Amphiphilic telechelic poly(N-isopropylacrylamide) in water: From micelles to gels*

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Abstract. We report the first study of aqueous solutions (0.025 gL⁻¹ to 46 gL⁻¹) of a telechelic poly(N-isopropylacrylamide) with octadecyl termini (C₁₈-PNIPAM-C₁₈, M_w: 37000, 320 NIPAM units, M_w/M_n = 1.07) obtained by reversible addition-fragmentation chain transfer (RAFT) free radical polymerization of N-isopropylacrylamide. Static and dynamic light scattering measurements and fluorescence spectroscopy, using 8-anilino-1-naphthalenesulfonic acid (ANS) as probe, yielded the concentration dependence of the size and aggregation number of C₁₈-PNIPAM-C₁₈ micelles in cold (20±C) dilute aqueous solutions. Concentrated solutions (c > 20 gL⁻¹) form transient gels exhibiting an oscillatory shear behavior that can be approximated by a single-relaxation Maxwellian model. Aqueous solutions of C₁₈-PNIPAM-C₁₈ undergo a phase transition upon heating to 31.5±C as determined by microcalorimetry. The heat-induced phase separation of dilute (0.025 gL⁻¹) C₁₈-PNIPAM-C₁₈ solutions yields a fluid that is colloidally stable at temperatures higher than 33°C. The overall results are consistent with a model assuming the formation of flowerlike micelles in the dilute regime and a network of micelles connected by telechelic chains in the concentrated regime.

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1 Introduction

Among the various families of hydrophobically modified water-soluble polymers, telechelic derivatives bearing hydrophobic end groups have attracted special attention over the years, primarily because of their ability to form flowerlike micellar aggregates which associate above a given polymer concentration, giving highly viscoelastic fluids [1]. Only few examples of such materials have been described, however, and of them, poly(ethylene oxide) (PEO) chains terminated by hydrophobic moieties (HM-PEO) are by far the best known, as they are the key structural components of several water-associative thickeners which have achieved industrial acceptance [2,3]. The hydrophilic to lipophilic balance of the HM-PEO has been shown to be of paramount importance in controlling the viscoelastic properties of their solutions. A number of studies have been carried out using monodisperse PEO chains terminated at either one or both ends with a hydrophobic group. The general conclusion is that, in water, isolated chains exist only when the polymer concentration is extremely low [4]. Beyond a critical association concentration, often so low that it cannot be detected, the chains associate forming rosettes or flower micelles consisting of a core made of the hydrophobic groups and a corona of PEO chains [5–7]. At still higher concentrations, HM-PEO chains form bridges between the rosettes, triggering significant viscosity enhancement and, eventually, leading to the formation of a gel phase [8–11]. This mechanistic scenario has emerged from a large number of investigations using various experimental tools, such as dynamic light scattering, which yields the hydrodynamic radius of the micelles [6,12–15], fluorescence spectroscopy, which allows one to assess the critical association concentration and the aggregation number of the micelles [5,9,10,16,17], ¹H NMR spectroscopy, which provides the self-diffusion coefficient of the molecules [13,18], small-angle X-ray and neutron scattering, which allow an evaluation of the size of the hydrophobic core [19,20], and rheology, which


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permits one to determine the disengagement rate of the hydrophobic group of a bridging chain from the core of one micelle [8,11,14,15].

Our research interests have focused on another water-soluble polymer, poly(N-isopropylacrylamide) (PNIPAM) and its hydrophobically modified derivatives. Like PEO, PNIPAM is a non-ionic polymer soluble in water at room temperature. The two polymers share a number of properties, and have often been compared with regard to their interactions with surfactants and with proteins [21,22]. But, in some important thermal and conformational properties, they markedly differ from each other. For instance, the lower critical solution temperature (LCST) of aqueous PEO solutions shows a strong molecular-weight dependence, while that of PNIPAM is almost independent of the molecular weight, exhibiting very flat cloud point lines. Also, PEO chains are inferred to adopt a loose helical form (11/2 helix) from MD simulation [23], and the size of each turn is such that it can accommodate one water molecule linked to the chain via hydrogen bonds. In contrast, PNIPAM chains are partially collapsed by the association of hydrophobic propyl groups. It seems therefore very interesting to compare the nature of association of polymers with different main chains, PEO and PNIPAM and identical hydrophobic groups at each chain end.

