A Novel Thermothickening Aqueous System Prepared from Hydrophobically-Modified Acrylamide Copolymer, Poly(*N*-isopropylacryl-amide) and Sodium Dodecyl Benzene Sulfonate and Its Mechanism Studies

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A Novel Thermothickening Aqueous System Prepared from Hydrophobically-Modified Acrylamide Copolymer, Poly(*N*-isopropylacryl-amide) and Sodium Dodecyl Benzene Sulfonate and Its Mechanism Studies

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A new thermothickening aqueous system was presented based on mixtures of hydrophobically-modified acrylamide copolymer (HM-PAM), poly(*N*-isopropylacryl- amide) (PNIPAM) and sodium dodecyl benzene sulfonate (SDBS). Unique in the thermothickening system, a maximum viscosity and the temperature (T_{max}) when reaching such viscocity change independently, reflects the presence of intermolecular interactions. The T_{max} of the new system suggests that its thermothickening behavior is correlated to the cloud point temperature (T_c) of PNIPAM, which can be easily adjusted to desired values by the addition of SDBS. The experimental data also indicate that the temperature between the rheological transition temperature (T_t) and T_{max} in HMPAM+PNIPAM+SDBS is within the range of 35–65°C, and the thermothickening behavior originates from the reinforcement of the association network between HMPAM, PNIPAM and SDBS. Consequently, the viscosity over the corresponding thermosensitive range upon cooling is higher than that upon heating.

Keywords: hydrophobically modified acrylamide copolymer, poly(*N*-isopropylacryl-amide), sodium dodecyl benzene sulfonate, viscosity, water-soluble polymers

1 Introduction

Complex water-based fluids containing polymers and surfactants find important practical applications in various domains such as paints, (1) cosmetics, (2) and oil recovery (3). However, these fluids often suffer from various limitations and deficiencies. Particularly, for water soluble polymers, the problems include shear degradation, viscosity loss in brines, and at high temperature, reaction with divalent ions, hydrolysis reactions, and microbial degradation. Among them, viscosity retention in brine and the problems at high temperature are considered to be of primary importance and the major weaknesses of currently available partially hydrolyzed polyacrylamides.

In attempts to overcome some of the aforementioned deficiencies in conventional water-soluble polymers, it has

been a common practice to crosslink the polymers in order to improve their resistances to thermal, as well as shear, degradation. Most of these attempts have, unfortunately been unsuccessful. More recently, an aqueous medium has been thickened by dissolving a hydrophobically modified water-soluble polymer, which contains a small portion of hydrophobic groups in the form of pendant lateral or terminal groups in the aqueous medium (4–6). While these polymers consist of a water-soluble polymer backbone and a number of low-critical-solubility-temperature (LCST) blocks or lateral groups, the thermo-sensitive moieties can undergo reversible microphase segregation with increasing temperature (7–9). For polymer concentrations higher than the overlap concentration of the chains, this transition provides a viscosity enhancement to the solution through inter-chain aggregation. Unfortunately, it is still difficult and often impractical to prepare such kinds of polymers that can be applied in oil fields, because the formation temperature and degree of mineralization in oil reservoir are very high. On the other hand, some references (10, 11) have disclosed that certain hydrophobically modified water-soluble polymers exhibit desired thickening

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profiles at specific temperatures in the presence of surfactants, but these systems are generally ineffective at low concentrations.

Very recently, we developed a new approach (12) to prepare thermothickening systems based on the mixtures of a hydrophobically-modified acrylamide copolymer (HMPAM) and poly(*N*-isopropylacrylamide) (PNIPAM). Their thermothickening mechanism was related to the LCST behavior of PNIPAM and the interaction between HMPAM and PNIPAM (13). In this study, to conveniently adjust the thermothickening behavior of HMPAM+PNIPAM over a wider temperature range, we have extended the HMPAM+PNIPAM complex study from a binary system to a HMPAM+PNIPAM+SDBS ternary system and explored its thermothickening mechanism in the new system.

