Photochromic Cross-Links in Thermoresponsive Hydrogels of Poly(*N*-isopropylacrylamide): Enthalpic and Entropic Consequences on Swelling Behavior

Mun-Sik Kang and Vinay K. Gupta*

Department of Chemical Engineering, University of Illinois, Urbana-Champaign, Urbana, Illinois 61801

Received: November 1, 2001; In Final Form: February 18, 2002

The preparation and properties of thermosensitive gels of poly(*N*-isopropylacrylamide) (PNIPAM) cross-linked with azoaromatic chromophores were investigated. Polymer gels were prepared with different concentration of the cross-linking agent, 4,4′-di[2-methacryloylamide]azobenzene (DMAAB). The gels were optically transparent and possessed a high absorption for ultraviolet light. Characterization of the equilibrium swelling in water revealed that an increase in cross-linking density caused a shift in the volume phase transition to lower temperatures. This shift in the transition temperature (T_c) was interpreted to arise from an increase in the unfavorable interactions between the solvent (water) and the polymer network due to the azoaromatic cross-links. A high cross-linker concentration also resulted in a decrease in the degree of equilibrium swelling due to an increase in the topological constraints of the PNIPAM chains. Below T_c, the shrinking dynamics of the PNIPAM gels with photochromic cross-links followed a Fickian diffusion behavior, and above T_c, the gels collapsed completely within 20 min. During the deswelling, irradiation of the gel and trans–cis photoisomerization of the cross-links were found to increase the expulsion of water from the swollen gels and decrease the water content of the gels by as much as 20–30%. This result contrasts with past studies on PNIPAM gels in which the azochromophore was present in the side chains and irradiation increased the swelling ratio. The largest decrease in water content ($\Delta R_{s,max}$) due to irradiation was observed near T_c, and the magnitude of the change, $\Delta R_{s,max}$, decreased with increase in cross-link density. The changes in swelling due to irradiation were attributed to entropic changes in the network due to irradiation.

Introduction

Responsive gels based on poly(*N*-isopropylacrylamide) (PNIPAM) have been the subject of wide interest.[1,2] These gels exploit the unique thermosensitive nature of PNIPAM, which in aqueous solutions exhibits a lower critical solution temperature (LCST) between 32 and 34 °C.[1–4] As a consequence of this thermosensitivity, polymer networks or gels that incorporate PNIPAM chains exhibit a dramatic volume phase transition near the LCST. Numerous experimental and theoretical studies have focused on the volume transition and explored the fundamental origins behind the phase transition.

Because the swelling and shrinking behavior of these hydrogels has potential uses in a wide variety of applications such as controlled release,[5] separations,[3,6,7] and actuators,[8] past investigations have sought to manipulate the swelling response by chemical modification of the polymer network. One frequent approach has been to use copolymers of PNIPAM and acrylic acid derivatives.[9,10] Other successful strategies have included modification of the side chains of PNIPAM with functional groups that either undergo changes such as ionization and photoisomerization or cause local heating by absorbing energy from visible light.[11,12] As a result, modulation of the volume transition of the gels can be accomplished by using environmental stimuli such as pH, ionic strength, or light.

In this paper, we focus on PNIPAM gels wherein the cross-links contain azobenzene groups that undergo photoisomeriza- tion and thereby alter the conformational balance within the network. While a similar strategy has been used in studies on elastomeric networks of polyacrylates and polyisobutylenes,[13,14] modification of gels of thermally responsive polymers such as PNIPAM has not been investigated. Here, we report the preparation of the PNIPAM gels with chromophoric groups. Because these gels are optically transparent and possess high absorption for ultraviolet light and because these properties are important in applications of hydrogels such as light-control windows,[15] we characterize the optical and swelling character- istics of the gels. The results reveal that the volume phase transition temperature depends on the density of cross-links and is related to the hydrophobic effect due to the azobenzene chromophores. Even though the cross-links constitute only a minor fraction of the network, irradiation by light modifies the degree of swelling by nearly 20–30%. The changes observed here differ from past reports[11,16] on PNIPAM gels that possessed azobenzene chromophores within side chains and indicate that different mechanisms underlie the light-controlled changes in swelling.

Experimental Section

Chemicals. All reagents, unless otherwise noted, were purchased from Aldrich Chemicals (Milwaukee, WI) and used without further purification. The solvents used in this study— pyridine, hexane, methanol, and DMF (Fisher)—were of reagent grade. Purified water was from an EasyPure UV system (Barnstead, IA).

