SHORT COMMUNICATIONS

Thermoresponsive Property Controlled by End-Functionalization of Poly(*N*-isopropylacrylamide) with Phenyl, Biphenyl, and Triphenyl Groups

Qian DUAN,[1] Atsushi NARUMI,[2] Yutaka MIURA,[1] Xiande SHEN,[1]
Shin-Ichiro SATO,[1] Toshifumi SATOH,[1,3] and Toyoji KAKUCHI[1,†]

[1]*Division of Biotechnology and Macromolecular Chemistry, Graduate School of Engineering,
Hokkaido University, Kita 13, Nishi 8, Kita-ku, Sapporo 060-8628, Japan*
[2]*National Institute of Advanced Industrial Science and Technology (AIST), Sapporo 062-8517, Japan*
[3]*Division of Innovative Research, Creative Research "Sousei", Hokkaido University, Sapporo 060-0808, Japan*

Poly(*N*-isopropylacrylamide) (PNIPAM) exhibits a coil-globule transition in aqueous solution at the lower critical solution temperature (LCST) of *ca.* 32 °C.[1] This interesting property has induced numerous studies about applications for PNIPAM and its derivatives,[2] while the PNIPAM with well-defined structures, such as the predicted molecular weight and narrow molecular weight distribution, has been demanded due to the increasing interest as thermoresponsive smart materials. Thus, the controlled polymerization of *N*-isopropylacrylamide (NIPAM) has been recently developed using living radical techniques.[3–5] For examples, 2-chloropropionates are reported to act as effective initiators for the atom transfer radical polymerizations (ATRP) of NIPAM; Masci *et al.* reported that the ATRP of NIPAM was performed in a mixed solvent of DMF and water using ethyl 2-chloropropionate as the initiator and CuCl/tris[2-(dimethylamino)ethyl]amine (Me₆TREN) as the catalyst system to produce PNIPAM with a controlled molecular weight and low polydispersity,[4b] and Stöver *et al.* reported that the ATRP of NIPAM by CuCl/Me₆TREN proceeded in a controlled manner using methyl 2-chloropropionate as the initiator and 2-propanol and *tert*-butyl alcohol as the solvents.[4f] In general, one of the significant merits for living polymerization is to produce end-functionalized polymers using suitably designed initiators. Especially, the hydrophobic end-group in the PNIPAM is known to affect its thermoresponsive property,[6] thus the polymerization of NIPAM using initiators with strong hydrophobic groups is of prime interest, because such a

method has high potential of becoming an easy, direct, and reproducible approach to afford the polymers with a tuned thermoresponsive property. However, there are few reports on the polymerization of NIPAM using such specially designed initiators.

In this communication, phenyl 2-chloropropionate (**1a**), (2′-phenyl)phenyl 2-chloropropionate (**1b**), (4′-phenyl)phenyl 2-chloropropionate (**1c**), and (2′,6′-diphenyl)phenyl 2-chloropropionate (**1d**) were prepared as the initiators for the ATRP of NIPAM. The polymerization of NIPAM was carried out using the initiating system consisting of **1a–d**/CuCl/Me₆TREN affording the end-functionalized PNIPAM with the hydrophobic groups, such as the phenyl, (2′-phenyl)phenyl, (4′-phenyl)phenyl, and (2′,6′-diphenyl)phenyl groups (**2a**, **2b**, **2c**, and **2d**, respectively) as illustrated in Scheme 1. In addition, we now report that the aqueous solutions of **2c** and **2d** showed an LCST at the very low temperature of *ca.* 21 °C due to the formation of the PNIPAM-aggregates with a high aggregation number, thus the initiators **1c** and **1d** are very useful tools for introducing a strong hydrophobic property into the chain-end of PNIPAM.

