Characteristic Role of Crosslinker on Thermally Induced Volumetric Contraction–Expansion Processes in Poly (*N*-isopropylacrylamide) Networks and Water Systems

Tadashi Tokuhiro,[1] Akira T. Tokuhiro[2]

[1]*Department of Chemistry, Missouri University of Science and Technology, Rolla, Missouri 65409*
[2]*Department of Mechanical Engineering, University of Idaho, Idaho Falls, Idaho 83402-1575*

ABSTRACT: In this work, the degree of crosslinking on the volumetric contraction–expansion processes of hydrogels made of poly(*N*-isopropylacrylamide) (NIPA) (initial amount: C_m) with varied amount (z) of crosslinking agent methylene-bis-acrylamide (BIS) in reference to most commonly used NIPA gel that was synthesized with $C_m = 700$ mM and $z = 8.6$ mM was investigated by applying our recently developed pycnometry. We focused on characteristic role of four polymeric NIPA residues directly bonded to a single BIS molecule by evaluating the total volume of gels per four NIPA residues directly bonded to a BIS molecule, plus associated water [v_{sp}(gel)(NIPA)$_{bonded}$)(T)], and the corresponding number of water molecules per four NIPA residues [N_s(gel)(NIPA)$_{bonded}$)(T)]. We elucidated how these quantities characteristically contribute to changes in the volumetric contraction–expansion processes of hydrogels. A comparison of these quantities with the corresponding quantities for (NIPA)$_{unbonded}$ residues clearly revealed a significant structural difference between (NIPA)$_{bonded}$ and (NIPA)$_{unbonded}$. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 3177–3184, 2009

Key words: *N*-isopropylacrylamide; density of hydrogel; crosslinking; gels; phase behavior; stimuli-sensitive polymers; structure-property relations

INTRODUCTION

Polymer gels are made of polymer networks (solid substances at room temperature) and solvent(s). They are two-component systems and form a phase different from phases of the respective components. When polymer gels are present in excess solvent(s), some polymer gels exhibit thermally reversible volumetric contraction–expansion as temperature varies.[1–13] Previous studies of these thermally sensitive polymer gels have primarily focused 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 absolute values of total volume [v(gel)] and mass [m(gel)] of gels nor the mass of polymer networks (m_p) 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.

One of the authors (T.T.) recently developed a pycnometric method for quantitative determination of the total volume of gels [v(gel)(T)], densities of polymer component [ρ_p(gel)(T)] and of solvent component [ρ_s(gel)(T) = m_s(gel)(T)/v(gel)(T)], and stoichiometry of polymer gels [m_p/m(gel)(T)] that are in equilibrium with excess solvent(s).[14,15] In application of this method to poly(*N*-isopropylacrylamide) (NIPA)–water system,[14] we introduced a new quantity, v_{sp}(gel)(T), that represents the total volume occupied by one single polymeric residue and its associated solvent molecules[15] expressed in units of nm^3 at a given temperature, T. Once v_{sp}(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 nanoscale.[15] In a similar way, we also evaluated the number of solvent molecules per single polymeric residue, N_s(gel)(T).[14,15] We note in addition that v_{sp}(gel)(T) includes any voids that may exist in gels.[16,17] By applying these metrics to polymer gels made of poly[*N*-(1,3-dioxolan-2-ylmethyl)-*N*-methyl-acrylamide] and water, methanol, or ethanol, we clarified the underlying reversed thermophysical mechanism between the hydrogel and gels made of alcohols.[15]

When we evaluated v_{sp}(gel)(T) and N_s(gel)(T) for hydrogels of (A) copoly[NIPA(1-x)/acrylic acid (x)(AAc)] [mean formula mass (FM)] and (B)

copoly[NIPA(1-x)/sodium acrylate (x)(NaAc)] (mean FM), where the mol fraction x is assumed at 0.0114 and 0.0457, we had to use mean FM of NIPA and AAc or NaAc according to the chemical composition of polymer networks. This approach clarified[18] that varying states of ionizable groups on temperature produced direct effects on volumetric contraction–expansion processes in the aforementioned hydrogels of copolymer networks differing from that in hydrogel of poly(NIPA). We were able to reveal further details at nanoscale by developing a means to evaluate gel volumes solely occupied by a single minor copolymer component, i.e., AAc or NaAc residue and associated water molecules, $v_{sp}(gel)(T)$(AAc or NaAc), by applying thermodynamic perturbation theory [here, the hydrogel of poly(NIPA) is an unperturbed system. When a small perturbation (ionizable group) is added to the hydrogel, the first-order perturbation effect on the unperturbed system can be evaluated by using the state function for the unperturbed state. Thus, $v(gel)$ [ionizable(x)] is the volume attributable to all ionizable groups].[19] These results revealed characteristic changes in the volumetric contraction–expansion processes near their swollen–shrunken state transitions.[18]

