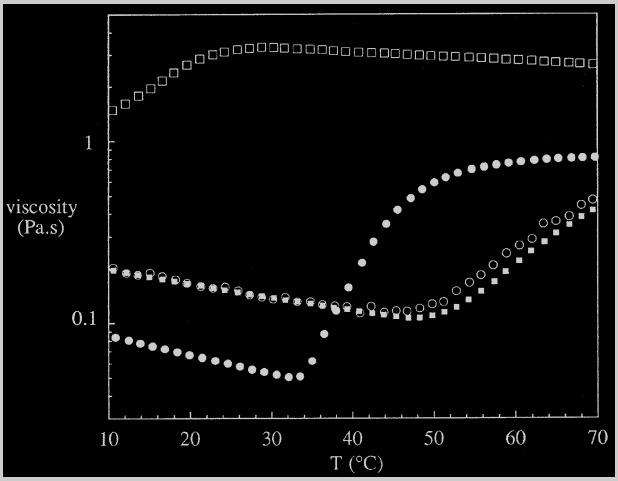
Full Paper: new family of thermoassociative graft copolymers has been recently synthesised using a two-step procedure. Schematically, their structure combines a weak polyelectrolyte backbone (poly(sodium acrylate), PAA) and thermosensitive side chains containing mainly N-isopropylacrylamide (NIPA). Taking advantage of this well controlled synthesis we have selectively varied the primary structure of the copolymers concerning the grafting extent, the length of the backbone, and the hydrophilic-lipophilic balance of the side chains by incorporating either hydrophilic or hydrophobic comonomers. The thermoassociative properties of the resulting copolymers were studied in semi-dilute solutions by rheology. It was clearly evidenced that the association temperature of the copolymers is selectively controlled in pure water (in the 0–100 °C range) by the chemical composition of the side chains. Moreover, the magnitude of the thermothickening effect is directly related to the modification extent while the absolute value of the viscosity is modulated by the length of the PAA backbone. Very sharp transitions were also evidenced by developing specific attractive interactions between the PNIPA grafts and the PAA backbone dependent on the pH of the solutions. In all the cases we demonstrate that the associative behaviour is well correlated to the thermodynamic properties of the precursors. A good knowledge of their phase diagrams in aqueous solution is therefore a very strong guideline for designing copolymers with responsive properties.



Variation of the viscosity with temperature for 3% solutions of PAA7/PNIPA10–31% (●), PAA7/PNIPA-AMPS-16% (o), PAA7/PNIPA-AAm-17% (■) and PAA7/PNIPA-BMA (□); shear rate = 100 s^{-1}

Thermoassociative graft copolymers based on poly(*N*-isopropylacrylamide): Relation between the chemical structure and the rheological properties

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(Received: May 7, 1999; revised: July 5, 1999)

Introduction

When dealing with thermothickening systems, we consider aqueous formulations whose viscosity increases reversibly upon heating. Basically there is no limitation at all for the temperature range as the requirements could be very different from one application to another, starting softly around the body temperature for biological purposes[1)] and going as high as 200 °C (or more) in the case of drilling fluids[2)] or well cementing processes. These unusual properties, triggered by the temperature were initially observed with semi-dilute solutions of cellulose derivatives[3–5)]. In that case, the associations are induced by a lower critical solution temperature (LCST) type phase separation. This demixing process remains confined at a local scale due to either the heterogeneous structure of the material combining hydrophilic and thermosensitive units (e.g. methyl cellulose) or to the stabilisation provided by added ionic surfactants in the case of more hydrophobic derivatives (e.g. ethyl hydroxyethyl cellulose). Starting from this idealised picture of reversible hydrophobic microdomains embedded into a hydrophilic matrix we developed a concept of thermoassociation with synthetic macromolecular systems in the recent years. The primary structure of our copolymers combines

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  1022-1352/2000/0805–0858$17.50+.50/0

a water-soluble backbone (poly(sodium acrylate), PAA) and LCST side-chains which were initially poly(ethylene oxide), PEO[2, 6–9]. These copolymers exemplify very nicely the initial concept of thermoassociation and allow to clarify the general mechanism.

The most important points are the following:

1) The LCST grafts thermodynamically control the association process. When using long side chains their segregation in aqueous solution proceeds similarly (temperature of phase separation, concentration of the phases) whether they are grafted or not. This can be used to predict the association temperature on the basis of the LCST phase diagram.

2) The primary structure of the copolymers has nevertheless an important weight upon the characteristics of the association clusters (size and aggregation number) and consequently on the functionality of the physical network.

More recently we moved to other thermosensitive side chains based on poly(*N*-isopropylacrylamide), PNIPA, derivatives[10]. When replacing PEO by PNIPA, the main idea was to use the wide chemistry of poly(N-substituted acrylamide) derivatives as well as their peculiar thermodynamic properties in water. In recent papers[10, 11] we confirmed the basic principles established with PAA-g-PEO copolymers with PNIPA grafts and extended the rheological studies to a wide range of added co-solutes like salts, neutral molecules and surfactants. When we started the present work the original idea was to correlate the macroscopic properties with the primary structure of the copolymers. One way is to consider the association through the thermodynamic properties of the grafts. It is well known for instance that the cloud point of aqueous solutions of PNIPA can be largely modified by introducing a few percent of comonomers (hydrophilic or hydrophobic) into the chains[12]. It is also possible to change other structural parameters related to the water-soluble backbone since, like for block copolymers, the hydrophilic chain itself contributes to the formation of the aggregates[13, 14]. The molecular weight of the backbone is one parameter, but the charge density of the main chain has also to be considered as it controls the magnitude of electrostatic repulsions. Moreover, varying the pH, one can tune the interactions between PAA and PNIPA from repulsive at intermediate or high pH to attractive at low pH.

In the first part of this paper we will describe the synthesis of thermoassociative graft copolymers by varying some structural characteristics, like length of the backbone, chemical nature of the side chains, grafting extent, and others. Then we will show how the thermothickening properties of the semi-dilute solutions could be influenced by changing this primary structure. The observed effects will be related to the precursor properties by means of phase diagrams, rheological behaviour and others.

