Hydrophobic Interactions of Poly(*N*-isopropylacrylamide) with Hydrophobically Modified Poly(sodium acrylate) in Aqueous Solution

G. Bokias,*,† D. Hourdet,† I. Iliopoulos,† G. Staikos,‡ and R. Audebert†,§

Laboratoire de Physico-chimie Macromoléculaire, Université Pierre et Marie Curie,
CNRS URA 278, ESPCI, 10 rue Vauquelin, 75231 Paris Cedex 05, France,
and Department of Chemical Engineering, University of Patras and Institute of
Chemical Engineering and High Temperature Chemical Processes, ICE/HT-FORTH,
P.O. Box 1414, GR-26500, Patras, Greece

Received June 17, 1997; Revised Manuscript Received October 15, 1997⊗

ABSTRACT: The interactions between poly(*N*-isopropylacrylamide), PNIPAM, and poly(sodium acrylate) hydrophobically modified with octadecyl groups, HMPA, in aqueous solutions, were studied by using viscometry and turbidimetry. The viscosity of mixtures of the two polymers, at 25 °C, may be several orders of magnitude higher than the viscosity of the corresponding mixtures of PNIPAM with the unmodified precursor poly(sodium acrylate). The higher the modification degree of the HMPA, the greater the viscosity enhancement. Furthermore, increasing the molar mass of PNIPAM leads to a more pronounced viscosity increase. The elevation of the phase separation temperature of PNIPAM in the PNIPAM/HMPA mixtures reveals, also, the development of interactions between the two polymers. These interactions are temperature-dependent, and a thermothickening behavior has been observed with increasing temperature.

Introduction

Aqueous formulations exhibiting high viscosities at rather low concentrations of dissolved materials find uses in a wide variety of applications: pharmaceuticals, cosmetics paints, enhanced oil recovery, etc.[1,2] Such formulations often contain, among others, hydrophobically modified water-soluble polymers (HMWSP). These polymers are based on a hydrophilic backbone, ionic or nonionic, to which some small amounts of very hydrophobic groups (long alkyl chains, for instance) have been attached. The interesting feature of HMWSP is their ability to produce highly viscous aqueous solutions above a threshold polymer concentration, $C°$. This viscosity enhancement, much higher than the viscosity of the unmodified precursor under the same conditions, is due to the strong tendency of their hydrophobic parts to form intermolecular aggregates in aqueous solutions.[3−10]

To improve the performance of these polymers, a small amount of surfactant may be used. The surfactant self-assembles around the hydrophobic parts of the HMWSP, creating mixed micelles.[11−22] The mixed aggregates may cross-link several HMWSP chains, depending on the relative polymer and surfactant concentrations. At constant polymer concentration, the viscosity first increases upon addition of surfactant, passes a maximum, and finally decreases. At high surfactant concentrations the mixed aggregates contain mainly surfactant molecules and only a few alkyl groups belonging essentially to the same HMWSP chain, rending the connectivity of the physical network looser.[11,12,13,17] HMWSP adsorb also on hydrophobic surfaces and can be used as stabilizers of hydrophobic particles[1,23,24] and of membrane proteins[25] in aqueous solution.

Another way to improve the rheological properties of such systems is by mixing two, appropriately chosen, HMWSP. The mixed aggregates formed between the alkyl groups of the two polymers lead to viscous solutions, like in the case of HMWSP/surfactant mixtures. Here again the rheological behavior (and the phase diagram) depends on the mixing ratio, i.e., on the efficiency of the formed hydrophobic cross-links.[26]

To our knowledge, the possibility of hydrophobic interactions between a HMWSP and a homopolymer exhibiting a lower critical solution temperature (LCST), like for instance poly(*N*-isopropylacrylamide), PNIPAM, has not been yet regarded, although it is possible to reveal interesting rheological phenomena. PNIPAM is maybe the most broadly studied LCST behaving water-soluble polymer.[27] Although it is soluble in water at low temperatures, its solubility decreases rapidly upon heating and, at ≅33 °C, it phase separates in a concentrated polymer solution in equilibrium with a dilute, essentially aqueous, phase. Therefore, PNIPAM has some inherent hydrophobicity and interacts with surfactants, like sodium dodecyl sulfate (SDS), forming polymer/surfactant complexes. These aggregates provide charges to the PNIPAM chains which, as a consequence, expand and the viscosity increases.[28−30] In addition, an elevation of the cloud point of PNIPAM is observed.[31,32]

In this study we report on the interactions between PNIPAM and poly(sodium acrylate) derivatives hydrophobically modified with octadecyl groups, HMPA. Special attention has been paid to the effect of the modification degree of HMPA and of the molar mass of PNIPAM on the rheological properties of the mixtures.

