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Temperature dependence of density of polymer gels: Effects of ionizable groups in copoly(*N*-isopropylacrylamide/acrylic acid or sodium acrylate)–water systems

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Abstract

Effects of ionizable groups in hydrogels of copolymer networks on the volumetric contraction–expansion process were investigated. Polymer networks used were: copoly[*N*-isopropylacrylamide (NIPA)$(1-x)$/acrylic acid (HAc) or sodium acrylate (NaAc)(x)] with mole fraction of minor component (x) assuming 0.0114 and 0.0457. From the temperature (T) dependence of total volume of gels, densities of the polymer and solvent (water) components, and stoichiometry, we evaluated (1) the volume of gels occupied by a single mean polymeric residue and associated water molecules (expressed in units of nm^3), *mean* v_{sp}(gel), and (2) number of water molecules per single mean polymeric residue, *mean* N_s(gel), from near 273 K to 323 K. These quantities (1) and (2) listed above showed how acid and salt forms affect differently on volumetric changes of gels over 50 K. We developed an approach to evaluate volumetric changes of gels solely caused by a single polymeric residue of a minor component ($x < 0.05$) plus associated water by applying thermodynamic first-order perturbation theory. They are *specific* $v_{sp}(\text{gel})(T)$ for a single HAc or NaAc polymeric residue plus associated water and the corresponding *specific* $N_s(\text{gel})(T)$. *Specific* $v_{sp}(\text{gel})(\text{HAc or NaAc})(T)$ and the corresponding *specific* $N_s(\text{gel}(T))$ revealed specific characteristics in thermal behavior near their respective transition temperatures from the swollen to shrunken states. We found these thermal changes shown at the nano-scale match very well with specific changes in the molality(T) of both ionizable groups. In fact, these are directly triggered by varying contents of water in gels. Based on the understanding of dissociative equilibrium attained by ionizable groups, we successfully replaced Na^+ in hydrogels of copoly[NIPA$(1-x)$/NaAc(x)] ($x = 0.0457$) by hydrogen ions. Absence of Na^+ in treated hydrogels was experimentally verified by ^{23}Na NMR and Na atomic absorption flame photometry. Discontinuity in the volumetric contraction–expansion process from the swollen to shrunken states and *vice versa* was not observed in contradiction to the previous reports [Hirotsu S, Hirokawa Y, Tanaka T. J Chem Phys 1987;87:1392–5. Matsuo SE, Tanaka T. J Chem Phys 1988;89:1695–703.] obtained by the conventional swelling experiments.

Keywords: Hydrogel of thermo-sensitive copolymer; *N*-Isopropylacrylamide; Density of hydrogel

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1. Introduction

Polymer gels are made of polymer networks (solid substances at room temperature) and solvent(s) and thus are two-component systems. It has been known that some polymer gels exhibit thermally reversible volumetric contraction–expansion as temperature varies [1–13]. The primary focus of previous studies has been on the *relative* volumetric changes of gels in reference to a standard volume of gels made of the same chemical composition of polymer networks. These studies were conducted mostly by determining the diameter (d) of small cylindrically shaped gel pieces (hereafter referred to as *conventional* swelling experiment). Since neither the total mass of gels nor the mass of polymer networks were experimentally determined, these conventional swelling experiments do not elucidate the determining role of the polymer and solvent components during the thermally reversible volumetric contraction–expansion of gels.

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One of the authors (T.T.) recently developed a pycnometry method for *quantitative* determination of the total volume of gels, densities of the polymer and solvent components, and stoichiometry of polymer gels that are in equilibrium with excess solvent(s) [14,15]. In application of this method to poly(NIPA)–water system [14], we introduced a new quantity, $v_{sp}(\text{gel})(T)$, that represents the total volume occupied by a single polymeric residue and its associated solvent molecules [15] expressed in units of nm^3 at a given temperature, T. Once $v_{sp}(\text{gel})(T)$ values are determined, we can *directly* compare the absolute values of the volumes of various gels made of *different* kinds of polymeric residues and/or of *different* solvent(s) at the nano-scale [15]. We note in addition that $v_{sp}(\text{gel})(T)$ includes any voids that may exist in gels [16,17]. In a similar way, we also evaluated the number of solvent molecules per single polymeric residue, $N_s(\text{gel})(T)$ [14,15]. By applying these metrics to polymer gels made of poly[*N*-(1,3-dioxolan-2-ylmethyl)-*N*-methyl-acrylamide (DIOMMA)] and water, methanol, or ethanol, we clarified the underlying reversible thermo-physical mechanism between the hydrogel and gels made of alcohols [15,18].

In the present study, we investigated the volumetric contraction–expansion processes in hydrogels of poly(NIPA) containing ionizable groups via pycnometry [14,15]. The polymer components used were: (A) copoly[NIPA$(1-x)$/acrylic acid (HAc)(x), and (B) copoly[NIPA$(1-x)$/sodium acrylate (NaAc)(x)], where the mole fraction x assumed values, 0.0114 and 0.0457. Our focus is on quantitatively understanding how ionizable components in the polymer networks affect volumetric changes in gels, as well as distinguishing any difference between the acid and salt forms of the same acid, at the nano-scale. We have also developed a means to evaluate $v_{sp}(\text{gel})(T)$ solely associated with a minor polymer component (HAc or NaAc containing ionizable group) in the case of copolymers. The corresponding $N_s(\text{gel})$ values assigned to a specific minor polymer component have also been evaluated. These new quantities elucidate the characteristic behavior of ionizable groups and its relation to the thermal response of hydrogels. These quantities, $v_{sp}(\text{gel})(T)$ and $N_s(\text{gel})(T)$, for both the mean and specific polymeric residue, are important measures that facilitate engineering applications of polymers because they directly link numerous polymer systems at the nano-scale to various macroscopic properties. An example in application to polymer gels and nano-to-macroscales is given in our recent study [19].

A quantitative comparison of present and previous studies also considers whether discontinuous volumetric changes that were reported in previous, conventional swelling experiments [1,2] are directly caused by the ionizable groups or are extraneous to the hydrogels of the above copoly(NIPA/HAc or NaAc) networks.

