Thermoassociating Poly(*N*-isopropylacrylamide) A–B–A Stereoblock Copolymers

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ABSTRACT: Properties of aqueous solutions of A–B–A stereoblock copolymers with an isotactic poly(*N*-isopropylacrylamide) (PNIPAM) as the other block (either A or B) and atactic PNIPAM as the other block were studied. Introduction of isotacticity lowered the solubility of the polymers in water at room temperature, but the copolymers were found to dissolve easily at 5 °C. Calorimetric scans of the polymer solutions did not reveal other transitions than the typical endotherm close to the cloud point of PNIPAM (32 °C). The transition temperature did not change with polymers with different lengths of the isotactic blocks, but the enthalpy change was significantly lowered compared with atactic PNIPAM. Polymers containing isotactic A blocks were found to exhibit thermothickening property, with enhanced viscosity at room temperature. The polymers formed hydrogels at room temperature at polymer concentrations above 45 g/L, while solutions of polymer containing an isotactic B block did not exhibit enhanced viscosity. Thermothickening was found to occur at lower temperature and lead to more elastic hydrogels with polymers with longer isotactic A block.

Introduction

Among the stimuli-sensitive polymers, poly(*N*-isopropylacrylamide) (PNIPAM) has attracted attention due to its sharp and reversible transition behavior and well-defined lower critical solution temperature (LCST) in aqueous medium around 32–34 °C.[1] However, most of the studies concentrate on atactic poly(*N*-isopropylacrylamide) (PNIPAM) which is soluble in water below its cloud point regardless of molecular weight. Introduction of stereoregularity changes the solubility of the polymers, making isotactic polymers insoluble in water and syndiotactic polymers only barely soluble.[2–4] As recent advances in controlled radical polymerization methods have made the tailoring of stereoregularity possible,[5] resulting polymer structures may be controlled to a great degree. Thus, stereoregular copolymers,[6] or stereoblock copolymers, with only one monomer but with defined blocks of certain stereoregularity may be prepared. Such polymers promise a great degree of versatility for the tailoring the properties of the polymers and their solutions.

An important group of water-soluble polymers are associative ones in which hydrophobic parts of the polymer molecules interact, self-assemble, and enhance the viscosity of aqueous solutions even at low polymer concentrations.[7] Associative PNIPAM polymers have been prepared in order to combine the associative properties with the stimuli responsiveness, as then either of these properties could be utilized to trigger changes in the polymer conformation and the degree of aggregation. Traditionally such polymers, the hydrophobically modified poly(*N*-isopropylacrylamides) (HM-PNIPAMs), have been prepared by copolymerization with non-water-soluble comonomers. Examples of HM-PNIPAMs include random copolymers of NIPAM and *n*-alkylacrylamides,[8–11] telechelic PNIPAM with alkyl chains,[12–14] and A–B–A block copolymers of PNIPAM with polystyrene A blocks.[15] In dilute aqueous solutions HM-PNIPAM chains associate, which often leads to micellization with core–corona structure consisting of hydrophobic core and hydrated PNIPAM corona layer. LCST still exists in HM-PNIPAMs, but the transition temperature decreases. The association phenomenon and lowering of the transition temperature have been observed also for the present partly stereoregular A–B–A block copolymers in dilute solution,[6] leading us to believe that the non-water-soluble isotactic blocks interact in an aqueous solution similarly as the hydrophobic groups in the case of HM-PNIPAMs.

Rheological characterization of aqueous PNIPAM solutions has been reported on unmodified[14,16,17] and hydrophilically[18–20] or hydrophobically[12] modified PNIPAM. Naturally, the interest has in most cases focused around the phase transition temperature of PNIPAM. Although temperature can serve as a trigger, for certain applications it may prove beneficial to have additionally a possibility to adjust the viscosity from low-viscosity solutions to gels or utilize the hydrophobic interactions for binding of non-water-soluble compounds.