Experimental Section

Polymers. The origin of poly(sodium acrylate), the modification reaction for the synthesis of the HMPA samples, and their characterization have been described elsewhere.[33,34] The modified polymers contain 1 mol %, 3 mol %, and 5 mol % of octadecyl side groups randomly anchored onto the polymer chain. They are denoted xC18, with $x = 1$, 3, or 5, respectively. For the sake of uniformity, the unmodified precursor poly(sodium acrylate) will be referred in the text as 0C18. The

---

* To whom correspondence should be addressed.

† Université Pierre et Marie Curie.

‡ University of Patras and Institute of Chemical Engineering and High Temperature Chemical Processes.

§ Dr. R. Audebert died after the submission of this manuscript. The coauthors would like to acknowledge his leadership in the field of associating polymers and to express their deep gratitude for his guidance and encouragement.

⊗ Abstract published in *Advance ACS Abstracts,* December 1, 1997.

S0024-9297(97)00884-X CCC: $14.00

polymerization degree of all these derivatives is ≈2000. As they are used in the sodium salt form, the pH of their aqueous solutions is pH > 8.

The polyacrylamide, PAM, synthesis and characterization were described elsewhere.[35] Its molar mass, estimated by viscometry, is 1.1×10^5 g mol^{-1} (polymerization degree ≈1500).

PNIPAM samples were prepared by radical polymerization in aqueous solutions, using the redox couple $(NH_4)_2S_2O_8$/$Na_2S_2O_5$ as initiator. Details on the synthesis are given elsewhere.[29] By changing the $Na_2S_2O_5$ to monomer ratio, we have obtained three samples of weight average molar mass 3.8×10^4, 3.0×10^5, and 6.5×10^5 g mol^{-1}. The molar mass was determined by size exclusion chromatography using the universal calibration method based on polystyrene standards TSK. A Waters 150-CV+ apparatus equipped with four Waters Ultra Styragel columns, thermostated at 40 °C, was used.[36] The elution solvent was tetrahydrofuran. Hereafter these samples will be referred to as PNIPAM-38, PNIPAM-300, and PNIPAM-650, respectively.

Rheology. For the more viscous solutions, viscosity experiments were performed with a Carri-Med controlled stress rheometer equipped with a cone and plate geometry. For the less viscous solutions a Contraves LS-30 viscometer was used. The constant temperature experiments were performed at 25.0 ± 0.1 °C. For the temperature scan experiments the Carri-Med controlled stress rheometer was used with an increasing temperature gradient of 1°C/min. In all cases, the viscosity at a shear rate of 10 s^{-1} is reported.

Turbidimetry. Turbidimetry experiments were performed using a thermostated water bath equipped with a magnetic stirrer. The cloud point temperature was determined by simple visual observation upon heating and cooling the sample. The heating/cooling rate was 0.5 °C/min. Repeated scans at much lower heating rates were performed close to the cloud point temperature. The accuracy of the reported values is better than 0.2 °C.

Sample Preparation. First, stock solutions of the various polymers in water were prepared. Water was purified with a Millipore system, combining inverse osmosis membrane (Milli-R) and ion exchange resins (Milli-Q). For both rheology and turbidimetry experiments, polymer mixtures were prepared by mixing the appropriate volumes of the corresponding stock solutions. The measurements were performed at least 24 h after mixing.

Results and Discussion

Rheology. Effect of Polymer Hydrophobicity. The viscosity behavior for mixtures of PNIPAM-300 with the various xC18 samples at $T = 25$ °C and shear rate 10 s^{-1} is presented in Figure 1. The total polymer concentration is 13 g L^{-1} for the mixtures containing 0C18 and 3C18 and 10 g L^{-1} for the mixture with 5C18. The results are presented as a function of the xC18 weight fraction, $W_{x\mathrm{C18}}$:

$$W_{x\mathrm{C18}} = \frac{m_{x\mathrm{C18}}}{m_{x\mathrm{C18}} + m_2} \qquad (1)$$

where $m_{x\mathrm{C18}}$ and m_2 are the masses of xC18 and PNIPAM, respectively, in the mixture.

Poly(sodium acrylate), 0C18, is a highly hydrophilic polymer, and it has been shown that it does not exhibit any special attractive interaction with the PNIPAM, at least at pH > 7.[37] Indeed, for the mixtures of 0C18 with PNIPAM the viscosity curve varies regularly within the values of the two pure components at the same concentration. The deviation from linearity is due to the polyelectrolyte nature of 0C18, which applies a faster increase in viscosity for the lower concentrations of this polymer (lower $W_{x\mathrm{C18}}$ values). For comparison, the viscosity curve of pure 0C18 in water is also shown, corresponding to $0 \le C_{0\mathrm{C18}} \le 13$ g L^{-1} (dotted line).