In this study, we investigated the volumetric contraction–expansion processes via pycnometry.[14,15] Our focus is on quantitatively understanding how the degree of crosslinking in the polymer networks affects on volumetric changes in gels at the nanoscale. We approached the problem from a different perspective than the work by Bromberg et al.[23] and Takata et al.[21] We investigated the thermal behavior of polymer networks as follows: (1) $v_{sp}(gel)(T)$ and the corresponding $N_s(gel)$ of four NIPA residues directly bonded to a BIS molecule and associated water molecules and (2) $v_{sp}(gel)(T)$ (mean FM) and $N_s(gel)(T)$(mean FM). These quantities revealed the characteristic role of crosslinkers and its relation to the thermal response of hydrogels. These quantities are important measures that facilitate potential engineering applications of polymer gels; that is, they directly link numerous polymer systems at the nanoscale to various macroscopic properties. An example of the application of polymer gels at nano-to-macroscales was presented with respect to the remediation of low-level radioactive particulate species in a recent study.[22]

MATERIALS AND METHODS

Synthesis of hydrogels consisted of poly(NIPA) with varied contents of crosslinker and chemical composition

Synthesis of polymer gels of a series of poly[NIPA (700 mM)/BIS(z)] with varied number of moles (z) of BIS and constant 700 mM NIPA was carried out by making a pregel aqueous solution as follows[1–13]:

1.9803 g (1/40 of 700 mM) recrystallized NIPA, 0.1 mL (5 wt % aqueous solution) N,N,N′,N′-tetramethylethylenediamine and 33.1 mg (1/40 of 8.6 mM) of BIS were dissolved in about 20 mL CO_2/O_2-free deionized water. The solution was bubbled with O_2-free N_2 gas for 20 min by adding 10 mg ammonium persulfate (chain reaction initiator) and marked up to 25 mL. After quickly transferring the solution into a test tube, it was bubbled with N_2 gas again for a few minutes. Multiple numbers of glass tubes (5 mm o.d., 30-mm long) were placed into the solution, and then it (with stopper) was left in a refrigerator (277 K) overnight for polymerization and gelation. Gel pieces thus formed were extracted from the glass tubes and were transferred in CO_2/O_2-free deionized water contained in a 500-mL plastic bottle. Water was replaced at least once in a day with fresh water over a week. Subsequently, the gel pieces were sliced into discs of ∼ 5 mm in thickness and were then lyophilized by freeze-drying method under vacuum ($<10^{-4}$ mmHg) over 36 h.[14,15,18]

Five samples taken from various portions of lyophilized gels were weighed at 2.00 ± 1.00 mg within ±10 μg accuracy and subjected for elemental analysis. Atomic weight percentages of carbon, hydrogen, and nitrogen were determined by using Perkin Elmer Model 2400 Elemental Analyzer.

Determination of density of polymer gels

By applying pycnometric method[14,15,18] to the hydrogels, we have determined $v(gel)(T)$, $\rho_p(gel)(T)$, $\rho_s(gel)(T)$, and $m_p/m(gel)(T)$ at temperatures (T) between near 273 K and close to 320 K. Here, m stands for mass (in gram). The amounts of lyophilized gels (polymer networks) (m_p) used in the determination of gels made with z = 20.0, 40.0, and 60.0 mM were 0.1194, 0.1185, and 0.1081 ($\times 1.0^{-3}$ kg), respectively. To avoid any absorption of CO_2 gas from the air, a small tube filled with NaOH pellets was attached to the stem on the left-hand side of an U-shaped pycnometer (section A in Fig. 1 of Ref. 14).

Experimental results and discussion

A comparison of chemical compositions of 4 poly (NIPA) with varied BIS contents are shown in Table I. It indicates that agreement between values found and calculated falls within the experimental limits of the method, and therefore, the following calculations were carried out by assuming the concentration of NIPA and BIS in pregel solutions.

Some representative values from the experiment for $v(gel)(T)$, $\rho_p(gel)(T)$, $\rho_s(gel)(T)$, and $m_p/m(gel)(T)$ at various temperatures are tabulated in Table II. The corresponding values for $v_{sp}(gel)(T)$(mean FM) and $N_s(T)$(mean FM) were evaluated from the four

TABLE I
Atomic Weight Percent of Hydrogen, Carbon, and Nitrogen in Poly(NIPA) Networks

z (mMol)	X	Theoretical H	Experimental H	Theoretical C	Experimental C	Theoretical N	Experimental N
8.6	0.0121	9.744	9.73	63.53	62.94	12.47	12.38
20	0.0278	9.676	9.54	63.34	61.55	12.59	12.28
40	0.0541	9.563	10.06	63.02	62.49	12.79	12.24
60	0.079	9.457	9.92	62.49	63.57	12.98	12.78

C_m is kept at 700 mM for all gels.

quantities under the assumption that mean FM can be obtained from the respective chemical compositions, i.e., mean FM = {FM (NIPA) × [700/(700 + z)] + FM (BIS) × [z/(700 + z)]}, where FM (NIPA) =

TABLE II
Some Representatives of the Experimental Values for v(gel)(T), ρ_p(gel)(T), ρ_s(gel)(T), and m_p/m(gel) for Poly[NIPA(700 mM)/BIS(Y)] Networks and Water

