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Positively Charged Amphiphilic Polymers Based on Poly(*N*-isopropylacrylamide): Phase Behavior and Shear-Induced Thickening in Aqueous Solution

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ABSTRACT: The phase behavior and rheological properties of hydrophobically modified copolymers based on a thermosensitive *N*-isopropylacrylamide backbone are reported. These polymers bear a rather high fraction (5−25 mol %) of octyl, dodecyl, or octadecyl side groups, and their solubility in water is ensured by positive charges, introduced to the same unit as the alkyl side group. Their phase behavior is governed by the competition between the hydrophilic character of the charges and the hydrophobic character of the alkyl groups. Thus, the cloud point temperature, T_{CP}, and the turbidity level above T_{CP} depend strongly on the alkyl length, the modification degree, and the polymer concentration. From the rheological point of view, the dodecyl- and octadecyl-modified polymers are powerful shear thickening materials in aqueous solution. The sharpness of this shear-induced thickening phenomenon and the critical shear rate at which it occurs depend on various factors: length of the alkyl groups, modification degree, polymer concentration, and temperature. Possible mechanisms responsible for this behavior are discussed.

Introduction

Hydrophobically modified water-soluble polymers (HM-WSP) have attracted an increasing interest over the past 15 years due to their original thickening properties in aqueous solutions.[1−4] Their structure generally consists of a hydrophilic backbone (usually nonionic or fully charged), with various hydrophobic groups, typically long alkyl chains, attached. In aqueous solution, these groups self-assemble to form hydrophobic aggregates. When the polymer concentration is lower than a characteristic value, $C_P°$, intrachain hydrophobic aggregates may form particularly when the polymer is nonionic. This leads to the shrinkage of the individual polymer chains and to a decrease in its viscosity, compared to that of the precursor, i.e., the corresponding unmodified polymer.[5−8] Conversely, at polymer concentrations higher than $C_P°$, interchain aggregation is favored, and a transient network can be formed. Above the so-called gelation threshold the dynamics of the system is governed by the effective lifetime of reversible junctions,[9,10] and the macroscopic result is a pronounced viscosity enhancement or gelation. These rheological properties are sensitive to the shear rate since the reversible junctions between the polymer chains, stabilized by the relatively weak hydrophobic interactions, can break and re-form under flow. The main consequence is the well-known shear-thinning behavior, reported for most of the associative polymer solutions. However, the opposite behavior, shear thickening, i.e., the viscosity enhancement under flow, is rarely observed in aqueous solution of water-soluble polymers.[11−15] In most cases shear thickening is not very pronounced and occurs only at rather low shear rates. In fact, when high shear rates are applied, the expected shear-thinning behavior is again observed. With the exception of some special cases,[11,12] this behavior is observed in aqueous solutions, mainly with polymers that are both charged and hydrophobically modified.[13−15] However, the most spectacular examples of shear-induced thickening have been observed in the fields of wormlike micelles, concentrated suspensions, and ionomers.[16] To explain the shear-thickening behavior of the latter systems, several theoretical approaches have appeared over the past 15 years.[17−20] Note that a strong shear thickening has been reported for mixtures of water-soluble polymers with colloidal particles.[21]

In this work we are interested in the shear-thickening behavior of hydrophobically modified copolymers based on *N*-isopropylacrylamide, NIPAM. These copolymers contain amphiphilic units combining an alkyl group with a cationic charge (Chart 1). Their synthesis and characterization are reported elsewhere.[22]

The well-known thermosensitive character of poly(*N*-isopropylacrylamide), PNIPAM, has been the subject of numerous studies during the past two decades.[23] In water, this polymer has a lower critical solution temperature (LCST) at around 33 °C. When the temperature, *T*, exceeds the LCST, the aqueous solution separates into two phases, with most of the polymer in the concentrated phase.[24] Macroscopically, one can easily determine the phase separation temperature, T_{CP}, as the solution turns cloudy when it reaches the two-phase region. As T_{CP} is approached, water becomes a progressively poor solvent for the PNIPAM, causing the chains to shrink and progressively the viscosity of the solution decreases.[24−26] T_{CP} can be adjusted to higher or lower temperatures by copolymerizing NIPAM with more or less hydrophilic comonomers.[27−29] For example, the introduction of charged comonomers into the PNIPAM chain leads to a substantial increase of its LCST,[29−33] due to the very high translational entropy contribution of the counterions. On the other hand, the copolymers of NIPAM with nonionic monomers containing long alkyl chains, such as octadecyl groups, show solubility

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Chart 1. Chemical Structure of the Hydrophobically Modified Polymers Based on NIPAM, Denoted PNIPAM*x*-*x*C*n*

