Association of Positively Charged Copolymers Based on *N*-Isopropylacrylamide with Hydrophobically Modified Poly(sodium acrylate) in Water

G. Bokias* and Y. Mylonas

Department of Chemical Engineering, University of Patras and Institute of Chemical Engineering and High-Temperature Processes, ICE/HT-FORTH, P.O. Box 1414, GR-26500 Patras, Greece

Received August 14, 2000

ABSTRACT: The association of positively charged copolymers based on *N*-isopropylacrylamide with a hydrophobically modified poly(sodium acrylate) derivative, containing 3 mol % octadecyl groups, PANa3C18, is investigated. The NIPAM-based copolymers, PNIPAM*x*, contain a fraction *x* of a positively charged comonomer, $0 \leq x \leq 25$ mol %. In PANa3C18/PNIPAM*x* aqueous mixtures the formation of mixed octadecyl/PNIPAM hydrophobic aggregates is strongly reinforced by the electrostatic attractions between the two polymers, leading to a pronounced viscosity increase. The maximum viscosity enhancement as well as phase separation phenomena are observed at a roughly constant polymer charge ratio, regardless of *x*. For PANa3C18/PNIPAM5 mixtures an important thermothickening behavior is observed, but this thermothickening ability weakens as *x* increases. The gradual loss of thermosensitivity with increasing *x* is also supported by fluorescence probing experiments and phase separation studies.

Introduction

Poly(*N*-isopropylacrylamide), PNIPAM, is a nonionic, rather hydrophobic water-soluble polymer, extensively studied over the past two decades and already finding numerous "smart" practical applications.[1,2] Basically, the great interest in this polymer is due to its moderate hydrophobic character, which is revealed by its lower critical solution temperature (LCST) behavior in water. PNIPAM is soluble in water at low temperature, but it phase separates as soon as temperature exceeds 33 °C.[3] The appearance of the two phases is accompanied by a large turbidity, and for simplicity we usually determine the cloud point, i.e., the temperature at which the solution turns cloudy. The hydrophobic character of PNIPAM is also revealed by its ability to associate with anionic surfactants. The most studied are the mixtures of PNIPAM with sodium dodecyl sulfate, SDS.[4,5] The formation of mixed PNIPAM/SDS aggregates introduces intrachain electrostatic repulsions, leading to the increase of the reduced viscosity of the polymer in dilute solution[6−8] and to the elevation of the cloud point upon addition of SDS.[4,5]

The hydrophobically modified derivatives of poly(sodium acrylate) containing *x* mol % pendent octadecyl groups, PANa*x*C18, are typical examples[9−11] of hydrophobically modified water-soluble polymers, HMWSP. In aqueous solution and above a threshold polymer concentration, *C*°, the octadecyl groups of several polymer chains form interpolymer hydrophobic aggregates.[12] These aggregates cross-link reversibly the polymer chains, and a transient network is formed. As a result, the aqueous PANa*x*C18 solutions are highly viscous when the polymer concentration exceeds *C*°.

It has been shown[13] that we can further improve the thickening properties of PANa*x*C18 derivatives even at concentrations lower than or near *C*° by simply mixing them with PNIPAM. Similarly to the PNIPAM/SDS mixtures, the PNIPAM chains are the nuclei onto which the octadecyl groups of various PANa*x*C18 chains are "adsorbed", forming mixed PNIPAM/octadecyl aggregates. A viscosity gain of 3−4 decades may be observed, depending on the mixture composition, the molecular weight of PNIPAM, and the modification degree *x* of the PANa*x*C18 samples. Moreover, as the hydrophobic character of PNIPAM strengthens upon heating, a significant thermothichening is also observed. Nevertheless, any thickening ability is lost when temperature exceeds ~40 °C, because PNIPAM chains become very hydrophobic and separate out from water.[13]