2. Experimental

2.1. Synthesis of polymer networks and preparation of hydrogels

Synthesis of polymer gels of a series of copoly[NIPA$(1-x)$/NaAc(x)] (where x ranges from 0.0114 to 0.0457) [21] was carried out by following a method described previously [1–10]. Synthesis of the corresponding copoly[NIPA$(1-x)$/HAc(x)] was carried out in a somewhat different manner than previous practice. Aqueous solutions (O_2- and CO_2- free water) containing appropriate amounts of HAc, NIPA, *N*,*N*′-methylene-bisacrylamide (BIS), and $NaHSO_3$ (replacing TEMED) were further degassed by injecting N_2-gas for 20 min, adding an initiator (APS), and finally marked up to 100 ml. The total concentration of all monomers was kept constant at 700 mM. A multiple number of glass tubes, 5 mm i.d. and 30 mm long, were placed into pre-gel solutions. The solutions (with a stopper) were left at 277 K overnight for polymerization and gelation. After extracting the gel pieces from the glass tubes, they were thoroughly washed with large amount of "CO_2-free" water. Subsequently, the gel pieces were sliced into discs of approximately 5 mm thickness, and were then lyophilized by freeze-drying over 36 h [14,15].

2.2. Determination of density of polymer gels

By applying pycnometry [14,15] to the synthesized hydrogels, we determined the following: volume of gels $v(\text{gel})(T)$, densities of the polymer component $\rho_p(\text{gel})(T)$ and of the solvent component $\rho_s(\text{gel})(T)$, and the stoichiometry of gels $m_p/m(\text{gel})(T)$ (where m stands for mass) at temperatures, T, between 273 K and 323 K. Experiments were repeated three times at the respective temperature by using gels taken from three different batches. The amount of lyophilized gels m_p (in the first batch) consisted of approximately a dozen gel discs made of $x = 0.0114$ and 0.0457 HAc [20]; corresponding to 0.0513 and 0.0521 g, respectively. For the gels made of NaAc (in the first batch), the amounts were 0.0843 and 0.0727 g, respectively. A small tube filled with NaOH pellets was attached to the stem on the left-hand side of a U-shaped pycnometer (Section A in Fig. (1) in Ref. [14]) in order to prevent absorption of CO_2 gas from air. Experiments were repeated three times by using different batches of polymer networks.

2.3. Determination of sodium ions in gels and chemical composition of polymer networks

^{23}Na NMR spectra were obtained at two resonance frequencies in several unwashed and washed hydrogel pieces (made of D_2O) with $x = 0.0457$. Spectra were also obtained for the collected washing solutions. The ^{23}Na NMR frequencies were 95.33 MHz [21] at 8.1 Tesla and 105.758 MHz [22] at 9.2 Tesla. The corresponding pulse widths for the 90° pulses were 19.0 and 12.5 μs, respectively.

The amount of sodium contained in swollen hydrogel pieces and the collected washing solutions was also determined by using a Perkin–Elmer Model 3200 atomic absorption flame photometer. Calibration of the flame absorbance *versus* concentration was performed with aqueous solutions of sodium chloride at 589.0 nm. Swollen hydrogel pieces were digested by concentrated nitric acid and made up to a definite volume with water.

Chemical compositions (C, N, and H) of the lyophilized specimens of various copolymer networks were determined by using a Perkin–Elmer Model 2400 elemental analyzer. Each specimen was weighed as 2.00 ± 0.5 mg with accuracy of ± 10 μg. Five samples taken from three batches were used for the respective copolymer.

3. Results and discussion

3.1. Effect and role of ionizable groups on the volumetric contraction–expansion of polymer gels: difference between acid and salt forms

The chemical compositions of copoly[NIPA($1-x$)/HAc(x) or NaAc(x)] at both $x = 0.0114$ and 0.0457, as determined by elemental analyses, deviated very slightly from those calculated from pre-gel solutions. Thus, subtle differences do not hold significance in the following discussion.

Experimental values for $v(\text{gel})(T)$, $\rho_p(\text{gel})(T)$, $\rho_s(\text{gel})(T)$, and $m_p/m(\text{gel})(T)$ in the first batch at various temperatures are tabulated in Table 1. The temperature dependence of $v_{sp}(\text{gel})(T)$ evaluated from those quantities tabulated in Table 1 together with those obtained in other batches are shown in Fig. 1(a) for $x = 0.0114$ and in Fig. 1(b) for $x = 0.0457$, respectively [23]. In fact, $v_{sp}(\text{gel})(T)$ of poly(NIPA) [24] is also plotted in Fig. 1(a) and (b) as reference. We must note that $v_{sp}(\text{gel})(T)$ spans a range from few tenths to few nm^3.

A consequence of differences in the state of ionizable groups on the thermal behavior in volumetric contraction–expansion of hydrogels is represented by the temperature dependence of the first derivative of $v_{sp}(\text{gel})(T)$ with respective to T, i.e., $[\mathrm{d}v_{sp}(\text{gel})(T)/\mathrm{d}T]$. A careful comparison of $\mathrm{d}v_{sp}(\text{gel})(T)/\mathrm{d}T$ between the acid and salt forms in the gels with $x = 0.0457$ reveals the following: (1) both $\mathrm{d}v_{sp}(\text{gel})(T)/\mathrm{d}T$ fall in the same range from the lowest temperature to about 294 K; however, (2) $\mathrm{d}v_{sp}(\text{gel})(T)/\mathrm{d}T$ in the salt form at temperatures above 294 K is much greater than that in the acid form. This difference clearly leads to an increase in the transition temperature T_{tr} from the swollen to the shrunken state in fact, in increasing order from poly(NIPA) to the salt form and to the acid form of the ionizable groups (Fig. 1(a) and (b)). Furthermore, we can say that the $v_{sp}(\text{gel})(T)$ values for copoly[NIPA($1-x$)/HAc or NaAc(x)] are greater than those of poly(NIPA) when $x = 0.0457$. Subsequently, $N_s(\text{gel})(T)$ evaluated from the above four quantities as listed in Table 1 and also from those in other batches reflect the direct influence of the ionizable groups in a manner similar to the trend given for $v_{sp}(\text{gel})(T)$. For example, a greater number of $N_s(\text{gel})(T)$ in copoly gels, in contrast to poly(NIPA) gels, are clearly shown in Fig. 2(b) ($x = 0.0457$). Finally, in contrast to the swollen state, both $v_{sp}(\text{gel})(T)$ and $N_s(\text{gel})(T)$ in the shrunken state converge to nearly the same values in *all* gels.