T (K)	v(gel) (m × 10^{-2})^3	ρ_p(gel) (kg m^{-3}) × 10^3	ρ_s(gel) (kg m^{-3}) × 10^3	m_p/m (gel) (%)
$Y = 20.0$ mM[a]				
277.2	2.550	4.682	1.061	4.227
280.7	2.477	4.821	1.076	4.228
284.2	2.227	5.362	1.078	4.738
287.1	2.138	5.584	1.080	4.914
290.7	2.043	5.845	1.080	5.1335
294.2	1.711	6.979	1.105	5.940
296.5	1.857	6.428	1.057	5.733
299.7	1.700	7.024	0.9512	6.876
303.7	1.330	8.980	0.9203	8.891
305.7	1.048	11.389	0.8666	11.61
308.2	0.2918	40.91	0.5712	41.73
$Y = 40.0$ mM[b]				
277.2	2.261	5.241	0.9480	5.239
280.7	2.080	5.697	0.9874	5.454
284.2	1.922	6.166	0.9820	5.908
287.1	1.876	6.318	0.9927	5.983
290.7	1.918	6.520	0.9786	6.246
294.2	1.572	7.539	0.9731	7.190
296.5	1.542	7.684	0.9418	7.543
299.7	1.432	8.273	0.9067	8.362
303.7	0.9894	11.98	0.9062	11.67
305.7	0.7823	15.15	0.8726	14.79
308.2	0.3031	39.09	0.7093	35.53
$Y = 60.0$ mM[c]				
277.2	1.826	5.919	0.8725	6.353
280.7	1.930	5.601	0.8878	5.934
284.2	1.686	6.412	0.8724	6.846
287.1	1.642	6.584	0.8643	7.079
290.7	1.625	6.652	0.8654	7.138
294.2	1.234	8.758	0.9030	8.841
296.5	1.307	8.268	0.8308	9.051
299.7	1.256	8.604	0.8498	9.194
303.7	0.8208	13.17	0.8086	14.01
305.7	0.6677	16.19	0.7084	18.60
308.2	0.3298	32.78	0.3775	46.47

[a] $m_p = 119.4$ mg.
[b] $m_p = 118.5$ mg.
[c] $m_p = 108.1$ mg.

0.1132 kg and FM (BIS) = 0.11542 kg. The temperature dependence of v_{sp}(gel)(T)(mean FM) and N_s(gel)(mean FM) thus evaluated in the four gels are shown in Figures 1 and 2, respectively. We can clearly see that there is no change in the transition temperature (T_{tr}) between the swollen and shrunken states with varying z values. Further, both v_{sp}(gel)(mean FM)(T) and N_s(gel)(mean FM)(T) in the shrunken state seem to converge to nearly the same value in all these gels. Figure 1 shows that v_{sp}(gel)(T)(mean FM) significantly decreases in gels with $z = 20$ mM from those with $z = 8.6$ mM; however, only a marginal decrease was observed with further increase in z. In comparison to v_{sp}(gel)(T)(mean FM), the corresponding decrease in N_s(T)(mean FM) exhibited rather systematic decrease with increasing z. This decrease in N_s(T)(mean FM) substantially contributes to a decrease in v_{sp}(gel)(mean FM)(T) even though we observed that (1) a large difference in the slope of the temperature
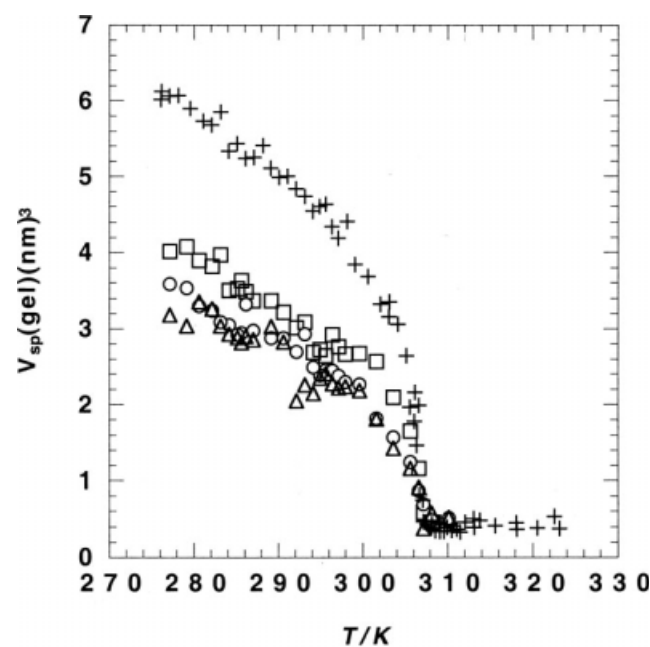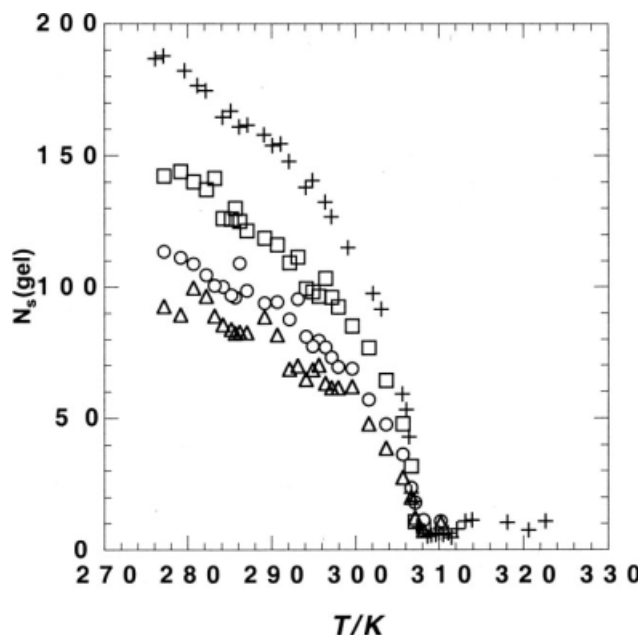

