# Impact of End-Group Association and Main-Chain Hydration on the Thermosensitive Properties of Hydrophobically Modified Telechelic Poly(*N*-isopropylacrylamides) in Water

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ABSTRACT: We examine the influence of the macromolecule chain length on the cloud point temperature ($T_{cp}$) and the temperature of the coil-to-globule transition ($T_M$) in aqueous solutions of hydrophobically modified (HM) telechelic poly(*N*-isopropylacrylamides) (PNIPAM) ranging in concentration from 0.01 to 35 g $L^{-1}$ (0.1−310 mmol of NIPAM $L^{-1}$). The telechelic HM-PNIPAM samples with *n*-octadecyl termini were obtained by RAFT polymerization of NIPAM in dioxane in the presence of *S*-1-*n*-octadecyl-*S*′-(α,α′-dimethyl-α″-*N*-*n*-octadecylacetamide)trithiocarbonate as a chain transfer agent. Their molar mass ($M_n$) ranged from 12 000 to 49 000 g $mol^{-1}$ with a polydispersity index lower than 1.20. The cloud point temperatures, measured by monitoring the temperature-induced changes in scattering intensity, decreased significantly with increasing polymer concentration, this effect being more pronounced with decreasing polymer molar mass. In contrast, the temperature of the PNIPAM chain coil-to-globule collapse (30 ± 1 °C) was only slightly affected by solution concentration and polymer molecular weight. These results are interpreted in terms of the coexistence of two phenomena: association of the *n*-octadecyl terminal groups and hydration of the PNIPAM chains.

## Introduction

Poly(*N*-isopropylacrylamide) (PNIPAM) in water exhibits a lower critical solution temperature (LCST), which has been investigated by a variety of experimental techniques in the dilute and concentrated regimes.[1−9] Several models have been described to account for the coil-to-globule collapse of PNIPAM in water[10,11] and the complex water/PNIPAM phase diagram.[12] The temperature-driven change in the conformation of single PNIPAM chains and the macroscopic phase separation reflect rather subtle changes in polymer/water interactions, primarily the release of water molecules from a polymer hydration layer into bulk water. It comes as no surprise, consequently, that slight changes in the chemical composition of PNIPAM have important consequences on the water/PNIPAM phase diagram.

Taylor and Cerankowski pointed out 30 years ago that the LCST of poly(*N*-alkylacrylamides), such as PNIPAM, can be raised or lowered via introduction of hydrophilic or hydrophobic comonomers, respectively.[13] Since then, there have been numerous attempts to exploit this property to create "intelligent" devices and systems able to respond reliably and repetitively to temperature jumps.[14,15] One approach has been to link to a PNIPAM chain a small number of long alkyl or perfluoroalkyl chains to generate hydrophobically modified (HM) PNIPAM.[16−21] The hydrophobic groups drive the self-assembly of the polymers, leading to the formation of polymeric micelles that exist as isolated entities in dilute cold aqueous solutions. Upon heating, dehydration of the PNIPAM chains triggers changes in the size and shape of the micelles, often leading to macroscopic aggregation. The phase transition temperature depends not only on the level of hydrophobe incorporation and on its chemical structure but also on its position on the chain. This effect can be traced to differences in the structure of the micelles formed by the various HM-PNIPAMs in cold water. Randomly modified HM-PNIPAMs adopt a loose micellar conformation in which the hydrophobic groups are partly exposed to water; the cloud point of their solutions is depressed significantly compared to that of PNIPAM solutions.[22,23] Polymers that carry a hydrophobic group at one chain end tend to form core-shell structures in which the hydrophobic core is insulated from the water by a brushlike corona of PNIPAM chains.[18,24,25] Micelles of yet another type form in solutions of HM-PNIPAM carrying a hydrophobic group at each chain end. Like all associating polymers, such as telechelic alkyl end-capped poly(ethylene oxides) or hydrophobically modified ethoxylated urethanes (HEUR),[26−28] telechelic HM-PNIPAMs form flowerlike associates consisting of loops of hydrated polymer chains having both end groups entrapped in the micellar core. In a preliminary light scattering study of aqueous dilute solutions of a telechelic HM-PNIPAM sample of $M_n \sim 35\,000$, we reported that near the transition temperature individual flower micelles collapse, forming globules with an uneven segment density distribution.[29] Several globules aggregate, yielding colloidally stable mesoglobules.[30]

The introduction of hydrophobic end groups affects the phase behavior of PNIPAM solutions in two ways. First, the miscibility of the polymer in water becomes poorer as a result of direct interactions between water and the alkyl chains. Second, the mixing entropy of the polymer chains is reduced due to the increase of their apparent molecular weight via micelle formation. Both factors favor phase separation, so that the lower critical solution temperature (LCST) tends to shift downward. However, association of the end chains does not affect the hydration of the main chains, except for segments near the

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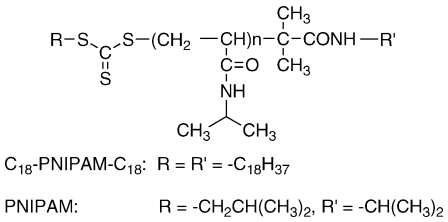


**Figure 1.** Structure of the polymers used in this study.

micellar core, because they remain exposed to water even when association takes place. Therefore, the telechelic PNIPAM/water system is an interesting example of the coexistence, without competition, of two phenomena: end-chain association and hydration.We have prepared a series of telechelic HM-PNIPAMs ($C_{18}$-PNIPAM-$C_{18}$, Figure 1) of varying molecular weights and examined their miscibility with water as a function of concentration. We determined the temperature that triggers the coil-to-globule collapse of the main chain, together with the thermodynamic values associated with the conformation change. The study reveals that, for a given polymer sample, the cloud point temperature, $T_{cp}$, detected by light scattering, differs significantly from $T_M$, the temperature corresponding to the maximum of the endotherm measured by microcalorimetry. From the data and theoretical considerations on end-chain association and main-chain hydration, we propose a model of the temperature-dependent interactions between water and telechelic HM-PNIPAM flower micelles.

## Experimental Section

**Materials.** All chemicals were purchased from Aldrich Chemicals, unless otherwise stated. Azobis(isobutyronitrile) (AIBN, 98%) was recrystallized from methanol. 2-Methyl-1-propanethiol (92%), *n*-octadecylthiol, isopropylamine (99.5+%), *n*-octadecylamine, carbonyldiimidazole, carbon disulfide (99.9%), sodium hydroxide, and tricaprylylmethylammonium chloride were used as received. *N*-Isopropylacrylamide (stabilized, 99%) was obtained from Acros Organics and was recrystallized from acetone/heptanes (4:6). 1,4-Dioxane and hexanes (ACP, ACS Reagent) were distilled over sodium under argon. All other solvents were reagent grade and used as received. Water was deionized with a Millipore Milli-Q system.

