

Rheological properties of thermoresponsive nanocomposite hydrogels

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ABSTRACT: Highly elastic and robust nanocomposite hydrogels based on *N*-isopropylacrylamide (NIPAM) and cationic (3-acrylamidopropyl) trimethylammonium chloride (AMPTMA) were synthesized by photopolymerization. Nanoscopic clay, laponite XLS, was added in the gels during the synthesis. The effect of a hydrophobic salt, lithium bis(trifluoromethane) sulfonimide (LiNTf₂), and clay content on the viscoelastic properties, swelling ratio, and stiffness of the nanocomposite hydrogels were investigated as a function of temperature. Synthetic clay served as a multifunctional cross-linker, producing hydrogels with enhanced elastic properties. Anionic NTf₂ binds to the cationic comonomer units and significantly affected the viscoelasticity and thermal properties. DSC measurements showed that the volume phase transition temperature and its enthalpy changed with the clay content and with introducing the cationic comonomer (AMPTMA) in the PNIPAM network. With the addition of either laponite XLS or the comonomer and 5 mM solution of LiNTf₂, a fourfold and fivefold increase in elastic modulus was obtained, respectively, compared to that of the homopolymer PNIPAM hydrogel. With increasing the temperature from 20 to 45°C for the copolymer gel with 10% AMPTMA in 5 mM LiNTf₂, the elastic modulus grew 15 times larger. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43123.

KEYWORDS: cationic copolymer of *N*-isopropylacrylamide; DSC; elasticity; photopolymerized nanocomposite hydrogels; rheological properties

Received 24 August 2015; accepted 2 November 2015

DOI: 10.1002/app.43123

INTRODUCTION

The term hydrogel is used for three-dimensional network structures of polymers which can absorb and retain high amount of water. Some of the hydrogels have extraordinary characteristics, such as good biocompatibility and transition in volume by a small change of environmental variables (pH, temperature, ionic strength, and so on).^{1–5}

Poly (*N*-isopropylacrylamide) (PNIPAM) has attracted attention because of its sharp reversible volume transition with temperature.⁶ PNIPAM has a lower critical solution temperature (LCST) of around 32–34°C in water, and hydrogels made of PNIPAM cross-linked with clay and/or *N,N'*-methylenebisacrylamide (BIS) shrink as temperature increases above LCST. This effect has led to a variety of applications for the hydrogels, such as drug delivery agents,^{7,8} biosensors,⁹ separation devices,¹⁰ and bioactuators.¹¹

However, conventional cross-linked hydrogels suffer from structural heterogeneity, insufficient sensitivity to stimuli, and they show low mechanical strength.¹² Nanocomposite hydrogels can be defined as hydrated three-dimensional networks where the chains are either physically or chemically cross-linked with each other and/or nanoparticles.^{6,13} During the last decades, several types of hydrogels such as slide-ring gels,¹⁴ double network

gels,¹⁵ and nanocomposite gels^{3,16} with high mechanical strengths have been prepared.

Mechanical properties and shear response of hydrogels have been studied with different methods, such as compression, tensile, small-angle neutron scattering, and dynamic rheological measurements.^{6,17–19} Application of the hydrogels in some fields requires a fundamental investigation on their rheological properties, such as elastic and loss moduli.^{3,20,21} Among the techniques, dynamic rheological techniques have attracted a high interest as an effective approach to study the structure of hydrogels.^{21–23}

PNIPAM hydrogels have been successfully prepared by photochemically initiated polymerization. However, no detailed investigations of the mechanical, structural, and viscoelastic properties of the nanocomposite PNIPAM hydrogels have been done so far.^{12,19,24–26} The stress–strain behavior and tensile strength of photopolymerized nanocomposite PNIPAM hydrogels with changing photoinitiator concentration have been reported by Haraguchi.¹² However, rheological properties of photopolymerized cationic nanocomposite copolymer gels of *N*-isopropylacrylamide²⁷ have not been investigated.