Experimental part

Materials

N-Isopropylacrylamide (NIPA), acrylic acid (AA) and butyl methacrylate (BMA) were purchased from ALDRICH, acrylamide (AAm) and acrylamido-2-methylpropanesulfonic acid (AMPS) from FLUKA. All monomers were used as received. Potassium persulfate and dimethyl sulfoxide (KPS and DMSO respectively, from PROLABO), 2-aminoethanethiol hydrochloride (AET, HCl, from FLUKA), disulfine blue (from PANREAC), dicyclohexylcarbodiimide (DCCI, from ACROS) 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).

Polymer synthesis

The polymerization of thermosensitive oligomers was carried out in a three necked flask equipped with a reflux condenser, a magnetic stirrer and a nitrogen feed. The monomers were dissolved in water and the resulting solution was deaerated during 1 h with nitrogen bubbling. The temperature was adjusted to 29 ($\pm 1\,^{\circ}$C) using a water bath. The initiators (KPS and AET, HCl) were dissolved separately in water and added rapidly to the preceding medium. 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. When BMA was used as comonomer the reaction was carried out in DMSO and the oligomer was recovered by precipitation in hot water ($40-50\,^{\circ}$C).

The poly(acrylic acid) precursor referred as PAA1, was synthesised by radical polymerization as reported previously[15]. Its weight average molecular weight, determined by size exclusion chromatography (SEC) is: $\overline{M}_w$ = 136000 g/mol. Another poly(acrylic acid) precursor, denoted PAA7, was purchased from SCIENTIFIC POLYMER PRODUCTS. Its weight average molecular weight was determined to be: $\overline{M}_w$ = 690000 g/mol.

Grafting reaction

The experimental procedure has already been described elsewhere[10, 11]. Briefly, the grafting reaction was carried out in NMP at $60\,^{\circ}$C where the required amounts of PAA, PNIPA and DCCI (coupling agent) were introduced successively. The reaction was allowed to proceed during 20 h. Afterwards the flask was immersed in a cold water bath and the dicyclohexylurea (by-product) 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 against pure water and recovered by freeze drying.

Analytical methods

^{1}*H NMR*: The characterization of precursors and graft copolymers was performed in D_2O using a BRUKER WP250 spectrometer (250 MHz).

Tab. 1. Synthesis conditions of functional oligomers and co-oligomers

Telomer	$[M]_0$[a)]	$[AET, HCl]_0$	$[KPS]_0$	$\overline{M}_n$[b)]	NIPA/X[c)]	NIPA/X[d)]
	mol/L	mol/L	mol/L		mol-%	mol-%
PNIPA5	0.85	0.042	0.017	5200	100/0	100/0
PNIPA10	1.28	0.026	0.013	9800	100/0	100/0
PNIPA-AAm	1.28	0.026	0.013	≈10000	85/15	85/15
PNIPA-AMPS	1.28	0.026	0.013	≈10000	95/5	96/4
PNIPA-BMA[e)]	1.28	0.026	0.013		90/10	93/7

a) Total monomer concentration.
b) Determined by SEC for PNIPA telomers and estimated for the cotelomers.
c) Initial feed composition.
d) Molar composition calculated using the ^{1}H NMR spectrum.
e) DMSO was used as solvent.

Potentiometric titration: The potentiometric titration of amino-terminated oligomers 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 oligomer solution to ensure that all the amine functions were under basic form.

Size exclusion chromatography (SEC): SEC was used to follow the conversion of the reactions and to characterise the polymers. The analyses were carried out using a Waters 6000 A chromatographic system equipped with four OH-pack columns, equilibrated at 20 °C in aqueous medium ($LiNO_3$ 0.5 mol/L). To follow the extent of grafting reactions, 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 a concentrated solution of NaOH were then added to the mixture in order to ionise the poly(acrylic) backbone and to enhance the solubility of the copolymer in the aqueous medium.

Rheological measurements: Viscosity measurements of semi-dilute copolymer solutions were performed on a CARRI-MED controlled stress rheometer (CSRH 100) 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). In the view of previous studies the heating rate chosen was always 2 °C/min.

Cloud point experiments: The cloud point of oligomer aqueous solutions was determined visually by following 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 ±0.1 °C.

Results and discussion

Synthesis and characterization

Functional oligomers and co-oligomers

In a previous paper we have reported the synthesis of graft copolymers combining a poly(sodium acrylate) (PAA) backbone and PNIPA side chains[10]. They were prepared according to a two-step procedure with 1) the synthesis of amino-terminated oligomers by telomerisation and 2) the grafting of the functional oligomers onto a poly(acrylic acid) precursor. We will now focus on the telomerisation and the grafting reaction of new PNIPA derivatives that mainly contain NIPA units (at least 85 mol-%) and another monomer, either hydrophilic (acrylamide, AAm or sodium acrylamido-2-methyl propane sulfonate, AMPS) or hydrophobic (butyl methacrylate, BMA). As long as hydrophilic comonomers are concerned, the same conditions as for NIPA alone hold for the telomerisation (Tab. 1). In each case the polymerization was followed by SEC and it could be checked if both monomers were incorporated into the chains. With BMA we took dimethylsulfoxide (DMSO) instead of water as a solvent since it could dissolve both monomers (NIPA, BMA) and initiators (potassium persulfate, KPS and aminoethanethiol hydrochloride, AET, HCl). The polymers were recovered by dialysing the reaction medium against pure water except for the PNIPA-BMA which was precipitated in hot water (40–50 °C) and for the PNIPA5 (low molecular weight) which was finally precipitated in diethyl oxide. We qualitatively checked if the cotelomer PNIPA-BMA had amino-end groups using the dye-partition test with disulfine blue as reported by Palit and coworkers[16]. This test was not applicable to the other two cotelomers since they were insoluble in chloroform. The

amino-end groups were then quantitatively determined by a potentiometric titration while the composition was estimated by ^{1}H NMR. It is rather difficult to give absolute molecular weights for the cotelomers as the SEC calibration was specific to PNIPA. Nevertheless the SEC traces of PNIPA10, PNIPA-AAm and PNIPA-AMPS were similar. As a result, we will assume that the three oligomers have the same average molecular weight: $\overline{M}_n \approx 10000$ g/mol (with a polydispersity index around 2). This was expected since the relative amounts of thiol were identical for the three syntheses. The average number of amino end group per oligomeric chain (f) was calculated by the following formula: $f = A \cdot \overline{M}_n$, where A is the total amine content per g of oligomer determined by potentiometric titration. For our oligomers f was always close to 1. The slight excess of amine functions can be attributed to traces of AET, HCl in the final product (not completely purified). The PNIPA-BMA was not characterized by SEC, because of its low solubility in water at 20 °C. The results of the different characterizations are summarised in Tab. 1. The composition of the copolymer is always close to that of the initial medium which is quite normal as the monomer conversion is quantitative in the time of the reaction (≈100%). As for the distribution of the different units inside the copolymer chains, we can only find information for the NIPA-AAm copolymerization. In that case, Chiklis and co-workers[17] have reported the following reactivity ratios: $r_{NIPA} = 0.5$ and $r_{AAm} = 1.0$. These values indicate that the heterogenity of the cotelomers, due to the composition drift with conversion, is rather low.