***S*-1-*n*-Octadecyl-*S*′-(α,α′-dimethyl-α″-acetic acid)trithiocarbonate.** Aqueous sodium hydroxide (6.17 mL, 50%, 1.26 mmol) was added dropwise over a period of 20 min to a solution of *n*-octadecylthiol (34.30 g, 0.12 mol), acetone (147 mL, 1.99 mol), and tricaprylylmethylammonium chloride (2.30 mL, 0.005 mol) kept at 10 °C under nitrogen. At the end of the addition, the reaction mixture was stirred for 20 min. A solution of carbon disulfide (7.2 mL, 0.12 mol) in acetone (63 mL, 0.42 mol) was then added dropwise over 20 min. The yellow solution obtained was allowed to stir for 10 min. Then, chloroform (14.4 mL, 0.18 mol) was added in one portion, followed by dropwise addition over 30 min of an aqueous sodium hydroxide solution (31.5 mL, 50%, 0.60 mol). The resulting reaction mixture was stirred overnight at room temperature. It was cooled to 10 °C, water (180 mL) was added, and the pH of the resulting solution was adjusted to 1.0 by addition of concentrated aqueous HCl (~80 mL). The unreacted acetone was removed by vigorous purging with nitrogen. The solid was collected with a Buchner funnel and washed with water to eliminate the excess of salt and with ethanol to eliminate residual water-insoluble side products. The product was recrystallized five times from hexanes. A bright yellow crystalline solid was obtained (44.74 g, 83 %); mp 79.9−81.5 °C. HRMS ($MH^+$) found: 448.23 *m*/z; calcd for: $C_{23}H_{47}O_2S_3$ 448.778 *m*/*z*. $^1$H NMR ($CDCl_3$): $\delta$ 0.88 (t, $J$ = 6.5 Hz, 3 H), 1.25 (br, 28 H), 1.39 (m, 2 H), 1.68 (q, $J$ = 7.5 Hz, 2 H), 1.73 (s, 6H), 3.29 (t, 2 H), 5.31 ppm (s, 1 H). IR: 2914, 2848 ($CH_2$), 1715 (C═O), 1458 ($CH_2$), 1280 (C−O), 1076 cm$^{-1}$ (C═S). UV ($CHCl_3$): $\lambda_{max}$ = 310 nm, $\epsilon$ = 13 100 L mol$^{-1}$ cm$^{-1}$.

***S*-1-*n*-Octadecyl-*S*′-(α,α′-dimethyl-α″-*N*-*n*-octadecylacetamide)-trithiocarbonate (CTA1).** A solution of carbonyldiimidazole (1.79 g, 0.011 mol) in dichloromethane (10 mL) was added dropwise to a solution of *S*-1-*n*-octadecyl-*S*′-(α,α′-dimethyl- α″-acetic acid)-trithiocarbonate (5.0 g, 0.011 mol) in dichloromethane (130 mL) kept under nitrogen. The reaction mixture was stirred at room temperature overnight until complete conversion of the starting acid, as judged by analytical thin-layer chromatography on silica gel plates (eluent: THF/hexane 3/7 v/v). A solution of *n*-octadecylamine (6.0 g, 0.022 mol) in dichloromethane (25 mL) was added dropwise to the mixture kept at 30 °C. At the end of the addition the mixture was kept at room temperature overnight. It was washed successively with aqueous HCl (0.1 M), saturated aqueous sodium carbonate, and brine. The organic phase was dried over $Na_2SO_4$ and filtered, and the solvent was evaporated using a rotary evaporator. The residual yellow oil was purified by flash chromatography over via silica (eluent 1:10 THF:hexanes). The solid obtained was recrystallized from hexanes (three times), yielding a yellow crystalline solid (1.21 g); mp 76.0−76.8 °C. HRMS ($MH^+$): found: 700.56 *m*/*z*; calcd for: $C_{42}H_{81}NOS_3$ 700.2769 *m*/*z*. $^1$H NMR ($CDCl_3$): $\delta$ 0.88 (t, 6 H), 1.25 (br, 56 H), 1.45 (t, 4 H), 1.63 (q, 4 H), 1.69 (s, 6 H), 3.19 (q, 2 H), 3.23 (t, 2 H), 6.49 (t, 1 H) ppm. IR: 3300 (NH str), 2969 ($CH_2$ ), 1651 (CO str, amide), 1076 (CS), 720 cm$^{-1}$. UV ($CHCl_3$): $\lambda_{max}$ = 310 nm, $\epsilon$ = 11 400 L mol$^{-1}$ cm$^{-1}$.

***S*-1-Isobutyl-*S*′-(α,α′-dimethyl-α″-acetic acid)trithiocarbonate.** Aqueous sodium hydroxide (1.3 mL, 50%, 1.645 mmol) was added dropwise over a period of 15 min to a solution of 2-methyl-1-propanethiol (1.2 mL, 11.08 mmol), acetone (6.7 mL, 91.2 mmol), and tricaprylylmethylammonium chloride (0.2 mL, 0.45 mmol) kept at 10 °C in an ice/water bath. At the end of the addition, the reaction mixture was stirred for 20 min. A solution of carbon disulfide (0.7 mL, 11.09 mmol,) in acetone (2 mL) was then added dropwise over 15 min. The yellow solution obtained was allowed to stir for 10 min. Then, chloroform (1.4 mL, 16.67 mmol) was added in one portion, followed by dropwise addition over 30 min of an aqueous sodium hydroxide solution (4.5 mL, 50%, 40.3 mmol). The resulting reaction mixture was stirred overnight. Water (16.35 mL) was added, followed by concentrated aqueous HCl (8.25 mL) to acidify the reaction mixture. The remaining acetone was removed by vigorous purging with nitrogen. The solid was collected with a Buchner funnel and washed with water and with ethanol. The product was recrystallized five times from hexanes. A bright yellow crystalline solid was obtained (1.5 g, 62%); mp 101.7−102.3 °C. HRMS ($MH^+$) found: 252.0312 *m*/z, calcd for: $C_9H_{16}O_2S_3$ 252.405 *m*/*z*. $^1$H NMR ($CDCl_3$): $\delta$ 1.02 (d, 6 H), 1.73 (s, 6 H), 1.98 (septet, 1 H), 3.2 (d, 2 H) ppm. IR: 2961($CH_2$ str), 1691 (CO str, carboxylic acid), 1056 (CS), 806 cm$^{-1}$ ($C(CH_3)_2$). UV ($CHCl_3$): $\lambda_{max}$ = 310 nm, $\epsilon$ = 11 700 L mol$^{-1}$ cm$^{-1}$.

***S*-1-Isobutyl-*S*′-(α,α′-dimethyl-α″-*N*-isopropylacetamide)-trithiocarbonate (CTA2).** A solution of carbonyldiimidazole (0.64 g, 3.96 mmol) in dichloromethane (5 mL) was added dropwise to a solution of *S*-1-isobutyl-*S*′-(α,α′-dimethyl-α″-acetic acid)trithiocarbonate (0.80 g, 3.96 mmol) in dichloromethane (25 mL) kept under nitrogen. The reaction mixture was stirred at room temperature for 7 h, until complete conversion of the starting acid, as judged by analytical thin-layer chromatography on silica gel plates (eluent: hexanes/THF, 10/1 v/v). A solution of isopropylamine (0.674 mL, 7.92 mmol) in dichloromethane (5 mL) was added dropwise to the mixture. At the end of the addition the mixture was kept at room temperature overnight. It was washed successively with aqueous HCl (0.1 M), saturated aqueous sodium carbonate, and brine. The organic phase was dried over $Na_2SO_4$ and filtered, and the solvent was evaporated using a rotary evaporator. The residual yellow oil was purified by flash chromatography over silica (eluent 1:10 THF:hexanes). The solid obtained was recrystallized from hexanes (three times), yielding a yellow crystalline solid (0.65 g, 70%); mp 55.1−55.8 °C. HRMS ($MH^+$): found: 293.0941 *m*/*z*; calcd for $C_{12}H_{23}NOS_3$: 293.502 *m*/*z*. $^1$H NMR ($CDCl_3$): $\delta$ 1.02 (d, 6 H), 1.1 (d, 6 H), 1.73 (s, 6 H), 1.97 (septet, 1 H), 3.2 (d, 2 H), 4.01 (s,1 H), 6.27 (septet, 1 H) ppm. IR: 3317 (NH, amide), 2969 ($CH_2$ ), 1646 (CO str, amide), 1536 (NH) 1086 (CS), 809 cm$^{-1}$