Recently it has been shown that the bulky hydrophobic anion NTf₂, often used as a counterion in cationic ionic liquids

Table I. Feed Compositions and Reaction Times

Parameters	Sample S1	Sample S2	Sample S3	Sample S4	Sample S5
NIPAM (mg)	251	251	251	211	251
BIS (mg)	1.6	1.6	1.6	1.6	1.6
AMPTMA(mg)	-	-	-	45	-
Water (mL)	1	1	1	1	1
Clay XLS (mg)	-	25.1	37.5	-	-
Irgacure (mg)	2.51	2.51	2.51	7.5	-
TiO ₂ (mg)	-	-	-	-	3.30
Time (min)	2.5	2.5	2.5	7	20

induces an upper critical solution temperature (UCST) behavior when bound to polycations. Under certain conditions, a copolymer of NIPAM and AMPTMA can even show both UCST and LCST behavior upon addition of NTf₂. Thus, investigation of its effect on the cationic PNIPAM-based networks is of interest.

Here, rheological properties of PNIPAM and PAMPTMA–PNIPAM hydrogels have been investigated at different temperatures. Two methods have been used to increase the elasticity of the gels. First, varying amounts of clay were added to PNIPAM homopolymer gels, and second, lithium bis(trifluoromethane) sulfonimide (LiNTf₂) was added in PAMPTMA–PNIPAM copolymer gels. Because oscillational rheology on hydrogels is often complicated because of the slippage of the samples, we try to characterize the gels by compression tests.

The polymerizations were very fast when conducted using a photoinitiator Irgacure 819. For comparison, a test sample was made with TiO₂ as an initiator.

EXPERIMENTAL

Materials

N-isopropylacrylamide (Acros Organics, 99%) was recrystallized from hexane. 3-acrylamidopropyl trimethylammonium chloride (Aldrich) was precipitated and washed with acetone and dried in vacuum. Water for preparation of polymer solutions was purified with ELGA purelab ultrapurification system. Lithium bis (trifluoromethane) sulfonimide (Aldrich, 99%) and NaCl (Fluka, 99%) were used as received. Two types of photoinitiators—bis(2,4,6-trimethylbenzoyl) phenylphosphineoxide (Irgacure 819) and TiO₂ (mixture of anatase and rutile)—were obtained from Sigma-Aldrich. Synthetic laponite XLS (92.32 wt % Mg_{5.34}Li_{0.66}Si₈O₂₀(OH)₄Na_{0.66}, 7.68 wt % Na₂P₂O₇) was provided from Rockwood Co. *N,N'*-methylenebisacrylamide (BIS) (Sigma-Aldrich) was used as received.

Preparation of the Photopolymerized Hydrogels

Aqueous dispersions containing clay (laponite XLS), BIS, monomer(s), and photoinitiator (Irgacure 819 or TiO₂) were prepared. The general procedure for the polymerizations was as follows.

One milliliter of water containing laponite XLS (25.1 mg), NIPAM (251 mg), BIS (1.6 mg), and Irgacure 819 (2.51 mg, as a methanol solution) was ultrasonicated for 10 min, stirred for 30 min, and bubbled with N₂ for 30 min before exposing the

mixture to UV light (370 nm, 10 mW/cm²) for 2.5 min in an ice bath. Care was taken to prevent temperature rising close to the phase separation temperature of PNIPAM. The gelled product was purified by immersion in water for 2 days.

CHARACTERIZATION

Differential Scanning Calorimetry (DSC)

DSC measurements were conducted using TA Instruments Q2000 DSC under a nitrogen atmosphere (50 mL/min). Prior to the heating scan, swollen hydrogels were kept in hermetically sealed aluminum pans at 0°C for 1 h. The measurements were conducted by heating the samples from 0 to 60°C, with a rate of 1°C/min.

Rheology

Rheological measurements were conducted using a TA Instruments AR2000 stress-controlled rheometer with a stainless-steel 20 mm plate–plate measuring head. Flat gel samples with diameters around 30 mm at 20°C were immersed in distilled water to avoid drying or syneresis of the gel upon compression and to avoid sample shrinking below the diameter of the plate upon heating. A Peltier heated plate was used for the temperature control. Oscillatory and compression measurements were made at temperatures from 20 to 45°C. Before the actual measurements, the samples were equilibrated for 1 h at each temperature. To establish the linear viscoelastic range for oscillatory measurements, strain sweeps were conducted at 20 and 45°C at 1 Hz frequency. Frequency sweeps were then made using strains within the linear viscoelastic regime (1% strain). For the oscillatory measurements, the samples were compressed to 0.01 N normal force to ensure proper contact with the sample and the plate. Then, for the compression measurements, the plate was lowered at a speed on 30 μm/s and normal force recorded. The compressive strain as well as normal stress were then calculated from the distance measurement and normal force. The compressive modulus was calculated from the linear slope at low strains.

