

# Designing new thermoreversible gels by molecular tailoring of hydrophilic-hydrophobic interactions

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We have shown that the lattice fluid hydrogen bond (LFHB) model can successfully quantify the first-order volume transition in hydrogels. The model predicts that a critical balance of hydrophilic and hydrophobic interactions is required for a gel to exhibit a discontinuous volume transition. In this work we will report the swelling behavior of a new thermoreversible copolymer hydrogel, which has been synthesized from two monomers, whose homopolymers do not show any volume transition in water in the observable range of temperatures. The discontinuous volume transition phenomenon in the copolymer gel was observed only at a critical balance of hydrophilic-hydrophobic interactions. The discontinuous nature of the volume transition is lost with a subtle change in the hydrophilic-hydrophobic balance. The copolymer gel was synthesized from 2-acrylamido 2-methyl propane sulfonic acid (AMPS), which is a hydrophilic monomer, and N-tertiary butylacrylamide (N-t-BAm), which is a hydrophobic monomer. The hydrophilic-hydrophobic balance in the gel was altered by either changing the composition of the co-monomers or by substituting the N-t-BAm with another hydrophobic monomer, N-isopropylacrylamide (NIPAm). © 2000 American Institute of Physics.  
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## INTRODUCTION

Thermoreversible gels such as cross-linked poly (N-isopropylacrylamide) (PNIPAm) show discontinuous swelling-collapse volume transition at a temperature close to the lower critical solution temperature (LCST) of the linear polymer.<sup>1</sup> The molecular causes for LCST transitions in PNIPAm have been extensively investigated experimentally<sup>2-5</sup> as well as theoretically.<sup>6-10</sup> It has been proposed that the volume transition occurs as a result of the breakage of the hydrophobic hydration layer,<sup>7</sup> or due to rearrangement of hydrophilic hydrogen bonds,<sup>8,9</sup> or due to a combination of these two effects.<sup>10</sup>

It has been our endeavor to consistently quantify the volume transition phenomenon in hydrogels and to relate it to the associated molecular events. We have used the lattice fluid hydrogen bond (LFHB) model to show that the volume transition occurs as a result of the rearrangement of hydrogen bonds in the gel-water system and is also due to the temperature-dependent hydrophobicity of the polymer.<sup>10</sup> The LFHB model also correctly predicts the effect of hydrophilic and hydrophobic co-monomers on the volume transition temperature of gels.<sup>11</sup> These predictions have been experimentally validated in several studies<sup>2,12,13</sup> and are useful in designing gels of controlled transition temperature. The LFHB model also successfully predicts complex phenomenon like the reentrant volume transition of PNIPAm gel in alcohol-water mixtures.<sup>14</sup>

One of the very important predictions of the LFHB model is that a hydrogel requires a fine balance of hydrophilic and hydrophobic interactions in order for it to exhibit a discontinuous volume transition in water. In the case of PNIPAm gel, the monomer itself has a unique hydrophilic-hydrophobic balance such that the gel can show a LCST behavior in experimentally observable temperature range. Other similar hydrophobic gels that have been studied are N-methyl acrylamide, N-ethyl acrylamide,<sup>15</sup> N-n-propylacrylamide, and N-cyclopropylacrylamide.<sup>16</sup> However, it is not necessary for a single monomer to have a balance of hydrophilic and hydrophobic interactions. Indeed, we will show in this work that the LFHB model predicts a first-order volume transition for a copolymer gel, whose individual monomers need not show discontinuous transitions. Further, in this work we will show for the first time that when a highly hydrophilic monomer (2-acrylamido 2-methyl propane sulfonic acid), whose homopolymer does not show LCST, is copolymerized with a highly hydrophobic monomer (N-tertiary butylacrylamide), whose homopolymer also does not show any LCST, then at a critical composition ratio the copolymer gel shows a distinct discontinuous LCST-type volume transition. We will also show that any subtle change in the hydrophilic-hydrophobic balance qualitatively changes the swelling behavior of the copolymer gel. Such a change can be introduced by either changing the composition of the comonomers by a small amount or by slightly changing the hydrophobic group in the gel. We have also compared our experimental results with the theoretical calculations of the LFHB model.

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Our present work is clearly different from earlier works on copolymer gels, since we show that a thermoreversible gel can be synthesized from two monomers whose homopolymers do not show LCST independently. We believe that our work will have implications in designing new thermoreversible gels from combinations of suitable monomers.

## THEORY

We will briefly summarize the extended LFHB theory as applied to a binary mixture of solvent (component 1) and a copolymer gel (component 2) made from co-monomers  $A$  and  $B$ . The total free energy of the system is given as the sum of the free energies of mixing and the elastic free energy of an affine network. The elastic free energy  $\Delta G_{el}$  is given by the theory of rubber elasticity as

$$\Delta G = \frac{3}{2} \left( \frac{\nu_e}{V_0} \right) \left\{ \left( \frac{V}{V_0} \right)^{2/3} - 1 - \frac{1}{3} \ln \left( \frac{V}{V_0} \right) \right\}, \quad (1)$$

where  $\nu_e$  is the moles of elastically active chains in the gel,  $V$  is the volume of the gel, and  $V_0$  is the volume at synthesis at a given temperature and pressure.