**Table 1. Polymerization Conditions and Properties of the Polymers Investigated ($M_n$, $M_w$ = Number- and Weight-Average Molecular Weight of Polymers; $n$ = Number of NIPAM Units per Chain)**

| polymer | [CTA] | [NIPAM]/[CTA] | [CTA]/[AIBN] | time (h) | $M_n$ (UV) | $M_n$ ($^1$H NMR) | $M_n$ (GPC) | $M_w/M_n$ (GPC) | $n$ |
|---|---|---|---|---|---|---|---|---|---|
| PNIPAM -10K | CTA2[a] | 100 | 5 | 1 | 10 300 | —[c] | 10 400 | 1.04 | 90 |
| $C_{18}$-PNIPAM-$C_{18}$-49K | CTA1[b] | 540 | 10 | 6 | —[d] | —[c] | 49 000 | 1.20 | 428 |
| $C_{18}$-PNIPAM-$C_{18}$-35K | CTA1[b] | 540 | 10 | 2 | —[d] | —[c] | 34 600 | 1.07 | 300 |
| $C_{18}$-PNIPAM-$C_{18}$-22K | CTA1[b] | 436 | 10 | 8 | 26 600 | 22 200 | 22 200 | 1.16 | 191 |
| $C_{18}$-PNIPAM-$C_{18}$-12K | CTA1[b] | 436 | 10 | 6 | 15 600 | 14 300 | 12 400 | 1.11 | 104 |

[a] Solvent: dioxane. [b] Solvent: dioxane/hexanes 5/1 v/v. [c] Cannot be determined by $^1$H NMR specrometry. [d] Cannot be determined by UV−vis spectroscopy.

($C(CH_3)_2$). UV ($CHCl_3$): $\lambda_{max}$ = 310 nm, $\epsilon$ = 10 500 L mol$^{-1}$ cm$^{-1}$.

**Polymerizations.** All RAFT polymerizations were performed in septa-capped 25 mm × 150 mm glass tubes using a FirstMate system from Argonaut Technologies, Inc. The tubes were loaded with *N*-isopropylacrylamide, the desired chain transfer agent (CTA1 or CTA2), and the solvent (1,4-dioxane or 1,4-dioxane/hexanes 5/1 v/v). The polymerization solutions were thoroughly degassed with nitrogen for 15 min at room temperature. They were then heated to 65 °C. The degassing was continued for another 15 min. The required amount of a degassed solution of AIBN in dioxane was added to each reaction mixture. The system was kept under nitrogen, and the polymerizations were allowed to proceed for the desired duration. At the end of the polymerization, the solutions were cooled to room temperature. The polymers were isolated by precipitation into diethyl ether. They were purified further by two consecutive precipitations from THF into diethyl ether. They were dialyzed extensively against water, using a membrane of suitable MW cutoff. End-group analysis of each polymer sample was performed by UV−vis spectroscopy, using the absorbance at 310 nm of the CTA employed and, in the case of the $C_{18}$-PNIPAM-$C_{18}$ samples, by $^1$H NMR spectroscopy, using the signal at $\delta$ 0.88 ppm attributed to the resonance of the protons of the terminal methyl group of the *n*-octadecyl chains and the signal at $\delta$ 4.01 ppm ascribed to the isopropyl methine proton. Specific conditions employed in each polymerization are given in Table 1, together with the molecular characteristics of the corresponding polymers.

**Instrumentation.** Proton NMR spectra were recorded on a Bruker AMX-400 (400 MHz) spectrometer. The chemical shifts are referenced to trimethylsilane (TMS). UV/vis spectra were measured with a Hewlett-Packard 8452A photodiode array spectrometer. Infrared spectra were recorded on a Bruker Vector 22 spectrometer equipped with a Harrick MVP ATR cell. Mass spectra were recorded on a Micromass Autospec TOF instrument equipped with a LSIM source (Centre Régional de Spectrométrie de Masse, Université de Montréal, Montréal, QC, Canada). Melting points were measured with a Büchi 535 melting point apparatus. Gel permeation chromatography (GPC) was performed with a GPC system consisting of an Agilent 1100 isocratic pump, a set of TSK-gel α-M and TSK-gel α-3000 (Tosoh Biosep) columns, a Dawn EOS multiangle laser light scattering detector (Wyatt Technology Corp.), and an Optilab DSP interferometric refractometer (Wyatt Technology Corp.); injection volume: 100 $\mu$L; flow rate: 0.5 mL min$^{-1}$; eluent: DMF; temperature: 40 °C. The d$n$/d$c$ value of PNIPAM was determined to be 0.088 cm$^3$/g at 690 nm in DMF at 40 °C using an Optilab DSP interferometric refractometer (Wyatt Technology Corp). It was assumed that hydrophobic modification of the PNIPAM polymer does not influence the d$n$/d$c$ value.

**Cloud Point Measurements by Light Scattering (LS).** LS experiments were performed on a CGS-3 goniometer (ALV GmbH) equipped with a He−Ne laser ($\lambda$ = 632 nm) and a C25P circulating water bath (Thermo Haake). The polymer concentration was varied from 0.025 to 35 g L$^{-1}$. Prior to the measurements, the solutions were filtered directly into the light scattering cell through 0.45 $\mu$m Millex Millipore PVDF filters. The intensity of scattered light was measured after equilibrating the sample at a given temperature for at least 20 min. The average of three consecutive runs (1 min each) was recorded. The cloud point temperature ($T_{cp}$) was determined from plots of the LS intensity vs temperature, taking as $T_{cp}$, the point corresponding to the abrupt increase of the scattering intensity (see Figure 2). The estimated error in $T_{cp}$ determined by this procedure is ±0.2 °C.

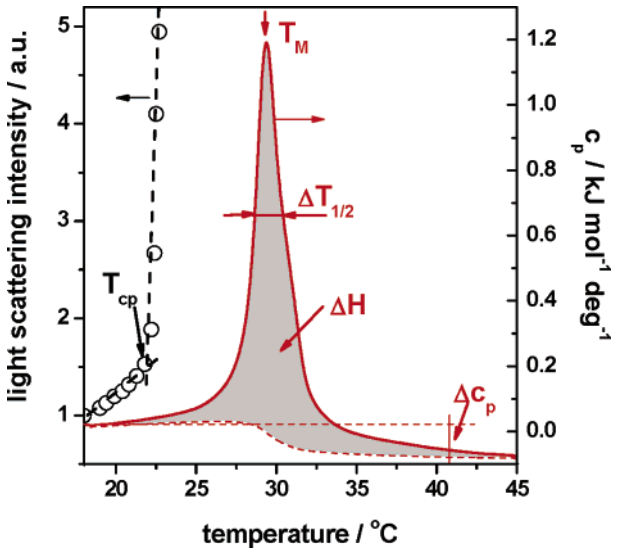


**Figure 2.** Microcalorimetric endotherm (heating rate: 1 °C min$^{-1}$) and changes with temperature of the scattered light intensity recorded for an aqueous solution of $C_{18}$-PNIPAM-$C_{18}$-35K (polymer concentration: 5.0 g L$^{-1}$).

