

Thermoassociative graft copolymers based on poly(*N*-isopropylacrylamide): effect of added co-solutes on the rheological behaviour

A. Durand¹, D. Hourdet^{*}

Laboratoire de Physico-Chimie Macromoléculaire, UMR 7615 (UPMC-CNRS-ESPCI), 10, rue Vauquelin F-75231 Paris Cedex 05, France

Received 25 November 1998; received in revised form 1 February 1999; accepted 10 February 1999

Abstract

Thermoassociative graft copolymers, poly(sodium acrylate)-graft-poly(*N*-isopropylacrylamide), PAA-g-PNIPA, were studied in aqueous solution, with various added co-solutes such as salt, neutral species and anionic surfactant. These additives induced important modifications in the characteristics of thermothickening phenomenon, which were compared with the solubility behaviour of the PNIPA precursor under the same conditions. For all the co-solutes used, we evidenced a strong correlation between the cloud point of the PNIPA/water/co-solute ternary system and the temperature of association of the PAA-g-PNIPA solubilised in the same medium. Fluorescence experiments were used to clarify the precise mechanism of co-solute effect: “solvent perturbation” or “polymer binding”. Potassium carbonate and glucose were shown to lower the quality of solvent for the PNIPA side chains so that the thermothickening phenomenon was shifted to lower temperatures. On the contrary, sodium dodecylsulphate and hexanol interact with PNIPA grafts through the formation of hydrophobic aggregates. © 1999 Elsevier Science Ltd. All rights reserved.

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

1. Introduction

Binary systems characterised by a phase separation upon heating are considered to have a lower critical solution temperature (LCST) [1]. It is well-known that in an aqueous medium, a large number of neutral molecules or polymers exhibit this kind of thermodynamic behaviour [2–4]. Although the solution is homogeneous at low temperature, a macroscopic phase separation appears when the temperature exceeds a critical value called the cloud point (CP) of the mixture. The LCST can be considered as the lowest CP of the system as it corresponds to the minimum of the phase diagram (Fig. 1). Such systems have been studied in detail for a long time, concerning the phase diagram [4], the influence of the polymer structure on the LCST behaviour [1,5] and the influence of the added co-solutes on the CP of the mixture [6]. Considering the last point related to ternary systems, a detailed examination is required to separate the large number of available co-solutes into different groups. A first classification is to consider only the chemical structure

of the added component, and consequently to distinguish the simple electrolytes, small neutral molecules and surfactants. This distinction is obviously linked to the kind of interaction that can be established between the added component and the other two compounds in the mixture (the water and the polymer). Basically, surfactants involve hydrophobic and sometimes electrostatic effects, while salts develop dipolar interactions and neutral molecules can induce hydrogen bonding or hydrophobic effect. A second classification can be done by separating the co-solutes according to their ability to develop interactions either with the solvent (water) or directly with the polymer. In this case, two main effects can be considered: (1) the binding of the co-solute by the polymer (this is generally the case with surfactants) or (2) the solvent perturbation by the co-solute (using salts or neutral molecules) [7]. Finally, a third possibility is to consider the effect of the added molecule on the CP of the system, and to separate the co-solutes that lower the CP from those that increase it [8,9]. On this basis we can easily separate the surfactants that generally tend to raise the CP [6,10] (but not always [11]) from the salts which usually lower it (with some well-known exceptions such as thiocyanates or iodides [8]). For salts, it is widely accepted to deal with “salting-in” and “salting-out” effects which are equivalent

^{*} Corresponding author.

¹ Laboratoire de Synthèse Macromoléculaire, UPMC, UMR 7610, case 184, 4 Place Jussieu, F-75252 Paris Cedex 05, France.

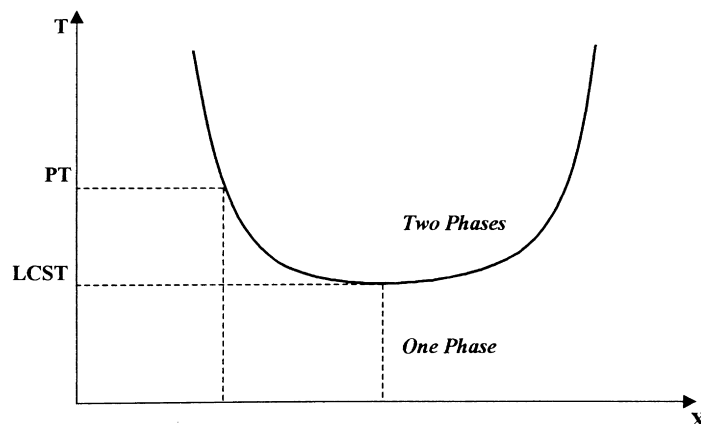


Fig. 1. Phase diagram of a binary system with a LCST.

to “raising the CP” and “lowering the CP”. In addition to these three classifications of co-solutes, many other possibilities are also possible.

Starting from these general considerations about the effect of co-solutes on the thermodynamic properties of aqueous systems having LCST, we can now focus on the “poly(*N*-isopropylacrylamide) (PNIPA)/water” binary mixture, a well known example. This system exhibits a LCST around 32°C [4]. Even if only a few salts have been examined considering their effect on the CP, the available data seem to indicate that they follow the classical Hofmeister series [12–14]. This effect is usually explained by mentioning that the presence of salt modifies the quality of the aqueous medium for PNIPA (compared with pure water). In the case of surfactants, the anionic species and particularly the sodium dodecylsulphate (SDS) are certainly the most studied. It has been shown that the SDS raises the CP very efficiently [10,15–22]. Eliassaf [14] reports that a dilute solution of PNIPA containing 1% SDS does not show any phase separation even upon boiling. The precise mechanism has been widely studied for about 15 years. It can be summarised as follows: above a critical aggregation concentration (much lower than the CMC), the SDS micelles are formed on PNIPA chains and tend to convert the neutral polymer into a polyelectrolyte. It is found that the hydrophilic/lipophilic balance (HLB) is modified considerably, and consequently the CP is shifted towards higher temperatures. As for the cationic surfactants, several studies which show that the global effect is qualitatively the same as compared with the anionic ones, but remain quantitatively less important are available [23–25]. Nevertheless, this is not a general rule for all surfactant molecules and it has been shown that some polymeric neutral surfactants tend to decrease the CP of PNIPA [11]. With these surfactants, it appears that hydrophobic interactions still exist between them and the PNIPA chains, but result in a decrease in the PNIPA hydration without any significant hydrophilicity brought about by the neutral polar head group (compared to the ionic head groups). As a result, the CP is decreased. As for the effect of small neutral

molecules on the CP of “PNIPA/water” system, it was studied in the case of molecules forming hydrogen bonds with water-like glucose [26] for instance, and also with mixtures of water and an organic solvent of PNIPA (like methanol or tetrahydrofuran) [27–30]. Although the effect can be complex (as for “water/organic solvent” mixtures), it appears that generally small neutral molecules lead to a decrease of the CP.