Preparation and Characterization of the Cross-Linked PNIPAM Gels. *N*−Isopropylacrylamide (NIPAM) was purified

* To whom correspondence should be addressed. Department of Chemi- cal Engineering, University of Illinois, Urbana-Champaign, 600 S. Mathews Avenue, Urbana, IL 61801. Email: vgupta@uiuc.edu. Fax: 217-333-5052. Tel: 217-244-2247.

by recrystallization from hexane and polymerized following standard literature procedures. Briefly, radical polymerization of NIPAM (1.33 mol/L) was initiated by 2,2′-azobisiso-butyronitrile (AIBN) in methanol solution at 60 °C. The solution was purged with nitrogen gas before polymerization. A photochromic compound, 4,4′-di[2-methacryloylamide]azobenzene (DMAAB), was used as a cross-linking agent. Synthesis of DMAAB has been reported previously.[17] After polymerization for 46 h, the gels were washed exhaustively with methanol and distilled water to remove any residual monomer and cross-linking agent. The gels were then dried under vacuum.

The molar ratio of the monomer NIPAM to the cross-linking agent DMAAB was varied from 15 to 200. The gels obtained were designated as $R_{m/c}$-XX where XX indicates the molar ratio of monomer to cross-linker. For comparison purposes, a PNIPAM gel (B-50) was also prepared using *N,N′*-methylene-bisacrylamide (MBAA) as the cross-linker. A fixed ratio of 50:1 of NIPAM to MBAA was used. Bulk FTIR spectrum of the gels was measured using a Nicolet Magna-IR 860 spectrometer by pelletizing a small amount of dried gel with KBr. UV−visible absorption spectrum of DMAAB and a thin film of the gel was measured using a Hewlett-Packard 8453 diode array spectrophotometer.

For swelling and shrinking studies, disks were cut from cylindrical samples that were prepared using a Teflon mold. Dry disks were immersed in water using a jacketed vessel and the temperature was maintained with a recirculating bath. The gels were immersed at a fixed temperature of 4 (±0.5) °C for 48 h to ensure equilibrium. To determine the equilibrium swelling of the cross-linked PNIPAM gels at a certain temperature, the sample was then immersed in purified water at a fixed temperature in the range 10−40 (±0.5) °C. After equilibration, the gels were taken out from water and weighed. In contrast to measurements of swelling based on the change in radius, the gravimetric method allows measurement of changes in the total volume of the gel, which can be interpreted within a theoretical framework. However, changes in temperature during the process of measurement and the presence of excess water are sources of error in the swelling ratio. Therefore, the time taken for measurement was minimized, and the gels were carefully wiped with wet tissue paper to remove any adherent water. The swelling ratio of samples, R_s, was estimated as $R_s = (W_s - W_d)/W_d$, where W_s and W_d were the weight of the swollen and dried samples, respectively. Measurements were performed for at least two different samples to ensure reproducibility.[18]

Shrinking kinetics of the gels were measured by equilibrating samples (in the dark) in water at 4 °C for 48 h and then transferring them to water at a higher temperature (10−40 °C). The samples were removed from water at specific intervals of time and as before, weighed quickly after removing excess water on the gel surface with a wet tissue paper. The amount of water released was measured by weighing the gel that had been immersed in water for a specific interval of time (W_t). Shrinking behavior of gels containing photochromic cross-links was also measured under irradiation by light. A 300 W ultraviolet lamp (model 66184, Oriel Corporation) equipped with an interference filter for 410 nm wavelength was used. The path length from source to sample was 10 cm. Because the UV lamp was equipped with a water filter and the gel was immersed in water, heating due to infrared components of light was negligible.

Results and Discussion

Characterization of Gel Properties. All PNIPAM gels cross-linked with DMAAB possessed a characteristic yellow color
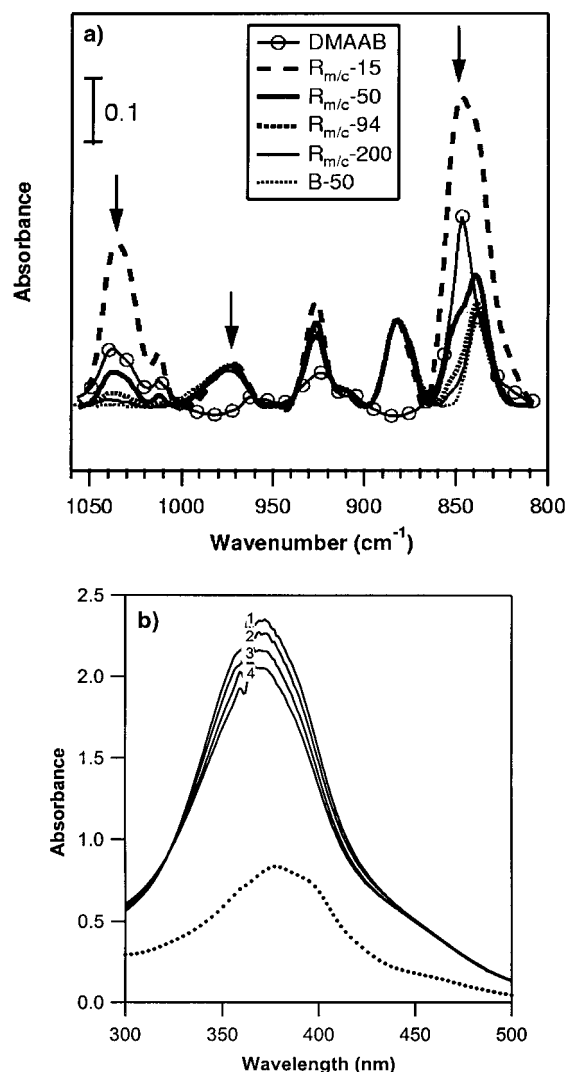