**High-Sensitivity Differential Scanning Calorimetry (HS-DSC).** HS-DSC measurements were performed on a VP-DSC microcalorimeter (MicroCal Inc.) at an external pressure of ca. 180 kPa. The cell volume was 0.520 mL. The heating rate was 1.0 °C min$^{-1}$. Data were corrected for instrument response time, a correction that takes into account the effect of scan rate on the data collected. Data were analyzed using the software supplied by the manufacturer. The polymer concentration of the solutions analyzed ranged from 0.1 to 11 g L$^{-1}$. The temperature of the phase transition ($T_M$) was taken at the maximum of DSC peak. The enthalpy of the transition ($\Delta H$) was determined from the area of the endotherm, and the difference in heat capacity after and before transition ($\Delta c_p$) was calculated from the position of the baseline before and after the phase transition (see Figure 2). At least three measurements were performed for each solution of a given concentration.

**Pressure Perturbation Calorimetry (PPC).** PPC measurements were performed on a VP-DSC microcalorimeter equipped with a pressure perturbation accessory (MicroCal Inc.). The pressure applied during the compression cycle was 500 kPa. The reference cell and sample cell volumes were identical (0.517 mL). The concentration of the solutions analyzed ranged from 1.0 to 11.0 g L$^{-1}$.

A detailed description of the method has been reported elsewhere.[22,31,32] In a differential calorimetric experiment, the sample and reference cells are filled respectively with a solute (polymer in our measurements) solution and with solvent. When both cells are subjected to the same pressure change $\Delta P$, the thermal

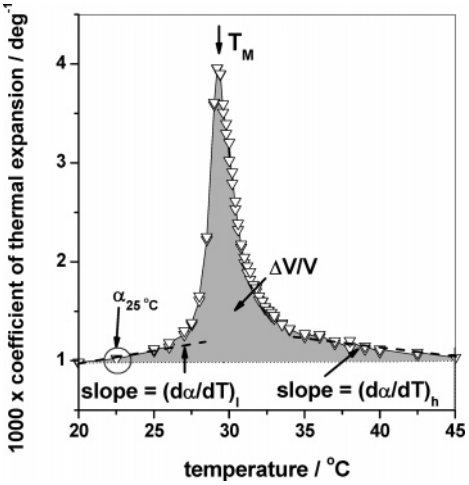


**Figure 3.** PPC scan recorded for an aqueous solution of $C_{18}$-PNIPAM-$C_{18}$-35K in water (polymer concentration: 5.0 g $L^{-1}$).

expansion coefficient, α, of the solute can be calculated from the equation

$$\alpha = \alpha_s - \frac{\Delta Q}{T \Delta P m_p \overline{V}_p} \quad (1)$$

where $\alpha_s$ is the thermal expansion coefficient of the solvent, $T$ is the temperature, $m_p$ and $\overline{V}_p$ are the polymer mass and partial molar volume in the solution, respectively, and $\Delta Q$ is the net heat (i.e., the difference between sample cell and the reference cell, that contains solvent only). The volume change $\Delta V$, which accompanies a transition in the system, is obtained by integration of the curve of the changes in the coefficient of thermal expansion with temperature, as indicated in eq 2, where we assume that $\Delta V$ is small compared to $V$. The value $\Delta V$ is expressed as a percent of $V$.

$$\frac{\Delta V}{V} = \int \alpha \, dT = \int \frac{1}{V}\left(\frac{dV}{dT}\right) dT \quad (2)$$

A typical PPC trace is shown in Figure 3, together with the graphical determination of the various parameters derived from the data: the transition temperature $T_{M,PPC}$, the area $\Delta V/V$, the value of the thermal expansion coefficient at 25 °C ($\alpha_{25}$), and the slope of the temperature dependence of the thermal expansion coefficient before and after the transition $(d\alpha/dT)_l$ and $(d\alpha/dT)_h$, respectively.

## Results and Discussion

**Preparation and Characterization of the $C_{18}$-PNIPAM-$C_{18}$ Samples.** The polymers were prepared by reversible addition−fragmentation chain transfer (RAFT) polymerization,[33−35] using a dialkyl trithiocarbonate chain transfer agent (CTA) prepared in two steps (Figure 4):[36] (1) a modified ketoform reaction,[37] involving the reaction, in the presence of sodium hydroxide, of carbon disulfide and either *n*-octadecanethiol (CTA1) or methyl-1-propanethiol (CTA2), alkylation with chloroform and acetone in the presence of a phase transfer catalyst, and acidification yielding a carboxyl-terminated trithiocarbonate;[36] (2) a carbonyldiimidazole-mediated amidation of the terminal carboxyl group with either *n*-octadecylamine (CTA1) or isopropylamine (CTA2). Both CTAs are crystalline solids. Their structure was confirmed by high-resolution mass analysis, $^1$H NMR, UV−vis, and FTIR spectroscopy.

Polymerizations of NIPAM were conducted at 65 °C for different reaction times and with different molar ratios of NIPAM/CTA using AIBN as an initiator in the presence of either CTA1, to prepare $C_{18}$-PNIPAM-$C_{18}$, or CTA2, to obtain PNIPAM samples devoid of hydrophobic termini (Table 1). The molecular weights of the polymers were measured by size exclusion chromatography using dimethylformamide as eluent, with combined refractometry and multiangle laser light scattering detection. In all instances the polydispersity index (PDI) was ≤1.20. In the case of polymers of sufficiently low molar mass ($M_n$ < 35 000 g $mol^{-1}$), molar mass data were confirmed by end-group analysis using the UV−vis absorbance at 310 nm of the trithiocarbonate chromophore and/or the $^1$H NMR spectrum of the polymers dissolved in chloroform-*d*. The areas of the characteristic triplet at $\delta$ 0.88 ppm ($J$ = 7.5 Hz), due to the resonance of the terminal methyl protons of the octadecyl chains, and of the broad singlet at $\delta$ 4.01 ppm, corresponding to the isopropyl methine proton resonance (Figure 5), were used to confirm the molecular weight of the telechelic PNIPAMs. The values of $M_n$ determined by GPC, UV−vis spectroscopy, and $^1$H NMR spectroscopy are in good agreement, given the expected precision of the measurements (Table 1).

**Cloud Point Measurements.** All telechelic PNIPAMs were soluble in cold water, forming fluid solutions as long as the polymer concentration was kept below ∼35 g $L^{-1}$, except in the case of aqueous $C_{18}$-PNIPAM-$C_{18}$-35K, which underwent gelation above a polymer concentration of 20 g $L^{-1}$. The solutions became turbid in response to an increase in temperature. The cloud point temperature, $T_{cp}$, taken as the temperature corresponding to the sharp increase in the intensity of the light scattered by the sample, was determined as a function of solution concentration for the four telechelic HM-PNIPAM samples. In a typical experimental procedure, it took ∼5 h to heat a sample from 20 to 40 °C, as the temperature was increased stepwise, and for each temperature setting, the sample was equilibrated for 20 min prior to carrying out light scattering experiments.[38] We confirmed that the cloud point values recorded by scattering

