Synthesis and thermoassociative properties in aqueous solution of graft copolymers containing poly(N-isopropylacrylamide) side chains

Alain Durand, Dominique Hourdet*

Laboratoire de Physico-chimie Macromoléculaire, UMR 7615, Espci-upmc-cnrs Espci, 10 rue Vauquelin, 75231 Paris cedex 05, France

Received 25 May 1998; accepted 17 July 1998

Abstract

New thermoassociative polymers were developed on the basis of the self-aggregation behaviour induced by heating of the ‘poly(N-isopropylacrylamide)/water’ binary system. The preparation of the graft copolymers involves a 2-step method with (1) the synthesis of amino end functionalised oligo-NIPA by radical polymerisation initiated with a convenient redox system based on thiol and (2) a ‘grafting onto’ reaction of the PNIPA chains on a poly(acrylic acid) backbone. In semi-dilute aqueous solution, the resulting graft copolymers exhibit a large viscosity enhancement upon heating as soon as the temperature exceeds the lower critical solution temperature (LCST) of the PNIPA side chains. The influence of various physicochemical parameters (copolymer concentration, shear rate) and structural characteristics (side chains length) on the thermothickening behaviour are examined and interpreted using the concept of thermally induced physical network.

© 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(N-isopropylacrylamide); Associative polymers; Thermothickening

1. Introduction

Important applications of water-soluble polymers (WSP) are related to the thickening and rheology modification of industrial fluids: small amounts of WSP introduced in an aqueous mixture can produce a viscosity increase of several orders of magnitude [1–3]. In the last three decades, many WSP were developed for these applications and several structures were proposed. The simplest one concerns polymers with very high hydrodynamic volume. For instance, these polymers can provide a high viscosity at low concentration but they are generally very sensitive to deformation and some mechanical degradation (loss of viscosity) can occur under high shear rate [4]. With the same idea, a polyelectrolyte would be efficient in pure water but in the presence of salt the thickening efficiency is weakened due to screening effect. An alternative route to these standard thickeners was developed using the concept of ‘associative polymers’. Their basic structure is constituted of a water-soluble chain, for the main part, with a few hydrophobic groups scattered along the chain. In semi-dilute aqueous solution, the hydrophobic parts self-aggregate into microdomains and give rise to a physical network with a large increase of viscosity [5–9].

Nevertheless, for all these systems, the viscosity generally decreases when temperature is raised and this can be an important drawback, especially for applications carried out in a wide range of temperatures. For most of these applications, like drilling fluids in deep subterranean formations, it would be more valuable to use polymer solutions whose viscosity remains independent of the temperature or even increases under heating. These unexpected properties, which reverse the Arrhenius law for flow, can be obtained only with particular polymers which we will call ‘thermoassociative polymers’ (or ‘thermothickening polymers’) and for which intermolecular associations are favoured on warming. Several aqueous systems which show such thermothickening behaviour have already been described [10–28]. In most cases, when temperature is raised, water becomes a bad solvent for one of the components which, as previously mentioned, starts to self-aggregate with the associative polymers. Among these systems several groups can be distinguished: aqueous solutions of cellulosic derivatives [10–12], triblock copolymers [13–15], polymer–surfactant mixtures [16–19], oligomeric surfactants [20], polymer mixtures [21] and graft copolymers [22–28]. Even if all these systems exhibit a thermoassociative behaviour, only the thermothickening graft copolymers, which we started to develop at the beginning of the 1990s, really allow a systematic approach to the key relations existing between the thermodynamic properties of the components,
the primary structure of the system and its flow properties with the temperature. Our initial copolymers were designed on the basis of a poly(sodium acrylate) (PAA) backbone with pendant poly(ethylene oxide) (PEO) side chains. Owing to their lower critical solution temperature (LCST) in water [29], the PEO side chains can self-associate reversibly into microdomains when the temperature is raised above the phase separation one (association temperature). This frustrated phase separation, which is maintained at a microscopic level thanks to the hydrophilic backbone, provides an important increase of the viscosity. From a wide set of data, which associate different experimental approaches like small angle neutron scattering, phase diagrams and rheological behaviour [22–26,30], we have shown that not only the association temperature, but all the viscosifying process of PEO graft copolymers were closely related to the thermodynamic properties of the PEO itself [24]. As a matter of fact, it was clearly evidenced that micro- and macro-phase separation proceed identically if we compare (1) the temperature of phase separation, (2) the number of PEO participating in the concentrated phase (at a given temperature) and (3) the PEO concentrations inside the dilute and concentrated phases (∼ microdomains). The important consequence is that the association behaviour can be easily predicted from the phase diagram of the ‘PEO/water’ binary system.

