

Synthesis and Solution Properties of Temperature-Sensitive Copolymers Based on NIPAM

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ABSTRACT: A kind of temperature-sensitive water-soluble polymers P(NIPAM-HEMA-AM) of N-isopropylacrylamide (NIPAM), hydroxyethyl methacrylate (HEMA) and acrylamide (AM) were synthesized by free radical aqueous solution copolymerization. The polymers were characterized by Fourier transform infrared spectrum (FTIR) method. Solution properties, such as the influences of monomer ratios and additives on the low critical soluble temperature (LCST) of the polymer solutions as well as the viscosity-temperature properties were studied. The results show that the polymer concentrations have no significant influence on the LCST of polymer solutions. The incorporation of HEMA units leads to a lower LCST, while AM units to a higher LCST. The additions of small molecules such as salt and surfactant also have significant effect on the LCST, the addition of NaCl decreases the LCST, while the addition of sodium dodecylbenzenesulfonate (SDBS) increases the LCST. The apparent viscosity of

polymer solutions depends on temperature. The 1.5 wt % aqueous solutions of P(NIPAM-HEMA-AM) exhibits good thermo-thickening behavior over 55°C, whereas the 0.8 wt % aqueous solutions do not show this behavior during the heating process. The aqueous solutions of P(NIPAM-HEMA-AM) are viscoelastic fluids, and the viscoelasticities mainly depend on temperature. Both the storage modulus (G') and loss modulus (G'') of 1.5 wt % polymer solutions increase with temperature. Over 55°C, G' exceeds G'' , and the polymer solutions are elasticity-dominated. In contrast, below 55°C, G'' is larger than G' , and the polymer solutions are viscosity-dominated. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 1099–1105, 2010

Key words: N-isopropylacrylamide; water-soluble polymer; rheology; temperature-sensitive polymer; low critical soluble temperature

INTRODUCTION

Current industrial practice, especially oil industry, favors the use of water-soluble polymers which are related to the thickening and rheology modification of industrial fluids. In the last several decades, many water-soluble polymers were developed for this applications.^{1–18}

Partially hydrolyzed polyacrylamide is the simplest water-soluble polymer. Its thickening properties mainly rely on its high molecular weight and physical entanglement of polymer chains due to the repulsion of carboxylate groups and hydrogen bonds of amido groups. It is efficient in pure water, but in the presence of salt the thickening efficiency is weakened. Furthermore, high shear rate causes the breakage of the polymer chains, resulting in the irreversible decrease of aqueous solution viscosity.

Polymers containing a small proportion of hydrophobic groups usually in the form of pendent side chains or terminal groups are also one of the impor-

tant water-soluble polymers due to the advantages of both polyelectrolyte and hydrophobic groups.^{4–8} In aqueous solutions, the hydrophobic groups aggregate to minimize their exposure to water and thereby form intermolecular or intramolecular association resulting in the hydrophobic microdomains. In semi-dilute aqueous solutions, intermolecular hydrophobic interactions lead to the formation of three-dimensional networks of polymer chains resulting in a rapid increase of the apparent viscosity. At high shear rate, the network structures are disrupted and the apparent viscosities of polymer solutions decrease. However, upon removal of shear the associations can reform and the viscosities completely recover their original values. Because of these unique solution properties the hydrophobically associating polymers have potential application in enhanced oil recovery (EOR). Recently, studies on hydrophobically modified polymers have been concentrated on the polymers containing acrylamide (AM) and one of hydrophobic monomers, which are mainly the derivatives of AM, acrylic esters, and its derivatives.^{4–8}

However, until now all of these water-soluble polymers cannot be subjected to heating, and the viscosity generally decreases when temperature is raised. But for the fluids work at high temperature,

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it would be more valuable to use polymer solutions whose viscosity remains independent on temperature or even increases under heating. These unexpected properties can only be provided by thermo-thickening polymers, which are also regarded as one of the potential oil displacement agents.