The use of positively charged NIPAM-based random copolymers, instead of the homopolymer PNIPAM, is expected to alter decisively the thickening properties of the corresponding mixtures with PANa*x*C18. Similarly to the behavior of mixtures of oppositely charged hydrophobically modified polymers,[14,15] the introduction of strong electrostatic attractions between PANa*x*C18 and the NIPAM-based copolymers, in addition to their tendency to form mixed hydrophobic aggregates, is expected to greatly improve the thickening ability of their mixtures. Moreover, the thermal sensitivity of NIPAM-based copolymers will weaken as their charge content increases. Indeed, the cloud point of random NIPAM-based copolymers containing 5 mol % charged groups is elevated at ~50 °C, while the cloud point of those containing 10 mol % charged groups is higher than 70 °C.[16−18] This will significantly influence the thermothickening ability of their mixtures with PANa*x*C18, and the observation of new interesting features is expected.

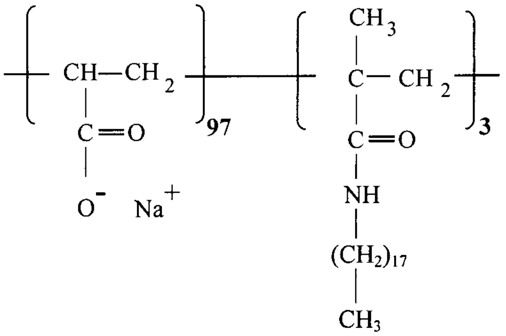
In this work, the investigation of the influence of the charge content of positively charged NIPAM-based copolymers on the behavior of their mixtures with PANa*x*C18 is presented. The study is performed with a sample of poly(sodium acrylate) containing 3 mol % octadecyl groups, randomly anchored on the polymer chain, denoted PANa3C18 (Scheme 1). The positively charged comonomer of the NIPAM-based copolymers is

---

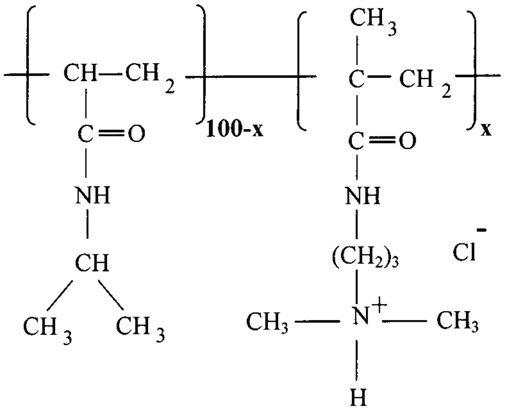
* To whom correspondence should be addressed. E-mail: bokias@chemeng.upatras.gr.

10.1021/ma001423o CCC: $20.00

Scheme 1



Scheme 2



the *N*,*N*-(dimethylaminopropyl)methacrylamide, MADAP, neutralized with HCl (Scheme 2).[19] These copolymers will be referred to as PNIPAM*x*, where *x* is the mole percentage of the charged MADAP units. We focus mainly on the thickening and thermothickening properties of the PANa3C18/PNIPAM*x* mixtures. Moreover, fluorescence probing experiments and phase behavior studies were performed, to have a better insight into their thermally induced properties.

The phase behavior of the mixtures is of interest, since mixing two oppositely charged polyelectrolytes usually leads to associative phase separation over almost the entire mixing interval.[20,21] However, when the two polyelectrolytes are hydrophobically modified, the phase separation domain is very reduced.[14,15] A similar behavior is expected to be observed also with the mixtures PANa3C18/PNIPAM*x*. Nevertheless, due to the thermal sensitivity of the NIPAM-based chain, we also expect interesting phenomena as a function of temperature.

Experimental Section

Polymers. Table 1 summarizes the main characteristics of the charged NIPAM−MADAP copolymers. The synthesis and characterization of these polymers are described elsewhere.[19] Details on the origin and characterization of PANa3C18 can be found elsewhere.[12] The weight-average molar mass of the precursor poly(sodium acrylate), PANa, is 150 000, and the threshold concentration $C°$ of the sample PANa3C18 is 0.01 g/cm^3 as estimated from rheology data.

