Rheological Behaviour of Poly(*N*-isopropyl acrylamide) in Water-Acetone Mixtures

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ABSTRACT

Atactic poly(*N*-isopropyl acrylamide) (PNIPAM) is a thermosensitive polymer in aqueous solutions. By modifying its structure with isotactic (i) rich blocks it has been shown that the thermal and structural properties of the solutions can be modified. For example, a triblock PNIPAM with isotactic endblocks forms hydrogels at temperatures close to room temperature. These gels phase separate at higher temperatures and dissolve when lowering the temperature.

The rheological properties of PNIPAM polymers in water-acetone mixtures were investigated to see how the acetone content affects solution behaviour.

Different arrangements of the atactic and isotactic block result in different complex viscosity as a function of temperature profiles and the block arrangement have an effect on the strength of the formed gel. It was also found that the acetone content influences the gelling behaviour of the PNIPAM systems to a large extent.

INTRODUCTION

In the recent years there has been an increasing interest in gel-forming polymers with thermosensitive properties. There are applications for these materials in various fields, e.g. materials for wound healing, viscosity adjustment of liquids and semisolids in production facilities, and pharmaceutical formulation with prolonged effect for application to the eye or the oral cavity. Polymers have been used as additives in crystallization in order to control and modify the properties of the crystallized product. In a previous study, Tian et al.[1] have shown that it was possible to modify the morphology of nitrofurantoin monohydrate (NF) crystals by addition of certain types of polymers to the crystallization solution. We have found that PNIPAM has similar properties. Because of poor water solubility of NF, acetone was added to increase the solubility of NF. It was observed that the addition of acetone changed the rheological behaviour of the polymer solution.

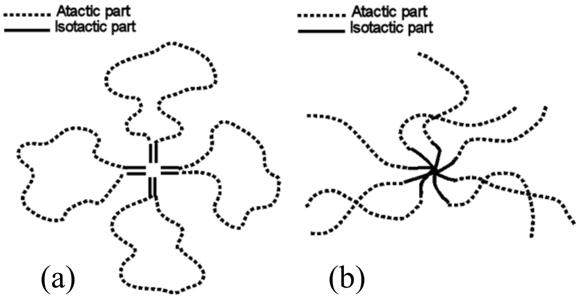

Figure 1. Schematic illustration of (a) flowerlike and (b) branched a-i-a micelles.

In this study four different PNIPAM block polymers were investigated. The polymers consist of atactic (a) and isotactic (i) blocks. At room temperature the atactic block is water soluble, whereas the isotactic block is not.[2,3] Nuopponen et al.[4] has found that in dilute conditions PNIPAM triblock polymers form flower-like or branched micelles depending on the order of atactic and isotactic blocks, see Fig. 1. Upon increasing the polymer concentration the interconnecting bridging chains between the micelles results in the gelling of the system in the case of flowerlike micelles.

The aim of this work was to characterize the rheological properties of four PNIPAM triblock polymers and to scrutinize the effect of the presence of acetone in the system.

MATERIALS AND METHODS

Samples

The following PNIPAM triblock polymers were investigated: i2-a28-i2 and i6-a68-i6, a12-i5-a12 and a12-i10-a12. The structure of a polymer can be identified from the abbreviation, e.g.: a12-i5-a12 means that the isotactic block is placed in the middle of the polymer chain surrounded by atactic blocks and the numbers gives the block sizes in kDa. 5 wt% stock solutions of each polymer were prepared and diluted with deionised water and acetone (HPLC grade) to a final concentration of 1 wt%. Four acetone to water ratios (v/v) were measured: 0:1, 0.25:1, 0.5:1 and 1:1. All measurements were conducted on freshly prepared solutions of PNIPAM, left to stand overnight at 5 ºC.

Rheology measurements

Oscillatory viscosity experiments were conducted with a TA AR-G2 rheometer using a cone and plate geometry, diameter of 60 mm. and 1º cone angle. A cover shield was used to reduce the evaporation of acetone as much as possible during the measurement. The sample temperature during the measurement was controlled with a Peltier element in the plate. Strain was set to 0.01 in all experiments. Initial experiment showed this value was in the linear viscoelastic regime. Frequency sweeps from 0.1 to 100 rad/s were conducted at fixed temperatures from 10ºC to 40 ºC with 1 or 5 ºC intervals. The dynamic moduli were monitored as a function of frequency and temperature. Complex viscosity (η*) (Eq. 1) was used to evaluate the overall gelling profile of the samples as it takes into account both the storage modulus (G') and the loss modulus (G''), where ω is the angular frequency:

$$\eta^*(\omega) = \frac{\sqrt{G'(\omega)^2 + G''(\omega)^2}}{\omega} \qquad (1)$$

RESULTS

Aqueous PNIPAM solutions

The four investigated aqueous PNIPAM solutions showed different complex viscosity dependence upon heating (Fig. 2).

