolytes. However, we may generally say that for EG measurements, acid–base equilibrium (~COOH=COO$^-$+H$^+$) was completely established over the entire range of α_n.

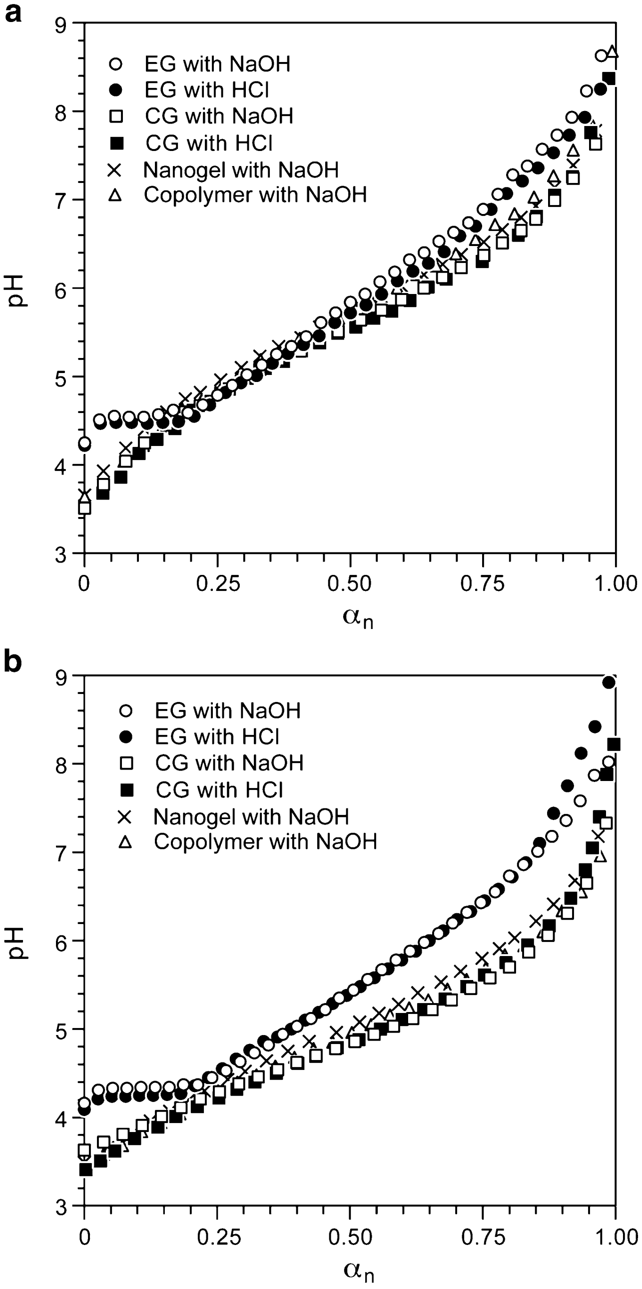

Fig. 3 Plots of equilibrium pH vs the degree of neutralization (α_n) at ionic strengths 0.025 M (**a**) and 0.1 M (**b**) for EG and CG. The titration of both gels with NaOH was followed by back titration with HCl, as shown in Fig. 1. Data for nanogel and copolymer samples listed in Table 1 are shown for comparison. Note that the nanogel and copolymer data in graph **a** were obtained in the absence of added NaCl (i.e., ionic strength≈0) in our previous study [16]

We now discuss the unique features of EG titration curves as mentioned in (1) to (4) above in terms of the distribution of COOH groups in the polymer network. In the copolymer or its gels, the AA monomer units have their COOH groups randomly distributed along a linear chain or within a cross-linked three-dimensional network of chains. From the results of these copolymer samples shown in

Fig. 3, it is clear that whether the COOH groups are bound to either the polymer chain or to its network (gel) has little influence on the potentiometric titration behavior. Then, it is reasonable to associate the different titration behavior of EG with the fact that PAA is entrapped within a NIPA network. As mentioned in the “Introduction,” PAA in an acidic pH range forms an interpolymer complex with PNIPA via hydrogen bonding [1–5]. All of our gel samples (including EG) used for titration with NaOH started completely in the acid form; therefore, under these conditions, the entrapped PAA chains could complex with the NIPA units in the network. The addition of NaOH should then break hydrogen bonds via dissociation of the COOH group. Such a process should be evident in the titration curves of EG at ionic strengths 0.025 and 0.1 M. Results for back titration with HCl can be interpreted as renewing the formation of hydrogen bonds between AA and NIPA segments in the EG network since we did not observe any hysteresis, i.e., the polymer system returned to its original state under acidic conditions.