Several aqueous systems which show such thermo-thickening behavior have already been described,^{9–18} and are mainly focused on polymers based on N-isopropylacrylamide (NIPAM).^{13–18} Generally, poly(N-isopropylacrylamide) solutions show no thermo-thickening behavior, but exhibit a coil-globule transition at about 32–34°C. The corresponding temperature is defined as the lower critical solution temperature (LCST). Below the LCST, the polymer solutions are swollen, hydrated, and hydrophilic, and above this temperature, the solutions become collapsed, dehydrated, and hydrophobic. Moreover, the LCST can also be controlled by incorporating more hydrophilic or hydrophobic monomers, namely, the modification of the hydrophilic/lipophilic balance (HLB) of polymer chains. The incorporation of hydrophobic monomers leads to a lower LCST and hydrophilic monomers to a higher LCST. At the same time, it is found that NIPAM-based polymers containing hydrophilic sequences, such as PAA-g-PNIPAM¹³ and CMC-g-PNIPAM¹⁴, exhibit significant thermo-thickening behavior. So it is possible to synthesize thermo-thickening polymers based on NIPAM by modifying the contents of hydrophilic or hydrophobic monomers.

In this article, the nonionic thermosensitive water-soluble copolymers P(NIPAM-HEMA-AM) of N-isopropylacrylamide (NIPAM), acrylamide (AM), and hydroxyethyl methacrylate (HEMA) were synthesized by free radical aqueous solution copolymerization, and the solution properties of P(NIPAM-HEMA-AM) were investigated.

EXPERIMENTAL SECTION

Materials

Acrylamide (AM) was purchased from Kelong Chemical Agent Factory (Chengdu, China) and was recrystallized twice from CHCl_3 . N-isopropylacrylamide (NIPAM) was manufactured from J&K Chemical. Hydroxyethyl methacrylate (HEMA) was obtained from A Johnson Matthey Co. Kalium persulfate and sodium bisulfite were both purchased from Haihong Chemical Agent Factory (Chengdu, China). All of these materials except AM were used without further purification.

Polymerization

The copolymers of NIPAM, HEMA, and AM were prepared by free radical aqueous solution copoly-

merization in aqueous solution using Kalium persulfate/sodium bisulfite as the redox free radical initiators. Each reaction was conducted in a 100-mL, three-necked, round flask equipped with a mechanical stirrer, nitrogen inlet and outlet. NIPAM, AM, and HEMA were added into the reaction flask, and then dissolved in deionized water. The mixture was stirred under N_2 until a clear homogeneous mixture was observed. The total monomer concentration in water was constant at 25% (w/w) and the initiator concentration was 0.3% (w/w) relative to the monomer feed. After the addition of initiators, the polymerization was conducted at 30°C for 12 h. The product was dissolved in mixtures of acetone and ethanol and was then precipitated in excess ether before drying in vacuum at room temperature for 24 h.

Measurements

FTIR spectrum was recorded on NICOLET-560 infrared spectrophotometer and the polymer was coated on the KBr crystal wafer before measurement.

Stock polymer solutions were prepared by dissolving the dried polymer in deionized water or aqueous salt solutions and being shaken gently on an orbital shaker for at least 5 days.

The transmittances of polymer solutions were measured at 650 nm on the Model 722 spectrometer (Shanghai Analysis Instrument Factory). The LCST was determined as a temperature exhibiting a 50% decrease in optical transmittance of the polymer solutions (0.8 wt %).

Relationship between apparent viscosity and temperature of 0.8 wt % polymer solutions was measured using Brookfield DV III rotational (cylinder) viscometer. These of 1.5 wt % were performed on a cone-and-plate rheometer with a cone angle of 4° and a diameter of 40 mm (Malvern Instruments Co., Gemini 200). The rheometer was equipped with a temperature control unit that was calibrated to give a temperature in the sample chamber within 0.1°C of the set value.

Oscillatory shear experiments were also conducted in the Gemini 200 rheometer system using a cone-and-plate geometry. Since measurements were carried out at elevated temperatures (up to 65°C), a layer of silicone oil was added to the sample to avoid evaporation of the solvent. At each temperature the sample was allowed to equilibrate for about 0.5h before measurements were commenced. The values of the strain amplitude (<5%, in this work the value was 1%) were checked in order to ensure that all experiments were conducted within the linear viscoelastic region, where G' and G'' were independent on the strain amplitude.

