ARTICLES

Thermoassociative Graft Copolymers: NMR Investigation and Comparison with Rheological Behaviour

Alain Durand,† Dominique Hourdet,* and Françoise Lafuma

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

Received: October 22, 1999; In Final Form: April 19, 2000

The thermoassociative properties of semidilute solutions of graft copolymers containing poly(*N*-isopropylacrylamide) (PNIPA) side chains are studied by ^{1}H NMR. Upon heating, the PNIPA grafts self-aggregate into hydrophobic microdomains and their ^{1}H NMR signal is no longer detectable. This phenomenon is attributed to the glassy structure of the aggregates' core and allows a direct detection of the aggregation process. On this basis it becomes possible to detect the formation of the microdomains by salting-out (with potassium carbonate) or their dissociation by adding an anionic surfactant (sodium dodecyl sulfate). The ^{1}H NMR observations are compared to the rheological data previously obtained and to small-angle neutron scattering measurements performed in similar conditions. A good correlation is evidenced between the macroscopic and microscopic transitions probed by the different techniques.

Introduction

Recently, new thermoassociative graft copolymers were developed in our laboratory on the basis of the LCST phase diagram of the "PNIPA/water" system.[1] Their structure consists basically of a sodium polyacrylate (PAA) backbone and PNIPA side chains. In semidilute solution, when the temperature increases above a critical value (the association temperature, T_{assoc}), the side chains self-aggregate into hydrophobic microdomains that act as reversible cross-links between macromolecules. Because of this microscopic phase separation, a large increase in viscosity can be obtained (it gains 1 order of magnitude within 10 deg under rather high shear rate, $\gamma = 100$ s^{-1}). The rheological properties of the aqueous solutions of these copolymers were studied in pure water[1] as well as in the presence of added cosolutes (salts, neutral molecules, and surfactants).[2] It was shown that the characteristics of the thermothickening phenomenon were largely modified in the presence of cosolutes and especially T_{assoc}. Moreover, the variation of T_{assoc} was readily predicted by considering the cloud point of the PNIPA precursors solubilized in the same environmental conditions. The data obtained by macroscopic measurements are useful to design aqueous systems suited to specific applications. Nevertheless, additional data related to the transitions undergone by the macromolecules and to the structure of the hydrophobic microdomains formed, are necessary to complete the picture of the mechanisms involved in the thermoassociative process.

Various techniques can be applied to study the molecular interactions between polymer chains and solvent molecules. Among them, many experiments were used to investigate the transitions of thermosensitive polymers or thermoassociative copolymers: fluorescence,[3,4] infrared absorption spectroscopy,[5] small-angle neutron scattering,[6−9] and nuclear magnetic resonance (NMR).[10,11] More particularly, proton NMR was used to study the phase transition of poly(*N*-isopropylacrylamide) (PNIPA) with temperature on gels[12−14] and linear polymers[15,16] as well. It was shown that when a PNIPA gel collapses upon heating above the critical temperature, the ^{1}H NMR signal of NIPA units progressively disappears. In other words, when temperature is increased, intensities of proton lines diminish due to the signal broadening. The same phenomenon was evidenced with PNIPA solutions and was explained in a similar way assuming that upon heating the water−NIPA interactions are replaced by NIPA−NIPA interactions that bring the NIPA units into solidlike aggregates where the motion of the functional groups are strongly reduced. As a result, the ^{1}H NMR signal of the aggregated NIPA units is of solid type and cannot be detected by the NMR device used. In the case of slow exchange, only the NIPA units that retain enough mobility give experimentally a NMR signal. As the temperature increases, strong NIPA−NIPA associations dominate so that almost no signal can be detected at 50 °C.[11]

Starting from these results about PNIPA, we tried to apply ^{1}H NMR to our thermoassociative graft copolymers in order to monitor the association upon heating on the viewpoint of the molecular interactions and their consequences on mobility. Furthermore, the ^{1}H NMR experiments can be carried out in the same conditions as the rheological ones so that a direct comparison of the association process is possible even if the time scales are necessarily different.

In this paper we will first investigate how the ^{1}H NMR spectrum of copolymer solutions is modified when temperature

* To whom correspondence should be addressed. E-mail: dominique.hourdet@espci.fr.

† Current address: Laboratoire de Chimie-Physique Macromoléculaire, Groupe ENSIC Nancy, UMR CNRS-INPL 7568, BP 451, F-54001 Nancy Cedex, France.

10.1021/jp993769a CCC: $19.00
Published on Web 08/31/2000

increases. Then, the ^{1}H NMR results will be compared to rheological experiments and some small-angle neutron scattering (SANS) results. The interpretation assumes the formation of quasi-solid (or glassy) aggregates induced by the microphase separation of the PNIPA grafts.

Experimental Section

Materials. *N*-Isopropylacrylamide (NIPA) and acrylic acid were purchased from Aldrich and Fluka, respectively, and were used as received. Potassium carbonate (from PROLABO), sodium dodecyl sulfate (from Fluka), and the deuterated sodium dodecyl sulfate (from EURISO-TOP) were of analytical grade.