Next, we discuss why the titration curve for EG exhibited little change for $\alpha_{\mathrm{n}}<0.25$ and a large linear increase over the α_{n} range of 0.25 to 0.8. The phenomenon of solution pH varying little upon addition of small amounts of acid or base is usually observed for buffer solutions. Then, a rapid change of pH is seen when the added amount of acid or base exceeds the solution’s buffering capacity. Such a buffering action can be usually observed around the half-neutralization point of a titration curve of weak acids with strong bases or weak bases with strong acids (see Fig. 4a). This was also the case when the copolymer or its gel having COOH groups was titrated with NaOH (see Fig. 3). A suppressed increase of pH with increasing α_{n} can be observed over the range of α_{n} from 0.3 to 0.7 for the copolymer and CG. Based on these observations, we hypothesize that, as shown in Fig. 4b, (1) microdomains composed of PAA chains surrounded by the NIPA network form within the EG via hydrogen bonding, (2) the addition of small amounts of NaOH increases the concentration of $\sim \mathrm{COO^{-}Na^{+}}$ within the domain, whereby (3) the domain, which then contains ~COOH and $\sim \mathrm{COO^{-}Na^{+}}$ groups, acts as a strong buffer like a concentrated $\mathrm{CH_3COO^{-}Na^{+}/CH_3COOH}$ solution. Moreover, (4) upon addition of more NaOH, over the buffering capacity, the titration curve then exhibits a linear increase due to breaking of hydrogen bonds with COOH groups. This interpretation makes it possible to rationalize

