

Effect of Adamantyl Methacrylate on the Thermal and Mechanical Properties of Thermosensitive Poly(*N*-isopropylacrylamide) Hydrogels

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ABSTRACT: A series of thermosensitive hydrogels containing adamantyl groups were fabricated by copolymerization of *N*-isopropylacrylamide and adamantyl methacrylate (AdMA). The thermal properties of such copolymeric hydrogels were studied by differential scanning calorimetry. The mechanical properties were emphasized through compression, tension, and dynamic mechanical analysis (DMA). Moreover, Rubber elasticity theory was used to evaluate the network parameters based on compressive stress–strain measurements. The results indicate that both the microstructure and physical properties strongly depend on the quantity of AdMA in the

copolymeric gels. As the content of AdMA increases, the volume phase transition temperature of hydrogels decreases linearly, and the mechanical strength can be significantly improved, the effective crosslinking density (v_c) increases monotonously, while the polymer–water interaction parameter (χ) decreases first and then increases with AdMA content. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 155–163, 2012

Key words: poly(*N*-isopropylacrylamide); adamantyl methacrylate; hydrogels; mechanical properties; structure–property relations

INTRODUCTION

Poly(*N*-isopropylacrylamide) (PNIPAM) is one of the most extensively studied thermosensitive hydrogels. The most interesting feature of these polymers is that they can display thermally reversible phase transitions in response to temperature change. The temperature when smart hydrogels exhibit phase transitions is called volume phase transition temperature (VPTT). It is $\sim 32^\circ\text{C}$ in aqueous solution, and can be shifted by copolymerization with hydrophobic or hydrophilic monomers.^{1,2} When the external temperature is below the VPTT, the PNIPAM hydrogel or its copolymer hydrates and absorbs plenty of water, but when the temperature is above its VPTT, it dehydrates quickly. Due to this unique thermosensitive property, PNIPAM hydrogels have been com-

monly utilized in many fields, such as the controlled delivery of medicinal drugs,³ tissue engineering,⁴ separation system,⁵ mechanical actuators,⁶ smart sensors,⁷ and intelligent fabrics.⁸

However, there are still some limitations in the current PNIPAM hydrogels, such as slow response rates, weak mechanical properties and inappropriate VPTT. In fact, many potential applications of conventional PNIPM hydrogels have been restricted and abandoned because of these limitations. Therefore, it is desirable to develop a new PNIPAM based hydrogel that could overcome all these disadvantages simultaneously, especially with stronger mechanical properties and variable VPTT.

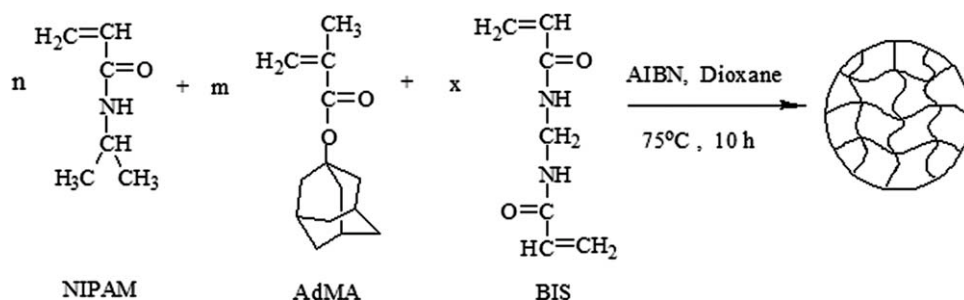
To improve the performance of PNIPAM hydrogels, many advanced ways and new technologies have been developed in recent years. Such as templating processes for creating polymerized hydrogels for applications in chemical sensing and device fabrication,⁹ the technology to obtain chemically crosslinked hydrogel layers with patternable properties,¹⁰ the significant advances in the field of nanocomposite hydrogels,¹¹ as well as the double-network hydrogels with extremely high mechanical strength.¹² All of these ways have given a striking improvement of PNIPAM hydrogels either in the temperature sensitivity or the mechanical properties. However, the excellent combination of properties needed for practical application was seldom reported. Here, we try to make some promotion in

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Scheme 1 Synthesis route of P(NIPAM-*co*-AdMA) hydrogels by free-radical solution copolymerization.

the combined properties of PNIPAM hydrogels simply by copolymerizing NIPAM and a special comonomer with adamantyl group.

Adamantane is a large, rigid, and hydrophobic molecule. When adamantyl groups are incorporated into polymers, they can significantly improve the material's thermal stability and mechanical properties.¹³ However, few studies have been reported about PNIPAM hydrogel system contained adamantyl in the network.^{14–16} In our recent research, we synthesized a comonomer of adamantyl methacrylate (abbreviated as AdMA), and fabricated a novel P(NIPAM-*co*-AdMA) hydrogel through the simple radical solution copolymerization approach. The effect of adamantyl part on the physical properties and microstructure of PNIPAM hydrogels has been systematically studied for the first time. Our anticipation is to obtain thermosensitive copolymer hydrogels with enhanced mechanical properties, improved thermal sensitivity, and adjustable VPTT.

