Viscometry—a useful tool for studying conformational changes of poly(*N*-isopropylacrylamide) in solutions

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Viscosity measurements as a function of temperature were used to characterize the phase transition when aqueous poly(*N*-isopropylacrylamide), poly(NIPAM), was heated past the lower critical solution temperature, *LCST*, at 32°C. Upon heating, the viscosity showed a large increase as the *LCST* was approached; this was attributed to intermolecular aggregation increasing the effective molecular weight of the polymer in solution. Beyond the *LCST*, reduction of viscosity was observed which is consistent with the viscometric properties of a diluted dispersion of colloidal particles.

(Keywords: viscosity; poly(*N*-isopropylacrylamide); conformation; water-soluble polymer; phase separation)

Introduction

Poly(*N*-isopropylacrylamide), poly(NIPAM), is a linear non-ionic polymer in the polyacrylamide family (*Figure 1*). The presence of the isopropyl group on the polymer chain gives the macromolecules a hydrophobic character. Hence, when the polymer is dissolved in water, the hydrophobic interactions cause the water molecules to reorganize and assemble a cage-like structure around the isopropyl groups[1].

It is well established that poly(NIPAM) possesses a lower critical solution temperature (*LCST*) of ~31°C[2]. A phase change occurs reversibly at this temperature which is found to be independent of molecular weight and concentration[3]. It is believed that phase separation occurs when a linear macromolecular chain collapses from an extended flexible coil to a compact and rather stiff globular state. This is commonly referred to as the 'coil–globule transition'. Various techniques were used such as turbidity[4,5], light scattering[6], fluorescence[7,8] and microcalorimetry[2,5,9]. All these techniques provide some information on the chain conformation near the phase transition point.

Presented in this communication is a first attempt to use viscometry to study conformational changes of aqueous poly(NIPAM) solution as it undergoes phase separation. Viscometry works by measuring the resulting stress from polymer chains as they are being subjected to a velocity gradient. It can be used to detect any changes as the polymer solution is being heated and since the stress exerted by the polymer chains is measured continuously, more information can be obtained. Interesting conclusions can be drawn from the results regarding the conformational changes of the polymer chains as poly(NIPAM) undergoes phase separation.

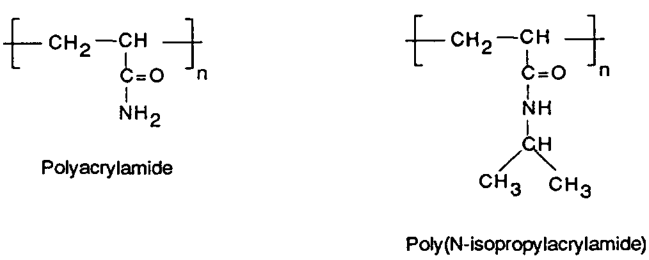
Experimental

N-isopropylacrylamide was recrystallized from a mixture of toluene and hexane. Potassium persulphate (KPS; analytical reagent, BDH Chemicals) and sodium dodecylsulphate (SDS; specially pure, BDH Chemicals) were used as purchased. Water was purified by passing distilled water through a Milli-Q Water System (Millipore Corporation).

The polymerization was carried out in a 1 litre four-necked glass reactor equipped with a condenser, a nitrogen inlet, thermometer and motor-driven stirrer which was set to run at 200 rev min^{-1}. The reactor was immersed in a water bath at 70°C. The reactor was charged with 7.51 g *N*-isopropylacrylamide, 500 ml deionized water and 0.059 g SDS. The solution was deoxygenated by nitrogen bubbling for 30 min. The reaction was started with the addition of 0.56 g of KPS dissolved in 10 ml water.

The surfactant, initiator fragments and unreacted monomer were removed from the polymer solution by dialysis against water. A 2.1 cm (i.d.) dialysis tubing (Spectrapor) was used. After 5 days and many changes of water, the conductivity of the dialysate remained unchanged.

Viscosities were measured in a Bohlin VOR rheometer fitted with a double gap concentric cylinder measuring system together with the most sensitive torsion bar. In the Bohlin VOR, the temperature was maintained with a computer-controlled water bath. Temperature calibration of the sample chamber was carried out with a thermoprobe as the bath temperature and the solution temperature were not the same. A temperature rise rate of 1°C min^{-1} was used for the present work.


Polyacrylamide

Poly(N-isopropylacrylamide)

Figure 1 Comparison of the structures of polyacrylamide and poly(NIPAM)

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Results and discussion

The phase behaviour of poly(NIPAM) was evaluated by measuring optical transmittance of polymer solutions at 500 nm as a function of temperature in a HP8452A spectrophotometer fitted with a HP89090A Peltier temperature controller. *Figure 2* shows a plot of reduced transmittance *versus* temperature of three different concentrations of poly(NIPAM). Phase separation as evidenced by the drastic reduction in the transmittance occurred at about the reported *LCST* of 32°C. The poly(NIPAM) phase above the *LCST* was present as stable colloidal dispersions, which presumably were electrostatically stabilized by the sulphate initiator residues. It was previously shown that the presence of a crosslinking monomer gives a colloidally stable poly(NIPAM) latex[10].

