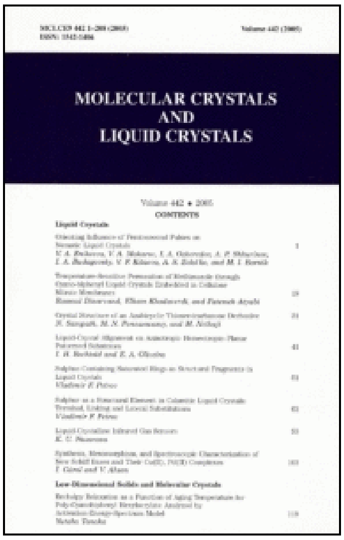


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644168

Synthesis and Association Behavior of Telechelic Poly(*N*-isopropylacrylamides) with Azobenzene End Groups

Norihito Ishii[a]; Rodolphe Obeid[b]; Xing-Ping Qiu[b]; Jun-ichi Mamiya[a]; Tomiki Ikeda[a]; Françoise M. Winnik[b]
[a] Chemical Resources Laboratory, Tokyo Institute of Technology, Midori-ku, Yokohama, Japan [b] Department of Chemistry and Faculty of Pharmacy, University of Montréal, Succursale Centre Ville, Montreal, Quebec, Canada

To cite this Article Ishii, Norihito , Obeid, Rodolphe , Qiu, Xing-Ping , Mamiya, Jun-ichi , Ikeda, Tomiki and Winnik, Françoise M.(2010) 'Synthesis and Association Behavior of Telechelic Poly(*N*-isopropylacrylamides) with Azobenzene End Groups', Molecular Crystals and Liquid Crystals, 529: 1, 60 — 70

To link to this Article: DOI: 10.1080/15421406.2010.495899
URL: http://dx.doi.org/10.1080/15421406.2010.495899

Mol. Cryst. Liq. Cryst., Vol. 529: pp. 60–70, 2010
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2010.495899

Synthesis and Association Behavior of Telechelic Poly(*N*-isopropylacrylamides) with Azobenzene End Groups

NORIHITO ISHII,[1] RODOLPHE OBEID,[2]
XING-PING QIU,[2] JUN-ICHI MAMIYA,[1]
TOMIKI IKEDA,[1] AND FRANÇOISE M. WINNIK[2]

[1]Chemical Resources Laboratory, Tokyo Institute of Technology, Midori-ku, Yokohama, Japan
[2]Department of Chemistry and Faculty of Pharmacy, University of Montréal, Succursale Centre Ville, Montreal, Quebec, Canada

*A telechelic poly(*N*-isopropylacrylamide) (PNIPAM) with azobenzene end-groups (telechelic Az-PNIPAM) was prepared by reversible addition-fragmentation chain transfer (RAFT) free radical polymerization of NIPAM. This polymer self-assembles in cold water forming nanoparticles with a hydrodynamic radius (R_H) of 8 nm and an aggregation number of 29 chains. The thermoresponsive behavior of Az-PNIPAM in water was investigated by turbidimetry and light scattering. In addition, the photoresponsive behavior of aqueous Az-PNIPAM was investigated by monitoring the changes with temperature of the solution and transmittance at 650 nm before and after irradiation at 366 nm.*

Keywords Azobenzene; liquid-crystalline molecules; reversible addition-fragmentation chain transfer (RAFT) polymerization; telechelic poly(*N*-isopropylacrylamide)

Introduction

Stimuli-responsive polymer gels and micelles have been studied extensively [1–3]. In particular, poly(*N*-isopropylacrylamide)s (PNIPAMs) and its derivatives have been explored due to their unique thermo-responsive properties in water [4–6]. One of the most interesting properties of PNIPAMs is the heat-induced change in its solubility in water. PNIPAM dissolves in cold water by forming hydrogen bonds between water molecules and the polymer amide groups. The solubility of PNIPAM is high in cold water but it decreases upon increasing the temperature. Water becomes a poor solvent for PNIPAM above 32°C. This useful property can be exploited in applications such as drug delivery system and cosmetics [7]. Winnik *et al.* reported the synthesis and solution properties of telechelic hydrophobically