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

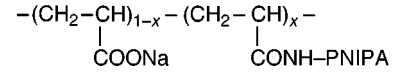
Analytical Methods. *^{1}H NMR.* ^{1}H NMR experiments were performed in D_2O using a Bruker WP250 spectrometer (250 MHz). For temperatures higher than room temperature, the tubes were stabilized at the desired temperature in a water bath before the experiment. To make quantitative comparisons between the spectra (at different temperatures), the integrations were normalized by the area of the peak of water protons at 25 °C.

Rheological Measurements. The viscosity analyses of aqueous solutions with temperature were carried out on a CARRI-MED controlled stress rheometer (CSRH 100) using a cone−plate geometry. The temperature was adjusted by a high power Peltier system that 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).

Small-Angle Neutron Scattering. SANS experiments were performed on spectrometer PACE in the Laboratoire Léon Brillouin (CEA-Saclay, France). The incident neutron wavelength was 14 Å with a corresponding sample−detector distance of 4.6 m. The scattered neutrons were collected according to scattering angle by an array of 30 circular detectors of 1 cm width. This configuration provides a scattering vector (q) ranging from 0.003 to 0.03 Å^{-1}. The diameter of the incident beam was 7.6 mm. The polymer solutions or the solvent alone was introduced into quartz cells (5 mm thick and 9 mm width), which were mounted in a temperature-controlled sample holder (precision ±0.5 °C). The solutions were prepared using D_2O as solvent. The details concerning the treatment of the data have been given in a preceding paper.[9]

Results

Structure of the Copolymers Studied. The thermoassociative copolymers used in this paper are graft copolymers combining a polyelectrolyte backbone (PAA) and thermosensitive PNIPA side chains randomly distributed:



The details of the synthesis of these copolymers are given in a previous paper;[1] their main characteristics are summarized in Table 1. The two copolymers used in the present study possess the same backbone (denoted PAA1) and approximately the same modification extent but differ by the length of the side chains.

^{1}H NMR and SANS Study of Aqueous Solutions. *Influence of Temperature.* The ^{1}H NMR spectrum of a solution of PAA1/PNIPA10−29% in D_2O ($C_p = 6\%$) at $T = 25$ °C is given on Figure 1. The assignments of the various peaks are given on the same picture. The peaks located at 1.0 and 3.7 ppm are specific to NIPA (denoted "e" and "f") and correspond to the hydrogen of the isopropyl group: −CH− and $-CH_3$ respectively. The peaks between 1.5 and 2.5 ppm come from the methylene and methyne groups of the PNIPA and PAA chains.

TABLE 1: Structural Characteristics of the Graft Copolymers

copolymer	length of side chains[a]	copolymer comp (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 polymerization 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.

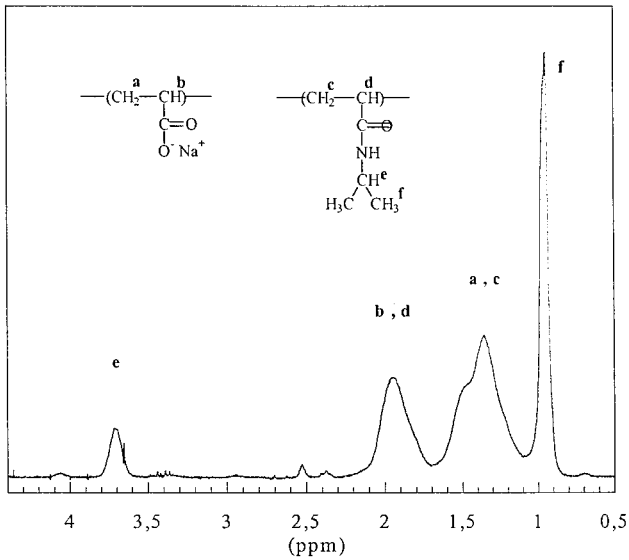


Figure 1. ^{1}H NMR spectrum of a solution of PAA1/PNIPA10−29% ($C_p = 6\%$ in D_2O). The temperature is 25 °C. The attributions of the peaks are indicated in the graph.

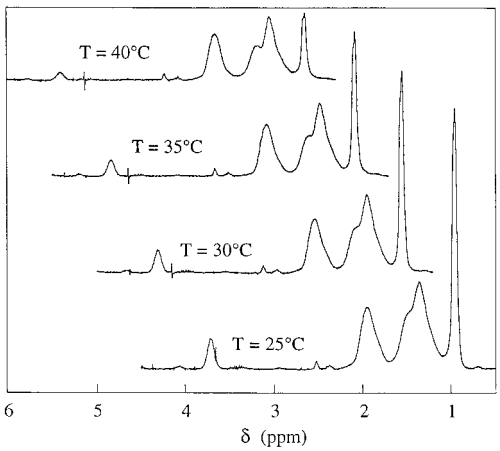


Figure 2. Evolution of the ^{1}H NMR spectrum of a solution of PAA1/PNIPA10−29% ($C_p = 6\%$ in D_2O) with temperature.

The influence of temperature on the spectrum is given on Figure 2 in the temperature range from 25 to 60 °C. For the sake of clarity, the NMR spectra were incremented by 0.5 ppm at each temperature. It is obvious that the spectrum is considerably modified when the temperature is raised.