Starting from these results, the aim of the present study was to extend the concept of thermoassociation to new macromolecular systems based on poly(N-isopropylacrylamide) (PNIPA), a well-known WSP which displays a LCST around 32°C in pure water [31–35]. When replacing PEO by PNIPA the main ideas were to use (1) the versatility of polyacrylamide derivatives chemistry and (2) the peculiar thermodynamic properties of these polymers in water. In this way we expect to develop new water-soluble polymers exhibiting well-defined thixotroping behaviours.

In the first part of this paper the synthesis of PAA-g-PNIPA graft copolymers, following a two-step process, will be described. Later, we will discuss the rheological properties of these polymers in water, especially the variation of viscosity with temperature and we will try to correlate the observed thixotrope behaviour to the thermodynamic properties of the binary system PNIPA/water.

2. Experimental

2.1. Materials

N-isopropylacrylamide (NIPA) and acrylic acid (AA) were purchased from ALDRICH and FLUKA, respectively, and were used as received. Potassium persulfate (KPS, from PROLABO), 2-aminoethanethiol hydrochloride (AET, HCl; from FLUKA), disulfine blue (from PANREAC), dicyclohexylcarbodiimide (DCCI, from ACCROS) and N-methylpyrrolidone (NMP, from SDS) were all analytical grade reagents. Water was purified with a MILLIPORE system combining inverse osmosis membrane (Milli RO) and ion exchange resins (Milli Q).

2.2. Polymer synthesis

The polymerisation of NIPA was carried out in a threenecked flask equipped with a reflux condenser, a magnetic stirrer and a nitrogen feed. The monomer was dissolved in water and the resulting solution was deaerated during 1 h with nitrogen bubbling. The temperature was adjusted to (29 ± 1)°C with a water bath. The initiators (KPS and AET,HCl) were separately dissolved in water and added rapidly to the NIPA solution. The reaction was allowed to proceed for 18 h. Then the polymer was recovered by dialysing the reaction medium against pure water (membrane cut-off = 6000 daltons) and freeze drying. For the very low molecular weights a special procedure was followed. The reaction medium, initially freeze dried, was redisolved in methanol. An appropriate amount of sodium hydroxide was then added to neutralise the hydrochloride ions. The salts which were not soluble in methanol gave a precipitate that was filtered off and the resulting clear solution was added dropwise into a large excess of diethylxide. After precipitation, the polymer was recovered by filtration and finally dried under vacuum.

The poly(acrylic acid) (PAA) precursor was obtained by radical polymerisation in aqueous medium as described elsewhere [36]. Its absolute average molecular weights, determined by Size Exclusion Chromatography (SEC), are: \( M_w = 37\ 000\ \text{g/mol} \) and \( M_n = 136\ 000\ \text{g/mol} \). This sample will be referred to as PAA1.

2.3. Grafting reaction

In a three-necked flask, equipped with a reflux condenser and a magnetic stirrer, PAA was dissolved in NMP during 18 h. The temperature was adjusted to 60°C with an oil bath. PNIPA and DCCI were separately dissolved in NMP. The solution of PNIPA was then introduced slowly to the reaction medium and 2 h later the DCCI was added dropwise to the mixture. The reaction mixture was sampled regularly in order to follow the reaction progress by SEC. After 20 h the flask was immersed in a cold water bath. The dicyclohexylurea by-product, formed by DCCI during the grafting reaction, gave an insoluble material which was filtered off. The copolymer was then progressively precipitated by dropwise addition of a concentrated NaOH solution. It was then recovered by filtration and washed several times with methanol. The solid product was further purified by ultrafiltration (membrane cut-off = 10 000 daltons) against pure water and finally recovered by freeze drying.
2.4. Analytical methods

2.4.1. $^1$H n.m.r.

$^1$H n.m.r. characterisation of precursors and graft copolymers was performed in D$_2$O using a BRUKER WP250 spectrometer (250 MHz).