---

Address correspondence to Tomiki Ikeda, Chemical Resources Laboratory, Tokyo Institute of Technology, R1-11, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan. Tel.: +81 45 924 5240; Fax: +81 45 924 5275; E-mail: tikeda@res.titech.ac.jp modified PNIPAMs [8,9], which form flower-like micelles in cold aqueous solution. The micelles exist as isolated entities in dilute cold aqueous solution and form large particles above the cloud-point temperature [10]. The azobenzene chromophore, which exhibits photochromism and liquid-crystalline properties, has been studied extensively as a molecule able to trigger changes in the properties of materials in response to photoirradiation [11–13] as a result of the reversible photoisomerization of the azo linkage. We report here the synthesis of a telechelic PNIPAM with azobenzene end-groups obtained by reversible addition-fragmentation chain transfer (RAFT) polymerization of NIPAM and further end-group transformation. The effect of the azobenzene end-groups on the self-assembly of the polymers in water and the photo/temperature responsive properties of the polymers in water were investigated by physico-chemical methods.

Experimental

Instrumentation and Measurements

All ^{1}H NMR spectra were recorded on a Lambda-300 (300 MHz) spectrometer. Gel permeation chromatography (GPC) was performed with a Japan Spectroscopy Co., model DG-980-50 system equipped with a refractive index detector and three Shodex columns (K803 + K804 + K805) eluted with DMF at 40°C. The molecular weight values were determined using a calibration curve obtained with PMMA standards. High sensitivity differential calorimetry (HS-DSC) measurements were performed on a VP-DSC microcalorimeter (MicroCal Inc.) at an external pressure of ca. 180 kPa. The cell volume was 0.517 ml. The heating rate was 1°C/min. The polymer concentration was 1.0 g/l, unless otherwise specified. The solutions for analysis were degassed at 25°C for 20 min. They were equilibrated at 10°C for 1 h before initiation of the heating process. The samples were heated from 10 to 80°C and cooled back immediately to 10°C. Four consecutive heating and cooling scans were performed in all cases. Data were corrected for instrument response time and analyzed using the software supplied by the manufacturer.

UV-Vis spectra were recorded with a JASCO, V-550 UV-visible spectrophotometer, which was used also for turbidity measurements, which yielded the cloud points (T_{cp}) of polymer solutions. The T_{cp} values were determined by spectrometric detection of the changes in turbidity (650 nm) of aqueous polymer solutions (1.0 g/l) heated at a constant rate (1°C/min). The cloud points reported are the temperatures corresponding to a 50% decrease of the solution transmittance.

Static (SLS) and dynamic light scattering (DLS) 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 ($\lambda = 633$ nm), and a C25P circulating water bath (Thermo Haake). SLS experiments yield the apparent weight-average molar mass ($M_{w,app}$) 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, known as the excess Rayleigh ratio $R(q, c)$ given by Eq. (1):

$$\frac{K(c - c_{\mathrm{mic}})}{R(q,c)} \cong \frac{1}{M_{\mathrm{w,app}}P(\Theta)} + 2A_2(c - c_{\mathrm{mic}}) \tag{1}$$

where c is the polymer concentration, c_{mic} is the concentration of micellization onset, q is the scattering vector ($q = (4\pi n/\lambda)\sin(\Theta/2)$, A_2 is the second virial coefficient, n is the refractive index of the solvent, λ is the wavelength of the light in the vacuum, and Θ is the scattering angle (30°–150°). The scattering constant is $K = 4\pi^2 n^2 (\mathrm{d}n/\mathrm{d}c)^2/N_A\lambda^4$, where $\mathrm{d}n/\mathrm{d}c$ is the refractive index increment and N_A is Avogadro's number. The $\mathrm{d}n/\mathrm{d}c$ of the derivatized PNIPAM was 0.074 ml/g for aqueous solutions at 24°C and a wavelength of 690 nm. In Eq. (1), it is assumed that the contribution of a single polymer chain to the scattering intensity is negligible, compared to that of the micelles. Data recorded for solutions of concentration c were analyzed according to the Zimm equation, assuming that the macromolecules are in a swollen conformation. In this case, the particle scattering function is $P(\Theta) = 1 - (q^2R_G^2)/3$, where R_G is the radius of gyration. Since $(q^2R_G^2)/3 << 1$, it may be assumed that $1/[1 - (q^2R_G^2)/3] \cong 1 + (q^2R_G^2)/3$. Thus, Eq. (1) becomes

$$\frac{K(c - c_{\mathrm{mic}})}{R(q,c)} \cong \frac{1}{M_{\mathrm{w,app}}}\left(1 + \frac{R_G^2}{3}q^2\right) + 2A_2(c - c_{\mathrm{mic}}) \tag{2}$$

The apparent mass of a polymer ($M_{\mathrm{w,app}}$) in a solution of concentration c was obtained by extrapolation of the scattered intensity $R(q, c)/(c - c_{\mathrm{mic}})$ to $q = 0$. The apparent radius of gyration of the scattering objects in a solution of concentration c was obtained by a mean-square linear fit of the inverse of the scattered intensity versus q^2 (see Eq. (2)).