The areas of the peaks specific to NIPA decrease dramatically upon heating and practically disappear at 60 °C. To quantify this evolution, the integrations of the peaks were normalized

by the area of the peak of water protons at each temperature. On this basis, we can calculate that the area of the peak denoted "e" is 3 times lower at 60 °C compared to its value at 25 °C. This implies that at $T = 60$ °C, 65% of the NIPA units is no longer detected by the NMR device. If we examine more particularly the peak of protons "e", which is far from the PAA signals, the half-height width is constant over the whole temperature range and it is also the case for the solvent peak. This means that the signal from the aggregated NIPA units with low mobility (a very large signal) is absolutely not detected and, as a result, the area of the remaining peak corresponds only to the protons "e" that keep enough mobility (on the ^{1}H NMR time scale). Finally, the ratio of the integration of peak "f" to that of peak "e" is equal to 6 at all temperatures, which is the expected value according to the chemical formula. As a result, the structural transition undergone by the NIPA units implies an arrested motion of the isopropyl group as a whole.

As for the peaks corresponding to methylene and methyne groups of NIPA and sodium acrylate (AA) units (denoted "a, b, c, d" on Figure 1), it is clear that the area decreases, but less than the others, which are specific to NIPA. More precise calculations show that we can assume that the signals due to NIPA progressively decrease while those from AA remain unmodified over the whole temperature range.

From this first set of experiments, we can conclude that on heating an aqueous solution of graft copolymer, the signal corresponding to the thermosensitive PNIPA side chains progressively decreases while those from the hydrophilic AA units remain unchanged.

The same experiment was performed with a 9% solution of PAA1/PNIPA5−14.5% in D_2O. Similar phenomena were observed except that the area of the peaks of NIPA units were unmodified until 35 °C and started to decrease only at 40 °C. Since the main difference between the two copolymers is the length of the PNIPA side chains (cf. Table 1), we can relate this to the lower hydrophobicity of the PNIPA5 chains compared to those of PNIPA10, which implies a lower thermosensitivity. This will be discussed later on the basis of rheological characterizations.

These results indicate that the coil−globule transition of the side chains can be detected with ^{1}H NMR experiments through the decrease of their signals (in given experimental conditions). This is another way to study the aggregation of the PNIPA side chains that is triggered off upon heating.

Influence of Potassium Carbonate, K_2CO_3. It was shown in a previous paper[2] that the introduction of salt (K_2CO_3, for instance) at a constant temperature could bring about the aggregation of the side chains by salting-out in a similar way as a temperature rise. Following this idea, we carried out ^{1}H NMR experiments at a constant temperature of 35 °C where the concentration of K_2CO_3 was varied in a solution of PAA1/PNIPA5−14.5% ($C_p = 3\%$). The results indicated that the effect of K_2CO_3 is qualitatively identical to that observed previously with temperature (data not shown). When the concentration of added K_2CO_3 is gradually increased, the peaks characteristic of NIPA are significantly diminished as soon as $[K_2CO_3] > 0.1$ M. So, as far as structural transitions are concerned, the salting-out effect of K_2CO_3 is very similar to the heat-induced dehydration of PNIPA chains.

Figure 3 shows the SANS data obtained with a 3% solution of PAA1/PNIPA5−14.5% containing various amounts of K_2CO_3 at a given temperature of 35 °C. Upon adding salt, a peak appears in the spectrum that indicates the formation of microdomains.[9]

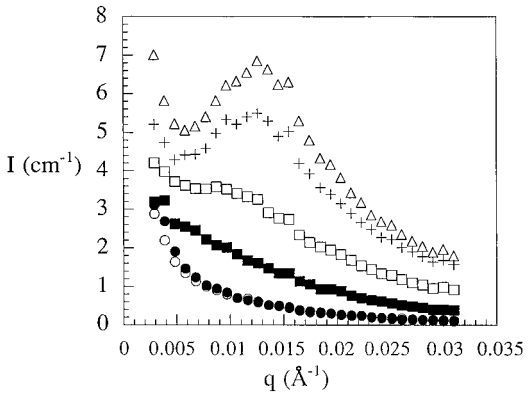


Figure 3. SANS intensities of 3% solutions of PAA1/PNIPA5−14.5% at various K_2CO_3 concentrations: 0 (●); 0.1 M (○); 0.3 M (■); 0.5 M (□); 0.8 M (+); 1 M (△). $T = 35$ °C.

More precisely, we can notice that, up to 0.1 M K_2CO_3, there is no significant difference with the reference spectrum obtained in pure water, which exhibits absolutely no peak. This fact is coherent with previously reported data,[2] which indicated that for a 3% solution of PAA1/PNIPA5−14.5% we have $T_{assoc} \approx 35$ °C only for 0.2 M of K_2CO_3. Thus, up to 0.1 M, no association occurs in the copolymer solution and the SANS spectrum remains unmodified.

For 0.3 and 0.5 M K_2CO_3, the scattered intensity is significantly higher than that recorded in pure water, but no peak can be clearly evidenced. In that range of salt concentration the solvent becomes poor for the PNIPA grafts and associations start. Finally, for 0.8 and 1 M K_2CO_3 added, the spectrum exhibits a peak with high intensity. These results show that the solvent is poor for the side chains that are gathered into concentrated microdomains. The scattering of these aggregates gives rise to a correlation peak in the SANS spectrum. We can see that the peak remains centered at the same position ($q_{max} \approx 0.013$ Å^{-1}). The position of the maximum is taken as a measure of the most probable distance between the aggregates (d): $d = 2\pi/q_{max}$. So, the results indicate that the mean distance between the microdomains remains unchanged at high salt concentrations (0.8−1 M). Similar results have been reported previously[9] concerning other thermoassociative graft copolymers.