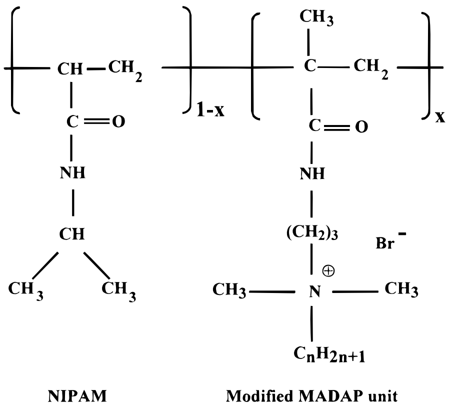


Table 1. Characteristics of the Precursors and the Hydrophobically Modified Polymers Used in This Study

			Br/C (w/w)		
polymer	$[\eta]^a$ ($cm^3\ g^{-1}$)	$M_w{}^b \times 10^{-6}$	analytical structure	titration[c] of Br^-	elemental analysis
PNIPAM5-5	220	1.0			
PNIPAM5-5C8			0.053	0.049	0.043
PNIPAM5-5C12			0.051	0.052	0.047
PNIPAM5-5C18			0.049	0.050	0.046
PNIPAM10-10	232	1.1			
PNIPAM10-10C8			0.097	0.092	0.091
PNIPAM10-10C12			0.096	0.103	0.118
PNIPAM10-10C18			0.088	0.090	0.094
PNIPAM25-25	280	1.5			
PNIPAM25-25C8			0.198	0.203	0.205
PNIPAM25-25C12			0.177	0.171	0.170

[a] The intrinsic viscosities, $[\eta]$, of the precursors were measured at 20 °C in 0.5 M $LiNO_3$ solution. The polymers were in their nonionic (amine) form. [b] Molar masses, M_w, were estimated from the relation $[\eta] = 0.047 M_w{}^{0.61}$ (0.5 M $LiNO_3$; $T = 20$ °C).[52] This relation has been established for PNIPAM, and therefore it provides only a very rough estimation of the molar mass of our copolymers. However, the influence of MADAP units to $[\eta]$ is not expected to be strong because of the conditions used: nonionic form of the precursors ($n = 0$) and relatively high ionic strength. Moreover the same synthesis procedure was applied for the three precursors. [c] The w/w calculations are based on the known chemical structure of the precursor, considering that an amount, equivalent to the titrated Br^- ions, of MADAP units are quaternized.

problems since now the LCST is shifted to very low temperatures as a result of the increased polymer hydrophobicity.[34-36] Generally, the incorporation of these groups is limited to low values (up to 5 mol % and, usually, less than 1%),[37-45] to preserve solubility in water. The copolymers studied here contain both charged groups and alkyl chains. Because of the competition between these two opposite characters, they present an interesting phase behavior in water. For the same reason, they exhibit a spectacular rheological behavior, remarkably different from the one usually observed with other associative polymers.

Experimental Part

Polymers. In Table 1 the polymers used in this study are listed. Their synthesis involves the following steps.[22] Initially, the precursors were synthesized in aqueous medium, via a copolymerization reaction between NIPAM and an amine group containing monomer, *N*,*N*-[(dimethylamino)propyl]-methacrylamide, MADAP. The second step consisted in the alkylation of the amine groups with an alkyl bromide in $CHCl_3$ at 59 °C. It has been shown that, under these conditions, the resulting copolymers have a rather random microstructure.[22] The molar mass of the precursors (the nonquaternized copolymers) was estimated around (1−1.5) × 10^6 from intrinsic viscosity measurements. No residual MADAP units have been detected, by acid−base titration, on the quaternized samples. Moreover, the Br^- titration and the elemental analysis data, shown in Table 1, confirm the complete quaternization of the precursors. For the sake of comparison, the properties of the precursors have been studied in the acid (cationic) form, and the data are reported in the Experimental Section together with those of the quaternized derivatives.

A precursor denoted, for instance, PNIPAM10-10 is a NIPAM−MADAP copolymer containing 10 mol % MADAP, and all the MADAP units are neutralized with HCl. A modified polymer denoted, for instance, PNIPAM10-10C18, is a NIPAM−MADAP copolymer containing 10 mol % MADAP fully quaternized with octadecyl bromide. For the general formula, PNIPAM*x*-*x*C*n*, see Chart 1.

Turbidimetry. The turbidity measurements were performed with a spectrophotometer SPF-500C from SLM AMINCO, equipped with a thermostated cell. The wavelength of the incident beam was 500 nm, and the scattered light at 90° was measured. The temperature was changed manually, and the sample was allowed to equilibrate for at least 15 min at each temperature.

Rheology. A Rheometrics RFS II fluids spectrometer, equipped with a Couette geometry, was used for the rheology measurements. The shear rate was increased continuously with a rate of ~10 s^{-1}/min. The samples that possessed shear thickening properties were allowed to relax for at least 20 min before starting the measurements.

Sample Preparation. For each copolymer, a concentrated solution was first prepared and allowed to equilibrate under gentle stirring for at least 24 h. The other concentrations were prepared by the appropriate dilution of the initial solution. All measurements were performed at least 24 h after sample preparation. Water was purified with a Millipore system, combining inverse osmosis membrane (Milli-R) and ion-exchange resins (Milli-Q).