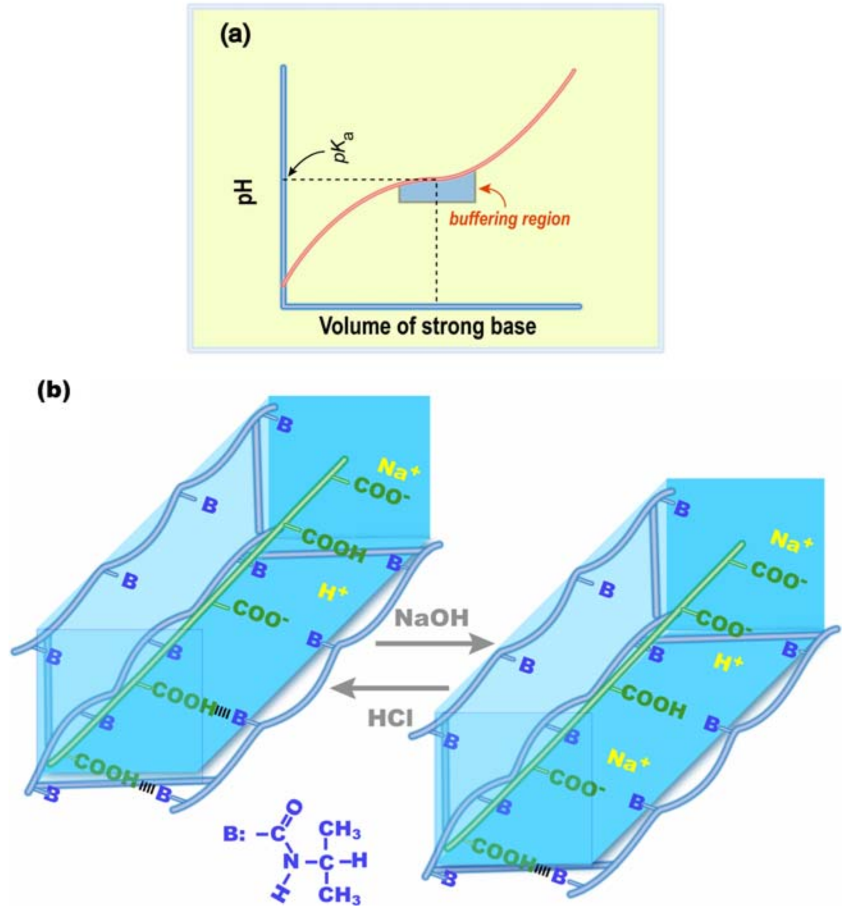

Fig. 4 Schematic illustration for understanding the pH change observed in the titration of EG at $\alpha_{\mathrm{n}}<0.25$. In **a**, typical titration curve of a weak acid (e.g., acetic acid) with a strong base (e.g., NaOH) is shown. Also shown in **b** is a part of the microdomain formed in the EG system

why a slight but significant pH jump appeared in the titration curve when only a minimal volume (0.05 ml) of NaOH was added.

Dependence of apparent dissociation constant on the degree of dissociation

Details of titration behavior can be studied by displaying how the apparent dissociation constant ($p\mathrm{K_a}$) varies with the degree of dissociation (α_d). $p\mathrm{K_a}$ can then be obtained from titration data using the following relations:

$$p\mathrm{K}_a = \mathrm{pH} - \log\left(\frac{\alpha_\mathrm{d}}{1-\alpha_\mathrm{d}}\right) \tag{1}$$

$$\alpha_\mathrm{d} = \alpha_\mathrm{n} + \left(\frac{C_{\mathrm{H}^+} - C_{\mathrm{OH}^-}}{C_\mathrm{p}}\right) \tag{2}$$

Here, C_{OH^+} and C_{OH^-} denote the molar concentrations of H^+ and OH^- ions, respectively. C_P is the molar concentration of COOH groups in the polymer sample. α_n is the degree of neutralization (see the previous section). Figure 5 shows the α_d dependence of $p\mathrm{K_a}$ obtained from the results in Fig. 3. Since we have found from Fig. 3 that there is no hysteresis between forward titration and back titration, only the results obtained by forward titration with NaOH are shown in Fig. 5. The main features of the α_d dependence of $p\mathrm{K_a}$ are as follows: (1) the entrapped gels (EG) showed a minimum value around $\alpha_\mathrm{d}\sim 0.25$, that is, a decrease of $p\mathrm{K_a}$ with increasing α_d from 0 to 0.25 and a linear increase of $p\mathrm{K_a}$ for α_d from 0.25 to 1.0. (2) CG exhibited only a monotonic increase of $p\mathrm{K_a}$ with α_d. (3) This feature of CG behavior was the same as that of the linear copolymer, as well as of the nanogel. (4) An increase of ionic strength leads to a decrease in $p\mathrm{K_a}$ for all the samples, but the magnitude of decrease of $p\mathrm{K_a}$ is smaller for EG than for the other samples.

It is well known that the pK_a is proportional to the free energy ($\Delta G(\alpha_\mathrm{d})$) required to remove a molar equivalent of protons at a given α_d and is written as

$$p\mathrm{K}_a = p\mathrm{K}^\mathrm{o} + 0.43\frac{\Delta G(\alpha_\mathrm{d})}{\mathbf{R}T} \tag{3}$$

where $p\mathrm{K}^\mathrm{o}$ denotes an intrinsic dissociation constant, which is a characteristic of an ionizing group under conditions where its interactions with other ionizing groups are absent. **R** is the gas constant, and T is the absolute temperature. One may understand the observed increase of $p\mathrm{K_a}$ as the result of interactions between H^+ and polymer-bound COO^- ions becoming stronger or at least more numerous, with increasing α_d. The nature of these interactions in polyelectrolyte systems is usually considered as electrostatic. When comparing results of EG and CG samples whose AA and NIPA compositions are nominally the same (see Table 1), we first notice that the values of $p\mathrm{K_a}$ for EG at a given α_d are generally greater than those for CG; in particular over the ranges where $\alpha_\mathrm{d}<0.2$ and $\alpha_\mathrm{d}>0.5$ and at both ionic strengths. This larger $p\mathrm{K_a}$ value means a greater $\Delta G(\alpha_\mathrm{d})$, which may be related to hydrogen bonding of PAA entrapped in the NIPA network. A similar mechanism has been reported to explain the titration data of poly(dicarboxylic acids) such as alternating copolymers of maleic acid (MA) with methyl vinyl ether or styrene [17], that is, very large $p\mathrm{K_a}$