The influence of the copolymer concentration at a given K_2CO_3 concentration of 1.0 M indicated that d varied with C_p according to a power law: $d \sim C_p^{-0.39}$. The exponent found experimentally is closed to the theoretical value of $^{-1}/_3$, which corresponds to the isotropic dilution of scattering objects of given size.

The SANS spectrum was also examined at higher value of q (asymptotic behavior) in the range 0.01 Å^{-1} < q < 0.1 Å^{-1} for all the salt concentrations at $T = 35$ °C. The intensity was found to decrease according to a power-law of the type: $I \sim q^{-x}$ where $2 < x < 3$. This show that the aggregates detected in the solution do not exhibit a sharp interface since in that case a value of 4 would be obtained for x as in the case of PAA grafted with poly(ethylene oxide) side chains.[9]

Influence of Sodium Dodecyl Sulfate, SDS. Aqueous solutions of PAA1/PNIPA10−29% ($C_p = 3\%$) were prepared with different concentrations of SDS ranging from 0 to 30 mM. The ^{1}H NMR spectra of these solutions were registered at a constant temperature of 55 °C in order to evidence the effect of the surfactant on the associated copolymers. The surfactant used

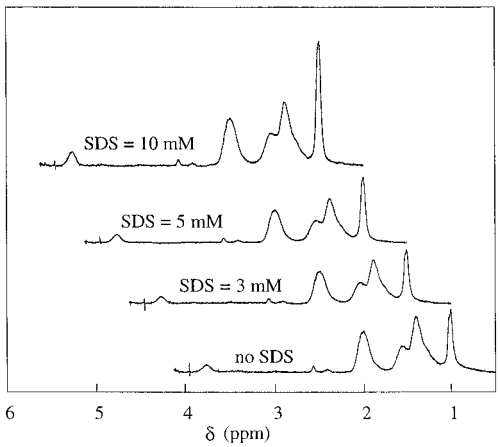


Figure 4. ^{1}H NMR spectrum of a solution of PAA1/PNIPA10−29% (C_p = 3% in D_2O) at various concentrations of SDS. The temperature is maintained at 55 °C.

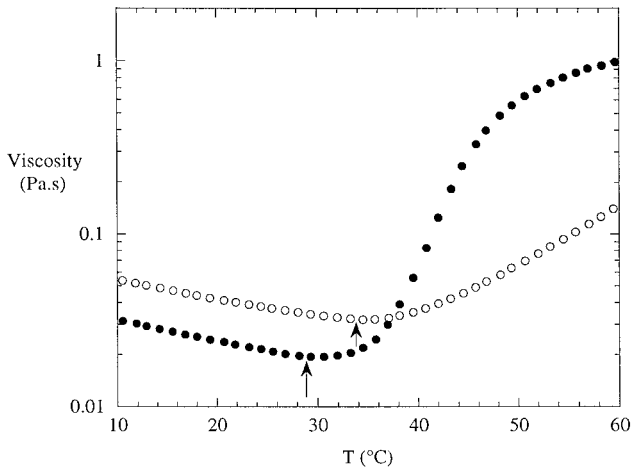


Figure 5. Variation of the viscosity with temperature for aqueous solutions of graft copolymers: PAA1/PNIPA10−29% (●), C_p = 6%; PAA1/PNIPA5−14.5% (○), C_p = 9%. The shear rate is 100 s^{-1}, and the heating rate is 2 °C/min. The arrows indicate the position of the association temperature (T_{assoc}).

was deuterated SDS so that no surfactant peaks could be observed and overlap with that of our copolymers. Typical spectra are given on Figure 4 and show that the introduction of SDS increases gradually the peaks of NIPA units, and when enough SDS is added, the areas of these peaks are identical to those calculated at 25 °C. So, at high temperature, the NIPA signal can be completely recovered by adding enough surfactant. This implies that the surfactant has an effect that is exactly opposite to those of temperature and salt. The temperature, like the salt, reduces the polymer−solvent interactions and then increases the interactions between specific units of the macromolecules (NIPA units). As a result, the PNIPA chains self-aggregate into solidlike microdomains and their ^{1}H NMR signals are no longer detected. On the contrary, the SDS molecules interact with the PNIPA chains and enhance their hydrophilicity by increasing the repulsions between charged micelles adsorbed at the surface of the chain. Then the newly solubilized PNIPA chains recover their mobility and become again observable at the time scale of the NMR device. Consequently, the intensity of the NIPA peaks tend to increase until it recovers its maximum value (measured at 25 °C) that is reached when all the PNIPA microdomains are disrupted.

A similar effect was evidenced by Badiger et al.[12] on PNIPA chemical gels equilibrated in SDS aqueous solutions. For instance, for large amounts of added SDS, they have shown that the swelling/collapse transition previously followed by NMR with ^{1}H line width was almost completely suppressed up to temperatures of 50 °C (when high amounts of SDS were added). The suppression of the local transitions in molecular mobility was related to the decrease of the hydrophobic character of the PNIPA gel decorated with SDS micelles.