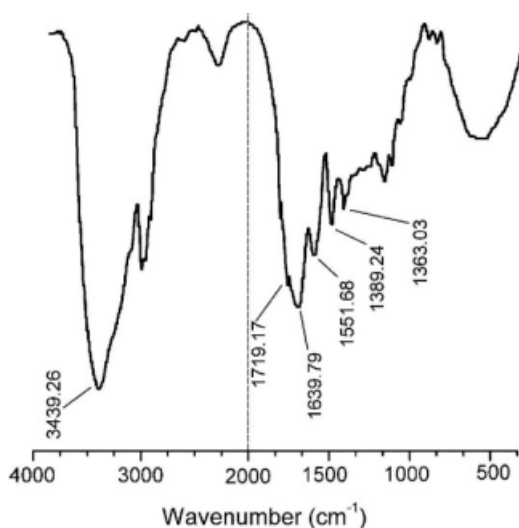


Figure 1 IR spectrum of P(NIPAM-HEMA-AM).

RESULTS AND DISCUSSION

Fourier transform infrared spectrum (FTIR)

The FTIR spectrum of P(NIPAM-HEMA-AM) is shown in Figure 1. It shows a strong absorption band at 3439.26 cm^{-1} which is attributed to the $-\text{NH}_2$ group. The absorption bands at 1639.79 and 1719.17 cm^{-1} confirm the presence of carbonyl group ($-\text{C}=\text{O}$) of acrylamide and ester carbonyl group ($-\text{COO}$) of HEMA, respectively. Furthermore, the iso-intensity double peaks corresponding to the symmetrical bending vibrations and the coupling split of bimethyl of isopropyl group are found at 1389.24 and 1363.03 cm^{-1} . These absorption peaks verify the success of copolymerization.

The lower critical solution temperature (LCST) of P(NIPAM-HEMA-AM)

To discuss the effects of reaction conditions on the temperature sensitivity of this copolymer, LCST of P(NIPAM-HEMA-AM) aqueous solution is first introduced. Figure 2 shows the development of transmittance of P(NIPAM-HEMA-AM) aqueous solutions with temperature at different concentration: 0.8 and 1.5 wt %. For 0.8 wt %, the polymer solutions are transparent liquid below 60°C , and the values of transmittance approach to 100%. With the increase of temperature, the aqueous solutions become cloudy gradually and yield a white fluid eventually, following the sharp decrease of transmittance from 100% to 50% in the range of $60\text{--}75^\circ\text{C}$. During this stage, the LCST can be determined to be 68.5°C according to the temperature which corresponds to a 50% decrease in optical transmittance. Above 75°C , the values of transmittance keep constant. When this solution is cooled down to below 60°C , it becomes transparent again. These results show high sensitivity and revers-

ibility to temperature of polymer solutions upon heating and cooling. It also can be seen that for polymer solutions with high concentration, such as 1.5 wt %, the starting point of the decrease of transmittance does not change. But the decrease of transmittance is sharper than that of 0.8 wt % polymer solutions because of the strong hydrophobic interactions of high concentration polymer solutions.

It is reported that this sharp decrease of transmittance of polymer solutions is attributed to the change in the hydrophilic–hydrophobic equilibrium of polymer chains.^{19–25} Increase of temperature enhances the hydrophobicity of polymer chains, enlarges hydrophobic regions of polymer solutions and facilitates polymer–polymer association by hydrophobic interactions, resulting in the precipitation of polymer chains eventually.