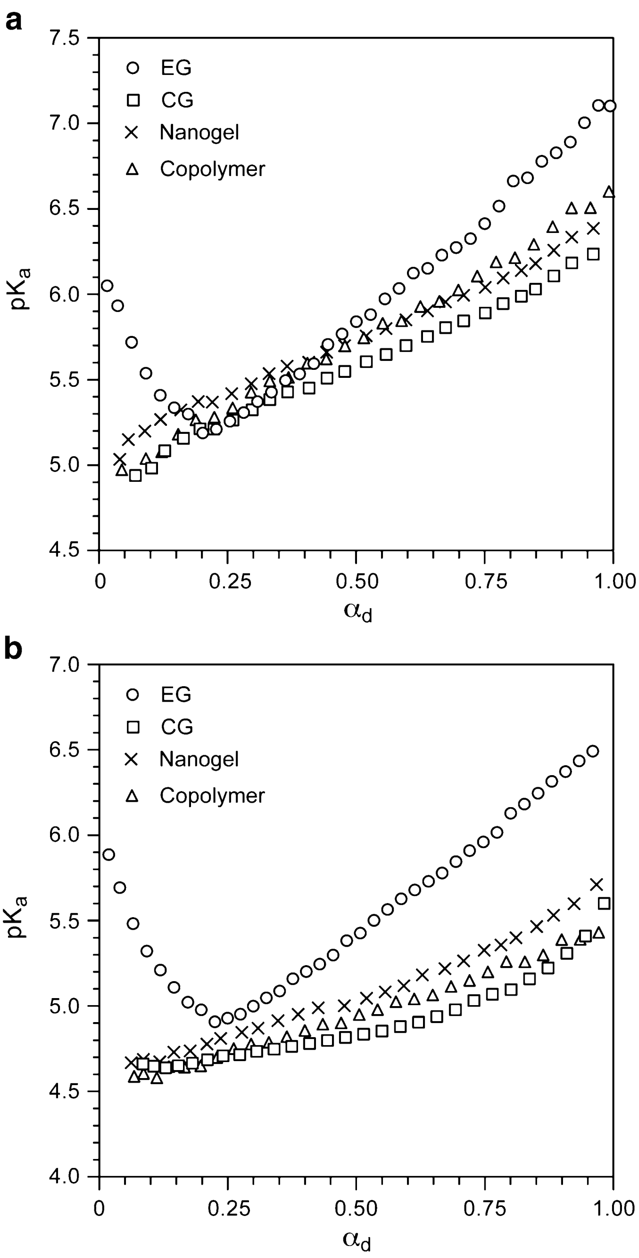

Fig. 5 Dependence of apparent dissociation constant ($p\mathrm{K_a}$) on the degree of dissociation (α_d) at ionic strengths of 0.025 M (**a**) and 0.1 M (**b**). Data obtained from titration curves with NaOH are shown in Fig. 1

values (5 to 9) were observed in the second half of the dissociation process (α_d>0.5) due to the formation of hydrogen bonds between the nearest neighboring ~COO$^-$ and ~COOH groups on MA segments. Such strong interaction between charged neighbors and uncharged groups along a polymer chain is referred to as "nearest-neighbor interaction", which was originally proposed by Katchalsky and his coworkers [18]. Thus, it is reasonable to interpret the decrease of pK$_a$ for α_d<0.25 in EG gels as meaning that the dissociation of H$^+$ ions becomes easier with increasing α_d due to partial breaking of hydrogen bonds. However, the dissociated H$^+$ ions still concentrate around the PAA polyion entrapped in the gel, resulting in only a small effect on the pH of the bulk solution outside the gel, as mentioned in the previous section (see Fig. 4).