Swelling Ratios

Swelling experiments of the hydrogels were made gravimetrically in the temperature range from 20 to 45°C after the sample surfaces had been wiped with paper to remove excess water. The hydrogel samples were allowed to swell in deionized water for at least 1 day at each temperature (mass of the swollen gel,

W_S). The dry weight of the hydrogels, W_D , was measured after drying the gels under vacuum for 24 h.

The swelling ratio (SR) of the hydrogels is defined as $SR = (W_S - W_D)/W_D$.

RESULTS AND DISCUSSION

Photopolymerizations

The monomer, NIPAM, and comonomer, AMPTMA, were photopolymerized in deionized water in the presence of a photoinitiator, the cross-linker BIS, and synthetic laponite XLS by exposing it to UV light (370 nm, 10 mW/cm²) for 2.5 min at 0°C. The type of photoinitiator had a key role on the polymerization and two types of photoinitiators were used: (1) a bis-cylphosphine photoinitiator (Irgacure 819) with UV absorption maxima at 295 and 370 nm and (2) nano TiO₂ (a mixture of anatase and rutile) which has antibacterial effects in the presence of the light.

Trials to prepare gels with only the clay as a potential cross-linker were not successful; the products were too heterogeneous to be studied further.

The resulting hydrogels showed different characteristics depending on factors such as the amount of clay and the choice of photoinitiator. The presence of the cationic AMPTMA repeating unit in the NIPAM network had a major impact on properties. The feed compositions of the samples chosen for swelling tests and mechanical characterization are shown in Table I.

Swelling Behavior

The swelling ratios of the hydrogels at different temperatures are shown in Figure 1. The swelling ratio at 20°C was highest (165) for the cationic copolymer PAMPTMA–PNIPAM. The swelling ratio of the sample S3 (clay content 15%) was 24. There is a relationship between the swelling ratio and the clay content of the hydrogels, higher clay content reducing the swel-

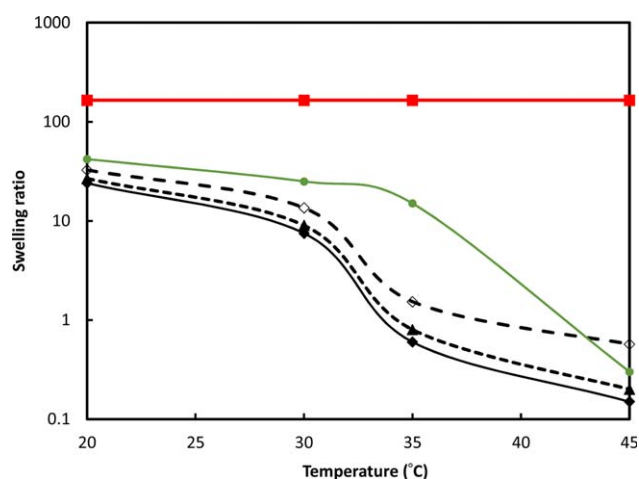


Figure 1. Swelling ratios of the hydrogels from 20 to 45°C. S1 (PNIPAM) (\diamond), S2 (PNIPAM + 10% XLS) (\blacktriangle), S3 (PNIPAM + 15% XLS) (\blacklozenge), S4 (PAMPTMA–PNIPAM in water) (\blacksquare), and S4 (PAMPTMA–PNIPAM in 5 mM LiNTf₂) (\bullet). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Calorimetric Data of the Photopolymerized Hydrogels

Sample	LCST (°C)	ΔH (KJ/mol)
S1	32.2	5.10
S2	33.8	3.28
S3	34	2.50
S4	–	–
S4 in 5 mM LiNTf ₂	38.60	0.01

ling. At temperatures above the LCST, all the hydrogels except the PAMPTMA–PNIPAM, shrank dramatically in volume.