The free energy of mixing is calculated from a mean-field assumption in which the mers of the two components 1 and 2 are randomly placed on a lattice. For the mixture of  $n_1$  molecules of component 1 and  $n_2$  molecules of component 2 ( $N = n_1 + n_2$ ), the mer length ( $r$ ), the characteristic mer volume ( $\nu^*$ ), and the characteristic mean-field mer-mer interaction energy ( $\varepsilon^*$ ) are given by

$$\frac{1}{r} = \frac{\phi_1}{r_1} + \frac{\phi_2}{r_2}, \quad (2)$$

$$\nu^* = \phi_1 \nu_1^* + \phi_2 \nu_2^*, \quad (3)$$

$$\varepsilon^* = \phi_1^2 \varepsilon_1^* + \phi_2^2 \varepsilon_2^* + 2 \phi_1 \phi_2 \xi_{12} (\varepsilon_1^* \varepsilon_2^*)^{0.5}. \quad (4)$$

Here,  $\phi$  is the volume fraction,  $r_i$  is the number of lattice sites occupied by a molecule of component  $i$ ,  $\nu_i^*$  is the characteristic mer volume of component  $i$ , and  $\varepsilon_i^*$  is the characteristic mer-mer interaction energy for component  $i$ . A pure component  $i$  is thus characterized by three parameters  $r_i$ ,  $\nu_i^*$ , and  $\varepsilon_i^*$ .  $\xi_{12}$  is the binary interaction parameter between components 1 and 2.

The characteristic parameters of the pure random copolymer are obtained from Eqs. (2) to (4) by assuming that the copolymer can be considered as a random mixture of the two homopolymers  $A$  and  $B$ , which form the copolymer  $A-B$ , and that the interaction parameter between the two homopolymers  $\xi_{AB}$  is unity. In using Eqs. (2) to (4) for the copolymer, the subscripts 1 and 2 are replaced by  $A$  and  $B$  representing the two homopolymers. The volume fraction of the mers of two homopolymers are calculated as

$$\phi_i = \frac{w_i / \rho_i^*}{\sum w_i / \rho_i^*}, \quad (5)$$

where  $w_i$  is the weight of the component  $i$  ( $i=A, B$ ) and  $\rho_i^*$  is its characteristic density.

In a mixture of the copolymer and water, the binary interaction parameter  $\xi_{12}$  is calculated as

$$\xi_{12} = \xi_{1A} \phi_A + \xi_{1B} \phi_B, \quad (6)$$

where the binary interaction parameter between water and the two homopolymers  $A$  and  $B$  are in general given as

$$\xi_{1i} = a_i T + b_i; \quad i = A, B. \quad (7)$$

The binary interaction parameter between the copolymer and water can be considered as simulating the ‘‘effective hydrophobicity’’ of the copolymer since the hydrophilic part of the interactions is considered separately in the hydrogen bonding terms in the mean-field frame work of the LFHB theory as summarized below.

Let there be  $i$  ( $i=1, m$ ) types of proton donors and  $j$  ( $j=1, n$ ) types of proton acceptors in the system of a gel and a solvent. The total number of donors and acceptors is given by

$$N_t^d = \sum_k d_i^k n_k \quad \text{and} \quad N_a^j = \sum_k a_j^k n_k, \quad (8)$$

where  $d_i^k$  and  $a_j^k$  are the number of donors of type  $i$  and acceptors of type  $j$  in component  $k$ . If  $N_{ij}$  is the total number of hydrogen bonds formed between an  $i-j$  donor-acceptor pair, then the number of undonated protons of type  $i$  and unaccepted protons of type  $j$  are given by

$$N_{io} = N_i^d - \sum_j N_{ij} \quad \text{and} \quad N_{oj} = N_a^j - \sum_k N_{kj}. \quad (9)$$

If  $E_{ij}^0$ ,  $S_{ij}^0$ , and  $V_{ij}^0$  are changes in the energy, entropy, and volume due to the formation of an  $i-j$  hydrogen bond, then the fraction of such  $i-j$  bonds formed is given by

$$\nu_{ij} = \left[ \nu_d^i - \sum_k \nu_{ik} \right] \left[ \nu_a^j - \sum_k \nu_{kj} \right] \exp(-G_{ij}^0/RT), \quad (10)$$

where

$$\nu_{ij} = \frac{N_{ij}}{rN}; \quad \nu_d^i = \frac{N_i^d}{rN}; \quad \nu_a^j = \frac{N_a^j}{rN}; \quad (11)$$

$$G_{ij}^0 = E_{ij}^0 + PV_{ij}^0 - TS_{ij}^0.$$

The free energy of mixing in the LFHB model can be calculated from the mixing rules given by Eqs. (2)–(4) and the hydrogen bonding fractions are given by Eq. (10). The details of the free energy of mixing terms are described in Lele *et al.*<sup>10</sup> From the free energy of mixing and the elastic free energy of Eq. (1), the chemical potential of water in the gel phase can be calculated as

$$\begin{aligned} \frac{\mu_1^G}{RT} = & \ln(\phi_1/\omega_1) + \left(1 - \frac{r_1}{r_2}\right) \phi_2 + r_1 \tilde{p} \phi_2^2 \chi_{12} \\ & + r_1 \left\{ -\frac{\tilde{p}}{\tilde{T}_1} + \frac{\tilde{p}_1 \tilde{\nu}}{\tilde{T}_1} + (\tilde{\nu} - 1) \ln(1 - \tilde{p}) + \frac{1}{r_1} \ln \tilde{p} \right\} \\ & + r_1 \sum_l^m \sum_j^n \nu_{lj} - \sum d_l^1 \ln \frac{\nu_d^1}{\nu_{io}} - \sum a_j^1 \ln \frac{\nu_a^1}{\nu_{oj}} \\ & + \left\{ r_1 \left( \frac{\nu_e}{V_0} \right) \nu_1^* \tilde{\nu} \left[ \left( \frac{V_0}{V} \right)^{1/3} - \frac{1}{2} \left( \frac{V_0}{V} \right) \right] \right\}, \quad (12) \end{aligned}$$