Results and Discussion

Turbidimetry. In Figure 1 the turbidity curves for the NIPAM copolymers modified with octyl groups (Figure 1a) or dodecyl groups (Figure 1b), at a polymer concentration $C_P = 0.02$ g cm^{-3}, are presented. For comparison, the turbidity curve obtained with a homopolymer PNIPAM of similar molar mass has also been plotted. When the temperature reaches T_{CP}, an abrupt increase in turbidity is observed for the PNIPAM solution. The onset of the turbidity curve, at 33 °C, corresponds to the cloud point of our sample. It should be noted that the precursors (PNIPAM5-5, PNIPAM10-10, PNIPAM25-25), under ionized form, are soluble in the whole temperature range, 0−100 °C, at this polymer concentration. This is obviously due to the incorporation of ionic groups into the polymer chain.

On the contrary, the solutions of the copolymers modified at 5 and 10 mol % with octyl groups (Figure 1a), although they are charged similarly to their corresponding precursors, turn turbid when temperature increases. When the content in charged octyl units increases, the cloud point is shifted to higher temperatures, so that PNIPAM25-25C8 does not exhibit any significant turbidity in the entire temperature range studied, at this polymer concentration. It seems that the hydrophobic character of the octyl groups is not strong enough to compensate for the strong hydrophilic character of the charges. Thus, the cloud point of these copolymers progressively increases as *x* increases. However, they still remain less hydrophilic than the corre-

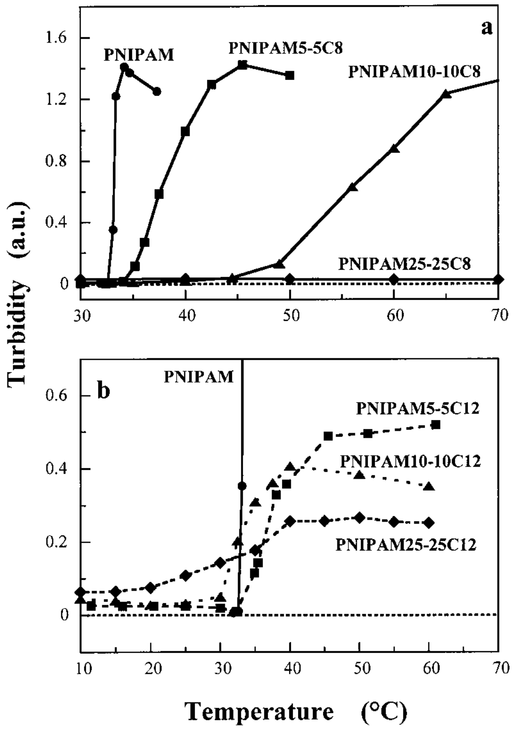


Figure 1. Turbidity curves for the octyl-modified (a) and dodecyl-modified (b) NIPAM-based copolymers. $C_P = 0.02$ g cm^{-3}. (●) PNIPAM, (■) PNIPAM5-5C8 or PNIPAM5-5C12, (▲) PNIPAM10-10C8 or PNIPAM10-10C12, (◆) PNIPAM25-25C8 or PNIPAM25-25C12.

sponding ionic precursors, which do not show any turbidity under these conditions.

Rather different is the behavior of the copolymers modified with dodecyl groups (Figure 1b). Now, the strong hydrophobic character of the dodecyl groups prevails, or at least compensates, the hydrophilic character of the charges. A slight decrease of T_{CP} is therefore observed as x increases. In addition, as in Figure 1a, the slope of the turbidity curves decreases when increasing x.

It is worth noting that all the charged hydrophobically modified polymers shown in Figure 1 (and also those given in the following figures) do not form two well-separated phases, even at temperatures much higher than the cloud point. Instead, they appear in the form of turbid suspensions, stable for several hours. These suspensions are probably stabilized by the charged units of the polymer, as was also observed by other researchers for slightly charged NIPAM-based polymers.[46,47]

A remarkable observation is that the turbidity of the C12 derivatives above the T_{CP} is lower than that of the corresponding C8 derivatives, and it seems even to decrease when x increases. This is further confirmed when comparing the 5-5Cn derivatives (Figure 2). Although the onset of the turbidity seems to follow the expected order, the turbidity at high temperatures becomes progressively weaker as the length of the alkyl group increases. Of course, the phase separation behavior depends also on the polymer concentration, but the general trends as a function of n and x are still the same.

