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# Network formation in poly(*N*-isopropyl acrylamide)/water solutions during phase separation

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Evidence from dynamic viscoelasticity measurements has been found for reversible network formation *via* the physical association of hydrophobic side-groups during phase separation at around 33°C in a 1.22 wt.% aqueous solution of poly(*N*-isopropyl acrylamide) (PNIPA) having a molecular weight of $2.1 \times 10^6$. The frequency $\omega$ dependence of the dynamic storage and loss moduli $G'$ and $G''$ showed homogeneous fluid behaviour at 25°C, while at 35°C, a plateau zone was found in the $G'$ *versus* $\omega$ curve and $G'$ was larger than $G''$, indicating the formation of a network. The increase in $G'$ was instantaneous at the phase separation temperature and was not a progressive process. © 1997 Elsevier Science Ltd. All rights reserved.

**(Keywords: poly(*N*-isopropyl acrylamide); network formation; sol–gel transition)**

## *Introduction*

Poly(*N*-isopropyl acrylamide) (PNIPA), containing both hydrophilic amide groups and hydrophobic isopropyl groups in its side-chains, is soluble in water as well as in less-polar solvents e.g. tetrahydrofuran and chloroform[1]. The PNIPA/water solution undergoes phase separation upon heating, exhibiting a lower critical solution temperature (LCST) at about 32°C[2]. In addition, the chemically cross-linked PNIPA hydrogel shows a sudden volume shrink in water when heated above 33.2°C[3]. These properties make PNIPA attractive not only in industrial applications but also in fundamental research.

The mechanism of phase separation in PNIPA/water solutions has been investigated intensively[1,4–7]. A hydrophobic interaction is considered to cause the PNIPA chains to associate, inducing phase separation if the solution is concentrated enough. However, neither the critical concentration nor binodals of this binary system have been reported so far. It is still unknown whether a pair of equilibrated liquid phases are formed after the phase separation at a given temperature.

We have discovered evidence for network formation during phase separation in PNIPA/water solutions through dynamic viscoelastic measurements. The influence of physically associative structure on the microstructure and rheology has been studied on some polymer solutions, involving hydrogen bonding, ionic coordination, and complexes[8–12]. In the case of neutral polymers, the strength of the interactions is strongly dependent on the hydrophobicity of the polymer[13–18]. This may be the first example of a physically associative network originating from simple hydrophobic bonding.

## *Experimental*

The *N*-isopropyl acrylamide (NIPA) monomer provided by Cohjin Co. was recrystallized twice from a benzene/*n*-hexane mixture prior to use. The polymerization was conducted in *tert*-butyl alcohol at 55°C for 8 h, with a monomer concentration of 1.073 mol $l^{-1}$ and 0.58 mol% azobis(isobutylonitrile) as initiator. The prepared poly(*N*-isopropyl acrylamide) (PNIPA) was purified by precipitation from acetone solution into *n*-hexane three times. The PNIPA sample was fractionated by phase separation in acetone/*n*-hexane mixtures at fixed temperatures for several times, and a fraction coded D55-2-1A was selected for use in this study[19]. The intrinsic viscosity $[\eta]$ of this sample was measured in methanol at 25°C ± 0.05°C with use of a modified Ubbelohde viscometer. The viscosity-averaged molecular weight $M_\eta$ of the sample was $2.1 \times 10^6$ as evaluated from $[\eta]$ using the Mark–Houwink–Sakurada equation developed by Chiantore *et al.*[20]. The index of molecular weight distribution $M_w/M_n$ determined with use of a Waters-150C gel permeation chromatograph was 1.62 for D55-2-1A referred to polystyrene standards.

Dynamic viscoelasticity measurements were made on an aqueous 1.22 wt.% solution of the sample D55-2-1A. We chose this concentration in order to produce a higher torque response and also to reduce the entanglement effect. The strain-controlled rheometer RFS-II of Rheometrics was used with a Couette fixture whose cup and bob diameters were 33.96 mm and 32 mm, respectively, and the length was 33.31 mm. The temperature was controlled by a computer-programmable circulator with a precision of ±0.05°C.

The steady-flow viscosity was measured at 25°C as a function of shear rate $\dot{\gamma}$ from 0.1 to 100 $s^{-1}$. Three types of dynamic viscoelasticity measurements were carried out on the same PNIPA/water solution. The first was of the complex modulus $G^*$ at 25 and 35°C over a shear strain $\gamma$ range 0.5–100% at a fixed angular frequency $\omega$ of 10 rad $s^{-1}$. The second was of the $\omega$ dependence of the storage and loss moduli $G'$ and $G''$ in the range of about 1–100 rad $s^{-1}$ at 25 and 35°C at a fixed strain of 20%. The last type of measurement was of $G'$, $G''$, and the complex viscosity $\eta^*$ as a function of temperature from 25 to 38°C, encompassing the LCST, at a constant $\omega$ of 10 rad $s^{-1}$ and $\gamma$ of 20%. The rate of temperature increase was controlled at 0.1°C $min^{-1}$.