Figure 1. Transmission IR spectra (a) of the $R_{m/c}$-15, $R_{m/c}$-50, $R_{m/c}$-94, $R_{m/c}$-200, and B-50 gels compared to the bulk spectrum of DMAAB. The spectra have been scaled to match the intensity of the peak at 970 cm^{-1}. Panel b shows the UV−visible absorption spectrum of a dark-stabilized, 0.01 M solution of the cross-linking agent DMMAB (dashed line) in DMF. The absorption of $R_{m/c}$-94 gel (film swollen in water at 25 °C) is shown after different times of irradiation: (1) 0 (dark-stabilized); (2) 30; (3) 60; (4) 120 min.

due to the aromatic azo bond and were transparent when swollen with water. In comparison, the gel B-50 prepared by cross-linking with MBAA was colorless. The yellow color deepened for gels prepared using a lower molar ratio ($R_{m/c}$) of NIPAM to DMAAB and was consistent with the incorporation of a higher fraction of photochromic cross-links in the gel.

The gels prepared with photochromic cross-links were characterized using transmission IR spectra and UV−visible spectroscopy (Figure 1).[19] The bulk IR spectra of the $R_{m/c}$-XX samples (Figure 1a) revealed absorption bands at 1035 and 846 cm^{-1} that were also present in the spectrum of the pure DMAAB. These bands arise from the in-plane and out-of-plane C−H bending vibrations of the aromatic ring in DMAAB. No such bands were observed in the sample B-50 prepared from MBAA. Because the absorption band at 970 cm^{-1} due to the isopropylacrylamide moiety was absent in DMAAB, all spectra were normalized with respect to its intensity. Figure 1a shows that the intensity of the band at 1035 cm^{-1} (and at 846 cm^{-1}), which corresponds to DMAAB, increased in proportion with the decrease in the ratio $R_{m/c}$ of monomer to cross-linker

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concentration. The band was most intense for $R_{m/c}$-15 and the least intense for $R_{m/c}$-200, which is consistent with a higher incorporation of the cross-linking agent within the former. Figure 1b shows the UV−visible spectrum of $R_{m/c}$-94 and the cross-linker DMAAB.[20] The dark-stabilized samples show a strong absorption from the azobenzene moiety in the UVB region (300−400 nm) with a slight shift of the maximum absorption to lower wavelength in the gel. Irradiation of the gel caused a slight decrease in the peak absorption and was indicative of the trans−cis isomerization. While the isomerization of DMAAB in solution is known[17] to show a significant conversion of trans to cis isomers within 40 min (80% drop in the maximum absorbance), isomerization in the network was significantly less with the maximum absorbance changing by less than 15% after 2 h of irradiation.[21]

The equilibrium swelling behavior (Figure 2a) of the $R_{m/c}$-XX series gels as a function of temperature revealed that gels with a high degree of swelling correspond to lower incorporation of DMAAB or lower cross-linking concentration. Similar behavior has been reported in past experimental studies on neutral PNIPAM gels.[1] A continuous volume phase transition was also observed as temperature was increased. The largest decrease in swelling was observed between 20 and 35 °C. A plot of the normalized slope of R_s with respect to temperature shows the transition temperature more clearly (Figure 2b). For B-50, the transition occurred near 32 °C, which is close to the value for the lower critical solution temperature of PNIPAM chains in aqueous solutions. In $R_{m/c}$-200, the DMAAB cross-links introduced a high degree of absorption for ultraviolet light but only negligibly influenced the volume transition temperature (T_c). In comparison, swelling behavior of gels $R_{m/c}$-15, $R_{m/c}$-50, and $R_{m/c}$-94 revealed a shift in T_c toward lower temperatures as the amount of DMAAB increased within the gel. The gel with the highest incorporation of DMAAB ($R_{m/c}$-15) showed a $T_c \approx 19$ °C, while $R_{m/c}$-50 and $R_{m/c}$-94 showed a transition temperature of ~23 and ~28 °C, respectively. In past studies,[22,23] no such shift in T_c with cross-linker concentration has been observed for PNIPAM gels prepared with MBAA.