The absolute values of both $v_{sp}(\text{gel})$ and $N_s(\text{gel})$ for polymer gels consisting of any *homo*-polymer networks and/or any single solvent component can be compared irrespective of the kind of polymer and/or solvent [14,15]. To evaluate $v_{sp}(\text{gel})$ and $N_s(\text{gel})$ for homo-polymer, we expressed $m_p =$ number of moles · formula mass (F.M.) of a polymeric residue [14,15]. As for copolymer made of the major (NIPA) and minor containing ionizable group, the *mean* F.M. (copolymer) is calculated by $[(1-x)\cdot \text{F.M. (major)} + x \cdot \text{F.M. (minor)}]$ where, x denotes the mole fraction of minor polymer component. Therefore, both $v_{sp}(\text{gel})$ and $N_s(\text{gel})$ evaluated should be regarded as values obtained in terms of *mean* field theory. Consequently, the direct effect on gel volume, solely caused by minor polymeric residue containing ionizable group, cannot be manifested by *mean* $v_{sp}(\text{gel})$.

Since all x values in *hetero*-copolymer systems are less than 0.05, the presence of minor component may be considered as small *perturbation* to the original NIPA hydrogel systems. By applying thermodynamic first-order perturbation theory [25], we developed an approach to evaluate the gel volume, $v_{sp}(\text{gel})$, consisting solely of a single residue of minor polymer component, plus associated water molecules. From the definition [14,15] of $v_{sp}(\text{gel})$ for hydrogel made of homo-polymer (NIPA) networks, we can calculate the total volume of hydrogels composed of any known number of NIPA polymeric residues. In hetero-polymers, the total volume of gels attributable to the NIPA residues plus associated water molecules can easily be evaluated by knowledge of the chemical composition of polymer network pieces (m_p). Here, this is noted as $v(\text{gel})^{\text{theor}}(\text{NIPA})(1-x)$. Since hydrogels of both homo- and hetero-polymer networks were synthesized by using the same total numbers of monomers (700 mM), the following relation must hold for hydrogels made of hetero-polymers [20]; that is,

$$\Delta v(\text{gel}) = v(\text{gel})^{\text{expt}}\{\text{poly}[\text{NIPA}(1-x)/\text{ionizable}(x)]\} - v(\text{gel})^{\text{theor}}(\text{NIPA})(1-x) \tag{1}$$

In Eq. (1), Δv denotes the difference in volume. It is logically appropriate to interpret $\Delta v(\text{gel})$ as arising exclusively from $v(\text{gel})[\text{ionizable}(x)]$. Hence we can evaluate the volume of gels exclusively occupied by a single polymeric residue (ionizable) plus the associated water molecules [*specific* $v_{sp}(\text{gel})(\text{ionizable})$]. Similarly, the *specific* $N_s(\text{gel})(\text{ionizable})$ can be evaluated [14,15]. In actual calculation, however, we note the subtle experimental differences seen in thermal characteristics among various systems as shown in Fig. 1(a) and (b). We note that the differences observed are much greater than the error associated with density measurements (see last paragraph in this section regarding the differences). Therefore, we did take experimental data points from smoothed curves drawn through small deviations for $v(\text{gel})(\text{T})$ in the evaluation of *specific* $v_{sp}(\text{gel})(\text{ionizable})$ and $N_s(\text{gel})(\text{ionizable})$. The temperature dependence of the results [*specific* $v_{sp}(\text{gel})(\text{ionizable})$] for hetero-polymer systems with $x = 0.0457$ are presented in Fig. 3(a). The corresponding results for *specific* $N_s(\text{gel})(\text{ionizable})$ are shown in Fig. 3(b).

Fig. 3(a) and (b) reveals distinct characteristics associated with the thermal behavior of respective polymeric (ionizable) residues, compared to much smaller values in the main polymeric (NIPA) residue. In the lower temperature region up to

Table 1
Representative experimental values for $v(\text{gel})(T)$, $\rho_p(\text{gel})(T)$, $\rho_s(\text{gel})$, and $m_p/m(\text{gel})$ for copoly[NIPA(1 − x)/HAc(x)] and copoly[NIPA(1 − x)/NaAc(x)] networks and water (first batch)

Acid form

$x = 0.0114$

T (°C)	v(gel) (cm^3)	ρ_p(gel) (g cm^{-3}) × 100	ρ_s(gel) (g cm^{-3})	m_p/m(gel)[a] (%)
7.9	2.175	2.359	0.9743	2.364
11.9	2.010	2.553	0.9980	2.494
15.9	1.614	3.179	1.006	3.064
20.4	1.611	3.056	1.008	2.942
22.9	1.646	3.117	0.9944	3.039
27.9	1.269	4.043	0.9949	3.905
30.9	1.062	4.829	0.9727	4.729
34.9	0.8117	6.324	1.002	5.936
35.4	0.6920	7.413	1.002	6.767
37.9	0.09679	53.00	0.8462	38.51
39.9	0.08407	61.02	1.075	36.22
41.9	0.05181	99.02	0.8311	54.37
43.7	0.06420	79.90	0.5716	58.30
47	0.08374	61.26	0.8156	42.89

$x = 0.0457$

T (°C)	v(gel) (cm^3)	ρ_p(gel) (g cm^{-3}) × 100	ρ_s(gel) (g cm^{-3})	m_p/m(gel)[b] (%)
5.0	2.250	2.316	1.006	2.251
10.0	2.028	2.568	0.9844	2.543
15.0	1.901	2.740	0.9947	2.681
20.1	1.764	2.953	0.9961	2.879
22.6	1.524	3.418	0.9957	3.319
27.6	1.473	3.538	0.9924	3.442
31.1	1.259	4.139	0.9694	4.094
34.1	1.035	5.032	0.9684	4.940
35.1	0.9216	5.653	0.9434	5.653
36.1	0.7931	6.569	0.9526	6.451
36.6	0.7186	7.251	0.9540	7.180
38.1	0.3493	14.92	0.9540	13.52
40.1	0.1950	26.71	0.8777	23.33
41.4	0.08467	61.53	0.5515	52.73
45.1	0.1733	30.06	0.8803	25.45