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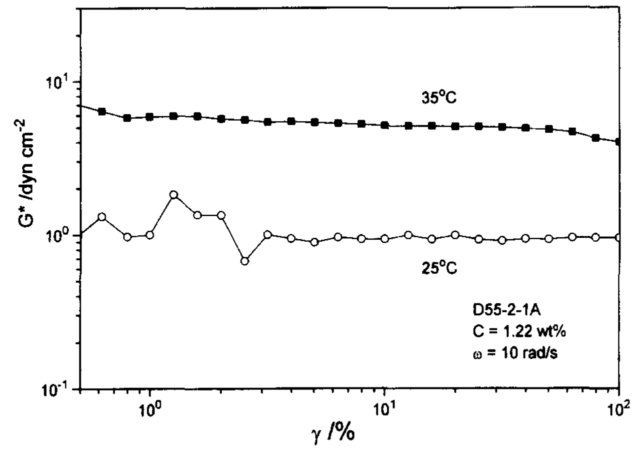

**Figure 1** Strain dependence of the dynamic complex modulus $G^*$ at 25 and 35°C, at an angular frequency $\omega$ of 10 rad $s^{-1}$

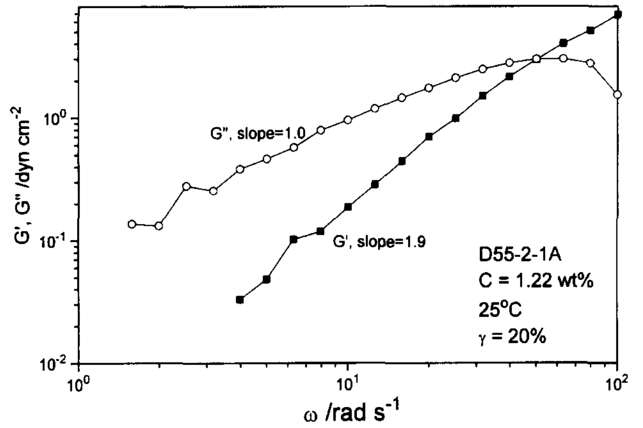

**Figure 2** The oscillatory frequency dependence of the dynamic storage and loss moduli $G'$ and $G''$ at 25°C at a strain $\gamma$ of 20%

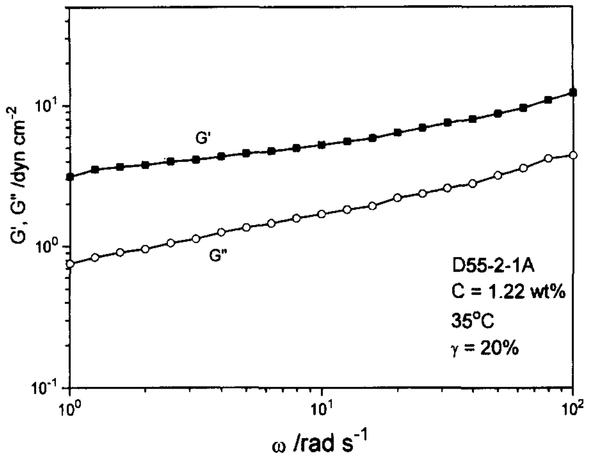

**Figure 3** The oscillatory frequency dependence of the dynamic storage and loss moduli $G'$ and $G''$ at 35°C at a strain $\gamma$ of 20%

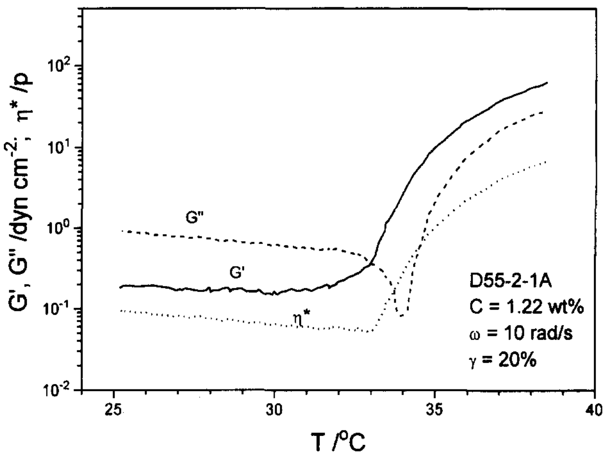

**Figure 4** Plots of dynamic oscillatory storage and loss moduli $G'$ and $G''$ and complex viscosity $\eta^*$ *versus* temperature at 20% strain and 10 rad $s^{-1}$ angular frequency

## *Results and discussion*

At first, it is essential to confirm the strain range in which the linear viscoelasticity can be observed from this PNIPA/water solution. *Figure 1* shows that the complex modulus $G^*$ is almost independent of the strain $\gamma$ at both 25 and 35°C when $\gamma$ is less than 50%. For the following experiments, the applied oscillatory strain is kept at 20% to produce enough torque and the results are processed within the framework of linear viscoelasticity[21]. It is worth noticing that 35°C is higher than the LCST at which the solution is already phase-separated.