Rheology. A controlled-stress rheometer (Rheometrics SR-200) equipped with a cone/plate geometry (diameter = 25 mm, angle = 2°) was used for most of the rheology measurements. The rheology measurements of the PANa3C18/PNIPAM mixtures were performed with a Contraves LS-30 viscometer equipped with a Couette geometry.

Fluorescence Probing. Steady-state fluorescence spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer. Pyrene was used as a fluorescence probe at a concentration 6 × 10^{-7} M. The excitation wavelength was 334 nm, and the intensities at 373 and 384 nm were used to calculate the first to the third peak intensity ratio (I_1/I_3). Pyrene was introduced by adding the appropriate volume of a stock pyrene solution 1 × 10^{-3} M in ethanol.

Table 1. Characterization of the NIPAM-Based Copolymers Used in This Study

polymer	MADAP content[a] (mol %)	$[\eta]^b$ (cm^3/g)	$M_w{}^c \times 10^{-6}$
PNIPAM		175	0.65
PNIPAM5	5	220	1.0
PNIPAM10	10	232	1.1
PNIPAM25	25	260	1.4

[a] Averaged values from potentiometric titration and ^{13}C NMR data. [b] $[\eta]$ is measured in a 0.5 M LiNO$_3$ aqueous solution at 20 °C. The copolymers were in the uncharged basic form. [c] M_w are estimated from the relation $[\eta] = 0.047M_w{}^{0.61}$, that it has been established for the homopolymer PNIPAM under these conditions.

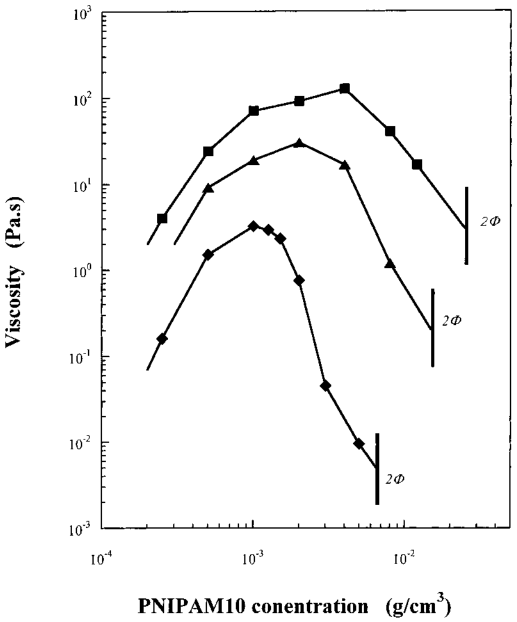


Figure 1. Variation of the viscosity of PANa3C18/PNIPAM10 mixtures with the PNIPAM10 concentration at a shear rate of 1 s^{-1} (T = 25 °C). The concentration of PANa3C18 is 1 × 10^{-2} (■), 5 × 10^{-3} (▲), or 2.5 × 10^{-3} g/cm^3 (◆).

Turbidimetry. A thermostated water bath equipped with a magnetic stirrer was used for the turbidimetry experiments. Cloud points were determined by simple visual observation upon heating the sample. The heating rate was ~0.5 °C/min.

Sample Preparation. The water used for the preparation of the various solutions was purified with a Seralpur water purification apparatus, combining inverse osmosis membrane and ion-exchange resins. Samples were prepared by mixing the appropriate volumes of the already prepared stock solutions of the corresponding polymers. The measurements were performed at least 24 h after the preparation of the samples. For the rheology and fluorescence probing experiments, the sample were left to equilibrate at the desired temperature for 15 min before measurement. All experiments are made at constant PANa3C18 concentration and increasing the PNIPAM*x* concentration.