The effect of the cross-linker concentration on swelling can be interpreted within the framework of the Flory−Rehner (FR) phenomenological model.[24] According to this formalism, the equilibrium swelling of a neutral polymer gel is determined by the condition of zero osmotic pressure (Π) in a solvent,

$$\Pi = \nu kT\left[\left(\frac{\phi}{2\phi_0}\right) - \left(\frac{\phi}{\phi_0}\right)^{1/3}\right] - \frac{kT}{V_s}[\phi + \ln(1 - \phi) +$$

$$\chi(\phi,T)\phi^2] = 0 \quad (1)$$

where the first term is the contribution from the elastic free energy (Π_e) and the second term is the free energy of mixing (Π_m). Here, T is the temperature, V_s is the molar volume of the solvent, ν is the number of effective polymer chains between cross-links per unit volume of the gel, and ϕ and ϕ_0 are the network volume fractions at swelling equilibrium and initial state, respectively. The Flory interaction parameter for the polymer and solvent, χ, depends on both ϕ and T. Past studies have shown that eq 1 or its adaptations can be successfully used to obtain the equilibrium swelling curve,[1,10,22,25]

$$V/V_0(T) = \phi_0/\phi \quad (2)$$

that captures the volume phase transition. Using a modified FR theory and experiments, Shibayama and co-workers[22,23] have reported that neutral PNIPAM gels cross-linked with MBAA show a decrease in V/V_0 with an increase in the cross-linker

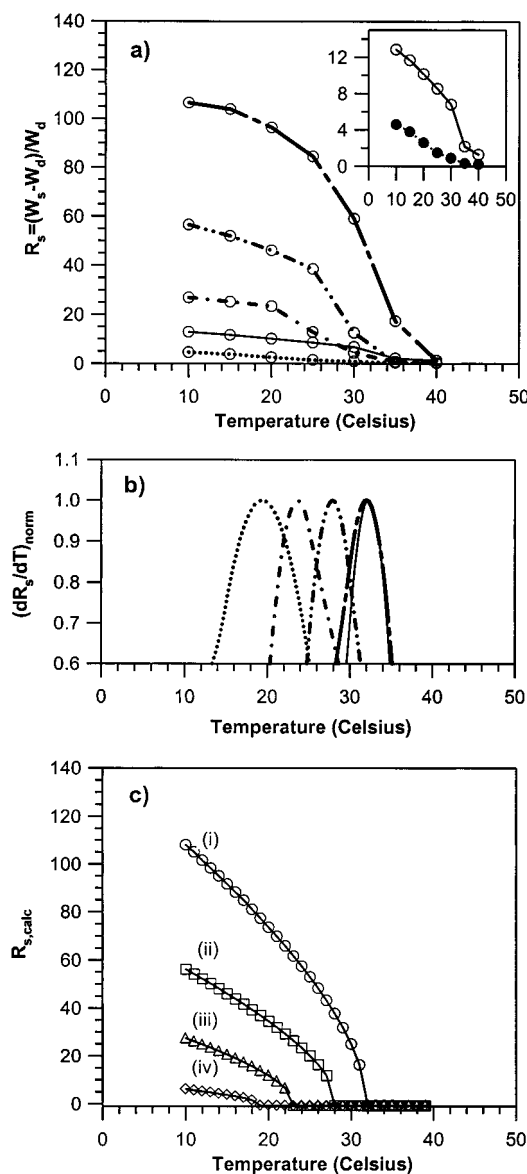**Figure 2.** Equilibrium swelling ratio as a function of temperature (a) for $R_{m/c}$-15 (dashed line), $R_{m/c}$-50 (dot−dash line), $R_{m/c}$-94 (dot−dot−dash line), $R_{m/c}$-200 (short−long dash line), and B-50 (solid line). The inset shows a magnified view for $R_{m/c}$-15 and B-50. All measurements were in the dark. Panel b shows a normalized slope with respect to temperature for the equilibrium swelling ratio. Panel c shows the theoretically estimated swelling ratios ($R_{s,calc}$) for different ΔH and ν values: (i) $\Delta H = -12.32 \times 10^{-21}$ J, $\nu = 0.0001$ mol/L (○); (ii) $\Delta H = -12.18 \times 10^{-21}$ J, $\nu = 0.00025$ mol/L (□); (iii) $\Delta H = -11.98 \times 10^{-21}$ J, $\nu = 0.0006$ mol/L (△); (iv) $\Delta H = -11.85 \times 10^{-21}$ J, $\nu = 0.005$ mol/L (◇). Parameters $\phi_0 = 0.14$, $\chi_2 = 0.518$, $\Delta S = -4.717 \times 10^{-23}$ J/K were held constant in lines i−iv. See text for discussion.

concentration, that is, increase in ν. The decrease in swelling ratio in Figure 2a with the ratio $R_{m/c}$ originates from a similar increase in topological constraints due to higher cross-link concentration.