2 Experimental

2.1 Materials

HMPAM and polyacrylamide (PAM) were prepared as reported elsewhere (12). Acrylamide (AM, 10.0 g), N-(4-vinylbenzyl)-N,N-dimethyloctadecan-1-aminium chloride (VBDMOAC, 0.639 g), and acrylic acid (AA, 3.41 g) were dissolved in deionized water (93.0 mL). After treated with a small amount of HCl (final pH = 2–3), the solution was deoxygenated with nitrogen for 1 h. The solution was then heated to 70 °C, and azodiisobutyronitrile (AIBN, 12.0 mg in 2.00 mL of methanol) was subsequently added to initiate the polymerization. After 6 h at 70°C, the formed polymer was isolated by adding an excess of ethanol and drying under high vacuum for 24 h. Copolymers (namely HMPAM) containing different amount of hydrophobic groups were prepared similarly by changing the amount of VBDMOAC. The schematic structure of HMPAM is shown in Figure 1.

The preparation of PNIPAM has been reported previously (12). Here is an improved synthesis: Deionized water (20.0 mL) and NIPAM (5.00 g) were added to a 100 mL container. After all NIPAM was dissolved in water, the polymerization was then initiated by consecutive additions of sodium bisulfite (6.60 mg in 6.60 mL of deionized water) and manganese sulfate anhydrous (1.90 mg in 1.90 mL of deionized water) via a syringe. The polymerization proceeded continuously at 15°C for 24 h, and subsequently the polymer purification was accomplished by dialyzing against water using a 8,000–10,000 molecular weight cutoff dialysis bag for a week. The polymer was recovered by freeze-drying.
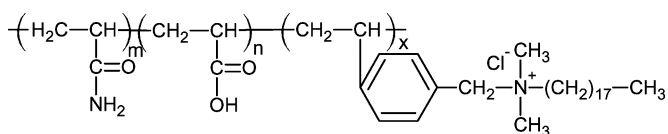

Fig. 1. Chemical structure of HMPAM.

Table 1. Chemical compositions of polymers

Polymer code	Feed ratio of VBDMOAC (mol%)	^{a}AA content (mol%)	$^b[\eta]$ dL g^{-1}
HMPAM	0.75	12.15	8.66
PAM	0	15.91	10.86
PNIPAM	0	0	2.55

a. Elemental analysis b. in 0.1 M NaCl solution at 25°C

The characteristics of the model polymer are given in Table 1.

2.1.1. *Sample preparation and measurement*

HMPAM and PNIPAM stock solutions were prepared by diluting the proper amount of polymers in deionized water. HMPAM solutions were neutralized with NaOH (final pH = 7–8). Mixtures containing desired compositions were prepared by mixing aqueous stock solutions of HMPAM and PNIPAM, and they were stirred for 24 h and equilibrated for 1 d at room temperature before use.

Viscosity measurements were carried out by using a Wells Brookfield DV III+ viscometer equipped with different sizes of spindles and a temperature-control water bath. Dynamic measurements were conducted by a Haake RS600, and the frequency ω was set at 6.28 rad s^{-1}. Turbidimetry experiments were performed by using a temperature-control water bath with a magnetic stirrer. The cloud point temperature T_c, above which, the polymer solutions become phased-separated, is also called phase transition temperature. In this paper, T_c was determined by simple visual observation upon heating and cooling the sample. The heating/cooling rate was 1°C/min. Repeated scans at much lower heating rates were performed at temperatures close to T_c.

3 Results and Discussion

A strong viscosity enhancement was observed when PNIPAM was added to the HMPAM's semi-dilute solution, which could be attributed to hydrophobic interactions between the two polymers. As PNIPAM was added to the HMPAM aqueous solution, the hydrophobic interactions between HMPAM and PNIPAM in water spontaneously occurred and resulted in the formation of polymer complexes. In our previous report, (12) we found that the viscosity of HMPAM+PNIPAM increased with temperature before reaching the T_c of PNIPAM. One reason could be that the inter-chain aggregation was enhanced because the inter-polymeric complexes formed by the main and graft-side groups in PNIPAM worked as hydrophobic segments. However, the system viscosity also exhibited a decreasing behavior above the T_c of PNIPAM. Typically in a thermothickening system, as the temperature increases, the viscosity of the polymer solution also rises, and there is a
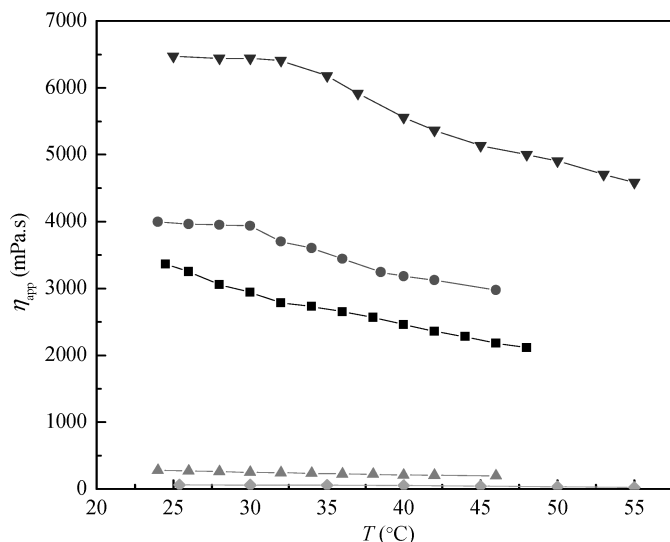
Fig. 2. Dependence of the apparent viscosity of various polymer solutions on temperature at a shear rate of 0.75 s^{-1}. 5000 mg/L HMPAM+400 mg/L SDBS (▼), 5000 mg/L HMPAM+ 3000 mg/L PNIPAM (●), 5000 mg/L HMPAM (■), 5000 mg/L PAM+3000 mg/L PNIPAM (▲) and 3000 mg/L PNIPAM+400 mg/L SDBS (♦).