Phase diagrams in aqueous solutions

In the following the polymer concentration will be denoted Cp and will be expressed in weight percent. The cloud point (Tp) of aqueous solutions of functional (co)oligomers with their concentration is given in Fig. 1. The introduction of a very low content of hydrophilic units in the chains gives rise to an important increase of Tp, especially when these units are ionic[18, 19] (see for example the curve of PNIPA-AMPS). We try to make a quantitative comparison for our NIPA-AMPS telomers using the results of Wang and co-workers[20] who synthesised NIPA-AMPS hydrogels. For 5 mol-% of AMPS units they report a collapse temperature of 43 °C which is close to our Tp value found when Cp = 1–2%. As for NIPA-AAm copolymers containing 15 mol-% of AAm units, we use the following references:

Taylor and co-workers[12] report Tp = 43 °C for Cp = 5%,
Priest and co-workers[21] report Tp = 46 °C for Cp = 0.03%.

These values are close to those of Fig. 1, if we remember that the oligomers studied in this work have a much lower molecular weight than those used by the quoted authors.

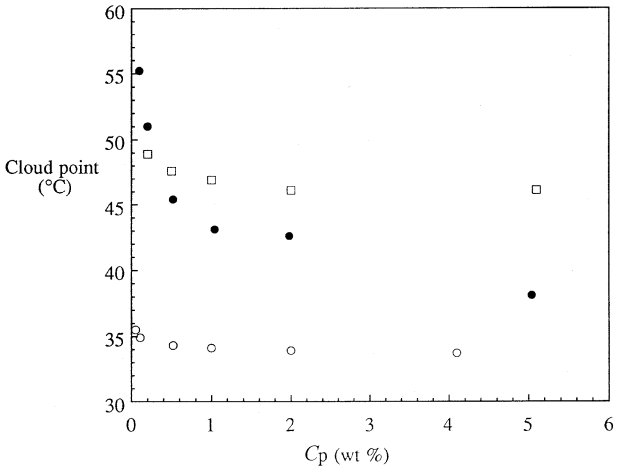

Fig. 1. Cloud point of oligomer solutions as a function of the concentration: PNIPA10 (○), PNIPA-AMPS (●) and PNIPA-AAm (□)

Compared with PNIPA10 we can see that the sensitivity of Tp towards the polymer concentration is much more pronounced for cooligomers. As a matter of fact, we can easily assume that when the phase separation takes place, the concentration of polymer in the supernatant will increase with its hydrophilicity (by the incorporation of hydrophilic units). The effect of charged units is especially strengthened at low concentrations (Cp < 0.5%) or higher Debye length, since we can see that the increase of the cloud point is more important for PNIPA-AMPS than for PNIPA-AAm. This is caused by the counter-ions translational entropy which is much more effective to solubilise PNIPA chains in water compared to the favourable enthalpic contribution of acrylamide units[20, 21].

These results show that the incorporation of hydrophilic monomers in the PNIPA chains allows to modify the LCST of the system in water and the shape of the phase diagram, especially in the low concentration area.

Finally, concerning the PNIPA-BMA copolymer, we just found a very small solubility area in the phase diagram which is located at relatively low temperatures (ca 4–5 °C) for Cp ≈ 0.5%.

Graft copolymers

The functional oligomers and co-coligomers were grafted onto a poly(acrylic acid) precursor in N-methylpyrrolidone (NMP) according to a procedure reported previously[10]. Two different acidic precursors were used, they are denoted PAA1 ($\overline{M}_w$ = 136000 g/mol) and PAA7 ($\overline{M}_w$ = 690000 g/mol). The characteristics of the different graft copolymers are given in Tab. 2. The polymers' nomenclature is:

Tab. 2. Synthesis and characterisation of graft copolymers

Copolymer	[PAA]	[telomer]	[DCCI]	Composition[a)]	Modification extent[b)]	Grafting yield
	g/mL	g/mL	[—NH_2]	wt.-%	%	%
PAA1/PNIPA5-14.5%	0.015	0.008	3.4	14.5	0.3	50
PAA1/PNIPA10-29%	0.012	0.012	4.7	29	0.4	67
PAA1/PNIPA10-17%	0.038	0.012	6.2	17	0.2	89
PAA7/PNIPA10-31%	0.010	0.010	5.6	31	0.4	71
PAA7/PNIPA-AAm-17%	0.015	0.015	4.5	17	0.2	39
PAA7/PNIPA-AMPS-16%	0.015	0.015	3.0	16	0.2	37
PAA7/PNIPA-BMA	0.011	0.011				

a) Weight percent of telomer calculated using ^{1}H NMR results.
b) Average number of side chains per 100 monomer units of the backbone (calculated from ^{1}H NMR and $\overline{M}_n$ values of Tab. 1).

PAA backbone/oligomeric side chain/composition (weight percent of oligomer)%.

The modification extent of a graft copolymer will be defined as the average number of side chains per 100 monomer units in the backbone. E.g., a value of 0.3% indicates that for 1000 monomer units of the backbone, 3 are grafted by a functional oligomer (on average), the other 997 are sodium acrylate units. Since all the reaction media are homogeneous during the grafting reaction, the normal expectation is that the side chains will be distributed randomly along the backbone. The grafting yield varies between 50 and 90% for most of the syntheses and it appears clearly that high molar ratios [DCCI]/[amine] (>6) are necessary to obtain quantitative grafting. Nevertheless this two-step synthesis (telomerisation + grafting) can be regarded as a suitable way to prepare grafted copolymers with a well controlled primary structure. Using this line of copolymers, where we have specifically modified the size of the backbone, the length of the side chains, their chemical nature and the modification extent we will now focus on the real weight of these parameters on the thickening behaviour in semi-dilute solution.