Results and Discussion

Thickening Properties. The viscosity behavior for PANa3C18/PNIPAM10 mixtures at 25 °C and shear rate 1 s^{-1} is presented in Figure 1. The concentration of PANa3C18 is well below, 2.5 × 10^{-3} and 5 × 10^{-3}

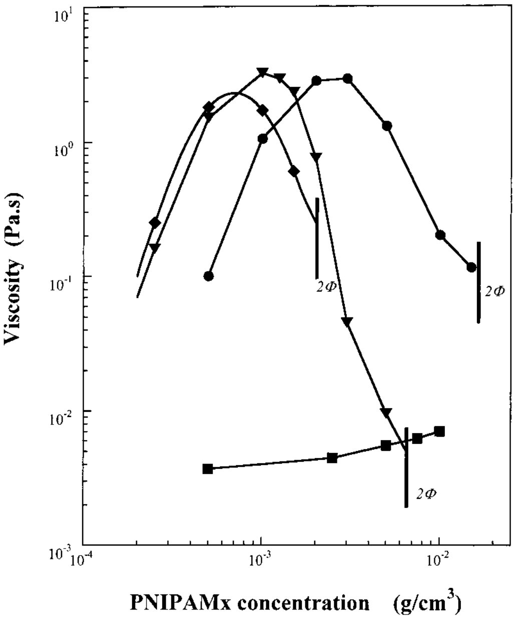


Figure 2. Variation of the viscosity of PANa3C18/PNIPAM*x* mixtures with the PNIPAM*x* concentration at a shear rate 1 s^{-1} ($T = 25$ °C). The concentration of PANa3C18 is 5×10^{-3} g/cm^3. (●) PANa3C18/PNIPAM5, (▼) PANa3C18/PNIPAM10, (◆) PANa3C18/PNIPAM25, (■) PANa3C18/PNIPAM.

g/cm^3, or near the threshold concentration of this polymer, 1×10^{-2} g/cm^3. In this concentration range the viscosity of the two components is very low (less than 2×10^{-2} Pa·s for PANa3C18 and less than 5×10^{-3} Pa·s for PNIPAM10). Nevertheless, when they are mixed, a remarkable viscosity enhancement is observed. Depending on the mixture composition, the viscosity gain may reach 3–4 decades. In all cases, the viscosity of the mixtures initially increases upon addition of PNIPAM10, passes through a maximum, and then decreases. For higher PNIPAM10 concentrations phase separation takes place. For the three sets of experiments, the viscosity maxima and the onset of phase separation are observed at roughly constant charge ratios of the cationic charges concentration over the sodium acrylate concentration. The maximum viscosity is observed at a charge ratio ~0.04, whereas phase separation occurs when the charge ratio reaches the value ~0.2–0.25. It should be noted that when mixing PNIPAM10 with the unmodified precursor, PANa, phase separation occurs at a much lower charge ratio. The higher charge ratio found for the PANa3C18/PNIPAM10 mixtures, comparable to that observed by Thuresson et al.,[14] confirms that the formation of mixed hydrophobic aggregates, containing octadecyl groups and NIPAM sequences, enlarges the miscibility composition region between the two oppositely charged polyelectrolytes.

Here, we have to note that the highest concentration of PANa3C18 is close to its C^o. At this concentration, this polymer forms mixed hydrophobic aggregates even with the homopolymer PNIPAM.[13] The transient network formed this way leads also to a viscosity enhancement, however clearly less pronounced than that for the PANa3C18/PNIPAM10 mixtures. In the latter case, the corresponding transient network is strongly reinforced by the electrostatic attractions between the two polymer components.