Recently, new thermoassociative graft copolymers were developed in our laboratory on the basis of the LCST phase diagram of the “PNIPA/water” system [31]. Their structure basically consists of a sodium polyacrylate (PAA) backbone and PNIPA side chains. In a semi-dilute solution, when the temperature increases above a critical value, the side chains self-aggregate into hydrophobic microdomains that act as reversible cross-links between macromolecules. Due to this microscopic phase separation, a large increase in viscosity can be obtained (it can gain several orders of magnitude within 10 degrees at rest). The main characteristics of the thermo-thickening behaviour were the association temperature (T_{ass}), the sharpness of the thermo-thickening process and the magnitude of the thickening (at a given shear rate). An overall description of the thickening mechanism needs to take into account the different components involved in the aggregation process, i.e. (1) the core formation (PNIPA), (2) the interfacial properties and (3) the corona building up with its bridging ability. Nevertheless, from our previous results it was clearly shown that the self-assembling properties of the graft copolymers, and especially the triggering temperature are closely related to the thermodynamic properties of the PNIPA grafts. In other words, this means that the association temperature (T_{ass}) of PAA-g-PNIPA copolymers in an aqueous solution can be accurately predicted using the CP of PNIPA precursor under the same conditions (concentration, ionic strength).

Starting from these results, it appears that the thermo-thickening behaviour, and especially the T_{ass} could be controlled by adding co-solutes to the aqueous solutions of PAA-g-PNIPA copolymers. Indeed, we can expect to observe similar effects between the microphase separation

Table 1
Structural characteristics of the graft copolymers

Copolymer	Length of side chains ^a	Copolymer composition (wt.%) ^b	Modification extent (%) ^c
PAA1/PNIPA5-14.5%	46	14.5	0.3
PAA1/PNIPA10-29%	87	29	0.4

^a Number average degree of polymerisation based on the number average molecular mass obtained by size exclusion chromatography.

^b Weight percent of PNIPA.

^c Average number of PNIPA side chains per 100 monomer units of the backbone.

in PNIPA grafted polymers in aqueous solution and macro-phase separation of the precursor binary system “PNIPA/water” [32]. In addition, co-solutes can also influence other characteristics of the phenomenon as e.g. salts can greatly modify the extent of electrostatic repulsions.

In this paper, we will investigate the role of various co-solutes on the rheological properties of PAA-g-PNIPA copolymers. The resulting properties will be compared to the thermodynamic behaviour of the “PNIPA/water” system and the fluorescence technique will be used to specify the nature of the interactions which take place between the various components of the ternary system.

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 carbonate and hexanol (from Prolabo), D+ glucose (from Sigma) and SDS (from Fluka) were all of analytical grade.

The absolute molecular weights of the poly(acrylic acid) used here, denoted as PAA1, were determined by size exclusion chromatography: $M_n = 37\ 000$ g/mol and $M_w = 136\ 000$ g/mol.

2.2. Analytical methods

¹H NMR. ¹H NMR characterisation of the graft copolymers was performed in D₂O using a BRUKER WP250 spectrometer (250 MHz)

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 provide a fast and precise control of the temperature during heating and cooling stages. The measuring unit was also equipped with a solvent trap in order to prevent water evaporation during the scanning experiments performed until rather high temperatures (up to 70°C).

Cloud point measurements. The determination of the CP of PNIPA aqueous solutions was done visually by following

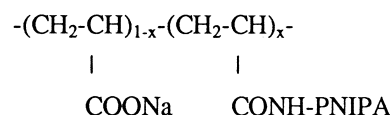
the variation of the turbidity with temperature. The aqueous solution (volume = 1 ml), initially equilibrated at room temperature in a sample tube equipped with a magnetic stirrer, was immersed in a thermostated cell with a circulating water bath. The heating rate was regulated around 0.5°C/min and the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

Fluorescence measurements. The measurements of fluorescence intensity were performed using a SPF-500C spectrofluorometer (AMINCO). The sample temperature of the cell was regulated owing to a circulating water bath. The sample cell contained a magnetic stirrer in order to improve the temperature equilibration. It was stopped during the measurements. The excitation wavelength was 334 nm. The bandpass was 5 nm for the excitation and 0.5 nm for the emission. The aqueous solutions were prepared first and then, the appropriate amount of a concentrated alcoholic pyrene solution (6×10^{-4} M) was added, using a microsyringe, so as to obtain a pyrene concentration of 6×10^{-7} M in the sample.

3. Results and discussion

3.1. Structure of the copolymers studied

The thermoassociative copolymers used in this paper are graft copolymers which combine a polyelectrolyte backbone (PAA) with the thermosensitive PNIPA side chains that are randomly distributed:



The details of the synthesis of these copolymers are given in a previous paper [31], their main characteristics are summarised in Table 1. The two copolymers have the same backbone (denoted by PAA1, as in the first article [31], Section 2) and approximately the same modification extent but differ in the length of the side chains.

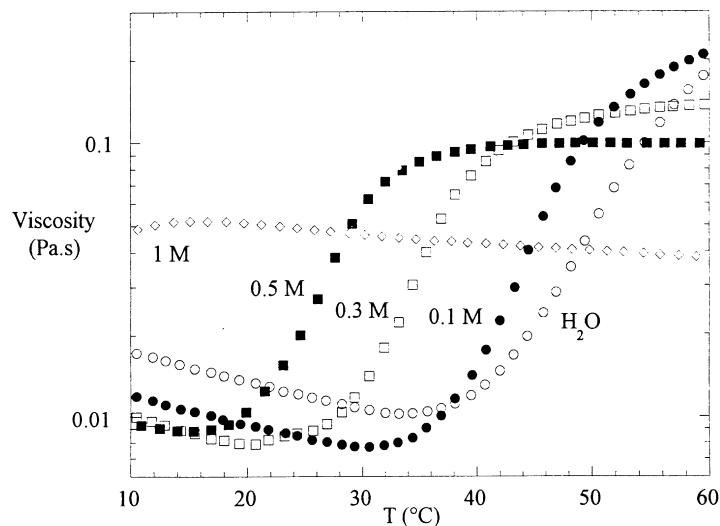


Fig. 2. Viscosity of a 3% solution of PAA1/PNIPA10-29% as a function of temperature at different concentrations of K_2CO_3 ; heating rate = $2^\circ C/min$; shear rate = $100 s^{-1}$.

3.2. Effect of additives on the rheological behaviour

In this part, all the rheological curves (viscosity versus temperature) were obtained at a fixed shear rate of $100 s^{-1}$, with a heating rate of $2^\circ C/min$. The concentrations of co-solutes are expressed in molality (mol/kg, symbol M), i.e. in mole per unit mass of solvent. As for the polymer concentrations, they are expressed in weight percent.

3.2.1. Effect of potassium carbonate, K_2CO_3

The viscosity–temperature curve for an aqueous solution of PAA1/PNIPA10-29% at 3% concentration, with different concentrations of K_2CO_3 , is given in Fig. 2. It appears that

the gradual introduction of this salt in the aqueous solution of copolymer does not change the overall behaviour for modest salt concentrations significantly. More precisely, a thermo-thickening effect is still observed up to about 0.5 M of K_2CO_3 and can be described using the same characteristics as pure water. On the contrary, for much higher concentrations (1 M for instance), a thermo-thickening behaviour is no longer obtained and replaced by a permanent associative character with a nearly constant viscosity over the whole temperature range.