Figure 1 Dependence of total gel volume [v_{sp}(gel)(mean FM)] on temperature and content of crosslinker (z mol) in poly(N-isopropylacrylamide) networks–water systems; plus: $z = 8.6$; square: $z = 20.0$; circle: $z = 40.0$; triangle: $z = 60.0$.

Figure 2 Dependence of specific number of water for NIPA residue [N_s(gel)(mean FM)] on temperature and content of crosslinker (z mol) in poly(N-isopropylacrylamide) networks–water systems; plus: $z = 8.6$; square: $z = 20.0$; circle: $z = 40.0$; triangle: $z = 60.0$.

dependence of v_{sp}(gel)(T)(mean FM) {$d[(v_{sp}$(gel)(T)(mean FM)]$/dT$]} between $z = 8.6$ and $z = 20$; and (2) all slopes are much steeper in the temperature range between 304 and 307 K. This indicates that overall the contraction of gel volume and loss of water are accelerated in the noted temperature range.

The influence of the degree of crosslinking on gel volumes beyond the results of v_{sp}(gel)(T)(mean FM) and N_s(gel)(T)(mean FM) were considered by specifically focusing on volumetric changes assigned to four NIPA residues that are directly bonded to a single BIS molecule and associated water molecules, that is v_{sp}(gel)(NIPA)$_{bonded}$ (expressed in units of nm^3). The content of z versus the number of moles of NIPA residue in all gels examined are less than 8%, and thus, as we have done in the previous study,[18] the application of first-order thermodynamic perturbation theory[19] to all systems examined seems to be acceptable in the evaluation of v_{sp}(gel)(NIPA)$_{bonded}$. However, the four (NIPA)$_{bonded}$ are characteristically different from the rest of NIPA residues since their configurations in polymer chain are more restricted than the rest. Therefore, we treated the four NIPA directly bonded to a BIS molecule, together with a single BIS, as one separate entity as a perturber to the reference system (gels with $z = z_0 = 8.6$). We begin with this understanding as our working postulate in the following analysis of experimental data. Since the number of (NIPA)$_{bonded} = 4z$, the

number of NIPA residues [(NIPA)$_{unbonded}$] that are not directly bonded to a BIS become $700 - 4z$. The calculated values for two different kinds of NIPA residues in four hydrogels are listed as Columns A_k(mol) and B_k(mol) in Table III, respectively. As the reference system also contains z_0 BIS and $4z_0$ in (NIPA)$_{bonded}$ molecules, we can only evaluate, in principle, changes in gel volume caused by the differences between other z and z_0. The value shown in column $\Delta A/B_0$ in Table III indicates that only the gel with $z = 20$ mM can appropriately be treated by perturbation theory with respect to the reference system (z_0). Thus, we treated all the gel systems containing higher z values (>20 mM) with respect to systems containing the nearest smaller z value as the reference. The reference system shifts successively starting from the original z_0. For example, gels with $z = 20$ mM is the reference system for gels with $z = 40$ mM and so on. We must note that accuracy of perturbation treatment gradually decreases in gels with higher z values as indicated in column $\Delta A/B_{k-1}$. The ratio of the number of moles of (NIPA)$_{unbonded}$ versus (NIPA)$_{bonded}$ shown as column B_k/A_k in Table III indicates the following: about 5 (=19.3/4) (NIPA)$_{unbonded}$ residues are present between each (NIPA)$_{bonded}$ in the reference system ($z_0 = 8.6$) and reduces to only 2(=7.75/4) (NIPA)$_{unbonded}$ in gels with $z = 20$. The ratio continues to decrease to merely 1 (=3.38/4) (NIPA)$_{unbonded}$ residue, and then to less than 1/2 (=1.92/4) for gels with $z = 40$ and 60, respectively. This means that the gel with $z = 60$ contains only one (NIPA)$_{unbonded}$ or zero residue between two (NIPA)$_{bonded}$ residues.