The swelling/deswelling time of the hydrogels can be discussed through monitoring the elastic and loss moduli as a function of time when temperature is switched around transition temperature. This phenomenon will be studied in detail in future works.

Differential Scanning Calorimetry

Analysis of the thermograms of the samples gives not only the onset temperature of the thermal collapse of the gels but also the enthalpy change associated with it. ΔH is related to the fraction of NIPAM units or segments which are free to undergo the deswelling process. The calorimetric data of the photopolymerized hydrogels are shown in Table II.

The first observation is that the introduction of AMPTMA in the polymerization suppresses the phase transition of PNIPAM in distilled water (sample S4), as has earlier been observed for solutions of linear PNIPAM–AMPTMA copolymers.²⁷ But in the sample S4 swollen in 5 mM salt solution of LiNTf₂, we can observe volume phase transition temperature, around 39°C upon heating (taken as the peak temperature of the endotherm). The same behavior is observed in the swelling studies. The transition point of this sample depends on the concentration of NTf₂ and composition of AMPTMA. The pure PNIPAM gel (S1) has the maximum heat flow at 32.2°C, while the addition of clay, samples S2 and S3, shifts the transition temperature to around 34°C. This indicates the interaction of the polymer

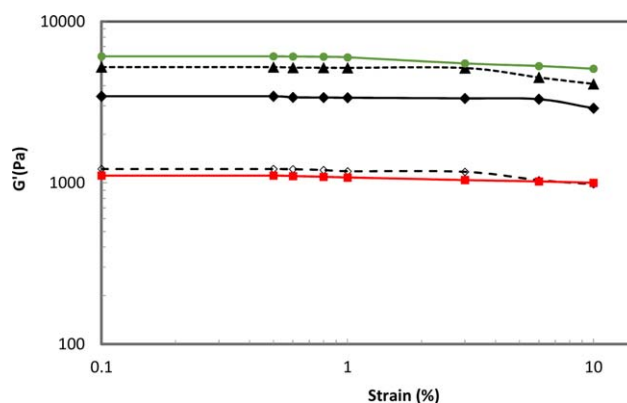


Figure 2. Oscillatory strain sweeps of the hydrogels at 20°C, frequency $\omega = 6.284$ rad/s. S1 (PNIPAM) (\diamond), S2 (PNIPAM + 10% XLS) (\blacktriangle), S3 (PNIPAM + 15% XLS) (\blacklozenge), S4 (PAMPTMA–PNIPAM in water) (\blacksquare), and S4 (PAMPTMA–PNIPAM in 5 mM LiNTf₂) (\bullet). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

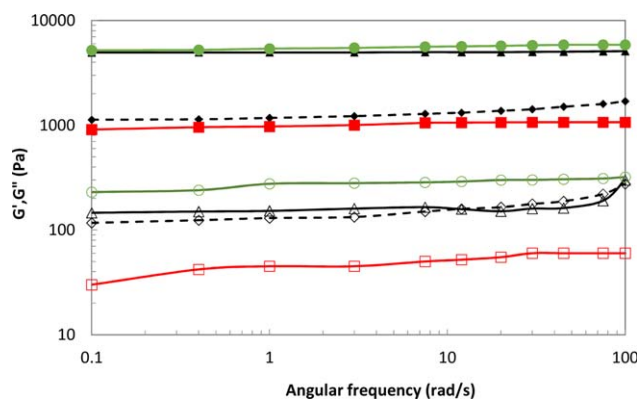


Figure 3. Frequency sweeps of the hydrogels at 20°C and 1% strain. S1 (PNIPAM) (G' \blacklozenge , G'' \blacklozenge), S2 (PNIPAM + 10% XLS) (G' \blacktriangle , G'' \blacktriangle), S4 (PAMPTMA–PNIPAM in water) (G' \blacksquare , G'' \square), and S4 (PAMPTMA–PNIPAM in 5 mM LiNTf₂) (G' \bullet , G'' \circ). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with the clay. The transition enthalpy, ΔH , decreases significantly with the increasing amount of clay, as was expected for systems where the conformational freedom of the PNIPAM chains decreases.