However, the results in Figure 2a−b differ from Shibayama's work because neither the theoretically estimated $V/V_0(T)$ curves nor the experiments showed a shift in T_c when the concentration of the cross-linker MBAA was varied. The reason underlying this difference is that change in MBAA concentration has a negligible influence on the effective Flory interaction parameter, χ, which is an important determining factor for T_c. In contrast, DMAAB is significantly more hydrophobic and even though the cross-links are a small fraction (~0.5−6.6% from reaction

stoichiometry) of the network, a change in the DMAAB concentration impacts χ. Increase in the DMAAB content leads to, plausibly, a higher value of χ and shifts the value of T_c to lower temperatures. Past results by Irie and co-workers[11,16] on aqueous solutions of PNIPAM chains that had azobenzene groups in the side chains support this interpretation. Irie et al. observed that the LCST for free PNIPAM chains shifts to lower temperatures with increase in the azobenzene content because of the increasing hydrophobicity associated with the side chain.

Calculation of the temperature dependence of swelling using eqs 1 and 2 supports the above interpretation. In these calculations, the temperature and concentration dependence of χ was estimated using the following form:[1,10,22,25]

$$\chi = \chi_1 + \chi_2 \phi = \frac{\Delta H - T\Delta S}{k_B T} + \chi_2 \phi \qquad (3)$$

The value of ϕ_0 in eq 1 was set from experimental values. A past study by Hirotsu[25] has reported estimates for $\chi_2 = 0.518$, $\Delta S = -4.717 \times 10^{-23}$ J/K, and $\Delta H = -12.462 \times 10^{-21}$ J. For simplicity, we assumed that only ΔH changes with cross-linker concentration. Therefore, the values of ΔH and ν were adjusted until the volume transition temperature and the swelling ratio at low temperatures approximated the values obtained from experiments. The plot of $R_{s,calc}$ in Figure 2c shows that curve i corresponds to the behavior shown by $R_{m/c}$-200, while curves ii, iii, and iv correspond to $R_{m/c}$-94, $R_{m/c}$-50, and $R_{m/c}$-15, respectively.

As expected, the cross-link density ν had no effect on T_c but only modified the degree of equilibrium swelling. The increase in the estimated cross-link parameter ν showed reasonable agreement with the change in the cross-linker concentration during the synthesis. For example, the change in R_s (Figure 2a) upon decreasing the molar ratio of NIPAM to DMAAB from 200 to 94 was matched well by the $R_{s,calc}$ (Figure 2c) when ν increased by a factor of 2.5 from 0.0001 to 0.00025. Similarly, the change in R_s with decrease in NIPAM/DMAAB from 94 to 50 was matched by a nearly 2-fold increase in ν from 0.00025 to 0.0006. While the shape of the theoretically estimated curves i–iv for $R_{s,calc}$ differed from the experimental results, the theoretical estimates supported the interpretation of experimental results in Figure 2a. A slight increase in ΔH caused a shift in T_c and a change of 0.5×10^{-21} J ($\sim$4%) in ΔH was sufficient to shift T_c from 32 to 19 °C.

Shrinking Dynamics of Swollen Gels. The rate of shrinking of a polymer network reveals important information on the dynamic interactions between the gel and the solvent. For PNIPAM gels with photochromic cross-links, the deswelling behavior of $R_{m/c}$-50 and $R_{m/c}$-94 was investigated by subjecting a gel swollen at 4 °C to a temperature jump to different temperatures ranging from 10 to 40 °C. For both materials, the extent of water loss became larger as the temperature of exposure for the swollen gel was increased and the rate of weight loss increased with the magnitude of the temperature jump. This behavior is illustrated in Figure 3a for $R_{m/c}$-94. It is evident that the largest change in water content occurred between 25 and 35 °C and corresponds to a rise in temperature above the volume transition temperature (T_c) for $R_{m/c}$-94. In the case of $R_{m/c}$-50, the largest change occurred between 20 and 30 °C (not shown) and was in agreement with the shift in T_c to lower temperature (cf. Figure 2b).