2.4.2. Potentiometric titration

The potentiometric titration of amino-terminated PNIPA was carried out with an automatic titrator TT-Processeur 2 (TACUSSEL). Before titration with HCl 0.01 mol/L, an excess of NaOH was added to the PNIPA aqueous solution to ensure that all the amine functions were under basic form.

2.4.3. Size exclusion chromatography (SEC)

SEC was used in this study, either to follow the conversion of the reactions or to characterise the molecular weight of the polymers.

For PNIPA synthesis, the reaction progress was checked with time using a Waters 6000A chromatographic system equipped with four ultrastyragel columns ($10^3, 10^4, 10^5$ and $10^6$ Å). The latter were equilibrated at room temperature in THF and detection at the column output was monitored using a differential refractometer (Waters R401). The samples, originated from a concentrated aqueous medium, were injected into the columns after dilution in THF to a final concentration of $(2–3) \times 10^{-3}$ g/mL, on the polymer weight basis.

For poly(acrylic) derivatives, analyses were carried out with a similar Waters system equipped with four Shodex OH-pak columns, equilibrated at $T = 20^\circ$C in aqueous solution (LiNO$_3$, 0.5 mol/L). To follow the extent of the grafting reaction, 0.5 mL were sampled from the reaction medium and diluted into 5 mL of LiNO$_3$, 0.5 mol/L. A few drops of concentrated solution of NaOH were then added to the mixture so as to ionise the poly(acrylic) backbone and to enhance the solubility of the copolymer in the aqueous medium.

2.4.4. Disulfine blue test

A qualitative detection of amino end groups of PNIPA oligomers was performed using the disulfine blue test. This was done following the procedure previously described by Palit et al. [37–39], except that the composition of the disulfine blue aqueous solution was slightly modified: sodium sulfate was added up to a concentration of 0.3 mol/L so as to ensure insolubility of PNIPA in the aqueous phase.

2.4.5. Rheological measurements

The viscosity analyses of aqueous solutions with temperature were carried out on a CARRI-MED controlled stress rheometer (RHEO) using a cone-plate geometry. The temperature was adjusted by a high power Peltier system which provided fast and precise control of the temperature during heating or cooling stages. The measuring unit was also equipped with a solvent trap in order to prevent water evaporation during the scanning experiments performed up to rather high temperatures (up to 70°C).

2.4.6. Cloud point measurements

The determination of the cloud point of PNIPA aqueous solutions was done visually by following the variation of the turbidity with temperature. The aqueous solution (volume = 1 mL), initially equilibrated at room temperature in a sample tube equipped with a magnetic stirrer, was immersed in a thermostated cell with a circulating water bath. The heating rate was regulated around 0.5°C/min and the cloud point was defined as the temperature at which the solution started to turn cloudy. The reproducibility of the determination was $\pm 0.1^\circ$C.

3. Results and discussion

3.1. Synthesis and characterisation

3.1.1. Amino-terminated PNIPA

The synthesis of functional PNIPA, which has already been described in the literature, is usually achieved by introducing an efficient chain transfer agent (CTA) in the polymerisation medium [40–43]. In the specific case of amino-terminated PNIPA, 2-aminoethanethiol hydrochloride (HCl$_2$N–CH$_2$–CH$_2$–SH or AET,HCl) is undoubtedly the best candidate since thiols are widely used and well-known CTA [40–42]. According to this peculiar type of polymerisation, usually called telomerisation, the CTA allows control of the end-groups of the polymer as well as its molecular weight: the more CTA introduced, the shorter will be the telomers. Consequently, telomerisation provides oligomers with both defined functional end groups and desired molecular weights [44,45]. In accordance with our
objectives, the reaction was carried out in aqueous medium using a redox couple where the oxidant was the potassium persulfate and the reducing agent, the thiol itself. According to our SEC analyses performed during the reaction, the polymerisation progress was evidenced to be very fast: 90% of the conversion was reached within less than one hour. Furthermore, during the reaction the pH of the aqueous medium dropped from 5.6 at the beginning to 2–2.5. This could be attributed to the formation of HSO\(_4^-\) (see reaction 1 in Scheme 1) as previously reported, for similar redox systems [46–48]. Moreover, as no polymerisation at all took place if only KPS was introduced as initiator, but the reaction started immediately if some AET,HCl was added, we may infer that step (1') given in Scheme 1 is negligible in our conditions. Regarding the next steps of the polymerisation process, i.e., the propagation and transfer reactions, we can assume that they follow the usual mechanism (reactions 2 to 4 in Scheme 1) as was reported, for example, for the telomerisation of NIPA with 3-mercaptopropionic acid as CTA by Takei et al. [49]. The functionalised polymers, which were purified either by dialysis or precipitation, were characterised in aqueous solution by SEC using a calibration curve based on PNIPA. As shown in Fig. 1, the length of the telomers synthesised is directly related to the initial concentration of AET,HCl in the reaction medium and \(M_w\) scales approximately with the opposite of the thiol concentration [AET,HCl]. Contrary to the thiol dependence of the molecular weight, the concentration of KPS does not seem to have any important effect on \(M_w\) (Fig. 1). This prevalent role of the reducing agent in the polymerisation process is a quite general mechanism which has already been reported for other redox systems containing KPS and for various acrylic monomers [36].