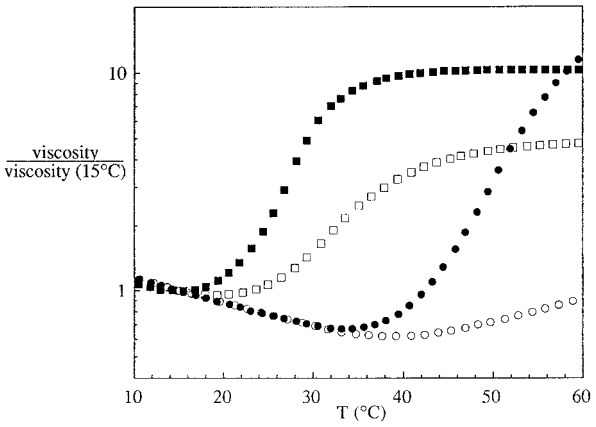

Fig. 2. Variation of the viscosity (divided by its value at 15 °C) of 3% solutions of PAA1/PNIPA10–29% (filled symbols) and PAA1/PNIPA 10–17% (open symbols) in: H_2O (○, ●) and K_2CO_3 0.5 M (□, ■); shear rate = 100 s^{-1}

Rheological properties

Influence of the modification extent

In Fig. 2 we compare the thermothickening behaviour of two copolymers differing only by their graft content (0.2% and 0.4%). As one can easily expect, the magnitude of the thermothickening process follows that of the modification. This is obviously related to the number of elastically active chains which participate in the formation of the physical network. Nevertheless if one could expect that a minimum number of PNIPA grafts is required to observe the formation of a physical network, increasing value will extend the phase separation process to higher scale length and finally a macroscopic phase separation will be reached. In practice we are limited with PNIPA to a maximum grafting ratio ranging between 1 and 2 mole-% which corresponds to PNIPA weight fractions of 51% and 68 wt.-%. The optimization of the thermoassociative properties has to be done between these two limits keeping in mind that the optimum value should be closely linked to the experimental conditions. As we can see on Fig. 2, the screening of electrostatic repulsions by added salt is very effective for the low modified sample both in viscosity level and dynamics of network formation.

The only parameter that remains constant between the two copolymers is the association temperature, T_{ass}, at which the initial decrease of the viscosity starts to slow down. This can be related to the phase diagram of PNIPA and to the low variation of Tp with concentration.

With PAA-g-PNIPA copolymers the grafting extent is therefore an interesting tool to selectively adjust the slope of the thermothickening process, keeping the association temperature constant. In this way one can prepare soft or

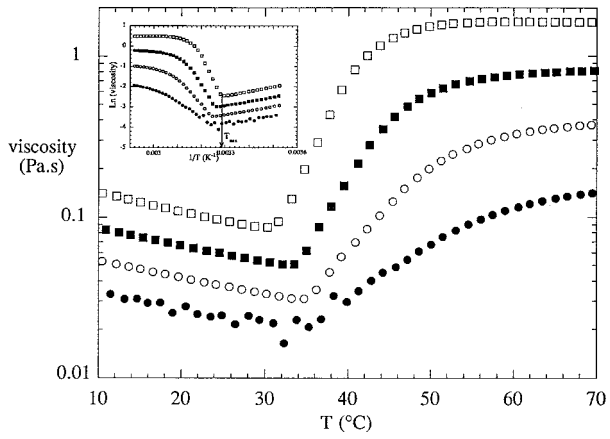

Fig. 3. Variation of the viscosity with temperature for aqueous solutions of PAA7/PNIPA10−31% at various concentrations: 0.8% (●), 1.5% (o), 3% (■) and 6% (□); shear rate = 100 s^{-1}. The association temperature is determined by plotting the same results under an "Arrhenius plot" (see inset)

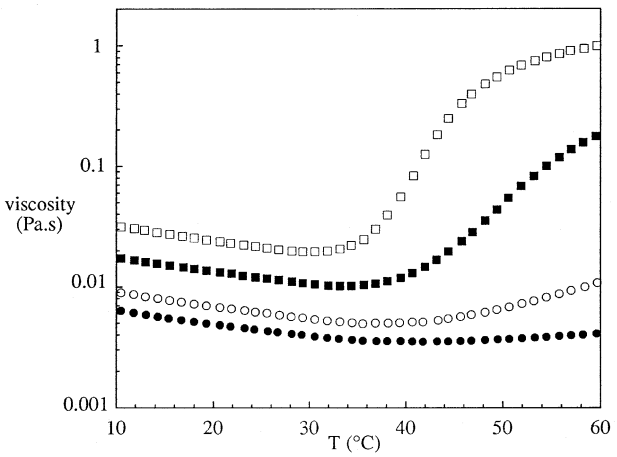

Fig. 4. Variation of the viscosity with temperature for aqueous solutions of PAA1/PNIPA10−29% at various concentrations: 0.8% (●), 1.5% (o), 3% (■) and 6% (□); shear rate = 100 s^{-1}

hard thickeners which could give answers to current technological problems.

Influence of the length of the PAA backbone

The thermothickening behaviour of PAA7/PNIPA10−31% in aqueous solutions is given in Fig. 3. The association temperature can be precisely determined by plotting the results in an "Arrhenius plot" (see inset of Fig. 3). Compared to the results obtained with PAA1/PNIPA10−29% (Fig. 4), we can see that T_{ass} is the same for the two copolymers at a given concentration. This demonstrates again that T_{ass} is fixed by the phase diagram of PNIPA side chains taking into account the PNIPA concentration as well as the whole environmental conditions, e.g. concentration of acrylate units, co-solutes.

On the contrary, the magnitude of the thermothickening effect largely depends on the size of the main chain. At low concentrations (Cp < 1.5%) the overlap between the backbones is very low, especially for PAA1 and this is unfavourable to the formation of intermolecular associations. As a result, the thermothickening effect of PAA1/PNIPA10−29% is, at low concentration, much lower compared to that of PAA7/PNIPA10−31%. At these concentrations, close to the overlap concentration, the strengthening of the thermoassociative effect is directly related to the number of elastically active chains. At higher concentrations (Cp > 3%) the magnitude of the thermothickening effect obtained with the PAA1/PNIPA-10−29% is almost equal and even greater compared to PAA7/PNIPA10−31% (Fig. 5). This inversion can be interpreted by considering the rheological behaviour of the two precursors PAA1 and PAA7 (Fig. 6). It is clear that the PAA7 solution is slightly shear-thinning whereas the PAA1 solution does not show any significant variation of the viscosity with γ in that range of shear rate.