If we focus on the K_2CO_3 concentrations lower than 0.5 M, we can distinguish several effects that seem to have various origins. First, for temperatures lower than T_{ass} , the viscosity decreases largely when K_2CO_3 is added,

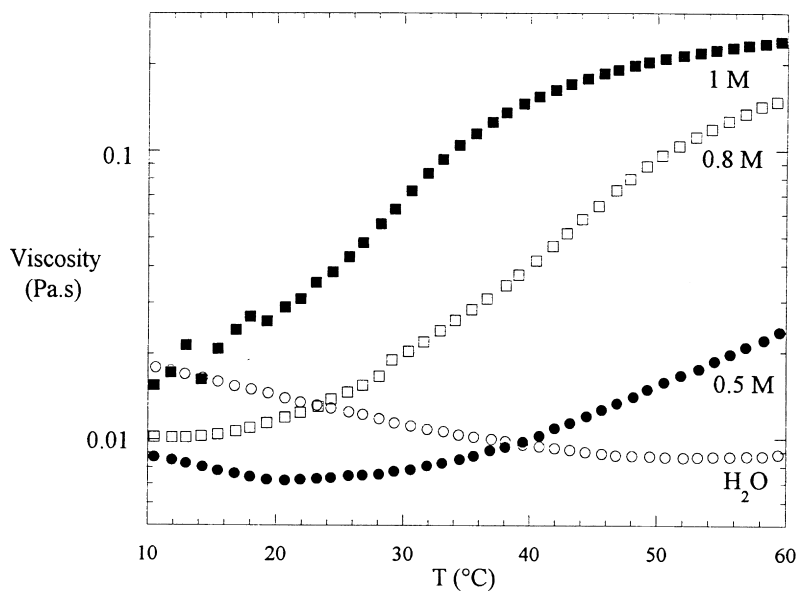


Fig. 3. Viscosity of a 3% solution of PAA1/PNIPA5-14.5% as a function of temperature at different concentrations of K_2CO_3 ; heating rate = $2^\circ C/min$; shear rate = $100 s^{-1}$.

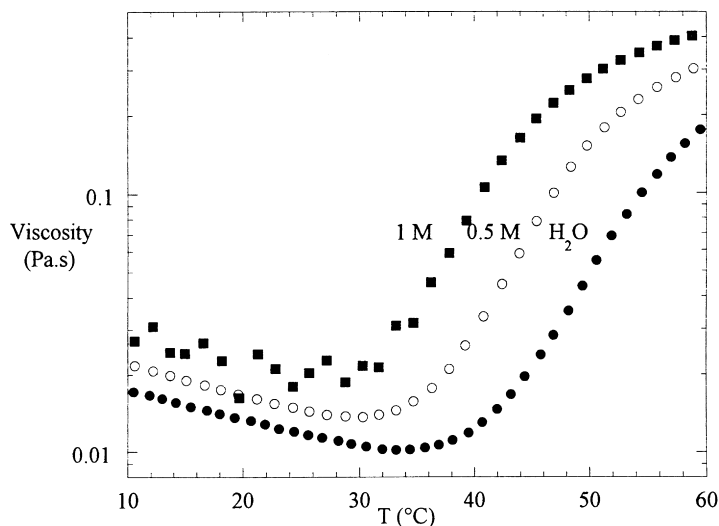


Fig. 4. Viscosity of a 3% solution of PAA1/PNIPA10-29% as a function of temperature at different concentrations of glucose; heating rate = 2°C/min; shear rate = 100 s⁻¹.

which is the classical behaviour of polyelectrolytes. It is well known that an increase in the ionic strength tends to lower the viscosity of charged polymers due to the screening of the electrostatic repulsions. Consequently, in the range $T < T_{\text{ass}}$, the copolymer behaves like a typical polyelectrolyte and the effect of K_2CO_3 is directly linked with the ionic strength. It is also evident that the association temperature tends to decrease when increasing amounts of K_2CO_3 are added. This effect is a direct consequence of the salting-out tendency of K_2CO_3 on the PNIPA side chains. This was reported for other polymers with LCST behaviour and can be quantitatively compared, in the case of PNIPA, to the salting-out effect of sodium sulphate[12]. The introduction of K_2CO_3 in the solution decreases the quality of the solvent for PNIPA side chains and favours their aggregation at a lower temperature compared to pure water. It also appears

that the sharpness of the thermo-thickening process is greater in the presence of salt than in pure water. This is again a consequence of the screening of the electrostatic repulsions by the increase of the ionic strength. Indeed, the association of the PNIPA side chains is weakened by the electrostatic repulsions between the polyelectrolyte backbones so that the thermoassociation is a rather progressive phenomenon as evidenced by the rheological measurements. When salt is added, the magnitude of the electrostatic contribution is greatly reduced and the association takes place more easily in a shorter range of temperature.

For higher concentrations of K_2CO_3 , the thermo-thickening phenomenon is no longer detected in the explored temperature range as the associations start at a temperature much lower than 10°C. It is worth mentioning that in these conditions, the viscosity of the solution has an extremely

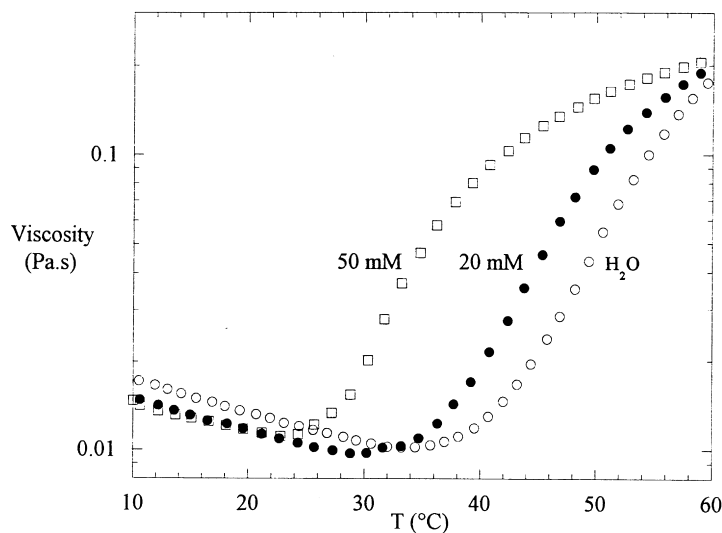


Fig. 5. Viscosity of a 3% solution of PAA1/PNIPA10-29% as a function of temperature at different concentrations of hexanol; heating rate = 2°C/min; shear rate = 100 s⁻¹.

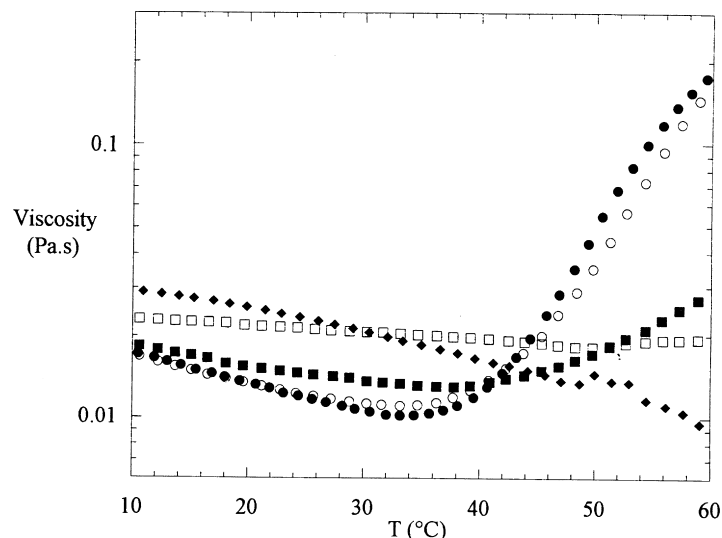


Fig. 6. Viscosity of a 3% solution of PAA1/PNIPA10-29% as a function of temperature at different concentrations of SDS (0, ●; 2 mM, ○; 5 mM, ■; 10 mM, □ 35 mM ◆); heating rate = 2°C/min; shear rate = 100 s⁻¹.

low sensitivity to the temperature, compared with the classical associative thickeners [33].