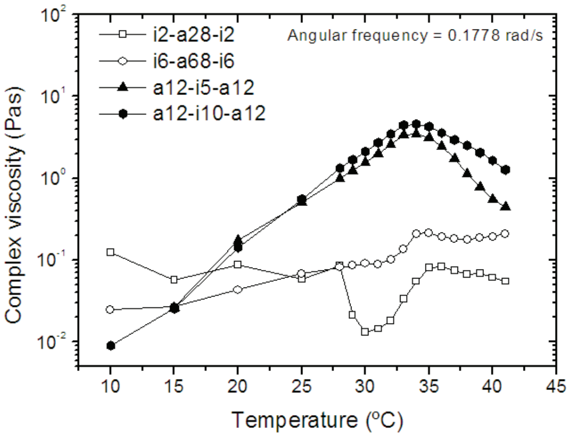

Figure 2. Complex viscosity (Pas) as a function of temperature of the four PNIPAM polymers in water.

Both a-i-a PNIPAMs displayed very similar complex viscosity upon heating profiles. When the temperature was increased from room temperature to ~30 ºC a solution to gel phase transition occurred. If the temperature was increased further above ~35 ºC a phase separation was observed.

The i2-a28-i2 PNIPAM was not able to form gel in water or in any of the measured acetone to water ratios. This was probably due to the low concentration and/or the short isotactic part, which was not able to form interconnected micelles. The drop in complex viscosity at around 28-30 ºC indicates the phase separation.

The i6-a68-i6 PNIPAM in water did not seem to gel within the measured temperature range, even though a rise in the complex viscosity was detected at 32°C, probably due to the low concentration used. However it was observed that a 5 wt% aqueous solution of this polymer gels even at 4 ºC.

Gelpoint determination

The gelpoint (GP) was determined, according to the method of Winter and Chambon[5], as the temperature where tan (δ) was frequency independent and the dynamic moduli have equal frequency dependency. Fig. 3 shows an example of the calculations.

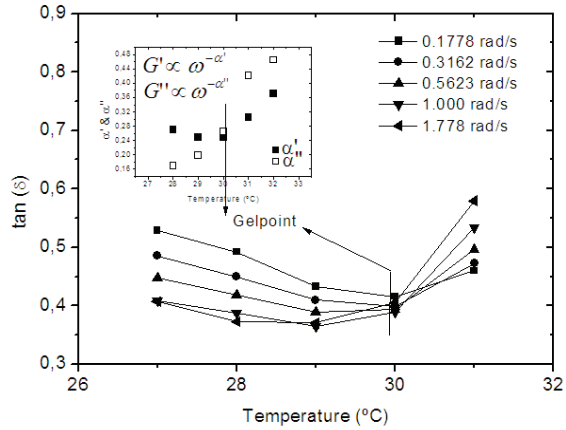

Figure 3. Gelpoint determination for 1% (w/v) a12-i5-a12 PNIPAM polymer in water.

The tan (δ) value was plotted against temperature for different angular frequency. The frequency independency was determined to be around 30 ºC in the example (Fig. 3). This was confirmed by plotting α' and α'' against temperature, where α' and α'' were determined as the slope of the linear region when plotting log (G') and log (G'') for each temperature against log (ω).

i6-a68-i6, a12-i5-a12 and a12-i10-a12 PNIPAM, 1 wt% in water, have similar gelpoints around 28-30 ºC. However, a gelpoint for PNIPAM i2-a28-i2 could not be determined.

Effect of acetone addition

The effect of acetone addition to the polymer solutions was investigated for PNIPAM a12-i5-a12, a12-i10-a12 and i6-a68-i6, as the i2-a28-i2 was not able to form a gel. In initial experiments (data not shown) it was observed that addition of acetone caused a decrease in complex viscosity above ~20 ºC, but at the same time it stabilized the complex viscosity above the phase separation temperature, possible by a reduced rate of phase separation.