This report describes the properties of aqueous solutions of PNIPAM A–B–A stereoblock polymers where an atactic PNIPAM block acts as a hydrophile and a short isotactic PNIPAM as a non-water-soluble sticker. While these polymers are of great interest for studies in dilute solutions, such as the colloidal stability of thermally responsive polymers[21] or the formation of mesoglobules,[22] we now focus on the properties of these polymers in more concentrated solutions, capable of forming gels.

Experimental Section

Materials. The synthesis of the stereoregular polymers via RAFT polymerization has been described in detail elsewhere.[6] The characteristics of the polymers are given in Table 1. Polymers are coded according to the tacticity of the blocks, atactic (a) or isotactic (i), and the number represents the molecular weight of the respective block in kg/mol.

Sample Preparation. Weighed polymer solutions were prepared from freeze-dried polymers dissolved to deionized water (Elga Purelab Ultra) and kept at 5 °C at least overnight before measurements. Samples for the NMR measurements in were made similarly, but instead of deionized water, deuterium oxide, D_2O (Euriso-Top), was used and spectra were referenced using signal from 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (Aldrich).

Differential Scanning Calorimetry (DSC). DSC measurements were performed with a Mettler 822e differential scanning calorimeter under a nitrogen atmosphere. Aqueous polymer solutions (3–12 mg) in aluminum pans were first kept at 0 °C for 1 h and heated using a rate of 1 °C min^{-1}.

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Table 1. Polymer Characteristics

sample[a]	macroRAFT [M_n (g/mol)]	M_n(theor) [g/mol]	M_n(SEC) [g/mol]	M_w/M_n	isotactic (%)
a24.3			24300		
i2-a28-i2	i4.2	32200	36700	1.29	11
i5-a70-i5	i10.2	80200	64700	1.31	13
a12-i5-a12	a24.3	29300	28900	1.32	16

[a] The sample codes refer to the lengths of the atactic block (a, kg/mol) and isotactic block (i, kg/mol).

NMR Spectroscopy. NMR measurements of the polymers in D_2O were measured using a Varian UNITYINOVA spectrometer operating at 300 MHz for protons equipped with a temperature control unit. The ^1H T_2 relaxation measurements from the methyne proton peak at 2 ppm were made using the Carr−Purcell−Meiboom−Gill spin–echo sequence using an array of ∼20 values ranging from 0.002 to 1 s. The self-diffusion coefficients, D_s, of the polymers were measured from the methylene proton peak at 1.5 ppm by the pulsed field gradient NMR method (PFG-NMR) using the stimulated echo sequence.[23] NMR spectra were recorded with field gradient pulse σ duration of 2 ms and dwell times Δ between 120 and 200 ms between the first and last 90° radio-frequency pulse. A series of spectra with linearly incremented gradient strengths from 0 to 65 G/cm were collected. The attenuation of the signal was measured as a function of the applied field gradient strength and the D_s calculated according to

$$\ln[I/I_0] = -(Y_M G\sigma)^2(\Delta - \sigma/3)D_s = -kD_s \quad (1)$$

where I and I_0 are the signal intensities with and without the gradients, γ_M is the gyromagnetic ratio, G is the applied gradient strength, σ is the length of the field gradient pulse, and Δ is the dwell time between the pulses. The gradient strength was calibrated with a water sample at the same temperature. Plotting the natural logarithm of the measured intensities against the gradient strength thus provides the D_s as the slope of the linear fit.

Rheology. TA AR2000 stress-controlled rheometer equipped with 40 mm aluminum 2° cone and a Peltier heated plate was used for the oscillatory and steady shear measurements between 5 and 25 °C. A rest period of at least 10 min was allowed after sample loading and temperature change. Oscillatory frequency and temperature sweeps were made using strains within the linear viscoelastic regime.