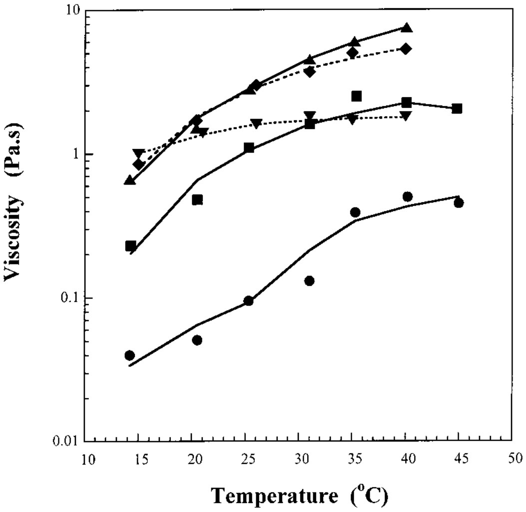


Figure 3. Temperature dependence of the viscosity of various PANa3C18/PNIPAM*x* mixtures at a shear rate 1 s^{-1} ($T = 25$ °C). The concentration of PANa3C18 is 2.5×10^{-3} g/cm^3. The concentration of PNIPAM5 is 5×10^{-4} (●), 1×10^{-3} (■), or 3×10^{-3} g/cm^3 (▲). The concentration of PNIPAM10 is 1×10^{-3} g/cm^3 (◆), and the concentration of PNIPAM25 is 5×10^{-4} g/cm^3 (▼).

The influence of the charge content of the PNIPAM chain on the thickening properties of the PANa3C18/PNIPAM*x* mixtures is presented in Figure 2. The PANa3C18 concentration is always 2.5×10^{-3} g/cm^3. At this low PANa3C18 concentration, no significant viscosity enhancement is observed for the mixtures of PANa3C18 with the homopolymer PNIPAM. The viscosity is less than 0.01 Pa·s and increases regularly upon addition of PNIPAM. On the contrary, the introduction of charges in the NIPAM chain enhances the interpolymer association and leads to an important viscosity increase even at this low PANa3C18 concentration. For the optimum mixture compositions, the viscosity is about 3 decades higher than the viscosity of the PANa3C18/PNIPAM system. Interestingly, for the three PANa3C18/PNIPAM*x* systems, the viscosity maximum is of the same order, regardless of the charge content of the copolymer PNIPAM*x*. Moreover, like in Figure 1, the maximum is observed at a constant charge ratio of about 0.05 ± 0.01. This constancy suggests that there exists an optimum mixture composition, where each PANa3C18 chain connects as much PNIPAM*x* chains as possible. Before the maximum, interconnections are favored, whereas after the maximum their number decreases. Finally, when the net charge of the polyelectrolyte complexes formed is not sufficient to keep them in solution, they separate out from water. Such a qualitative description of the bell-shaped viscosity variations at constant HMWSP concentration is widely recognized now for their mixtures with micelles,[22] and it has been also suggested for protein/HMWSP mixtures.[23,24]

Thermal Sensitivity. The influence of temperature on the thickening properties of some PANa3C18/PNIPAM*x* mixtures is presented in Figure 3. For the mixtures of PNIPAM5 with PANa3C18 a considerable viscosity increase is observed when temperature increases. This increase is about 1 order of magnitude for the PANa3C18/PNIPAM5 mixtures in the temperature range 15–40 °C. Note that a similar viscosity enhancement with temperature was also observed for mixtures of PANa3C18 with the homopolymer PNIPAM at a higher PANa3C18 concentration.[13] In that case, the thermothickening behavior was attributed to the fact that the temperature increase strengthens the hydrophobic character of PNIPAM and leads to a stronger association of the PNIPAM chains with the octadecyl groups of PANa3C18.

For the PANa3C18/PNIPAM*x* mixtures, thermothickening properties become smoother as the charge content of the NIPAM-based chain increases, so that the viscosity of the PANa3C18/PNIPAM25 mixture is almost constant with temperature. This tendency, verified for several mixtures of PANa3C18 with the three copolymers at various compositions (results not shown here), is apparently related to the decreasing thermosensitive character of the copolymers PNIPAM*x*: as *x* increases, the PNIPAM sequences are shorter and less sensitive to temperature changes. Therefore, it is possible to control the viscosity profile as a function of temperature, from strong thermothickening to temperature independent, just by controlling the charge content of the NIPAM-based copolymer.