First-order thermodynamic perturbation theory[19] was applied in a successive way as described in the preceding paragraph by exactly following our previous procedure.[18] Namely, v(gel)[(NIPA)$_{unbonded}$]^{theor}(T)(Z_k) in units of (m $\times 10^{-2}$)^3 was calculated by taking v_{sp}(gel)(z_{k-1})(T)(mean FM) in units of nm^3 in the reference system (z_{k-1}) and then applying the difference in stoichiometry contained in z and m_p values between these two systems. Then, v(gel)[(NIPA)$_{bonded}$](T)(z_k) [in units of (m $\times 10^{-2}$)^3] was evaluated by using the following relationship:

$$\Delta[v(\text{gel})(T)(Z_k)][\text{in units of } (\text{m} \times 10^{-2})^3]$$
$$= [v(\text{gel})^{expt}(T)(Z_k)] - [v(\text{gel})(\text{NIPA}_{unbonded})^{theor}(T)(Z_k)]$$

where Δ stands for the difference, and v(gel)^{expt}(T)(Z_k) are taken from the second column of Table II. It is logical to consider $\Delta[v(\text{gel})(T)](z)_k$) as originating solely from all residues consisting of one BIS and four (NIPA)$_{bonded}$ molecules plus associated water molecules. To obtain v_{sp}(gel)[(NIPA)$_{bonded}$)(T)(z_k)] in units of nm^3, we need to use the mean FM

TABLE III
Number of Moles of Polymeric NIPA Residues Directly Bonded to BIS and Unbonded to BIS

System (k)	z (mM)	A_k (mol)[a](NIPA)$_{bonded}$	B_k (mol)[b](NIPA)$_{unbonded}$	$\Delta A^c(\times 100)$	$\Delta A/B_{k-1} \times (100)$	$(\Delta A/B_0)$	B_k/A_k	N'
0	8.6	34.4	665.6	–	–	–	19.3	19.3[d]
1	20.0	80.0	620.0	+45.6	6.8	(6.8)	7.75	8.29
2	40.0	160.0	540.0	+80.0	12.9	(18.9)	3.38	4.15
3	60.0	240.0	460.0	+80.0	14.8	(30.9)	1.92	2.76

[a] $4z$
[b] $700 - 4z$.
[c] $\Delta A = A_k - A_{k-1}$.
[d] Set equal to the B_k/B_k value, where $k = 0$.
$k = 0$: $A(A + B) = 2.41 \times 10^4$ in units of 3.602×10^{-13} nm^6, where Avogadro constant $= 6.022 \times 10^{23}$/mol.

of the residue consisting of one BIS and four NIPA molecules (0.12139 kg).

The results for Δv_{sp}(gel)[(NIPA)$_{bonded}$)$(T)(Z_k)$] in gels with $z = 20$, 40, and 60 mM with respect to $z = 8.6$, 20, and 40 mM, respectively, are presented in Figure 3. The corresponding plots for ΔN_s(gel) [(NIPA)$_{bonded}$)$(T)(Z_k)$] are also shown in Figure 4. The positive and negative signs in both Figures 3 and 4 imply increase and decrease in the respective quantity. To make a comparison to v_{sp}(gel)(T)(mean FM), Δv_{sp}(gel)[(NIPA)$_{bonded}$)$(T)(Z_k)$] in Figure 3 are adjusted to the volume occupied by one-fourth of one BIS, four NIPA, and associated water molecules. The same adjustment was also applied to ΔN_s(gel) [(NIPA)$_{bonded}$)](T) (Fig. 4). Changes in Δv_{sp}(gel) [(NIPA)$_{bonded}$)](T) when compared with v_{sp}(gel) (T)(mean FM) revealed that addition of BIS that is

bonded to four NIPA caused a significant decrease in gel volume and number of water for gels with $z = 20$. In fact, Δv_{sp}(gel)[(NIPA)$_{bonded}$)](T) in the swollen state remained virtually constant at those for $z = 40$ in spite of the doubling in amount of BIS. Further addition of BIS to $z = 60$ did not affect the general trend seen in gels of $z = 40$ with a slight increase in the absolute quantity. These results are compatible with arguments for changes in the B_k/A_k ratio in the preceding paragraph. Namely, addition of BIS is gradually depleting NIPA residues that were previously accounted for v_{sp}(gel)[(NIPA)$_{unbonded}$)](T). The corresponding changes seen ΔN_s(gel)[(NIPA)$_{bonded}$)] (T) in gels with $z = 40$ and 60 indicate somewhat more delicate changes with increasing temperature as follows: (1) a further decrease observed at lower temperature in gels with $z = 40$ gradually levels off
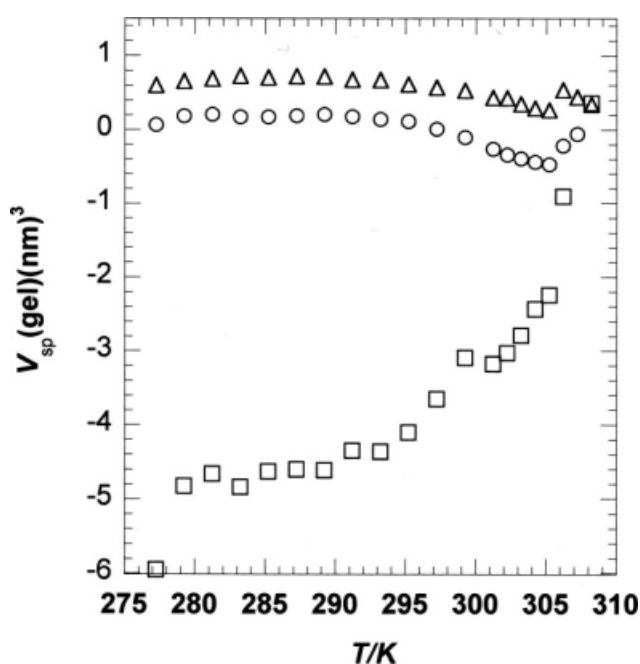