where

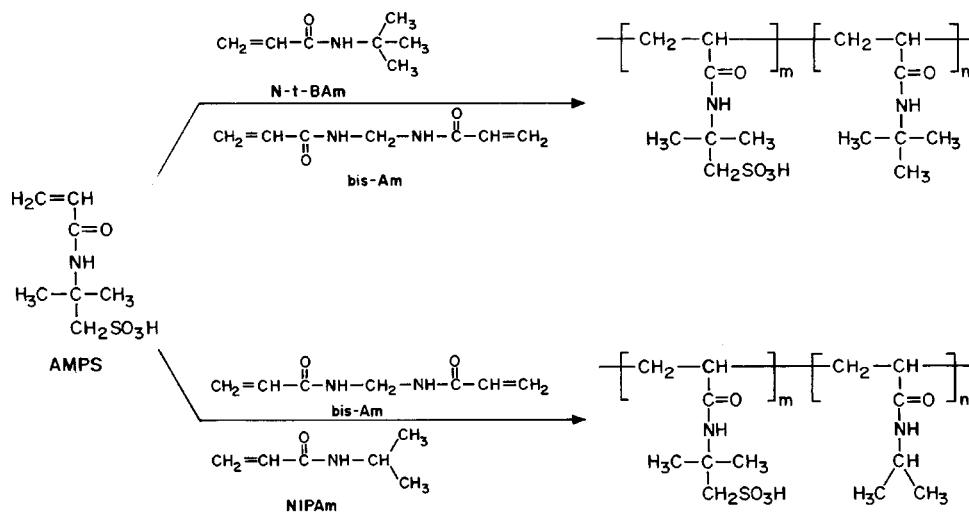


FIG. 1. Reaction scheme for the synthesis of copolymer gels.

$$\chi_{12} = \frac{\varepsilon_1^* + \varepsilon_2^* - 2\xi_{12}(\varepsilon_1^* \varepsilon_2^*)^{1/2}}{RT}, \quad (13)$$

and  $\tilde{\rho}$  is the reduced density of the mixture which is related to the reduced pressure  $\tilde{P} = P/P^*$  and reduced temperature  $\tilde{T} = T/T^*$  by the equation of state

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T} \left\{ \ln(1 - \tilde{\rho}) + \tilde{\rho} \left[ 1 - \left( \frac{1}{r} - \sum_i^m \sum_j^n \nu_{ij} \right) \right] \right\} + \frac{\nu_e}{V_o} \tilde{T} \nu^* \left[ \left( \frac{V_o}{V} \right)^{1/3} - \frac{1}{2} \left( \frac{V_o}{V} \right) \right] = 0. \quad (14)$$

In the first line of Eq. (12), the first two terms are the combinatorial entropy contribution and the third term is the energetic (effective hydrophobic) contribution. The term in the second line represents the effect of the pure component properties, while those in the third line represent the hydrogen bonding contribution. The fourth line represents the elastic energy contribution.

The equilibrium swelling capacity of the gel,  $q = 1/\phi_2$ , can be calculated from the condition that the swelling pressure of the gel at equilibrium is equal to zero. Thus,

$$\Pi = \mu_1^G - \mu_1^0 = 0, \quad (15)$$

where  $\mu_1^0$  is the chemical potential of pure water outside the gel. Equation (13) can be solved by simultaneously solving Eqs. (10), (12), and (14). These are the main equations constituting the model.

The model parameters for a copolymer gel-water mixture include nine pure component parameters (three for each component), one binary interaction parameter ( $\xi_{12}$ ), three hydrogen bonding parameters ( $E_{ij}^0, S_{ij}^0, V_{ij}^0$ ) for each  $i-j$  type of hydrogen bond, and the crosslink density ( $\nu_e/V_o$ ). Parametric values are discussed in the Results and Discussion section.

## EXPERIMENT

### Materials

2-acryloylamido-2-methyl propane sulfonic acid (AMPS) was purchased from Fluka. N-tertiary-butyl-

acrylamide (N-t-BAm) and methylene bis-acrylamide (bis-Am) were all obtained from Aldrich Chemical Company Inc. N-isopropyl acrylamide (NIPAm) was purchased from Polysciences Inc. (Warrington, PA) and dimethyl sulfoxide (DMSO), analytical reagent (AR) grade, was obtained from S.d. fine chemicals, Mumbai, India. The initiator azo isobutyronitrile (AIBN) was procured from SAS Chemical Co., Mumbai, India. Deionized distilled water was prepared in the laboratory using standard procedures.

### Synthesis of gels

We have synthesized the gels by copolymerizing either the N-t-BAm or the NIPAm monomer with the AMPS monomer in different mole ratios. The copolymerization was carried out in DMSO using bis-Am as a cross linker and AIBN as a free radical initiator. The reaction scheme is shown in Fig. 1. The desired amounts of monomers with defined mole ratios along with the cross-linking agent and the initiator were taken in a beaker and dissolved in DMSO with constant stirring under nitrogen gas bubbling. The reaction mixtures were poured into test tubes and sealed. The reaction was carried out at 65–70 °C for 24 hrs. The cylindrical gels obtained were immersed in water for 48 hrs in order to wash away the unreacted reactants. During this time fresh water was added frequently. The washed gels were dried in an oven at 50 °C to constant weight. A series of copolymer gels, N-t-BAm-co-AMPS (referred to as Bu-AMPS) and NIPAm-co-AMPS (referred to as ip-AMPS), were prepared with different mole ratios to study the effect of the concentration of the hydrophobe on the swelling behavior. All gels were clear and transparent except the N-t-BAm homopolymer gel. In the case of 10 mole % as well as 20 mole % cross linker, the gels were very soft and difficult to handle. Therefore in the present work, the gels were prepared by using 30 mole % cross-linking agent.

## CHARACTERIZATION OF THE COPOLYMER GELS

### Swelling measurements

Dry gel samples of known weights were immersed in excess distilled water and kept in sealed containers, which

were placed in a temperature-control bath (Julabo F25) of  $\pm 1^\circ\text{C}$  accuracy until equilibrium was reached. This took approximately 96 hrs. The samples were removed and blotted dry. The swelling ratio of the copolymer gels was determined gravimetrically. The equilibrium weights of the swollen samples at each temperature were determined. The swelling ratios of the copolymer gels were calculated from the ratio of the weight of the equilibrated gel to the original weight.

$Q$  = weight of the equilibrated gel/original weight of the gel.