The presence of amino endgroups in the polymers was checked qualitatively using a specific dye-partition test, involving disulfine blue (DB test), which was reported by

![](image)

> **Fig. 1.** Weight average molecular weight of telomers determined by SEC as a function of ● AET,HCl initial concentration; \([K_2S_2O_8]_0 = 0.015 \text{ mol/L}, [M]_0 = 0.77 \text{ mol/L} \). □ K\(_2S_2O_8\) initial concentration; \([\text{AET,HCl}]_0 = 0.025 \text{ mol/L}, [M]_0 = 1.29 \text{ mol/L} \).

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Characterisation of amino-terminated PNIPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Telomer</td>
<td>([M]_0 ) (mol/L)</td>
</tr>
<tr>
<td>PNIPA5</td>
<td>0.85</td>
</tr>
<tr>
<td>PNIPA10</td>
<td>1.28</td>
</tr>
<tr>
<td>PNIPA13</td>
<td>1.24</td>
</tr>
<tr>
<td>PNIPA12</td>
<td>0.77</td>
</tr>
</tbody>
</table>

^a Determined by SEC.

^b Total amine content/g of PNIPA, from potentiometric titration.

^c Average number of amino endgroups per chain given by \(f = A \times M_w\).
Palit and co-workers [37–39]. Since this test requires a polymer which is soluble in organic phase and insoluble in water we have modified it slightly for a specific application to PNIPA, as reported in the experimental section. For the telomers synthesised according to our procedure, the DB test always gave a positive answer which means that part of the polymer chains contain amino endgroups. Of course, we verify that the DB test was negative when either AET,HCl or unfunctionalised PNIPA (polymer chains synthesised with AIBN as initiator) were used. Beside this qualitative test, a quantitative determination of the amino endgroups was effectively done by potentiometric titration of the different telomers. As we can see in Table 1, the functionality of the telomers lies roughly around 1 except for the PNIPA sample with the shortest molecular weight (PNIPA5). In that case, the high value of the functionality \( f = 2.2 \) seems unrealistic since it would imply two amine groups per chain and, consequently, a very different termination process. Compared to the three other samples, which were purified by ultrafiltration, we are more inclined here to attribute this high level of amine groups in the sample to the presence of AET,HCl which would have been only partly removed during the precipitation process.

Among the various telomers which were prepared, only PNIPA5 and PNIPA10 will be used in the following grafting reactions.

### 3.1.2. Graft copolymers

Poly(acrylic acid)-g-poly(N-isopropylacrylamide) graft copolymers (PAA/PNIPA) were prepared according to the classical reaction of amines with carboxylic acids in the presence of a coupling agent (DCCI) and in an aprotic solvent (NMP) (see Scheme 2) [50]. As described in the experimental section, the grafting reaction was monitored by SEC which can also help to check the efficiency of the purification procedure. As previously reported with ampholylecters [39,42], the coupling reaction is very fast and proceeds in less than 1 h. Nevertheless, the final grafting yields calculated from \(^{1}\text{H} \text{n.m.r.} \) (Table 2), are not very high (around 50\%) compared to the 70–100\% obtained with most of the grafting reactions involving aminopolyethers derivatives. According to our previous experiments [39,42], we can expect to improve the grafting efficiency of amino-PNIPA by increasing the amount of carbodiimide up to \([\text{DCCI}]/[\text{–NH}_2] \) ratios around 10.