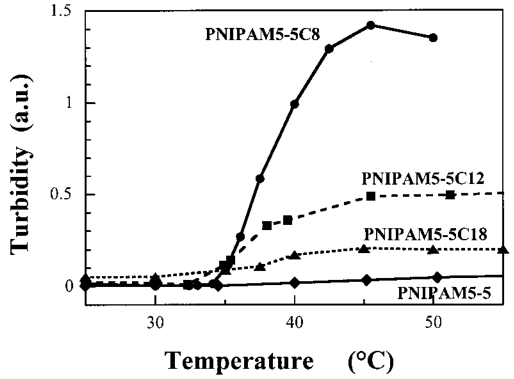


Figure 2. Influence of the alkyl length on the turbidity behavior of the NIPAM-based copolymers containing 5 mol % amphiphilic units. $C_P = 0.02$ g cm^{-3}. (◆) PNIPAM5-5, (●) PNIPAM5-5C8, (■) PNIPAM5-5C12, (▲) PNIPAM5-5C18.

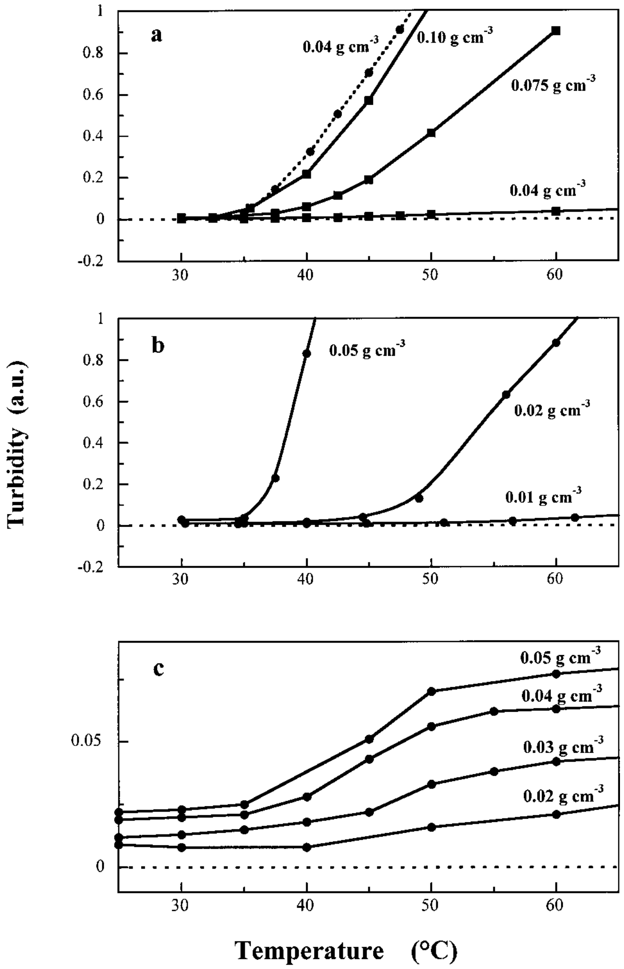


Figure 3. Concentration dependence of the turbidity behavior of (a) PNIPAM10-10 (■) and PNIPAM5-5 (●), (b) PNIPAM10-10C8, and (c) PNIPAM10-10C18.

The effect of the polymer concentration on the turbidity behavior is shown in Figure 3. It is remarkable that even the precursors, in their charged form, turn turbid at high temperatures provided that the polymer concentration is high enough (Figure 3a). Apparently, at high polymer concentration, the self-screening of the charged groups reduces their ability to keep these copolymers soluble, a phenomenon also observed with NIPAM−(sodium acrylate) copolymers.[48] The polymer concentration effect depends on the charge density of the polymer in the expected order; i.e., PNIPAM5-5 exhibits higher turbidity than PNIPAM10-10 (compare curves at $C_P = 0.04$ g cm^{-3} in Figure 3a), while PNIPAM25-25 does not show any turbidity in the temperature range studied, at least for C_P up to 0.1 g cm^{-3}. Figure 3b,c confirms that the effect of the polymer concentration is also observable for the hydrophobically modified derivatives. The C8 derivative forms more turbid solutions than the precursor, while the C18 one exhibits a remarkably low turbidity even at $C_P = 0.05$ g cm^{-3}. (Note that in Figure 3c the *y*-axis scale has been expanded.) The C12 derivatives show an intermediate behavior. It has not been possible to perform turbidity measurements for the PNIPAM10-10C18 at higher concentrations because it forms extremely viscous solutions or gels that are difficult to handle. However, visual inspection of these samples confirms the very low turbidity at high temperatures.