characteristic maximum viscosity point at a specific temperature T_{max}, which is unique in each polymer system. Therefore, the HMPAM+PNIPAM mixture solution only exhibited a thermothickening behavior over 25–35°C, where the T_{max} was closely related to the T_c of PNIPAM.

Figure 2 shows the variation of the apparent viscosity (η_{app}) of various polymer systems at different temperatures. In the presence of HMPAM, PAM+PNIPAM and PNIPAM+SDBS, the viscosity decreases with temperature between 22.5 and 55°C. However, in HMPAM+PNIPAM and HMPAM+SDBS, a viscosity enhancement over 25–35°C was observed. As shown in Figure 2, for HMPAM+PNIPAM and HMPAM+SDBS, their T_{max}'s were all lower than 35°C. With the temperature range considered for practical applications, a challenge now arises: how can the T_{max} be extended to higher temperatures?

3.1 PNIPAM + SDBS Binary Systems

Surfactants are knowingly able to change many behaviors of PNIPAM drastically, especially the water solubility and T_c. While in pure water, the T_c of PNIPAM is about 33°C. In the presence of surfactants, the phase separation of PNIPAM is suppressed, and its T_c increases. As revealed in Figure 3, the T_c of PNIPAM+SDBS were measured as a function of the surfactant concentration. When the concentration of SDBS below ∼ 300 mg/L, the T_c remained constant at 33°C. Upon further increase of the SDBS concentration, the T_c was successively elevated to about 54°C at 1200 mg/L. The results were in good agreement with those of Meewes et al. (14). Therefore, SDBS may be used to
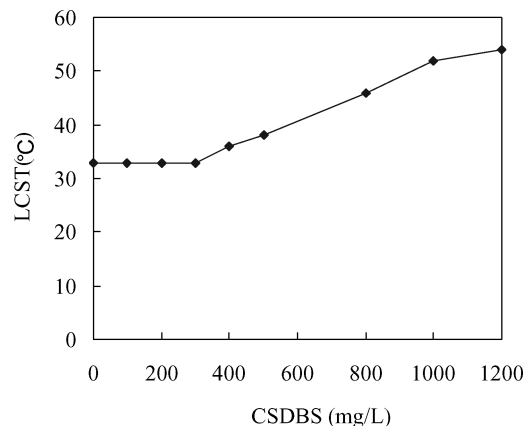

Fig. 3. Phase map of PNIPAM-SDBS-H$_2$O, C_{PNIPAM} = 3000 mg/L.

adjust the T_{max} of HMPAM+PNIPAM, because the thermothickening behavior of HMPAM+PNIPAM is related to the T_c of PNIPAM (13).