Two graft copolymers were prepared following this procedure with the same backbone but with two different PNIPA side chains (see Table 2). Since the reaction medium is homogeneous (PAA and PNIPA are completely soluble in NMP) we can expect that the distribution of the side chains along the backbone is random. This was demonstrated by Magny et al. [51] in similar conditions with alkylamines but in our situation, where the grafting molar ratios are very low (below 1\%), this remains impossible to prove experimentally.

### 3.2. Rheological properties in aqueous solution

#### 3.2.1. Thermothickening behaviour

A typical thermothickening behaviour in semi-dilute solution is presented in Fig. 2 with a 6\% solution of PAA1/PNIPA10–29\% in pure water. For comparison, we plot on the same picture the results obtained with a mixture of PAA1 (under the polyacrylate form) and PNIPA10 at a total concentration of 6\% and with the same composition as that of the copolymer. For the mixture, and as expected for usual fluids, the shear flow curve displays a continuous decrease of viscosity on the whole range of temperature, with only small perturbations around 34°C. At this temperature, the PNIPA10 starts to phase separate macroscopically (the solution becomes turbid) but the viscosity does not display any important variation as (1) it is mainly the polyelectrolyte which contributes to the viscosity of the solution and (2) there are no specific interactions between the two phases. If we focus now on the graft copolymer solution we can easily define a transition temperature \( T_{\text{ass}} \) which separates the rheological behaviour in two parts.

Below \( T_{\text{ass}} \), the copolymer solution behaves as the previous mixture and we can see that the viscosities are almost the same in this range. Now, when the temperature reaches the ‘critical’ value, the PNIPA side chains start to self-aggregate but the covalently-linked polyelectrolyte backbones stabilise the PNIPA phase at the microscopic level. In semi-dilute solutions, the PNIPA microdomains are connected through the highly soluble PAA chains into a physical 3-dimensional network with the expected viscoelastic properties. One can see that the macroscopic transition, i.e., the viscosity, is not abrupt but proceeds continuously with increasing temperature, starting from a weak segregation regime around \( T_{\text{ass}} \) (with side chains interactions comparable to kT) and going towards an expected strong segregation regime well above \( T_{\text{ass}} \). The association temperature can be precisely determined by plotting the results under an Arrhenius plot (see inset of Fig. 2). We obtain here \( T_{\text{ass}} \sim 30^\circ\text{C} \) which is not very far from the LCST of the PNIPA10, but we will come back later to this point.

In order to check the influence of experimental parameters onto the transition behaviour of the copolymer solution, we have applied to a given sample different heating
rates varying between 1 and 5°C/min. The various thermoviscosifying curves obtained were almost perfectly superimposed, which means that the associative phenomenon is rather fast and that we can rule out any kinetic effect. For all the following studies, we will keep an intermediate heating rate value of 2°C/min.

Following the same idea, we have verified the reversibility of the thermothickening process by comparing the 2 plots obtained on heating and cooling. As expected from the previous data, the two curves obtained are very similar and we can conclude that in our experimental conditions, each step of the association process results from a true thermodynamic equilibrium.

From a general point of view, for a given sample, its thermothickening behaviour can be characterised using at least three parameters:

- the association temperature: \( T_{\text{ass}} \) (see Fig. 2),
- the sharpness of the thermothickening process that we can define as the initial slope of \( \eta = f(T) \) for \( T > T_{\text{ass}} \),
- the magnitude of the thickening for a given shear rate: \( \eta_{\text{max}} / \eta_{\text{min}} \).

These parameters will be used later to describe the modifications of the thermothickening process caused by various physicochemical variables.