Results and Discussion

The characteristics of the studied polymers are listed in Table 1. The atactic homopolymer a24.3 and the polymer having atactic A blocks, a12-i5-a12, were directly soluble in water up to the studied concentrations (90 g/L) at room temperature. On the other hand, the polymers i2-a28-i2 and i5-a70-i5 having isotactic A blocks were only barely soluble in water at room temperature but dissolved completely upon cooling to 5 °C even at concentration of 90 g/L, both forming transparent viscous solutions. Upon heating the aqueous polymer solutions above 32 °C, they become cloudy and, at the studied concentrations, precipitate. Figure 1 displays the photographs of a 90 g/L solution of i2-a28-i2, taken directly from 5 °C, at room temperature, and after heating up to 50 °C. As may be seen in the figure, the solution is clear viscous liquid at low temperatures but further viscosifies upon warming to room temperature and behaves as a hydrogel. This behavior was common for the solutions of polymers with isotactic A blocks, i2-a28-i2 and i5-a70-i5, and with concentration >45 g/L both formed clear gels at room temperature which do not flow in the tube-inversion test.

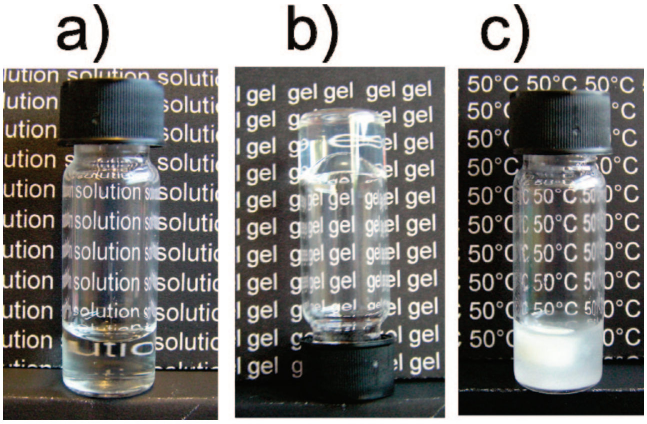

Figure 1. Photograph illustrating i2-a28-i2 45 g/L polymer solution at (a) 5 °C, (b) room temperature, and (c) 50 °C.

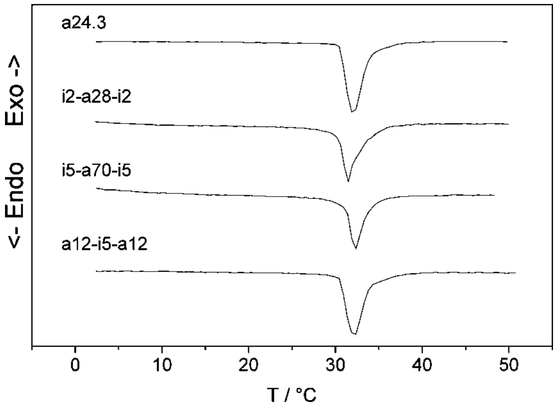

Figure 2. Thermograms of 90 g/L polymer solutions.

Table 2. Calorimetric Data of the Aqueous Polymer Solutions

sample[a]	peak/°C	ΔH/J/g	ΔH/kJ/mol/NIPAM unit	ΔH/kJ/mol/atactic NIPAM unit [b]
a24.3	32.05	4.85	6.06	6.06
i2-a28-i2	31.51	4.04	5.09	5.85
i5-a70-i5	32.03	3.90	4.86	5.57
a12-i5-a12	32.14	4.30	5.27	6.35

[a] Concentration 90 g/L. [b] Enthalpy calculated using M_n(theo) data from Table 1.

In order to study the effect of the stereoregular blocks, the polymer solutions were measured with DSC (see Figure 2 and Table 2). The atactic reference a24.3 and the stereoblock copolymers show endothermic transitions at nearly the same temperature, around 32 °C, upon heating (taken as the peak temperature of the endotherm). The enthalpy of the phase transition (ΔH) per repeating monomer unit for the atactic a24.3 sample corresponds to literature values.[1,24] A comparison between the atactic polymer and the stereoblock copolymers shows that the copolymers containing isotactic blocks have significantly lower transition enthalpy, especially when normalized with respect to the NIPAM units (see Table 2). The calorimetric runs of i5-a70-i5 at lower concentration, from 15 to 45 g/L (data not shown), had the same endothermic transition temperature and enthalpy per repeat unit as with the 90 g/L sample. Calculating the transition enthalpies of the stereoblock copolymers per atactic NIPAM units as shown in Table 2 indicates that the enthalpies correspond rather well to the enthalpy of atactic reference. As no transitions apart from the endotherms at around 32 °C were seen in the thermograms and as the enthalpy clearly decreases with introduction of the isotactic blocks, it can be concluded that at the concentrations studied the endothermic enthalpy change comes from the atactic PNIPAM. Compared with the microcalorimetry experiments in dilute solutions where no significant reduction of endothermic enthalpy change at demixing temperature was observed,[6] the calorimetric studies at higher concentrations show that parts of the isotactic blocks are associated with such a degree that they