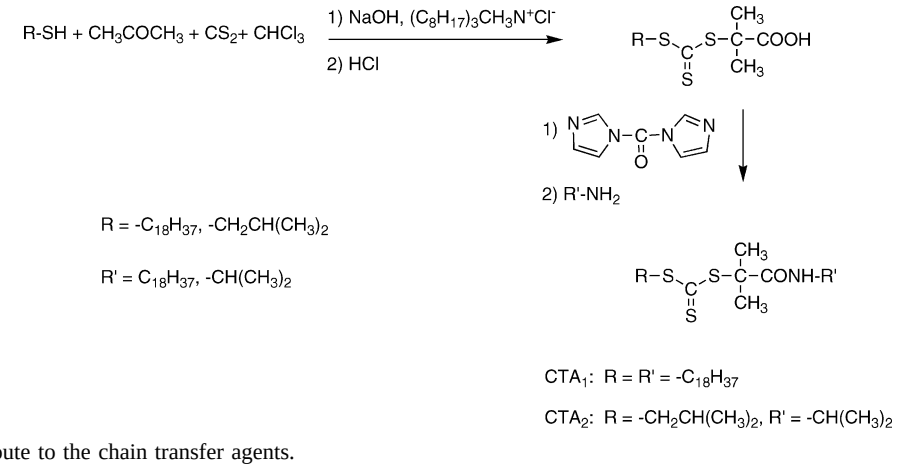


**Figure 4.** Synthetic route to the chain transfer agents.

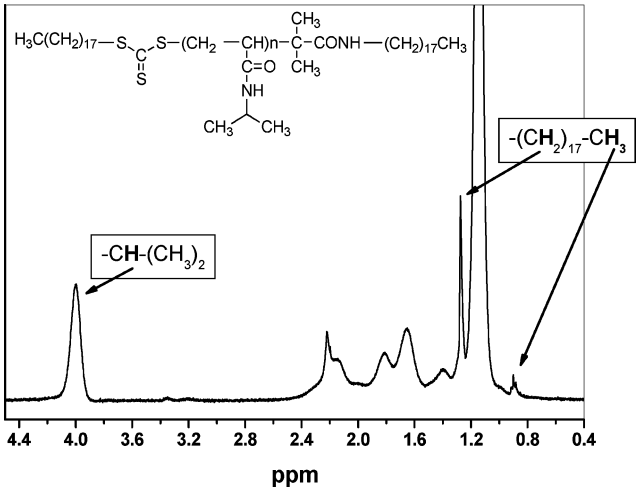


**Figure 5.** $^1$H NMR spectrum of $C_{18}$-PNIPAM-$C_{18}$-22K in $CDCl_3$.

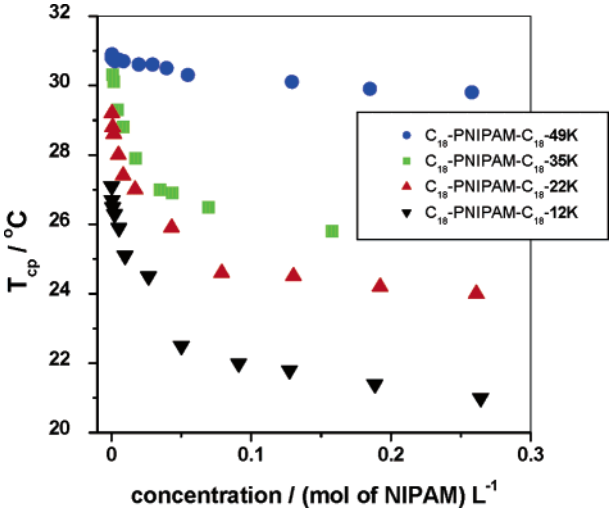


**Figure 6.** Plot of the changes of the cloud point $T_{cp}$ of aqueous solutions of various telechelic HM-PNIPAM samples as a function of polymer concentration.

intensity were not affected by more than ±0.2 °C for solutions heated at a faster rate.

Several trends emerge. The $T_{cp}$ values recorded for telechelic HM-PNIPAM solutions of identical concentration (Figure 6 and Figure 7, bottom) decrease with decreasing polymer molar mass, from a value of 30.7 °C ($C_{18}$-PNIPAM-$C_{18}$-49K, 1.0 g L$^{-1}$) to 25.1 °C ($C_{18}$-PNIPAM-$C_{18}$-12K, 1.0 g L$^{-1}$). In the case of the polymer of lowest molar mass, $T_{cp}$ drops by nearly 5.5 °C over a concentration range of ∼0.1 (mol of NIPAM) L$^{-1}$ (or 11 g L$^{-1}$), before leveling toward a constant value. In contrast, the $T_{cp}$ value of solutions of the polymer of highest molar mass is independent of concentration, except for very dilute solutions ($c$ < 0.6 g L$^{-1}$), which exhibit a slightly higher $T_{cp}$. The behavior of solutions of $C_{18}$-PNIPAM-$C_{18}$-49K is nearly the same as that of the PNIPAM/water system for which horizontal cloud point lines have been reported.[39,40]

**High-Sensitivity Differential Scanning Calorimetry.** Next, we monitored the heat-induced phase transition of aqueous telechelic HM-PNIPAM solutions by microcalorimetry, a technique that yields the changes of the partial heat capacity, $c_p$, of a solution as a function of temperature. In all measurements, the heating rate was 1 °C min$^{-1}$ and the solutions were heated from 10 to 70 °C. Thermograms recorded for aqueous solutions of four telechelic HM-PNIPAMs of fixed concentration (5.0 g L$^{-1}$ or ∼44 mM NIPAM L$^{-1}$) are presented in Figure 7

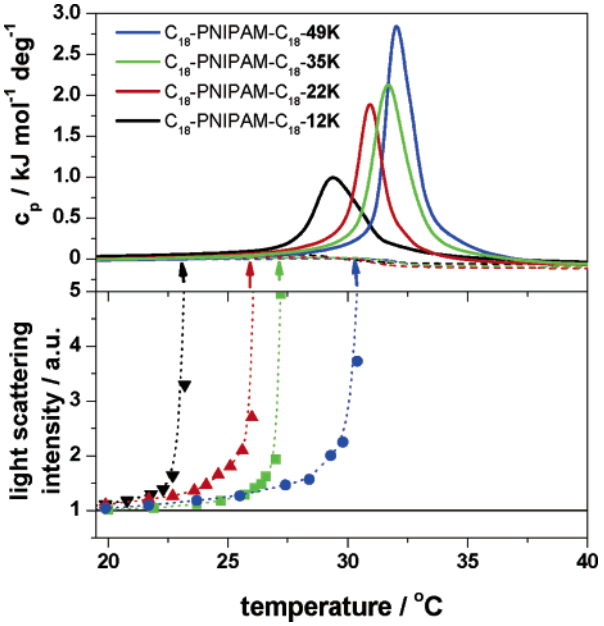


**Figure 7.** (top) Microcalorimetric endotherms recorded for aqueous solutions of telechelic HM-PNIPAM and (bottom) changes with temperature of the light scattering intensity recorded for aqueous solutions of telechelic HM-PNIPAMs (polymer concentration: 5 g L$^{-1}$). The arrows indicate the cloud point values.

(top). Four parameters can be extracted from the thermograms (see Experimental Section): $T_M$, the temperature corresponding to the transition maximum; $\Delta H$, the enthalpy of the transition; $\Delta T_{1/2}$, the width of the endotherm at half-height; and $\Delta c_p$, the difference in partial heat capacity after and before the transition (Table 2).