In our previous study,¹⁷ the influence of AdMA content on morphologies and swelling properties of the prepared copolymer hydrogels was mainly discussed. The results showed that at a certain value of AdMA content, both the pore structure and swelling properties of the copolymer hydrogels exist in an optimum state, where there is perfect pore structure and a fast response to temperature change.

In this study, we extend this work to investigate the effect of AdMA content on the thermal and mechanical properties of the P(NIPAM-*co*-AdMA) copolymer hydrogels, and we also use the rubber elasticity theory to derive the network parameters based on compression measurements for well understanding the correlation between structure and properties. This relationship can be a good instruction to design expected thermosensitive hydrogels according to required properties.

EXPERIMENTAL

Materials

1-Adamantanol (>99%) and Methacryloylchloride (>99%) were purchased from local providers and

used as received. Triethylamine (analytical grade) was treated by molecular sieves before used. *N*-isopropylacrylamide (NIPAM) was purchased from TCI and recrystallized from *n*-hexane. *N,N'*-methylene-bis-acrylamide (BIS, Shanghai chemical Reagent, China) and *N,N'*-azobisisobutyronitrile (AIBN, Tianjin Kermel Chemical Reagent, China) were recrystallized within ethanol. Dioxane and dichloromethane (analytical grade) were redistilled and then treated with molecular sieves before used.

Synthesis of AdMA

Comonomer AdMA was synthesized according to the procedure of McCaffrey et al.¹⁸ At 0°C, under the protection of nitrogen, 10.45 g (0.1 mol) methacryloylchloride was added dropwise to a stirred solution of 7.60 g (0.05 mol) of 1-adamantanol and 15.18 g (0.15 mol) of triethylamine and 0.05 g phenothiazine in 150 mL of dichloromethane. After 27 h of stirring, the mixture was first filtrated, and then washed with NaOH solution followed by saturated NaCl solution. After dried over MgSO₄ and removed of the solvent by rotatory evaporation, then treated by column chromatography (silicagel, CH₂Cl₂), pure AdMA was obtained as a pale and transparent oil.

Structure characterization of AdMA

The chemical structure of AdMA was studied by using superconducting nuclear magnetic resonance (¹H and ¹³C) spectrometer (NMR, DRX-400, BRUKER) with deuterated chloroform (CDCl₃) as the solvent and Fourier transform infrared (FTIR) spectrometer (FTIR, RFX-65A, Analect) in the range of 400–4000 cm⁻¹.

Preparation of P(NIPAM-*co*-AdMA) hydrogels

A series of P(NIPAM-*co*-AdMA) hydrogels with different mass ratios of AdMA to NIPAM were prepared by free radical solution copolymerization as shown in Scheme 1. All the copolymerization was performed in dioxane, with the AIBN as initiator, BIS as crosslinker, at 75°C for 10 h. In all cases, the

crosslinker/monomer ratio, the initiator/(monomers and crosslinker) ratio were fixed at 3/100 (w/w), 1.2/100 (w/w), respectively. The concentration of the polymerization solution was 0.15 g/mL. Finally, the obtained samples were named as NA_i , where i represent the value of mass percentage of AdMA to NIPAM in feed, including that the pure PNIPAM was named as NA0.

Take AdMA3 for example, a typical procedure of copolymer preparation is as follows: 0.4000 g NIPAM, 0.0120 g AdMA, and 0.0124 g BIS were dissolved into 3 mL dioxane in a 25-mL eggplant-type flask, then 0.0051 g AIBN was added. Subsequently, the reaction system was dispersed using ultrasonic waves for 20 min followed by vacuumizing-filling in nitrogen gas for three times. Then the flask was sealed under nitrogen atmosphere and kept into oil bath at 75°C for 10 h. After copolymerization, the synthesized hydrogels were firstly washed in dioxane. Then the hydrogels were immersed into distilled water at 20°C for 24 h, and then transferred into 40°C hot water for about 10 min. Such treatment in water was repeated for at least three times and the water was replaced after every cycle to make sure that the unreacted materials and linear copolymers were eliminated completely.

Structure characterization of hydrogels

The structure of hydrogels was characterized by FTIR using the freeze-dried hydrogels. The samples were directly analyzed using a FTIR spectrometer (FTIR, RFX-65A, Analect) in a KBr flake.

Measurements of VPTTs

The VPTT of swollen hydrogel was investigated by differential scanning calorimetry (DSC) using a DSC Q200 from TA Instruments. Before measurements, all the samples were kept into deionized water at 10°C for at least 24 h to reach equilibrium. The samples were scanned from 0 to 40°C, at a rate of 2°C/min with the nitrogen flow 50.0 mL/min. The VPTT values were recorded as the maximum of the transition peaks.