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 (τ) 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 $1/(\tau q^2)$ to $q = 0$ yields the value of D, which is related to the average hydrodynamic radius R_H of the scattering objects by Eq. (3):

$$D = \frac{k_B T}{6\pi\eta_s R_H} \tag{3}$$

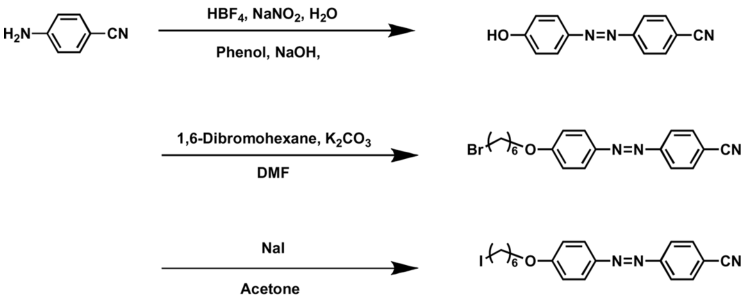
where η_S the viscosity of the solvent, k_B is the Boltzmann constant, and T is the absolute temperature.

Materials

4-Cyano-4′-(6-bromohexyloxy)azobenzene was prepared following a reported procedure [14] starting from 4-nitrobenzonitrile. Water was deionised with a Millipore Milli-Q system.

Synthesis

Synthesis of 4-Cyano-4′-(6-iodohexyloxy)azobenzene (I6Az) (Scheme 1). 4-132#Cyano-4′-(6-bromohexyloxy)azobenzene (1.0 g, 2.6 mmol) and sodium iodide (3.9 g, 26 mmol) were dissolved in acetone (40 ml). The mixture was heated



Scheme 1. Synthetic routes of I6Az.

at reflux with stirring for 3 h. It was cooled to room temperature and the acetone was removed under vacuum. The solid residue was dissolved in chloroform, washed with water, dried over anhydrous $MgSO_4$, filtered. The solvent was removed from the filtrate with a rotary evaporator, yielding solid, which was recrystallized from hexane/CH_2Cl_2 (8/2 v/v) Yield: 1.0 g, 88%.

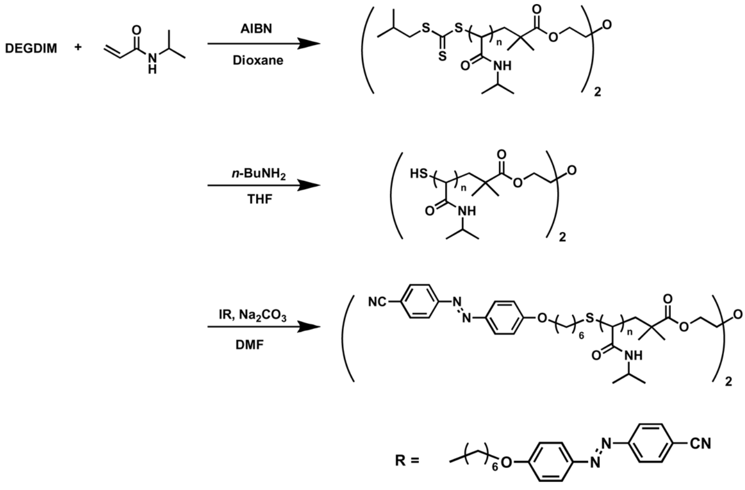
^{1}H NMR ($CDCl_3$) ppm, δ 1.59 (m, $CH_2ICH_2C\boldsymbol{H_2}$), 1.89 (m, $CH_2IC\boldsymbol{H_2}$ and -$OCH_2C\boldsymbol{H_2}$), 3.24 (t, $C\boldsymbol{H_2}I$), 4.08 (t, -$OC\boldsymbol{H_2}$), 7.02 (d, Ar-$\boldsymbol{H}$), 7.80 (d, Ar-$\boldsymbol{H}$), 7.95 (d, Ar-$\boldsymbol{H}$).