The complex viscosity of the 1 wt% a12-i5-a12 PNIPAM solutions were changing dramatically as a function of temperature and with different solvent composition (Fig. 4).

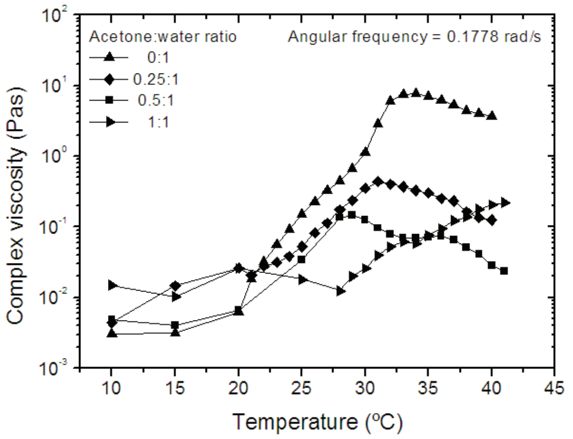

Figure 4. Complex viscosity (Pas) as a function of temperature showed for the a12-i5-a12 PNIPAM polymer at four acetone:water ratios.

The complex viscosity in gelling range was decreased with increasing acetone content. The gelpoint was found to be around 29-30 ºC for the following ac:w ratios: 0:1, 0.25:1 and 0.5:1, independent of the acetone content. For the solution with 1:1 ac:w ratio no gelling was observed, and no gelpoint was found. The increase in complex viscosity for the 1:1 ac:w ratio above 28 ºC was probably due to acetone evaporation during measurement, which would increase the concentration of a12-i5-a12 and shift the ac:w ratio towards lower value.

Similar to the findings for a12-i5-a12 the complex viscosity for a12-i10-a12 solutions also strongly depends on temperature and solvent composition (Fig. 5). The complex viscosity in the gelling range was decreased when increasing the ac:w ratio above 0.25:1. The solution with 0.25:1 ac:w ratio showed a more distinct phase transition from solution to gel, and with further temperature increase a more distinct phase separation compared to the solution with 0:1 ac:w ratio. For the solutions with 0.5:1 and 1:1 ac:w ratio no gelling was observed, and no gelpoint was found. The gelpoint for the 0:1, 0.25:1 ac:w ratios gelpoint was found to be 28 and 30 ºC. The increase in complex viscosity for the 1:1 ac:w ratio above 32 ºC was probably due to acetone evaporation during measurement, as discussed earlier.

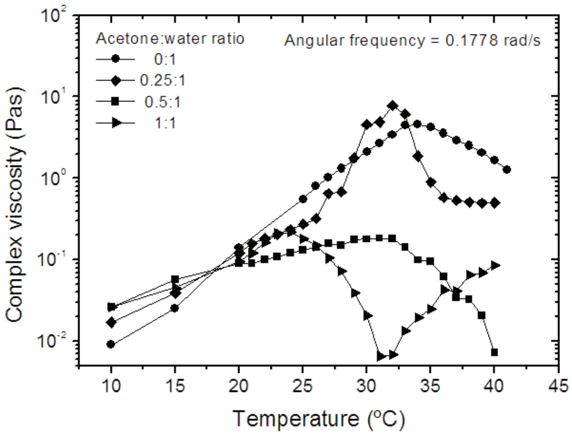

Figure 5. Complex viscosity (Pas) as a function of temperature showed for the a12-i10-a12 PNIPAM polymer at four acetone:water ratios.

The rheological behaviour of 1 wt% i6-a68-i6 deviates strongly from what was observed for a12-i5-a12 and a12-i10-a12 (Fig. 6). An increasement in the ac:w ratio caused an increase in the complex viscosity, which was the opposite effect observed compared to the a-i-a type polymers. With 0:1 and 0.25:1 ac:w ratios no gelling was seen and no gelpoint was found. At 0.5:1 and 1:1 ac:w ratios gelling was observed, and the gelpoints were determined to be 28 ºC. The increased acetone content seems to stabilize the gelability of this polymer, probably by interacting with the hydrophobic core of the flowerlike micelles.