Salt form

$x = 0.0114$

T (°C)	v(gel) (cm^3)	ρ_p(gel) (g cm^{-3}) × 100)	ρ_s(gel) (g cm^{-3})	m_p/m(gel)[c] (%)
4.9	2.908	2.899	0.9806	2.872
7.9	2.615	3.223	0.9758	3.198
11.9	2.451	3.439	0.9823	3.383
15.9	2.206	3.822	0.9877	3.726
20.4	1.948	4.328	0.9823	4.220
22.9	1.790	4.711	1.001	4.496
27.9	1.467	5.745	1.014	5.361
30.9	1.353	6.230	1.012	5.799
34.4	0.6559	12.85	0.9992	11.40
35.4	0.1353	62.33	1.267	32.97
35.9	0.09917	85.01	1.229	40.88
37.9	0.1053	80.06	1.262	38.81
39.9	0.04475	188.4	2.275	45.3
41.9	0.1165	72.34	0.8933	44.75
43.7	0.05484	153.7	1.045	59.53
47.0	0.0411	205.2	1.772	53.66

(*continued*)

$x = 0.0457$

T (°C)	v(gel) (cm^3)	ρ_p(gel) (g cm^{-3}) × 100	ρ_s(gel) (g cm^{-3})	m_p/m(gel)[d] (%)
5.0	3.261	2.230	1.009	2.162
7.9	2.990	2.432	1.004	2.364
11.9	3.006	2.419	1.002	2.357
15.9	2.340	3.106	1.015	2.968
20.4	2.125	3.421	1.015	3.262
22.9	2.256	3.223	1.009	3.096
27.9	1.641	4.430	1.027	4.134
30.9	1.331	5.464	1.014	5.114
34.9	0.8882	8.185	0.9840	7.679
35.4	0.6418	11.33	1.033	9.878
35.9	0.4915	14.79	1.053	12.31
37.9	0.2129	34.15	1.085	23.94
39.9	0.09237	78.70	1.752	31.00
41.9	0.07194	101.1	1.495	40.34
43.7	0.02010	361.7	3.231	52.82

[a] $m_p = 0.0513$ g.
[b] $m_p = 0.0521$ g.
[c] $m_p = 0.0843$ g.
[d] $m_p = 0.0727$ g.

about 295 K, *specific* v_{sp}(gel) and N_s(gel) for all residues decrease linearly with differing slopes. From 295 K to (respective) T_{tr}, variations with increasing temperature reveal characteristics related to the chemical property of respective polymeric residues. Each ionizable group exhibits a sharp rise and fall within a narrow temperature range just below their respective T_{tr}. This is in contrast to a gradual decrease in both *specific* v_{sp}(gel) and N_s(gel) for poly(NIPA). These specific changes for the ionizable residues are directly related to changes in the degree of ionic dissociation of ionizable groups (see next paragraph).

Here, it is appropriate to consider all ionizable groups as acting independently in polymer gels for $x < 0.05$ and thus reaching a measure of chemical equilibriums as a whole. This equilibrium can be expressed as Eqs. (2) and (3) for the acid and salt form, respectively:

$$K_a = \left[-\text{RCOO}^-\right]\left[\text{H}^+\right]/\left[-\text{RCOOH}\right] \tag{2}$$

$$K = \left[-\text{RCOOH}\right]\left[\text{OH}^-\right]/\left[-\text{RCOO}^-\right] \tag{3}$$

Note that both $-\text{RCOOH}$ and $-\text{RCOO}^-$ structurally belong to the polymer components in gels and interact with water that contain either hydrogen or hydroxyl ion, and/or sodium cations.

Since experimental determination of the degree of ionization in polymer gel systems is hard to achieve at this present [26], we took a different approach to evaluate the effect of ionizable groups on the thermal behavior of polymer gels. We chose 2-methyl-propanoic acid (or the corresponding sodium salt), $CH_3{-}CH(COOH){-}CH_3$ or $CH_3{-}CH(COO^-Na^+){-}CH_3$ as our model system [27] to represent the polymeric residue containing ionizable group. We then calculate K ($=K_w/K_a$) from Eq. (3) by using the value of pK_a ($=4.84 \pm 0.2$) [28] for this acid and K_w [29]. Next, either $[\text{H}^+]$ (or

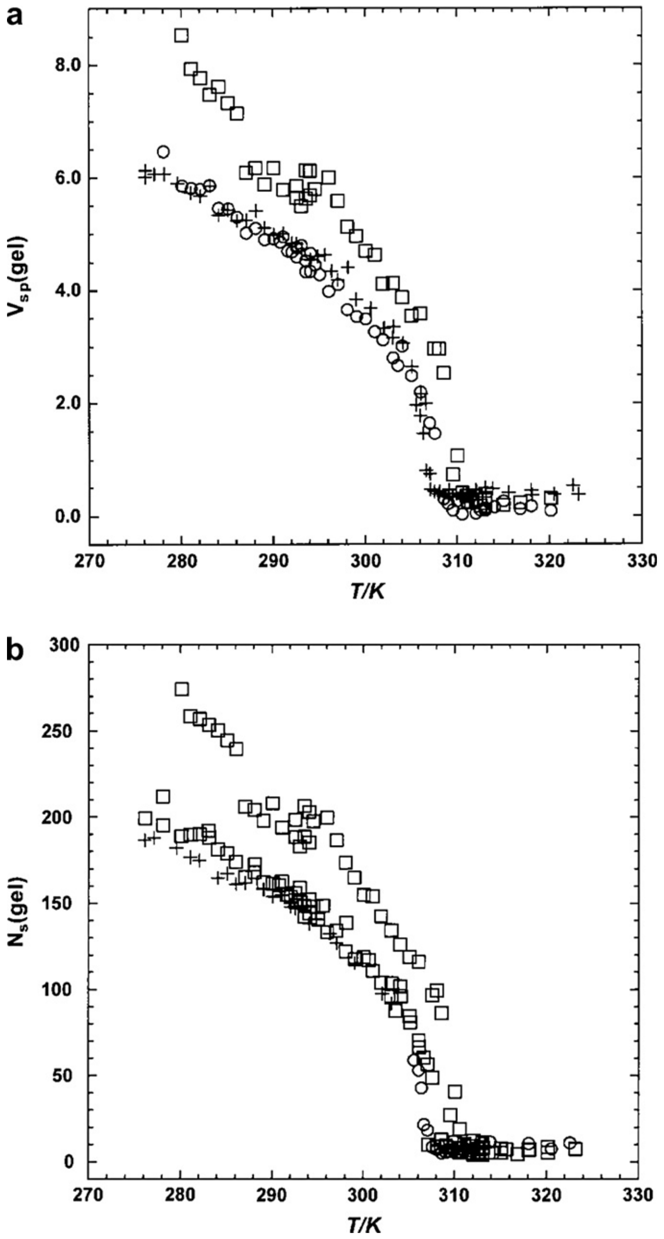

Fig. 1. Temperature dependences of *mean* v_{sp}(gel) (in units of nm^3) in hydrogels made of copoly[NIPA$(1-x)$/HAc(x)] (□) or copoly[NIPA$(1-x)$/NaAc(x)] (○): (a) $x = 0.0114$; and (b) $x = 0.0457$. The corresponding values in the hydrogels of poly(NIPA) [14,24] (+) are also shown as the reference.