### Mechanical properties (compression test)

A compression accessory fitted to a UTM (universal testing machine, model Instron 4204) was used to obtain the stress-strain data on swollen specimens having dimensions of 25 mm length and 12 mm diameter. An appropriate load cell was fitted to the instrument and the tests were done at a crosshead speed of 10 mm/min. The linear portion of the compression-strain curve was used to compute the modulus.

### Fourier-transform infrared (FT-IR) study of copolymer gels

The infrared absorption spectra of the copolymer gels were measured by a Shimadzu model 8300 FTIR spectrophotometer. The dried samples were pelletized with KBr and the transparent pellets were used for scanning.

## RESULTS AND DISCUSSIONS

Figure 2 shows qualitative predictions of the LFHB model for the swelling behavior of copolymer gels in which one of the monomers is highly hydrophilic while the other is highly hydrophobic. The homopolymer gel of the hydrophobic monomer remains in a collapsed state in water in the temperature range of 5 to  $100^\circ\text{C}$  as shown by curve 1, whereas the homopolymer of the highly hydrophilic gel shows a UCST- (upper critical solution temperature) type swelling behavior in the same temperature range as shown by curve 2. Thus, none of the homopolymers shows a first-order discontinuous LCST-type volume transition. However, at a proper composition of these two monomers, the LFHB model predicts a discontinuous-type swelling behavior as shown by curve 3. This clearly indicates that a proper balance of hydrophilic and hydrophobic interactions is essential for a gel to exhibit a first-order discontinuous volume transition. As the hydrophilicity increases, the hydrophilic-hydrophobic balance is disturbed and consequently the LCST behavior is lost. At a higher hydrophilic monomer composition, the decrease in swelling with temperature (LCST-type behavior) is balanced by the increase of swelling with temperature (UCST-type behavior), resulting in a swelling plateau as shown by curve 4. At still higher hydrophilic monomer content, the swelling behavior changes to UCST-type, i.e., the swelling ratio increases with temperature. Thus the model predicts qualitatively different swelling behaviors such as a collapsed state, discontinuous LCST type, continuous LCST type, swelling plateau, and UCST-type swelling with respect to temperature.

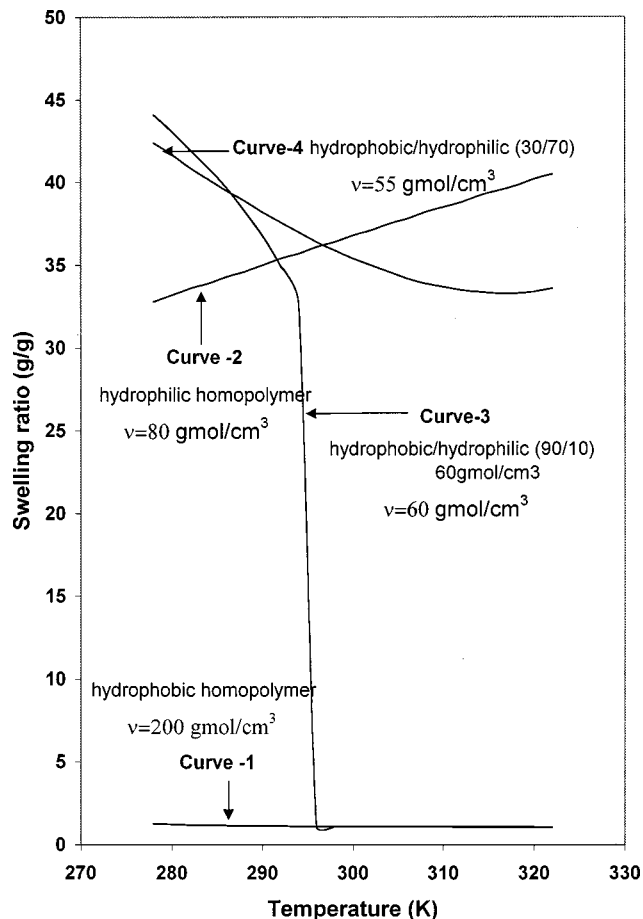


FIG. 2. Qualitative predictions of the LFHB model for the swelling behavior of copolymer gels. The hydrogen bonding parameters are the same as indicated in Table I, the pure component parameters are the same as in Table II, the binary interaction parameters are reported in Table III, the copolymer compositions and cross-link densities are given in the figure.

We will now show that the qualitative model predictions are indeed validated experimentally for copolymer gels. Figure 3 presents the swelling behavior of a series of copolymer gels in which AMPS is used as the highly hydrophilic monomer and N-t-BAm is used as the highly hydrophobic monomer. The lines through the experimental points are the trend lines and are drawn for the sake of clarity. The swelling capacity of the pure PAMPS gel increased with increase in temperature, while the pure poly (N-t-BAm) gel did not swell in water in the temperature range studied. However, when a small amount of AMPS comonomer was copolymerized with N-t-BAm, the swelling behavior of the copolymer gel was qualitatively different from that of the homopolymer gels. The copolymer gel Bu-AMPS-10/1 (1 mole of N-t-BAm and 0.1 mole of AMPS) showed a sharp discontinuous LCST-type swelling-collapse phenomena in water as the temperature was raised from  $14$  to  $16^\circ\text{C}$ . Also, at the transition temperature of  $15^\circ\text{C}$ , the gel showed the coexistence of a swollen and a collapsed phase as shown in Fig. 4. With a slight increase in the AMPS content of the copolymer gel such as in the case of Bu-AMPS (10/2), a continuous decrease in swelling was observed with increasing temperature. Another significant observation was that the copolymer gel, Bu-AMPS (10/2), did not attain a fully collapsed state. With