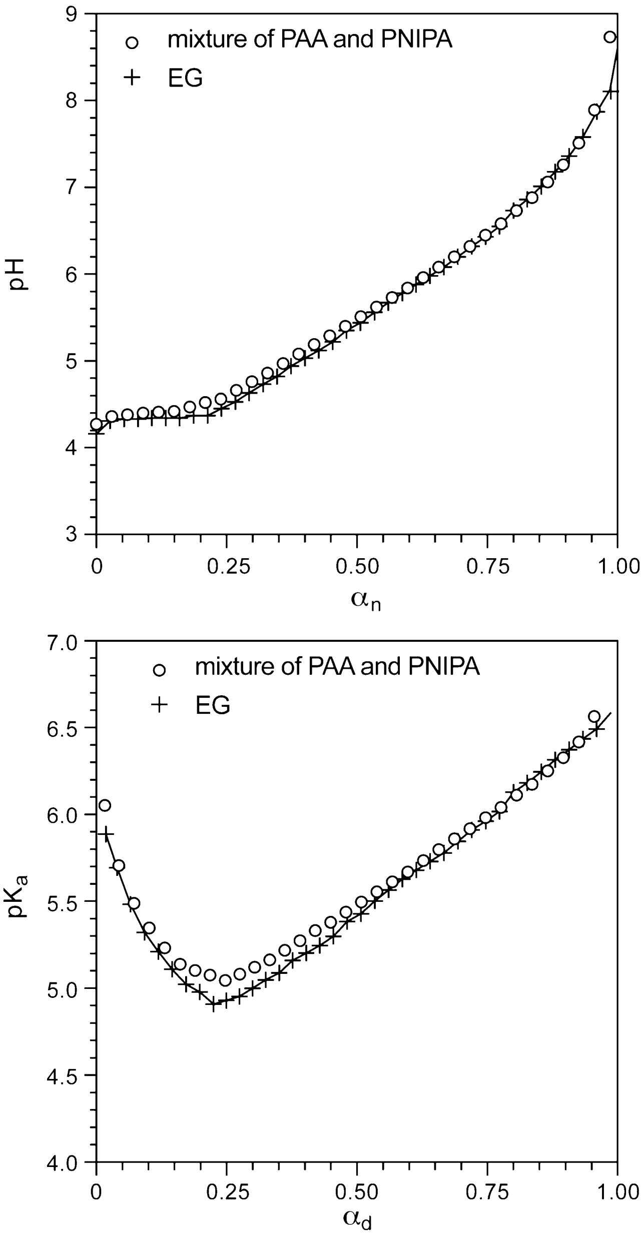

Fig. 6 Comparison of the titration curves of EG with those for an aqueous mixture of PAA and pure NIPA polymer

To support our argument further, back titration data for EG were compared with those of an aqueous mixture of PAA (as sodium salt) and PNIPA (AA to NIPA unit ratio~ 1:4). As shown in Fig. 6, good agreement was observed for both pH versus α_n and pK$_a$ versus α_d curves when data for the entrapped gel and mixed solution were compared. Back titration of the mixed solution with HCl led to a decrease of pH, until the system became turbid at α_n~0.27 (pH~4.66) due to the formation of large particles of an intrapolymer complex between PAA and NIPA polymers. The hydrodynamic radii (<R_h>) of these complexes were about 500 nm as estimated from dynamic light scattering (e.g., see [19] for details of the measurements). Thus, titrations for α_n< 0.27 were performed on an inhomogeneous system, somewhat similar to our suspension of finely divided EG gel particles here. The quantitative agreement observed in the data in Fig. 6 strongly suggests the same interaction in both the EG system and in the mixed PAA and NIPA polymer system, that is, pH-dependent complex formation can take place even in cross-linked gel systems in which PAA is entrapped within a NIPA network.