Interestingly, these three parameters can be compared to those used to describe the swelling behaviour of temperature-sensitive hydrogels. For instance Harsh et al. [52] defined the transition temperature, the sharpness of the transition and the degree of swelling as the key parameters for temperature-sensitive cellulose ether hydrogels. Although the thermodynamic phenomenon involved here is the same, the interactions between the polymeric chains are favoured upon heating, the macroscopic transition has a very different magnitude. For hydrogels, which can best be compared with an isolated chain (dilute solution) rather than with a semi-dilute solution of polymer, the thermoinduced interactions which are extended to the whole system lead to a strong collapse of the system (macroscopic phase separation). For our graft copolymers the thermosensitive chains are a minority and they are spread along a very hydrophilic backbone. Consequently, only local interactions can be generated with the temperature. They give rise either to an increase of viscosity in the semi-dilute regime or to a decrease of the hydrodynamic volume of the copolymer chain in dilute solutions.

### 3.3. Effect of copolymer concentration

The viscosity at constant shear rate of the sample PAA1/PNIPA10–29% is plotted versus the temperature for various copolymer concentrations in Fig. 3. Two main effects can be underlined.

First of all, the association temperature is lowered when the copolymer concentration increases. More precisely \( T_{\text{ass}} \) is shifted from 32 to 30 and 26°C when the concentration...
raises from 3, 6 and 9%, respectively. This lowering of the self-association temperature of the PNIPA side-chains probably originates from the well-known salting-out effect usually observed with simple electrolytes. As a matter of fact, we have to keep in mind that the copolymer backbone is a polyelectrolyte and consequently the polysalt or ionic concentration increases linearly with the copolymer concentration.

The second point concerns the sharpness of the thickening curve which seems also dependent on the copolymer concentration, especially between 3 and 6%. Once more, we can use the fact that, as previously mentioned, the ionic strength increases in the same order as the copolymer concentration. As the associative mechanism proceeds through a subtle equilibrium between electrostatic repulsions and hydrophobic attractions, one can easily state that the associations will be favoured at higher ionic strength either by adding salt or by increasing the polyelectrolyte concentration. Of course the viscosity of the 3D network is proportional to the number of physical cross-links, or to the total number of elastically active chains, and this number increases with the copolymer concentration.

Finally, we can mention that for \( C_p = 6 \) and 9% the viscosity reaches a plateau about 25°C above \( T_{\text{ass}} \), the maximum that one could correlate to the strong segregation regime. For \( C_p = 3\% \) the slope is much lower and the plateau cannot be reached in the experimental temperature range \( (T < 60^\circ C) \) as the competition between electrostatic and hydrophobic interactions remains stronger.

3.4. Effect of shear rate

The shear rate dependence of the viscosity of a 6% solution of PAA1/PNIPA10–29% is shown in Fig. 4. For temperatures below \( T_{\text{ass}} \), the viscosity does not exhibit any detectable shear rate dependence over the explored range.
(50–800 s\(^{-1}\)). On the contrary when \(T > T_{\text{ass}}\) the solution becomes clearly shear-thinning which is consistent with the network formation through weak associations (hydrophobic interactions). From these curves a clear transition in the solution microstructure is displayed since upon heating the rheological behaviour is modified and a shear rate sensitivity appears. In order to better quantify this effect we have plotted the viscosity against the shear rate at different temperatures (Fig. 5). Again we can see that the sensitivity to shear rate is highly enhanced by heating. The exponent of the power-law which fits the shear-thinning behaviour of these systems varies from \(-0.4\) to approximately \(-0.8\) when the temperature is raised from 45 to 60°C, respectively. Of course, from a technological point of view, the shear rate at which the thermothickening cancels, i.e., when the viscosity falls down to that of the polymer backbone, could be a relevant parameter. If we take the data of Fig. 4 we can extrapolate a ‘critical’ shear rate ranging around \(6 \cdot 10^4\) s\(^{-1}\) at 60°C.

As a concluding remark, we can say that the shear rate influences mainly the magnitude of the viscosity at the plateau but the two other parameters, i.e., the thermothickening sharpness and the association temperature, remain unchanged.