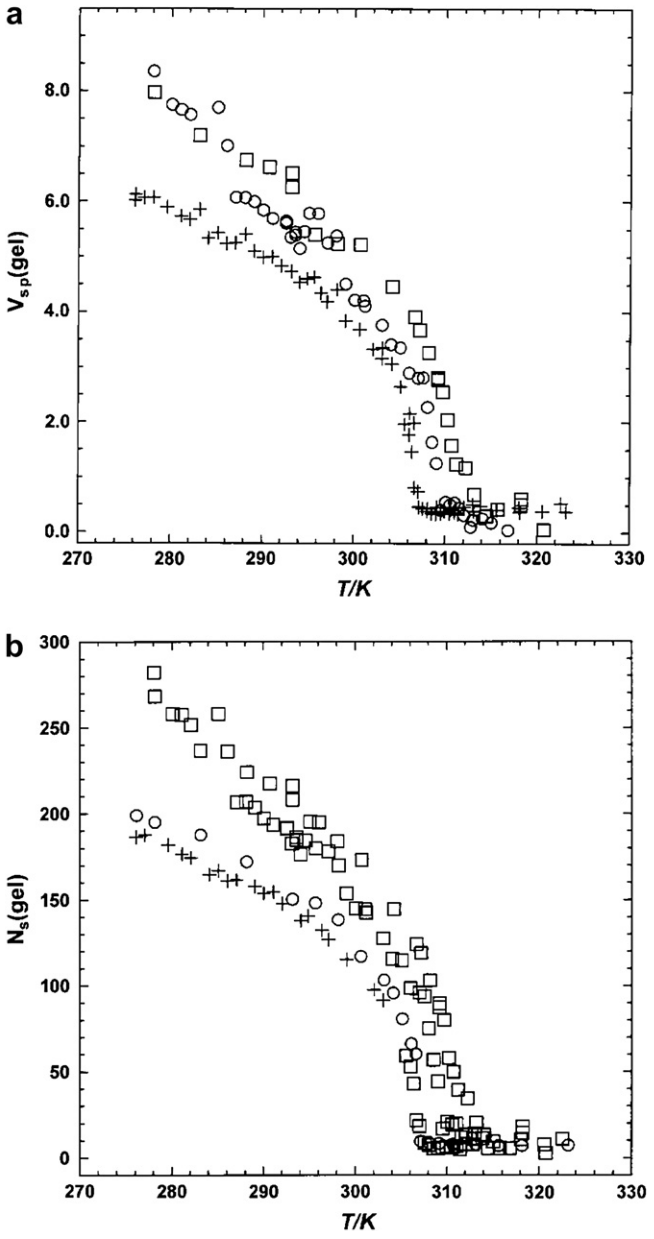

Fig. 2. Temperature dependences of *mean* N_s(gel) in hydrogels made of copoly[NIPA$(1-x)$/HAc(x)] (□) or copoly[NIPA$(1-x)$/NaAc(x)] (○) networks: (a) $x = 0.0114$; and (b) $x = 0.0457$. The corresponding values in the hydrogels of poly(NIPA) [14,24] (+) are also shown as the reference.

[$-$RCOO$^-$]) in Eq. (2) or [OH$^-$] [or $-$RCOOH] in Eq. (3) must be evaluated at various temperatures as the water content in gels changes with temperature. If we take the amount of HAc or NaAc used in the synthesis of gels as the original amount of $-$RCOOH for the acid form and $-$RCOO$^-$ for the salt form, respectively, we can express [H$^+$] or [OH$^-$] *versus* the amount of water in gels in units of molality (not in molarity) at various temperatures by solving quadratic equations describing the respective ionic dissociations. Since the difference [28] in pK_a values between 283 K and 298 K is less than 0.3%, the temperature dependence of K or K_a was not included in the calculation. Results thus obtained for [H$^+$] and [OH$^-$] are plotted as *pseudo pH* values in Fig. 4.

Gradual changes in the temperature dependence of *pseudo pH* throughout the swollen state clearly indicate progression in extent of dissociative ionization and ultimately become pronounced beyond the respective T_{tr} (Fig. 4). Namely, the solvent component in the acid form becomes more acidic, contrary to behavior in the salt form. Small and broad dips in *pseudo pH* values centered at 307 K (Fig. 4) indicate that delicate changes occur in the dissociative ionization of both ionizable groups. Sharp changes in *specific* v_{sp}(gel)(HAc or NaAc) and *specific* N_s(gel)(HAc or NaAc) within a few Kelvins around 307 K (Fig. 3(a) and (b)) exactly match with the behavior in *pseudo pH*. Solving the quadratic equations