Polymerization. A solution of the chain transfer agent (synthesized according to references [15,16]) (DEGDIM, 124 mg, 0.22 mmol), the initiator (AIBN, 3.5 mg, 0.022 mmol), and the monomer (NIPAM, 2.0 g, 18 mmol) in 1,4-dioxane (10 ml) was placed in a round-bottom flask with rubber septa. The solution was deoxygenated by bubbling nitrogen for 30 min at room temperature. The reaction flask was placed in an oil bath preheated to 65°C. The polymerization was allowed to proceed for 4 h under constant magnetic stirring. At the end of this polymerization, the solution was cooled to room temperature. The polymer, α,ω-di(isobutylthiocarbonylthio)-poly(*N*-isopropylacrylamide), was isolated by precipitation in diethyl ether. It was purified further by two consecutive reprecipitations from THF into diethyl ether. Yield: 1.90 g, 88%.

^{1}H NMR ($CDCl_3$) ppm, δ 1.01 (d, -$CH_2CH(C\boldsymbol{H_3})_2$), 1.13 (s, -$NHCH(C\boldsymbol{H_3})_2$), 1.27–2.30 (multipeaks, polymer backbone protons), 3.15 (s, -$SC\boldsymbol{H_2}$), 3.61 (s, -$OC\boldsymbol{H_2}$), 3.95 (s, -$NHC\boldsymbol{H}$), 4.16 (s, -$C(=O)OC\boldsymbol{H_2}$), 6.40 (bs, -$C(=O)N\boldsymbol{H}$).

Preparation of Telechelic α,ω-Dimercapto Poly(N-isopropylacrylamide)s (SH-PNIPAMs). *n*-Butylamine (0.78 g, 0.16 mmol) and tris(2-carboxyethyl) phosphine hydrochloride (TCEP, trace amount), were added to a solution of α,ω-di(isobutylthiocarbonylthio)-poly(*N*-isopropylacrylamide) (0.70 g 0.2 mmol) in THF (10 ml) (Scheme 2). The resulting solution was stirred for 1 h at room temperature under a nitrogen atmosphere. The product was recovered by precipitation in diethyl ether and purified by two consecutive reprecipitations from THF into diethyl ether. Yield: 0.71 g. ^{1}H NMR ($CDCl_3$) ppm, δ 1.12 (s, -$NHCH(C\boldsymbol{H_3})_2$), 1.30–2.20 (multiplets, polymer backbone protons), 3.67 (s, -$OC\boldsymbol{H_2}$), 3.96 (s, -$NHC\boldsymbol{H}$), 4.15 (s, -$C(=O)OC\boldsymbol{H_2}$), 6.40 (bs, -$C(=O)N\boldsymbol{H}$).

Preparation of Telechelic α,ω-Diazobenzene PNIPAM. Sodium carbonate (1.7 g, 16 mmol) was added to a solution of I6Az (0.062 g, 0.14 mmol, 1.2 equiv.) and



Scheme 2. Synthetic routes of telechelic Az-PNIPAM.

telechelic SH-PNIPAM (1.2 g, 0.12 mmol) in distilled DMF (10 ml). A crystal of TCEP was added to the mixture to prevent disulfide bond formation. The solution was stirred under nitrogen for 24 h. The polymer was recovered by precipitation in diethyl ether and purified by two consecutive reprecipitations from THF into diethyl ether. Yield: 0.99 g, 79%.

^{1}H NMR ($CDCl_3$) ppm, δ 1.14 (s, -NHCH($C\boldsymbol{H}_3$)$_2$), 1.30–2.30 (multiplets, polymer backbone protons), 3.67 (s, -$OC\boldsymbol{H}_2$), 3.97 (s, -NHC$\boldsymbol{H}$), 4.17 (s, -C(=O)OC$\boldsymbol{H}_2$), 6.40 (bs, -C(=O)N$\boldsymbol{H}$), 6.98 (d, Ar-$\boldsymbol{H}$), 7.74 (m, Ar-$\boldsymbol{H}$), 7.93 (m, Ar-$\boldsymbol{H}$).