The origin of this surprising turbidity behavior is possibly due to the ability of the alkyl groups to self-assemble, in aqueous solutions, in micellar-like structures stabilized by the charged groups. Indeed, the formation of micellar structures for nonionic hydrophobically modified PNIPAM, below the LCST, has been demonstrated.[34,35,45] These structures are better organized as the alkyl length (*n*) or the alkyl content (*x*) increases. However, for the nonionic copolymers, the micellar structures are disrupted at temperatures above the LCST, and a phase separation similar to that of the homopolymer takes place.[35] In the case of our copolymers, the charges seem to stabilize the formed micellar structures and operate against the full collapse of the polymer chains and the formation of a polymer-rich phase. Indeed, Spafford et al. have recently reported[45] that anionically charged NIPAM-based copolymers, containing a small fraction (1 mol %) octadecyl groups, phase-separates at higher temperatures compared to the charged nonhydrophobic analogues. In our systems, where the fraction of charged alkyl groups is rather high, the stabilization of such micellar-like aggregates is more favorable. It is expected that these mixed aggregates contain the alkyl groups and NIPAM segments in the center, while the cationic charges are located on the surface. The repulsive electrostatic interactions between the aggregates prevent the system from phase separation. Within this model, the amphiphilic units of the copolymer are expected to behave as added surfactant. Indeed, it is well-known that PNIPAM associates with surfactants, such as sodium dodecyl sulfate.[49,50] This association starts below the LCST of PNIPAM and persists above it. As a result, the macroscopic phase separation, detected by the appearance of turbidity, is shifted to higher temperatures, and even then, the turbidity of the mixed system is less pronounced than in the absence of surfactant. To fully clarify the mechanism behind the observed turbidity behavior of our copolymers, more studies are needed for the detailed characterization of the structures formed below and above the LCST.

Rheology. In Figure 4 is presented the rheological behavior of copolymers containing 10 mol % MADAP, at $T = 25$ °C and $C_P = 0.05$ g cm^{-3}. The precursor, PNIPAM10-10, exhibits a typical behavior for a semidilute polymer solution: after a Newtonian plateau, a shear-thinning behavior is observed at higher shear rates. The behavior of PNIPAM10-10C8 is similar with the exception that the curve is shifted to lower viscosity values. This is a general observation for all the octyl-modified samples (results not shown here), which is in agreement with the "phase behavior" of these polymers: the introduction of the octyl groups results in a slight increase of their hydrophobicity (turbidity results) and in the moderate shrinkage of the polymer chain (rheological results) but does not lead to any dramatic change of the copolymer behavior in water, compared to the corresponding precursors.

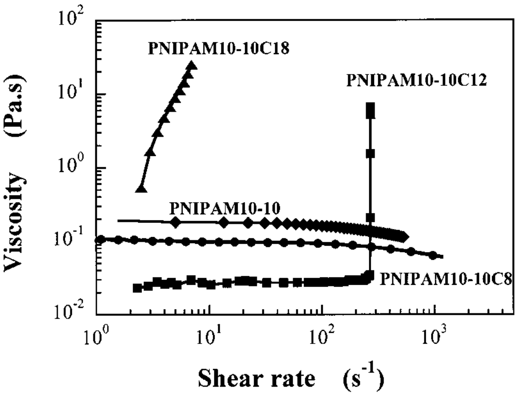


Figure 4. Viscosity as a function of shear rate for the NIPAM-based copolymers modified at 10 mol % with alkyl groups of various length. $C_P = 0.05$ g cm^{-3}. (◆) PNIPAM10-10, (●) PNIPAM10-10C8, (■) PNIPAM10-10C12, (▲) PNIPAM10-10C18.

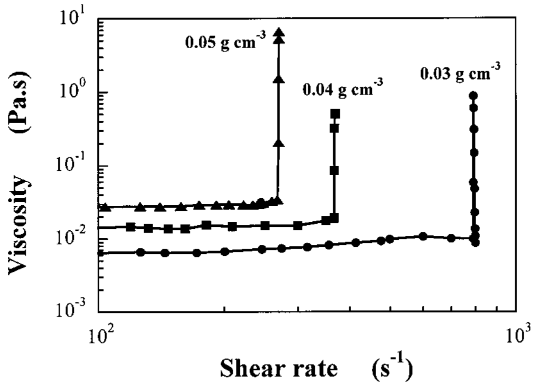


Figure 5. Influence of the polymer concentration on the shear-thickening properties of the copolymer PNIPAM10-10C12 at 25 °C: (▲) $C_P = 0.05$ g cm^{-3}, (■) $C_P = 0.04$ g cm^{-3}, (●) $C_P = 0.03$ g cm^{-3}.

On the contrary, the copolymers modified with longer alkyl chains display an unusual rheological behavior. At low shear rates, PNIPAM10-10C12 has a viscosity significantly lower than the precursor, indicating that the copolymer coil has now shrunk greatly. Indeed, at this concentration, the cloud point of this copolymer is ~27 °C, only slightly higher than the temperature of the viscosity measurement (25 °C). The viscosity remains low up to a critical shear rate, γ_{cr}. At this shear rate, a rheological transition takes place and the solution becomes gellike. The increase in viscosity is so abrupt that the apparatus fails to give reliable measurements at $\gamma > \gamma_{cr}$. For this reason, in Figures 4−6 no data are given for $\gamma > \gamma_{cr}$.