Influence of reaction conditions on the LCST of P(NIPAM-HEMA-AM)

As aforementioned, temperature plays an important role on the change of hydrophilic–hydrophobic

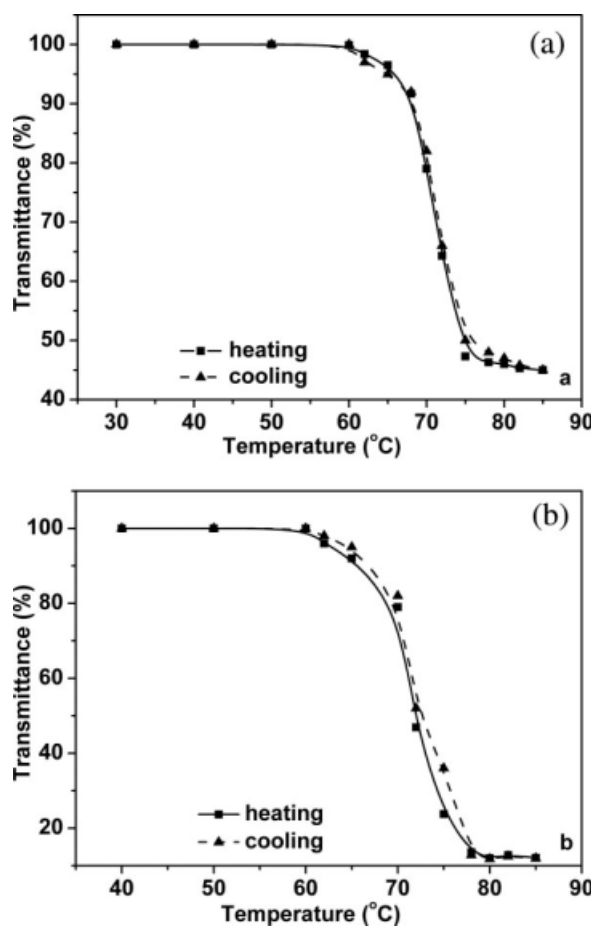


Figure 2 The development of transmittance of P(NIPAM-HEMA-AM) aqueous solutions with temperature at different concentrations. NIPAM : HEMA : AM = 60 : 1 : 39. (a) 0.8%; (b) 1.5%.

TABLE I
The LCST of 0.8 wt % P(NIPAM-AM-HEMA) Solutions with the Same Content of HEMA

No.	HEMA/ mol %	AM/ mol %	NIPAM/ mol %	LCST/°C
1	1	24	75	48.0
2	1	29	70	53.8
3	1	34	65	60.8
4	1	39	60	68.2

equilibrium of polymer chains. For random copolymers, experimental results show LCST can be mainly affected by polymer composition, such as the content of hydrophilic or hydrophobic units.^{7,23,26–30}

In the following discussions the polymer compositions corresponding to the monomer feed ratios will be used.

Table I shows the LCST of 0.8 wt % P(NIPAM-HEMA-AM) aqueous solutions at fixed molar fraction of HEMA units. An increase of the LCST is observed with the increase of the molar fraction of AM units. This is because that the excess incorporation of hydrophilic units AM enhances the hydrophilicity of polymer chains, and eventually enhances the solubility of polymer.

Table II shows the LCST of 0.8 wt % P(NIPAM-HEMA-AM) aqueous solutions at fixed molar fraction of AM, and a decrease of the LCST is observed with the increase of the molar fraction of HEMA units. The incorporation of hydrophobic units HEMA enhances the hydrophobicity of polymer chains. When raising the temperature, the polymer chains rapidly separate from aqueous solution and leads to the decrease of LCST.

Table III shows the LCST of 0.8 wt % P(NIPAM-HEMA-AM) aqueous solutions at fixed molar fraction of NIPAM units. Similarly, due to the hydrophobicity of HEMA, a decrease of the LCST is also observed with the molar fraction of HEMA.

These results show that the LCST of the polymer solutions is significantly influenced by the composition of the polymer: The increase of the ratio of hydrophilic to unit leads to the increase of LCST, whereas the decrease of this value leads to the decrease of LCST.