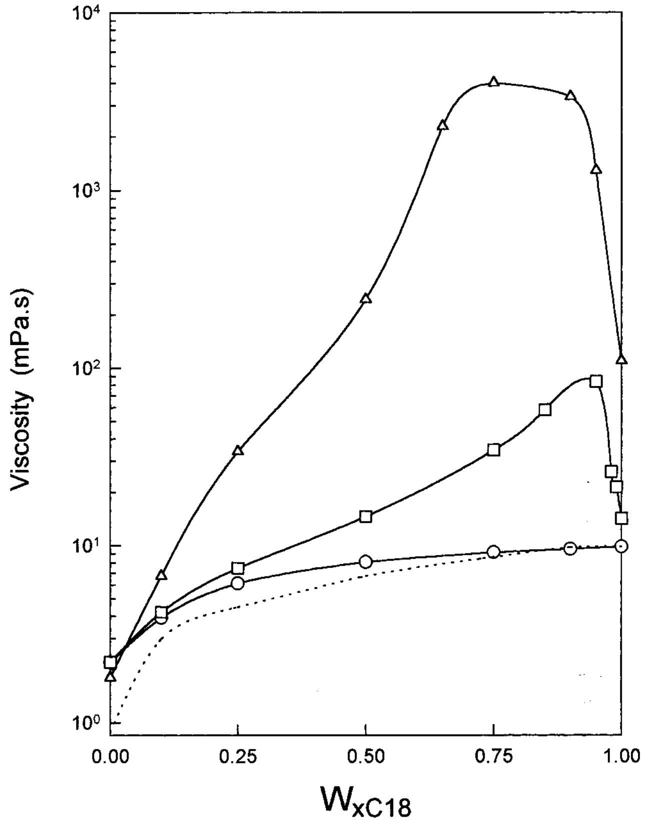
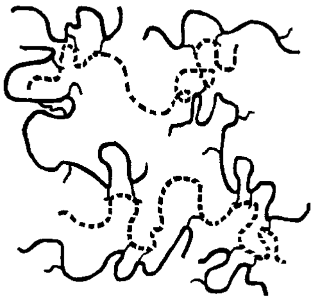


Figure 1. Variation of the viscosity of PNIPAM-300/xC18 mixtures with the mixture composition. ($T = 25$ °C): (○) 0C18; (□) 3C18; (△) 5C18. The total polymer concentration is 13 g L^{-1} for the mixtures PNIPAM-300/0C18 and PNIPAM-300/3C18 and 10 g L^{-1} for the mixtures PNIPAM-300/5C18. The dotted line represents the viscosity behavior of a pure 0C18 aqueous solution in the absence of PNIPAM-300 but at the same concentration as the actual 0C18 concentration in the corresponding mixtures.

When 0C18 is replaced by 3C18 or 5C18, we observe a considerable viscosity enhancement, which is very pronounced for mixtures rich in xC18, $W_{x\mathrm{C18}} \ge 0.5$. That reminds us of the rheological behavior of xC18 mixtures with micelles or proteins, where a pronounced viscosity maximum (or even gelation) is observed at compositions rich in xC18.[12,21,38] The hydrophobic character of PNIPAM is quite important at $T = 25$ °C, as this temperature is close to its LCST (≅34 °C for our samples). It is now well established that due to this hydrophobic character PNIPAM associates rather strongly with surfactants while more hydrophilic polymers, like PAM, do not. Therefore, the formation of mixed aggregates between the highly hydrophobic C18 groups of our polymers and the PNIPAM chains is quite expectable. In some way, the PNIPAM chains play the role of the hydrophobic or amphiphilic nuclei, onto which the C18 groups aggregate. The PNIPAM and HMPA chains are therefore cross-linked via the mixed aggregates (Chart 1). On a macroscopic scale, this is revealed by the spectacular viscosity increase. Of course, the cross-linking efficiency depends on the HMPA/PNIPAM ratio.