If we now consider the same experiments with the PAA1/PNIPA5-14.5% (Fig. 3), similar remarks apply. The thermo-thickening phenomenon, which is almost undetectable in pure water, is progressively shifted to lower temperatures and becomes more efficient on the whole range of salinity explored.

3.2.2. Effect of small neutral molecules: glucose and hexanol

The effects of glucose and that of a primary alcohol, hexanol, on the viscosity–temperature curve of a 3% aqueous solution of PAA1/PNIPA10-29% are shown in Figs. 4 and 5, respectively. The two neutral co-solutes have similar effects as they both lead to a lowering of T_{ass} . Within the concentration range of the experiment, it is found that the displacement of the thermoassociative phenomenon reaches around 10°C at higher concentration. For glucose, the concentrations are qualitatively compared to those of K₂CO₃ in Fig. 2, but the resulting effect is clearly less pronounced. As for hexanol, the concentrations used are approximately 20 times lower than that required with glucose to obtain the same effect on T_{ass} (50 mM against 1 M, respectively). This fact indicates that the mechanism involved is not the same. More precisely, if we refer to the criteria proposed by Molyneux [7], for glucose, where the concentrations are around 1 M, we are in the “solvent perturbation” case. Further, it was shown that the addition of saccharides into an aqueous solution of PNIPA decreased the CP.

On the contrary, in the case of hexanol, for which the concentrations are less than 100 mM, we should be in the “polymer binding” case [7], where the effect is due to specific interactions between the polymer and the co-solute. The

resulting complex is in this case less soluble than the individual partners. The effects of various primary alcohols on the CP of ethyl(hydroxyethyl) cellulose (EHEC) were shown to be largely dependent on the length of the alkyl chain, and hexanol appeared to be very efficient in the same range of concentrations. Hence, this is another indication of possible specific interactions taking place in the mixture.

The influence on the association temperature is the only aspect that we can compare between the salt and the neutral molecules. As with the neutral molecules, no other effect can be observed either on the sharpness of the thermo-thickening process or on the viscosity for $T < T_{\text{ass}}$. This is not surprising as these two effects were attributed to the variation of ionic strength triggered out by the salt.

3.2.3. Effect of an anionic surfactant (SDS)

The variation of viscosity with temperature, for an aqueous solution of PAA1/PNIPA10-29% at 3% concentration, is shown in Fig. 6 for different concentrations of SDS ranging from 0 to 35 mM. The main result is that the thermo-thickening phenomenon is greatly altered by the presence of SDS when the concentration of surfactant exceeds 3 mM and is finally completely suppressed at 35 mM. Moreover, a more accurate examination of the curves reveal that the interactions between the SDS and the PNIPA side chains give rise to opposite effects on viscosity whether the temperature is below or above the association temperature.

Firstly, if we consider the part where $T < T_{\text{ass}}$, the PNIPA grafts of the copolymer, which are under good solvent conditions, can interact with the SDS above a critical association concentration (CAC). As a result when the amount of SDS increases, more surfactant molecules bind to the PNIPA grafts and convert them into charged chains. In this way the binding of SDS at low temperature increases

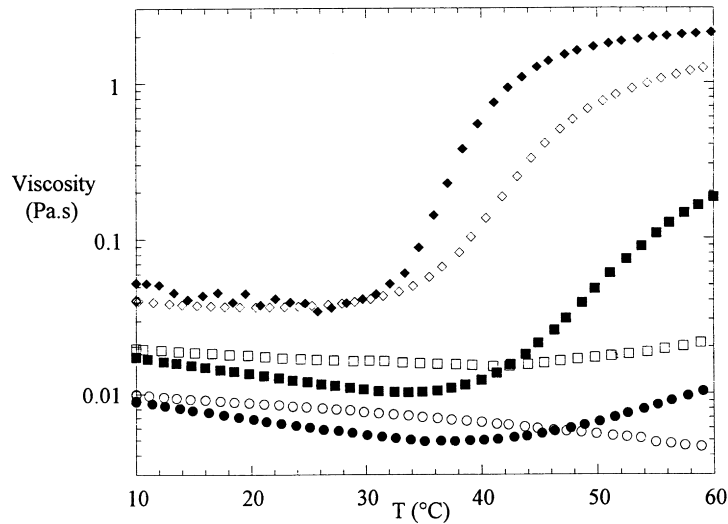


Fig. 7. Viscosity of a solution of PAA1/PNIPA10-29% as a function of temperature at various copolymer concentrations (1.5% \circ \bullet , 3% \square \blacksquare , 9% \diamond \blacklozenge), in pure water (filled symbols) and in SDS 7 mM (open symbols); heating rate = $2^\circ\text{C}/\text{min}$; shear rate = 100 s^{-1} .

the electrostatic repulsions inside and between the polymer chains. The consequence of this additional electrostatic effect is to increase the viscosity and to change its dependence on temperature. It is worth mentioning that the hydrophobicity of the PNIPA side chains is known to increase with temperature, and this favours an increase of the binding of SDS upon heating (decrease of the CAC).

In the temperature range preceding the demixing of PNIPA, the resulting increase of electrostatic repulsions upon heating tends to lower the slope of the η - T curves originally attributed to the Arrhenius-type behaviour [34] ($\eta = a e^{b/T}$). As expected, this peculiar behaviour is cancelled as soon as the PNIPA chains are fully saturated with SDS (see Fig. 6, with SDS = 35 mM). In this case, we

return to the initial slope, which is also very close to the one obtained with pure water.

In the temperature range where $T > T_{\text{ass}}$, that is to say when the copolymers tend to associate, the SDS-bound micelles on the PNIPA side chains hinder the formation of microdomains in the same way as they tend to raise the CP of PNIPA in water (in this case, bound micelles prevent the macroscopic precipitation of the polymer). If we use the results published recently by Lee et al. [35], concerning the effect of SDS on the demixing of PNIPA upon heating, we take the surfactant to polymer ratio (S/P) as a key parameter. According to the results obtained from small angle neutron scattering, two coexisting states can be defined: one is constituted by colloidal particles corresponding to the precipitated polymer stabilised by SDS molecules, and the

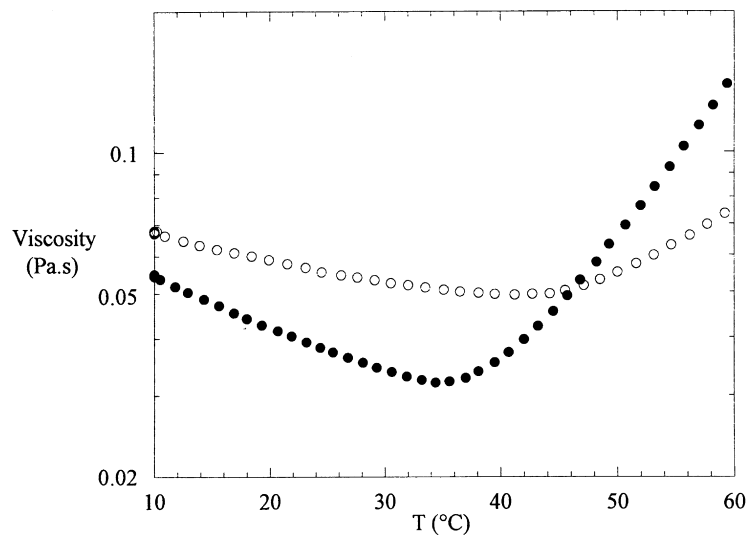


Fig. 8. Viscosity of a 9% solution of PAA1/PNIPA5-14.5% as a function of temperature in pure water (\bullet) and in SDS 7 mM (\circ); heating rate = $2^\circ\text{C}/\text{min}$; shear rate = 100 s^{-1} .