PNIPAM10-10C18 presents a similar pronounced shear-thickening behavior (Figure 4). Although at rest the solution seems to be very fluid (visual observation when smoothly tilting the sample), the shear-thickening behavior is observed at very low shear rates. Consequently, it has not been possible to measure the plateau viscosity at low γ for this copolymer.

The influence of the polymer concentration on the shear thickening properties of PNIPAM10-10C12 is presented in Figure 5. When the polymer concentration decreases, the viscosity at low shear rate decreases and γ_{cr} increases. Obviously, a higher stretching of the

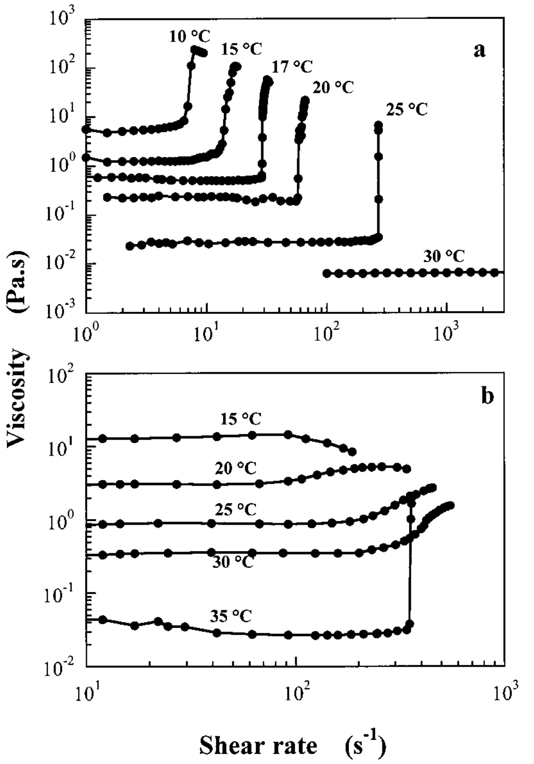


Figure 6. Temperature dependence of the shear-thickening properties of PNIPAM10-10C12 (a) and PNIPAM5-5C12 (b). $C_P = 0.05$ g cm^{-3}.

polymer chains is needed to achieve interchain connectivity.

The temperature dependence of the rheological behavior of PNIPAM10-10C12 and PNIPAM5-5C12 at $C_P = 0.05$ g cm^{-3} is given in Figure 6. For both copolymers, a progressive increase of the viscosity at low shear rate is observed as the temperature decreases. This can be attributed to the combined effect of several factors: (a) Improvement of the solvent quality at lower temperatures resulting in the unfolding of the polymer chains. This is due to the thermosensitive nature of the PNIPAM segments. (b) Increase of the friction coefficient between segments of different polymer chains. In this term are included two contributions. The first is related to the usual backbone-to-backbone contacts. The second is due to the formation of interchain hydrophobic aggregates. For PNIPAM10-10C12, there is a simultaneous shifting of γ_{cr} to lower values: for instance, γ_{cr} decreases from $\sim$250 s^{-1} at 25 °C to $\sim$7 s^{-1} at 10 °C (Figure 6a). The rheological transition remains very abrupt regardless of the temperature.

For PNIPAM5-5C12, the temperature effect is qualitatively different (Figure 6b). As the temperature decreases, the shear-thickening transition becomes smoother, and pure shear thinning is observed at 15 °C. A sharp shear-thickening behavior is only seen close to the cloud point ($\sim$35 °C).

From the plateau values of the viscosity ($\gamma < \gamma_{cr}$), it is possible to estimate the activation energy of the flow process, E_a. In fact, PNIPAM5-5C12, PNIPAM10-10C12, and the corresponding precursors present an Arrhenius type behavior as a function of the temperature. The data are summarized in Table 2. For the sake of comparison, E_a for a PNIPAM solution has been included. The precursors, PNIPAM5-5 and PNIPAM10-10, have an activation energy close to that of PNIPAM. The incorporation of dodecyl groups in the copolymers results in a clear enhancement in E_a, which can be attributed to the stronger attractive interactions between macromolecules. It is evident that E_a increases with increasing polymer hydrophobicity: it passes from 180 to 235 kJ/mol when the dodecyl content increases from 5 to 10 mol %.