There have been only few comparative studies of the association properties of HM-PEO and HM-PNIPAM, due to difficulties experienced in preparing PEO and PNIPAM samples of similar architecture: PEO can only be modified at the chain ends, whereas PNIPAM, which can be decorated easily with hydrophobic chains grafted along the main chain [24–29], is not readily modified on the chain ends. It has proven possible to prepare semi-telechelic HM-PNIPAMs bearing a hydrophobic group at one chain end, and several studies have been conducted to understand their association in water. There has been a single report on the preparation of telechelic PNIPAMs, for which the end groups were modified with carboxylic acids [30]. We succeeded recently in preparing telechelic PNIPAM samples of narrow molecular-weight polydispersity that bear an octadecyl group at each chain end [31]. The polymers were obtained via radical polymerization with reversible addition-fragmentation chain transfer (RAFT) [32], using a chain transfer agent bearing two n-octadecyl chains (C_{18}). Among the various samples prepared, we selected one telechelic polymer (C_{18}-PNIPAM-C_{18}) (Fig. 1) consisting of ~320 NIPAM units, with molecular weight comparable to that of the telechelic PEO (PEO-35 K), which has been investigated in great details by several research groups [5,6,8,11–13,17,20]. We examined the properties of aqueous solutions of this telechelic PNIPAM in the dilute and concentrated regimes, via static and dynamic light scattering, fluorescence spectroscopy, and rheology. As this telechelic PNIPAM, like PNIPAM itself [33], exhibits a lower critical solution temperature (LCST) in water at ca. 32 °C, the effect of temperature on its solution properties was assessed as well using the same techniques, complemented by microcalorimetry.

2 Materials and methods

2.1 Polymer synthesis and characterization

The telechelic PNIPAM derivative (Fig. 1) $M_w = 37000$, $M_w/M_n = 1.07$ was synthesized by the RAFT polymerization technique as described in detail elsewhere [31]. Briefly, polymerization of N-isopropylacrylamide (NI-PAM) was carried out in dioxane at 65 °C in the presence of azobis(isobutyronitrile) (AIBN) as initiator and S-n-octadecyl-S-(α,α-dimethyl-α′-n-octadecylacetamide)trithiocarbonate (Fig. 1) as RAFT agent. The polymer structure was ascertained by $^1$H NMR spectroscopy (Bruker 500 MHz spectrometer). Molecular-weight characteristics were obtained using a GPC system consisting of an Agilent 1100 isocratic pump, a set of TSK-gel α-M and a TSK-gel α-3000 (Tosoh Biosep) columns, a Dawn EOS multi-angle laser light scattering detector (Wyatt Technology Corp.) and an Optilab DSP interferometric refractometer (Wyatt Technology Corp.); injection volume: 100 µL; flow rate: 0.5 mL min$^{-1}$; eluent: DMF, 40 °C. UV/Visible spectra were measured with a Hewlett Packard 8452A photodiode array spectrometer.

2.2 Differential Scanning Calorimetry (DSC)

DSC measurements were performed on a VP-DSC microcalorimeter (MicroCal Inc.) at an external pressure of ca. 180 kPa. The cell volume was 0.517 mL. The heating rate was 1.0 °C min$^{-1}$. Data were corrected for instrument response time and analyzed using the software supplied by the manufacturer. The polymer concentration was 5.0 g L$^{-1}$.

2.3 Light scattering (LS)

Static (SLS) and dynamic (DLS) light scattering experiments were performed on a CGS-3 goniometer (ALV GmbH) equipped with an ALV/LSE-5003 multiple-τ digital correlator (ALV GmbH), a He-Ne laser ($λ = 632$ nm), and a C25P circulating water bath (Thermo Haake). The temperature was 20 °C unless otherwise stated. The polymer concentration was varied from 0.025 to 5 g L$^{-1}$. Prior
to the measurements, the solutions were filtered directly into the light scattering cells through 0.45 \mu m Millex Milipore PVDF filters.