At temperatures below the LCST, we found that the viscosity of the PNIPA/water solution under investigation was almost independent of shear rate as long as $\dot{\gamma}$ is less than 10 $s^{-1}$, exhibiting Newtonian-like behaviour. (For a real Newtonian fluid the storage modulus $G'$ should be zero.) With increasing shear rate, the solution shows a shear-thinning effect instead of the shear-thickening found in many associative polymer solutions[22,23].

*Figure 2* shows the angular frequency $\omega$ dependence of the storage and loss moduli $G'$ and $G''$ of a solution having a concentration of 1.22 wt.% at 25°C. In the low $\omega$ region, $G'$ and $G''$ are proportional to $\omega^{1.9}$ and $\omega^{1}$, respectively, which is characteristic of a viscous liquid. Limitations on the range of frequency and torque must have prevented us achieving a theoretical low-frequency limit of $\omega^2$ for $G'$. With increasing frequency, the curve of $G''$ *versus* $\omega$ shows a maximum at $\omega = 70$ rad $s^{-1}$. In contrast, $G'$ increases monotonically with $\omega$, showing no sign of the appearance of a plateau zone in this $\omega$ region. The above results indicate that below the LCST the PNIPA/water solution is a homogeneous fluid.

To examine the structure change in the PNIPA/water solution after phase separation, we conducted the same dynamic viscoelasticity measurements at 35°C. *Figure 3* illustrates the results. It is surprising that there is evidence of network formation because there is a plateau in the $G'$ *versus* $\omega$ curve and $G''$ is smaller than $G'$ over the whole $\omega$ region. The inclination of the curves for $G'$ and $G''$ *versus* $\omega$ can be attributed to the presence of a molecular weight distribution in the network strand chain between the adjacent cross-linkers. This distribution makes the storage function less flat and smoothes out the maximum and minimum in the loss function[21]. This phenomenon demonstrates that the PNIPA chains in the PNIPA/water solution associate with each other to form a physically cross-linked gel-like state at 35°C. We consider that the hydrophobic interactions between the PNIPA chains act as the physical joints in the PNIPA/water solution after phase separation.

In order to trace the network formation process, we determined $G'$, $G''$ and the complex viscosity $\eta^*$ with the temperature increasing at a rate of 0.1°C $min^{-1}$, and at a fixed $\omega$ of 10 rad $s^{-1}$ and a $\gamma$ value of 20%, which ensured that these measurements were in the linear range. *Figure 4* shows the results for a 1.22 wt.% PNIPA/water solution. When the temperature is below 32°C, $G'$ is lower than $G''$ and $\eta^*$ slightly decreases with temperature, which is characteristic of an ordinary fluid having a small positive flowing activation energy. At about 32°C, $G'$ starts to increase sharply and overtakes $G''$ at 33.0°C. In contrast, $G''$ exhibits a deep minimum at 34°C. After phase separation, $G'$ becomes almost proportional to the temperature, showing a rubber-like property.

This phenomenon is reversible when the solution is cooled down and is reproducible when the cooled solution is re-heated. These results suggest that a physically cross-linked network is formed instantaneously at the phase separation temperature, instead of being a progressive process. The cross-linker is constrained at temperatures above the LCST, showing an infinite relaxation time, but it can be reversibly loosened by cooling down below the LCST.

## *Concluding remarks*

The above observations show that a physically cross-linked network is formed in a PNIPA/water solution at the phase separation temperature. According to the authors' knowledge, this is the first report concerning a sol–gel transition in the PNIPA/water system induced by heating. As discussed previously[7], at the phase separation temperature, the hydrated shell around the hydrophobic parts of the PNIPA chain that is dissolved in water is partially destroyed and the isopropyl side-chains approach each other within the van der Waals radius, resulting in so-called hydrophobic bonding. N.m.r. measurements[7] have shown that the relaxation rate of the methyl proton in the isopropyl groups decreases with increasing temperature, illustrating a mobility loss due to the bonding.

When the solution concentration is higher than the overlap concentration, hydrophobic bonding can cause intermolecular aggregation, which plays the role of physical cross-linkers in the network formation that we observed. The effects of molecular weight and concentration on network formation would permit us to understand the hydrophobic interaction as well as the dynamic behaviour of chain molecules exhibiting physical association. Further work on these aspects is in progress. Owing to a structural analogy, revealing the nature of this transition may be helpful in understanding the denaturation and folding of proteins.

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