3.2 HMPAM+PNIPAM+ SDBS Ternary Systems

The temperature dependences of the apparent viscosity in ternary systems of HMPAM, PNIPAM and SDBS are shown in Figure 4. Compared with the binary system of HMPAM+PNIPAM, the ternary systems exhibited a higher T_{max} and a larger viscosity enhancement. In all examples shown in Figure 4(a), the C_{PNIPAM} was kept constant at 3000 mg/L. When C_{HMPAM} = 3000 mg/L and C_{SDBS} = 400 mg/L, the viscosity started to increase at 35°C, and the T_{max} became 53°C. This rheological transition (thermothickening behavior) started at 35°C, thus the rheological transition temperature T_t was 35°C. This rheological transition temperature in HMPAM+PNIPAM+SDBS fitted well with the T_c observed in PNIPAM+SDBS, since they were both 35°C. As C_{SDBS} further increased, the peaks of the plots became flatter and the T_{max} moved to a higher temperature. In more concentrated polymer solutions, i.e., C_{HMPAM} = 5000 mg/L shown in Figure 4(b), the thermothickening behavior was more obvious and the T_{max} was extend to 63°C at C_{SDBS} = 1200 mg/L.

In these mixtures, the viscosity increased with the temperature and their viscoelastic properties could be characterized by their shear storage G', shear loss G'' and the phase angle δ (tanδ = G''/G'). In Figure 5, G', G'' and tanδ are plotted against temperature for a mixture containing HMPAM (5000 mg/L), PNIPAM (3000 mg/L) and SDBS (400 mg/L). It was observed than G' was higher than G'', and the G' and G'' curves were almost mutually parallel. The results can be explained as follows: first, in such system, the concentration of HMPAM is much larger than its critical associating concentrations (CAC, 1800 mg/L), therefore an association network can be formed with HMPAM molecules due to strong intermolecular interactions;
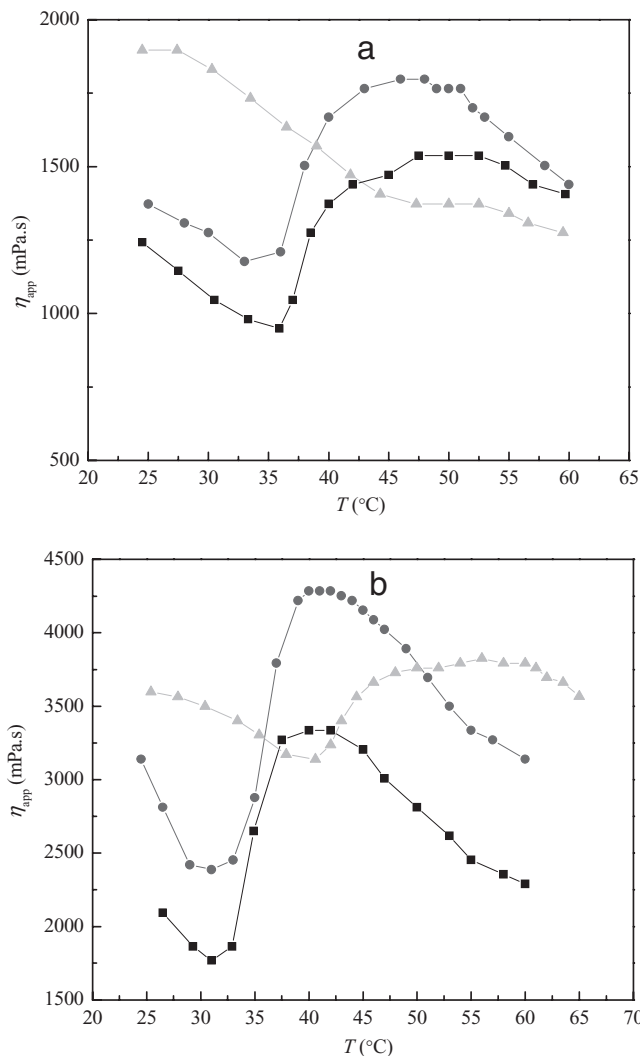
Fig. 4. Temperature dependences of the apparent viscosity for mixtures of HMPAM, PNIPAM and SDBS: C_{PNIPAM} = 3000 mg/L, (a) C_{HMPAM} = 5000 mg/L, (b) C_{HMPAM} = 3000 mg/L, (■)C_{SDBS} = 400 mg/L (•) C_{SDBS} = 700 mg/L (▲)C_{SDBS} = 1200 mg/L.

second, in the presence of PNIPAM and SDBS, the network structure becomes larger and more open, which results in elastic components in the viscoelastic properties that are much larger than its viscous components; finally, $G' > G''$.