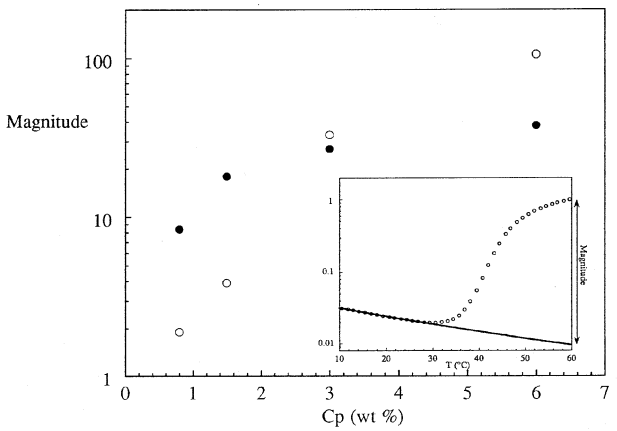

Fig. 5. Variation of the magnitude of the thermothickening effect as a function of the copolymer concentration for aqueous solutions of: PAA1/PNIPA10−29% (o) and PAA7/PNIPA10−31% (●); shear rate = 100 s^{-1}. The magnitude A_η is defined as the ratio of the viscosity at 60 °C to the value obtained by extrapolating the initial decrease to 60 °C (see inset)

To further investigate this problem we are using the description of physical networks proposed by Tanaka and Edwards[22]. Generally, the viscoelastic properties are theoretically described in a non entangled regime, i.e. when the number of monomer units between two associative side chains (stickers) is much smaller compared to the number of monomers between physical entanglements. In that case the properties are dominated by the life time of a sticker into the hydrophobic clusters. In our case, the backbone has a high molecular weight and at high concentration the previous hypothesis does not hold, since the relaxation time of the hydrophobic chain is no longer negligible compared to the lifetime of the sticker. This is what we observe with the PAA7 derivative at Cp = 6% where entanglements, which are responsible for the shear sensitivity of the backbone, weaken the physical network.

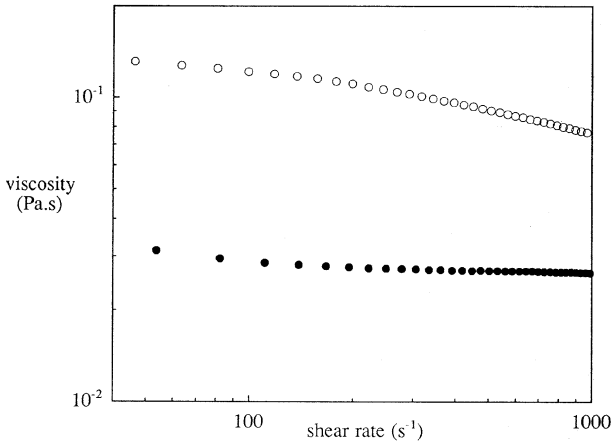

Fig. 6. Variation of the viscosity with shear rate for 3% solutions of PAA1 (●) and PAA7 (o) at a given temperature of 25 °C

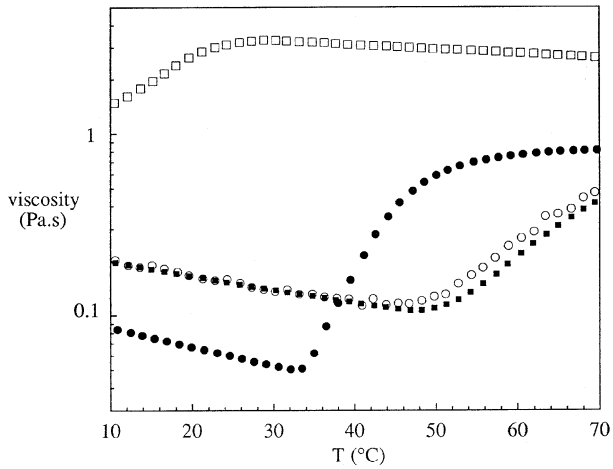

Fig. 7. Variation of the viscosity with temperature for 3% solutions of PAA7/PNIPA10−31% (●), PAA7/PNIPA-AMPS-16% (o), PAA7/PNIPA-AAm-17% (■) and PAA7/PNIPA-BMA (□); shear rate = 100 s^{-1}

From a practical point of view, the use of thermoassociative graft copolymers with a very long backbone could be interesting for the low concentrations domain ($Cp \leq 1\%$) since:

1. the viscosity of the solution is higher,
2. overlap is noticeable and favours intermolecular associations and a significant thermothickening effect.

Nevertheless, at higher concentrations and under high shear rates ($\gamma > 100\ s^{-1}$), the sensitivity of long backbones to mechanical stress weakens the physical network and limits the performance of the associative system.

Influence of the chemical nature of the side chains

a) Control of the thermothickening behaviour

As underlined in a previous section, the incorporation of hydrophilic or hydrophobic units in the PNIPA chains (co-oligomers) can be used to adjust the temperature of phase separation in water (cloud point). The thermothickening behaviour of graft copolymer solutions combining the PAA7 backbone and different side chains (PNIPA-BMA, PNIPA10, PNIPA-AMPS and PNIPA-AAm) is depicted in Fig. 7. As we can see, the copolymers exhibit a distinct associative behaviour with the hydrophilicity of the comonomer as it would be anticipated from the cloud point data reported in a previous section. For the hydrophobic comonomer (BMA) T_{ass} is much lower than 10 °C so that the viscosity of the solution is almost constant over the whole temperature range. The copolymer has a permanent associative character instead of a thermoassociative tendency since the solubility of the side chains is considerably reduced. This effect is similar to the salting-out of PNIPA side chains by adding K_2CO_3[11]. Nevertheless, the incorporation of a hydrophobic comonomer only increases the attractive component between the side chains while the introduction of K_2CO_3 salt also lowers the repulsive forces, i.e. the electrostatic repulsions between the PAA backbones.