EXPERIMENTAL

Materials

N-Isopropylacrylamide (NIPAM) (97%, Aldrich) was recrystallized twice from hexane/toluene (10/1, v/v) and stored in an inert atmosphere at −30 °C. Tris(2-(dimethylamino)ethyl)amine (Me₆TREN) was synthesized according to the published procedure.[7] 2-

---

[†]To whom correspondence should be addressed (Tel/Fax: +81-11-706-6602, E-mail: kakuchi@poly-mc.eng.hokudai.ac.jp).
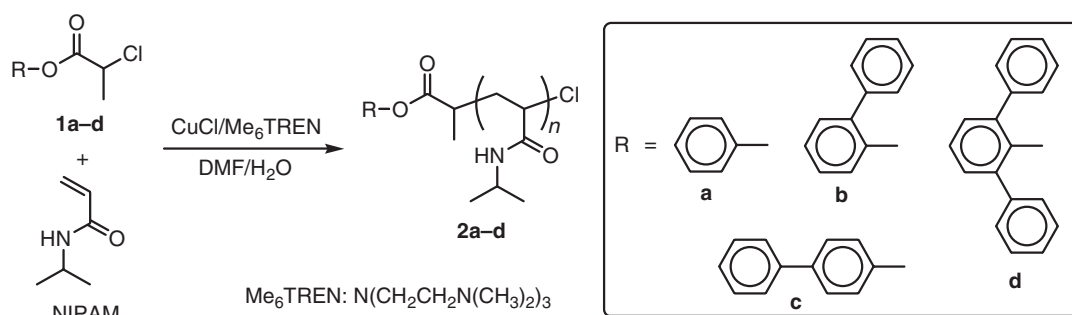
Scheme 1.

Phenylphenol (> 98.0%), 4-phenylphenol (> 99.0%), and 2-chloropropionyl chloride (> 95%) were purchased from Tokyo Kasei Kogyo Co., Ltd., and used without purification. Phenol (>99.0%, Acros Organics Company), 2,6-diphenylphenol (97%, Acros Organics Company), copper(I) chloride (CuCl, 99.999%, Aldrich), *N*,*N*-dimethylformamide (> 99.5%, Kanto Chemical Co., Inc.), and all other reagents were used as received.

Instruments

Size exclusion chromatography (SEC) was performed at $40\,^{\circ}$C using a Jasco high performance liquid chromatography (HPLC) system (PU-980 Intelligent HPLC pump, CO-965 Column oven, RI-930 Intelligent RI detector, and Shodex DEGAS KT-16) equipped with a Shodex Asahipak GF-310 HQ column (linear, $7.6\,$mm $\times\ 300\,$mm; pore size, $20\,$nm; bead size, $5\,\mu$m; exclusion limit, 4×10^4) and a Shodex Asahipak GF-7M HQ column (linear, $7.6\,$mm $\times\ 300\,$mm; pore size, $20\,$nm; bead size, $9\,\mu$m; exclusion limit, 4×10^7) in DMF containing lithium chloride ($0.01\,$M) at a flow rate of $0.4\,$mL·min^{-1}. The number-average molecular weight (M_n) and polydispersity (M_w/M_n) of the polymers were calculated on the basis of a polystyrene calibration.

A static laser light scattering (SLS) measurement was performed using an Otsuka Electronics CALLS-1000 light scattering spectrometer ($\lambda = 632.8\,$nm). The refractive index increment (dn/dc) was measured using an Otsuka Electronics DRM-1021 double-beam differential refractometer ($\lambda = 632.8\,$nm). Ultraviolet–visible (UV–vis) spectra were measured with a $10\,$mm path length using a Jasco V-550 spectrophotometer, which used a deuterium lamp as the light source for the UV range (190–350 nm) and a halogen lamp for the visible range (330–900 nm), equipped with an EYELA NCB-1200 temperature controller.

Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) measurements were performed using a Voyager-DE STR mass spectrometer with $20\,$kV acceleration voltages. The

positive ions were detected in the reflector mode ($20\,$kV). A nitrogen laser ($337\,$nm, $3\,$ns pulse width, 10^6–$10^7\,$W/cm^2) operating at $3\,$Hz was used to produce the laser desorption, and 500 shots were summed. The spectra were externally calibrated using 2,5-dihydroxybenzoic acid with a linear calibration. Samples for MALDI-TOF MS were prepared by mixing the polymer, a matrix (1,8-dihydroxy-9(10*H*)-anthracenone; dithranol), and a cationizing agent (sodium trifluoroacetate) in THF.