Xerogel density (ρ_2) measurements and swelling experiments

1. The xerogel density measurements: The xerogel density ρ_2 was measured with specific gravity bottle method. Before measurements, all the hydrogel specimens were dried exhaustively in a vacuum oven at 60°C for several days. Since xerogels will swell in water, so hexane was chosen as the nonsolvent in the tests. The experiments were performed as follows: First,

revise the hexane's relative density to water at 20°C with the specific gravity bottle attached with a little thermometer, then test each of the sample's density according to the specific gravity bottle method.

2. Swelling experiments: four xerogel samples were chosen for equilibrium swelling experiments. First, the xerogels were weighed, respectively, as m_d . Then all the samples were immersed into deionized water of 20°C for 48 h to reach swelling equilibrium. The swollen samples were then weighed as m_w .

With the obtained xerogel density ρ_2 , and the results from swelling experiments, the equilibrium volume swelling ratio (SR_v) at 20°C can be calculated from the following expression:

$$SR_v = \frac{m_d/\rho_2 + (m_w - m_d)/\rho_1}{m_d/\rho_2} \quad (1)$$

In which ρ_1 is the density of water at 20°C (0.998 g/cm³). The polymer volume fraction in swollen state (ϕ_{2s}) was then obtained as $1/SR_v$.

Measurements of mechanical properties for hydrogels

Dynamic mechanical analysis (DMA) for the swollen hydrogel samples were conducted on a Biodynamic Mechanical Instrument (electroforce 3200, BOSE) in a dynamic compression mode to measure the dynamic storage modulus (E'), the dynamic loss modulus (E''), and the loss tangent ($\tan \delta$) as functions of frequency. Before measurements, all the samples were kept in deionized water of 25°C for at least 48 h to reach swelling equilibrium, then the hydrogels were cut into cylindrical shape of around 10 mm radius and 5 mm length, and vacuum grease was used to cover the samples surface to prevent dehydration during testing. The measurements were carried out at the same temperature of 25°C from an initial frequency of 0.01 Hz to a final frequency of 50 Hz, with a frequency increment of 1 Hz.

For tensile measurements, the swollen hydrogel samples were also equilibrated at 25°C and then cut into strips of (5 × 10 × 20 mm³). The experiments were also carried out on the Biodynamic Mechanical Instrument (electroforce 3200, BOSE) in a static tensile mode under the following conditions: test temperature was 25°C, the sample length between the jaws was 1.5 mm and the extension speed was 3 mm/min. For instrument limitation, not all the tensile tests were performed to the break point, but to an ultimate extension of 6 mm.

As to the measurements of compressive stress and strain, the hydrogels were in the equilibrium

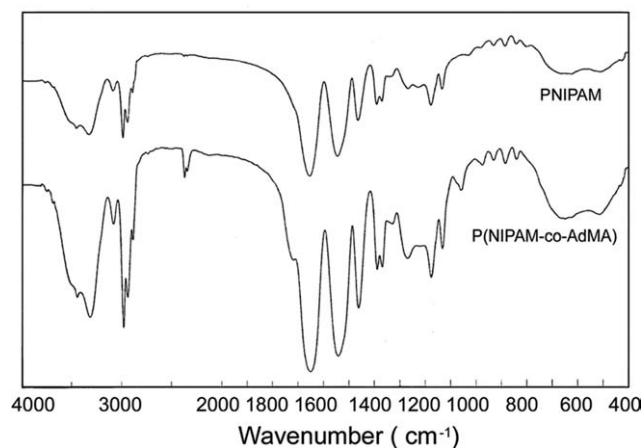


Figure 1 FTIR spectra of PNIPAM and P(NIPAM-co-AdMA) hydrogels.

swollen state at 20°C and made into cylindrical shape with a diameter of 15 mm and a thickness of 10 mm. The experiments were conducted on a Texture Analyzer (CT3, Brookfield) under the following conditions: test temperature = 20°C, test speed = 0.5 mm/s, and the ultimate deformation = 20%.

RESULTS AND DISCUSSION

The characterization of AdMA

Both the NMR and FTIR spectra have confirmed the structure of AdMA we prepared. The results are listed as follows:

^1H NMR (200 MHz, CDCl_3): δ (ppm) = 1.62 (br, CH_2 , 6H), 1.87 (s, CH_3 , 3H), 2.13 (br, CH_2 , 6H), 2.15 (s, CH, 3H), 5.45 (s, $\text{CH}_2=$, 1H), 5.98 (s, $\text{CH}_2=$, 1H); ^{13}C NMR (200 MHz, CDCl_3): δ (ppm) = 18.3 (CH_3), 30.8, 36.2, 41.2, 80.4, 124.2 ($\text{CH}_2=$), 138.0 ($\text{CH}_2=\text{C}$), 166.5 (C=O); IR (KBr): 2913, 2856, 1714 (C=O), 1635 (C=C), 1454, 1332, 1295, 1174, 1056 cm^{-1} .