When hydrophilic comonomers are incorporated in the side chains, T_{ass} is increased by about 15 °C independently on the comonomer used. The presence of either 4 mol-% of AMPS or 15 mol-% of AAm in the side chains leads to similar behaviours which is consistent with the cloud point data. We can compare the effect of hydrophilic comonomers in the PNIPA side chains with the addition of an anionic surfactant: SDS. As reported earlier[11], a similar increase of T_{ass} can be obtained by adding SDS which micellizes onto the PNIPA side chains. This is equivalent to adding adsorbed charges onto the side chains.

From these results we can conclude that the incorporation of comonomers into the side chains provides a very selective way to control the association tendency of the grafts. An important characteristic of the associating behaviour of the side chains is the value of T_{ass} and its evolution with the composition of the grafts. This will be investigated in the following section.

b) Relation between T_{ass} and the cloud point of the thermosensitive precursors

In a previous paper we showed that, for copolymers grafted with PNIPA10 side chains, T_{ass} was very close to the cloud point of the PNIPA10 precursor in the same environmental conditions. Of course it is necessary to take into account the salting-out effect of the sodium acrylate units which lower this value compared to pure water. Starting from these results, we obtain a general formula which can predict the cloud point when there is no other solute added:

$$Tp = Tp_{H2O} - a_{ANa}Cp_{ANa} \quad (1)$$

Tab. 3. Comparison between the association temperature (T_{ass}) obtained from rheological measurements performed on graft copolymers and the phase separation temperature (Tp) determined with the oligomeric precursors in the same environmental conditions.

Copolymer	Cp	T_{ass}	Tp	$T_{ass}-T$p
	wt.-%	°C	°C	°C
PAA7/PNIPA10−31%	0.8	34	34	0
	1.5	33	33	0
	3.0	32	31.5	0.5
	6.0	30	28.5	1.5
PAA7/PNIPA-AMPS-16%	0.8	55	52	3
	1.5	47	48.5	–1.5
	3.0	43	44	–1
	6.0	37	38	–1
PAA7/PNIPA-AAm-17%	0.8	56	49	7
	1.5	52	47.5	4.5
	3.0	45.5	45	0.5
	6.0	40	41	–1

where T_{H2O} is the cloud point in pure water as given by one of the phase diagrams of Fig. 1, C_{ANa} is the concentration of sodium acrylate units (in wt.-%). The value of a_{ANa} was determined experimentally: $a_{ANa} = 1.27$ °C/%.

Using Eq. (1) the values of Tp can be calculated for three different graft copolymers solutions and compared to the values deduced from rheological experiments (see Tab. 3). The results display that, except for some low concentrations (Cp ≤ 1.5%), T_{ass} is always close to Tp. It has to be noted that for the two copolymers PAA7/PNIPA-AMPS-16% and PAA7/PNIPA-AAm-17% T_{ass} is difficult to determine accurately when Cp ≤ 1.5%, since the thermothickening effect starts smoothly and close to the end of the experimental temperature range.

Once again, these comparisons clearly indicate that for a graft copolymer with long side chains ($\bar{M}_n \approx 10000$ g/mol) the thermodynamic properties of the grafts control the association. The phase diagram is thus a useful guideline for the design of thermoassociative graft copolymers with desired association temperatures.

Influence of the ionisation degree of the backbone

All the graft copolymers mentioned here possess a PAA backbone, which is initially under a fully ionised form. Since we have seen that the electrostatic repulsions play an important role in the formation of the hydrophobic microdomains we have progressively decreased the degree of ionisation of the backbone (denoted α) by adding different amounts of hydrochloric acid (HCl). It is worth mentioning that the copolymer is no longer soluble if we go down to low α values ($\alpha \rightarrow 0$), a complex coacervation (hydrogen bonding) takes place between carboxylic groups and NIPA units[23]. The thermothickening behaviour of the PAA7/PNIPA-AMPS-16% at various degrees of ionisation is depicted in Fig. 8.

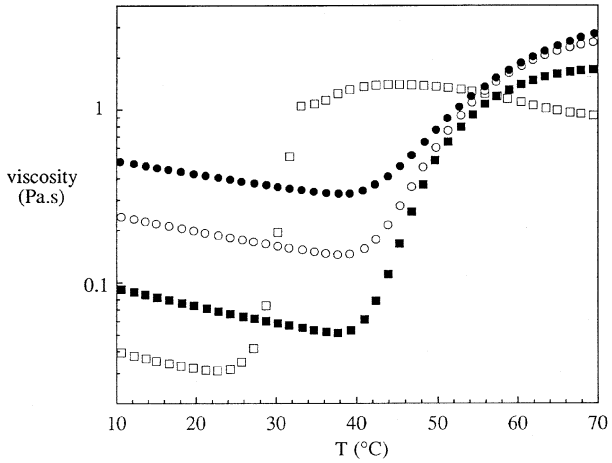

Fig. 8. Variation of viscosity with temperature for a 6% solution of PAA7/PNIPA-AMPS-16% at various ionisation degrees: 1 (●), 0.75 (o), 0.49 (■) and 0.33 (□); shear rate = 100 s^{-1}

The α values are calculated from the amount of HCl introduced assuming a 1:1 stoichiometry.

Several effects can be distinguished along the whole temperature range.

For low temperatures, T < 20 °C, the acidification of the backbone gives rise to a continuous decrease of the viscosity. This effect has two origins:

1) the increase of the ionic strength of the solution according to the following reaction

$$—COONa + HCl \rightarrow —COOH + NaCl \quad (2)$$

2) the decrease of the charged units in the main chain.

In order to discriminate between these two effects we performed complementary experiments where equivalent amounts of NaCl were added to the initial copolymer solutions (α = 1) (see Fig. 9). The comparison with the curve obtained when HCl is added shows that:

- for α = 0.75, the two curves are nearly superimposed so that the effect is entirely due to the ionic strength,
- for α < 0.50, the viscosity is significantly lower when HCl is added, compared to NaCl, so that other effects have to be considered.