3.5. Effect of side chains length

If we consider the variation of the viscosity with temperature of an aqueous solution of PAA1/PNIPA10–29% at various concentrations (Fig. 6) we can notice that the viscosity profiles are somewhat different from the ones obtained with the PAA1/PNIPA10–29% in the same conditions. Although the general behaviour remains the same (with the main characteristics as those described in a preceding section), great differences can be found for the association temperature and the slope of the thermothickening part. Especially, we can notice that for a 3% solution of PAA1/PNIPA5–14.5% almost no thermothickening effect can be observed. In the same way, the magnitude of the thickening cannot be evaluated from these curves as the plateau is far from being reached, even at 9%. The differences between the two copolymers becomes obvious if they are compared in the same conditions (see Figs 3 and 6). This indicates clearly that the formation of microdomains and the resulting macroscopic properties are strongly dependent on the side chains length. The two copolymers have indeed the same hydrophilic backbone and approximately the same modification extent (molar ratio), whereas the length of the grafted PNIPA is two times larger for the PAA1/PNIPA10–29% compared to the PAA1/PNIPA5–14.5%. Several explanations can be found to justify these expected differences between the two copolymers.

First of all, we can assume reasonably that the shorter the PNIPA chain, the lower its hydrophobic character and the higher is its LCST or phase separation temperature. According to this it follows that for graft copolymers having the
same grafting ratio and studied at the same copolymer concentration, the association temperature of the low side-chain derivative will be shifted towards higher temperature. Moreover, this trend will be strengthened if we take into account some concentration dependence of the ‘PNIPA/water’ phase diagram. As a matter of fact, and according to the same previous assumptions, the relative PNIPA concentration is always two times larger in a solution of PNIPA10 derivative compared to a PNIPA5 one.

Secondly, it could be interesting to compare the associative behaviour of our graft copolymers to the rheology of solutions of hydrophobic ethoxylated urethane (HEUR) studied by Annable and co-workers [53]. For these systems, which self-associate in water by their alkyl moieties and give very nice interconnected flowers in concentrated solution, it was shown (1) that a minimum of 6 methylene groups is necessary to provide hydrophobic associations and (2) that for longer hydrophobic chains which form aggregates, the activation energy of disengagement of an alkyl chain from a hydrophobic cluster increases linearly with the chain length \( \Delta H \approx 1 \text{ kT} \) per methylene group. If we apply these results qualitatively to the thermoassociative graft copolymers, it becomes obvious that for a given grafting ratio, the sharpness of the thromoassociation must decrease when the length of the PNIPA side-chain decreases. This effect is particularly important in our system where strong electrostatic repulsions exist between the polyelectrolyte backbones and we can easily imagine that in some cases these repulsions can prevent the formation of hydrophobic associations above, the ‘cloud point’ of the PNIPA grafts. More generally, they just delay the self-aggregation process towards higher temperature or when the hydrophobic interactions become strong enough to provide persistent association under steady-shear flow. Consequently, one can try to modify the balance between hydrophobic and electrostatic interactions and then the rheological behaviour by changing the ionic strength (added salt) or the dielectric constant of the solution. Such experiments will be reported in a forthcoming paper.

### 3.6. Relation between \( T_{\text{ass}} \) and the cloud point of PNIPA

From the previous discussion, it appears that the association process, induced by heating, proceeds through a thermodynamic balance between antagonistic forces. The variation of the viscosity with temperature depicts macroscopically the modifications which take place at each equilibrium step but it remains difficult to estimate separately the respective weight of the different forces on the key parameters of the thermoassociation. Nevertheless, we can expect to obtain further information by comparing the theroassociation behaviour of the graft copolymers with the thermodynamic properties of the precursors. Of course the cloud point of PNIPA aqueous solution has been widely reported in the literature, with a LCST around 32°C [32,33], but its dependence on the polymer concentration and molecular weight has been paid surprisingly less attention.

For our two PNIPA precursors, the cloud point determination was performed optically at various concentrations and at a given heating rate of 0.5°C/min (Fig. 7). It appears clearly that below a concentration of 0.5% the precipitation temperature \( T_p \) starts to rise sharply and even becomes difficult to determine precisely. Conversely, at high concentrations the cloud point is almost constant for PNIPA10 \( T_p \approx 34°C \) whereas it still remains concentration-dependent until 2.5% \( T_p \approx 37°C \) for the shorter chains. Since the graft copolymers contain mainly ionised monomers, coming from the polyelectrolyte backbone, it is important to evaluate the influence of added poly(sodium acrylate) on the cloud point of PNIPA. The results, obtained with a 1% aqueous solution of PNIPA10 and presented in Fig. 8, show that the cloud point of the PNIPA precursor

![Fig. 7. Cloud point of PNIPA5 (○) and PNIPA10 (●) in water as a function of concentration; heating rate = 0.5°C/min.](image1)