SLS experiments yield the weight-average molar mass ($M_w$) and the $z$-average root-mean square radius of gyration ($R_g$) of scattering objects in dilute solution, based on the angular dependence of the excess absolute scattering intensity with respect to the solvent $I(q, c)$:

$$\frac{K_c}{I(q, c)} \cong \frac{1}{M_w} \left( 1 + \frac{R_g^2}{3q^2} \right) + 2A_2c,$$

where $c$ is the polymer concentration, $q$ the scattering vector ($q = (4\pi n/\lambda)\sin(\Theta/2)$), $A_2$ the second virial coefficient, $n$ the refractive index of solvent, $\lambda$ the wavelength of the light in vacuum, and $\Theta$ the scattering angle (30°–150°). The scattering constant is $K = 4\pi^2 n^2 dn/dc^2/N_A\lambda^4$, where $dn/dc$ is the refractive index increment and $N_A$ is Avogadro’s number. The $dn/dc$ of hydrophobically end-capped PNIPAM was approximated as 0.162 cm$^3$/g, the value determined for non-modified PNIPAM. The apparent mass of a polymer ($M_{w,\text{app}}$) in a solution of concentration $c$ is obtained by extrapolation of the scattered intensity $I(q, c)/c$ to $q = 0$. The apparent radius of gyration is obtained by a mean-square linear fit of the inverse of the scattered intensity versus $q^2$ (see Eq. (1)), under the assumption that $dn/dc$ is the same in the entire volume of the scattering object. The calculations were performed using the software supplied by the manufacturer of the instrument.

In DLS experiments, one measures the normalized time autocorrelation function of the scattered intensity, which can be expressed in terms of the autocorrelation function of the concentration fluctuations. In our experiments, the relaxations had always a diffusive character with a characteristic time ($\tau$) inversely proportional to $q^2$. A cumulant analysis was applied to obtain the diffusion coefficient ($D$) of the scattering objects in solution. Extrapolation of the first reduced cumulant ($\tau D^{-1}$) to $q = 0$ yields the value of $D$, which is related to the average hydrodynamic radius $R_h$ of the scattering objects via the relation

$$D = \frac{kT}{6\pi \eta_h R_h},$$

where $k$ is the Boltzmann constant, $\eta_h$ the viscosity of the solvent, and $T$ the temperature.

In some cases, the average relaxation time was determined by the CONTIN analysis based on the inverse Laplace transform of the normalized dynamical correlation function of polymer concentration fluctuations. This method is more appropriate for solutions characterized by several relaxation mechanisms. It was found that the relaxation times obtained using this method coincide, within experimental uncertainties, with those calculated by cumulant analysis.

### 2.4 Fluorescence measurements

Steady-state fluorescence spectra were recorded on a Varian Cary Eclipse spectrometer. The temperature control of the samples was achieved using a water-jacketed cell holder connected to a Cary circulating water bath. The temperature of the sample fluid was measured with a thermocouple immersed in a water-filled cell placed in one of the four cell holders in the sample compartment. All measurements were carried out at 20°C unless otherwise stated. 8-Anilino-1-naphthalenesulfonic acid (ANS, Aldrich) was used as a fluorescence probe (concentration: $2.5 \times 10^{-5}$ M). The slit settings were 5 nm for both excitation and emission. Emission spectra were recorded with an excitation wavelength of 350 nm. Solutions were kept in the dark at 5°C for 12 h prior to measurements and were not degassed.

### 2.5 Linear viscoelastic measurements

Dynamic oscillatory tests were conducted with a rheometer (ARES, Rheometric) in the cone-plate geometry. The cone radius was 2.5 cm, and the gap angle between the cone and the plate was 0.1 rad. The storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, were measured as a function of angular frequency, $\omega$. The amplitude of the oscillatory strain was kept small ($\leq 0.2$) to ensure the linearity of the moduli measured. Measurements were carried out at 20.5°C with a 46 gL$^{-1}$ aqueous C$_{18}$-PNIPAM-C$_{18}$ solution.

### 3 Results and discussion

#### 3.1 Thermal properties of aqueous solutions of C$_{18}$-PNIPAM-C$_{18}$

The telechelic polymer C$_{18}$-PNIPAM-C$_{18}$ was soluble in water at or below room temperature up to a concentration of at least 46 gL$^{-1}$, the highest concentration tested. All solutions became turbid when heated above $\sim 31$°C. The temperature dependence of the partial heat capacity of an aqueous C$_{18}$-PNIPAM-C$_{18}$ solution (5 gL$^{-1}$) was monitored by microcalorimetry to determine the thermodynamic parameters of the phase transition: the temperature of maximum heat capacity, $T_m$, the width of the transition at half-height $\Delta T_{1/2}$, the heat of transition ($\Delta H$), and the difference in the heat capacity before and after the transition ($\Delta C_p$) (Fig. 2). The value of $T_m$ for C$_{18}$-PNIPAM-C$_{18}$ is ca. 0.5°C lower than the transition temperature of unmodified PNIPAM. In contrast, in the case of HEUR solutions, the decrease in LCST, compared to unmodified EO chains, usually reaches several tens of degrees [34], and depends on the polymer molecular weight.