We can notice that T_{ass} remains unchanged when the degree of ionisation is varied between 1 and 0.5. For lower values (here α = 0.3) T_{ass} decreases significantly (about 15 °C) and the thickening effect is very sharp; the viscosity gains more than one order of magnitude within 6 degrees. The sharpness of the transition indicates that we are close to the conditions of complex coacervation mentioned previously. Additional comments can be done by comparing T_{ass} with the cloud point value calculated according to the following equation:

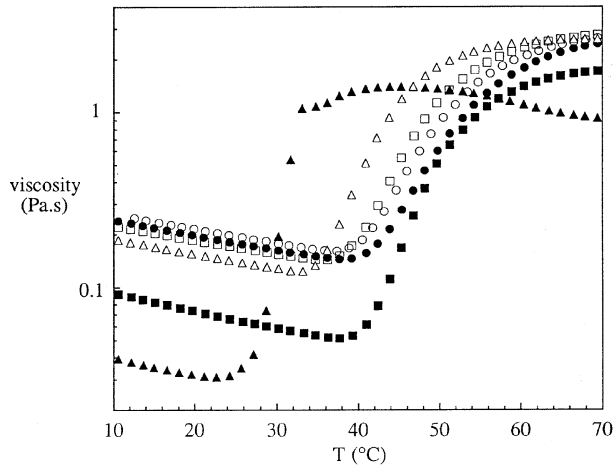

Fig. 9. Comparison of the curves obtained with a 6% solution of PAA7/PNIPA-AMPS-16% by adding HCl or a molar equivalent amount of NaCl. α = 0.75 (●) and 0.2 M NaCl (o); α = 0.49 (■) and 0.3 M NaCl (▫); α = 0.33 (▲) and 0.5 M NaCl (Δ)

$$Tp = Tp_{H2O} - a_{ANa}Cp_{ANa} - a_{AH}Cp_{AH} - a_{NaCl}C_{NaCl} \qquad (3)$$

where Cp_{AH} is the concentration of acrylic acid units in wt.-% and C_{NaCl} the concentration of NaCl (in mol/kg of water denoted M). In Eq. (3) the terms a_{ANa} and a_{NaCl} account for salting-out effects of the sodium acrylate units and of the sodium chloride issued from the acid-base reaction (Eq. 2). Complementary experiments allow to determine the value of a_{NaCl} which is around 12 °C/M. The term a_{AH} accounts for the influence of the acid units on the PNIPA behaviour. Since the numerical value of this term is not known, we will use the difference between T_{ass} and Tp to describe the influence of acid units (Tab. 4). We can see clearly that for α values ranging between 0.5 and 1, T_{ass} and Tp are almost identical, indicating that the acid units have no significant effect. On the contrary when α decreases down to 0.3, T_{ass} is 14 °C lower than Tp. In that case, there are enough acid units along the PAA backbone to give rise to strong hydrogen bonding with NIPA units. Moreover, since the position of the charges are not fixed on the backbone the acid units can easily gather around the NIPA microdomains whereas the acrylate units are rejected in the outer part of the network. This prevents a macroscopic phase separation.

These results clearly illustrate the importance of the repulsive contribution of the main chain in the formation of the physical network: the charges of the PAA backbone can efficiently maintain an osmotic pressure in the network in order to avoid any phase separation ("collapse" of the physical network). Moreover, the role of pH as a driving-force for the associations is emphasized. The interesting pH range is around 3.5–4, since large acid sequences are required to develop significant hydrogen bonds with PNIPA grafts. These interactions disrupt the hydration of the side chains and as a result T_{ass} is abruptly decreased as if they were more hydrophobic. Nevertheless the equilibrium between the forces is very subtle and if the contribution of the backbone is overturned from repulsive to attractive the copolymer no longer remains stable and a phase separation occurs at pH below 3.5.

Tab. 4. Comparison between T_{ass} (deduced from rheological data) and Tp (calculated according to Eq. (3) with a_{AH} = 0) for 6% solutions of PAA7/PNIPA-AMPS-16%

Ionisation degree	pH	T_{ass}	Tp	$T_{ass} - Tp$
		°C	°C	°C
1	≥8.0	37	38	–1
0.75	≈5.4	38	36	2
0.49	≈4.5	37	37.5	–0.5
0.33	≈3.8	22.5	36.5	–14

Mixtures of different polymers

In previous sections, we have seen that it was possible to control the rheological properties of aqueous solutions through the primary structure of the copolymer. For a given copolymer one can modify the macroscopic properties by adding effective cosolutes but another interesting alternative concerns the mixture of copolymers.

First of all, we shall consider the effect of adding increasing amounts of the PAA1 precursor to a 3% solution of PAA1/PNIPA10–29% (Fig. 10). Three effects are detected:

1) at T < T_{ass}, the viscosity increases,
2) T_{ass} decreases,
3) the thermothickening effect is lowered and almost completely cancelled out when 4.2% of PAA1 is added.

The first point is caused by the increase of the total concentration of polymer in the solution (from 3% to 7.2% upon adding PAA1). The point 2) is a consequence of the "salting-out" effect of sodium acrylate units on PNIPA side chains which was previously detailed. Using the Eq. (1) we can account conveniently for this variation (data not shown). To explain the decrease of the thermothickening upon adding PAA1 (point 3) we must consider that the thermoassociative polymer chains (PAA1/PNIPA10–29%) are progressively surrounded by PAA1 chains that are absolutely inactive in the formation of the physical network. In other words, the PAA1 chains hinder the formation of aggregates at least by steric considerations. Of course more studies are needed to give a more accurate picture of this macromolecular organisation, but the occurrence of a phase separation between the two polymers does not seem to take place in this case.

A similar experiment was then performed with PAA1/PNIPA5–14.5% instead of PAA1. In that case we mixed two thermoassociative copolymers differing only by the

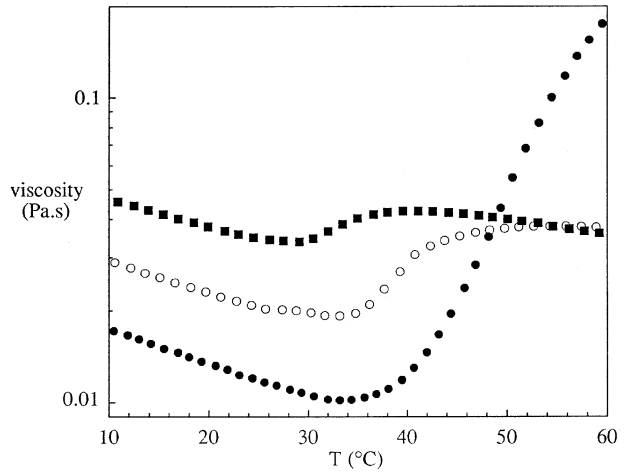

Fig. 10. Variation of the viscosity with temperature for a 3% solution of PAA1/PNIPA10−29% with different concentrations of PAA1 added: 0% (●), 2.1% (o) and 4.2% (▫); shear rate = 100 s^{-1}