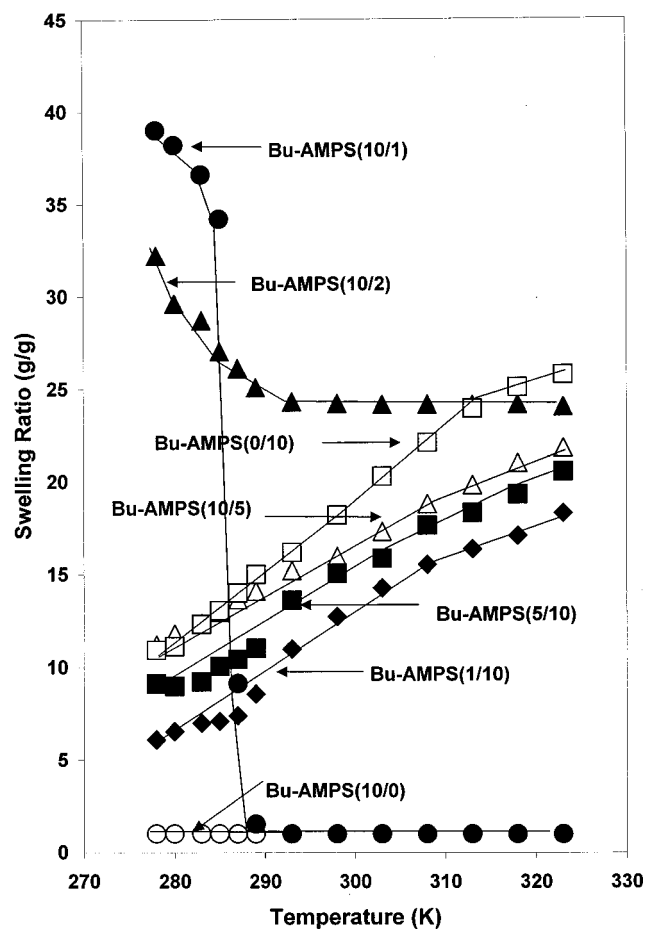


FIG. 3. Swelling behavior of AMPS-co-*N-t*-BAm copolymer gels.

further increase in the content of AMPS comonomer, no volume transition phenomenon was observed in the temperature range of 5 to 100 °C. In fact all the copolymer gels with higher AMPS content showed a UCST- (upper critical solution temperature) type swelling behavior.

It is clear from the foregoing results that a fine balance of hydrophobic-hydrophilic interactions results in discontinuous LCST-type transition for the Bu-AMPS (10/1) gel. As the hydrophilicity increases due to increasing AMPS content, the balance is disturbed and consequently the LCST behavior is lost. For the Bu-AMPS (10/2), the hydrophobic

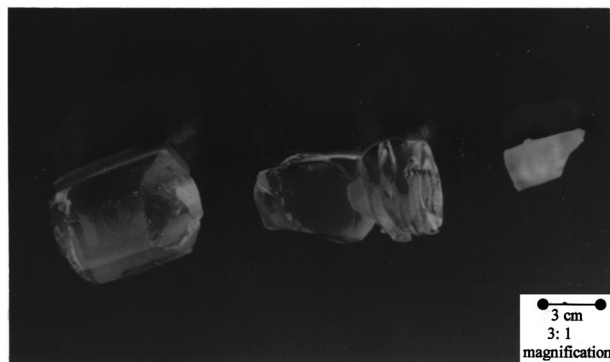


FIG. 4. Coexistence of a swollen and a collapsed phase at the transition temperature.

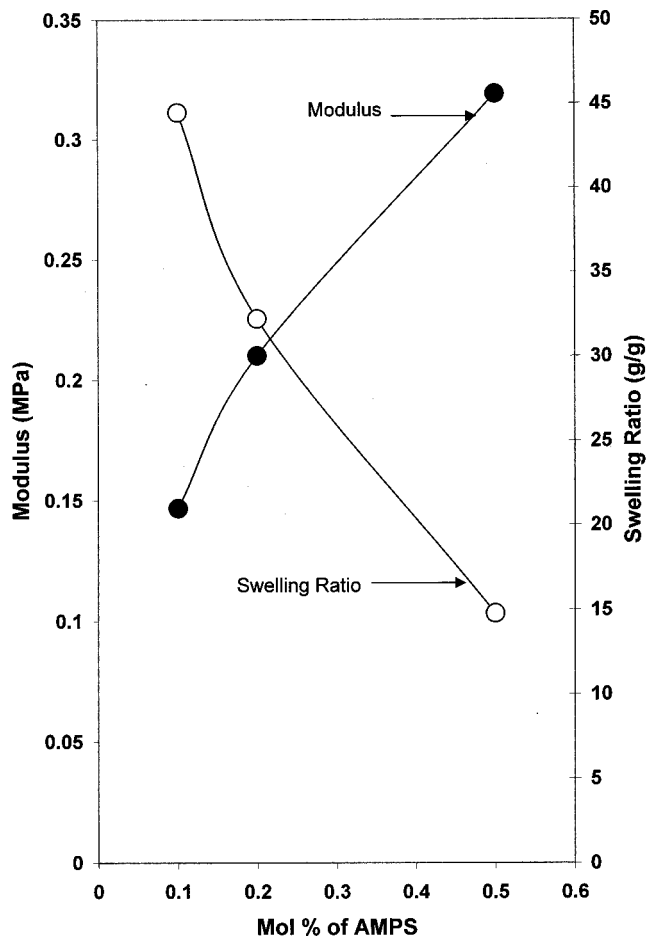


FIG. 5. Correlation between AMPS content, modulus and swelling behavior of the copolymer gels.

contribution of the decrease in swelling with temperature is balanced by the hydrophilic contribution of the increase in swelling with temperature. Hence a swelling plateau is observed. With further increase in hydrophilicity, the swelling capacity of the copolymer gel increases with increase in temperature. A comparison of Figs. 2 and 3 indicates that the *N-t*-BAm-AMPS copolymer gel indeed shows all the different swelling behavior predicted by the LFHB model.