There are other subtle differences between the phase transition thermodynamics of PNIPAM and its telechelic analogue. For example, the transition is sharper in the case of C$_{18}$-PNIPAM-C$_{18$ solutions and the heat of the transition is slightly smaller for the end-capped polymer compared to the unmodified analogue (see Ref. [35]). We note (Fig. 2) that the heat capacity of C$_{18}$-PNIPAM-C$_{18}$ at temperatures higher than the phase transition temperature is smaller than that of the polymer solution below...
the transition temperature, as observed in the case of PNIPAM solutions [35]. Such a decrease in heat capacity indicates that during the phase transition the number of polymer/water contacts decreases, in analogy with events occurring during the heat-induced refolding of proteins following cold denaturation [36]. Interestingly, the amplitude of the change in solution heat capacity before and after the transition ($\Delta c_p$) is significantly larger for solutions of the end-capped polymer, compared to PNIPAM solutions [35]. This effect, together with the differences in $T_m$ and $\Delta H$, hints at subtle differences in polymer/water interactions between telechelic PNIPAM and the unmodified polymer.

The thermodynamic properties of aqueous C$_{18}$-PNIPAM-C$_{18}$ also differ from those of PNIPAM grafted at random in N,N-dimethyl formamide (DMF), a good solvent of the polymer, with a low level of octadecyl groups, for which both $\Delta H$ and $\Delta c_p$ values are identical, within experimental uncertainty, to those of PNIPAM (see Ref. [35]).

### 3.2 Telechelic PNIPAM aqueous solutions below the cloud point

Dilute solutions of C$_{18}$-PNIPAM-C$_{18}$ in water ($c < 5\, \text{g}\, \text{L}^{-1}$) were probed by light scattering and fluorescence spectroscopy. From static light scattering (SLS) measurements of solutions of C$_{18}$-PNIPAM-C$_{18}$ in N,N-dimethyl formamide (DMF), a good solvent of the polymer, we determined the weight-average molecular weight of the polymer ($\sim 37000$). Similar measurements, but carried out with aqueous solutions of the polymer, yielded a much larger $M_w$ value even for very dilute solutions (i.e. $c = 0.025\, \text{g}\, \text{L}^{-1}$, $M_{w,app} \approx (9.5 \pm 0.6) \times 10^5 \, \text{Da}$) [37], implying that, in water and below the solution cloud point, C$_{18}$-PNIPAM-C$_{18}$ exists as micellar aggregates. The apparent $M_w$ of the polymer remains constant until the concentration reaches 0.6 $\text{g}\, \text{L}^{-1}$. Further increase in concentration results in a significant enhancement of $M_{w,app}$ which attains a value of $3.2 \times 10^6$ ($c = 4\, \text{g}\, \text{L}^{-1}$). If one compares the $M_{w,app}$ value in the low-concentration range to that of isolated polymer chains ($\sim 37000$), one may infer that the C$_{18}$-PNIPAM-C$_{18}$ aggregation number (i.e. the number of polymer chains per micelle) is approximately $25 \pm 3$. The steep increase in $M_{w,app}$ in solutions in the 0.6 to 4 $\text{g}\, \text{L}^{-1}$ range indicates either bridging between individual rosettes or an increase in the rosette size. The estimated aggregation number reaches a value of $\sim 80$ chains in solutions of 4 $\text{g}\, \text{L}^{-1}$. The second virial coefficient of micelles in water (0.025 < $c$ < 0.6 $\text{g}\, \text{L}^{-1}$) $A_2 = 3.6 \times 10^{-4} \, \text{mol cm}^3 \, \text{g}^{-2}$, estimated from the concentration dependence of the intensity of scattered light (see Eq. (1)) takes a positive value implying that water is a good solvent for C$_{18}$-PNIPAM-C$_{18}$ micelles below the LCST. Taken together, the SLS measurements suggest that telechelic PNIPAM forms core-shell micellar structures, with associated hydrophobic octadecyl chains protected from the water surroundings by a corona of hydrated PNIPAM chains.