Examination of the Concentration of the Onset of Micellization (c_{mic})

The c_{mic} was determined using Nile Red. Solutions containing a constant Nile Red concentration (10 μM) and varying amounts of polymer (1.8×10^{-4} to 3.0 g/l) were prepared, starting from a stock solution (3.0 g/l). UV-visible absorption spectra of the solutions were recorded from 500 to 650 nm.

Photoresponsive Behavior

The transmittance at 650 nm of aqueous solutions of the telechelic Az-PNIPAM (0.2 g/l) was measured as a function of temperature before and after irradiation of the solutions at 366 nm (1 mW/cm^2).

Results and Discussion

Synthesis of Telechelic Diazobenzene PNIPAM (Az-PNIPAM)

The telechelic diazobenzene PNIPAM (Az-PNIPAM) was prepared in three steps, as depicted in Scheme 2. First, NIPAM was polymerized at 65°C in dioxane in the presence of the difunctional CTA diethylene glycol di(2-(1-isobutyl)sulfanylthiocarbonylsulfanyl-2-methylpropionate (DEGDIM) and AIBN acting as an initiator. The polymerization was left to proceed to high conversion (~95%) [8]. The

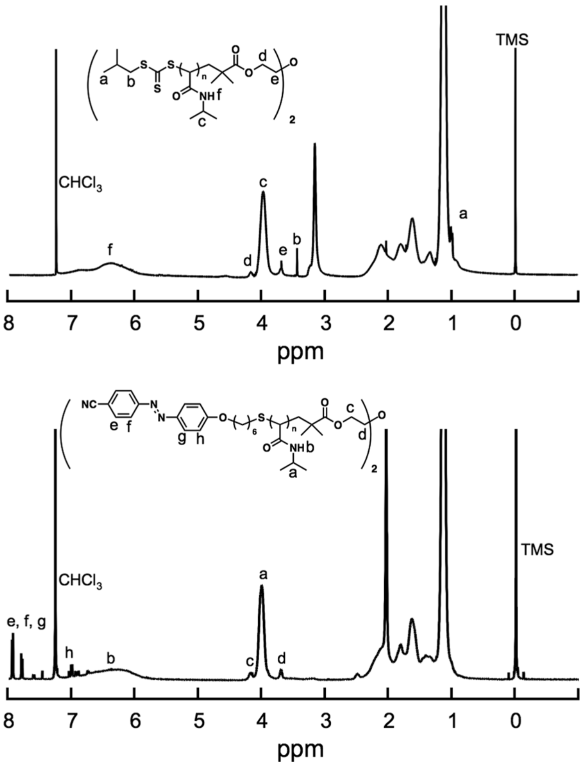


Figure 1. ^{1}H NMR spectrum of telechelic iBu-PNIPAM (top) and telechelic Az-PNIPAM (bottom).

[NIPAM]/[DEGDIM] molar ratio in the polymerization mixture was adjusted to attain a polymer of molecular weight ~10,000 g/mol. The GPC elution profile of the polymer was monomodal and symmetrical and the polydispersity index of the polymer was 1.08. The structure of the polymer was ascertained by analysis of its ^{1}H NMR spectrum in $CDCl_3$ (Fig. 1, top). It is possible to calculate the number average molecular weight from the ^{1}H NMR spectrum of the polymer, using the value of the integral of the signals due to *H*c (3.97 ppm) and *H*e (3.67 ppm) [8]. The number average molecular weight was determined also from the UV-vis spectrum of the polymer, which exhibits a strong absorbance centered at 310 nm ascribed to the thiocarbonylthio moiety, which can be used to calculate the M_n value ($M_n = w/c_{CTA}$), where w is the weight of polymer (in g) and $c_{\rm CTA}$ is the amount of thiocarbonylthio residues in the sample (in mole). The values of the number average molecular weight from ^{1}H NMR spectrum and the UV–vis spectrum are in good agreement with the value obtained by GPC (Table 1).