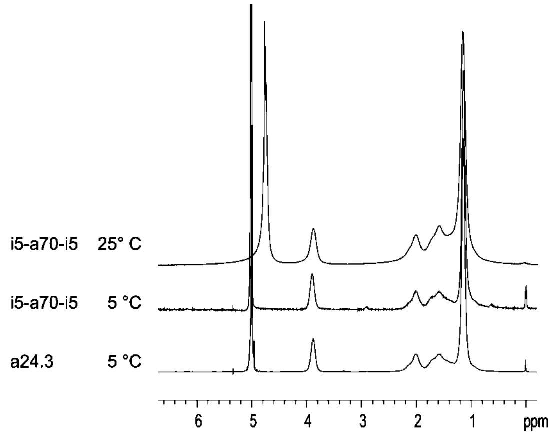

Figure 3. ^1H NMR spectra of the PNIPAM solutions (polymer concentration 55 g/L).

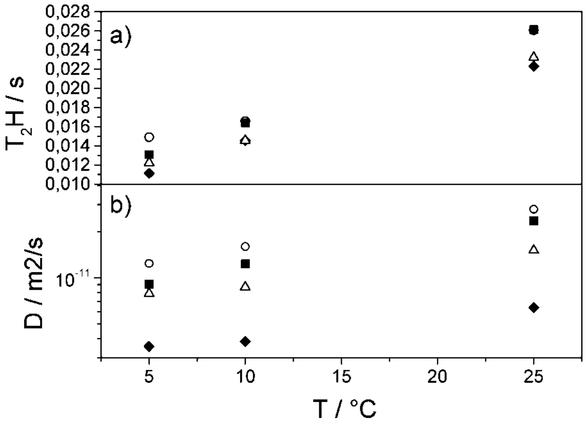

Figure 4. T_2H relaxation times (a) and diffusion coefficients (b) of polymer solutions in D_2O: (○) a24.3, (■) a12-i5-a12, (△) i2-a28-i2, and (◆) i5-a70-i5.

do not interact with water similarly as atactic PNIPAM. This indicates that the degree of association may change with polymer concentration.

^1H NMR spectra were measured for the samples at concentrations of 55 g/L. Figure 3 shows the ^1H NMR spectra of the polymer solutions in D_2O: sample a24.3 at 5 °C and i5-a70-i5 at 5 and 25 °C. Comparison of the spectra shows that in D_2O the isotactic blocks do not give any detectable signal. For the i5-a70-i5, the only notable feature in the spectra is the broadening of the lines due to the slowed dynamics as the sample macroscopically gels. For the other samples, no signals arising from the isotactic blocks or changes due to temperature could be seen in the spectra. The T_2H relaxation times are shown in Figure 4. Though the differences between the samples are small, it can be concluded that the samples having isotactic A blocks, i2-a28-i2 and i5-a70-i5, have shorter relaxation times, indicating more restricted mobility. This restricted mobility originates from the association of the polymers due to the insolubility of the isotactic blocks. Diffusion measurements further confirm the association as the i2-a28-i2 and i5-a70-i5 have significantly lower diffusion coefficients D_s than the atactic a24.3 or a12-i5-a12 at all temperatures. It is noteworthy that all the NMR parameters show linear relationships with respect to temperature. Thus, it is unlikely that an abrupt phase change in the samples takes place, as for example the demixing of atactic PNIPAM results in significant changes in the intensities of different protons in the NMR spectra.[25] As DSC and NMR evidently probe only the atactic part of the polymers, characterization on a macromolecular scale is needed.