From a dynamic light scattering (DLS) study of aqueous C$_{18}$-PNIPAM-C$_{18}$ solutions above the critical association concentration, we determined the hydrodynamic radius ($R_h$) of C$_{18}$-PNIPAM-C$_{18}$ micelles, based on their experimental mutual diffusion coefficient (Eq. (2)). In solutions of 0.025 < $c$ < 0.6 $\text{g}\, \text{L}^{-1}$ (20 $^\circ\text{C}$) the value of $R_h$ remains constant (17.5 $\pm$ 2 nm). It increases steeply for $c > 0.6\, \text{g}\, \text{L}^{-1}$, reaching a value of $\sim 50$ nm ($c = 0.4\, \text{g}\, \text{L}^{-1}$) (Fig. 3a). The radius of gyration ($R_g$) obtained form SLS data (Eq. (1)) follows a similar trend (Fig. 3b). The ratio $R_g/R_h$ takes a value of $\approx 1.35$ for polymer solutions of $c < 0.6\, \text{g}\, \text{L}^{-1}$ and decreases with increasing concentration.
to reach a value of $\sim 0.9$ (Fig. 3c). The ratio $R_g/R_h$ is rich in information on the concentration-induced changes in the conformation of polymer chains. Random coils are characterized by a ratio of 1.5, whereas for uniform non-draining spheres it is $\sim 0.77$ [38]. Our results indicate that in solutions of $0.025 < c < 0.6 \text{gL}^{-1}$ the chains forming the micellar corona adopt a loose conformation, suggesting that the PNIPAM are highly hydrated. When the micelles grow, $R_g/R_h$ decreases to ca. 0.9, indicating densification of the micellar structure. This densification may be an indication of the release of water molecules from the PNIPAM corona due to the crowding of looped chains as the number of polymers forming a rosette increases.

To confirm this hypothesis, we set about to determine the aggregation number by fluorescence spectroscopy, using pyrene as a probe. However, our attempts failed due to the fact that the trithiocarbonate group, incorporated in the polymer structure at the junction between the PNIPAM chain and the hydrophobe (Fig. 1), is a powerful quencher of pyrene fluorescence. We carried out instead a series of measurements using a different fluorescent dye, 8-anilino-1-naphthalenesulfonic acid (ANS). Like pyrene, ANS reports on the micropolarity of its environment. Both the emission intensity ($I$) and the wavelength of maximum emission ($\lambda_{\text{max}}$) vary as ANS passes from a polar environment, such as water, to a non-polar medium, such as the core of micelles: the emission intensity increases and $\lambda_{\text{max}}$ undergoes a blue shift [39]. Although ANS is preferentially solubilized in non-polar media, it has a significant solubility in water, therefore the spectroscopic features detected from ANS-doped C$_{18}$-PNIPAM-C$_{18}$ solutions presented next will reflect a distribution of probe molecules within the micelles and in water.

Polymer concentration-dependent spectra of ANS in aqueous C$_{18}$-PNIPAM-C$_{18}$ solutions and in water are presented in Figure 4a, together with the changes in total fluorescence intensity and in $\lambda_{\text{max}}$ (Fig. 4b) for $0.06 < c < 8 \text{gL}^{-1}$. Significant changes in the ANS spectral features occur as the polymer concentration increases. Most remarkably, the emission intensity undergoes a steep increase as the polymer concentration exceeds $\sim 0.6 \text{gL}^{-1}$, the concentration corresponding to the decrease in $R_h$ detected by DLS (Fig. 3a) and attributed to a densification of the micelles. It should be noted too that the emission intensity of ANS remains very weak for $0 < c < 0.1 \text{gL}^{-1}$, a concentration range for which polymer rosettes exist, as demonstrated by DLS and SLS measurements. This implies that the average environment of the probe in solutions in this polymer concentration range is rather polar, suggesting either i) that ANS is primarily located in water and not in the micelle hydrophobic core, or ii) that ANS is indeed solubilized in the micelles, but that within the micelles it is located primarily within the corona or at the barrier surface between their hydrophobic core and the corona. Turning to the changes in $\lambda_{\text{max}}$ (Fig. 4b), we note that the ANS emission in polymer solutions of $c < 0.2 \text{gL}^{-1}$ presents features typical of hydrophilic environment. As the polymer concentration increases beyond $0.2 \text{gL}^{-1}$, the value of $\lambda_{\text{max}}$ gradually shifts to shorter wavelengths, nearing a limiting value for solutions of $c > 1 \text{gL}^{-1}$. The leveling off of $\lambda_{\text{max}}$, together with the sharp increase of the emission intensity that take place as the polymer concentration exceeds $\sim 0.6 \text{gL}^{-1}$ express the increased hydrophobicity of the probe environment. These data give further support to the conclusion drawn from DLS measurements, namely the existence of a polymer concentration regime for which the number of polymer chains within a rosette increases to an extent such that it forces the release of polymer-bound water molecules, in order to accommodate the steric requirements of the polymer chains.