Shrinking behavior for a wide number of thermally responsive gels has been reported and is understood in terms of a "collective diffusion" that combines network diffusion through the aqueous phase and network rearrangement. Two approaches are fre-
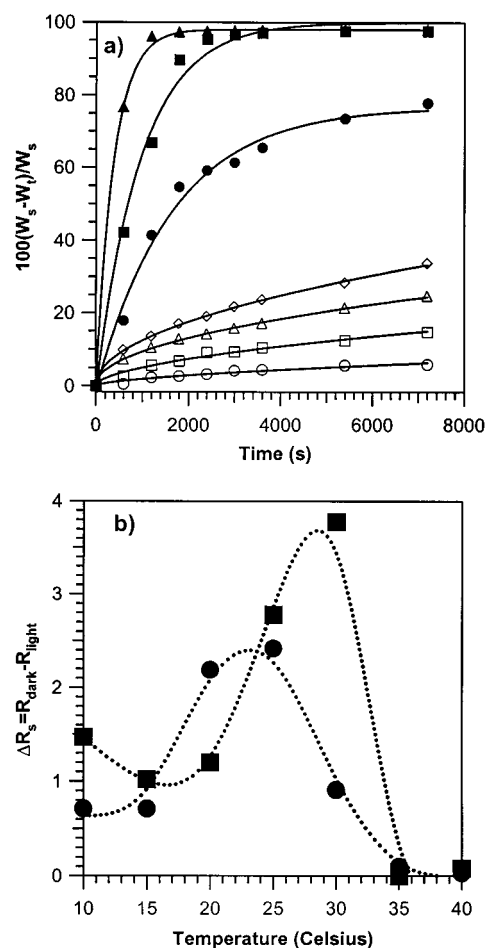

Figure 3. Change in water content as a function of time (a) for $R_{m/c}$-94. The gel was swollen at 4 °C and subjected to a temperature jump: (○) 4–10; (□) 4–15; (△) 4–20; (◇) 4–25; (●) 4–30; (■) 4–35; (▲) 4–40 °C. The lines are fit to the experimental data. For temperatures below 30 °C a power law, $y = kt^n$, was used. For $T \geq 30$ °C an exponential fit, $y = k\,e^{-t/\tau}$, was used. Panel b shows the net difference in the swelling ratio of water for $R_{m/c}$-50 (●) and $R_{m/c}$-94 (■) before and after 2 h of irradiation. Lines are drawn as guide to the eye.

quently used to interpret shrinking kinetics. One approach relies on the Tanaka–Fillmore[26] model or its generalizations[27] and incorporates the elasticity of the polymer network along with an effective diffusivity. A second approach relies on modeling the shrinking (or swelling) as an unsteady-state diffusion process.[28] The latter predicts that the rate of water release follows a time dependence of $t^{1/2}$. Figure 3a shows that for $T < T_c \cong 30$ °C the shrinking of the photochromic $R_{m/c}$-94 gel can be adequately described by a dependence of the form t^n with n lying between 0.49 and 0.60. In contrast, once the temperature exceeded the phase transition temperature, the $t^{1/2}$ dependence could no longer be used to accurately describe the kinetics of shrinking. An exponential fit was observed to be a better description for the results corresponding to 30, 35, and 40 °C. Complete collapse of the gel was observed for $T > T_c$.

Past studies have often observed a similar departure from $t^{1/2}$ Fickian diffusion kinetics when the temperature jump exceeds the critical transition temperature.[7] The exact nature of the departure has been reported to depend on the chemical and physical structure of the gel. For example, shrinking of PNIPAM gels cross-linked with MBAA near T_c has been known to occur in multiple stages with different rates of water loss.[23,29] Kitada and co-workers have shown that the characteristic time for these processes can be altered by manipulating the pressure during gelation.[30] Incorporation of hydrophobic comonomers

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with NIPAM can also lead to gels with a sigmoidal shrinking behavior.[31] Visual observations indicate that all of these effects stem from either heterogeneities in the gel or formation of a dense skin layer that restricts outward permeation of water. The latter leads to a build-up of internal pressure followed by formation and swelling of bubbles on the gel surface with expulsion of water through the bubbles. In the case of the present study, in which gels were prepared with DMAAB in the cross-links, visual observation of the gel showed the presence of patches of dense skin and bubbles when the gel was subjected to a temperature jump $T > T_c$. However, in contrast to previous studies of different PNIPAM gels, neither multiple stages with different rates of water loss nor a sigmoidal pattern in the shrinking kinetics was observed for these gels.

Effect of Irradiation. Azobenzene is known to exhibit trans—cis isomerization upon irradiation with UV light and cis—trans isomerization by thermal relaxation. Past studies have explored the photoisomerization of azobenzene chromophores incorporated as cross-links in elastomeric networks of polyacrylates and polyisobutylene. Stadler and Weber[14] have shown that in swollen gels of polyisobutylenes trans—cis isomerization of the cross-links causes a decrease in the entropy of the polymer chains in the network and that the elastic retractive forces produce a faster cis—trans isomerization. This indicates that the behavior of the azo groups in cross-links differs from isomerization of azobenzene groups in either side chains or free chains.