Figure 3 Dependence of specific gel volume for (NIPA)-$_{bonded}$ [v_{sp}(gel)(NIPA)$_{bonded}$] on temperature and content of crosslinker (z mol) in poly(N-isopropylacrylamide) networks–water systems; square: $z = 20.0$; circle: $z = 40.0$; triangle: $z = 60.0$.
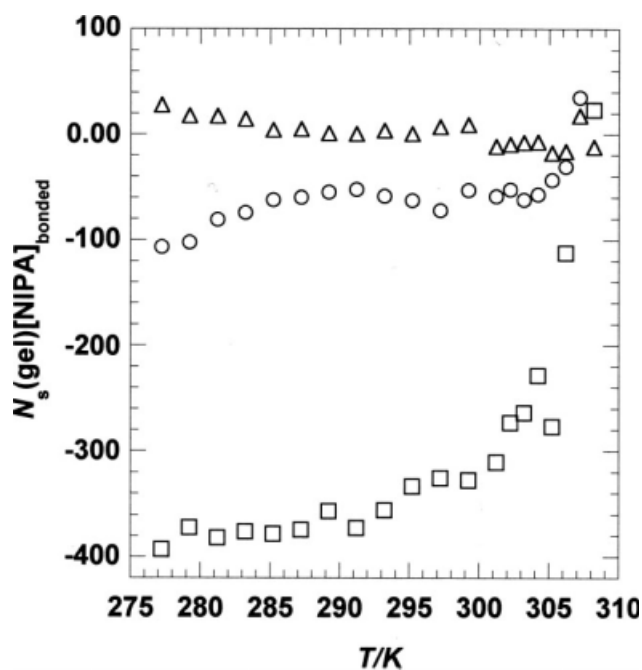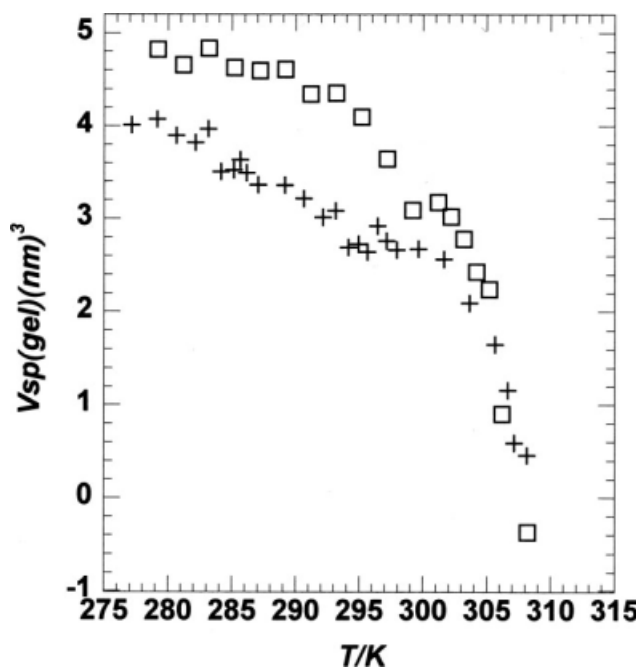
Figure 4 Dependence of specific number of water molecules for (NIPA)$_{bonded}$ [N_s(gel))(NIPA)$_{bonded}$] on temperature and content of crosslinker (z mol) in poly(N-isopropylacrylamide) networks–water systems; square: $z = 20.0$; circle: $z = 40.0$; triangle: $z = 60.0$.

Figure 5 Temperature dependence of specific gel volumes for $(NIPA)_{bonded}$ and $(NIPA)_{unbonded}$ in poly(N-isopropylacrylamide) networks–water systems; square: $(NIPA)_{bonded}$; plus: $(NIPA)_{unbonded}$.

toward higher temperature; and (2) an opposite trend in gels with $z = 60$ versus $z = 40$ is noticeable at lower temperature, although it also levels off at higher temperature.