3.3 Thermothickening Mechanism

Although the thermothickening behavior in the ternary systems is clearly related to the T_c of PNIPAM, the details of the thermothickening process are still rather unclear. To understand its mechanism, it is instructive to investigate the interactions between various components in the system first. It is widely known that HMPAM associates strongly with surfactants by forming mixed micelles (15, 16). The rheological behaviors of these mixed micelles are strongly
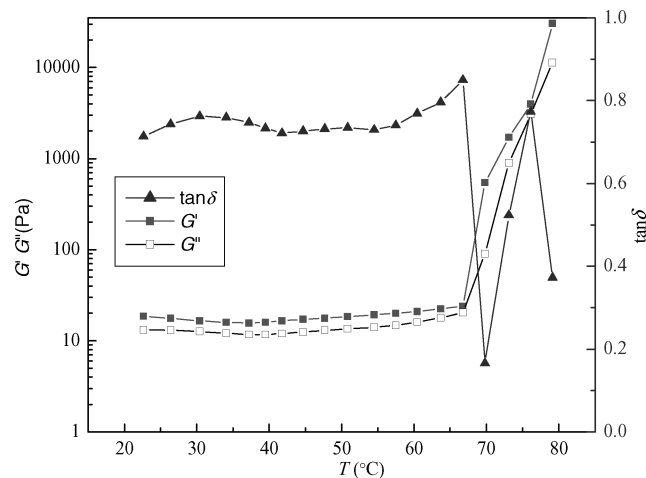

Fig. 5. Temperature dependences of the storage modulus (G'), loss modulus (G'') and the loss tangent value (tanδ) for mixtures of HMPAM, PNIPAM and SDBS, ω = 6.28 rad/s.

dependent on the molar ratios of micelles to alkyl polymer lateral groups. Figure 6 shows the effect of SDBS to the viscosity of various polymer solutions. The viscosity of HMPAM solutions initially increased with the addition of SDBS. It reached a maximum, and then decreased rapidly. Such results have been reported previously by many investigators (17, 18). However, in HMPAM+PNIPAM, the viscosity initially decreased with the addition of SDBS, and then increased while C_{SDBS} rose to approximately 500 mg/L, which corresponded to the critical micellization concentration (*cmc*) of SDBS, 418 mg/L.

A possible mechanism involved in the viscosity change of HMPAM+PNIPAM+SDBS is proposed in Scheme 1. According to the hydrophobic character, when SDBS is added
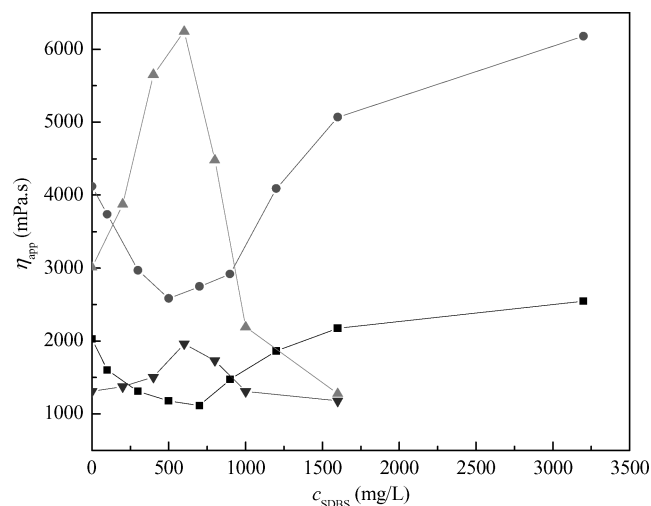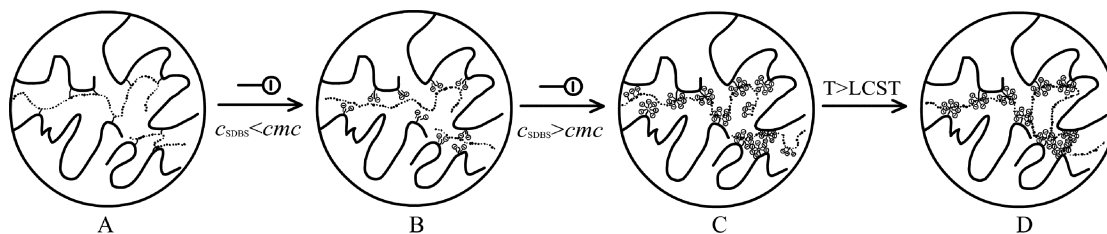

Fig. 6. Variation of the apparent viscosity of various polymer solutions with the surfactant concentration (▼) 3000 mg/L HMPAM, (▲) 5000 mg/L HMPAM, (■) 3000 mg/L HMPAM+ 3000 mg/L PNIPAM, (•) 5000 mg/L HMPAM+3000 mg/L PNIPAM.