Because the volume phase transition in PNIPAM gels is dependent on the network entropy and because the isomerization of cross-links can impact this entropy, we investigated the effect of irradiation on the shrinking of $R_{m/c}$-50 and $R_{m/c}$-94 at different temperatures. The gels were swollen with water under dark conditions over a prolonged period at 4 °C. After immersion in water at a given temperature, gravimetric measurements of the amount of water expelled from a swollen gel were performed as a function of time while the gel was irradiated with light from a UV lamp. As a control, we also measured the response for the B-50 gel, which has no chromophoric groups. No effect of irradiation was seen on the swelling ratio (R_s) for B-50 gel, and the difference, $\Delta R_s = R_{s,dark} - R_{s,light}$ remained close to zero. In contrast, the gels cross-linked with DMAAB showed several distinct effects of light irradiation (Figure 3b).

First, for both $R_{m/c}$-50 and $R_{m/c}$-94, the amount of water expelled was larger (ΔR_s was positive) upon irradiation than under dark conditions. Second, the maximum in ΔR_s was close to the temperature at which the volume phase transition occurred. Third, $\Delta R_{s,max}$ was larger in the case of the $R_{m/c}$-94 gel than $R_{m/c}$-50. The value of $\Delta R_{s,max}$ shows that irradiation reduced the swelling ratio by nearly 30% of the value that was observed in the dark for $R_{m/c}$-94 and by 20% for $R_{m/c}$-50. To ensure that these effects were due to chemical changes in the chromophore and not due to macroscopic changes in temperature caused by irradiation, the temperature of the solvent was monitored during irradiation. Because no rise in temperature was observed and because B-50 did not show any effect of light irradiation, we believe that photochromism of the cross-links underlies ΔR_s.[32]

Results in Figure 3b show a stark contrast with past results on a gel wherein the azobenzene was present in the PNIPAM side chains and not the cross-links. In past studies, Irie et al. reported that trans—cis isomerization of azobenzene groups in side chains of a PNIPAM gel increased the volume change on swelling (or retention of water) by nearly 25%.[11] This difference in water retention upon irradiation did not show a maximum below T_c but remained constant with temperature. Furthermore,
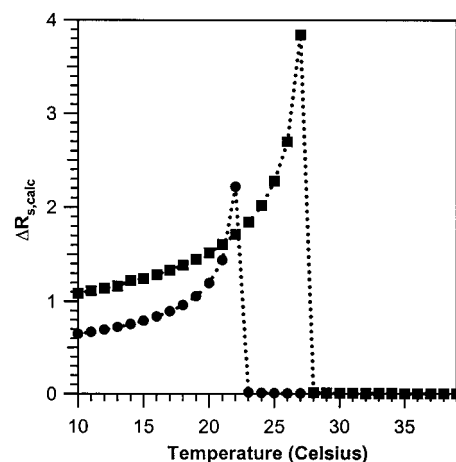

Figure 4. Theoretically estimated change ($\Delta R_{s,calc} = R_{s,calc} - R'_s$) in swelling ratios due to entropy change. The value of R'_s was calculated using $\Delta S = -4.7255 \times 10^{-23}$ J/K, $\Delta H = -12.18 \times 10^{-21}$ J, $\nu = 0.00025$ mol/L (●) and $\Delta S = -4.7245 \times 10^{-23}$ J/K, $\Delta H = -11.98 \times 10^{-21}$ J, $\nu = 0.0006$ mol/L (■). See text for discussion.

irradiation shifted the transition to higher temperatures. Irie at al. interpreted their observations on the basis of the fact that the cis isomer is more hydrophilic relative to the trans isomer. We believe that changes in hydrophilicity due to trans—cis isomerization do not account for our experimental results because a similar effect would lead to a negative ΔR_s and not a positive ΔR_s as shown in Figure 3b. Furthermore, ΔR_s shows a maximum near T_c and is not constant with temperature. Another major difference between the present study and the past work is that the azobenzene content in the side chains of the gel was ~11% and significantly more than the chromophore content in the cross-links of $R_{m/c}$-94 and $R_{m/c}$-50 gels.