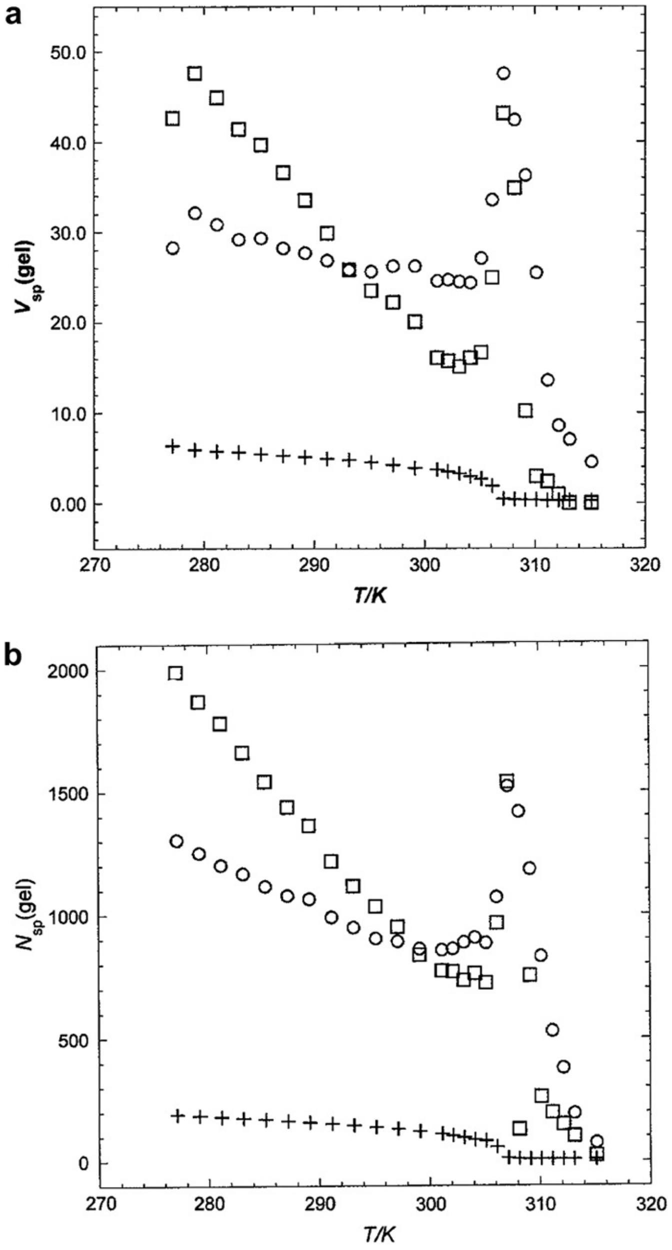

Fig. 3. Temperature dependences of: (a) *specific* V_{sp}(HAc), V_{sp}(NaAc) and V_{sp}(NIPA) (in units of nm^3) in hydrogels made of copoly[NIPA($1-x$)/HAc(x)] (□), copoly[NIPA($1-x$)/NaAc(x)] (○) where $x = 0.0457$, and poly-(NIPA) [14,24] (+); and (b) .the corresponding values of *specific* N_{sp}(gel).

reveals that greater decrements in the water content throughout contraction of gels are responsible for these changes. Thus, this may in fact be the origin of characteristic behavior of copolymer gels in volumetric contraction–expansion process. Exact correspondence of characteristic behavior substantiated at both molecular and nano-scale levels were also revealed in other experimental observations: (1) significant change in dynamics of water (HOD) in gels as determined by both self-diffusion coefficient [30] and proton NMR spin-lattice relaxation time (T_1) [31]; and (2) characteristic changes in the line-shape of proton NMR spectra for polymer networks [32]. When these results are integrated, a plausible mechanism for the volumetric contraction–expansion process in gels is suggested at the nano-scale. It is of interest to compare our results with recent developments obtained by other approaches [33–35].

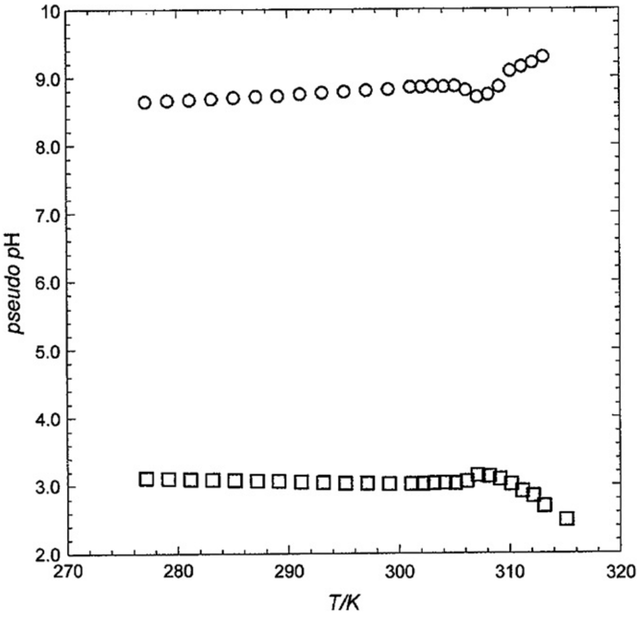

Fig. 4. Temperature dependences of concentration of hydrogen ions (in molality) (*pseudo pH*). In hydrogels made of copoly[NIPA($1-x$)/HAc(x)] (□) and in copoly[NIPA($1-x$)/NaAc(x)] (○) where $x = 0.0457$.

3.2. Comparison of the present results with previous experimental results obtained by the conventional swelling experiments [1,2]. Physical nature of the transition between the swollen and shrunken states

To compare the volumetric changes obtained here to conventional swelling experiments [1,2] we must express the gel volumes in compatible forms. In short, both methods must have the same reference. The major differences in conventional swelling experiments from the present method are as follows: (1) only *relative* swelling ratios with respect to a gel reference made of the same chemical compositions were obtained at various temperatures, [$(d(T)/d_0$] where d represents the diameter of a cylindrically shaped gel piece; (2) the states of newly synthesized, and unwashed gels were taken as the reference points [d_0] for the respective gels; (3) the mass of polymer networks in a gel piece was not determined; and (4) no experimental determination was attempted at temperatures lower than 293 K.