The parameters obtained for C$_{18}$-PNIPAM-C$_{18}$ micelles may be compared with those of telechelic PEO of similar molecular weight. For instance, $R_h$ and $N_{\text{agg}}$ values of $21 \pm 2$ nm and $33 \pm 9$, respectively, were reported for micelles of C$_{18}$-PEO-C$_{18}$ sample of $M_w = 35000$ in water (ca. 800 EO units, concentration $0.2$–$1.8 \text{gL}^{-1}$) [6, 11]. These values are of the same order of magnitude as the values determined here for telechelic PNIPAM. This qualitative agreement between data reported for the two
polymers brings strength to our description of the association of C$_{18}$-PNIPAM-C$_{18}$ in water.

### 3.3 Telechelic PNIPAM aqueous solutions above the cloud point

Several phenomena occurred as solutions of C$_{18}$-PNIPAM-C$_{18}$ were heated through their cloud points. They were observed via SLS, DLS and fluorescence spectroscopy using ANS as reporter molecule. A sharp increase in scattering intensity was observed by SLS within a narrow temperature range, 23 ± 1°C in the case of a 4 g L$^{-1}$ polymer solution and 31 ± 1°C, in the case of a dilute solution (0.025 g L$^{-1}$). These observations are reported in terms of changes of $M_{w,app}$ as a function of solution temperature (Fig. 5a). In solutions of high polymer concentration (4 g L$^{-1}$), large micellar aggregates exist below the cloud point (Fig. 3). They grow significantly upon heating, inducing macroscopic phase separation which precluded any attempts to determine molecular parameters of these solutions for temperatures higher than 25°C. For dilute solutions (0.025 g L$^{-1}$), however, the size of the scattering objects can be determined even well above the phase transition (Fig. 5b) using both SLS and DLS. As discussed earlier in dilute solutions kept below the cloud point, telechelic PNIPAM forms micelles for which the radius of gyration $R_g$ is larger than the hydrodynamic radius $R_h$. As the temperature increases, $R_g$ decreases reaching a minimum (∼11.5 nm) as the temperature reaches ∼29.5°C, a value slightly below the phase transition temperature. Further heating triggers an increase of $R_g$ which levels off when the temperature reaches ∼32°C. This increase can be attributed to the association of several rosettes via interaction of collapsed dehydrated chains on the corona of individual micelles. The hydrodynamic radius of the micelles smoothly increases with the solution temperature in a ∼2°C range surrounding the phase transition temperature measured by microcalorimetry.