Synthesis and characterization of P(NIPAM-co-AdMA) hydrogels

The FTIR spectra of the pure PNIPAM and P(NIPAM-co-AdMA) copolymer hydrogels are shown in Figure 1. From the FTIR spectra, we can see that both the curves of pure PNIPAM and P(NIPAM-co-AdMA) copolymers appear the characteristic absorption peaks of NIPAM at 3317 cm^{-1} (N-H), 1654 cm^{-1} (N-C=O) and 1548 cm^{-1} (C=N). While the important difference between the two curves is that P(NIPAM-co-AdMA) shows the characteristic absorption peaks of ester groups at 1714 cm^{-1} , indicating the presence of AdMA structure. The results of FTIR spectroscopy confirm that AdMA units have been incorporated into PNIPAM hydrogel network.

VPTTs of hydrogels

The variation of volume phase transition with temperature determined by DSC is shown in Figure 2. According to Figure 2, obviously, the VPTTs decrease almost linearly with the increasing feed ratio of AdMA to NIPAM. This result can be attributed to the strong hydrophobicity of AdMA. Since the phase-transition behavior is caused by the reversible formation and breakage of hydrogen bonding between water and hydrophilic groups, and the hydrophilic/hydrophobic balance between hydrophilic and hydrophobic groups within the PNIPAM polymer chains.¹⁹ The inclusion of AdMA content changes these complicated interactions for its strong hydrophobicity, which can prevent hydrogen bonding among the amide groups and water. Thus, less energy is needed to break the hydrogen bonding; the phase transition can take place at lower temperature. In addition, as temperature increases, the hydrophobic adamantyl groups enhance the hydrophobic association interaction among the hydrophobic groups within the neighboring polymer chains, which also contributes to the decrease of VPTTs. Such influence of AdMA content on the VPTT is basically consistent with other hydrophobic comonomers, for example *N*-tertbutylacrylamide (NtBAM).²⁰ However, our data show that the AdMA can control the VPTT more efficiently which is due to the much stronger hydrophobicity of AdMA. The obtained linear relationship between VPTT and AdMA content

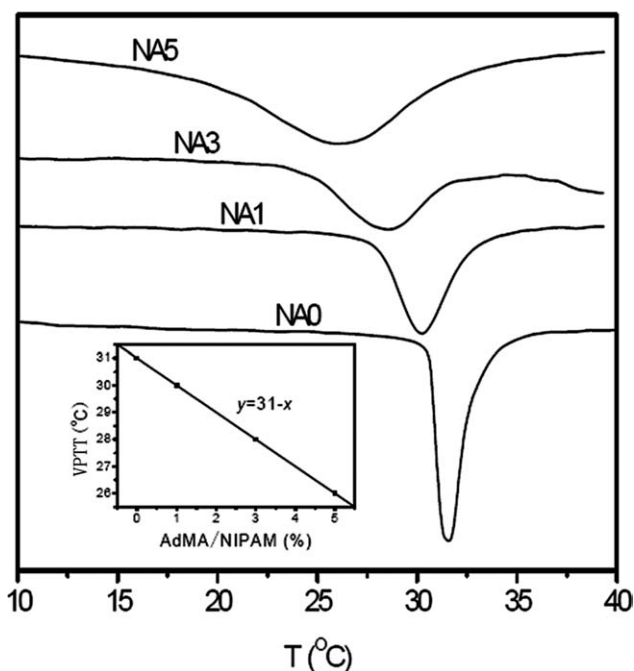


Figure 2 DSC curves of P(NIPAM-co-AdMA) hydrogels with various content of AdMA, and the VPTT as a function of mass percentage of AdMA/NIPAM in feed.

TABLE I
Xerogel Densities (ρ_2), Equilibrium Swelling Ratio Volume (SR_v), Polymer Volume Fractions in Swollen (ϕ_{2s}), and in Relaxed (ϕ_{2r}) State for P(NIPAM-co-AdMA) Gels of Four Different Monomer Mass Ratios in Feed at 20°C

20°C	ρ_2 (kg/dm ³)	SR_v	ϕ_{2s}	ϕ_{2r}^a
NA0	1.024	29.160	0.034	0.128
NA1	1.028	27.580	0.036	0.127
NA3	1.045	20.110	0.050	0.125
NA5	1.062	13.510	0.074	0.123

^a Denotes the polymer volume fraction in the gel in its relaxed state that is prior to swelling, the values were derived from the initial monomer concentration according to this equation: $\phi_{2r} = V_d(\text{dried})/V_r(\text{relaxed})$.

in feed can be a good instructor to prepare hydrogels with designed VPTT.

However, it can be seen that the transition range became broader with the AdMA content increasing. This may be attributed to the chemical heterogeneity of the copolymers. Since the copolymerization rate constant of the two monomers may be different from each other, the copolymers prepared by free radical polymerization at high polymerization yield would necessarily contain chains with different molar ratios of monomer units.^{21,22} Subsequently, these chains will behave differently during the phase transition. Therefore, the range of VPTTs for such chemically heterogeneous poly(NIPAM-co-AdMA) copolymers will be broader than that of chemically homogeneous pure PNIPAM.