The other interesting information we get from Figure 1 is the effect of the hydrophobic substitution of HMPA. 5C18 is, by far, more efficient than 3C18, despite the fact that the total polymer concentration is lower for the 5C18/PNIPAM-300 system (10 g L^{-1}) than for 3C18/PNIPAM-300 (13 g L^{-1}). On the other hand, 1C18 does not show any viscosity enhancement when mixed with

Chart 1. Schematic Representation of the Proposed Association Mechanism between PNIPAM and HMPA[a]



[a] The C18 side groups of HMPA adsorb onto the PNIPAM chain and form mixed aggregates that cross-link the system. Note that this illustration is not intended to be drawn to scale. Especially the size and the composition of the mixed aggregates are still unknown. Key: (solid line) HMPA; (dashed line) PNIPAM.

PNIPAM-300 and follows the same curve as 0C18 (data not shown). It is obvious that by increasing the C18 content of the HMPA polymers, we increase their hydrophobic character. In the pure HMPA solutions, this is revealed by a decreasing C° (the threshold polymer concentration for aggregation) and, at $C > C^\circ$, by a greater viscosity enhancement as a function of C. According to previous studies, $C^\circ \approx 3\%$, 1%, and 0.3% for 1C18, 3C18, and 5C18, respectively.[33,39] Under the experimental conditions used here, 1C18 is well below its C° and has no tendency to form aggregates, 3C18 is close to C°, especially for $W_{3C18} > 0.5$, while 5C18 is above C° essentially for all the W_{5C18} studied. It seems, therefore, that there is a qualitative correlation between the tendency of xC18 to form hydrophobic aggregates and its capacity to associate with PNIPAM. Again, we can note the similarity in behavior with other mixed systems containing HMPA for which the viscosity enhancement was found to increase when the hydrophobic substitution of HMPA increases.[11,12,18,22,38]

Effect of PNIPAM Molar Mass. Figure 2 presents the viscosity of mixtures of 3C18 with PAM and with three PNIPAM samples. The same conditions as in Figure 1 are used. The total polymer concentration is 13 g L^{-1} for all the mixtures. As expected, the highly hydrophilic PAM does not exhibit any viscosity enhancement when mixed with 3C18. Similarly to the 0C18/PNIPAM system, the viscosity curve varies regularly within the values of the two pure components. It has been well established that poly(sodium acrylate) does not associate with PAM under the pH conditions used in this study, pH > 7.[35]

On the other hand, Figure 2 clearly shows the effect of PNIPAM molar mass. The higher the molar mass, the more pronounced the viscosity enhancement. By increasing the molar mass, each PNIPAM chain can form an increased number of mixed aggregates with several 3C18 chains, which results in a more efficient cross-linking of the system and therefore a higher viscosity.

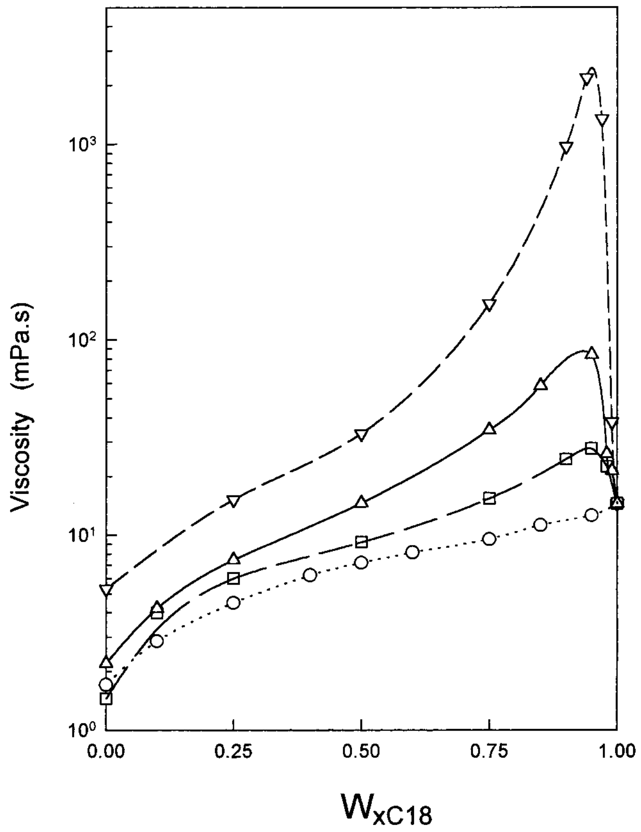


Figure 2. Variation of the viscosity as a function of the mixture composition for mixtures of 3C18 with PAM (○), PNIPAM-38 (□), PNIPAM-300 (△), or PNIPAM-650 (▽). T = 25 °C. The total polymer concentration is 13 g L^{-1}.