Visual comparison of the thermograms and the turbidity plots of aqueous telechelic HM-PNIPAMs (Figure 7, top and bottom, respectively) reveals that for each solution $T_{cp}$ is significantly lower than $T_M$. Also, while the $T_{cp}$ values decrease markedly as a function of increasing solution concentration (Figure 6), the $T_M$ values vary to a much lesser extent. For all polymer solutions, they are independent of concentration, except for concentrations less than ∼0.6 g L$^{-1}$ or ∼5 mM NIPAM L$^{-1}$ (Figure 8). This is in strong contrast with the behavior of PNIPAM solutions, for which it is usually observed that the maximum of the endotherm ($T_M$) corresponds well to the onset of turbidity increase.[41]

A systematic upward shift of the LCST with molecular weight was reported several years ago by Alami et al. in a study of the cloud points of aqueous telechelic poly(ethylene oxide)s.[42] In a recent study on the solution properties of thermosensitive telechelic poly(ethylene oxide-*co*-poly(propylene oxide)) bearing dodecyl end groups, Mori et al. also noted that the solution cloud point increases with the length of the polymer chain.[43] Such a miscibility improvement or shrinkage of the phase-separated region is a natural tendency, since for a fixed polymer concentration, the concentration of hydrophobic groups becomes smaller with increasing molecular weight. We observe a similar tendency for telechelic HM-PNIPAM solutions. End-chain association does not affect the coil-to-globule transition to the same extent as the cloud point because release of the bound water molecules upon heating takes place independently of association, in the ideal limit. Therefore, $T_M$ is expected to remain independent of polymer molecular weight. Since the sharp chain collapse seen in dilute aqueous PNIPAM solutions is mainly due to a cooperative dehydration,[12] i.e., bound waters

**Table 2. Thermal Properties of Aqueous Telechelic HM-PNIPAM Solutions (Polymer Concentration 1.0 g $L^{-1}$)**

| polymer | $T_{cp}$/°C | $T_M$/°C | $\Delta T_{1/2}$/°C | $\Delta H$/kJ/mol | $\Delta c_p$/J/(mol deg) | $\Delta V/V$/% | $1000\alpha_{25}/deg^{-1}$ | $d\alpha/dT^a/deg^{-2}$ |
|---|---|---|---|---|---|---|---|---|
| PNIPAM-10K | 31.8 | 32.8 | 3.5 | 6.93 | −107 | 1.50 | 0.99 | $5 \times 10^{-7}$ |
| $C_{18}$-PNIPAM-$C_{18}$-49K | 30.7 | 31.9 | 1.1 | 5.91 | −117 | 1.24 | 1.00 | $7 \times 10^{-6}$ |
| $C_{18}$-PNIPAM-$C_{18}$-35K | 28.8 | 31.6 | 1.2 | 5.19 | −123 | 1.17 | 0.95 | $6 \times 10^{-6}$ |
| $C_{18}$-PNIPAM-$C_{18}$-22K | 27.0 | 30.9 | 1.1 | 4.13 | −135 | 1.05 | 0.96 | $4 \times 10^{-6}$ |
| $C_{18}$-PNIPAM-$C_{18}$-12K | 25.1 | 29.4 | 1.4 | 3.55 | −150 | 0.98 | 1.12 | $2 \times 10^{-6}$ |

[a] Value calculated in the temperature range from 10 to 20 °C, thus for $T < T_M$ (see text).

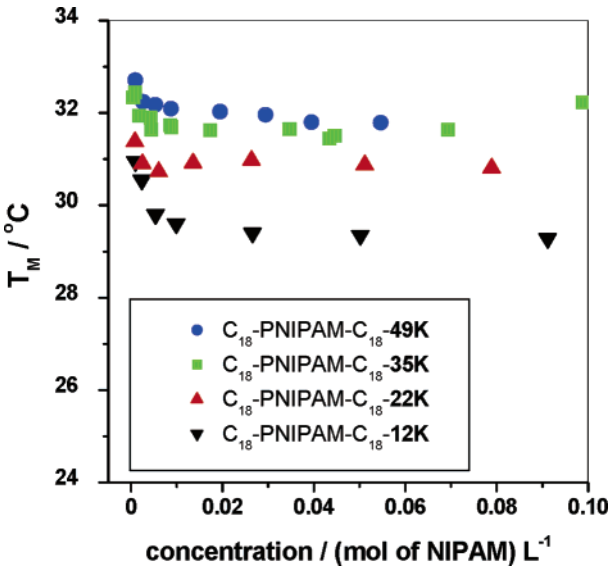


**Figure 8.** Plot of the changes of the temperature $T_M$ of maximum heat capacity of aqueous solutions of various telechelic HM-PNIPAM samples as a function of polymer concentration.

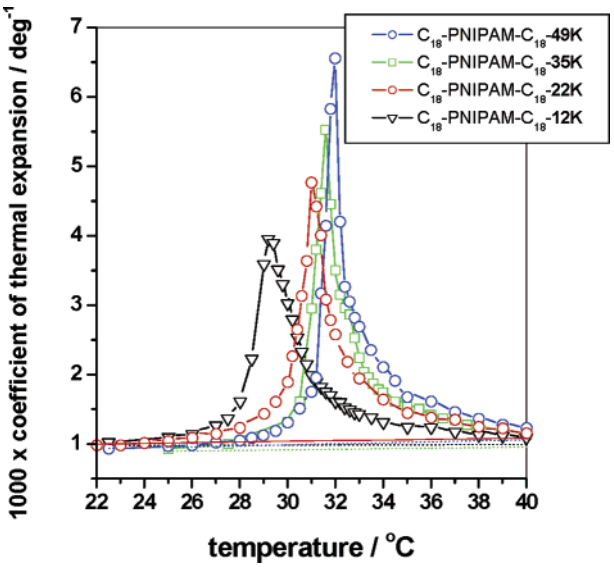


**Figure 9.** Temperature dependence of the coefficient of thermal expansion (α) of aqueous solutions of various telechelic HM-PNIPAM samples; (polymer concentration: 5 g $L^{-1}$).

are dissociated into the bulk not independently but in groups, the molecular-weight dependence of $T_M$ is also expected to be weak.

The enthalpy of the transition increases with increasing molar mass of telechelic HM-PNIPAM and, for a given sample, is independent of solution concentration (Table 2). It is lower than the value registered for the phase separation of PNIPAM solutions measured by us under the same conditions[22] and reported earlier by various groups.[5,44,45] The heat evolved upon phase separation is attributed to the release of water molecules bound to the polymer chain into bulk water. As the heat evolved during the phase transition of telechelic HM-PNIPAMs is smaller compared to PNIPAM, one has to conclude that fewer water/polymer H-bonds are broken, per NIPAM unit, during their heat-induced phase transition. This tendency may be taken as an indication that near the core of the micelles the PNIPAM chains are crowded to such an extent that the monomer density is sufficiently high to prevent formation of water/polymer hydrogen bonds. The temperature of the transition is not expected to change much as a result of the presence of such regions inaccessible to water molecules, given that $T_M$ depends only weakly upon the polymer molecular weight.