![Fig. 8. Cloud point of a 1% aqueous solution of PNIPA10 as a function of PAA concentration; heating rate = 0.5°C/min.](image2)
4. Conclusions

The aim of the present study was to extend the concept of thermoassociative copolymers to the poly(acrylamide) derivatives. In order to reach this objective, we have settled the bases to prepare well-defined graft copolymers according to a two-steps method, which involves the synthesis of functionalised PNIPA followed by their grafting onto a poly(-acrylic acid) backbone. As expected from their primary structure, the PAA-g-PNIPA exhibit very interesting thermothickening properties in aqueous solution that we can describe using some key parameters like the association temperature, the sharpness and the magnitude of the thermothickening.

As previously reported with poly(ethylene oxide) derivatives, \( T_{\text{ass}} \) is closely related to the cloud point of the grafted chains measured in equivalent conditions (the presence of the backbone must be taken into account). In other words, the loss of entropy due to the attachment of the LCST side-chain at one end has a negligible effect on its thermodynamic properties or phase diagram behaviour. This is true for sufficiently long PNIPA chains or at least when the repulsions are partly screened by addition of a simple electrolyte as previously evidenced with poly(ethylene oxide) graft copolymers [23–25]. Nevertheless, when decreasing the size of the LCST grafts, the strong electrostatic repulsions existing in pure water between the poly-electrolyte backbones can prevail and overcome the hydrophobic associations at a given temperature. At least these electrostatic repulsions tend to delay the association phenomenon towards higher temperatures and decrease the sharpness of the thermoviscosifying process. Taking into account the close agreement between the phase diagram of the binary system ‘PNIPA/water’ and the properties of the PAA-g-PNIPA in aqueous solution, we may infer that the triggering temperature could be easily controlled by using different cosolutes which are known to modify the cloud point of PNIPA. In the same way, we can imagine that for a given copolymer and at a given concentration, the sharpness of the thermoviscosifying process could be increased to some extent either by increasing the ionic strength (adding salt) or by decreasing the degree of ionisation of the weak polyelectrolyte (adding acid). Finally, the magnitude of the thickening process, at a given shear rate, will depend basically on two parameters (1) the number of elastically active chains in the network and (2) the life time of a ‘sticky’ chain inside a hydrophobic cluster. If the first parameter can be adjusted through the copolymer concentration or the primary structure (grafting ratio), the life time of the LCST side-chain inside the micro-domain can be modified by playing with the chemical nature of the precursors, either the water-soluble backbone and/or the LCST side-chain, or by changing the equilibrium between the forces, by adding a cosolute for example.

From this short discussion simply based on two PAA-g-PNIPA studied in pure water, it appears that the promising thermothickening properties obtained with these new graft copolymers could be controlled by a wide set of

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>( C_p ) (%)</th>
<th>( T_{\text{ass}} ) (°C)</th>
<th>( \Delta T_p ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAA1/PNIPA10–29%</td>
<td>3</td>
<td>32</td>
<td>31</td>
</tr>
<tr>
<td>PAA1/PNIPA10–29%</td>
<td>6</td>
<td>30</td>
<td>29</td>
</tr>
<tr>
<td>PAA1/PNIPA10–29%</td>
<td>9</td>
<td>26</td>
<td>26</td>
</tr>
<tr>
<td>PAA1/PNIPA5–14.5%</td>
<td>3</td>
<td>≈44</td>
<td>36</td>
</tr>
<tr>
<td>PAA1/PNIPA5–14.5%</td>
<td>6</td>
<td>39</td>
<td>32</td>
</tr>
<tr>
<td>PAA1/PNIPA5–14.5%</td>
<td>9</td>
<td>34</td>
<td>28</td>
</tr>
</tbody>
</table>

Comparison between the association temperature \( T_{\text{ass}} \), obtained from rheological measurements performed on graft copolymers, and the phase separation temperature \( T_p \) determined with the PNIPA precursors in the same environmental conditions.
parameters, either relative to their primary structure or external, like salts, neutral molecules, etc. Such studies are currently being carried out and will be reported in a subsequent paper.

Acknowledgements

We wish to thank Rhodia Chimie for financial support of this work and particularly Dr D. Charmot and P. Corpart for helpful discussions.

References