TABLE II
The LCST of 0.8 wt % P(NIPAM-AM-HEMA) Solutions with the Same Content of AM

No.	AM/ mol %	HEMA/ mol %	NIPAM/ mol %	LCST/°C
1	39	1	60	68.2
2	39	3	58	62.5
3	39	5	56	54.3
4	39	8	53	48.2

TABLE III
The LCST of 0.8 wt % P(NIPAM-AM-HEMA) Solutions with the Same Content of NIPAM

No.	NIPAM/ mol %	HEMA/ mol %	AM/ mol %	LCST/°C
1	60	1	39	68.2
2	60	3	37	61.1
3	60	5	35	50.0
4	60	7	33	44.7

To simplify the discussion in this article, the polymers studied in the following sections are based on this composition (NIPAM : HEMA : AM = 60:1:39) if there is no special statement.

Influence of small molecules on the LCST of P(NIPAM-HEMA-AM)

Salts are known to influence the phase behavior of aqueous solutions of NIPAM-based polymers, because they disrupt the hydration structure surrounding the polymer chains. Sodium chloride (NaCl) is a typical example as shown in Figure 3. The introduction of NaCl in the solution decreases the quality of the solvent for polymer chains, favors their aggregation at a lower temperature compared with pure water, and enhances the hydrophobic intra-actions or interactions of polymer chains [Fig. 3(b,c)], which eventually leads to the precipitation of polymer chains.^{15,31}

Figure 4 shows the influence of NaCl on the LCST of 0.8 wt % aqueous solutions of P(NIPAM-HEMA-AM). It can be seen that the LCST of these two polymer solutions decrease linearly with NaCl, though the monomer ratios are different.

Being different with NaCl, additions of surfactants are often used to obtain a stable aqueous dispersion of hydrophobic solutes. Several studies reveal that the surfactant molecules adsorb onto polymer chains by means of their hydrophobic tails, either individually or in micellar form.^{32–34} Figure 5 shows the influence of sodium dodecylbenzenesulfonate

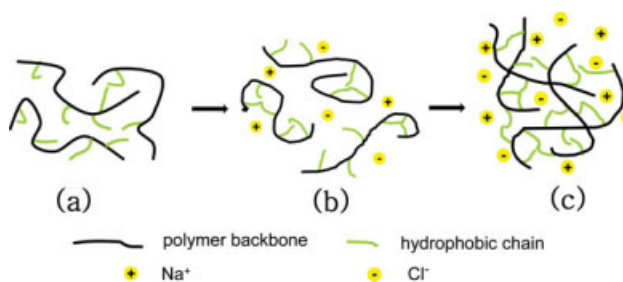


Figure 3 A schematic illustration of the effects of addition of NaCl on the structural reorganization of the polymer chains with temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

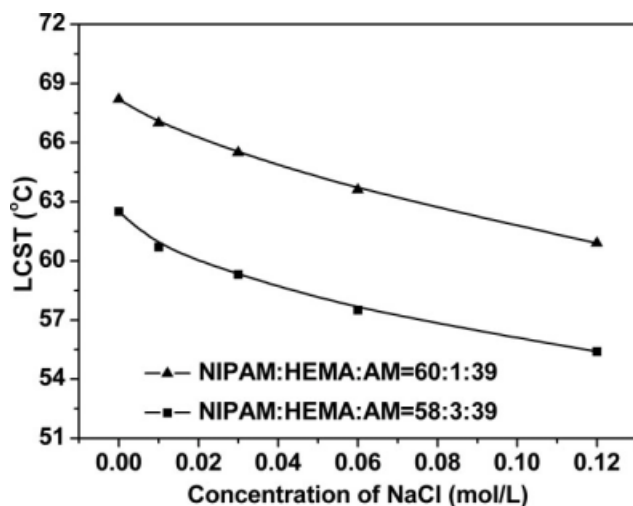


Figure 4 Influence of NaCl on LCST of 0.8 wt % P(NIPAM-HEMA-AM) solutions.