Another observation worthy of note is that the viscosity of most of the mixtures seems to reach a plateau at 40−45 °C. Because of water evaporation problems, we did not perform viscosity measurements at higher temperatures. However, we confirmed by simple visual inspection that the solutions with mixture compositions well below the phase separation charge ratio remain viscous and homogeneous even at higher temperatures. This is important as it suggests that the PANa3C18/PNIPAM*x* mixtures can find uses as (thermo)thickeners in a large temperature region, compared to the PANa3C18/PNIPAM mixtures, where phase separation occurs always at $T \sim 40$ °C, accompanied by a dramatic viscosity decrease.[13]

More information on the thermosensitive character of the PANa3C18/PNIPAM*x* association can be obtained by fluorescence spectroscopy using pyrene as a fluorescence probe. As known, the ratio I_1/I_3 of the intensity of the first vibrational band over the intensity of the third vibrational band of the fluorescence emission spectrum of pyrene is sensitive to the polarity of the microenvironment experienced by this probe. High I_1/I_3 values, of the order of 1.8−2, reveal a highly polar aqueous microenvironment, and low I_1/I_3 values, of the order of 1−1.2, are typical for a micellar microenvironment.[25] Note that aqueous PNIPAM solutions at temperatures just above the cloud point are characterized by an intermediate I_1/I_3 value of about 1.5.[26]

Figure 4 presents the variation of the ratio I_1/I_3 with temperature, for mixtures of PANa3C18 at a concentration of 5×10^{-4} g/cm^3 with each PNIPAM*x* copolymer at a concentration of 2.5×10^{-4} g/cm^3. The values of the ratio I_1/I_3 for the pure polymers (in the figure are presented only PNIPAM25 and PANa3C18) are slowly decreasing with temperature from ~1.73 to ~1.65, revealing that pyrene experiences a polar aqueous microenvironment. On the contrary, the hydrophobicity of the PANa3C18/PNIPAM*x* mixtures is significant already at 25 °C, the decrease of the I_1/I_3 ratio being more important as *x* increases. Moreover, all mixtures become gradually more hydrophobic with temperature, as the ratio I_1/I_3 decreases upon heating to 45 °C. This change is more pronounced for the mixtures of PANa3C18 with PNIPAM5 or PNIPAM10 and very smooth for the mixture PANa3C18/PNIPAM25, which is considerably hydrophobic already at room temperature. The temperature dependence of the ratio I_1/I_3 of the PANa3C18/PNIPAM*x* mixtures is in accordance with the viscosity−temperature profiles of these mixtures at much higher concentrations. The mixtures of PNIPAM5 or PNIPAM10 with PANa3C18 exhibit important thermothickening properties as their hydrophobic character increases considerably upon heating, while the viscosity of the PANa3C18/PNIPAM25 mixture is almost constant with temperature since its hydrophobic character changes very smoothly in the same temperature range.

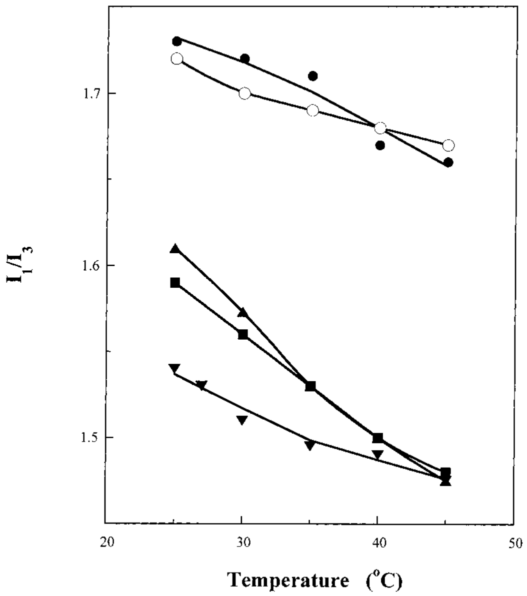


Figure 4. Influence of temperature on the ratio I_1/I_3 for mixtures containing 5×10^{-4} g/cm^3 PANa3C18 and 2.5×10^{-4} g/cm^3 PNIPAM5 (▲), PNIPAM10 (■), or PNIPAM25 (▼). (○) Pure PANa3C18: 5×10^{-4} g/cm^3. (●) Pure PNIPAM25: 2×10^{-3} g/cm^3.