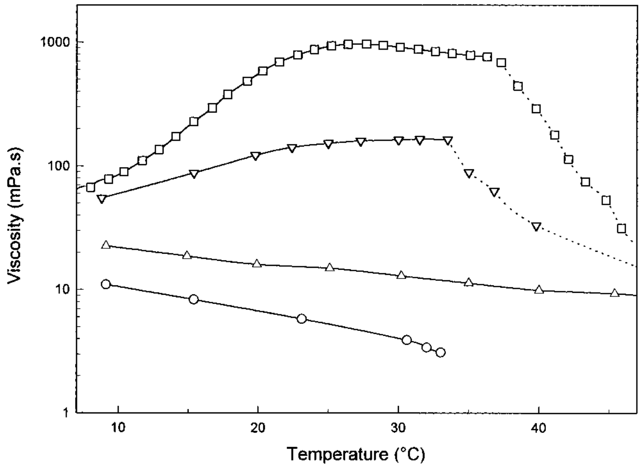


Figure 3. Temperature dependence of the viscosity of the polymers PNIPAM-650 (○) and 3C18 (△) and of PNIPAM-650/3C18 mixtures at two mixture compositions, $W_{xC18} = 0.75$ (▽) and $W_{xC18} = 0.90$ (□). The total polymer concentration is 13 g L^{-1}, and the shear rate, 10 s^{-1}.

Effect of Temperature. Another way to monitor the hydrophobic interactions between PNIPAM and the HMPA samples is by varying the temperature. In Figure 3 we have plotted the viscosity of PNIPAM-650, of 3C18, and of two mixtures of these polymers at $W_{3C18} = 0.75$ and $W_{3C18} = 0.90$ as a function of the temperature. The total polymer concentration for all solutions is 13 g L^{-1}, and the shear rate, 10 s^{-1}. For the two pure polymer solutions we observe a normal Arrhenius behavior; i.e., there is a continuous viscosity decrease as the temperature increases. On the contrary, the temperature dependence of the viscosity for the two polymer mixtures is completely different. Although initially, at $T \cong 10$ °C, the viscosity is rather low, it increases considerably as T increases, until the temperature reaches about 25 °C. At higher temperatures, the viscosity is rather constant or decreases slightly. At an even higher temperature we observe a rapid viscosity decrease in a temperature interval of $\cong$5 °C. Simultaneously, the viscosity measurements start to exhibit fluctuations, indicating that now PNIPAM phase separates from the solution. Indeed, the onset of this rapid viscosity decrease coincides well with the phase separation temperature observed visually (see also Figure 4), at least for the PNIPAM richer mixtures where we could observe visually the cloud point of the solution.

The clear thermothickening behavior at lower temperatures is probably the most interesting feature of these curves. However, the exact interpretation of this phenomenon is not easy. We must note that it takes place in a temperature region not much lower than the LCST of PNIPAM where the hydrophobic character of PNIPAM increases drastically with temperature, resulting in a more efficient cross-linking between the two polymers and therefore a higher viscosity. A similar increased association as a function of temperature was observed for PNIPAM/SDS mixtures.[29,40] Finally, note that the thermothickening behavior of HMPA/PNIPAM systems is reversible and essentially the same curves were obtained when decreasing temperature scans were applied to these systems.

The question to answer now is why does the viscosity level off, and even decrease, above a given temperature? To the strengthening of the hydrophobic interaction, which tends to increase the viscosity, is superimposed the normal Arrhenius behavior, which decreases the viscosity as a function of *T*. The resulting apparent viscosity of the mixture can therefore be considered as a result of these two opposite acting mechanisms. Moreover, when the critical temperature is approached, the dimensions of the PNIPAM coil decrease, as reflected by the decrease of the hydrodynamic radius.[41] That possibly affects the composition and the number of the mixed aggregates formed per PNIPAM chain, which in turn should influence the system behavior. Nevertheless, the exact contribution of this last effect on the viscosity of the mixture is not obvious to estimate.

The thermothickening behavior observed here is rather unusual and has been reported only for a small number of systems. The most common examples offer the comb or block copolymers consisting of a backbone (or main block) that is very hydrophilic and bear grafts (or blocks) exhibiting LCST behavior. At temperatures close to the LCST, the tendency of the LCST parts to phase separate induces the formation of intermolecular aggregates that cross-link the polymer chains. Nevertheless, the system still remains one phase because of the hydrophilic parts of the polymer (backbone or blocks). The final result is a reversible thermothickening (or thermogelling) behavior, as at temperatures lower than the LCST no aggregates are formed.[42−46] The same principle holds also for some polymer/surfactant mixtures, where the thermothickening behavior is due either to the polymer[47] or to the surfactant temperature sensitivity.[48]

Turbidimetry. The variation of the cloud point of HMPA/PNIPAM mixtures gives additional evidence for the development of interactions between the two polymers. In Figure 4 we have plotted the phase separation temperature of the mixtures of PNIPAM-650 with 3C18 or with the precursor 0C18, as a function of the mixture composition, W_{xC18}. The total polymer concentration is always 13 g L^{-1}. For the 3C18/PNIPAM-650 mixtures we have superimposed the data of the phase separation temperature determined by viscosity, as described in Figure 3.