Altogether, temperature dependency of both $\Delta v_{sp}(gel)[(NIPA)_{bonded})](T)$ and $\Delta N_s(gel)[(NIPA)_{bonded})]$ (T) strongly related to how many $(NIPA)_{unbonded}$ residues are still available for bonding to BIS molecule for generating new $(NIPA)_{bonded}$ residues. Substantial changes observed in the temperature dependence of the slope of $v_{sp}(gel)(NIPA)(T)$(mean FM) and of $N_s(gel)(T)$(mean FM) at temperatures between 304 and 307 K, noted in the preceding section, are now clearly indicated by the reversal of temperature dependence of $\Delta v_{sp}(gel)[(NIPA)_{bonded})](T)$ and of $\Delta N_s(gel)[(NIPA)_{bonded})]$ in gels with $z = 40$ and 60. Since T_{tr} is reported to be 306.6 ± 0.5 K[1–13] in gels with $z = 8.6$ mM and is the same for others with varied z values, the sudden directional changes must be related to that conformational changes in polymer networks took place from expanded (swollen state) to possibly compact form (shrunken state). This kind of sudden changes were also observed in temperature dependence of the self-diffusion coefficient and of proton NMR spin-lattice relaxation time of water as well as proton NMR spectra of polymer networks.[23] These facts suggest that both gel volumes and number of water molecules approach a possible lower limit in the swollen state.

In consideration of the discussion just described, $\Delta v_{sp}(gel)[(NIPA)_{bonded})](T)$ determined in gels with z

$= 20$ may represent the gel volume for $(NIPA)_{bonded})$ (T), irrespective of z values when $(NIPA)_{unbounded}$ are freely available. Then, $v_{sp}(gel)[(NIPA)_{bonded})](T)$ may directly be compared with $v_{sp}(gel)[(NIPA)_{unbonded})]$ (T) obtained from the reference ($z = 8.6$). Such a comparison is presented in Figure 5 together with the corresponding comparison for number of water molecules, $N_s(gel)$ (Fig. 6). Both $v_{sp}(gel)[(NIPA)_{bonded})]$ (T) and $v_{sp}(gel)[(NIPA)_{unbonded})](T)$ have nearly the same values from 304 K to T_{tr}. This is also true for $N_s(gel)[(NIPA)_{bonded})](T)$ and $N_s(gel)$ $[(NIPA)_{unbonded})](T)$. A completely reversed trend in temperature dependence of gel volume versus number of water molecules at temperatures below about 300 K reveals that a significant structural difference exists between gel($(NIPA)_{bonded})(T)$ and gel $(NIPA)_{unbonded})(T)$. In fact, the gel($(NIPA)_{bonded})(T)$'s volume contracts gradually from 278 to 300 K by about 40%; however, the associated water molecule loss is merely 15–20% over the same temperature range. On the other hand, contraction of gel($(NIPA)_{unbonded})(T)$ primarily arises from the loss of water molecules by about 40% in the same temperature range. The corresponding contraction of volume is about 25%. These facts indicate that water molecules associated with $(NIPA)_{bonded}$ are more tightly bound than those associated with $(NIPA)_{unbonded}$.

Bromberg et al. studied[20] dependency of swelling on the length of subchain in hydrogels made of a series of different amounts, c_m, (0.5–10.1 mM) of N,N'-dimethyl-acrylamide and varied amount, c_{xl}, (1.9–33
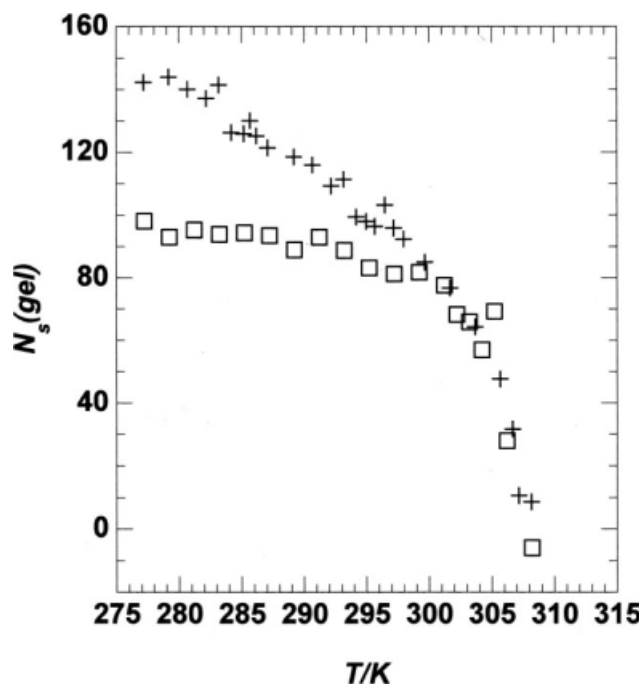
Figure 6 Temperature dependence of specific numbers of water molecules for $(NIPA)_{bonded}$ and $(NIPA)_{unbonded}$ in poly(N-isopropylacrylamide) networks–water systems.

mM) of crosslinker (BIS) at 20°C. They found that the swelling of the gel is related to the average length of a subchain N. Here, N is defined as the number of monomeric links along the polymer between two connected crosslinks. After a rather lengthy theoretical development in describing how polymer networks emerged in the course of synthesis of polymer gels, they theoretically arrived at eq. (1) for N,

$$N \approx 1/[L^6 c_{xl}(c_m + c_{xl})]. \qquad (1)$$

Here, L is the microscopic length scale associated with a single monomer size. They used equilibrium swelling data to relate N to c_m and c_{xl}, since it is extremely cumbersome to directly measure N. The original definition of N was formulated on the basis of hypothetical two crosslinks and one-dimensional monomeric links between them to derive N. Here, we view the one crosslinker (BIS) as a link to four one-dimensional monomeric (main) links. Thus, the crosslinker plays the central role for developing four monomeric links. As such, we view NIPA monomers directly bonded to a BIS molecule [expressed as (NIPA)$_{\text{bonded}}$] as a part of c_{xl} and subtract from c_m (see Table III). By adopting our notation and chemical composition of gels, we have rewritten eq. (1) as eq. (1′),