Our experimental data in Figs. 3 and 6 indicate that as the hydrophilic AMPS content in the gel increases the swelling capacity decreases. This is surprising since the swelling capacity of the gel can be expected to increase with increase in the hydrophilic content. However, the results of the compression test shown in Fig. 5 indicate that the modulus of the gels increases with AMPS content. Modulus is the measure of overall cross-link density of the gel. Our data show that as hydrophilic AMPS content increases, the cross-link density of the gel increases and hence the equilibrium swelling capacity of the copolymer gels decreases. We believe that since our synthesis procedure for copolymer gels does not provide any control over the cross-link density, the observed decrease in the swelling ratio with increase in AMPS content is due to the higher cross-link density of the copolymer gel. The higher cross-link density may be due to a combination of covalent cross-links from bis-Am as well as physical cross links from interpolymer hydrogen bonds such as those reported by Bensberg<sup>17</sup> and Lee *et al.*<sup>18</sup> We have examined the

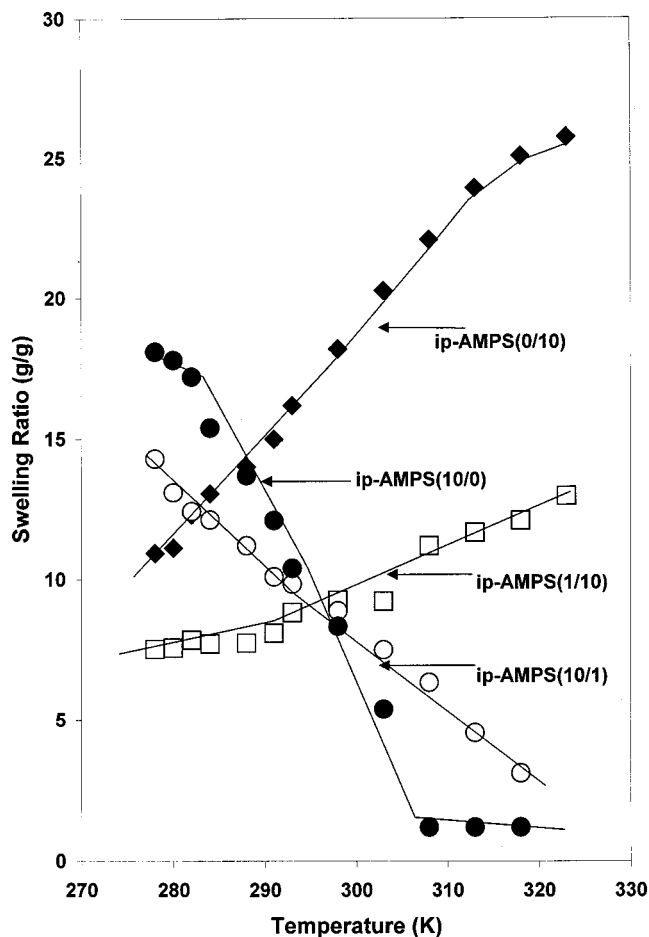


FIG. 6. Swelling behavior of AMPS-co-NIPAm copolymer gels.

copolymer gels by FT-IR spectroscopy to check the presence of interpolymer hydrogen bonding interactions in copolymer gels. No shift in peaks was observed for the hydrogen bonding groups (C=O, —NH, —OH, S=O) in the copolymer gel. This observation clearly indicates that the presence of interpolymer hydrogen bonding interactions is negligible. Hence the increase in cross-link density as the AMPS content increases is not due to the interpolymer hydrogen bonds. Our theoretical calculations also indicate that the contribution of physical cross links is negligible. From the experimentally determined modulus, we have calculated the cross-link density of the copolymer gels by using Eq. (16). For Bu-AMPS (10/1) and Bu-AMPS (0/10), the cross-link density values are 60 and 240 gmol/cm<sup>3</sup>, respectively, and the same values were used for the quantitative calculations using the LFHB model,

$$\sigma = \gamma kT \left( \alpha - \frac{1}{\alpha^2} \right). \quad (16)$$

Figure 6 shows the effect of temperature on the equilibrium swelling ratio of the ip-AMPS copolymer gels. The lines through the points are only the trend lines and are drawn for the sake of clarity. Pure poly (NIPAm) gel is found to undergo a sharp volume transition at 32 °C. A significant change in swelling behavior is observed with the incorporation of a small amount of hydrophilic group. The

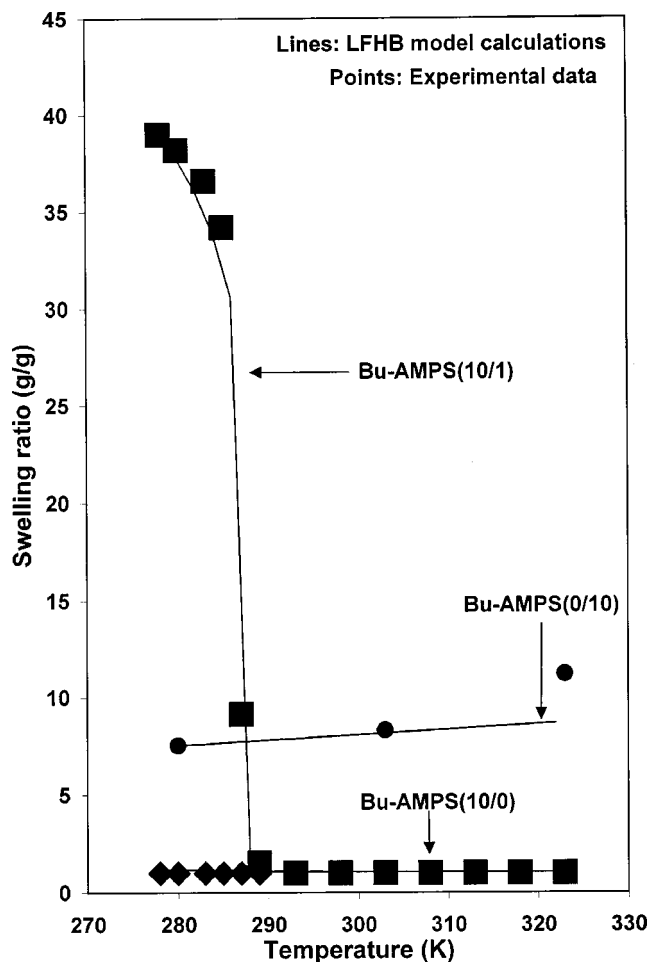


FIG. 7. Quantitative comparison of experimental data with the model calculations for AMPS-co-N-t-BAM copolymer gels.

ip-AMPS (10/1) gel (NIPAm 1.0 mol and AMPS 0.1 mol) shows a continuous LCST-type swelling behavior. The sharp volume transition seen in PNIPAm gel is lost with the incorporation of a small amount of AMPS. In all other compositions, as the AMPS content increases, the LCST behavior disappears and the swelling capacity tends to increase with temperature.