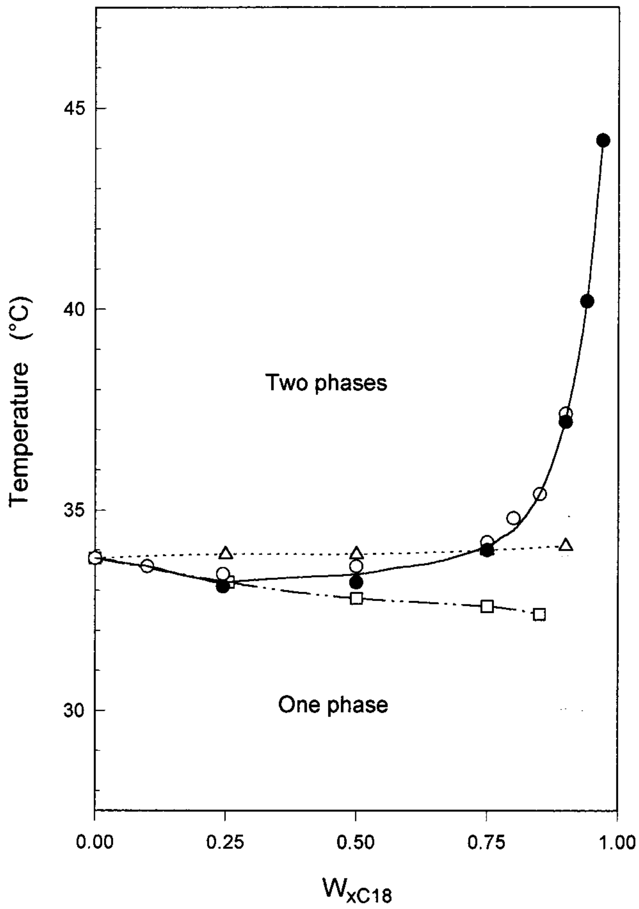


Figure 4. Variation of the phase separation temperature of PNIPAM-300/0C18 (□) and PNIPAM-300/3C18 (○, ●) mixtures as a function of the mixture composition. The total polymer concentration is 13 g L^{-1}. Open symbols refer to the cloud point determination by visual observation, and filled symbols refer to the phase separation temperature revealed from viscosity−temperature curves like in Figure 3. The dotted line (△) represents the cloud point curve of a pure PNIPAM-300 aqueous solution in the absence of *x*C18 but at the same concentration as the actual 0C18 concentration in the corresponding mixtures.

For the sake of comparison we have also plotted the cloud point of PNIPAM-650 solutions in the absence of *x*C18 but at the same concentration as the actual PNIPAM-650 concentration in the mixtures. As expected, it is almost constant (about 34 °C), depending only slightly on the polymer concentration.[49,50] Addition of the unmodified poly(sodium acrylate), 0C18, to the PNIPAM solutions leads to a continuous decrease of the cloud point as W_{xC18} increases. The influence, therefore, of 0C18 on the phase separation temperature of PNIPAM-650 corresponds, as expected, to the addition of salt to the PNIPAM solutions. For most salts, the LCST decreases continuously as the salt concentration increases.[48]

The charge density of 3C18 is practically the same as for 0C18, leading to the plausible supposition that the above mentioned salt effect should be the same as for 0C18. Nevertheless, if it still takes place, this is happening only in the PNIPAM rich mixtures and at $W_{3C18} > 0.3$ it starts to be less pronounced than in the corresponding 0C18/PNIPAM-650 mixtures. In addition, for the 3C18-rich mixtures ($W_{xC18} > 0.8$) we observe a rather significant elevation of the phase separation temperature. We can note here that this composition region corresponds to the high-viscosity region in Figure 2.