Discussion

Definition of the Fraction of "Immobilised NIPA Units". Since the line width of the peak of protons "e" does not vary with temperature, the integration of the remaining fine peak leads to the amount of NIPA units that keep enough mobility to be detected. This value can be compared to the total amount of NIPA units that should be detected, which corresponds to the integration of this peak at T = 25 °C. At any temperature it is then possible to calculate the fraction of "immobilized (or frozen) NIPA units" that is given by the equation

$$F(T) = 1 - S_e(T)/S_e(25\ °C) = 1 - S_f(T)/S_f(25\ °C)$$

where S_i is the value of the integration of the peak of protons "i" (i = e or f).

The evolution of F with temperature allows quantifying the decrease of the NIPA signals and to compare the evolution of the ^{1}H NMR spectrum to the rheological behavior, as will be done in what follows.

Comparison with Rheology and SANS. The thermothickening behavior of aqueous solutions PAA-*g*-PNIPA copolymers was already described in preceding papers.[1,2] The variation of the viscosity of aqueous solutions of PAA1/PNIPA10−29% and PAA1/PNIPA5−14.5% is given on Figure 5 at a constant shear rate of 100 s^{-1}. After an initial decrease, a large viscosity enhancement is observed above the association temperature (T_{assoc}), which is largely dependent on intrinsic parameters (side chains length, ...) and on more external ones (shear rate, cosolutes, ...). In particular, it has been shown that the addition of K_2CO_3 gives rise to a decrease of T_{assoc}, which is similar to the decrease of the cloud point of the aqueous solution of PNIPA precursors. On the contrary, the addition of SDS brings about an increase of T_{assoc} as could be anticipated from the data about the PNIPA precursor and also a decrease of the magnitude of the thermothickening effect which is completely canceled out at sufficiently high SDS concentrations. In this section we will examine how these rheological results are correlated to ^{1}H NMR observations.

The variations of the frozen fraction F and of the viscosity (logarithmic scale) with temperature are compared in Figure 6 for an aqueous solution of PAA1/PNIPA10−29% (C_p = 6%). As we can see, the two evolutions are very similar and this evidences unambiguously the correlation between the progressive decrease of the PNIPA signals and the thermothickening phenomenon. More precisely, in that solution F reaches 0.65 at 60 °C, which means that even 30 °C above T_{assoc}, there are still NIPA units that keep a relative mobility at the ^{1}H NMR time scale. It has to be underlined here that F is not the fraction of elastically active chains since the "frozen chains" can be involved in intramolecular as well as intermolecular associations. Nevertheless, our results show that the variation of F and the increase of the viscosity are correlated. As a matter of fact, the ^{1}H NMR experiments allow probing how the aggregated chains are progressively frozen inside the microdomains' core. In other words, these experiments focus on one aggregate while it does not give information about the connectivity of the aggregates,

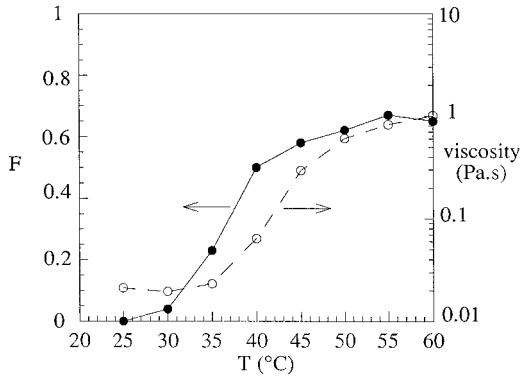


Figure 6. Variation of F (●) and of the viscosity at $\gamma = 100\ s^{-1}$ (○) with temperature for a solution of PAA1/PNIPA10−29% ($C_p = 6\%$ in D_2O).

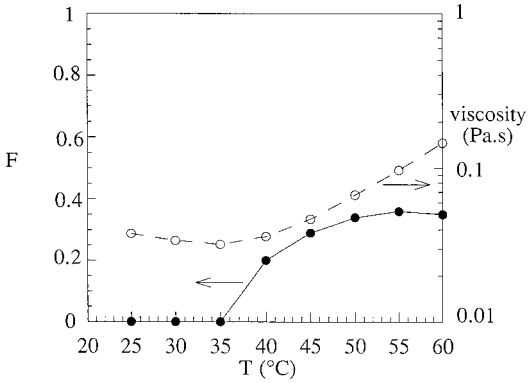


Figure 7. Variation of F (●) and of the viscosity at $\gamma = 100\ s^{-1}$ (○) with temperature for a solution of PAA1/PNIPA5−14.5% ($C_p = 9\%$ in D_2O).

which is studied by rheological experiments. These two techniques thus appear to be complementary and the results presented here show that the data obtained are correlated.

The same remarks apply for a 9% solution of PAA1/PNIPA5−14.5% (cf. Figure 7) and in that case we see that F starts to increase approximately at the same temperature where the thermothickening process is detected in rheological measurements. For this solution, F reaches only 0.4 at 60 °C, a lower value that can be related to the worse thermothickening properties measured in rheology. We can notice that, although the viscosity increases continuously above 35 °C, F reaches a plateau at a value of 0.4 at about 50 °C. These results exhibit that above the microphase separation of PNIPA, the gelation process continues to proceed. One of the main reasons is that the disengagement rate of PNIPA side chains from the clusters is a continuous decreasing function of the temperature.