The rheological behavior of the solutions corresponds well to the visual inspection of the polymer solutions. As seen in the flow curves in Figure 5, the 90 g/L solutions of a24.3 and a12-i5-a12 show Newtonian behavior at both 5 and 20 °C. The viscosity of these rather concentrated solutions is only roughly a magnitude higher than that of water, this reflecting the relatively small molecular weight of the polymers. The viscosity further decreases when the solutions are heated to 20 °C, showing behavior typical for aqueous solutions of linear PNIPAM below demixing temperature.[14] Quite to the contrary, the A−B−A polymers, having isotactic A blocks, have already at 5 °C much higher viscosities regardless of comparable molecular weight. Heating the 90 g/L i5-a70-i5 and i2-a28-i2 solutions further increases the viscosity although the samples are well below the cloud point of atactic PNIPAM. The flow curves of the solutions of the polymers with isotactic A blocks at room temperature show a typical feature of associating polymers, a change of slope of the flow curve or a slight increase in viscosity, at around shear rate of 1 1/s. Both the enhanced viscosity compared with the atactic reference and the increase in apparent viscosity, thermothickening, clearly indicate the formation of associations between the polymer molecules.

Many hydrophobically associating polymers in aqueous solution exhibit strain hardening behavior under oscillatory shear. Usually the phenomenon is understood to originate from the increased number of intermolecular interactions between adjacent chains at increasing deformation and/or simultaneous stretching of the chains inducing increased rigidity.[26] In the present study the oscillation strain sweep tests were made in order to probe the nature of the association of the polymers with respect to temperature and are shown in Figures 6 and 7. In Figure 6 the 90 g/L solution of i5-a70-i5 shows behavior typical for viscoelastic liquids at 5 °C, the loss modulus G'' being higher than the storage modulus G' and the moduli showing linear region at low strains before the shear thinning region. At 9 °C, G' is higher than G'' at low strains, and a characteristic strain hardening behavior typical for solutions of associating polymer is seen upon increasing strain. Increasing the temperature monotonically increases the value of the G'. In Figure 7 strain sweeps are shown for the 90 g/L i2-a28-i2 solution. Both G' and G'' are lower than those for a i5-a70-i5 solution with equal concentration, and the strain hardening behavior begins to develop at a higher temperature. Although the mass ratios between isotactic/atactic blocks between these two polymers are nearly the same, this behavior obviously originates from the longer isotactic blocks in the case of i5-a70-i5. It shows that the isotactic PNIPAM segments are indeed hydrophobic and act as polymeric stickers in the case of triblock copolymers, similarly as what has been accomplished using modification of atactic PNIPAM by alkyl chains or by using segments of hydrophobic polymers. To the authors' knowledge, such behavior has not been reported for PNIPAM (co)polymers below LCST, which has been known to induce a thermothickening effect in associative polymers.

The frequency sweeps of i5-a70-i5 solution of different concentration are shown in Figure 8. The elastic modulus builds up with increasing concentration, and for the lowest concentration, 24 g/L, the solution behaves as a viscous liquid. For gel-like 90 g/L samples the properties were measured upon lowering the temperature, shown in Figure 9. Cooling the solution clearly decreases the values of the elastic modulus, and samples which are gel-like at room temperature behave as viscous liquids at 5 °C. Some hysteresis can be seen when the data are compared with the strain sweeps in Figure 5 and 6, as the values of the moduli do not cross for the 90 g/L i5-a70-i5 sample, and the temperature at which the moduli of the 90 g/L i2-a28-i2 sample cross upon cooling is lower than that observed upon heating.