Comparing the N-t-BAM copolymer gels with the NIPAm gels, it is seen that the more hydrophobic N-t-BAM homopolymer gel did not swell in water while the PNIPAm gel showed a distinct LCST-type volume transition. Similarly, when the monomers are copolymerized with AMPS at 1.0:0.1 mol ratio, the N-t-BAM copolymer gel showed a distinct discontinuous volume transition, whereas the NIPAm-based gel showed a continuous transition at the same composition. The chemical structures of the hydrophobes are given in Fig. 1 and the only difference between the N-t-BAM and NIPAm is that in N-t-BAM there is an additional methyl group. This shows that subtleties of hydrophilic-hydrophobic balance play a vital role in determining the volume transition phenomenon of the copolymer gels.

Figure 7 shows a quantitative comparison between the experimental swelling behavior of the N-t-BAM-co-AMPS gels and LFHB model calculations. The lines through the

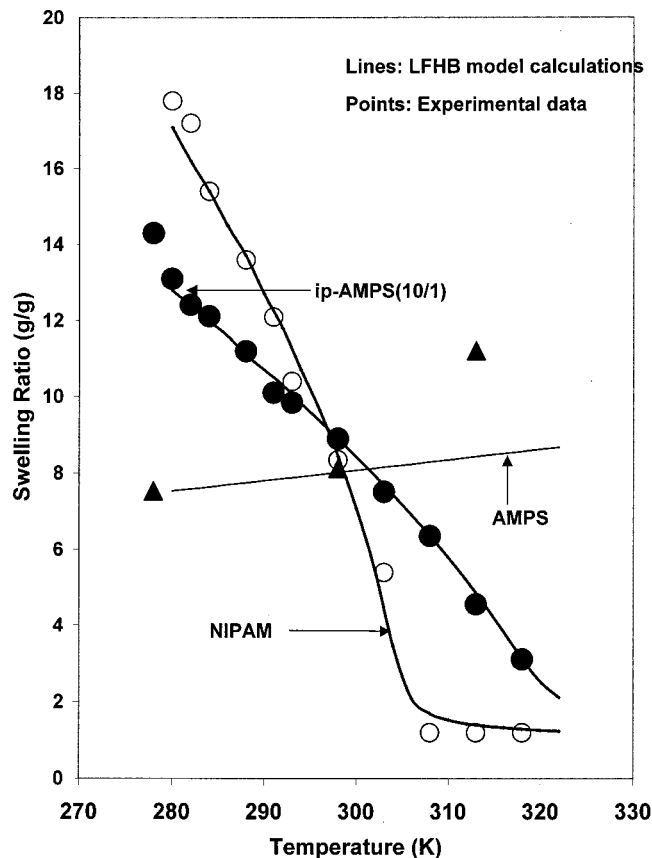


FIG. 8. Quantitative comparison of experimental data with the model calculations for AMPS-co-NIPAm gels.

experimental data points are the calculations of the LFHB theory. For the homopolymer AMPS and N-t-BAm gels the model parameters are fixed such that the predicted swelling behavior compares well with the experimental data. Now keeping all model parameters constant, the model successfully predicts a first-order volume phase transition at 15 °C for the Bu-AMPS (10/1) copolymer gel. However, the LFHB

model could not predict quantitatively the swelling behavior of Bu-AMPS (10/2). The model predicted a discontinuous volume transition at a higher temperature for Bu-AMPS (10/2), whereas the experimental swelling data show a swelling plateau as a function of temperature. A swelling plateau was predicted for a copolymer gel containing a higher composition of AMPS content as shown in Fig. 2.

Figure 8 shows the experimental and predicted swelling behavior of NIPAm-AMPS copolymer gels. The lines through the experimental data points are the calculations of the extended LFHB theory. Both the model as well the experimental observations showed a first-order transition for the PNIPAm gel. But a slight increase in hydrophilicity by copolymerizing NIPAm with AMPS qualitatively changed the swelling behavior of the gel.

The hydrogen bonding parameters used for all calculations in this paper are reported in Table I. For the copolymers, the LFHB model requires pure component properties of the homopolymers. In the absence of any data for the pure component properties of N-t-BAm, NIPAm, and AMPS, we have assumed the pure component values of polymethyl methacrylate for AMPS and NIPAm homopolymers, and those of poly (n-butyl methacrylate) for the N-t-BAm homopolymer are the same. These values have been reported by Sanchez and Lacombe<sup>19-21</sup> and have been successfully used by us in our earlier work.<sup>10-12,15</sup> The rationale for the choice of poly (n-butyl methacrylate) parameters for N-t-BAm is that it is more hydrophobic than poly (methyl methacrylate), whose parameters have been used for poly (NIPAm). Table II gives the pure component properties assumed for poly (NIPAm), poly (AMPS), and poly (N-t-BAm). It is found that the qualitative predictions of the swelling behavior of the copolymer gels do not depend very significantly on the values of the pure component parameters.