Conductometric titration

We performed conductometric titrations of CG and EG with NaOH in order to gain a better understanding of the pH

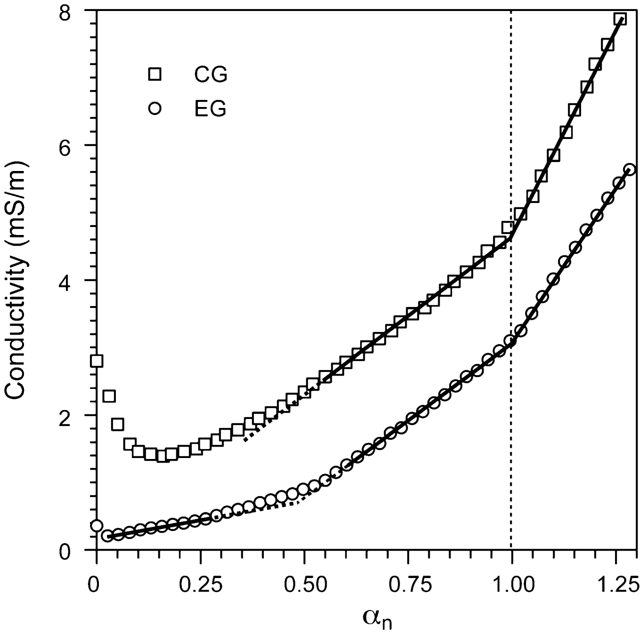

Fig. 7 Results of conductometric titration of CG and EG with NaOH in the absence of added NaCl. The concentrations of both titrant and sample are 20% of those used in potentiometric titrations

titration behavior of the EG sample. Figure 7 shows results of conductometric titrations for copolymer gel (CG) and entrapped gel (EG). As mentioned in the "Experimental" section, we used a more diluted suspension of the gel particles for conductometric titrations. However, we still cannot neglect the effect of gel particles between the platinum black electrodes in the conductance cell on the conductivity measured for the bulk solution. The conductivity data obtained are therefore somewhat compromised by the presence of these gel particles and we cannot expect the conductivity values to be quantitatively correct. Nevertheless, it is still possible to compare changes of conductivities with addition of NaOH. It is well known that the measured conductance of an electrolyte solution depends primarily on the concentration and types of ions. For example, when a strong polyacid such as poly(vinylsulfonic acid) is titrated with NaOH, the measured conductance decreases linearly until $\alpha_n=1.0$, then it shows a linear increase (i.e., a "V-shaped" curve with a break point at $\alpha_n=1.0$; e.g., see Fig. 9.3.2 in [20]). This feature is similar to ones seen in titration curves for low-molecular-weight electrolyte systems (e.g., HCl–NaOH system). The decrease in proton concentration for $\alpha_n<1.0$ and increase in hydroxyl ion concentration for $\alpha_n>1.0$ may be qualitatively understood as being due to the fact that both ions exhibit anomalously high mobilities in aqueous solutions and follow a specific transport mechanism [21]. In the case of weak polyacids such as PAA [20], the measured conductance shows a decrease at low α_n but a linear increase at $\alpha_n<0.4$, followed by a leveling off around $\alpha_n\sim0.5$, and again a linear increase for $\alpha_n>1.0$. These conductivity changes can be explained in terms of a decrease of the proton concentration in the initial titration stage, then an increase of the sodium ion concentration with increasing α_n up to $\alpha_n=1.0$, coupled with the facts that the mobility of a polyion is much lower than that of small ions (e.g., counterions), as well as that many counterions are localized around a polyion. Our results for CG and EG in Fig. 7 may be categorized as titrations of weak polyacids, particularly for the case of CG. Note that complete agreement cannot be expected between the titration profiles of weak polyacids and the corresponding gels because the latter substance contains all the polyion charges within their body. In the range of $\alpha_n<0.5$, however, differences were observed between CG and EG results. For the EG system, the slope of the linear portion of the conductivity curve showed a very slight increase around $\alpha_n\sim0.3$. Recall that below this degree of ionization there was a marked difference between the potentiometric titration results for EG and GC. The conductivity data suggest that the increase of free sodium ions per addition of NaOH titrant to the EG system is smaller for $\alpha_n<0.3$ than for $\alpha_n>0.3$, supporting our model shown in Fig. 4. A quantitative analysis of time-dependent conductivity change upon addition of NaOH has been attempted to study the complexation of PAA with neutral polymers as the Brønsted polybase (e.g., see [22]); however, there are remaining problems (in both experiment and theory) in the application of such a quantitative method to the present gel systems for the reason mentioned in the beginning of this section.