Further insight into the mechanism of the phase transition of telechelic HM-PNIPAMs can be gained by comparing the heat capacity, $c_p$, of solutions below and above $T_M$, as it is known that the transfer of nonpolar solutes into aqueous media is associated with a significant increase of the heat capacity.[46] Thus, the heat capacity of a native protein is lower than that of the denatured protein. Conversely, renaturation of a protein results in a decrease of its heat capacity.[47,48] Referring to the top section of Figure 7, we note that the partial heat capacity of solutions after the transition is smaller than that of the solution before the transition, ($\Delta c_p < 0$, Table 2). The same trend has been observed by us[22] and others in thermograms of aqueous PNIPAM.[5,49,50] It is usually taken as evidence of a decrease in the number of polymer/water contacts as a result of the phase transition, in analogy with the heat-induced refolding of proteins after cold denaturation. Interestingly, the $\Delta c_p$ values increase with decreasing telechelic polymer molecular weight. This is not the case for PNIPAM itself: the $\Delta c_p$ values are essentially independent of molecular mass.[1] The tendency of $\Delta c_p$ to become increasingly more negative upon decreasing polymer molecular weight suggests that there are differences in the hydration of the flower micelles depending on the length of the corona-forming chains and that there are more water/*n*-octadecyl chains contacts in the flower micelles with shorter PNIPAM loops, leading to higher values of $c_p$ below $T_M$.

**Pressure Perturbation Calorimetry.** PPC scans yield the changes with temperature of the thermal expansion coefficient (α) of a polymer in solution. Plots recorded for solutions of telechelic HM-PNIPAM (Figure 9) can be divided in four temperature ranges. Below the onset of the transition α remains constant. It undergoes a sharp increase for a temperature nearing the $T_M$ value of each polymer, reaches a maximum value for $T \sim T_M$, and decreases as the temperature further increases. The fact that the temperature corresponding to the maximum of the PPC trace nearly coincides with $T_M$ but not $T_{cp}$ is further evidence that the transition detected by calorimetry reflects the release of polymer-bound water molecules into bulk water. The phase separation observed at $T_{cp}$, which is induced by interactions of the hydrophobic termini, is not detectable by PPC.

The change in the volume of the hydration layer of the polymer during the phase transition, expressed as $\Delta V/V$ in percent of the partial volume of the polymer (eq 2, Experimental Section), can be extracted from PPC scans by integration of the changes in α as a function of temperature. It is the sum of

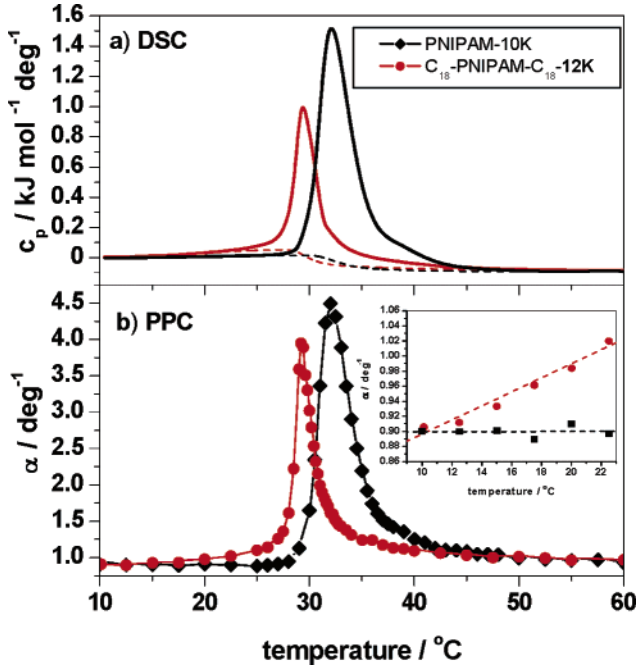


**Figure 10.** Microcalorimetric endotherms (top) and temperature dependence of the coefficient of thermal expansion (α) (bottom) of aqueous solutions of PNIPAM-10K and telechelic $C_{18}$-PNIPAM-$C_{18}$-12K; polymer concentration: 5 g/L$^{-1}$. Inset: expansion of the low-temperature region for the PPC scans.

the changes in the intrinsic volume of the polymer chains, assumed to remain constant during the transition, and the change in the volume of the water molecules as they escape from the structured layer of hydration of the polymer. The $\Delta V/V$ values decrease with decreasing HM-PNIPAM molar mass (Table 2), the trend also exhibited by the $\Delta H$ values (see above), strengthening our hypothesis that, as the micellar loops shorten, polymer−water hydrogen bonds are replaced by polymer/polymer hydrogen bonds.

**Phase Transitions of Aqueous PNIPAM and Aqueous Telechelic HM-PNIPAM Solutions: Similar, Yet Different.** In the course of a study on the effect of molar mass on the phase transition of PNIPAM samples of narrow size distribution, we prepared by RAFT polymerization a PNIPAM of molar mass similar to that of the shortest telechelic HM-PNIPAM of the series of this study. This sample, PNIPAM-10K, carries an *N*-isopropyl group at one end and an isobutyl group at the other. The two end groups are neutral and mimic the structure of the polymer repeat units. Relevant molecular data are listed in Table 1. Thermograms recorded for the two solutions are presented in Figure 10 (top), together with the changes with temperature of the expansion coefficients of the two solutions (Figure 10, bottom).

The values of $T_M$, $\Delta H$, and $\Delta V/V$ are significantly lower for solutions of the telechelic sample $C_{18}$-PNIPAM-$C_{18}$-12K, compared to PNIPAM-10K (Table 2). As discussed previously, $\Delta H$ and $\Delta V/V$ report on the changes in hydration of the polymer chain as the solution undergoes phase transition. The differences noted between the two samples concur and indicate that fewer water molecules are released (per mol NIPAM unit) during the transition of the telechelic HM sample compared to PNIPAM. The $T_M$ values for the two polymers are quite similar, as the polymer dehydration occurs cooperatively and independently on polymer molecular weight and presence of associations (vide supra).

Included in Figure 10 (bottom inset) is an expanded view of the PPC traces recorded between 10 and 22 °C for solutions of the two polymers. Note that the slope, $(d\alpha/dT)_l$, in the low-temperature region is steeper in the PPC trace recorded for the solution of telechelic HM-PNIPAM, compared to the solution of PNIPAM. This difference disappears in the high-temperature domain, where the slope $(d\alpha/dT)_h$ is negative and in the range $(2-7) \times 10^{-6}$ deg$^{-2}$ for both samples. Hepler pointed out several years ago that solutes that decrease the structure of water have a large positive α value at low temperature and $d\alpha/dT < 0$, whereas solutes acting as structure makers in water are characterized by a small positive or even negative α value and $d\alpha/dT > 0$.[51] The α value of the monomer, NIPAM, in water becomes progressively more positive as temperature increases, indicating that NIPAM is a structure maker in water.[52] The difference in $d\alpha/dT$ values observed in cold solutions of PNIPAM and its telechelic counterpart suggests that the hydrophobic groups linked to the polymer reinforce the structure-making character of polymer.

## Conclusions

Linking hydrophobic termini to a hydrophilic polymer chain results in a decrease of the cloud point temperature of this polymer. The cloud point depression is a direct consequence of the association of telechelic polymers into micelles and networks, which leads to an effective molecular weight higher than that of the corresponding PNIPAM homopolymer. Thus, the mixing entropy of telechelic polymers is lower than that of the homopolymer, and they tend to demix. This phenomenon was reported by Alami et al. in their study of telechelic PEO samples, for which the cloud point can drop by as much as 100 °C, depending on the polymer chain length.[42] We report here that the same effect takes place in the case of telechelic PNIPAM, albeit to a lesser degree. Calorimetric measurements and miscibility studies of HM-PNIPAM aqueous solutions have allowed us to detect experimentally the temperature, $T_M$, of the coil-to-globule collapse of the PNIPAM chain and the $T_{cp}$ of the solution. The $T_M$ value is almost the same for all polymers, independently of their molecular weight, and it is always higher than $T_{cp}$. Other parameters related to the PNIPAM chains dehydration mechanism, such as $\Delta H$ and $\Delta V/V$, indicate that fewer water molecules, per NIPAM units, are released from the hydrophobically end-modified polymer chains, at fixed polymer concentration, compared to PNIPAM. Inter- or intrapolymeric hydrogen bonds may form at the expense of water/polymer H-bonds as a consequence of chain crowding in the vicinity of the hydrophobic core.