Xerogel densities and swelling results

As revealed in Table I, it is found that with increasing in the content of AdMA, the ρ_2 increases. This is consistent with theoretical prediction because that

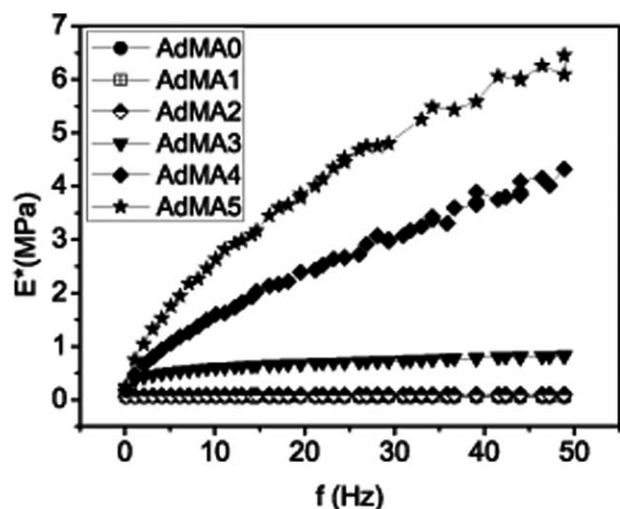


Figure 3 E^* as a function of frequency for six copolymer hydrogels with various AdMA content.

AdMA has much larger molecular weight than NIPAM. The SR_v decreases with AdMA content at the same temperature of 20°C, and the ϕ_{2s} increases. There are two possible factors contributing to this result: One is that the VPTTs of hydrogels decrease with AdMA content, so the gap of the same experimental temperature 20°C below each sample's VPTT decreases. Another may be that the effective crosslink densities increase with AdMA content. It is well known that less crosslinked materials are thermodynamically expanded more freely than highly crosslinked ones. Since the crosslinker percentage in polymers for all the samples concerned is the same, so there is a chance that incorporating AdMA part can virtually increase the effective crosslink densities of copolymer hydrogels.

Dynamic mechanical properties

Due to the viscoelastic nature of most hydrogels, comparative studies under dynamic loading are crucial for evaluating the mechanical properties of hydrogels. Figure 3 depicts the frequency dependence of dynamic complex modulus (E^*) for the six hydrogel samples with different concentrations of AdMA in feed, and Figure 4 presents the evolutions of dynamic loss tangent ($\tan \delta$) with frequency for these six hydrogels. In fact, the storage (elastic) modulus (E') and loss (viscous) modulus (E'') were both determined as functions of frequency, but the obtained values were more usefully expressed as complex modulus $|E^*|$ and loss tangent $\tan \delta$. $|E^*|$ provides a measure of stiffness under dynamic conditions, while $\tan \delta$ is an indicator of internal dissipation.²³

$$|E^*| = \sqrt{E'^2 + E''^2} \quad (2)$$

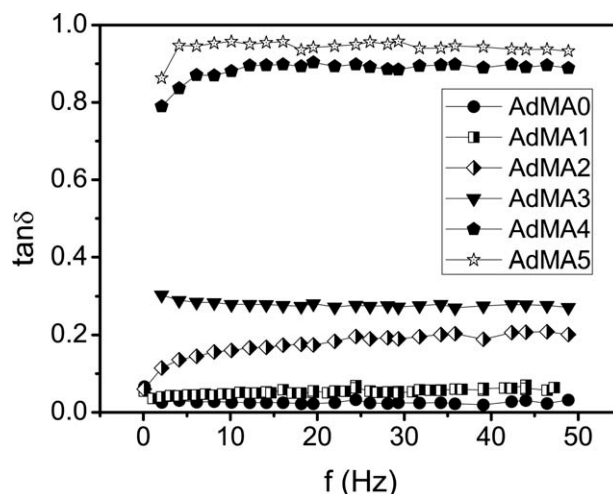


Figure 4 $\tan \delta$ as a function of frequency for six copolymer hydrogels with various AdMA content.

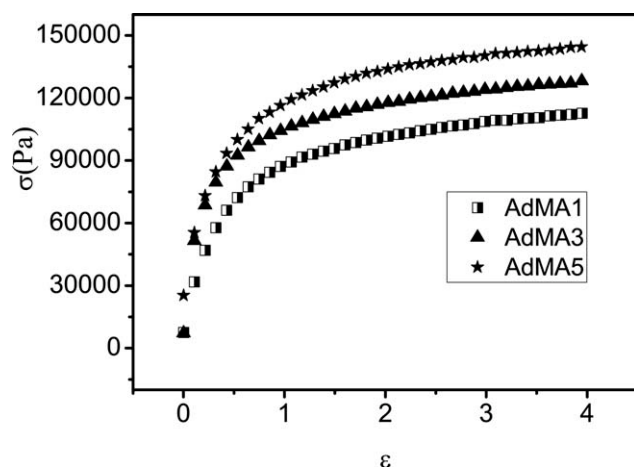


Figure 5 Tensile stress-strain curves of copolymer hydrogels with various content of AdMA in the equilibrium swollen state at 25°C.