Re-evaluation of previous data [1] was carried out as follows. Since the diameter of a newly synthesized gel piece ($d_0 = 1.35$ mm) was chosen as the reference diameter, the reference volume of a gel piece, V_0(gel), can be calculated as $(\pi/4)(1.35)^3 = 1.93\ mm^3$ if we assume that the height of cylindrical gel piece equals its diameter d_0. Gel volumes at T, $v(\text{gel})(T) = V_0(\text{gel})[d(T)/d_0]^3$, can be calculated from the swelling ratio at T [$d(T)/d_0$] shown in Fig. 1 ([1]). Then, the relative change in gel volumes with varying temperature,

v(gel)(T)/v_0(gel), were calculated by choosing the gel volume obtained at 293 K as the new reference, v_0(gel)(new). A comparison of the previous and current results of v(gel)(T)/v_0(gel)(new) *versus* T for hydrogels of copoly[NIPA($1-x$)/HAc(x) or NaAc(x)] is shown in Fig. 5(a) and (b) for $x = 0.0114$ and $=0.0457$, respectively. Inspection of Fig. 5(a) reveals that previous data for gels with $x = 0.0114$ nearly follow an identical trend to the present for the salt form, without discontinuity. As for gels with $x = 0.0457$, the previous data below 299 K closely follow the current data in the salt form rather than those in the acid form. However, the previous data start to deviate significantly from the current data at temperatures above 299 K and, discontinuously approach the current values in the shrunken state of the salt form at above 312 K. In the present work on hydrogel samples of copoly[NIPA($1-x$)/HAc or NaAc(x)] shown in Fig. 5(a) and (b), we did not observe the reported discontinuous trend in gel volume. In comparison, it is highly likely that the gel samples used in previous studies [1,2] contained sodium ions contrary to their unsubstantiated statement (see more details in Appendix) that sodium ions were absent (experimental evidence was not presented). In fact, in the above assumption, they did not account for the contribution from the counter ions based on Flory's equation. Since the contribution of each term in Flory's equation was not presented [1,2], their theoretical evaluation with respect to the discontinuity is inconclusive. Altogether, without mechanistic arguments, it is difficult to accept any claims of discontinuous volumetric changes in gels containing ionizable groups greater than 4 mM, around the respective T_{tr}.

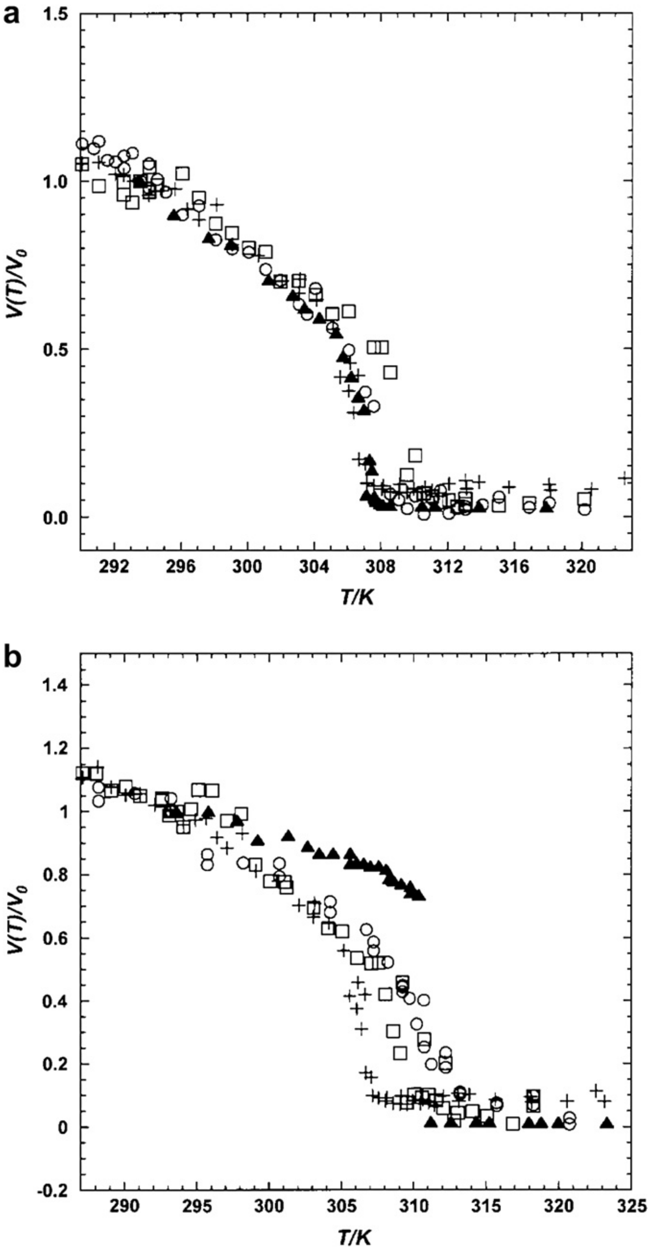

Fig. 5. Comparison of the relative $V(T)$ *versus* $V(T = 293\ \mathrm{K})$ in hydrogels of copoly[NIPA($1-x$)/HAc(x)] (□), copoly[NIPA($1-x$)/NaAc(x)] (○) and poly(NIPA) [14,24] (+) where: (a) $x = 0.0114$; (b) $x = 0.0457$ together with previous results [1,2] (▲).

It should be pointed out that the greatest volumetric expansions were actually observed from freshly synthesized gels [V_0(gel)(old)] to gels of any composition that attained equilibrium with excess water at 293 K (Fig. 1 [1,2]). Expansion in excess of one hundred was observed in gels with high contents of ionizable groups. Thus, the relative volumetric changes between 293 K and the respective T_{tr} look smaller than the above changes because of the choice of the reference [V_0(gel(old))]. It is apparent that the shortage of water (solvent) in pre-gel solutions was the major contributor to incomplete expansions of gel pieces that were freshly synthesized. These facts herein described suggest that we cannot compare the volumetric contraction–expansion of different gel systems in the same graph [15] because the physical state of freshly synthesized gels of different composition are not identical, even though the macroscopic volume [V_0(gel)(old)] are designed to be the same (use of capillary tubes of the same size). The synthetic condition (polymerization and gelation occurred within the same volume of capillary tubes) used in the previous studies [1,2] does not mean that the physical natural state of polymer gels made of different chemical constituents is identical. It is important to recognize that all measurements in the conventional swelling experiments, as well as the current pycnometric measurements, were all conducted with gels that were in equilibrium with excess water (solvent) except for newly synthesized gels. When one considers the past studies [1,2], the lack of consensus with respect to a reference has perhaps impeded investigation of the nature of the volumetric expansion–contraction processes of polymer gels.