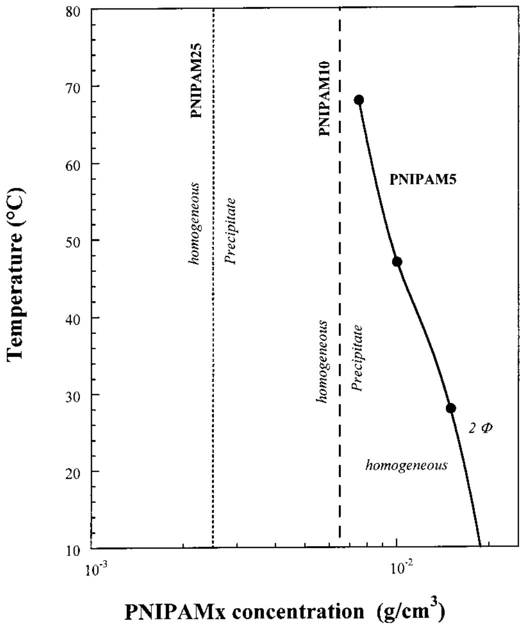


Figure 5. Phase behavior of mixtures containing 2.5×10^{-3} g cm^{-3} PANa3C18 and PNIPAM5 (●), PNIPAM10 (- - -), or PNIPAM25 (···).

Phase Behavior. The gradual loss of the thermosensitive features with increasing *x* is also reflected in the phase behavior of the PANa3C18/PNIPAM*x* mixtures. Thus, as is observed in Figure 5, the aqueous mixtures of PNIPAM5 with PANa3C18 exhibit lower critical solution temperature properties, and they separate into two phases upon heating. The results presented in this figure are performed at a constant PANa3C18 concentration of 2.5×10^{-3} g/cm^3. When the concentration of PNIPAM5 is lower than 1×10^{-2} g/cm^3, these mixtures are clear in the whole temperature range studied, 10−80 °C, while when it is higher than 2.5×10^{-2} g/cm^3, they phase separate, regardless of temperature. Nevertheless, for intermediate PNIPAM5 concentrations, turbidity appears only if temperature reaches a certain value. The cloud points determined that way are gradually shifted toward lower temperature as the PNIPAM5 concentration increases. Such a thermosensitive phase behavior is not the case for the mixtures of PANa3C18 with the other two copolymers, PNIPAM10 or PNIPAM25. Depending on the PNIPAM*x* concentration, these mixtures are either fully homogeneous or precipitated out from water regardless of temperature. The characteristic concentrations where the phase separation appears are indicated in Figure 5 by the vertical dashed and dotted line for PNIPAM10 and PNIPAM25, respectively, and they correspond to a constant charge ratio of ∼0.2−0.3. This constancy, similar to that observed in Figure 1, probably suggests that to obtain soluble interpolymer PANa3C18/PNIPAM*x* complexes, their net charge should overcome a critical value. We have not investigated the composition of the two phases, but an associative phase separation mechanism is the most probable, as in the usual formation of polyelectrolyte complexes.[20]

Conclusion

We investigated the association of positively charged NIPAM-based copolymers, PNIPAM*x*, with the negatively charged hydrophobically modified poly(sodium acrylate) derivative, PANa3C18. Since both electrostatic and hydrophobic interactions stabilize the interpolymer complexes, the PANa3C18/PNIPAM*x* mixtures exhibit a striking thickening efficiency, as compared to single PANa3C18 solutions or to mixtures of PANa3C18 with the uncharged homopolymer PNIPAM.

The rheology response of the mixtures to temperature changes can be successfully tuned by changing the charge content *x* of the PNIPAM*x* copolymers. When *x* is low, their mixtures with PANa3C18 preserve an important thermothickening ability, while the thermothickening properties become gradually smoother with increasing *x*. Another important advantage of the PANa3C18/PNIPAM*x* mixtures is their ability to maintain the thickening properties in a wider temperature region, as compared to the corresponding mixtures of PANa3C18 with the homopolymer PNIPAM. Interestingly, a roughly constant viscosity as a function of temperature is obtained for mixtures with $x = 25$ mol %.