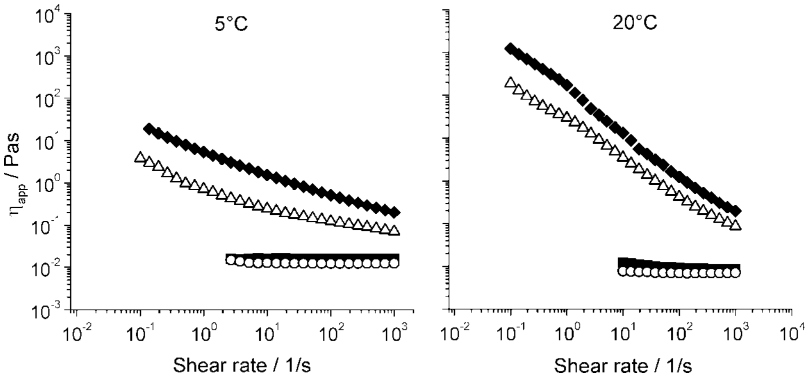

Figure 5. Flow curves of 90 g/L solutions: (○) PNIPAM(a24.3), (■) a12-i5-a12, (△) i2-a28-i2, and (◆) i5-a70-i5.

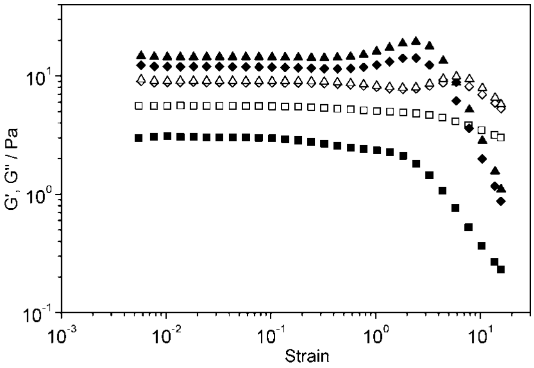

Figure 6. Strain sweeps of 90 g/L i5-a70-i5 solution at oscillation frequency 6.283 rad/s at 5 °C (*G′* (■), *G″* (□)), 9 °C (*G′* (◆), *G″* (◇)), and 13 °C (*G′* (▲), *G″* (△)).

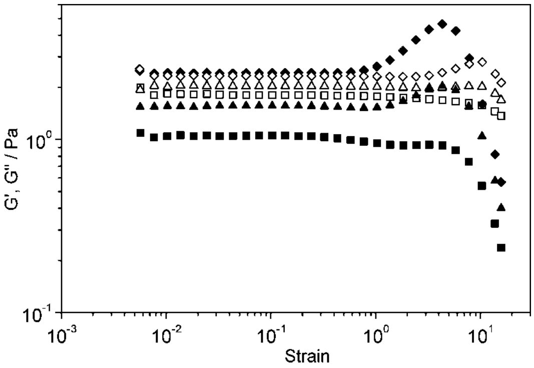

Figure 7. Strain sweeps of 90 g/L i2-a28-i2 solution at oscillation frequency 6.283 rad/s at 12 °C (*G′* (■), *G″* (□)), 14 °C (*G′* (▲), *G″* (◇)), and 16 °C (*G′* (◆), *G″* (△)).

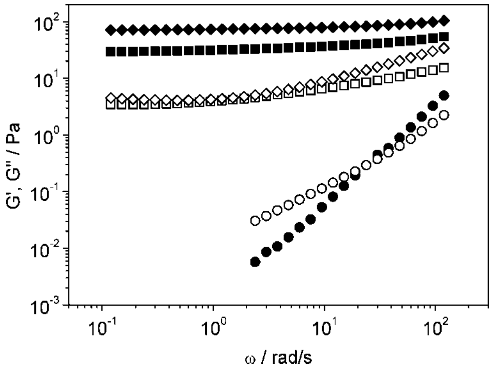

Figure 8. Frequency sweeps of 90 g/L i5-a70-i5 solutions at 20 °C: 25 g/L (●, *G′*; ○, *G″*), 46 g/L (■, *G′*; □, *G″*), and 90 g/L (◆, *G′*; ◇, *G″*).