Next, we examined the experimental practice used in the conventional swelling experiments in order to compare it to our approach. One of the most significant differences in experimental practice between this investigation and others [1–12] is the size of gel pieces. Here, both approaches used disc-shaped gel pieces. If we assume that the height of a gel piece is the same as the diameter, the volume of a gel piece [$(\pi/4)d^3$] used in the conventional swelling experiment is about 1.93 mm^3 in contrast to about 98.2 mm^3 in the present experiment. The ratio of volume of gel is about 1 *versus* 51. The ratio of diameter is 1 *versus* 3.67. Previous studies indicated that the rate of volumetric changes *versus* time is proportional to approximately the 1.8 power of the diameter of gel pieces [2,36,37]. This means that the rate of volumetric changes in the present experiment should take about 10 times longer than in the conventional swelling experiments if similarity in approach to thermal equilibrium is assumed. Since we left our samples at least three full days (72 h = 4,320 min) to attain equilibrium, the conventional experiments would approximately require at least 430 min (7.2 h) before a re-determination would take place. Since neither kinetic data nor observations made in the course of conducting the conventional swelling experiments were reported [1,2], it is not possible to evaluate how the volumetric contraction–expansion process progressed with time.

In contrast, our experimental results for the volumetric contraction–expansion processes occurring at the molecular level were substantiated as follows: (1) by means of proton NMR spectra of polymer networks [38], (2) by proton relaxation times of both polymer and solvent (water) components [31]; and (3) by determination of the self-diffusion coefficient of water [30] in samples consisting of sub-micron gel pieces (100 nm in diameter). These measurements clearly exhibit that gel pieces undergo some sort of the transient state (with rather long lifetime) before attaining new thermal equilibrium in transition from the swollen to shrunken states and *vice versa*. Macroscopically, transparent gel pieces (in swollen state) quickly become optically translucent (white) and subsequently require an extended period of time to reach a new thermodynamic state (shrunken) that is again transparent (homogeneous). Such observations were also not reported in previous works [1,2]. Both the short and long time span changes in optical properties are macroscopic manifestations of the transient/dynamic change in state (swollen to shrunken and *vice versa*) occurring at the nano-scale. It is evident that further studies, including a phenomenological model are needed to link the molecular level changes to changes in macroscopic properties.

4. Conclusion

The effect and roles of the ionizable groups on the thermal contraction–expansion processes in hydrogels of copoly[NIPA($1-x$)/Hac or NaAc(x)] were experimentally investigated. Evaluation of v_{sp}(gel) for the specific polymeric residues of a minor polymer component, as compared to the main NIPA polymer networks were achieved within the frameworks of thermodynamic first-order perturbation theory. The gel volumes, *specific* v_{sp}(gel) for both $-$RCOOH and $-COO^{-}Na^{+}$ groups thus evaluated exhibited characteristic behavior with temperature variation, particularly in a narrow temperature range near their respective transition temperature T_{tr}. The macroscopic changes in gel volume are attributable to delicate nano-scale level changes in the dissociative ionization of the respective ionizable groups and this change is attributed to thermal motions of water molecules in and out of gels. On the basis of this dissociative ionization, complete replacement of sodium ions by hydrogen ions in copoly[NIPA($1-x$)/NaAc(x)] was experimentally achieved.

Acknowledgments

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Appendix. Replacement of sodium cations in hydrogels of copoly[NIPA(1 − *x*)/NaAc(*x*)] by hydrogen ions

When Hirotsu et al. [1] performed the conventional swelling experiment on hydrogels made of a series of copoly [NIPA(700 mM − y)/acrylic acid (HAc)(y)], where y ranges from 1 to 128 mM in pre-gel solutions, they synthesized gels by using NaAc instead of HAc. Gels thus synthesized were treated as follows (quoting from Ref. [1]): "Gels were immersed in a large amount of water to wash away residual chemicals. Water was repeatedly changed until the diameter of the gel reaches an equilibrium value, which took approximately a week. During this process, *it may be safe to assume that all the sodium cations, originating from the sodium acrylate groups, are replaced by protons*. We have followed this procedure [1] to prepare copoly[NIPA($1-x$)/NaAc(x)] networks where x [20] were 0.0114 and 0.0457. Subsequently, the lyophilized polymer gels were obtained by the freeze-drying method.

Since the polymeric residue containing ionizable group, $-CH_2-CH(COO-Na^{+})-CH_2-$ can establish an equilibrium as shown by Eq. (3), this equilibrium can shift toward the r.h.s. when H^{+} (as HCl) is added to the system. Then, the system eventually becomes gels containing $-CH_2-CH(COOH)-CH_2-$ immersed in an aqueous solution of sodium chloride. This means all sodium cations can be removed from the polymer networks by adding for examples an acidic solution. This was actually carried out for the above samples. Fully swollen gel pieces made of copoly[NIPA($1-x$)/NaAc($x = 0.0457$)] were immersed in an aqueous solution of HCl (pH = 2) at room temperature for a week. After removing the supernatant liquid, new HCl solution (pH = 2) was added. This process was repeated three times, after which gels were washed with a large amount of water (H_2O) during several weeks in order to remove excess hydrogen ions. Finally, replacement of water (H_2O) in gel pieces was carried out by immersing gels in fresh D_2O several times. The fully deuterated specimens immersed in D_2O were used for acquiring ^{23}Na NMR signals. All supernatant liquids were collected and condensed by evaporation and was eventually made into a D_2O solution. A strong ^{23}Na NMR signal was obtained in a sample made of copoly[NIPA$(1-x)$/NaAc$(x=0.0457)$] prior to the above treatment with aqueous solution of HCl (1024 accumulations). In contrast, no ^{23}Na NMR signal was detected in the treated sample (32,768 accumulations). A strong ^{23}Na NMR signal was also obtained in the washed solution with the same acquisition condition as for non-treated sample. These measurements experimentally prove that all Na ions present in the original specimen were transferred to the acidic solution.

Additional experimental evidence of the presence and absence of sodium ions in the untreated and treated samples, respectively, was given by atomic absorption flame photometry (AA) for sodium. The amount of sodium found in the digested sample for dried gel pieces that weighed 38.9 mg of copoly[NIPA$(1-x)$/NaAc$(x=0.0457)$] was 2.11×10^{-5} mol. This is compared with the value (2.26×10^{-5} mol) calculated from the chemical composition of pre-gel solution. The average value for treated samples obtained by the same AA procedure was determined to be negligibly small.

Altogether, these two independent measurements prove the presence of sodium cations in the original (untreated) sample and virtually the complete absence of sodium cations in the treated samples. This provides strong evidence that the washing procedure used by Hirotsu et al. and others [2,8,10] actually did not replace sodium cations in the polymer gels by hydrogen ions.

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