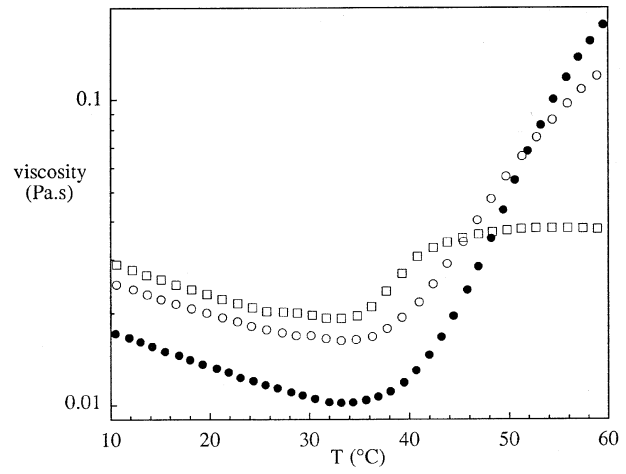

Fig. 11. Comparison of the $\eta = f(T)$ curves obtained with 1) a 3% solution of PAA1/PNIPA10−29% (●), 2) the same solution with 2.1% of PAA1 added (▫) and 3) the same solution with 2.4% of PAA1/PNIPA5−14.5% added (o); shear rate = 100s^{-1}

length of the PNIPA side chains ($\overline{M}_n$ = 5000 and 10000 g/mol). From the curves reported in Fig. 11, we can see that the mixing behaviour is very different if we take the PAA-PNIPA copolymer or its PAA precursor. As a PAA1/PNIPA 5−14.5% aqueous solution does not exhibit significant thermothickening properties under those conditions, we can assume that mixed aggregates of PNIPA5 and PNIPA10 are formed between the two copolymers. The resulting effect is not so important probably because of the limited associative properties of PNIPA5 grafts. Nevertheless it emphasises the possibility of forming mixed associations implying different types of side chains.

If we now examine the thermothickening properties of a mixture of PAA7/PNIPA10-31% and PAA7/PNIPA-AMPS-16% (Fig. 12) we can notice two major trends.

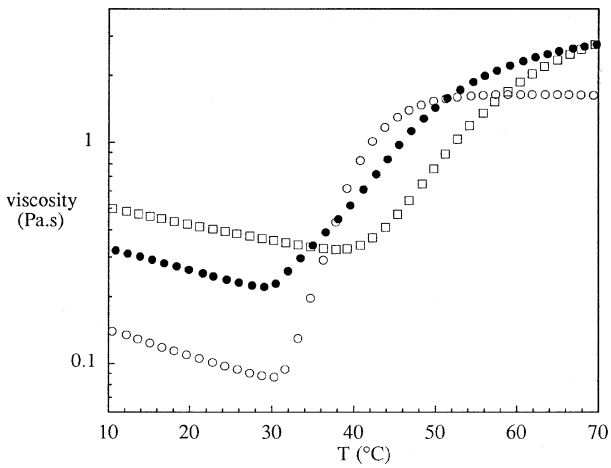

Fig. 12. $\eta = f(T)$ curves obtained with 1) a 6% solution of PAA7/PNIPA10−31% (0), 2) a 6% solution of PAA7/PNIPA-AMPS-16% (▫) and 3) a mixture containing 3.6% of PAA7/PNIPA10−31% and 3% of PAA7/PNIPA-AMPS-16% (●); shear rate = 100 s^{-1}

Note that in this case we have maintained the total copolymer concentration constant.

First of all, the association is triggered out by the more hydrophobic side chains:

$$T_{\text{ass mixture}} = 29.5\,^{\circ}\text{C} \text{ while } T_{\text{ass PAA7/PNIPA10-31\%}} = 30\,^{\circ}\text{C}.$$

Taking into account the thermodynamic behaviours described previously, this result could be anticipated. The second point concerns the dynamic of the thermothickening process. As judged by the slope of the curves, it seems that the formation of mixed microdomains with temperature is controlled by the less hydrophobic component or more exactly by the less associative one.

Conclusion

The synthesis of thermoassociative graft copolymers has been described through a two-step procedure: 1) the synthesis of functional oligomers carrying an amino end group and 2) the grafting of these oligomers onto a poly(acrylic acid) precursor. On this basis we have shown that it was possible to control almost all the main structural parameters of the graft copolymers in order to adjust their solution properties.

Several effects have been detailed and can be divided into two groups, those related to the dynamics of the physical network and those concerning the interactions in the pseudo-ternary system (grafts, backbone, solvent). The grafting extent and the length of the PAA backbone are important parameters in relation to the number of elastically active chains. While the normal trend would be to increase these parameters, there are some important drawbacks associated with:

1) the macrophase separation which can occur at high grafting extents,
2) the increase of the entanglements with the molecular weight (at a given concentration) and the interference of the shear-thinning behaviour of the backbone with the physical network.

From a thermodynamic point of view, we have shown that the chemical nature of the grafts can be used to control the association temperature of the copolymers. A good knowledge of the phase diagram of the grafts is therefore a useful tool to predict under which conditions, either in pure water or with added co-solutes, the copolymer will start to associate. Then the settlement of the microdomains will depend on the competition between attractive and repulsive forces. In previous studies we have shown that strong electrostatic repulsions between the backbone can slow down the formation of hydrophobic clusters. Ionic strength is therefore a possible way to strengthen the association process. This can be done very simply by adding salt or by decreasing the degree of ionisation of the backbone. Nevertheless with this second option we can also modify the attractive interactions between the backbone and the grafts, which can lead to a complex coacervation of the copolymer.

The thermodynamic behaviour of these thermoassociative graft copolymers is now well understood and it has been clearly established that the phase separation of the side chain precursors is the driving-force of the association process. Nevertheless, the dynamics and the morphology of the hydrophobic microdomains still have to be examined more deeply (e.g. the variation of the number of elastically active chains with temperature, the dynamics of the associations). These studies are currently carried out at our department in order to complete the picture of these responsive systems.

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

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