Next, the isobutylthiocarbonylthio termini of the polymer were converted to thiols by aminolysis, using a 10-molar excess of *n*-butylamine, with respect to thiocarbonylthio groups, in order to ensure completeness of the reaction. Aminolysis proceeded rapidly at room temperature, reaching near completion within 1 h, as confirmed by the disappearance of the absorbance at 310 nm in the UV-vis spectrum of the polymer. Finally, the telechelic dithiol PNIPAM was reacted with 4-cyano-4′-(6-iodohexyloxy)azobenzene in DMF containing sodium carbonate. The evolution

Table 1. Number average molecular weight

M_n (g/mol)			
GPC[a]	NMR[b]	UV-vis[c]	M_w/M_n (GPC)[a]
10500	11500	11800	1.08

[a]GPC condition: Flow rate 1 ml/min, Solvent DMF, Temperature 40°C.
[b]$M_n = [Hc]/[He] \times 4 \times M_o + M_{DEGDIM}$.
[c]$M_n = w/c_{CTA}$.

of the reaction was assessed by measuring the residual thiol concentration in aliquots of the reaction mixture taken at various time intervals. A reaction time of 24 h was sufficient to ensure completion of the reaction. The level of end-group functionalization was 99.5%, as determined by UV-vis spectroscopy.

Self-Assembly of Telechelic Az-PNIPAM in Water

Spectroscopic and light scattering experiments were carried out in order to confirm the presence of micellar assemblies in aqueous solutions of telechelic Az-PNIPAM, to characterize the assemblies in terms of size, aggregation number and concentration of the onset of micellization (c_{mic}) (Table 2), and to assess the effect of changes in solution temperature on the polymer self-assembly. The c_{mic} of the telechelic Az-PNIPAM in water was determined by UV-vis spectroscopy using Nile red as absorption probe. Nile red is poorly soluble in water. However in micellar solution, the dye is solubilized within the hydrophobic core of the micelles, and, consequently, the dye absorbance increases significantly. The absorbance at 582 nm of mixed solutions of Nile red (10 μM) and telechelic Az-PNIPAM was measured as a function of polymer concentration for solutions kept at 10°C. The absorbance remained very low for solutions of $c_{pol} < 0.03$ g/l. It increased sharply as the polymer concentration exceeded this value, reaching a plateau value for $c > 0.06$ g/l. The c_{mic} value of the telechelic Az-PNIPAM in water (0.056 g/l) was determined from a plot of the absorbance at 582 nm vs c_{pol}. It was taken as the concentration of the onset of absorbance increase (Fig. 2). The size of micelles and their aggregation number in water (1.0 g/l) at 8°C were 8 nm and 29 polymer chains, as determined, respectively by DLS and SLS.

Temperature Dependence of the Self-Assembly of Telechelic Az-PNIPAM in Water

Aqueous solutions of telechelic Az PNIPAM became turbid in response to an increase in temperature. Their cloud point temperature ($T_{cp} = 21°C$) was determined

Table 2. c_{mic} and light scattering data for solution of a telechelic Az-PNIPAM sample in dilute aqueous solution

c_{mic} (g/l)	N_{agg} SLS	$M_{w,app}$ (g/mol)	R_G (nm)	R_G/R_H	R_H(nm) $T = 8°C$
0.056	~29	2.9×10^5	17.5	1.6	8.0

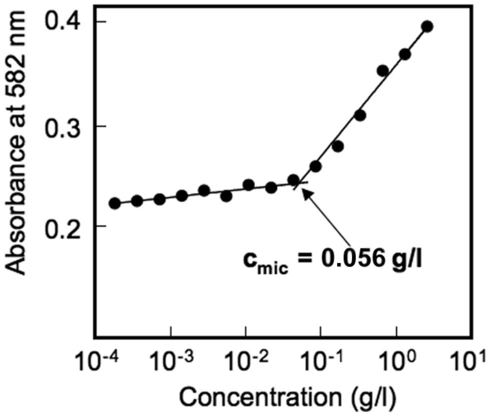


Figure 2. The concentration of the onset of micellization using the absorption spectra of Nile red as a probe.

by measuring the changes in turbidity (650 nm) of an aqueous telechelic Az PNIPAMs solution (1.0 g/l) heated at a constant rate (1°C/min). The T_{cp} value reported here is the temperature for which the solution transmittance falls below 50% (Fig. 3a). The heat-induced phase transition of a telechelic Az-PNIPAM aqueous solution was monitored also by microcalorimetry. A thermogram recorded for an aqueous solution of telechelic Az-PNIPAM (1.0 g/l) (Fig. 3b) presents a sharp endotherm with a maximum (T_M) at 25.5°C and a transition enthalpy (ΔH) of 1.25 kcal/mol NIPAM units. The temperature of the endotherm onset (10°C) corresponds well to the cloud point value recorded by turbidimetry, as observed previously [17]. The changes in the micellar size as a function of solution temperature