The influence of copolymer concentration on F at 55 °C is given in Figure 8 for solutions of PAA1/PNIPA10−29%. As we can see, the variation of F is located in the range 0.6−0.8 when C_p increases from 1.5 to 9%. The variation of the "thickening magnitude" in the same range of copolymer concentration is shown in the inset. This "thickening magnitude" is defined as the ratio of the viscosity at 60 °C to that obtained with the nongrafted PAA backbone in the same conditions. Since the "thickening magnitude" observed increases considerably, we can deduce that C_p acts mainly through the entanglements between the chains. More precisely, when C_p increases, it seems that slightly more side chains get frozen into the aggregates (probably due to the increase of the ionic strength) so that the variation of F with C_p is smooth. On the contrary, an increase in polymer concentration is highly favorable to intermolecular

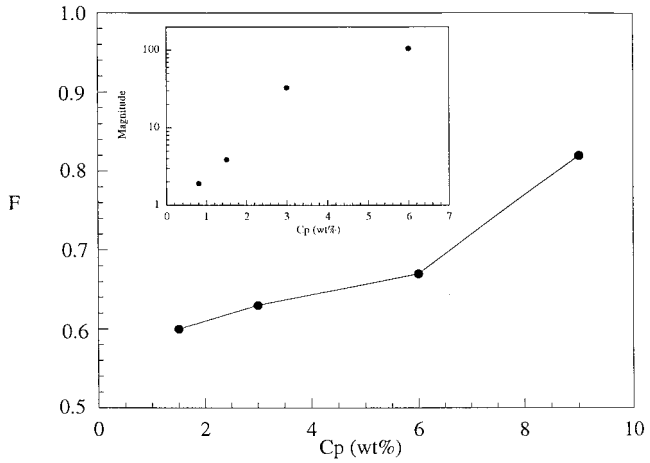


Figure 8. Influence of copolymer concentration (C_p) on F for a PAA1/PNIPA10−29% solution in D_2O at a given temperature of 55 °C. The inset shows the variation of the thickening magnitude in the same range of copolymer concentration. The thickening magnitude is defined as the ratio of the viscosity at 60 °C to the value obtained with the nongrafted PAA backbone in the same conditions.

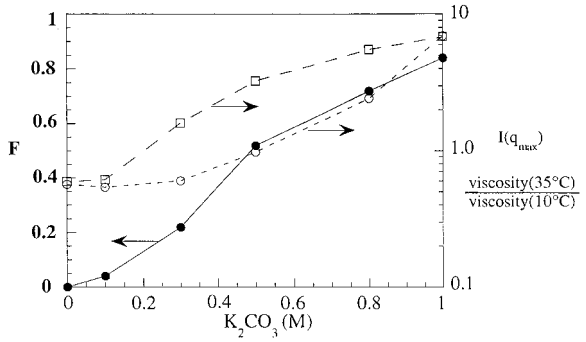


Figure 9. Variation of F (●), $I(q_{max})$ (□), and the viscosity divided by its value at 10 °C at $\gamma = 100\ s^{-1}$ (○) with the concentration of added K_2CO_3 for a solution of PAA1/PNIPA5−14.5% ($C_p = 3\%$ in D_2O) at a given temperature of 35 °C.

associations, that is to say to the connectivity of the physical network. It results in a large increase of the magnitude of the thickening effect. Here we notice again a difference in the sensitivity of the two techniques to an experimental parameter like the polymer concentration.

In the same way, at a given temperature of 35 °C, we can compare the evolutions of F and of the viscosity upon adding K_2CO_3 into a 3% solution of PAA1/PNIPA5−14.5% (cf. Figure 9). The comparison is qualitatively identical to that done with experiments where temperature was varied. The introduction of K_2CO_3 induces the aggregation of PNIPA side chains, which brings about a thickening effect and a decrease of the PNIPA NMR signal. In the same figure we have also reported the value of the SANS intensity at q_{max}. The variation of $I(q_{max})$ and that of F with the concentration of K_2CO_3 are very similar. This indicates that the incorporation of the PNIPA grafts into hydrophobic microdomains by salting-out as detected either by ^1H NMR or by SANS is described in the same way. So, the same phenomenon (thermoassociation) is depicted through its main consequences: formation of aggregates in the solution (=scattering objects) and formation of "low mobility" regions (the aggregates' core) where the NIPA units have a low mobility on the ^1H NMR time scale. The variation of the viscosity with the addition of K_2CO_3 is rather different from the other two since it involves specific concepts such as the ionic strength effect and the number of elastically active chains (intra- and intermolecular associations).

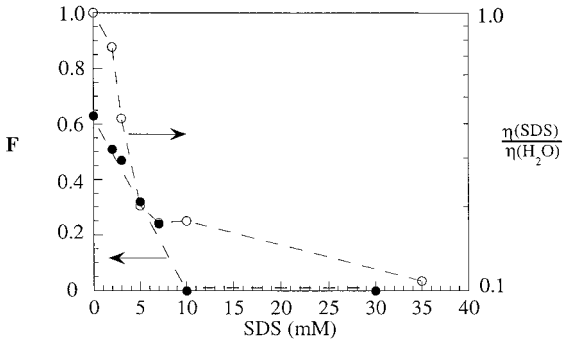


Figure 10. Variation of F (●) and of the viscosity divided by its value in H_2O (○) as a function of the concentration of SDS for a solution of PAA1/PNIPA10−29% (C_p = 3% in D_2O) at a given temperature of 55 °C.