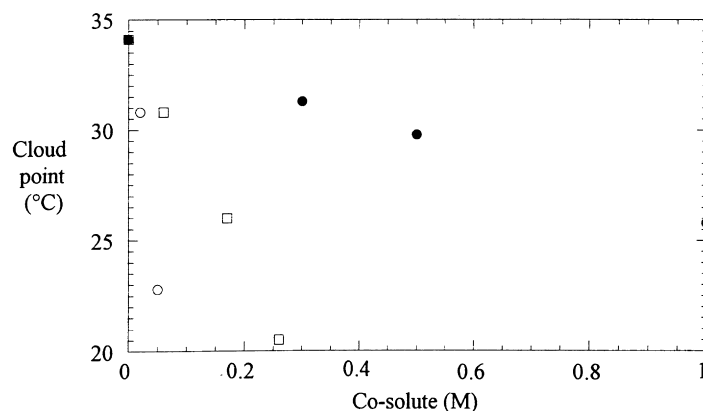


Fig. 9. Cloud point of a 1% solution of PNIPA10 as a function of the concentration of glucose (●) and hexanol (○) and K_2CO_3 (□).

other is formed by isolated PNIPA chains saturated by SDS. These two states are in equilibrium above the CP of PNIPA in water and the introduction of more surfactant tends to shift the equilibrium towards the isolated necklaces at a given temperature. They only report results at $T = 40^\circ C$, but we may infer that when the temperature is raised, the equilibrium is displaced toward the formation of colloidal particles at a given level of surfactant/polymer ratio (S/P). With our graft macromolecules, when the SDS is progressively added to the associated chains a part of PNIPA side chains start forming microdomains as described before, while an increasing part of the PNIPA side chains remain isolated with bound micelles. On heating the solution, the equilibrium is shifted towards the formation of microdomains but the process is much slower than in the case of pure water (compare the curve in pure water and that at 5 mM). Finally, for sufficiently high SDS concentrations, all the side chains are decorated by the SDS micelles and the thermoassociation is no longer possible (see the curve obtained with 35 mM of SDS).

Following this interpretation it seems that the important parameter is the S/P ratio, with P considering the PNIPA sides chains of the copolymer. The same parameter was used in a recent article about EHEC/SDS mixtures [36]. Consequently, if we keep the concentration of surfactant a constant and decrease the concentration of the copolymer in the solution, the thermo-thickening phenomenon should be progressively reduced and finally completely cancelled out for low polymer concentrations or high S/P ratios. These experiments are presented in Fig. 7 for PAA1/PNIPA10-29% and each curve is compared to that obtained for pure water. We can see that for a given SDS concentration of 7 mM and at a polymer concentration of 9%, the thermo-thickening effect is only slightly reduced compared with pure water whereas at 1.5% concentration, no effect can be observed.

Hence, when polymer conc./wt.% = 3%, more than 10 mM of SDS are required to suppress the thermoassociation whereas for polymer conc./wt.% = 1.5% only 7 mM are enough.

Finally, we can examine the influence of the length of the side chains. In Fig. 8 the viscosity–temperature curve for a 9% solution of PAA1/PNIPA5-14.5% is shown in pure water and with 7 mM of SDS. As can be seen, the effect is qualitatively the same as for the PAA1/PNIPA10-29%, which contains longer PNIPA side chains.

3.3. Comparison between T_{ass} and the cloud point of PNIPA

In a previous article [31], we have shown that the association temperature is closely related to the CP of PNIPA side chains. It appeared that, in pure water, for the longer side chains $T_{ass} = CP$, whereas for the shorter one, the association temperature could be higher than the CP by six degrees due to the hydrophilicity of the backbone (penalty of the polyelectrolyte corona formation) which delays the association.

Starting from these results we can check in the same way if the dependence of T_{ass} with added co-solutes can be related to the thermodynamic properties of the ternary system “PNIPA/water/co-solute”. In Fig. 9, we report the influence of various co-solutes on the CP of PNIPA10 at 1% concentration. The three additives tend to decrease the CP of the solution with an increasing efficiency in the order: glucose < K_2CO_3 < hexanol. In the case of glucose and K_2CO_3 the CP decreases linearly with the co-solute concentration.

More precisely, the results obtained with glucose agree with that previously reported by Kim et al. [26] who used the polymers with approximately the same molecular weights. It was found that K_2CO_3 decreased the CP of PNIPA10 solution more efficiently, and its effect can be compared to another divalent salt like sodium sulphate [12]: for K_2CO_3 the slope is around $-52^\circ C/M$ and for Na_2SO_4 it is close to $-43^\circ C/M$. The effect of hexanol is much stronger, compared to glucose and K_2CO_3 . Karlström et al. observed a similar effect of hexanol on the CP of EHEC aqueous solutions [37]. Quantitatively the decrease was more important but it is difficult to make such comparison as the two copolymers have very different structures.

Table 2

Comparison between T_{ass} and the CP of PNIPA precursor as a function of the concentration of added K_2CO_3

K_2CO_3 added (M)	T_{ass} of a 3% solution of PAA1/PNIPA10-29% ($^{\circ}\text{C}$)	CP of PNIPA10 ($^{\circ}\text{C}$)	T_{ass} of a 3% solution of PAA1/PNIPA5-14.5% ($^{\circ}\text{C}$)	CP of PNIPA5 ($^{\circ}\text{C}$)
0	32	31	≈ 44	36
0.1	29	27	40	31
0.2	≈ 25	21.5		
0.3	20	16	30	20
0.5	≤ 10	6	19	10
0.8			≤ 10	-5
1.0	$\ll 10$	-20	$\ll 10$	-15

Using these results we can calculate the CP of PNIPA10 and PNIPA5, as previously described, taking into account the presence of the polyelectrolyte backbone and the concentration of PNIPA. The values obtained are compared to the association temperature determined from the rheological measurements in Tables 2 and 3. It can be deduced that for the longer side chains the association temperature is always very close to the CP of the PNIPA precursor under the same conditions (concentration, ionic strength, etc.). However, for the shorter side chains, the CP is significantly lower than the association temperature as it was already observed for the experiments carried out in pure water. The same explanation holds as in pure water: the hydrophilicity of the PAA backbone is particularly important for short side chains and tends to delay the association to higher temperatures.

The CP of PNIPA10 was also measured as a function of the concentration of SDS added at a constant concentration of PNIPA10 of 0.9% (Fig. 10). It should be noted that in a solution of PAA1/PNIPA10-29% at 3% concentration, the effective concentration of PNIPA10 side chains is approximately 0.9%. We can see that the CP is practically constant up to 5 mM (the variation does not exceed 2°C in magnitude), where it starts to increase faster and finally becomes higher than 100°C when the concentration is around 20 mM. In a second set of experiments, we determined the CP of PNIPA10 solutions at various polymer concentrations with a constant SDS concentration of 7 mM (Fig. 11). In the same figure, we have also reported the values of the CP in pure water. It appears that the increase of the CP due to the presence of SDS becomes higher when the concentration of

PNIPA10 is decreased. Above 2% there is no noticeable increase of the CP due to the addition of SDS, while below 0.1% no CP can be detected up to 100°C . All these results can be explained on the basis of the S/P ratio which can be tuned, playing either with the concentration of SDS or the PNIPA, keeping the other a constant.