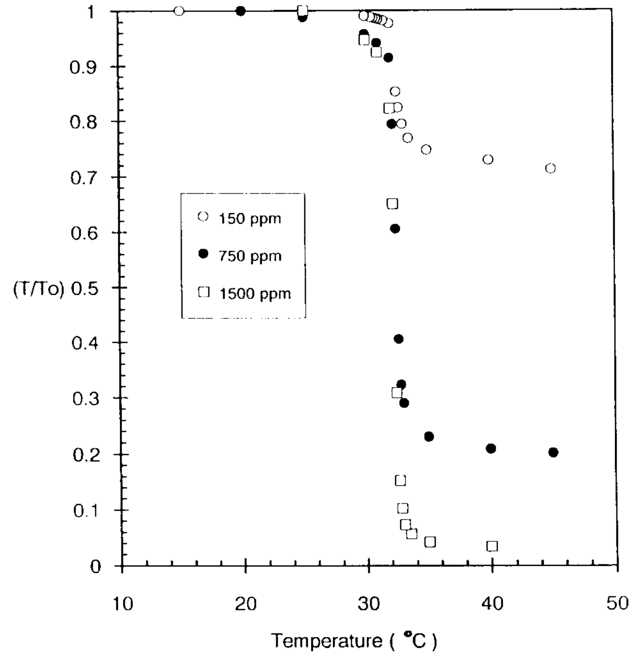

Figure 2 Reduced transmittance *versus* temperature of poly(NIPAM)

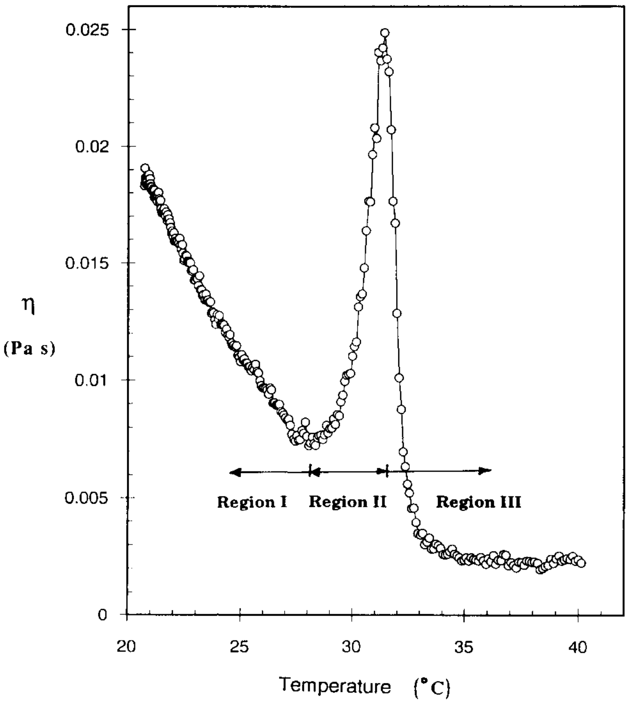

Figure 3 Viscosity–temperature curve of 1.5 wt% poly(NIPAM) solution. $\dot{\gamma} = 5.81\ s^{-1}$

Figure 3 shows the viscosity of 1.5 wt% poly(NIPAM) in water as a function of temperature at a shear rate of 5.81 s^{-1}. The results indicate that as the polymer solution is heated, the viscosity of the solution decreases according to the well-known Arrhenius relationship. However, this decrease ceases at ~28°C. Beyond this point, the viscosity increases by about a factor of three with temperature up to the *LCST*. This minimum point (between regions I and II) depends on polymer concentration, shear rate and the presence of surfactant[11]. At temperatures greater than the *LCST*, the viscosity decreases sharply and reaches a steady value of ~2.5×10^{-3} Pa s.

The results presented in *Figure 3* can be divided into three different regions and a possible explanation for each region is described below.

Region I. As the polymer was being heated, the Brownian motion of the molecules was increased which could disrupt the 'water cage' surrounding the hydrophobic segments of the macromolecules. Further increases in temperature would result in larger proportions of the hydrophobic segments being exposed since the water cages had been disrupted. In this environment, interactions between the hydrophobic segments of the polymer chains would be favourable and might start to occur.

Region II. It is reasonable to assume that when the polymer solution approached the *LCST*, the hydrophobic isopropyl groups should associate by hydrophobic bonding. The increase in viscosity in region II indicated that some of this association is intermolecular leading to an apparent increase in molecular weight. Similar phenomena have been reported for other systems such as hydrophobically modified hydroxyethyl cellulose[12]. Fujishige *et al.*[3] demonstrated using light scattering that phase separation was preceded by coil–globule transition and intermolecular aggregation near the *LCST*. However, Winnik[7] reported that no intermolecular aggregation occurred near the *LCST* using the fluorescence probe technique. Our present study suggests that intermolecular aggregation occurred well below the *LCST* and depended on the polymer concentration, shear rate and the presence of surfactant[11]. It lends support to the suggestion of Heskins and Guillet[2] who inferred from the viscosity-average molecular weight data that the polymer was associating as the temperature approached the *LCST*.

Region III. Region III represents the phase separated polymer that existed as colloidal particles which became unstable as the temperature was further increased. The drastic decrease in the viscosity was representative of the viscosity of dilute colloidal systems. Some flocculation and eventual coagulation occurred as the solution was further heated and sheared.

Conclusions

The present study indicates that prior to phase separation in semidilute poly(NIPAM) solution at the *LCST*, the polymer molecules exhibit significant intermolecular association. Viscometry can provide additional new information on the polymer coil conformation as they undergo phase separation.

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