(SDBS) on the LCST of the 0.8 wt % polymer solutions. The addition of SDBS does not show any change of transmittance during the entire temperature range studied. Similar results have been reported in many articles, and the precise mechanism has been widely studied.^{15,31} It can be summarized as shown in Figure 6: Due to the hydrophobic interactions between polymer chains and surfactants, surfactants are absorbed onto the hydrophobic regions of polymer chains [Fig. 6(b)], which eventually leads to the formation of micelle on these hydrophobic regions. This structure can be called as the complex structure of surfactants and polymer chains [Fig. 6(c)]. It is this complex structure that tends to convert the neutral polymer into a polyelectrolyte, causes an improved solubility of polymer chains, and results in the modification of the hydrophilic/hydrophobic balance of polymer. Consequently the LCST is shifted toward higher temperature. However, because of the disappearance of long hydrophobic chain of sodium benzene sulfonate (SBS), just like NaCl, the addition of SBS decreases the LCST (Fig. 5). It further proves that it is the formation of the complex structure of surfactants and polymer

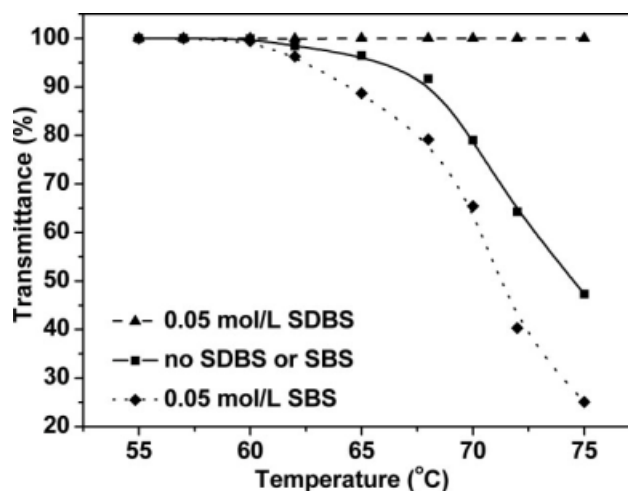


Figure 5 Influence of SBS and SDBS on the transmittance of 0.8 wt % P(NIPAM-HEMA-AM) solutions.

chains that causes the elevation of LCST of polymer solutions.

Rheological behavior

In Figure 7, the viscosities of polymers at different concentrations are plotted as a function of the temperature. It can be seen that the apparent viscosity of 0.8 wt % polymer solutions decreases with the increase of temperature, and merely no thermo-thickening behavior exhibits. But at higher polymer concentrations, such as 1.5 wt %, the polymer solutions show spectacular thermo-thickening behavior: As temperature increases from 55 up to 68°C, a dramatic viscosity enhancement is observed. This transition in the rheological behavior fits well with the phase transition observed in the light transmittance results: from a transparent liquid at $T < 60^\circ\text{C}$ gradually to a cloudy one with the increase of temperature. The correlation between another rheological transitions and phase transitions is found at near 70°C where the fluid becomes totally white and the viscosity begins to decrease with temperature because of the precipitation of polymer chains.

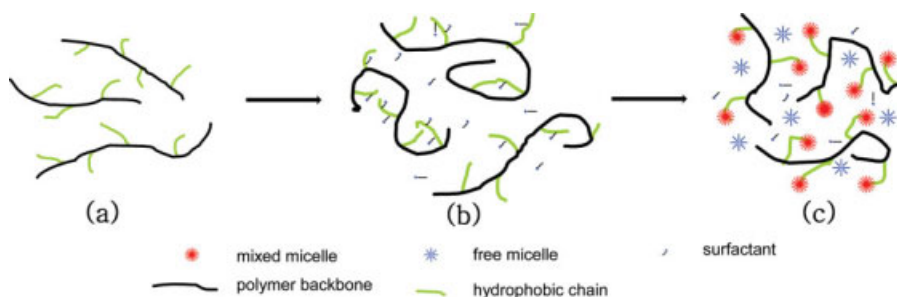


Figure 6 A schematic illustration of the effects of addition of surfactants on the structural reorganization of the polymer chains with temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