TABLE 2: Fraction of Frozen NIPA Units at 55 °C in Water and in the Presence of SDS

copolymer concn (%)	F(55 °C) in pure water	F(55 °C) in [SDS] = 7 mM	S/P
1.5	0.60	0.13	0.46
3	0.63	0.24	0.23
9	0.82	0.75	0.08

As for the experiments involving surfactant (cf. Figure 10), the evolutions of F and of the viscosity with the concentration of SDS added, at a fixed temperature of 55 °C, are very similar. In a previous paper[2] it was proposed that the introduction of SDS at $T > T_{assoc}$ extracts the PNIPA side chains from the microdomains, which progressively cancels out the thermothickening effect. The ^{1}H NMR results show that, when the PNIPA side chains are extracted from the hydrophobic aggregates, they recover enough mobility and their NMR signal is again detected. This correlation is demonstrated by the two identical variations of F and the viscosity with [SDS]. Moreover, $F = 0$ when [SDS] $\approx$ 10 mM, which means that all the microdomains are dissociated. Considering that F decreases almost linearly with [SDS], we may infer that the complexes between PNIPA side chains and SDS follow a given stoichiometry, as was already suggested by Lee et al. in a recent paper.[17] Starting from rheological results, we showed that in the presence of SDS, the effect observed on the thermothickening phenomenon was controlled by the ratio of the SDS concentration to that of PNIPA side chains (expressed in weight fraction) denoted S/P. The ^{1}H NMR results indicate that the microdomains are completely dissociated at S/P = 0.33. This value is consistent with that found by Lee et al.[17] who studied the phase separation of PNIPA. They showed that at 40 °C and for S/P = 0.4 all the macromolecules of PNIPA behave as isolated necklaces carrying SDS micelles. To check the relevance of the S/P ratio with ^{1}H NMR experiments we examined several solutions of PAA1/PNIPA10−29% at T = 55 °C varying the copolymer concentration but maintaining [SDS] = 7 mM. The values of F are given in Table 2 and each value is compared to that obtained with the same copolymer concentration but in pure water. These results show that when S/P < 0.1, the influence of SDS on F is relatively limited. When S/P > 0.4, F is dramatically decreased by the interactions that take place between the PNIPA side chains and the surfactant molecules. The same holds for rheological experiments:[2] at C_p = 9% the introduction of 7 mM SDS did not modify the viscosity−temperature curve compared to pure water. On the contrary, at C_p = 1.5% the addition of 7 mM SDS into the solution almost completely canceled the thermothickening phenomenon.

Formation of Solidlike Aggregates. The formation of hydrophobic aggregates takes place in the same thermodynamic conditions as the phase separation of the PNIPA precursors, which underlines the similarity between macro- and microphase separation. Many authors showed that at T > 32 °C, the concentrated phase (which contains almost all the PNIPA macromolecules initially dissolved) is structurally close to a solid phase and the mobility of the NIPA units is relatively low. So, provided that the exchange between the aggregates and the surrounding solution is slow enough (on the ^{1}H NMR time scale), the NMR signal decreases dramatically. Taking into account the results presented here, we can say that the same phenomenon takes place with the graft copolymers when $T > T_{assoc}$ and that the PNIPA side chains self-assemble into solidlike aggregates where the molecular mobility is considerably reduced. Nevertheless, since the PAA backbone is highly hydrophilic (and prevents a macroscopic phase separation) all the NIPA units cannot participate in the solid microphase formed upon heating. We must notice that ^{1}H NMR does not allow distinguishing intramolecular and intermolecular associations.

Importance of Side Chain Structure. Similar ^{1}H NMR experiments carried out with solutions of graft copolymers with poly(ethylene oxide) (PEO) side chains (not shown here) indicated that no significant modification of the spectrum could be detected when the association was triggered by adding K_2CO_3. Following our interpretation it means that the PEO side chains undergo no significant loss of mobility during the aggregation process on the ^{1}H NMR time scale. We can consider the glass transition temperature (T_g) data to get information about the variation of chain mobility.

The T_g of the PNIPA10 was measured by differential scanning calorimetry and found to be around 130 °C. This value is consistent with that given in the literature[18] and since it is relatively high we can estimate using the relation proposed by Bueche[19] that an aqueous solution containing 70 wt % PNIPA has a glass transition around 70 °C. This hypothesis was recently confirmed experimentally by Bar et al.[20] who show that the right part of the binary phase diagram (PNIPA/H_2O) is kinetically delimited by the glass transition temperature of the PNIPA−H_2O mixture. According to their results, for C_p = 80 wt %, a glass transition was observed, which freezes the macroscopic phase separation normally observed upon heating a PNIPA solution. As a result, we may infer that, above T_{assoc}, the aggregates core reaches a glassy state where the mobility of the NIPA units is low referring to the ^{1}H NMR time scale. If we now turn to PEO, the reported value of T_g is −72 °C,[19] which means that aggregates with a glassy core are not expected, even at very high concentration. So, the glass transition data are coherent with the differences observed in the structural characteristics of the microdomains when replacing PEO by PNIPA as thermoassociative side chains.