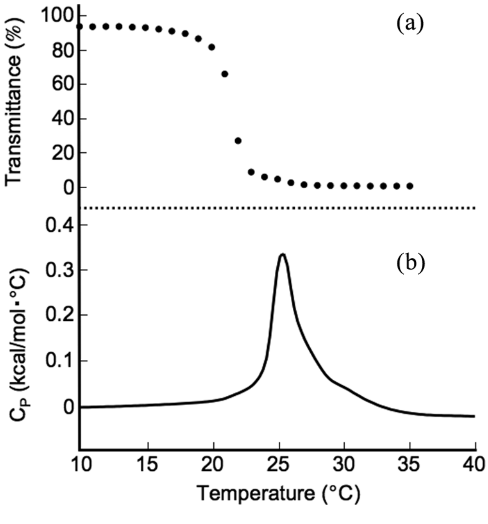


Figure 3. Changes in transmittance as a function of temperature of the telechelic Az-PNIPAM in water (a) and temperature dependence of the specific heat capacity of the telechelic Az-PNIPAM in water upon heating and cooling at a rate of 1°C/min (b).

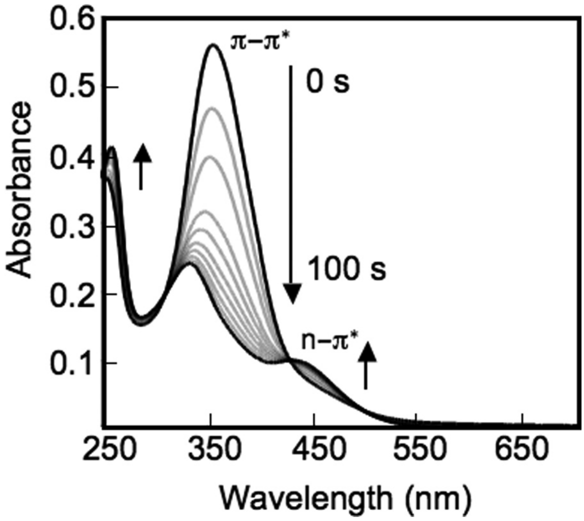


Figure 4. Changes in the absorption spectra of the telechelic Az-PNIPAM in water (0.14 g/l) upon photoirradiation (1 mW/cm^2) at 366 nm.

were monitored by DLS measurements. The hydrodynamic radius of the micelles underwent a sharp increase as the solution temperature reached 21°C, signaling the formation of an intermicellar network. For T = 25°C, the size of the aggregates exceeded the limit of detection (~800 nm) of the light scattering system employed. Further heating of the solution triggered a significant shrinking of the aggregates, which had a hydrodynamic radius of 270 nm and narrow size distribution for T = 34°C, a temperature for which collapsed PNIPAM chains have a tendency to form compact mesoglobules [17].

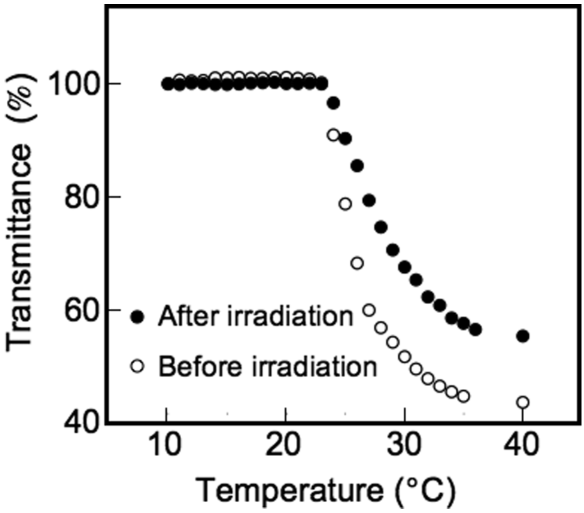


Figure 5. Changes in transmittance of probe light in solution of the telechelic Az-PNIPAM as a function of temperature before and after irradiation at 366 nm.