Phenyl 2-Chloropropionate (1a)

2-Chloropropionyl chloride ($17.6\,$g, $138\,$mmol) was gradually added to a solution of phenol ($10.0\,$g, $106\,$mmol) and NaOH ($5.5\,$g, $138\,$mmol) in water ($50\,$mL) at $0\,^{\circ}$C. After stirring at room temperature for $3\,$h, the reaction mixture was extracted with dichloromethane ($30\,$mL $\times$ 3). The combined extracts were washed with a 5% NaOH aqueous solution ($50\,$mL $\times$ 3) and brine ($100\,$mL $\times$ 3), dried over Na$_2$SO$_4$, and evaporated to dryness. The residue was distilled (bp 48–52 $^{\circ}$C, $0.020\,$mmHg) to yield **1a** as a colorless liquid ($15.6\,$g, 79.5%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ: 7.40 (dd, 2H, $J = 7.8, 8.3$ Hz), 7.26 (d, 1H, $J = 7.8$ Hz), 7.14 (d, 2H, $J = 8.3$ Hz), 4.63 (q, 1H, $J_1 = 6.8$ Hz, $J_2 = 10.2$ Hz), 1.82 (d, 3H, $J = 6.8$ Hz). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 168.6, 150.4, 129.5, 126.3, 121.1, 51.3, 21.3. *Anal.* Calcd for C$_9$H$_9$O$_2$Cl: C, 58.55; H, 4.91; Cl, 19.20. Found: C, 58.37; H, 4.93; Cl, 19.45.

(2′-Phenyl)phenyl 2-chloropropionate (1b)

2-Chloropropionyl chloride ($6.00\,$g, $47.3\,$mmol) was gradually added to a solution of 2-phenylphenol ($6.20\,$g, $36.4\,$mmol) and pyridine ($4.30\,$g, $54.4\,$mmol) in dry dichloromethane ($20\,$mL) at $0\,^{\circ}$C. After stirring at room temperature for $2\,$h, the reaction mixture was applied to squat column chromatography on silica gel with hexane/ethyl acetate (10/1, $R_f = 0.45$) to remove the insoluble salts. The combined eluents were evaporated and the residue was purified by flash column chromatography on silica gel with hexane/ethyl acetate (20/1) to give a colorless liquid. The liquid

was distilled (bp 135–137 °C, 0.35 mmHg) to yield **1b** (7.20 g, 75.9%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ: 7.42–7.32 (m, 8H), 7.18 (d, 1H, $J = 7.8$ Hz), 4.41 (q, 1H, $J_1 = 6.8$ Hz, $J_2 = 10.2$ Hz), 1.53 (d, 3H, $J = 6.8$ Hz). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 168.4, 147.4, 137.0, 134.9, 131.0, 129.0, 128.6, 128.3, 127.6, 126.8, 122.3, 52.2, 21.2. *Anal.* Calcd for C$_{15}$H$_{13}$O$_2$Cl: C, 69.10; H, 5.03; Cl, 13.60. Found: C, 69.10; H, 5.03; Cl, 13.71.

(4′-Phenyl)phenyl 2-chloropropionate (1c)

The procedure for **1b** was used for the synthesis of **1c** with 2-chloropropionyl chloride (6.0 g, 47.3 mmol), 4-phenylphenol (6.2 g, 36.4 mmol), and pyridine (4.30 g, 54.4 mmol). The crude product was recrystallized from hexane/dichloromethane to afford **1c** as white needles (7.55 g, 79.6%). $R_f = 0.45$ (hexane/ethyl acetate $= 10/1$). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.63–7.55 (m, 4H), 7.46–7.42 (m, 2H), 7.38–7.34 (m, 1H), 7.22–7.34 (m, 1H), 7.22–7.18 (m, 2H), 4.65 (q, 1H), 1.86 (d, 3H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 168.7, 149.8, 140.2, 139.5, 128.8, 128.3, 127.5, 127.1, 121.4, 52.3, 21.4. *Anal.* Calcd for C$_{15}$H$_{13}$O$_2$Cl: C, 69.10; H, 5.03; Cl, 13.60. Found: C, 69.07; H, 5.03; Cl, 13.55.