Conclusion

The aim of this study was to complete the rheological characterization of the thermoassociative properties of graft copolymers with PNIPA side chains. Using ^{1}H NMR experiments, it was possible to probe important changes in the environment of the PNIPA chains when the aggregation took place. When the solvent quality is too low for PNIPA grafts they self-assemble into hydrophobic aggregates, which possess a solidlike core. The NIPA units engaged in the glassy core undergo an important loss of mobility on the ^{1}H NMR time scale, which gives rise to a decrease of their signals in the spectrum either upon heating or by addition of K_2CO_3. These transitions detected by ^{1}H NMR are well correlated to the

rheological observations and SANS measurements, which ensures that it is the same phenomenon (thermoassociation) that is observed at two different scales (the whole solution and the NIPA units). A deeper ^{1}H NMR investigation could be imagined in order to get insight into the dynamic transitions undergone by the various parts of the macromolecules: transverse relaxation, ^{13}C NMR. While the signals of the PNIPA side chains were particularly considered in this study, other experiments could focus on the signals of the PAA backbone. In addition, the CP MAS technique could allow studying the signals of the aggregated side chains provided that they keep enough mobility.

The formation of the solid aggregates is related to the glass transition of the PNIPA rich phase, which can overcome the working temperature when the chains are gathered into concentrated aggregates. This implies that the use of different thermosensitive precursors can modify the morphology of the microdomains. The comparison is illustrated by the comparison of PEO and PNIPA side chains. Several experiments could be imagined in order to modify the glassy structure of the core. For instance, what would happen if an aqueous solution of PAA1/PNIPA10−29% were heated well above the T_g of PNIPA? What would happen if a specific plasticizer of PNIPA were introduced in the solution? Are the aggregated NIPA units going to recover their initial mobility and the ^{1}H NMR signal appear again? How are the thermothickening properties related to the solid or liquid structure of the aggregates? Such studies are currently being carried out in our laboratory in order to progress into a more efficient design of the thermothickening systems.

Acknowledgment. We want to thank Rhodia for the financial support of this work and particularly Dr. D. Charmot and Dr. P. Corpart for helpful discussions. We also thank Dr. J.-P. Cotton (LLB, Saclay) for his precious help in SANS experiments. The help of Dr. C. Tribet in ^{1}H NMR experiments is also gratefully acknowledged.

References and Notes

(1) Durand, A.; Hourdet, D. *Polymer* **1999**, *40*, 4941.
(2) Durand, A.; Hourdet, D. *Polymer* **2000**, *41*, 545.
(3) Winnik, F. M. *J. Chem. Phys.* **1989**, *93*, 7452.
(4) Schild, H. G.; Tirrell, D. A. *Langmuir* **1991**, *7*, 665.
(5) Shibayama, M.; Morimoto, M.; Nomura, S. *Macromolecules* **1994**, *27*, 5060.
(6) Shibayama, M.; Tanaka, T.; Han, C. C. *J. Chem. Phys.* **1992**, *97*, 6829.
(7) Shibayama, M.; Tanaka, T.; Han, C. C. *J. Chem. Phys.* **1992**, *97*, 6842.
(8) Shibayama, M.; Tanaka, T. *J. Chem. Phys.* **1995**, *102*, 9392.
(9) Hourdet, D.; L'Alloret, F.; Durand, A.; Lafuma, F.; Audebert, R.; Cotton, J.-P. *Macromolecules* **1998**, *31*, 5323.
(10) Ibbett, R. N.; Philp, K.; Price, D. M. *Polymer* **1992**, *33*, 4087.
(11) Forder, C.; Patrickios, C. S.; Armes, S. P.; Billingham, N. C. *Macromolecules* **1996**, *29*, 8160.
(12) Badiger, M. V.; Rajamohanan, P. R.; Kulkarni, M. G.; Ganapathy, S.; Mashelkar, R. A. *Macromolecules* **1991**, *24*, 106.
(13) Tokuhiro, T.; Amiya, T.; Mamada, A.; Tanaka, T. *Macromolecules* **1991**, *24*, 2936.
(14) Lele, A. K.; Hirve, M. M.; Badiger, M. V.; Mashelkar, R. A. *Macromolecules* **1997**, *30*, 157.
(15) Ohta, H.; Ando, I.; Fujishige, S.; Kubota, K. *J. Mol. Struct.* **1991**, *245*, 391.
(16) Zeng, F.; Tong, Z.; Feng, H. *Polymer* **1997**, *38*, 5539.
(17) Lee, L.-T.; Cabane, B. *Macromolecules* **1997**, *30*, 6559.
(18) *Polymer Handbook*; Brandrup, J., Immergut, E. H., Ed.; Wiley-Interscience: New York.
(19) Bueche, F. *Physical Properties of Polymers*; Wiley: New York, 1962.
(20) Bar, A.; Ramon, O.; Ladyzhinski, I.; Cohen, Y.; Mizrahi, S. Phase transition and changes in physical properties of hydrophobic hydrogels during drying. Polymer Networks 98; International Conference, Trondheim, Norway; Poster P49.