Photoresponsive Behavior of the Telechelic Az-PNIPAM in Water

Photoirradiation ($\lambda = 366\,\text{nm}$) of an aqueous telechelic Az-PNIPAM solution resulted in a decrease of the π-π^* band of the azobenzene chromophore centered at 352 nm and an increase of the n-π^* transition band at 257 and 446 nm (Fig. 4), confirming the occurrence of the *trans-cis* photoisomerization of the azobenzene moiety in the telechelic Az-PNIPAM aqueous solution. Next, the cloud point of telechelic Az-PNIPAM (0.2 g/l) in aqueous solution was measured before and after irradiation at 366 nm (Fig. 5). The temperature, at which transmittance started to decrease, was nearly the same before and after photoirradiation. However, the transmittances at 40°C of the two samples were different, which may be taken as an indication of a change in the morphology of the aggregates formed by the polymers carrying different isomers of azobenzene end-groups.

Conclusions

By using RAFT polymerization we prepared a telechelic PNIPAM of narrow molecular weight distribution modified with an azobenzene moiety on each chain end. The telechelic Az-PNIPAM in water above 0.056 g/l forms micellar assemblies. The size of the micelle and the aggregation number of this polymer in water (1.0 g/l) were 8 nm and 29 polymer chains at 8°C. Upon heating above the cloud point (21°C), micelles associate into larger objects (1,400 nm) as the solution temperature reaches 25°C: this temperature corresponds to the temperature of the phase transition of telechelic Az-PNIPAM in water. Further heating of the solution triggered a shrinking of the aggregate size, which is 270 nm at 34°C. Furthermore, The temperature, at which transmittance started to decrease, was nearly the same before and after photoirradiation. However, the final values of transmittance were different between the two samples. These results indicate that Az-PNIPAM in water shows the photoresponsive behavior. Further work is in progress aimed at progresses of the photoresponsiveness and liquid-crystalline property.

References

[1] Szczubiaka, K., Ishikawa, K., & Morishima, Y. (2000). *Langmuir*, *16*, 2083.

[2] Obeid, R., Maltseva, E., Thünemann, A. F., Tanaka, F., & Winnik, F. M. (2009). *Macromolecules*, *42*, 2204.

[3] Jiang, X., Lavender, C. A., Woodcock, J. W., & Zhao, B. (2008). *Macromolecules*, *41*, 2632.

[4] Pelah, A., Seemann, R., & Jovin, T. M. (2007). *J. Am. Chem. Soc.*, *129*, 468.

[5] Sundararaman, A., Stephan, T., & Grubbs, R. B. (2008). *J. Am. Chem. Soc.*, *130*, 12264.

[6] Morimoto, N., Ohki, T., Kurita, K., & Akiyoshi, K. (2008). *Macromol. Rapid Commun.*, *29*, 672.

[7] Sugiyama, K., Hanamura, R., & Sugiyama, M. (1997). *J. Polym. Sci. Part A: Polym. Chem.*, *35*, 3349.

[8] Segui, F., Qiu, X. P., & Winnik, F. M. (2008). *J. Polym. Sci. Part A: Polym. Chem.*, *46*, 314.

[9] Kujawa, P., Tanaka, F., & Winnik, F. M. (2006). *Macromolecules*, *39*, 3048.

[10] Koga, T., Tanaka, F., Motokawa, R., Koizumi, S., & Winnik, F. M. (2008). *Macromolecules*, *41*, 9413.

[11] Yamada, M., Kondo, M., Mamiya, J., Yu, Y., Kinoshita, M., Barrett, C. J., & Ikeda, T. (2008). *Angew. Chem. Int. Ed.*, *47*, 4986.

[12] Han, K., Su, W., Zhong, M., Yan, Q., Luo, Y., Zhang, Q., & Li, Y. (2008). *Macromol. Rapid Commun.*, *29*, 1866.

[13] Lin, L., Yan, Z., Gu, J., Zhang, Y., Feng, Z., & Yu, Y. (2009). *Macromol. Rapid Commun.*, *30*, 1089.

[14] Robello, D. R. (1990). *J. Polym. Sci., Part A: Polym. Chem.*, *28*, 1.

[15] Qiu, X. P., & Winnik, F. M. (2007). *Macromolecules*, *40*, 872.

[16] Qiu, X. P., Tanaka, F., & Winnik, F. M. (2007). *Macromolecules*, *40*, 7069.

[17] Kujawa, P., Aseyev, V., Tenhu, H., & Winnik, F. M. (2006). *Macromolecules*, *39*, 7686.