As a matter of fact, we noted that, at a constant copolymer concentration of 3% (Fig. 6), the thermothickening effect is greatly reduced when the SDS concentration reaches 5 mM. In the same concentration range, the CP of PNIPA10 precursors start to increase rapidly with the SDS concentration. In the same way, at a constant SDS concentration of 7 mM, we observed that the thermothickening effect of a 9% PAA1/PNIPA10-29% solution was only slower than in pure water. In this case, the corresponding concentration of PNIPA10 precursor is around 2.5% which is too high for the 7 mM of SDS added to have any noticeable influence (Fig. 11). From these experiments, it is clear that the same interactions take place between PNIPA10 and SDS, either the PNIPA chains are alone in solution or grafted onto the polyacrylic backbone. An important increase of the CP corresponds to a lowering of the thermothickening effect.

Considering the association temperature, we suggest that the effect of co-solutes can be readily predicted, at least qualitatively, by the thermodynamic data related to the PNIPA precursor. Quantitative predictions are possible, especially when modifying the quality of the solvent for the PNIPA chains, playing with “salting-out” phenomenon for instance.

3.4. Study of microscopic interactions by fluorescence

During the preceding experiments we tried to correlate the association behaviour to the thermodynamic properties of the LCST grafts from a macroscopic point of view using rheological and phase separation analyses. Nevertheless, two co-solutes can produce similar macroscopic effects involving different molecular mechanisms. In our case, we would like to distinguish the effects of the two kinds of co-solutes: solvent perturbation and specific binding to macromolecules.

As far as hydrophobic interactions are concerned, a good way to do this is to use a fluorescent probe like pyrene. If the

Table 3

Comparison between T_{ass} and the CP of PNIPA10 as a function of the concentration of various co-solutes

Added co-solute	T_{ass} of a 3% solution of PAA1/PNIPA10-29% ($^{\circ}\text{C}$)	CP of PNIPA10 ($^{\circ}\text{C}$)
Glucose 0.5 M	28	28
Glucose 1.0 M	≈ 25	24
Hexanol 0.02 M	28	29
Hexanol 0.05 M	22	21

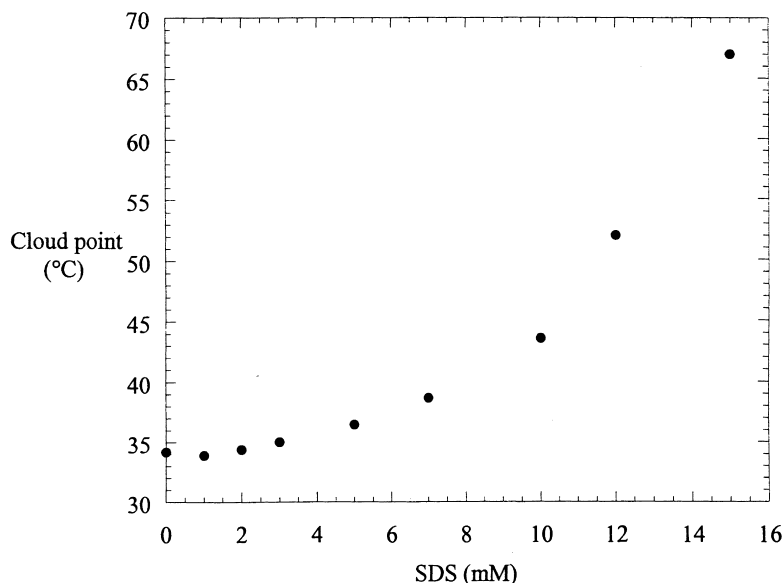


Fig. 10. Cloud point of a 0.9% solution of PNIPA10 as a function of SDS concentration.

co-solute introduced into the polymer solution binds specifically to the polymer by a hydrophobic effect, the well-known intensity ratio I_{11}/I_{13} of the two vibronic bands of the emission spectrum of pyrene located at 372.5 and 383 nm, respectively, which is near 2 in pure water, would drop to values well below 1.8 (e.g. 1.2 for SDS micelles). As the thermoassociative behaviour is based on the thermal enhancement of a hydrophobic effect, pyrene fluorescence seems to be a good way of studying the phenomenon.

We start with fluorescence experiments concerning the copolymer alone with only limited amounts of added sodium chloride in order to check how the thermoassociative phenomenon is sensed by the pyrene probe. The sodium chloride was added so as to screen the electrostatic

repulsions that are important at the low concentration used (0.1%).

We first consider the variation of I_{11}/I_{13} with temperature for a 0.1% solution of PAA1/PNIPA10-29% with NaCl 0.1 M as the solvent (Fig. 12). For comparison, we plot the same experiments for PAA1 at 0.07% concentration and PNIPA10 at 0.03% concentration. As can be seen, for the copolymer solution, a clear transition is observed from ca 1.85–1.60 when the temperature increases from 20 to 50°C. The transition temperature is approximately 34°C. We must emphasise that the copolymer solution remains clear over the entire temperature range. It is interesting to note that nearly the same transition is observed with the solution of PNIPA10 and at the same temperature. Obviously, the latter is due to the phase separation which

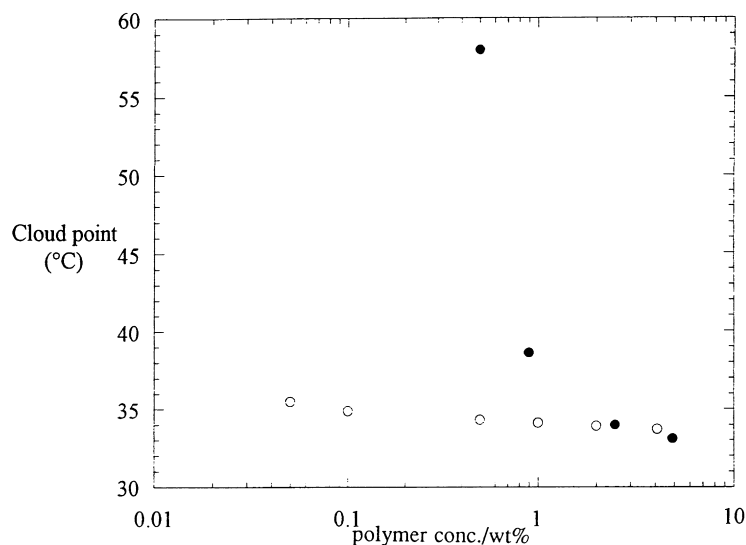


Fig. 11. Cloud point of a solution of PNIPA10 in SDS 7 mM (filled symbols) and pure water (open symbols) as a function of polymer concentration.