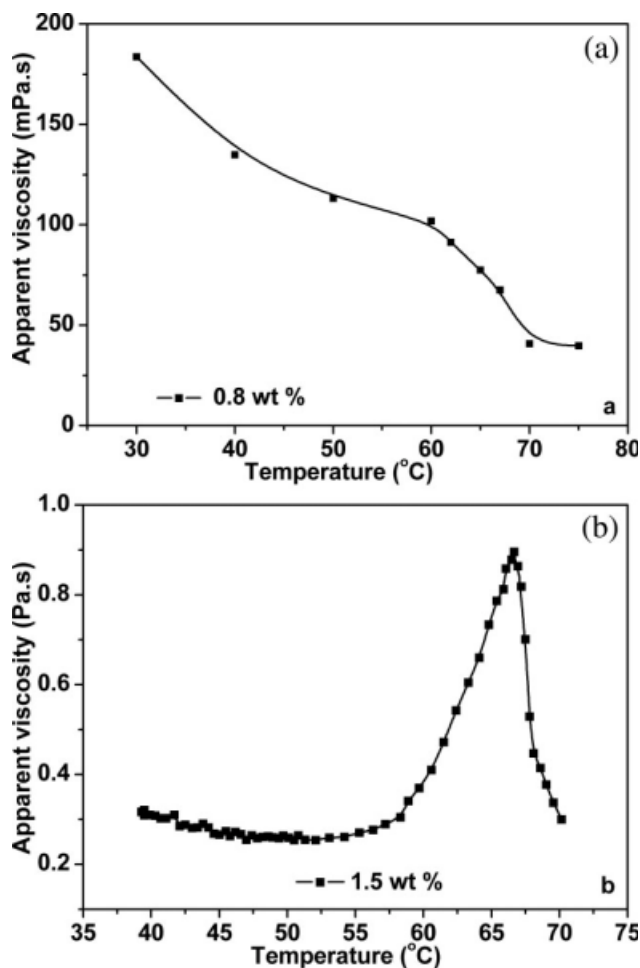


Figure 7 Influence of temperature on the viscosity of P(NIPAM-HEMA-AM) aqueous solutions at different concentrations. (a) 0.8%; (b) 1.5%. (shear rate: 1 s^{-1}).

The threshold temperature to observe the thermo-thickening is defined as association temperature (T_{ass}), which is concomitant with the starting point of the increase of viscosity. To high concentration solutions, such as 1.5 wt %, when temperature is lower than T_{ass} , viscosity is low, and in this temperature region, because of the balance of hydrophobic association and temperature-induced chain movement, viscosity keeps nearly constant as shown in Figure 8. With the increase of temperature the hydrophobic interactions are enhanced, polymer chains aggregate to form intermolecular hydrophobic microdomains [Fig. 8(b2)]. The formation of these microdomains leads to the high-viscosity physical networks, and results in the thermo-thickening behavior eventually. However, higher temperature causes further increase of hydrophobic interactions of polymer chains, leads to both the collapse of the physical networks and the precipitation of polymer chains, and results in the decrease of viscosity of polymer solutions [Fig. 8(c2)]. For low concentration solutions, such as 0.8 wt %, the hydrophobic interac-

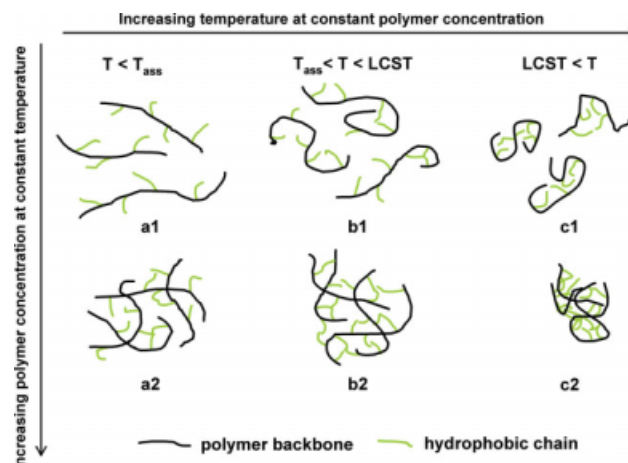


Figure 8 A schematic illustration of the effects of polymer concentration on the structural reorganization of the polymer chains with temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tions trigger the formation of intramolecular hydrophobic microdomains [Fig. 8(b1)], and no physical networks form, so the viscosity decreases with the increase of temperature. But the polymer chains can also precipitate because of the strong intramolecular hydrophobic interactions [Fig. 8(c1)], and there is also a phase transition which is consistent with that of the 1.5 wt % polymer solutions.