The curve of the 3C18/PNIPAM-650 system strongly reminds us of the corresponding behavior of PNIPAM/SDS mixtures and it can be explained in a similar way, i.e., by assuming the formation of mixed hydrophobic aggregates between PNIPAM and 3C18. This corresponds to an indirect introduction of charges to the PNIPAM chain, as 3C18 is a polyelectrolyte. The highly hydrophilic units of 3C18 enable the solubility of the PNIPAM above 34 °C. This can explain the elevated phase separation temperatures at high $W_{x\mathrm{C18}}$. At low $W_{x\mathrm{C18}}$, on the other hand, the HMPA does not associate efficiently with all the PNIPAM chains. Thus, the normal phase separation temperature was observed and, in this region, the cloud point varies like in the case of 0C18/PNIPAM-650 mixtures.

Conclusions

Both rheology and turbidimetry have revealed the ability of PNIPAM to interact strongly with hydrophobically modified poly(sodium acrylate) in aqueous solutions. This specific interaction is due to the hydrophobic character of the two polymers: at 25 °C the hydrophobicity of PNIPAM is high, as this temperature is close to its LCST, and the HMPA polymers, although they are composed of the hydrophilic poly(sodium acrylate) backbone, they contain also the highly hydrophobic octadecyl groups. The high hydrophobicity of both polymers is a prerequisite for the development of attractive interpolymer interactions. If poly(sodium acrylate) is not hydrophobically modified, no association is observed. The same holds when we use the hydrophilic polymer PAM instead of PNIPAM.

The elevation of the phase separation temperatures of the mixtures is similar to that observed when PNIPAM is mixed with ionic surfactants, like SDS. This similarity suggests that mixed hydrophobic aggregates are also formed in the case of HMPA/PNIPAM systems, involving the PNIPAM chains and the C18 groups of the HMPA. These mixed aggregates act as cross-linkers between the PNIPAM and HMPA chains and consequently the viscosity of the mixtures increases.

The results of this study clearly show the interest of using mixtures of amphiphilic polymers to improve the rheological properties of aqueous formulations. Furthermore, a thermothickening behavior can be obtained if one of the polymers exhibits a LCST. Preliminary results with other LCST polymers (poly(ethylene oxide), hydroxypropylcellulose) confirm that the above described behavior is quite general. Nevertheless, it is obvious that further research is needed in order to understand the details of the association mechanism and to characterize the network and the aggregates formed by those systems.

Acknowledgment. This work was supported by the European Union under the contracts CHRX-CT94-0655 (Human Capital and Mobility program) and ERBFMBICT960831 (Research Training Grant for G.B's postdoctoral stay in Paris). I.I. acknowledges financial support from the Greek General Secretariat for Research and Technology (PENED program, contract 1442,3.2) for his short-term stay in Patras University.

References and Notes

(1) *Polymers in Aqueous Media Performance through Association*; Glass, J. E., Ed.; Advances in Chemistry Series 223; American Chemical Society: Washington, DC, 1989.

(2) Russo, P. *Reversible Polymeric Gels and Related Systems*; ACS Symposium Series 350; American Chemical Society: Washington, DC, 1987.

(3) Wang, T. K.; Iliopoulos, I.; Audebert, R. In *Water Soluble Polymers. Synthesis, Solution Properties and Applications*; Shalaby, S. W., McCormick, C. L., Butler, G. B., Eds.; ACS Symposium Series 467; American Chemical Society: Washington, DC, 1981.

(4) Biggs, S.; Hill, A.; Selb, J.; Candau, F. *J. Phys. Chem.* **1992**, *96*, 1505.

(5) Ringsdorf, H.; Venzmer, J.; Winnik, F. M. *Macromolecules* **1991**, *24*, 1678.

(6) Sinquin, A.; Hubert, P.; Dellacherie, E. *Langmuir* **1993**, *9*, 3334.

(7) McCormick, C. L.; Nonaka, T.; Johnson, C. B. *Polymer* **1988**, *29*, 731.

(8) Schulz, D. N.; Kaladas, J. S.; Maurer, J. J.; Bock, J.; Pace, J. J.; Schulz, W. W. *Polymer* **1987**, *28*, 2110.

(9) Landoll, L. M. *J. Polym. Sci., Polym. Chem.* **1982**, *20*, 443.

(10) Valint, P. L.; Bock, J. *Macromolecules* **1988**, *21*, 175.

(11) Sarrazin-Cartalas, A.; Iliopoulos, I.; Audebert, R.; Olsson, U. *Langmuir* **1994**, *10*, 1421.

(12) Iliopoulos, I.; Olsson, U. *J. Phys. Chem.* **1994**, *98*, 1500.

(13) Biggs, S.; Selb, J.; Candau, F. *Langmuir* **1992**, *8*, 838.

(14) Winnik, F. M.; Ringsdorf, H.; Venzmer, J. *Langmuir* **1991**, *7*, 905.