(2′,6′-Diphenyl)phenyl 2-chloropropionate (1d)

The procedure for **1b** was used for the synthesis of **1d** with 2-chloropropionyl chloride (3.2 g, 25.3 mmol), 2,6-diphenylphenol (4.8 g, 19.5 mmol), and pyridine (2.45 g, 31.0 mmol). The crude product was recrystallized from hexane/diethyl ether to afford **1d** as white needles (5.11 g, 77.8%). $R_f = 0.31$ (hexane/ethyl acetate $= 10/1$). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.45–7.34 (m, 13H), 4.11 (q, 1H), 1.23 (d, 3H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 167.8, 144.6, 137.2, 135.8, 130.2, 129.1, 128.2, 127.7, 126.8, 52.0, 21.0. *Anal.* Calcd for C$_{21}$H$_{17}$O$_2$Cl: C, 74.89; H, 5.09; Cl, 10.53. Found: C, 74.72; H, 5.11; Cl, 10.42.

Polymerization

A typical procedure is as follows; A mixture of CuCl (35.7 mg, 0.36 mmol) and Me$_6$TREN (82.9 mg, 0.36 mmol) in DMF (3 mL) was placed on one side of an H-shaped glass ampoule and stirred at room temperature. DMF (4.8 mL), deionized water (1.2 mL), NIPAM (2.04 g, 18 mmol), and **1a** (66.57 mg, 0.36 mmol) were added to the other side of the ampoule and stirred for 15 min. Argon was bubbled through both mixtures for 15 min to remove any oxygen. After sealing, both mixtures were mixed, and heated at 20 °C for 70 min. The polymerization was stopped by exposure to air. The reaction mixture was diluted with DMF and passed through an alumina column to remove the copper complex. The polymer was purified by dialysis using a cellophane tube in DMF. After 3 d, the DMF was removed by distillation under vacuum at room temperature. The obtained polymer was dissolved in water and freeze-dried overnight under vacuum (818 mg; conv., 40%). $M_{n,SEC} = 6070$, $M_w/M_n = 1.24$, $M_{n,MS} = 3010$.

RESULTS AND DISCUSSION

Synthesis of End-Functionalized Poly(N-isopropylacrylamide) with Arryl Group

Four types of 2-chloropropionates, such as phenyl 2-chloropropionate (**1a**), (2′-phenyl)phenyl 2-chloropropionate (**1b**), (4′-phenyl)phenyl 2-chloropropionate (**1c**), and (2′,6′-diphenyl)phenyl 2-chloropropionate (**1d**) were prepared as initiators for the polymerization of *N*-isopropylacrylamide (NIPAM) by CuCl/tris[2-(dimethylamino)ethyl]amine (Me$_6$TREN). The initiators **1** showed a good solubility in DMF, therefore, the mixture of DMF and water was used as the solvents. The conversion of NIPAM was directly determined from the ^{1}H NMR spectra of the polymerization mixtures in DMSO-d_6.[5c] The respective polymerization mixtures were purified by alumina column chromatography and dialysis, followed by freeze-drying to give products as white solids. Initially, the products were characterized using size exclusion chromatography (SEC) to reveal the trends.