Conclusions

We studied the dissociation behavior of two polyelectrolyte gels, composed of macroscopic but finely divided NIPA networks, either copolymerized with AA or within which PAA was entrapped, using potentiometric titration with NaOH and back titration with HCl. The results obtained were compared with data for an un-cross-linked linear AA–NIPA copolymer and also for a nanogel consisting of a cross-linked AA–NIPA copolymer. The nominal compositions (AA–NIPA) of all these reference materials were similar to the present finely divided, macroscopic, irregularly sized and shaped CG. We determined that the titration curves of these macroscopic CG agreed well with those for comparable copolymers and nanogels. This showed that our titration method, which involved slow titrant addition rates and long equilibration times, was appropriate for studying the dissociation behaviors of polyelectrolyte gels. The two architecturally different gels, i.e., the CG and the EG, exhibited marked differences in their titration behavior. The CG behaved similar to a typical polycarboxylic acid, while the behavior of the EG was characterized by very little pH change at low degrees of neutralization ($\alpha_n<0.25$), followed by a more substantial pH change that was linear with α_n from 0.25 to 0.8. These features can be understood as the result of the formation of hydrogen bonds between entrapped PAA chains and the surrounding NIPA network.

Acknowledgment This work was supported in part by Grant-in-Aids for Scientific Research to E.K. from the Japan Society for the Promotion of Science (no. 18655089 and no. 20550183).

References

1. Iliopoulos E, Audebert R (1991) Macromolecules 24:2566
2. Staikos G, Bokias G, Karayanni K (1996) Polym Int 41:345
3. Staikos G, Karayanni K, Mylonas Y (1997) Macromol Chem Phys 198:2905
4. Vasile C, Bumbu GG, Mylonas Y, Cojocaru I, Staikos G (2003) Polym Int 52:1887
5. Burova TV, Grinberg NV, Grinberg VY, Kalinina EV, Lozinsky VI, Aseyev VO, Holappa S, Tenhu H, Khokhlov AR (2005) Macromolecules 38:1292
6. Ikawa T, Abe K, Honda K, Tsuchida E (1975) J Polym Sci Polym Chem Edn 13:1505
7. Osada Y (1979) J Polym Sci Polym Chem Edn 17:3485

8. Bokias G, Staikos G, Iliopoulos E, Audebert R (1994) Macromolecules 27:427
9. Kokufuta E, Wang B, Yoshida R, Khokhlov AR, Hirata M (1998) Macromolecules 31:6878
10. Ilmain F, Tanaka T, Kokufuta E (1991) Nature 349:400
11. Kokufuta E (2001) Phase transitions in polyelectrolyte gels. In: Radeva T (ed) Physical chemistry of polyelectrolytes. Surfactant science series. vol. 99. Marcel Dekker, New York, pp 591–685
12. Kokufuta E (2001) Langmuir 21:10004, (The Bob Rowell festschrift special issue); and other references therein
13. Nurkeeva ZS, Khutoryanskiy VV, Mun GA, Bitekenova AB, Kadlubowski S, Shilina YA, Ulanski P, Rosiak JM (2004) Colloid Surf A 236:141
14. Rafelski SM, Theriot JA (2004) Annual Review Biochem 73:209
15. Ramon O, Kesselman E, Berkovici R, Cohen Y, Paz Y (2001) J Polym Sci B Polym Phys 39:1665
16. Suzuki H, Wang B, Yoshida R, Kokufuta E (1999) Langmuir 15:4283
17. Kokufuta E (1980) Polymer 21:177
18. Katchalsky A, Mazur J, Spitnik P (1957) J Polym Sci 23:513
19. Kokufuta E, Ogawa K, Doi R, Kikuchi R, Farinato RS (2007) J Phys Chem B 111:8634
20. Rice SA, Nagasawa M (1961) Polyelectrolyte solutions. Academic, London, pp 450–452
21. Tuckerman ME, Marx D, Parrinello M (2002) Nature 417:925
22. Okubo T (1980) Biophys Chem 11:425