Rheological Measurements

Oscillatory strain sweeps at 20°C and 45°C show that the samples exhibit linear viscoelastic behavior up to around 3% strain, Figure 2. Above 3% strain, the elastic moduli of the hydrogels then gradually decreased, indicating most likely slippage of the plate. Consequently, 1% strain was selected for frequency sweeps.

The frequency sweeps of the gels are shown in Figure 3. To understand the effect of various parameters, such as the clay content, added salt, and cationic comonomer on the viscoelastic properties of the hydrogels, the oscillatory measurements were done at 20°C. It can be seen that the elastic and/or loss moduli of all hydrogels followed a similar trend. At all frequencies, elastic modulus is higher than the loss modulus. Moduli slightly increased with increasing angular frequency. As expected, the

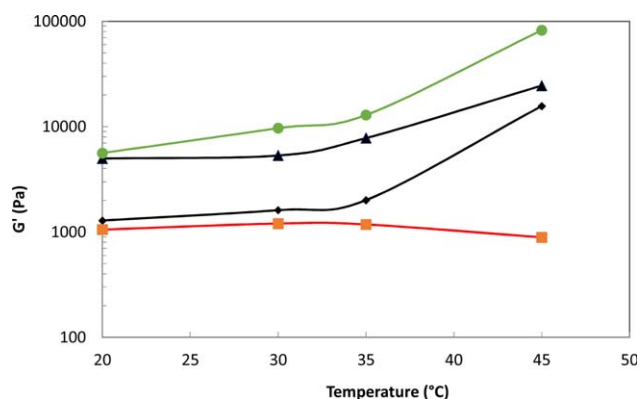


Figure 4. Oscillatory storage modulus of the hydrogels at $\omega = 7.538$ rad/s. S1 (PNIPAM) (\blacklozenge), S2 (PNIPAM + 10% XLS) (\blacktriangle), S4 (PAMPTMA–PNIPAM in water) (\blacksquare), and S4 (PAMPTMA–PNIPAM in 5 mM LiNTf₂) (\bullet). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 5. Photopolymerized PNIPAM hydrogel containing 10% clay (sample S2): (a) before and (b) after stretching. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

presence of clay in the PNIPAM network (S2) significantly increased the modulus. The modulus of PAMPTMA–PNIPAM network in water (S4) was slightly lower than that of the homopolymer gel, showing the effect of larger swelling ratio. However, S4 swollen in 5 mM LiNTf₂ had the highest elastic properties. This shows that NTf₂ binds to the cationic groups strongly enough to act as an additional cross-linking agent.

To understand the influence of temperature on the elastic properties of hydrogels, oscillatory measurements were carried out at different temperatures from 20 to 45°C at $\omega = 7.538$ rad/s, as shown in Figure 4.

It can be observed that the elastic properties of all hydrogels but the S4 (PAMPTMA–PNIPAM in water) followed a similar trend, i.e., increasing temperature increased the elastic moduli of the hydrogels. At $T = 45^\circ\text{C}$ (above the LCST), the elastic moduli of the hydrogels (except S4) has increased considerably. As an example, the elastic modulus of S1 at $T = 45^\circ\text{C}$ is 12 times higher than at $T = 20^\circ\text{C}$.

High elasticity and flexibility of the homopolymer hydrogels can be seen in Figure 5.

To determine the stiffness of the prepared hydrogels, compression tests were carried out at 20°C, and the result is shown in Figure 6. The samples were squeezed around 1,000 μm and the normal force was then measured as a function of time. The sample S4 swollen in 5 mM LiNTf₂ was the stiffest hydrogel,