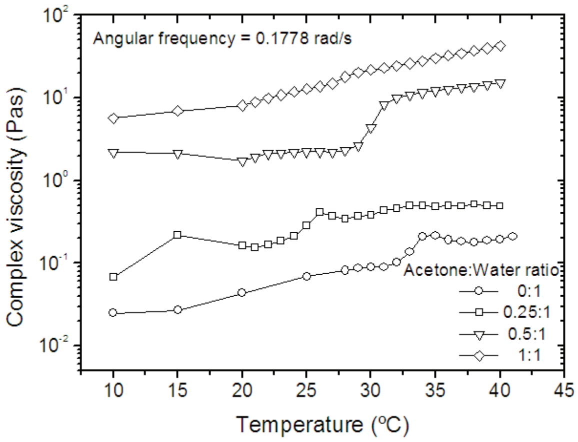

Figure 6. Complex viscosity (Pas) as a function of temperature showed for the i6-a68-i6 PNIPAM polymer at four acetone:water ratios.

Chen et al.[6] have investigated the effect of methanol addition to PNIPAM solutions. They found that addition of methanol decrease the intrinsic viscosity. Chen et al.[6] and Costa et al.[7] have investigated addition of several organic solvent to aqueous PNIPAM solution. They found that addition of methanol, ethanol, acetone, propanol, isopropanol or DMSO decreases the phase separation temperature (lower critical solution temperature). These findings are in consistence with the findings for a-i-a type PNIPAM polymers in this study, but not for the i-a-i type polymers.

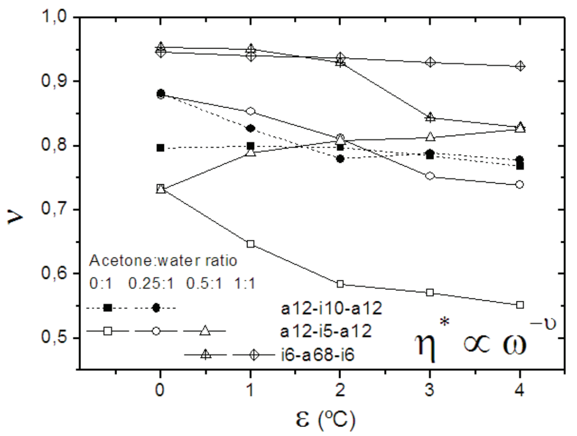

Figure 7. The frequency dependency of the complex viscosity (υ) against degrees above the gelpoint. ε is temperature distance from the gelpoint (ºC).

Gelstrength

Frequency dependency of the complex viscosity, $\eta^* \propto \omega^{-\nu}$ $(0 \leq \nu \leq 1)$, gives a measure of how solid-like the gel was. The value of ν close to 0 indicates a viscous-like behaviour, while a high ν value indicates more elastic and solid-like behaviour. The relationship between υ and the temperature at and above the gelpoint was shown in Fig. 7, for those PNIPAM solutions where gelling was observed. The maximum solidness of all the gels were reached at the gelpoint, except for the a12-i5-a12 PNIPAM polymer in 0.5:1 ac:w ratio. The solidness of the a12-i5-a12 PNIPAM at 0.5:1 ac:w ratio continued to increase for 1-4 ºC above the gelpoint. This behaviour was not seen for any other ac:w ratios or for other PNIPAM triblock polymers in this study. For the a12-i10-a12 with no acetone present (0:1 ac:w ratio) and the i6-a68-i6 with the highest measured acetone content (1:1 ac:w ratio) increasing the temperature 1-4 ºC above the gelpoint did not affect the solidness of the gel. For the remaining PNIPAM solutions and ac:w combinations it was observed they were becoming more viscous-like when increasing the temperature above the gelpoint, which indicated that phase separation was taking place. The temperatures, where the phase transition from solution to gel occurred and when the phase transition began, were found in a narrow temperature range. It can be concluded that by changing the temperature a few degrees centigrade around the gelpoint, it is possible to change the gel properties of PNIPAM block polymer to a large extent.

CONCLUSION

The solvent composition has a great influence on gelling properties of PNIPAM triblock polymers, both the a-i-a and the i-a-i type. This effect was greatly dependent on the placement of the isotactic blocks in the polymer chains, thus the shape of the micelles the polymer was able to form. The temperature range where the polymer was in the gel phase was narrow and was followed by a phase separation. It was observed that the complex viscosity changed dramatically during phase transition from solution to gel and later during phase separation. Changes in the complex viscosity changes will affect various properties for example the diffusion rate of molecules dissolved in the polymer solution. Changes in diffusion rate will have influence on crystallization of molecules, e.g.: it will affect the nucleation, nucleation rate and crystal growth and by this means properties of the final crystalline product.

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