The increase in temperature of polymer solutions leads to the phase transition which can be characterized by their storage, G' , and loss G'' moduli. The temperature dependence of G' and G'' for 1.5 wt % P(NIPAM-HEMA-AM) solutions at constant frequency, 1 Hz, is shown in Figure 9. It can be seen that the aqueous solutions of P(NIPAM-HEMA-AM) are viscoelastic liquid, and both G' and G'' increase

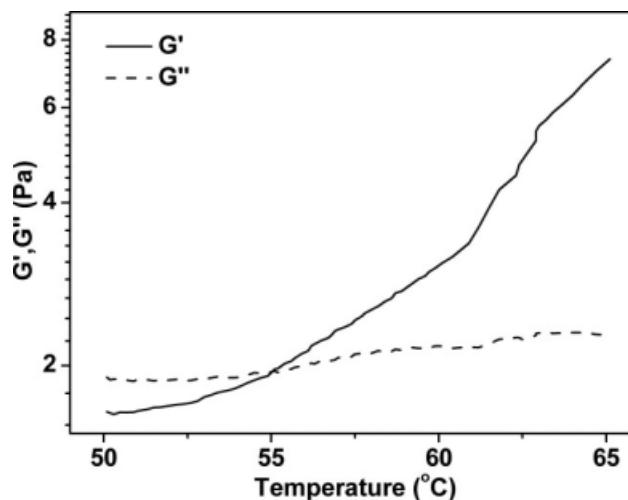


Figure 9 Temperature dependencies of the dynamic moduli of 1.5 wt % P(NIPAM-HEMA-AM) solutions of at frequency 1 Hz.

with the increase of temperature. At low temperature (below 55°C) the viscous features of polymer predominate ($G'' > G'$), whereas over 55°C, the G' curve overtakes the G'' one, indicating the predominance of the elastic response. The increasing elastic behavior of these polymers with temperature is characteristic of the entangled physical networks. The intersection point corresponds to the association temperature T_{ass} , being lower than the phase transition temperature.

What should be mentioned here is the difference between association temperature and LCST: at one point, with the continuing increase of temperature, the hydrophobic interactions between polymer chains are enhanced, following the formation of the physical networks, and the viscosity of polymer solutions begins to increase. This point is called association temperature, and corresponds to the intersection point in Figure 9. But at this point, the polymer solutions are still clear. Continuing to heat, the hydrophobic interactions are further enhanced, and the polymer chains begin to precipitate from solutions, resulting in the decrease of light transmittance. The LCST is determined as a temperature exhibiting a 50% decrease in light transmittance of the polymer solutions. And during this precipitation process, the viscosity begins to decrease.

CONCLUSIONS

Novel temperature-sensitive copolymers P(NIPAM-HEMA-AM) of NIPAM, HEMA and AM have been prepared by free radical aqueous solution copolymerization using kalium persulfate/sodium bisulfite as the redox free radical initiator. The LCST of the polymer solutions can be controlled by changing the monomer ratios of polymer: The increase of HEMA content leads to a lower LCST, while the increase of AM leads to a higher LCST. Another way to achieve such control would be the addition of small molecules. NaCl primarily disrupt the configuration of water molecules, whereas the SDBS used interacts with the polymer itself. So the addition of NaCl decreases the LCST, whereas the addition of SDBS increases the LCST. The aqueous solutions are viscoelastic fluids, and the viscoelasticity strongly depends on temperature. Below T_{ass} , the elastic modulus is lower than the loss modulus. Above T_{ass} , the elastic modulus is higher than the loss modulus and the polymer solutions show good thermo-thickening behavior.

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