The calculations of the hydrogen bonding terms in the chemical potential require solving nine simultaneous equations represented by Eq. (10) for three pairs of donors and

TABLE I. Hydrogen bonding parameters. [ $a_3^2 = d_3^2 = 0$  for Bu-AMPS (10/0) and ip-AMPS (10/0);  $a_1^2 = d_1^2 = 8, 6, 94,$  and  $56$  for Bu-AMPS (10/1), Bu-AMPS (10/2), ip-AMPS (10/1), ip-AMPS (10/0);  $a_3^2 = 2, 8,$  and  $86$  for Bu-AMPS (10/1), Bu-AMPS (0/10), and ip-AMPS (10/1);  $d_3^2 = 1, 4,$  and  $43$  for Bu-AMPS (10/1), Bu-AMPS (0/10), and ip-AMPS (10/1).]

H bonding parameters	Donors → Acceptors ↓	—NH	—OH	—SO <sub>3</sub> H
		$d_1^2 = 8, 6, 94, 56$	$d_2^2 = 2$	$d_3^2 = 0, 1, 4, 43$
$E_{ij}^0$ (J/gmol)	—C=O $a_1^2 = 8, 6, 94, 56$	$-3.24 \times 10^3$	$-16.0 \times 10^3$	$-3.24 \times 10^3$
$S_{ij}^0$ (J/gmolK)		$-9.9$	$-25.8$	$-10.0$
$V_{ij}^0$ (cm <sup>3</sup> /gmol)		$-0.85$	$-0.85$	$-0.85$
$E_{ij}^0$ (J/gmol)	—OH $a_2^2 = 2$	$-12.5 \times 10^3$	$-16.595 \times 10^3$	$-25.00 \times 10^3$
$S_{ij}^0$ (J/gmolK)		$-17.8$	$-26.6$	$-10.6$
$V_{ij}^0$ (cm <sup>3</sup> /gmol)		$-0.85$	$-4.2$	$-0.85$
$E_{ij}^0$ (J/gmol)	—SO <sub>3</sub> H $a_3^2 = 0, 2, 8, 86$	$-12.5 \times 10^3$	$-25.00 \times 10^3$	$-12.5 \times 10^3$
$S_{ij}^0$ (J/gmolK)		$-7.8$	$-10.0$	$-7.8$
$V_{ij}^0$ (cm <sup>3</sup> /gmol)		$-0.85$	$-0.85$	$-0.85$

TABLE II. Molecular parameters.

Component	$P^*$ (Mpa)	$T^*$ (K)	$\rho^*$ (kg/cm <sup>3</sup> )	MW(g/mol)
PN-t-BAm	503	699	1269	1000
PNIPAm	503	699	1269	10000
PAMPS	431	627	1125	1000
Water	475	578	853	18

acceptors. The donors and acceptors, along with their hydrogen bonding energies, entropies, and volume changes are listed in Table I. The hydrogen bonding parameters for the poly (NIPAm)-water system are the same as those reported in our earlier work. The parameters corresponding to the hydrogen bonding between the terminal sulfonic acid group on the AMPS monomer and the other donors and acceptors in the mixture are assumed to be such that hydrogen bonds formed are much stronger than those formed by the amide group.

The values of cross-link density of the gels required for quantitatively fitting the experimental data are calculated from the experimentally modulus values and are given in Table III. It is seen that Bu-AMPS (10/1) has lower cross-link density and thereby maximum swelling as observed experimentally.

The effective hydrophobicity of the copolymer gel is represented by  $\xi_{12}$ . The binary interaction parameter required for fitting the experimental swelling data are listed in Table III. A lower value of  $\xi$  indicates higher hydrophobicity. It is seen from the values of  $\xi$  that the effective hydrophobicity of all gels is slightly temperature dependent and that the value of  $\xi$  at any temperature decreases with increasing hydrophobicity of the co-monomer. It is found that  $\xi$ , along with the hydrogen bonding energies and entropies, and the number of donors and acceptors, together determine the volume transition behavior of the gels. Thus, the theory predicts that a critical contribution of the hydrophilic-hydrophobic interactions is necessary for discontinuous nature of volume transition of gels.

## CONCLUSION

We have synthesized a new thermoreversible copolymer gel from a highly hydrophilic monomer (AMPS) and a

TABLE III. Binary interaction parameters and cross-link density.

Gel	Components	$\xi$	$(\nu_e/\nu_0)$ (gmol/cm <sup>3</sup> )
Bu-AMPS(10/0)	N-t-BAm	$1.451 - 1.8 \times 10^{-3}T$	200
Bu-AMPS(10/1)	N-t-BAm	$1.451 - 1.8 \times 10^{-3}T$	60
	AMPS	$1.0 - 0.0 \times 10^{-3}T$	
Bu-AMPS(0/10)	AMPS	$1.0 - 0.0 \times 10^{-3}T$	240
ip-AMPS(10/0)	NIPAm	$1.5 - 1.56 \times 10^{-3}T$	60
ip-AMPS(10/1)	NIPAm	$1.5 - 1.56 \times 10^{-3}T$	120
	AMPS	$1.0 - 0.0 \times 10^{-3}T$	

highly hydrophobic monomer (N-t-BAm), such that the homopolymer gels do not show any LCST-type discontinuous volume transition in the observable range of temperature. At a critical hydrophilic-hydrophobic balance, the copolymer gel Bu-AMPS (10/1) showed a discontinuous volume transition at 15 °C with the coexistence of swollen and collapsed states. A subtle change in the hydrophilic-hydrophobic balance by changing either the composition of the monomers or by substituting N-t-BAm with a less hydrophobic NIPAm altered the swelling behavior of the copolymer gels qualitatively. Such mechanistic insights into the nature of volume transition could be useful in designing new thermoreversible gels with desired transition temperatures. Contrary to the expectation, a decrease in swelling ratio with increase in AMPS content was observed and the compression test results indicated that such a decrease in swelling ratio is attributed to the increase in overall cross-link density of the gel. We have also shown that the extended LFHB model can quantitatively predict the swelling of the copolymer gels. We believe our work will provide quantitative guidance for designing new thermoreversible gels by consideration of new suitable monomers.

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