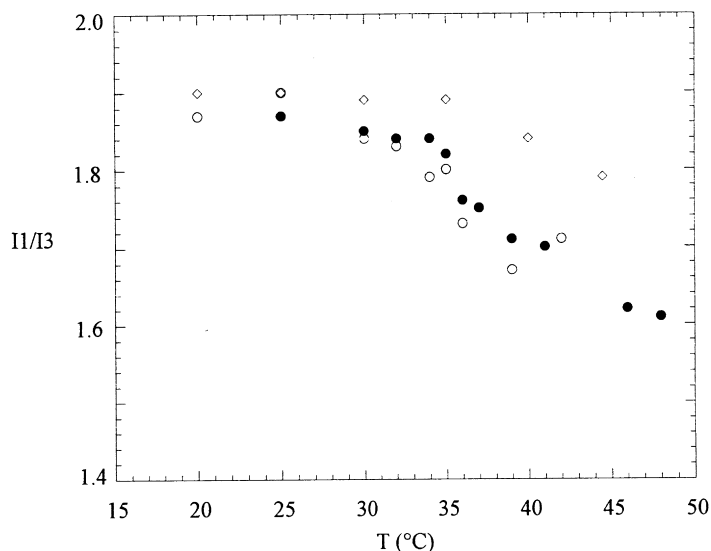


Fig. 12. Fluorescence intensity ratio $I1/I3$ as a function of temperature for various solutions in NaCl 0.1 M: 0.1% PAA1/PNIPA10-29% (●), 0.07% PAA1 (◇) and 0.03% PNIPA10 (○); [Pyrene] = 6×10^{-7} M.

takes place upon heating as has been shown already by Schild [38]. For the solution of PAA1, no transition is observed and $I1/I3$ is always above 1.8.

These results show clearly that the graft copolymer undergoes a transition, which implies the formation of hydrophobic microdomains in the solution. Moreover, this transition is entirely due to the PNIPA side chains and is absolutely similar to the CP phenomenon from the fluorescent viewpoint. Obviously, at a macroscopic scale, the two phenomena are clearly distinct. On the one hand the polymer phase separates and the solution becomes turbid. While on the other hand the segregation is limited to a microscopic scale and the solution remains clear.

It is clear that the thermoassociation can be readily detected by a fluorescent probe. We used this technique to

examine the effects of added co-solutes on the thermoassociative behaviour.

We now consider the variation of $I1/I3$ for a 0.1% solution of PAA1/PNIPA10 29% with K_2CO_3 0.1 M as the solvent (Fig. 13). The same transition, as with NaCl, is observed but the transition temperature is clearly lower. Hence, K_2CO_3 induces the formation of hydrophobic microdomains in the solution at lower temperature compared to NaCl solution at the same concentration.

The same experiments were carried-out with hexanol (Fig. 14). In this case, we note that no transition is detected. The intensity ratio is close to 1.20 over the whole temperature range (from 20 to 45°C). If this experiment is reproduced under the same conditions but without introducing the copolymer (Fig. 14, open circles), the intensity ratio is much

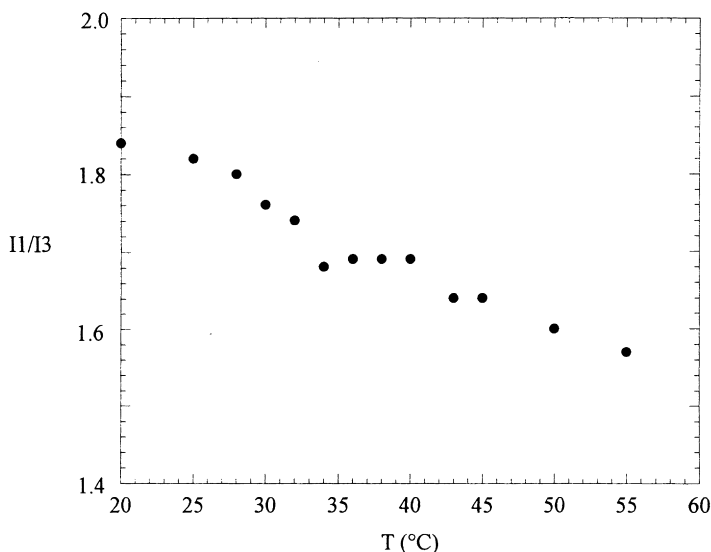


Fig. 13. Fluorescence intensity ratio $I1/I3$ as a function of temperature for a 0.1% solution of PAA1/PNIPA10-29% in K_2CO_3 0.1 M; [Pyrene] = 6×10^{-7} M.

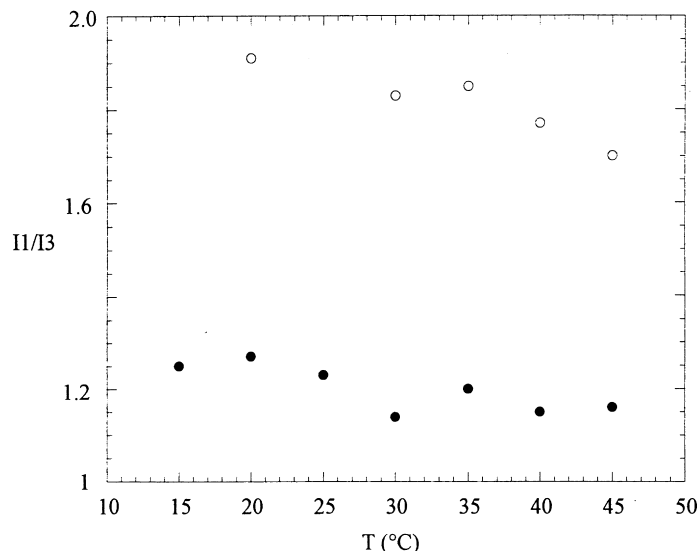


Fig. 14. Fluorescence intensity ratio I1/I3 as a function of temperature for hexanol 50 mM (○) and for a 0.1% solution of PAA1/PNIPA10-29% in hexanol 50 mM (●); [Pyrene] = 6×10^{-7} M.

higher and close to 1.80. These results demonstrate that hexanol forms hydrophobic aggregates in the presence of PNIPA side chains. If the hexanol is alone in water, at concentrations ≤ 0.05 M no hydrophobic aggregates can be detected. When the PNIPA side chains are covered by hexanol aggregates, they become more hydrophobic and the association temperature is lowered. The same phenomenon is likely to be responsible for the lowering of the CP of PNIPA10 precursor. We can conclude that although hexanol and glucose have qualitatively the same effect on the association temperature, the mechanism involved is very different. For glucose we can say that it is mainly the quality of the aqueous solvent which is depressed, while with hexanol the hydrophobic interactions take place with the PNIPA

chains. This is also coherent with the lower concentrations used with hexanol compared to those required with glucose to observe a significant shift of the association temperature.

Finally, we can also use fluorescence to study the interactions between the graft copolymers and SDS. In the case of this surfactant, the rheological results indicate that direct interactions take place between SDS molecules and the PNIPA side chains as the thickening properties are dramatically altered upon adding SDS. We also mention that the important parameter was the stoichiometric ratio of surfactant to NIPA units. It was shown by fluorescence experiments [10] that the SDS forms hydrophobic aggregates with PNIPA at concentrations much lower than its CMC and we have reproduced the same experiments with our graft