The changes in Figure 3b are more consistent with the reasoning by Stadler and Weber for the isomerization of azobenzene in cross-links of an elastomeric network. They proposed that trans—cis isomerization of the cross-links causes a local stress field and lower entropy of the network. Because lower entropy of the network in turn leads to increase in unfavorable interaction of the network with the solvent, the effect of irradiation proposed by Stadler and Weber can, plausibly, account for the increased expulsion of water from the PNIPAM gels cross-linked with DMAAB. In the PNIPAM gels, the volume phase transition amplifies the entropic effect and a measurable change in ΔR_s is observed. The above hypothesis suggests that a shift in T_c to lower temperatures should occur upon irradiation. However, no such effect was apparent in our experiments indicating that either the magnitude of the shift was small or the measurement was not possible with the discrete temperatures used in this study. Furthermore, the smaller $\Delta R_{s,max}$ in $R_{m/c}$-50 compared to $R_{m/c}$-94 indicates that cross-link density plays a role. Analogous to the polyisobutylene networks with azobenzene cross-links, a higher cross-link density lowers the cis fraction obtained upon irradiation and in turn leads to the smaller value of $\Delta R_{s,max}$ in the $R_{m/c}$-50 sample.

Theoretical estimates of ΔR_s (Figure 4) support the above reasoning. To capture the effect of irradiation, ΔS in eq 3 was varied from the value that was used to estimate curves ii and iii in Figure 2c. A swelling ratio R'_s was estimated, and the difference, $\Delta R_{s,calc} = R_{s,calc} - R'_s$, was estimated at each temperature, where $R_{s,calc}$ is the value plotted in Figure 2c. The general shape of the estimated $\Delta R_{s,calc}$ shown in Figure 4 matches the experimental observations and shows an increase as T_c is approached. While experiments reveal a broad maximum in ΔR_s, the calculated values show a much sharper change in

ΔR_s with temperature. Good agreement between the estimated $\Delta R_{s,max}$ and experimental $\Delta R_{s,max}$ was obtained with only a small change in ΔS ($\sim(7.5-8.5) \times 10^{-26}$ J/K). Thus, a variation in entropy of less than 0.2% was sufficient for a macroscopic change of $20-30\%$ in the swelling ratio. These results suggest that incorporation of photochromic cross-links within a thermoreversible gel and isomerization of the cross-links have entropic and enthalpic consequences that can form the basis for modulation of the volume phase transition and the swelling behavior of the gels.

Conclusions

The preparation and properties of thermosensitive gels of PNIPAM that are cross-linked with azoaromatic chromophores were investigated. As in past studies, a high cross-linker concentration resulted in a decrease in the degree of equilibrium swelling due to an increase in the topological constraints of the PNIPAM chains. In addition to this change in swelling ratio, the increase in cross-linking density also caused a shift in the volume phase transition temperature (T_c) to lower values, which was attributed to the increase in unfavorable enthalpic interactions between the solvent (water) and the polymer network due to the azoaromatic cross-links. The shrinking dynamics of the PNIPAM gels with photochromic cross-links were found to follow a Fickian diffusion behavior for $T < T_c$. Irradiation of the gel and trans$-$cis photoisomerization of the cross-links were found to decrease the water content of the gels. The largest decrease in water content ($\Delta R_{s,max}$) was observed when the irradiation was performed near T_c. Irradiation caused a decrease in swelling by as much as $20-30\%$ of the value observed in the dark. This result contrasted with the behavior reported in past studies for PNIPAM gels in which the azochromophore was present in the side chains. The changes in swelling due to irradiation were attributed to entropic changes in the network due to irradiation. Furthermore, an increase in the cross-link density was found to reduce the magnitude of these changes and decrease $\Delta R_{s,max}$.

References and Notes

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(18) The continuity of the swelling data and shrinking kinetics for all of the samples for multiple measurements indicates that temperature variations, if any exist during the time of the brief period of gravimetric measurements, do not cause undue variations.

(19) We attempted to degrade the gel using a strongly alkaline solution to measure the concentration of the azo moiety. However, even after several days, no degradation was observed.

(20) The UV−visible absorption of DMAAB was measured in DMF because it was insoluble in aqueous solutions.

(21) Changes in the absorption spectrum with irradiation could not be measured as a function of temperature because of experimental constraints. Because the azobenzene moiety has a strong molar absorptivity, measurements in Figure 1b had to be performed with an extremely thin film of the gel suspended in water. Increase in temperature led to warping/folding of the film, and therefore, an accurate absorption spectrum could not be obtained. The use of mechanical means to keep the gel stretched during temperature jumps is not possible because the additional mechanical stress would result to results that would be inconsistent with the other experiments in which swelling of a "free" disklike gel was measured.

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(32) Prediction of the magnitude of ΔR_s from changes in absorbance (A) of the azobenzene chromophore (cf. Figure 1b) is difficult because a one-to-one relation between ΔA and ΔR_s does not exist. Prediction of the magnitude of ΔR_s from changes in absorbance requires a geometric description of the network wherein the fractional trans-to-cis conversion has to be related to the change in elastic free energy, which is not possible at this time.