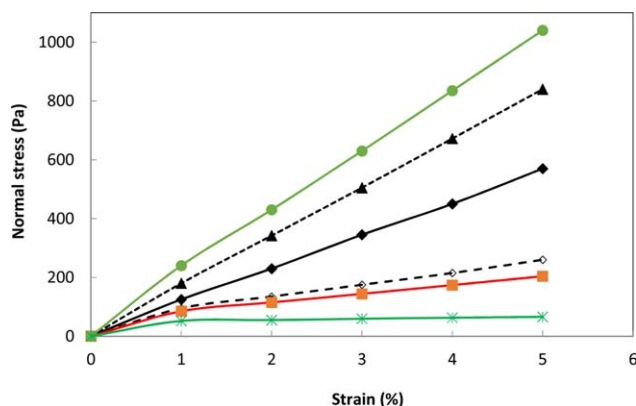


Figure 6. Stress–strain curves obtained by compression tests of various samples at 20°C. S1 (PNIPAM) (\blacklozenge), S2 (PNIPAM + 10% XLS) (\blacktriangle), S3 (PNIPAM + 15% XLS) (\blacklozenge), S4 (PAMPTMA–PNIPAM in water) (\blacksquare), S4 (PAMPTMA–PNIPAM in 5 mM LiNTf₂) (\bullet), and S1–TiO₂ (\times). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Young's Modulus of the Hydrogels at 20, 30, and 45°C

T (°C)	Sample S1 E (KPa)	Sample S2 E (KPa)	Sample S4 in 5 mM LiNTf ₂ E (KPa)	Sample S3 E (KPa)	Sample S4 in water E (KPa)	Sample S1 in TiO ₂ E (KPa)
20	3.63	15.50	18	9.94	3.16	0.18
30	5.40	16.10	21.12	13.20	3.60	1.98
45	46.20	75.30	243.30	70.41	2.70	24.64

i.e., the highest normal force at a certain time. This is indicating the strong binding of the bulky hydrophobic anion to the polymer. In addition, the clay content in the polymer network had a positive effect on the stiffness of the PNIPAM hydrogels (S2 and S3).

The sample prepared with TiO₂ as a photoinitiator had low stiffness. A motivation for using TiO₂ as an initiator might be its antibacterial property. If stiff antibacterial gels are what are wanted, a mixture of Irgacure 819 and TiO₂ would be a suitable initiator system.

Young's Modulus and Elasticity of the Hydrogels

The Young's modulus, E , was determined at different temperatures (20, 30, and 45°C) from the slope of the stress-strain curve. The Young's modulus at 45°C is much higher than that at 20 and 30°C, see Table III. It is clearly observed from Table III that the elasticity of the hydrogels except the PAMPTMA-PNIPAM in water (S4) followed a similar trend, increasing temperature increasing the elasticity of the hydrogels. The PAMPTMA-PNIPAM gel in 5 mM LiNTf₂ is very elastic, especially at temperature above the LCST. Above the LCST, the elasticity of most of the hydrogels (S1, S1-TiO₂, S2, S3, and S4 in 5 mM LiNTf₂) significantly improved, the S4 with LiNTf₂ being superior, however. Better improvement in elasticity of the samples with clay can be seen in the hydrogels with 10% clay, sample S2, because 10% is percolation threshold of filler and for 15%, sample S3, passes this threshold.

CONCLUSIONS

A series of PNIPAM-based hydrogels have been investigated. Homopolymeric PNIPAM gels were prepared either with or without added clay. Copolymer gels were prepared of a mixture of AMPTMA and NIPAM. The motivation for the addition of cationic repeating units to the polymer was based on a recent finding that a hydrophobic anion NTF₂ binds to the cations and decreases the solubility of the polymer to such an extent that UCST behavior may be observed.²⁷

By incorporating synthetic laponite XLS to the hydrogel, the rheological properties and stiffness of the hybrid hydrogels were improved. However, the combination of a cationic monomer and a bulky hydrophobic counterion led to much stronger gels. The viscoelasticity and stiffness of the prepared hydrogels were in the order of S4 (PAMPTMA-PNIPAM) in 5 mM LiNTf₂ > S2 (PNIPAM-10% clay) > S1 (PNIPAM) > S4 (PAMPTMA-PNIPAM-water) > S5 (PNIPAM-TiO₂).

The syntheses by photopolymerization were very fast. A comparative gel sample was prepared by using TiO₂ as the initiator. The resulting gels, however, were not reasonably strong.

The overall conclusion is that strong thermally responsive PNIPAM gels may be obtained by adding a suitable amount of nanoscopic clay filler to the reaction mixture or by using ionic interactions between the polymer and added salt. The interactions between the additives and the polymer could well be seen by measuring the ΔH associated with the thermal collapse of PNIPAM. In both methods, the number of elastically effective cross-links is increased.

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