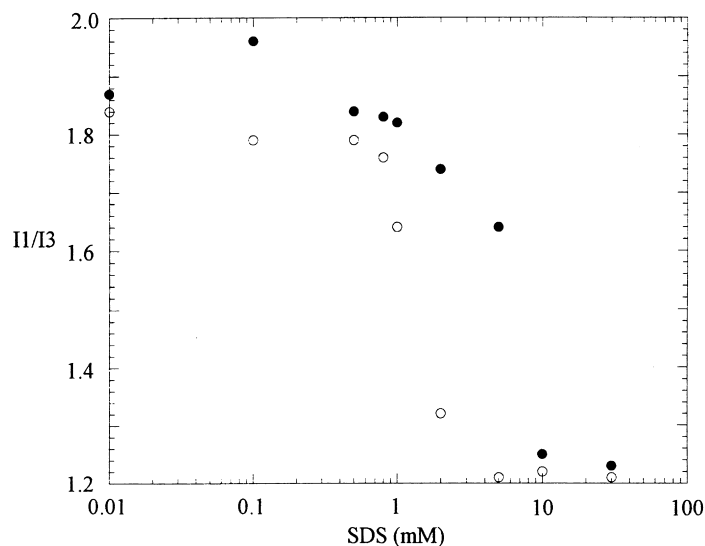


Fig. 15. Fluorescence intensity ratio I1/I3 as a function of SDS concentration for a 0.1% solution of PAA1/PNIPA10-29% (●) and in pure water (○); [Pyrene] = 6×10^{-7} M.

copolymer at a constant temperature. This was done with a PAA1/PNIPA10-29% solution at 0.1% concentration at 25°C (Fig. 15). In this case, the I1/I3 ratio drops from approximately 1.80–1.20 at a critical SDS concentration close to 0.001 M. By comparison, the same drop occurs in pure water at a higher concentration, close to 0.008 M, which is the CMC of SDS. These results clearly demonstrate that the SDS molecules form micelles with the PNIPA side chains of the graft copolymers despite the electrostatic repulsions due to the polyelectrolyte backbone. The organisation of the adsorbed micelles is probably greatly affected when the temperature is increased above the association temperature. But the main effect is the ionic perturbation of the phase separation process, which weakens and finally cancels out the thermo-thickening behaviour. Finally, we conclude that although hexanol also forms hydrophobic aggregates on the PNIPA chains, like SDS, the resulting effect is opposite and without strong modification of the magnitude of the thermo-thickening effect due to the absence of an ionic character.

4. Conclusions

The aim of this study was to check how the thermo-thickening behaviour of PAA-g-PNIPA was influenced by the addition of various co-solutes. As a previous paper [31] clearly showed that the thermoassociative phenomenon is closely related to the phase separation behaviour of PNIPA precursors, we studied specific additives selected for their known effect on the CP of PNIPA. As expected we demonstrated that the thermo-thickening characteristics could be predicted, at least qualitatively, by the thermodynamic data obtained with PNIPA. Quantitative predictions are also possible for the variation of T_{ass} in the presence of salt, glucose and hexanol. The magnitude of the perturbation induced by SDS on the rheological behaviour can be estimated by measuring the influence of the same amount of surfactant on the CP of PNIPA precursor. Fluorescence was applied successfully to identify the phenomenon at the origin of the variation of the association behaviour (solvent quality alteration or specific binding of co-solutes).

The results reported here emphasise the possible control of the thermo-thickening characteristics owing to some external parameters (presence of co-solutes). Another way to achieve such control would be to change the primary structure of the graft copolymers. In this case we could study the internal parameters. Several characteristics of the thermoassociative phenomenon could be modulated in this way as it has been already shown for associative polymers. Such studies are currently carried out in our laboratory and will be reported in a subsequent paper.

Acknowledgements

We want to thank RHODIA CHIMIE for the financial support of this work and particularly Dr D. Charmot and P. Corpart for helpful discussions.

References

- [1] Taylor LD, Cerankowski LD. *J Polym Sci: Polym Chem Ed* 1975;13:2551.
- [2] Klug ED. *Food Technol* 1970;24:51.
- [3] Bailey FE, Callard RW. *J Appl Polym Sci* 1959;1:56.
- [4] Heskins M, Guillet JE. *J Macromol Sci: Chem* 1968;A2(8):1441.
- [5] Ito S. *Kobunshi Ronbunshu* 1989;46:437.
- [6] Pandya K, Lad K, Bahadur P. *J Macromol Sci: Pure Appl Chem* 1993;A30:1.
- [7] Molyneux P. *Water: a comprehensive treatise*. In: Franks F, editor. Chapt. 7, vol. 4, 1975.
- [8] Saito S. *J Polym Sci: Part A-1* 1969;7:1789.
- [9] Nwankwo I, Xia DW, Smid J. *J Polym Sci* 1988;26:581.
- [10] Schild HG, Tirrell DA. *Langmuir* 1991;7:665.
- [11] Cho CS. *Macromol Rapid Commun* 1994;15:727.
- [12] Schild HG, Tirrell DA. *J Phys Chem* 1990;94:5154.
- [13] Park TG, Hoffman AS. *Macromolecules* 1993;26:5045.
- [14] Eliassaf J. *J Appl Polym Sci* 1978;22:873.
- [15] Wu C, Zhou S. *J Polym Sci, Part B: Polym Phys* 1996;34:1597.
- [16] Schild HG, Tirrell DA. *Macromolecules* 1992;25:4553.
- [17] Wu XY, Pelton RH, Tam KC, Woods DR, Hamielec AE. *J Polym Sci, Part A: Polym Chem* 1993;31:957.
- [18] Tam KC, Wu XY, Pelton RH. *J Polym Sci, Part A: Polym Chem* 1993;31:963.
- [19] Kokufuta E, Suzuki H, Sakamoto D. *Langmuir* 1997;13:2627.
- [20] Mears SJ, Deng Y, Cosgrove T, Pelton R. *Langmuir* 1997;13:1901.
- [21] Meewes M, Ricka J, De Silva M, Nyffenegger R, Binkert T. *Macromolecules* 1991;24:5811.
- [22] Ricka J, Meewes R, Nyffenegger R, Binkert T. *Phys Rev Lett* 1990;65:657.
- [23] Wada N, Kajima Y, Yagi Y, Inomata H, Saito S. *Langmuir* 1993;9:46.
- [24] Inomata H, Goto S, Otake K, Saito S. *Langmuir* 1992;8:687.
- [25] Tam K, Ragaram S, Pelton RH. *Langmuir* 1994;10:418.
- [26] Kim YH, Kwon IC, Bae YH, Kim SW. *Macromolecules* 1995;28:939.
- [27] Asano M, Winnik FM, Yamashita T, Horie K. *Macromolecules* 1995;28:5861.
- [28] Winnik FM, Ottaviani MF, Bobmann SH, Pan W, Garcia-Garibay M, Turro NJ. *Macromolecules* 1993;26:4577.
- [29] Winnik FM, Ottaviani MF, Bobmann SH, Pan W, Garcia-Garibay M, Turro NJ. *Macromolecules* 1992;25:6017.
- [30] Winnik FM, Ringsdorf H, Venzmer J. *Macromolecules* 1990;23:2415.
- [31] Durand A, Hourdet D. *Polymer* 1999;40:4941.
- [32] Yoshioka H, Mikami M, Mori Y. *J Macromol Sci: Pure Appl Chem* 1994;A31:121.
- [33] Bokias G, Hourdet D, Iliopoulos I, Staikos G, Audebert R. *Macromolecules* 1997;30:8293.
- [34] Anderade EN, Da C. *Nature* 1930;125:12.
- [35] Lee LT, Cabane B. *Macromolecules* 1997;30:6559.
- [36] Kjøniksen AL, Nystrom B, Lindman B. *Macromolecules* 1998;31:1852.
- [37] Karlstrom G, Carlsson A, Lindman B. *J Phys Chem* 1990;94:5005.
- [38] Schild HG. In: Shalaby SW, McCormick CL, Butler GB, editors. *Water soluble polymers, synthesis, solution properties and applications*, ACS Symposium Series 467, Chap. 16, 1990.