Contrary to the situation below the transition temperature, in the high-temperature domain the $R_g$ values, obtained from SLS data, are consistently smaller than $R_h$ for a given temperature. The changes of the $R_g/R_h$ ratio (Fig. 5c) give information about the evolution of the C$_{18}$-PNIPAM-C$_{18}$ micelles conformation upon heating. In solutions of $c < 0.6$ g L$^{-1}$ and when $T < 26.5$°C, the ratio $R_g/R_h$ equals 1.35, implying a rather loose and highly hydrated conformation of the corona PNIPAM chains. Upon increasing the temperature, the $R_g/R_h$ ratio decreases, reaching a minimum of ∼0.35 at $T = 30$°C, indicating densification of the micellar structures. An analogous behavior was observed by Wu et al. in their study of the heat-induced collapse of a single high molecular weight PNIPAM, NIPAM copolymers [40,41], and other hydrophobically modified polymers [42]. The fact that the $R_g/R_h$ value is smaller than theoretically predicted for hard spheres (ca. 0.77) was attributed to the formation of molten globules, i.e. aggregates for which the surface has a lower density than the center. The rosettes of telechelic PNIPAM may undergo the same transformation upon heating, the core of micelles heated to ∼30°C consisting of closely packed octadecyl chains surrounded by collapsed PNIPAM chains. Such micelles may be viewed as molten globules where the denser core consists of the n-alkyl chains. In solutions heated above 30°C, several collapsed rosettes aggregate via interaction of dehydrated PNIPAM chains that form a hydrophobic medium into which the octadecyl chains can be solubilized as isolated entities, leading to composition-homogeneous associates for which the $R_g/R_h$ ratio approaches the value predicted based on the hard-sphere limit (Fig. 5c). If we assume micelles to be perfectly non-draining, i.e., the solvent flow does not penetrate the corona or the core, then the hydrodynamic radius should be equal to the micelle radius. However, the PNIPAM chains in the corona are expected to be highly hydrated. The water molecules bound to the chains via hydrogen bonds move together with the polymer chains, and, consequently, micelles are expected to exhibit a non-draining behavior. In solutions heated above 30°C, the chains inside the inner micelle core are highly collapsed, so that the ratio of the mass density of the corona to that of the core is less than 1. Simple calculations indicate that assuming that the core radius is half the micelle radius, the ratio $R_g/R_h$ reaches 0.3 in the small density ratio limit. Thus, the experimental $R_g/R_h$ value observed may be a consequence of density inhomogeneity within polymer micelles.
been detected previously in the case of pyrene-labeled solutions of longer chain length (Fig. 6). A sudden increase in fluorescence intensity together with a sharp shift of \( \lambda_{\text{max}} \) from 520 nm to 492 nm (Fig. 7) were detected as the solution was heated from 10 to 50 °C. These effects signal a change in the micropolarity sensed by ANS that passes from the hydrophilic environment of highly hydrated rosettes formed in cold micellar solutions to the hydrophobic medium of collapsed and associated polymeric micelles.

The hydrophobic nature of the nanoparticles formed during the phase transition of dilute C_{18}-PNIPAM-C_{18} solutions was confirmed via fluorescence probe measurements. Emission spectra of an ANS-containing solution of the polymer (0.1 g L\(^{-1}\)) were recorded as the solution was heated from 10 to 50 °C. A sudden increase in fluorescence intensity together with a sharp shift of \( \lambda_{\text{max}} \) from 520 nm to 492 nm (Fig. 7) were detected as the solution temperature reached ~ 29 °C. These effects signal a change in the micropolarity sensed by ANS that passes from the hydrophilic environment of highly hydrated rosettes formed in cold micellar solutions to the hydrophobic medium of collapsed and associated polymeric micelles.

3.4 Telechelic PNIPAM aqueous solutions above the gelation threshold

Aqueous solutions of C_{18}-PNIPAM-C_{18} of sufficiently high concentration form transient gels. The threshold concentration, estimated by the inversion tube method, was ~ 20 g L\(^{-1}\). The oscillatory shear responses of aqueous telechelic PNIPAM transient gels, monitored at 20.5 °C for a solution of \( c = 46 \text{ g L}^{-1} \) (well beyond the gelation threshold), suggested viscoelastic features of the gel with a primarily viscous response at low frequency and a crossover at high frequency (Fig. 8). The storage and loss moduli \( G' \) and \( G'' \) of the gel exhibit a nearly single-relaxation Maxwell behavior specified by equations (3) and (4):

\[
G'(\omega) = \frac{G'_\infty \omega^2 \lambda^2}{1 + \omega^2 \lambda^2},
\]

and

\[
G''(\omega) = \frac{G''_\infty \omega}{1 + \omega^2 \lambda^2}.
\]

Here, \( \omega \) is the angular frequency, and \( G''_\infty \) and \( \lambda \) are the high-frequency modulus and relaxation time of the
transient gel, respectively. The relaxation time evaluated from the \(G''\) peak frequency is 0.2 s.