In general, the effect of the end group is likely to appear for low weight molecular polymers. Thus, we targeted the preparation of the end-functionalized PNIPAM's with a series of hydrophobic groups, in which the molecular weights are relatively low. Hence, NIPAM was polymerized using the feed ratio of $[\text{NIPAM}]_0/[\mathbf{1}]_0/[\text{CuCl}]_0/[\text{Me}_6\text{TREN}]_0 = 50/1/1/1$. After the polymerization in DMF/water of 13/2 at 20 °C for 50 min, the NIPAM conversions reached 29, 43, 46, and 79% for the systems using **1a**, **1b**, **1c**, and **1d**, respectively. Surprisingly, the initiator **1a–d** showed a different tendency for the NIPAM polymerization. The feed ratio of $[\text{NIPAM}]_0/[\mathbf{1}]_0 = 50/1$ was the recipe for polymers with a short chain as described above, hence, the chloropropionate moieties in **1a–d** might show a different activity at an early stage for the polymerization. However, the SEC traces of the products exhibited one sharp peak with low polydispersity indices (M_w/M_n's) between 1.21–1.25. The number average molecular weights ($M_{n,SEC}$'s) were 4830, 6080, 7970, and 10400 for the products using **1a**, **1b**, **1c**, and **1d**, which increased with the increasing NIPAM conversions (29, 43, 46, and 79%). These results suggested that the respective systems proceeded in a controlled manner.

In order to elucidate the effect of the end-functional group for PNIPAM on the thermoreponsive property, we turned our attention to the preparation of the poly-

Table I. Polymerization of NIPAM with **1** and characterization of product **2**

Initiator	Time (min)	Conv.[b] (%)	Product	$M_{n,theor}$[c]	$M_{n,SEC}$[d]	M_w/M_n[d]	$M_{n,MS}$[e]	$M_{w,MS}$[e]
1a	70	40	**2a**	2450	6070	1.24	3010	3460
1b	50	43	**2b**	2690	6080	1.24	3020	3480
1c	40	44	**2c**	2750	5940	1.24	2850	3240
1d	15	49	**2d**	3110	6070	1.26	3390	3800

[a]Solvent, DMF/water (v/v, 13/2); temp., 20 °C; $[NIPAM]_0/[1]_0/[CuCl]_0/[Me_6TREN]_0 = 50/1/1/1$; $[NIPAM]_0 = 2.0$ M. [b]Determined by ^{1}H NMR spectrum of the reaction mixture in DMSO-d_6. [c]$M_{n,theor} = M_{NIPAM}[NIPAM]_0 conv/100[1]_0 + M_1$. [d]Determined by SEC using polystyrene standards. [e]Determined by MALDI-TOF-MS.

mers with similar molecular weights using **1a**, **1b**, **1c**, and **1d**. After the polymerization times of 70, 50, 40, and 15 min, the NIPAM conversions reached 40, 43, 44, and 49% for the systems using **1a**, **1b**, **1c**, and **1d**, providing the products with the $M_{n,SEC}$ (M_w/M_n) of 6070 (1.24), 6080 (1.24), 5940 (1.24), and 6070 (1.26), respectively, as listed in Table I. However, the $M_{n,SEC}$ values are significantly higher than the theoretical number average molecular weights ($M_{n,theor}$'s) calculated on the basis of monomer conversion, though similar phenomena have been previously reported in many studies.[4f,5b] Hence, the obtained polymers were characterized using matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS), which is known as a convenient method to determine the molecular weight of PNIPAM.[3c,4f,5b,5c] The MALDI-TOF MS spectrum show one main series of peaks, which has a regular interval of *ca.* 113.1 of the molar mass of the monomer, NIPAM. Table I lists the number average molecular weight calculated from the MALDI-TOF MS ($M_{n,MS}$). The $M_{n,MS}$'s of 3010, 3020, 2850, and 3390 were in good agreement with the $M_{n,theor}$'s of 2450, 2690, 2750, and 3110 for the products using **1a**, **1b**, **1c**, and **1d**, respectively. The MALDI-TOF MS analysis gave more important information, *i.e.*, the obtained polymers contain initiating chain-ends defined by the used initiators and the chlorine in the terminating chain-ends. The initiator was completely consumed after the polymerization based on the HPLC analysis. In addition, the polymerization system without **1** produced no polymer after 3 d. These results indicated that the products were assigned to the end-functionalized PNIPAM's with phenyl, (2′-phenyl)phenyl, (4′-phenyl)phenyl, and (2′,6′-diphenyl)phenyl groups, **2a**, **2b**, **2c**, and **2d**, respectively.