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## References and Notes

(1) Schild, H. G. *Prog. Polym. Sci.* **1992**, *17*, 163.
(2) Winnik, F. M. *Polymer* **1990**, *31*, 2125.
(3) Winnik, F. M. *Macromolecules* **1990**, *23*, 233.
(4) Tam, K. C.; Wu, X. Y.; Pelton, R. H. *J. Polym. Sci., Polym. Chem. Ed.* **1993**, *31*, 963.
(5) Tiktopulo, E. I.; Bychkova, V. E.; Ricka, J.; Ptitsyn, O. B. *Macromolecules* **1994**, *27*, 2879.
(6) Wang, X.; Qiu, X.; Wu, C. *Macromolecules* **1998**, *31*, 2972.
(7) Maeda, Y.; Higuchi, T.; Ikeda, I. *Langmuir* **2001**, *17*, 7535.
(8) Stieger, M.; Richtering, W. *Macromolecules* **2003**, *36*, 8811.
(9) Kita, R.; Wiegand, S. *Macromolecules* **2005**, *38*, 4554.
(10) Matsuyama, A.; Tanaka, F. *J. Chem. Phys.* **1991**, *94*, 781.
(11) Wu, C.; Zhou, S. *Macromolecules* **1995**, *28*, 5388.

(12) Okada, Y.; Tanaka, F. *Macromolecules* **2005**, *38*, 4465.
(13) Taylor, L. D.; Cerankowsky, L. D. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 2551.
(14) Kikuchi, A.; Okano, T. *Adv. Drug Deliv. Rev.* **2002**, *54*, 53.
(15) Gil, E. S.; Hudson, S. M. *Prog. Polym. Sci.* **2004**, *29*, 1173.
(16) Schild, H. G.; Tirrell, D. A. *Langmuir* **1991**, *7*, 1319.
(17) Ringsdorf, H.; Venzmer, J.; Winnik, F. M. *Macromolecules* **1991**, *24*, 1678.
(18) Chung, J. E.; Yokoyama, M.; Suzuki, K.; Aoyagi, T.; Sakurai, Y.; Okano, T. *Colloids Surf. B* **1997**, *9*, 37.
(19) Chung, J. E.; Yokoyama, M.; Aoyagi, T.; Sakurai, Y.; Okano, T. *J. Controlled Release* **1998**, *53*, 119.
(20) Zhang, Y. B.; Li, M.; Fang, Q.; Zhang, Y. X.; Jiang, M.; Wu, C. *Macromolecules* **1998**, *31*, 2527.
(21) Kujawa, P.; Goh, E. C. C.; Calvet, D.; Winnik, F. M. *Macromolecules* **2001**, *34*, 6387.
(22) Kujawa, P.; Winnik, F. M. *Macromolecules* **2001**, *34*, 4130.
(23) Cao, Z.; Liu, W.; Gao, P.; Yao, K.; Li, H.; Wang, G. *Polymer* **2005**, *46*, 5268.
(24) Winnik, F. M.; Davidson, A. R.; Hamer, G. K.; Kitano, H. *Macromolecules* **1992**, *25*, 1876.
(25) Winnik, F. M.; Adronov, A.; Kitano, H. *Can. J. Chem.* **1995**, *73*, 2030.
(26) Winnik, M. A.; Yekta, A. *Curr. Opin. Colloid Interface Sci.* **1997**, *2*, 424.
(27) Pham, Q. T.; Russel, W. B.; Thibeault, J. C.; Lau, W. *Macromolecules* **1999**, *32*, 2996.
(28) Beaudoin, E.; Borisov, O.; Lapp, A.; Billon, L.; Hiorns, R. C.; Francois, J. *Macromolecules* **2002**, *35*, 7436.
(29) Kujawa, P.; Watanabe, H.; Tanaka, F.; Winnik, F. M. *Eur. Phys. J. E* **2005**, *17*, 129.
(30) Aseyev, V.; Tenhu, H.; Winnik, F. M. In *Self-Organization of Amphiphilic Copolymers in Aqueous Media*; Khokhlov, A. R., Ed.; Springer-Verlag GmbH: Heidelberg, Germany, in press.
(31) Lin, L.-N.; Brandts, J. F.; Brandts, M.; Plotnikov, V. *Anal. Biochem.* **2002**, *302*, 144−160.
(32) Brandts, J. F.; Lin, L.-N. *Thermochim. Acta* **2004**, *414*, 75.
(33) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559.
(34) Rizzardo, E.; Chiefari, J.; Mayadunne, R. T. A. In *Controlled/Living Radical Polymerization—Progress in ATRP, NMP, and RAFT*; Matyjaszewki, K., Ed.; American Chemical Society: Washington, DC, 2000; Vol. 768, pp 278−295.
(35) Moad, G.; Chong, Y. K.; Postma, A.; Rizzardo, E.; Thang. S. H. *Polymer* **2005**, *46*, 8458.
(36) Lai, J. T. *Tetrahedron Lett.* **2001**, *42*, 557.
(37) Gilman, H.; Wilder, G. R. *J. Am. Chem. Soc.* **1955**, *77*, 6644.
(38) Detailed analysis of the scattering results will be reported in a forthcoming publication.
(39) Afroze, F.; Nies, E.; Berghmans, H. *J. Mol. Struct.* **2000**, *554*, 55−68.
(40) Durme, K. V.; Van Mele, B.; Loos, W.; Du Prez, F. E. *Polymer* **2005**, *46*, 9851−9862.
(41) Garret-Flaudy, F.; Freitag, R. *J. Polym. Sci., Part A* **2000**, *38*, 4218.
(42) Alami, E.; Rawiso, M.; Isel, F.; Beinert, G.; Binana-Limbele, W.; Francois, J. *Adv. Chem. Ser.* **1996**, *248*, 343.
(43) Mori, T.; Shiota, Y.; Minagawa, K.; Tanaka, M. *J. Polym. Sci., Part A* **2005**, *43*, 1007.
(44) Cho, E. C.; Lee, J.; Cho, K. *Macromolecules* **2003**, *36*, 9929.
(45) Ding, Y.; Ye, X.; Zhang, G. *Macromolecules* **2005**, *38*, 904.
(46) Makhatadze, G. I.; Lopez, M. M.; Privalov, P. L. *Biophys. Chem.* **1997**, *64*, 93.
(47) Privalov, G. P.; Privalov, P. L. *Methods Enzymol.* **2000**, *323*, 31.
(48) Privalov, P. L. *J. Chem. Thermodyn.* **1997**, *29*, 447.
(49) Schild, H. G.; Tirell, D. A. *J. Phys. Chem.* **1990**, *94*, 4352.
(50) Tiktopulo, E. I.; Uversky, V. N.; Lushchik, V. B.; Klenin, S. I.; Bychkova, V. E.; Ptitsyn, O. B. *Macromolecules* **1995**, *28*, 7519.
(51) Hepler, L. G. *Can. J. Chem.* **1969**, *47*, 4613.
(52) Laukkanen, A.; Valtola, L.; Winnik, F. M.; Tenhu, H. *Macromolecules* **2004**, *37*, 2268.

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