$$\tan \delta = \frac{E''}{E'} \quad (3)$$

As shown in Figure 3, The E^* of hydrogels can be controlled by varying the mass ratios of AdMA to NIPAM in feed. The general trend is that the E^* increases with increasing AdMA concentration and frequency. However, for hydrogels with a low concentration of AdMA or with no AdMA at all ($\leq 2\%$ within experimental range), E^* does not exhibit a strong dependence either on the frequency or on AdMA concentration. All the three curves lie rather close to each other over the whole frequency scale observed. While as the AdMA percentage increases further, such as, for the NA3, NA4, and NA5 hydrogels, the behavior of E^* displays significantly different from that of the former three. At each given frequency, the E^* increases remarkably with increasing AdMA content and for each sample, the E^* exhibits monotonic increase with frequency. Moreover, the higher the AdMA content, the stronger the dependence of E^* on frequency becomes. This is because at the experimental temperature, the hydrogels with higher AdMA content contain relatively less water, thus in the denser networks, relaxation processes can possibly occur and produce increasing frequency dependence.²⁴ The results of E^* suggest that the stiffness of the copolymer hydrogels increase with AdMA content.

As shown in Figure 4, the $\tan \delta$ of all the hydrogels show almost no dependence upon the frequency over the whole range of frequency examined, suggesting that both the E' and E'' exhibit the same increasing tendency with frequency. However, the trend is that they all increase with increasing AdMA content, concretely, when the weight percentage of AdMA in feed is below 3%, the $\tan \delta$ increases slowly from 0.05 for NA0 to 0.3 for NA3, while when the weight ratio

percentage of AdMA reaches 4 and 5%, the $\tan \delta$ increases rapidly to ~ 0.9 . However, all the $\tan \delta$ of the samples examined are within the range from 0 to 1, indicative of more elastic solid behavior.²³

The trend demonstrated in Figure 4 can be explained as follows: the bulk, rigid adamantyl groups restrict the flexibility of polymer chains in the crosslinked networks. When the hydrogels are subjected to dynamic loading over a certain range of frequency, strain will lag behind stress, giving rise to part of energy loss. The more the content of adamantyl groups, the further the strain lags behind stress, so the internal loss increases with increasing AdMA content in copolymer hydrogels.

Tensile properties

Figure 5 shows the tensile stress-strain curves for three samples with different weight percentage of AdMA to NIPAM in feed, in which stress (σ) denotes the applied tensile force per unit cross-sectional area of the undeformed hydrogel specimen, and strain (ϵ) denotes the ratio of the changed length (Δl) to the initial length (l_0) of hydrogel. Here only the three samples were exhibited in tensile tests, but without the pure PNIPAM hydrogel NA0 as comparison, because the NA0 hydrogels were so weak and brittle that they were difficult to withstand any normal tensile tests. As shown in Figure 5, it is obvious that all the copolymer samples display much higher toughness. The stresses to deform the hydrogels increase with AdMA content. This indicates the promotion of the elastic properties of the hydrogels, in agreement with above results revealed from dynamic mechanical measurements.

Therefore, the addition of AdMA to PNIPAM can effectively enhance the mechanical properties of the obtained hydrogels, and the mechanical properties can be easily controlled by changing the amount of

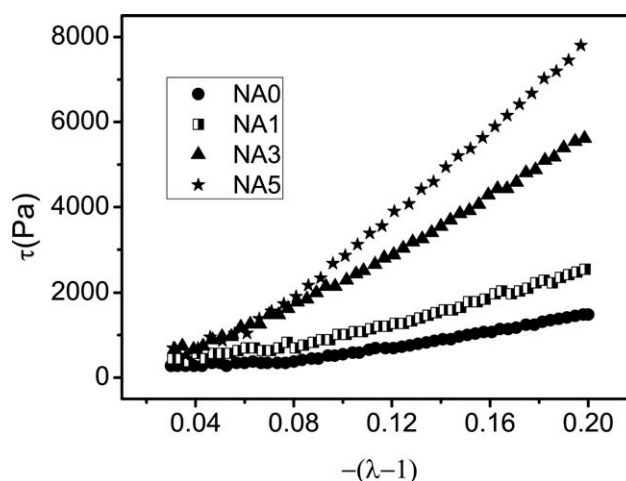


Figure 6 Compression stress (τ) versus strain $[-(\lambda - 1)]$ plots for swollen hydrogels with various AdMA content in the equilibrium-swollen state at 20°C.