Thermoresponsive Property

Clear aqueous solutions were obtained for **2** with the $M_{n,MS}$'s of *ca.* 3000 in cold water, which became turbid by raising the temperature. The transmittance at 500 nm (%) of an aqueous solution of **2** (2 mg/mL) was measured using UV–vis spectroscopy upon rais-
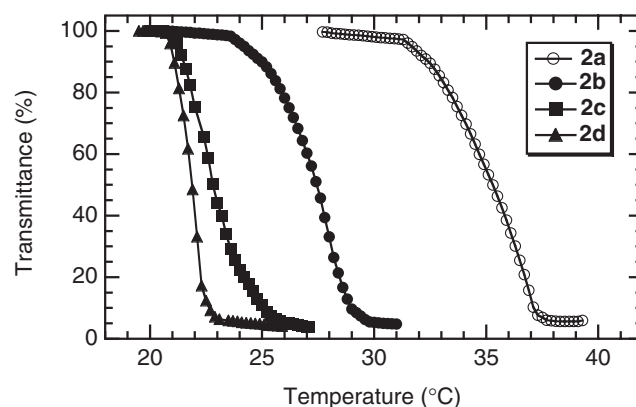

Figure 1. Cloud point curves for the aqueous solutions of **2a–d**.

ing the temperature at the heating rate of 0.1 °C/5 min to determine the LCST. Figure 1 shows the transmittance versus temperature plots (cloud point curves). We used the 90% transmittance points (90% T) as the LCST. The LCST's of the aqueous solutions of **2a**, **2b**, **2c**, and **2d** were 31.5, 23.8, 21.2, and 20.9 °C, respectively. Therefore, the hydrophobic end-groups in **2b–d** acted as an efficient unit for lowering the LCST.

The hydrophobic end-groups in **2** should aggregate in water, which is expected to affect the thermoresponsive property of **2**. Thus, the aggregation property of **2** in water was characterized by the static laser light scattering (SLS) measurement at a temperature below the LCST. The $M_{w,SLS}$ of 2490 was relatively lower than the weight average molecular weight estimated from the MALDI-TOF MS, $M_{w,MS}$, of 3460 for **2a**. On the other hand, **2b**, **2c**, and **2d** showed $M_{w,SLS}$'s of 31300, 337000, and 3503000, which were significantly greater than the respective $M_{w,MS}$'s of 3480, 3240, and 3800 (Table II). Thus, **2b–d** formed PNIPAM-aggregates in cold water below the LCST, in which the driving force is the low solubility of the hydrophobic end-groups. The aggregation number for the PNIPAM-aggregates of **2**, N_{agg}, which was defined as the $M_{w,SLS}$ divided by the $M_{w,MS}$, was calculated as 9, 104, and 920 for **2b**, **2c**, and **2d**, respectively, as listed in Table II. A possible explanation of the

Table II. Aggregation and thermoresponsive properties of **2**

Sample	LCST (°C)	$M_{w,MS}$[a]	$M_{w,SLS}$[b]	N_{agg}[c]
2a	31.5	3460	2490	—
2b	23.8	3480	31300	9
2c	21.2	3240	337000	104
2d	20.9	3800	3503000	920

[a]Determined by MALDI-TOF-MS. [b]Determined by SLS measurement in water at 15 °C. [c]$N_{agg} = M_{w,SLS}/M_{w,MS}$.

result that the LCST's decreased with the increasing N_{agg}'s is as follows. The liquid–solid phase transition of an aqueous PNIPAM solution is derived from the coil-globule transition of the PNIPAM chains at the LCST.[1] PNIPAM-aggregates with high N_{agg}'s were already formed in the cold aqueous solutions of **2b–d**, which prompted a transition to occur into the insoluble globule-form at the lower temperature. Consequently, the end-functionalization of PNIPAM with biphenyl and triphenyl groups by using initiators for the controlled radical polymerization was shown to be one direct approach to construct the polymer with a tuned themoresponsive property.