Acknowledgment. This work was supported by the Operational Program for Education and Initial Vocational Training on Polymer Science and Technology, 32a, 33H6. Prof. G. Staikos and Dr. I. Iliopoulos are thanked for stimulating discussions and useful suggestions.

References and Notes

(1) Schild, H. G. *Prog. Polym. Sci.* **1992**, *17*, 163.
(2) *Biorelated Polymers and Gels*; Okano, T., Ed.; Academic Press: New York, 1998.
(3) Heskins, M.; Guillet, J. E. *J. Macromol. Sci., Chem. A2* **1968**, *8*, 1441.
(4) Schild, H. G.; Tirrell, D. A. *Langmuir* **1991**, *7*, 665.
(5) Schild, H. G. *ACS Symp. Ser.* **1991**, *No. 467*; Chapter 17.
(6) Eliassaf, J. *J. Appl. Polym. Sci.* **1978**, *22*, 873.
(7) Tam, K. C.; Wu, X. Y.; Pelton, R. H. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 963.
(8) Staikos, G. *Macromol. Rapid Commun.* **1995**, *16*, 913.
(9) *Polymers in Aqueous Media: Performance through Association*; Glass, J. E., Ed.; Advances in Chemistry No. 223; American Chemical Society: Washington, DC, 1989.
(10) *Polymers as Rheology Modifiers*; Schulz, D. N., Glass, J. E., Eds.; ACS Sumposium Series No. 462; American Chemical Society: Washington, DC, 1991.
(11) *Water-Soluble Polymers: Synthesis, Solution Properties and Applications*; Shalaby, S. W., McCormick, C. L., Buttler, G. B., Eds.; ACS Sumposium Series No. 467; American Chemical Society: Washington, DC, 1991.
(12) Wang, T. K.; Iliopoulos, I.; Audebert, R. *Polym. Bull.* **1988**, *20*, 577.
(13) Bokias, G.; Hourdet, D.; Iliopoulos, I.; Staikos, G.; Audebert, R. *Macromolecules* **1997**, *30*, 8294.
(14) Thuresson, K.; Nilsson, S.; Lindman, B. *Langmuir* **1996**, *12*, 530.
(15) Tsianou, M.; Kjøniksen, A.-L.; Thuresson, K.; Nyström, B. *Macromolecules* **1999**, *32*, 2974.
(16) Chen, G.; Hoffman, A. S. *Nature* **1995**, *373*, 49.
(17) Qiu, X.; Kwan, C. M. S.; Wu, C. *Macromolecules* **1997**, *38*, 22759.
(18) Matsukata, M.; Hirata, M.; Gong, J. P.; Osada, Y.; Sakurai, Y.; Okano, T. *Colloid Polym. Sci.* **1998**, *276*, 77.
(19) Bokias, G.; Hourdet, D. Manuscript in preparation.
(20) Smid, J.; Fish, D. Polyelectrolyte Complexes. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley-Interscience: New York, 1988; Vol. 11, p 720.
(21) Piculell, L.; Lindman, B. *Adv. Colloid Interface Sci.* **1992**, *41*, 149.
(22) Goddard, E. D.; Ananthapadmanabhan, K. P. In *Interaction of Surfactants with Polymer and Proteins;* CRC Press: Boca Raton, FL, 1992.
(23) Petit, F.; Audebert, R.; Iliopoulos, I. *Colloid Polym. Sci.* **1995**, *273*, 777.
(24) Borrega, R.; Tribet, C.; Audebert, R. *Macromolecules* **1999**, *32*, 7798.
(25) Zana, R. In *Surfactant Solutions: New Methods of Investigation;* Zana, R., Ed.; Surfactant Science Series Vol. 22; Marcel Dekker: New York, 1987.
(26) Schild, H. G. *ACS Symp. Ser.* **1991**, *No 467*; Chapter 16.

MA001423O