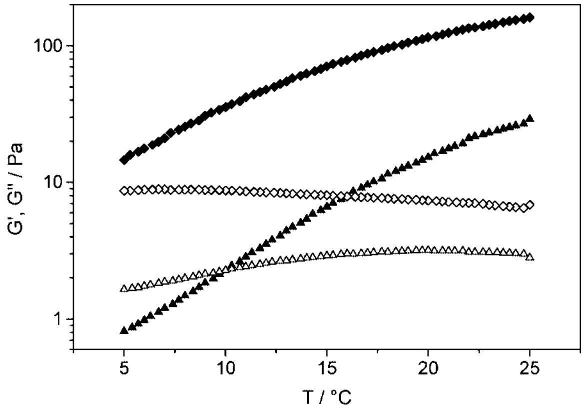

Figure 9. Oscillation temperature sweep upon cooling the 90 g/L i5-a70-i5 (◆, *G′*; ◇, *G″*) and i2a28-i2 solutions (▲, *G′*; △, *G″*). Cooling rate = 0.2 °C/min; oscillation frequency = 6.283 rad/s.

The observed thermothickening is rather unexpected as the increase of thermal motion is likely to speed up molecular dynamics and lead to weaker rheological properties as no LCST is detected. In this sense the presently studied polymers with isotactic A blocks differ significantly from many other associative polymers studied in aqueous solutions. For example, hydrophobically modified acrylamides[27] have been reported to exhibit a decrease in viscosity upon heating due to the decreasing friction between monomer units and the solvent. Also, we have earlier reported on a hydrophobically modified 4-armed star polymer comprising of water-soluble poly(acrylic acid) core and short hydrophobic polystyrene stickers which forms hydrogels at room temperature that soften and behave as viscous liquids upon heating.[28] However, a recent report on hydrophobically modified poly(sodium acrylate), PAANa, grafted with hydrophobic side chains has showed that it is possible to create aqueous thermothickening solution with incorporation of non-water-soluble side chains. The authors studied PAANa grafted with either poly(*n*-butyl acrylate), PNBA, poly(*n*-butyl methacrylate), PNBMA, or poly(*N*-(*tert*-butyl)acrylamide), PTBA.[29] It is interesting to note that the viscosity of the solutions decreased with temperature apart from the polymer grafted with PTBA, which showed mild thermothickening. Although PTBA is not soluble in water (not even at low temperatures), the authors state that its insolubility is further enhanced with increasing temperature. Though insoluble in water, PTBA units are not fully dehydrated at room temperature, and the residual water molecules interact with the polar groups. We believe that same explanation applies to the currently studied isotactic PNIPAM blocks. As is evident from the solubility data, the solubility of the isotactic blocks in water is enhanced at lower temperatures. We postulate that the isotactic structure of the polymer chain leads to different structured water shell than with atactic PNIPAM due to steric constraints. The residual water molecules still interact with the polar groups and rearrange upon heating/cooling. The calorimetric data suggest that this restructuring process is entropic in the case of isotactic PNIPAM, in contrast with the LCST behavior of atactic PNIPAM which is mainly enthalpic. The restructuring of the water shell upon heating increases the interchain association capability. This interesting property of stereoregular PNIPAM allows the properties of these solutions be controlled by tailoring the polymer structure or by adjusting the polymer concentration or temperature. The fact that these stereoblock copolymers consist only of widely studied PNIPAM makes them interesting candidates for example for biomedical applications.

Conclusions

Stereoblock A−B−A copolymers of poly(*N*-isopropylacrylamide) (PNIPAM) were studied. It was found that polymers containing isotactic A blocks were barely soluble in water at room temperature but dissolved easily at 5 °C. At the concentrations studied (>40 g/L) all the polymers had the same phase transition temperature close to the LCST of atactic PNIPAM, but the transition enthalpy decreased in the case of the polymers containing isotactic blocks, coming entirely from the atactic block. Isotactic sequences did not change the ^{1}H NMR spectra of the polymers in D_2O solutions, but the T_2H relaxation times and diffusion coefficients were lower compared with the atactic reference polymer, indicating more restricted motion of the atactic blocks due to interchain association of the polymers. Rheological characterization showed increasing viscosity and evolution of associations with increasing temperature in the case of copolymers with isotactic A blocks well below the phase transition temperature of atactic PNIPAM (∼32 °C). At room temperature clear gels were obtained at polymer concentrations above 45 g/L for polymers having isotactic A blocks. The observed thermothickening is explained by the decreasing polymer–water interactions of the isotactic block with increasing temperature.

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