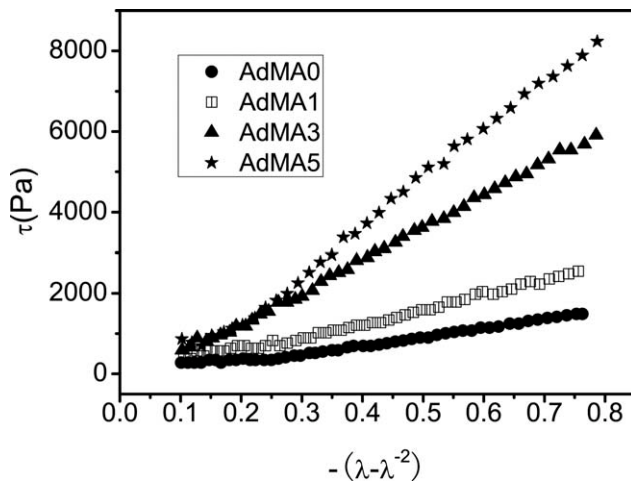


Figure 7 Compression τ versus $-(\lambda - \lambda^{-2})$ plots for swollen hydrogels with various AdMA content in the equilibrium swollen state at 20°C.

AdMA in feed. Hence, it is believed that these mechanically tunable hydrogels modified by AdMA will have great potential applications in many fields.

Compression properties and network characteristics

To investigate the relationship among the swelling behavior, mechanical properties, and network structures of the current copolymer hydrogels, compression stress-strain measurements with small deformation were made and combined with the rubber elasticity theory to evaluate the network parameters of this series of copolymeric hydrogels. Texture analysis is a technique that is usually used for the mechanical characterization of food materials, while in the recent years, it has been also employed as a useful tool in the field of hydrogel research.^{25,26} Here all the compression stress-strain measurements were just obtained in the aid of Texture analysis.

Figures 6 and 7, respectively, illustrate the compression τ versus $-(\lambda - 1)$ and compression τ versus $-(\lambda - \lambda^{-2})$ plots of the P(NIPAM-*co*-AdMA) hydrogels with different AdMA content in the equilibrium swollen state at 20°C. Where τ denotes the applied compressive force per unit cross-sectional area of the undeformed swollen hydrogel specimen, and λ is the ratio of the deformed length (l) to the undeformed length (l_0) of hydrogel. So the strain is $-(\lambda - 1)$ (for compression, it is negative), and the $-(\lambda - \lambda^{-2})$ is defined as compression deformation factor. As shown in Figure 6, it can be seen that all the samples show a linear dependence between stress and strain over the strain range given ($R > 0.99$). So the Young's modulus E could be obtained as the slopes of τ versus $-(\lambda - 1)$. The plots in Figure 7 of τ versus $-(\lambda - \lambda^{-2})$ are also shown accurately linear over the entire strain range studied. It was

said that the PNIPAM and its copolymer chains in the swollen state could be regarded as flexible polymer chains just like polymers in the rubbery state,²⁷ and the results from our mechanical measurements also showed that the P(NIPAM-*co*-AdMA) hydrogels had elastic behaviors, so the rubber elasticity theory was used here to derive the network parameters based on the compression stress-strain measurements. For a swollen network system prepared from solution, the effective crosslinking density (ν_e) can be evaluated from the following rubber elasticity equations by the gaussian chains model^{28,29}:

$$\tau = G(\lambda - \lambda^{-2}) \quad (4)$$

$$G = RT\nu_e\phi_{2s}^{1/3}\phi_{2r}^{2/3} \quad (5)$$

where the shear modulus G is determined as the slope of τ versus $-(\lambda - \lambda^{-2})$ plot according to the eq. (1), R is the gas constant ($8.314 \text{ J k}^{-1} \text{ mol}^{-1}$), T is absolute temperature (293 K).

As we know, the above classic rubber elasticity equations are established on many ideal hypotheses. To make it more reasonable to apply this statistical theory into the real network, we modify the eq. (2) partly as follows:

$$G = \frac{\overline{\gamma^2}}{\gamma_0^2} \left(1 - \frac{2}{f}\right) \left(1 - \frac{2M_c}{M_n}\right) RT\nu_e\phi_{2s}^{1/3}\phi_{2r}^{2/3} \quad (6)$$

In which $\overline{\gamma_0^2}$ is the mean square end-to-end distance of an equivalent free random coil and $\overline{\gamma^2}$ the mean square end-to-end distance of a crosslinked random coil. $\overline{\gamma^2}/\overline{\gamma_0^2}$ is used for modifying the ideal hypothesis $\overline{\gamma^2} = \overline{\gamma_0^2}$. According to Graessley,³⁰ the value of $\overline{\gamma^2}/\overline{\gamma_0^2}$ should be 0.5 in the case that a crosslinker functionality equals to 4. Since in the highly swollen state, a real network exhibits the properties much closer to the random network,³¹ so under this model, another emendation factor $(1 - 2/f)$ is introduced, in which f denotes the functionality of crosslinker. Finally, considering the imperfection of formed network chains, we also introduce the correction factor of $(1 - 2M_c/M_n)$, where M_c is the molar mass between crosslinks and M_n the number-average molecular weight of the primary chains before crosslinking, but we have been hitherto unable to find any proper modified value of it for real hydrogel network system, here we treat it as unity in a similar manner as Ma et al.³²