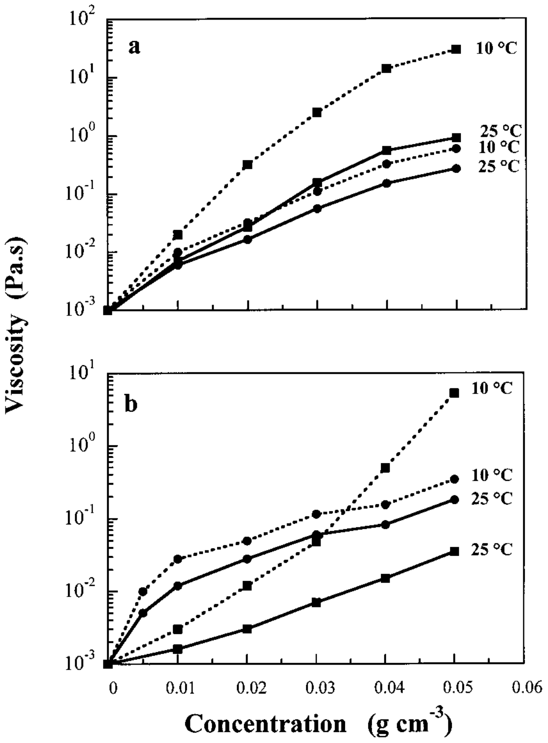


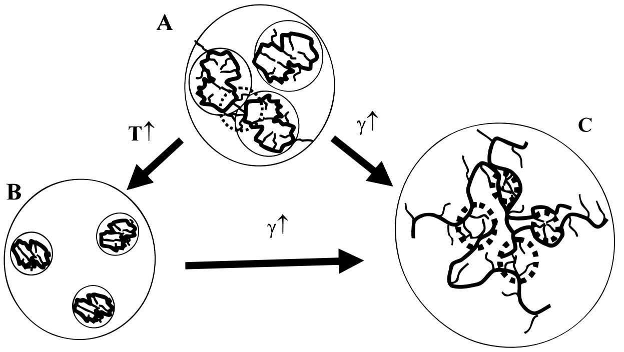
Figure 7. Low shear rate viscosity versus polymer concentration for (a) PNIPAM5-5 (●) and PNIPAM5-5C12 (■) and (b) PNIPAM10-10 (●) and PNIPAM10-10C12 (■). Temperature: 25 °C (solid curves) and 10 °C (dotted curves). Shear rate: 1 s^{-1}.

Table 2. Activation Energy, E_a, of the Flow Process at Low Shear Rate of the Precursors and the Dodecyl-Modified Products ($\gamma < \gamma_{cr}$; $C_P = 0.05$ g cm^{-3})

	E_a (kJ/mol)	
polymer	precursor	C12 derivative
PNIPAM5-5	40	180
PNIPAM10-10	30	235
PNIPAM	40	

The viscosity at low shear rates gives information about the conformation of the polymer chains and the association between them. In parts a and b of Figure 7, the low shear rate viscosity ($\gamma = 1$ s^{-1}) has been plotted as a function of polymer concentration for the two modified polymers, PNIPAM5-5C12 and PNIPAM10-10C12, respectively. The results, at 10 and 25 °C, are compared to those obtained with the corresponding precursors, which display the typical viscosity increase as a function of C_P. A similar viscosity increase is observed for PNIPAM5-5C12 at 25 °C (Figure 7a). The corresponding viscosity curve is shifted to higher values in the whole concentration range, although the difference with the precursor curve at 25 °C is not much pronounced. However, at 10 °C, the viscosity enhancement for PNIPAM5-5C12 is much more important, reaching 2 orders of magnitude for the most concentrated solutions. When the hydrophobic level is increased, the change of the viscosity is clearly more significant (Figure 7b). For PNIPAM10-10C12 at 25 °C,

Chart 2. Schematic Representation of the Possible Mechanism Behind the Shear-Thickening Properties of the NIPAM-Based Hydrophobically Modified Polymers in Aqueous Solution[a]



[a] For the sake of clarity, we have drawn individual polymer coils in the states A and B, although the phenomenon is observed in the semidilute concentration region. At rest (state A), polymer chains form mainly intrachain hydrophobic aggregates, with a possibility of some interchain junctions. When shear is applied, these aggregates are deformed. Above γ_{cr}, additional interchain hydrophobic junctions are formed, and the system behaves as a reversible network (state C). By increasing temperature (state B), the polymer chains shrink and the intrachain hydrophobic aggregates are reinforced. Now, higher shearing is needed to pass to state C.

i.e., close to the cloud point temperature, viscosity values are lower by 1 order of magnitude in the whole concentration range compared to the viscosity of the corresponding precursor. The same comment also holds at 10 °C in the low-concentration region. However, now the viscosity increases dramatically with concentration, so that at $C_P = 0.05$ g cm^{-3} the viscosity of PNIPAM10-10C12 is about 1 order of magnitude higher than that of the precursor.

The behavior of PNIPAM10-10C12, at 10 °C, strongly resembles the behavior of nonionic hydrophobically modified polymers: their viscosity is lower than that of the precursor, and it increases rapidly, exceeding the viscosity of the precursor, when the polymer concentration increases.[5−8] In those cases, it has been shown that the hydrophobic groups form mainly intrachain aggregates at low concentrations, explaining the low-viscosity values. As the concentration increases, the polymer chains start to overlap and interchain aggregation occurs. The interchain hydrophobic aggregates now connect several polymer chains, inducing a large viscosity enhancement. When the temperature increases to 25 °C, the cloud point of the polymer is approached. As the polymer now “feels” a poor solvent, the coils contract, favoring intrachain aggregates, resulting in low-viscosity values for a much larger concentration regime.