Sch. 1. Schematic representation of the possible mechanism behind the thermothickening behavior of the ternary system. (solid line) HMPAM, (dashed line) PNIPAM.

to HMPAM+PNIPAM, SDBS can be absorbed onto the hydrophobic groups in the HMPAM chain preferentially instead of in the PNIPAM chain itself; subsequently it disrupts the weak network formed by the HMPAM and PNIPAM mixture micelles and leads to a decrease in viscosity (state B). When C_{SDBS} further increases, the mixture micelles are formed again by these three components, and a reversible network is reestablished (state C). So the viscosity gradually recovers.

The viscosity behavior of the ternary system with a successively heating and cooling is illustrated in Figure 7. The mixture contained HMPAM (5000 mg/L), PNIPAM (3000 mg/L) and SDBS (400 mg/L). Although the viscosity variation in both heating and cooling had the same feature, the viscosity in cooling over 30–40°C was much larger than that in heating. This can be attributed to the irreversible association network between HMPAM, PNIPAM and SDBS. During these two processes, the interaction between SDBS and PNIPAM is stable. However, before heating and T < 25°C, the interaction between PNIPAM and HMPAM is rather weak due to the hydrophilic character of PNIPAM, and only a few PNIPAM chains participate in the formation of mixed micelles. Upon heating and at temperatures close to the T_c of PNIPAM, the LSCT parts tend to have

phase separation, and its hydrophobicity increases, which leads to an increase in intermolecular interactions between PNIPAM, HMPAM and SDBS (state D). Simultaneously, some of these formed networks between PNIPAM, HMPAM and SDBS are irreversible upon cooling. As a result, the viscosity between T_t and T_{max} upon cooling is higher than that upon heating.

4 Conclusions

A binary system based on the mixture of hydrophobically-modified acrylamide copolymer (HMPAM) and poly(*N*-isopropylacrylamide) (PNIPAM) exhibits a thermothickening behavior over 25–35°C. Its thermothickening mechanism is related to the hydrophobic interaction between HMPAM and PNIPAM, and its T_{max} is dependent to the T_c of PNIPAM. By adding a surfactant SDBS, it is possible to tune the T_c of PNIPAM at desired values, because the phase separation of PNIPAM can be suppressed in the presence of the surfactant. Our experimental data also show that the T_{max} of HMPAM+PNIPAM can be adjusted to 65°C by using surfactants. These results are important for many industrial applications such as enhanced oil recovery. For HMPAM+PNIPAM+SDBS, G' is much higher than G'' between T_t and T_{max}, which suggests that the ternary system has a typical elastic behavior. Furthermore, tanδ decreases slightly when $T > 33$°C and then remained constant over 42–65°C, indicating that the thermothickening behavior of this ternary system is subject to the reinforcement of the association network between HMPAM, PNIPAM and SDBS. Spontaneously, the formed network upon heating can be reversed. As a result, the viscosity over the corresponding thermosensitive range upon cooling is higher than that upon heating.
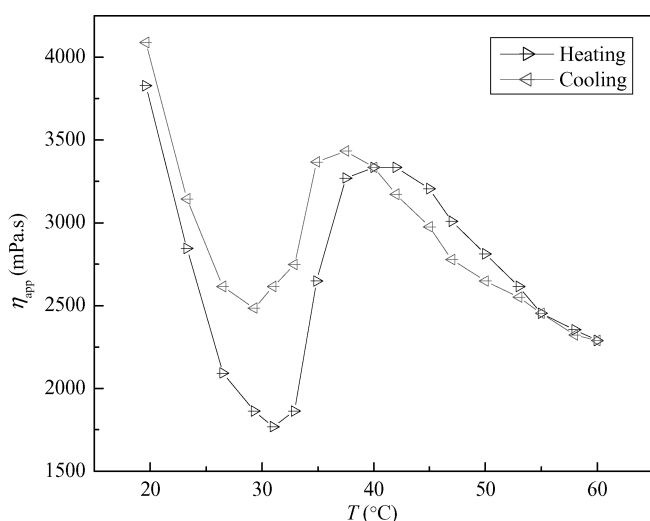
Fig. 7. Effect of one cycle of temperature on the apparent viscosity of mixture.

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