$$N' = 1/[L^6 A(B + A)], \qquad (1')$$

where A and B are given in the 3rd and 4th columns of Table III. If we equate N' to B/A given in the eighth column of Table III, L in eq. (1′) becomes an unknown quantity to be determined. By setting N' = 19.3 for gel with z = 8.6 mM, L was determined to be 1.22 nm. We then obtained values of N' for other gels with z = 20.0, 40.0, and 60.0 mM by using this L value. The results are listed in Table III. These values should be compared with B_k/A_k listed in Table III. A rather good agreement between N' and B/A may be regarded as fortuitous; however, they present a somewhat unified viewpoint when we consider that the agreement emerged from rather quite different focus. In our approach, we treated NIPA residues differently according to how they would practically be involved in polymer networks, i.e., directly bonded to BIS or not bonded to BIS [expressed by B_k/A_k]. This is in contrast to considering the probabilistic occurrence of creating crosslinks [expressed by N (or N')].[20]

We also note the work by Takata et al. on the preparation of temperature dependence of thermosensitive gels.[21] They introduced a conceptual crosslinking density C_x defined as $2C_{\text{BIS}}/[2C_{\text{BIS}} + C_{\text{NIPA}}]$. If we rewrite this definition by adopting Bromberg et al.'s notation, it can be expressed as $2c_{xl}/[2c_{xl} + c_m]$. We noted that although theoretical model behind this equation is similar to Bromberg et al.,

is without consideration of the statistical probability for the formation of those crosslinks. They represent a three-dimensional polymer network by virtual polymer networks made of one-dimensional monomer links connected to two crosslinks and expressed the fractional number of crosslinkers as the density of crosslinking. The results obtained by SANS experiments are analyzed on the basis of the equation within the theoretical scope of Flory,[24] Huggins,[25,26] and de Gennes.[27] Some notable conclusions are as follows: (1) inhomogeneity of polymer networks explicitly depends on preparation temperature and c_{xl} and (2) c_{xl} saturation threshold was observed in relation to C_x. We have noted that fact (2) is as we described earlier.

Because our experimental determination of gel volumes extends from 277 K to nearly 310 K, we were able to study the characteristic role of crosslinker beyond that reported by Bromberg et al. That is, the gel networks exhibit non-Gaussian elasticity within the theoretical scope of Flory,[24] Huggins,[25,26] and de Gennes.[27] We note the following experimental differences upon which conclusion should be carefully drawn. Bromberg et al.[20] defined the degree of swelling, $S = (W_s - W_d)/W_d$, where W_s and W_d denote weights of gels swollen in equilibrium with excess water at 20°C and of gels dried at 90°C for 3–5 days, respectively. The definition of S can be rewritten with our notation as, $S = [m(\text{gel})(T) - m_p]/m_p = m_s(\text{gel})(T)/m_p$. Here, S is the stoichiometric relationship of gel that is in equilibrium with water at a given temperature T and not the direct definition of change in volume of gels. So, the temperature dependence of $m_s(\text{gel})(T)/m_p$ is not the same as that of volume of gels as was presented in our previous study.[14] The important difference between the two experimental procedures should also be noted. In our case, $m(\text{gel})(T)$ and $m_s(\text{gel})(T)$ are determined while gels are in equilibrium with excess water at a given T and while the physicochemical properties of gel pieces are intact within pycnometry. The absence of water in lyophilized gel (m_p) was examined by a proton solid-state NMR method; no quantification of water content in dried gel by Bromberg et al. was mentioned. Lastly, from an application perspective,[22] it is still premature to link these results at the nanoscale to any macroscopic properties. There is simply a shortage of data on macroscopic physical properties of hydrogels such as the bulk modules of elasticity.

CONCLUSION

The influential extent of the degree of crosslinking in poly(NIPA) networks on the thermally induced volumetric contraction–expansion processes of hydrogels was analyzed by focusing on the thermal

behavior of both NIPA residues directly bonded to a single BIS molecule [(NIPA)$_{bonded}$] and those constitute the usual —CH$_2$—CHR— polymer chains, where R stands for *N*-isopropylamide group [(NIPA)$_{unbonded}$]. It was found that the [(NIPA)$_{bonded}$] occupy more volume but retain less in terms of number of water molecules from 278 to about 300 K. Contraction of volume of [(NIPA)$_{unbonded}$] primarily arises from loss of water in the above temperature range. In this sense, [(NIPA)$_{unbonded}$] are predominantly responsible for the thermally induced volumetric contraction–expansion processes of hydrogels that are in equilibrium with water in the above temperature range. However, the thermal behavior of both NIPA residues at above 304 K to T_{tr} are nearly identical. These represent characteristic role of crosslinker in the aforementioned thermal processes.

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