Steiger and Richtering [43] examined the rheological behavior of a 4.7 wt% aqueous solution of unmodified PNIPAM of molecular weight \(M = 3.9 \times 10^6\), a sample in which the polymer concentration is about the same as that of the samples studied here, but the size of the polymer is much larger than that of the polymer employed here. They reported that their sample behaved as predicted by the Cox-Mertz rule, i.e., coincidence of the non-Newtonian viscosity \(\eta(\dot{\gamma})\) and the magnitude of the dynamic viscosity 
\[
|\eta'(\omega)| = (G'^2 + G''^2)^{1/2}/\omega \text{ for a shear rate } \dot{\gamma} = \omega.
\]

The relaxation time \(\lambda\) of this sample of unmodified PNIPAM, estimated from the reported \(\eta(\dot{\gamma})\) data, is \(\lambda = 0.7\) s at 20°C. From this \(\lambda\) value, the relaxation time of a PNIPAM chain of \(M = 3.7 \times 10^4\) is estimated to be \(\lambda_{\text{neat}} < 6.5 \times 10^{-4}\) s at 20°C. This \(\lambda_{\text{neat}}\) value is orders of magnitude smaller than the \(\lambda\) value (= 0.2 s) observed for a solution of C18-PNIPAM-C18. This fact demonstrates that the relaxation of the C18-PNIPAM-C18 solution is governed by the thermal dissociation of the aggregated domains of C18 end groups and that the PNIPAM backbone chains connecting these domains behave as well-equilibrated gel network strands in the time scale of this dissociation. This hypothesis is confirmed also by the fact that a relaxation time of ca. 0.8 s (25°C) was reported in a study of a 4 wt% solution of a telechelic polymer with molecular characteristics similar to those of C18-PNIPAM-C18, i.e., C18-poly(ethylene oxide)-C18 (\(M_w \sim 35000\)) [8].

The value of the high-frequency modulus \(G'_{\infty}\) evaluated from the \(G''\) data (Fig. 8) is 2.1 kPa. The number density of the effective network strands, \(\nu_{\text{eff}}\), evaluated from this \(G'_{\infty}\) (Eq. (5)),
\[
\nu_{\text{eff}} = \frac{G'_{\infty}}{kT},
\]
where \(k\) is Boltzmann constant and \(T\) the absolute temperature, is \(5.3 \times 10^{-23}\) m\(^{-3}\), a value close to the nominal chain number density, \(\nu^0 = 7.5 \times 10^{-23}\) m\(^{-3}\), evaluated from the concentration and molecular weight of the PNIPAM chains. The coincidence of experimental and calculated values suggests that most chains are incorporated in the gel network to sustain its transient elasticity.

We noted, however, that the oscillatory shear responses of telechelic PNIPAM gels deviate slightly from the Maxwellian behavior at low frequencies (dashed lines, Fig. 8). This deviation may be due to the motion of thermally dissociated network fragments. If thermal scission does not occur simultaneously at all aggregating ends, fairly large network fragments may form. These are expected to move rather slowly and such slow dynamics can dominate the relaxation at very low frequencies.

Overall, the features of the end-capped PNIPAM gel are similar to those of telechelic poly(ethylene oxides) within the linear-response region, for which the main mechanism of stress relaxation was identified to be the thermal dissociation of the aggregating gel network due to the detachment of one hydrophobic moiety from the micelle [8,11]. Nonlinear flow properties, however, may significantly differ due to the difference in the tension-elongation curve of the main chains. Initial flow experiments for C18-PNIPAM-C18 gels point to a stress overshoot with shear thinning in the stationary state. Details will be reported in a forthcoming article.

4 Conclusions

By using RAFT radical polymerization we synthesized a telechelic PNIPAM of narrow molecular-weight size distribution, bearing an octadecyl chain on each chain end. This polymer in dilute aqueous solution below the LCST forms small rosettes composed of ca. 25±3 polymer chains. Evidence from light scattering and fluorescence measurements points to the formation of larger and more hydrophobic aggregates in solutions of polymer concentration above 0.6 g.L\(^{-1}\). At still higher concentrations, significant viscosity enhancement is observed, such that fluids of concentration higher than 20 g.L\(^{-1}\) undergo gelation. The oscillatory shear behavior of this gel can be approximated by a single-relaxation Maxwell model, at least in the high-frequency range. The main mechanism of stress relaxation is ascribed to the dissociation of one end of a PNIPAM bridging chain from the core of a micelle.

Aqueous solutions of telechelic PNIPAM exhibit a temperature-induced phase transition. Near the transition temperature, micelles start to collapse forming mesoglobules with an uneven segment density distribution. Upon further heating, the globules aggregate and behave as a colloidally stable hard-spheres dispersion, in the case of dilute polymer solutions. Concentrated solutions tend to aggregate, triggering macroscopic phase separation.

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References

37. LS experiments could not be performed for polymer concentrations smaller than 0.025 gL$^{-1}$ because the light scattering signal becomes very noisy and of the order of that of the solvent.
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