REFERENCES

1. a) M. Heskins and J. E. Guillet, *J. Macromol. Sci. Pt. A, Chem.*, **2**, 1441 (1968).
   b) H. G. Schild, *Prog. Polym. Sci.*, **17**, 163 (1992).
2. Some recent publications:
   a) M. Arotçareéna, B. Heise, S. Ishaya, and A. Laschewsky, *J. Am. Chem. Soc.*, **124**, 3787 (2002).
   b) T. O. Collier, J. M. Anderson, A. Kikuchi, and T. Okano, *J. Biomed. Mater. Res.*, **59**, 136 (2002).
   c) G. Q. Wang, K. Kuroda, T. Enoki, A. Grosberg, S. Masamune, T. Oya, Y. Takeoka, and T. Tanaka, *Proc. Natl. Acad. Sci. U. S. A.*, **97**, 9861 (2000).
   d) A. Okamura, M. Itayagoshi, T. Hagiwara, M. Yamaguchi, T. Kanamori, T. Shinbo, and P. C. Wang, *Biomaterials*, **26**, 1287 (2005).
   e) S. Ohya, H. Sonoda, Y. Nakayama, and T. Matsuda, *Biomaterials*, **26**, 655 (2005).
3. For nitroxide-mediated polymerization (NMP) of NIPAM:
   a) E. Harth, A. Bosman, D. Benoit, B. Helms, J. M. J. Fréchet, and C. J. Hawker, *Macromol. Symp.*, **174**, 85 (2001).
   b) K. Kuroda and T. M. Swager, *Macromolecules*, **37**, 716 (2004).
   c) T. Schulte, K. O. Siegenthaler, H. Luftmann, M. Letzel, and A. Studer, *Macromolecules*, **38**, 6833 (2005).
4. For atom transfer radical polymerizations (ATRP) of NIPAM:
   a) D. J. Kim, J.-y. Heo, K. S. Kim, and I. S. Choi, *Macromol. Rapid Commun.*, **24**, 517 (2003).
   b) G. Masci, L. Giacomelli, and V. Crescenzi, *Macromol. Rapid Commun.*, **25**, 559 (2004).
   c) H. Kong, W. Li, C. Gao, D. Yan, Y. Jin, D. R. M. Walton, and H. W. Kroto, *Macromolecules*, **37**, 6683 (2004).
   d) C. Li, N. Gunari, K. Fischer, A. Janshoff, and M. Schmidt, *Angew. Chem., Int. Ed.*, **43**, 1101 (2004).
   e) J. N. Kizhakkedathu, R. Norris-Jones, and D. E. Brooks, *Macromolecules*, **37**, 734 (2004).
   f) Y. Xia, X. Yin, N. D. A. Burke, and H. D. H. Stöver, *Macromolecules*, **38**, 5937 (2005).
5. For reversible addition fragmentation chain transfer (RAFT) polymerizations of NIPAM:
   a) F. Ganachaud, M. J. Monteiro, R. G. Gilbert, M.-A. Dourges, S. H. Thang, and E. Rizzardo, *Macromolecules*, **33**, 6738 (2000).
   b) C. Schilli, M. G. Lanzendörfer, and A. H. E. Müller, *Macromolecules*, **35**, 6819 (2002).
   c) B. Ray, Y. Isobe, K. Morioka, S. Habaue, Y. Okamoto, M. Kamigaito, and M. Sawamoto, *Macromolecules*, **36**, 543 (2003).
   d) B. Ray, Y. Isobe, K. Matsumoto, S. Habaue, Y. Okamoto, M. Kamigaito, and M. Sawamoto, *Macromolecules*, **37**, 1702 (2004).
   e) S. Yusa, Y. Shimada, Y. Mitsukami, T. Yamamoto, and Y. Morishima, *Macromolecules*, **37**, 7507 (2004).
   f) C. M. Schilli, M. Zhang, E. Rizzardo, S. H. Thang, B. Y. K. Chong, K. Edwards, G. Karlsson, and A. H. E. Müller, *Macromolecules*, **37**, 7861 (2004).
6. J. E. Chung, M. Yokoyama, K. Suzuki, T. Aoyagi, Y. Sakurai, and T. Okano, *Colloids Surf., B*, **9**, 37 (1997).
7. M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 41 (1966).