(15) Winnik, F. M.; Ringsdorf, H.; Venzmer, J. *Langmuir* **1991**, *7*, 912.

(16) Goddard, E. D.; Leung, P. S. *Colloids Surf.* **1992**, *65*, 211.

(17) Tanaka, R.; Meadows, J.; Williams, D. A.; Phillips, G. O. *Macromolecules* **1992**, *25*, 1304.

(18) Magny, B.; Iliopoulos, I.; Audebert, R.; Piculell, L.; Lindman, B. *Prog. Colloid Polym. Sci.* **1992**, *89*, 118.

(19) Nystrom, B.; Thuresson, K.; Lindman, B. *Langmuir* **1995**, *11*, 1994.

(20) Biggs, S.; Selb, J.; Candau, F. *Polymer* **1993**, *34*, 580.

(21) Iliopoulos, I.; Wang, T. K.; Audebert, R. *Langmuir* **1991**, *7*, 617.

(22) Magny, B.; Iliopoulos, I.; Zana, R.; Audebert, R. *Langmuir* **1994**, *10*, 3180.

(23) Lundberg, D. J.; Glass, J. E. *J. Coatings Technol.* **1992**, *64*, 53.

(24) Buscall, R.; Corner, T. *Colloids Surf.* **1986**, *17*, 39.

(25) Tribet, C.; Audebert, R.; Popot, J. L. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 15047.

(26) Thuresson, K.; Nilsson, S.; Lindman, B. *Langmuir* **1996**, *12*, 530.

(27) Schild, H. G. *Prog. Polym. Sci.* **1992**, *17*, 163.

(28) Eliassaf, J. *J. Appl. Polym. Sci.* **1978**, *22*, 873.

(29) Staikos, G. *Macromol. Rapid Commun.* **1995**, *16*, 1995.

(30) Tam, K. C.; Wu, X. Y.; Pelton, R. H. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 963.

(31) Schild, H. G.; Tirrell, D. A. *Langmuir* **1991**, *7*, 665.

(32) Schild, H. G. *ACS Symp. Ser.* **1991**, No. 467, Chapter 17.

(33) Wang, T. K.; Iliopoulos, I.; Audebert, R. *Polym. Bull.* **1988**, *20*, 577.

(34) Magny, B.; Lafuma, F.; Iliopoulos, I. *Polymer* **1992**, *33*, 3151.

(35) Perrau, M. B.; Iliopoulos, I.; Audebert, R. *Polymer* **1989**, *30*, 2112.

(36) Lesec, J.; Millequant, M.; Patin, M.; Teyssie, P. In *Chromatographic Characterization of Polymers. Hyphenated and Multidimensional Techniques*; Provder, T., Barth, H. G., Urban, M. W., Eds.; Advances in Chemistry Series 247; American Chemical Society: Washington, DC, 1995.

(37) Bokias, G. Thesis. University of Patras, Greece, 1994.

(38) Petit, F.; Audebert, R.; Iliopoulos, I. *Colloid Polym. Sci.* **1995**, *273*, 777.

(39) Unpublished data of the Paris group.

(40) Kokufuta, E.; Zhang, Y.-Q.; Tanaka, T.; Mamada, A. *Macromolecules* **1993**, *26*, 1053.

(41) Wu, C.; Zhou, S. *Macromolecules* **1995**, *28*, 5383.

(42) Doelker, E. *Adv. Polym. Sci.* **1993**, *107*, 199.

(43) Brown, W.; Schillen, K.; Almgren, M.; Hridt, S.; Bahadur, P. *J. Phys. Chem.* **1991**, *95*, 1850.

(44) Hourdet, D.; L'Alloret, F.; Audebert, R. *Polymer* **1994**, *35*, 2624.

(45) Suto, S.; Nishibori, W.; Kudo, K.; Karasawa, M. *J. Appl. Polym. Sci.* **1989**, *37*, 737.

(46) Vos, S.; Moller, M.; Visscher, K.; Mijnlieff, P. F. *Polymer* **1994**, *35*, 2644.

(47) Carlsson, A.; Karstrom, G.; Lindman, B. *Colloids Surf.* **1990**, *47*, 147.

(48) Loyen, K.; Iliopoulos, I.; Audebert, R.; Olsson, U. *Langmuir* **1995**, *11*, 1053.

(49) Schild, H. G.; Tirrell, D. A. *J. Phys. Chem.* **1990**, *94*, 4352.

(50) Ricka, J.; Meewes, M.; Nyffenegger, R.; Binkert, Th. *Phys. Rev. Lett.* **1990**, *65*, 657.

MA970884F