The possible mechanism involved in the shear-thickening behavior of these NIPAM-based hydrophobically modified polymers has been sketched in Chart 2. At low temperatures and low shear rates, the polymer chains form mainly intrachain aggregates, with a probability of interchain connections, depending on the polymer concentration and the modification degree. When the shear rate reaches a critical value γ_{cr}, the deformation (elongation) of the compact coils or aggregates becomes sufficient to establish new physical contacts with their neighbors and to induce the formation of some extra interchain aggregates which stabilize more efficiently the transient interchain network. Upon heating, the (thermosensitive) polymer chains shrink more, and the intrachain aggregates are favored toward the interchain ones. In this case, a higher shear rate is needed to shift the intrachain ↔ interchain equilibrium to the right side. The description is equivalent when the polymer concentration is decreased. In this case, the polymer chains have less contacts, and the interchain aggregates are disfavored toward the intrachain ones. A higher shear rate is therefore needed to deform efficiently the polymer chains and to enable the formation of interchain aggregates.

We note again that this is only a schematic description of the possible mechanism behind the observed phenomenon. The polymer chains and the aggregates, in Chart 2, are not drawn to scale. Furthermore, at this polymer concentration, the solution is in the semidilute regime,[51] which is difficult to sketch without losing clarity in the chart. To get more insight into the shear-thickening mechanism, several questions need to be answered such as the following: Is the shear-thickening phenomenon just due to the balance between intra- and interchain association? Does the total concentration of aggregates change under shearing? Do the NIPAM units participate in the formation of mixed aggregates?

To answer these questions, further studies are underway. Fluorescence techniques, light scattering, and X-ray scattering could give information on the size of the aggregates and of the polymer coil. In this context, PNIPAM5-5C12 might be an excellent candidate since it presents the entire spectrum of behavior from shear thinning to pronounced shear thickening as a function of temperature (see Figure 6b). The role of the nature of the backbone will be investigated by replacing NIPAM with the more hydrophilic *N*,*N*-dimethylacrylamide.

Conclusion

Compared to most of the associative water-soluble polymers, the hydrophobically modified copolymers presented in this work are characterized by two special features: (a) they consist of a thermosensitive backbone, and (b) they contain equal amounts of charges and side alkyl groups, each charge being directly linked to the alkyl group. The combination of these two features results in a complex phase behavior and in spectacular rheological properties.

When the alkyl groups are not very long, for instance octyl groups, the hydrophilic character of the positive charges prevails over the hydrophobic contribution of the alkyl chains. Thus, the cloud point of these copolymers increases as the content of the charged octyl units increases. Nevertheless, their overall hydrophobicity seems higher than the corresponding unmodified precursors.

Increasing the length of the alkyl groups to dodecyl (and finally to octadecyl) results in pronounced changes in the phase and rheological behavior of the copolymers. The hydrophobic character of the dodecyl groups seems strong enough and prevails over the hydrophilic character of the charges. For instance, the cloud points are shifted to lower temperatures as the content of the charged dodecyl units increases. On the other hand, the octadecyl derivatives, despite their strong hydrophobic character, exhibit a very low turbidity at high temperatures, i.e., when $T > T_{CP}$.

The rheological properties of the aqueous solutions of these copolymers are also remarkable. At low shear rate, the polymer coils adopt a rather compact conformation, probably due to the formation of intrachain hydrophobic aggregates. Under flow, the disruption of some of these aggregates and their replacement by interchain ones leads to a dramatic viscosity enhancement or even gelation in some cases. Although a displacement of the equilibrium from intrachain to interchain aggregates should take place under flow, a complete interpretation of the mechanism governing the shear-induced thickening is not yet available. Certainly, the relative hydrophobicity of the PNIPAM backbone and the possibility of interactions with the side alkyl groups should be taken into account.

The copolymers modified with dodecyl groups offer a nice example of how one can effectively control the rheological response of an associative polymer solution by an appropriate choice of the chemical structure and of the external conditions. At low temperatures (i.e., in good solvent conditions), the less modified derivatives (e.g., PNIPAM5-5C12) exhibit the thickening properties usually observed with associative water-soluble polymers. It was observed that, by increasing the temperature, these thickening properties weaken at zero shear rate, but a strong thickening is observed at higher γ. This shear-induced thickening becomes more and more dramatic as the cloud point temperature is approached. In fact, it appears possible to control the rheological transition (the critical shear rate domain and the extent of viscosity enhancement) by the choice of the modification degree of the polymer, the length of the alkyl groups, and the polymer concentration.

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(51) In fact, the overlap concentration, $C^* \approx 1/[\eta]$, can be estimated from the data of Table 1. We find $C^* \approx 0.4$ g cm^{-3} in 0.5 M LiNO$_3$, and of course, it will be much lower in pure water. The estimation of C^* for the modified derivatives is more complicated due to intrachain aggregation.

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