Therefore, the effective crosslinking densities ν_e of these hydrogels can be yielded from eqs. (4) and (6), and the molar mass between crosslinks (M_c) thereby was calculated via the following expression:

$$M_c = \rho_2/\nu_e \quad (7)$$

Then it is also of interest to derive the copolymer-water interaction parameter χ according to the following equation:³³

TABLE II
Mechanical Properties and Network Parameters Based on Compression Stress-Strain Measurements for P(NIPAM-co-AdMA) Hydrogels with Various Content of AdMA

Sample Code	E (Pa)	G (Pa)	v_e (mol/cm ³)	M_c (g/mol)	χ	E/G
NA0	9373	2242	4.390E-05	23,295	0.466	4.181
NA1	15,262	3644	7.030E-05	14,626	0.447	4.188
NA3	33,547	8021	14.060E-05	7433	0.446	4.182
NA5	50,595	12104	18.750E-05	5661	0.483	4.180

$$\ln(1 - \phi_{2s} + \phi_{2s} + \chi\phi_{2s}^2 + v_e V_1 (\phi_{2s}^{1/3} \phi_{2r}^{2/3} - 2\phi_{2s} f^{-1})) = 0 \quad (8)$$

In which V_1 is the molar volume of swelling liquid, for water at 293 K, the value is 18.04 mL/mol.

As a result, all the obtained values of E , G , v_e , M_c , and χ are summarized in Table II for P(NIPAM-co-AdMA) copolymer hydrogels of four different compositions. As shown in Table II, it can be seen that the Young's modulus E and shear modulus G are both increase remarkably with the increasing content of AdMA, which demonstrates that the mechanical strength can be controlled quantitatively. In addition, it is interesting to find the value of E/G almost a constant around 4.18, in the reasonable value range according to Huglin et al.³⁴

Moreover, the increase in content of AdMA is also accompanied by an increase in v_e and a decrease in M_c . This may be due to the rigidity, hydrophobicity, and large volume of adamantyl groups. By the hydrophobic associations of hydrophobic groups, a large number of hydrophobic association domains are formed, which act as the physical crosslinking points in network of hydrogels.³⁵ Consequently, the effective crosslinking density v_e shows almost proportional to the mass percentage of AdMA/NIPAM in feed, which gives a good explanation of the notable rise in mechanical strength of copolymeric hydrogels with AdMA content.

As to the polymer-water interaction parameter χ , it exhibited a little different from previous reports.^{36,37} According to the general theory, the χ should increase with hydrophobic content all along. But our results showed that the χ was not a monotonous function of AdMA content, as is shown in Table II, it decreased with increasing AdMA content down to a minimum value and thereafter increased at higher AdMA content. This result demonstrated that the incorporation of hydrophobic AdMA parts within a limited amount could improve the swelling properties of the copolymeric hydrogels. This had been confirmed by the equilibrium swelling experiments in our previous article,¹⁷ in which the rates of change of equilibrium swelling ratios with temperature were in the order NA3 > NA1 > NA0 > NA5, in accordance with the trend of χ with AdMA content. Unfortunately, the complex interaction

among the present copolymers, which resulted in such change of χ cannot be explained fully here, but will be explored further in our later work.

For each of the samples studied, the crosslinker content is constant and only the ratio of AdMA to NIPAM is varied, so the data demonstrates that the content of AdMA in initial feed can have a great effect on the network parameters of copolymer hydrogels produced, consequently affect their physical properties.

CONCLUSION

In this article, a novel copolymer hydrogel P(NIPAM-co-AdMA) with different AdMA content was prepared, and the effect of AdMA content on the thermal and mechanical properties of P(NIPAM-co-AdMA) thermosensitive hydrogels was mainly studied. The results show that the VPTTs of the hydrogels decreased almost linearly with AdMA content. The mechanical properties and network parameters also strongly depend on the content of AdMA in copolymeric hydrogels. The incorporation of AdMA part can virtually increase the physical crosslinking points of the copolymeric hydrogels, and thus increase the overall effective crosslink density. So the mechanical properties were shown improved remarkably with increasing AdMA content. The polymer-water interaction parameter χ exhibited a nonmonotonous function of AdMA content. That is, as AdMA content increased in copolymeric hydrogels, the χ first decreased within limited concentration, then increased at higher AdMA content. The results demonstrated that there existed in an optimized AdMA content for swelling properties of the present copolymeric hydrogels. So by controlling proper AdMA content, it is possible to obtain thermosensitive PNIPAM hydrogels with excellent combination properties of appropriate VPTT, desirous swelling ability and high mechanical strength, which will lead to more applications in wider fields.

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