

THERMOSENSITIVITY OF NARROW-DISPERSED POLY(*N*-*n*-PROPYLACRYLAMIDE) PREPARED BY ATOM TRANSFER RADICAL POLYMERIZATION*

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Abstract Controlled polymerization of *N*-*n*-propylacrylamide was achieved by atom transfer radical polymerization (ATRP) in a *N,N*-dimethylformamide-water mixture (50 vol%) at room temperature with methyl 2-chloropropionate as initiator and CuCl/tris(2-dimethylaminoethyl)amine as the catalytic system in a ratio of 1:1:1. High molecular weight homopolymers (up to 3.7×10^4) with narrow molecular weight distribution (less than 1.2) were obtained. The living character of the polymerization was further demonstrated by self-blocking experiment. An inverse molecular weight dependence of the cloud point of narrow-dispersed poly(*N*-*n*-propylacrylamide) aqueous solution was determined by turbidimetry and differential scanning calorimetry, especially for the low molecular weight samples.

Keywords: Atom transfer radical polymerization; *N*-*n*-propylacrylamide; Polyacrylamide; Thermosensitive polymers.

INTRODUCTION

Some of poly(*N*-alkylacrylamide)s are water-soluble and can undergo abrupt phase transitions in water from a soluble to an insoluble state when the temperature is raised above a critical point (lower critical solution temperature, LCST). Such polymers have attracted much research interest because of their technological importance and potential biomedical applications^[1–4]. The best known of this family of polymers is probably poly(*N*-isopropylacrylamide) (PiPA), which shows an LCST at *ca.* 32°C^[5]. The thermosensitive polymers obtained from conventional free radical polymerizations are usually polydisperse with broadened thermal transitions^[6, 7]. Polymers of well-defined structure and molecular weight are desired and can be prepared by controlled radical polymerization methods, the most used of which include atom transfer radical polymerization (ATRP)^[7–19], nitroxyl-mediated polymerization^[20] and reversible addition-fragmentation chain transfer polymerization^[21]. ATRP has a good tolerance for the functional groups of monomers^[9]. Recently, some research groups have successfully prepared polyacrylamides by using alkyl chlorides rather than bromides as initiators in conjunction with CuCl/tris(2-dimethylaminoethyl)amine (Me₆TREN) as catalyst system in polar solvents^[7, 13–17]. Stöver and co-workers^[12] have reported the successful ATRP of *N,N*-dimethylacrylamide (DMA) and DMA/*N*-phenylacrylamide random copolymers in methanol or methanol/water mixtures. They also obtained well-defined PiPA in 2-propanol or *tert*-butyl alcohol at room temperature, with a polydispersity index (PDI) between 1.1 and 1.2 and degrees of polymerization of up to 300 without excess catalysts^[7, 15]. Masci *et al.*^[16] described the ATRP of *i*PA by the use of a *N,N*-dimethylformamide (DMF)-water mixture (50 vol%) at

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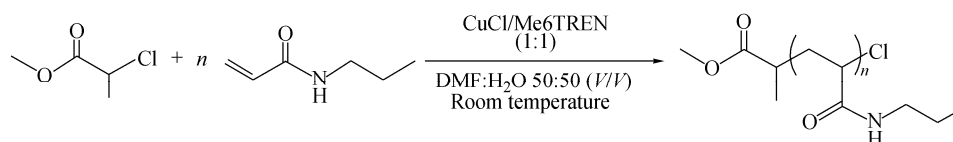
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20°C, and controlled molecular weight (up to 2.2×10^4) and low PDI (1.19) were obtained by using higher catalyst/initiator ratios (2:1). Most research efforts have focused on the ATRP of DMA and iPA, yet little attention was paid on other *N*-alkyl substituted acrylamides.

Poly(*N*-*n*-propylacrylamide) (PnPA) exhibits a reversible liquid-solid phase separation with an LCST around 22.5°C^[22, 23]. Only a few studies have been reported on PnPA even though this polymer may be useful as a fluorescent molecular thermometer^[24], in precipitation separation systems^[25], and as nonadhesive liquid embolism materials^[26] and thermoresponsive hydrogels^[27]. To the best of our knowledge, no study has been reported on the controlled polymerization of this monomer.

The molecular weight (MW) dependence of the cloud points of some of polyacrylamides has been an active yet controversial topic. The LCST of PiPA was reported to be inversely dependent^[6, 7, 15, 28], directly dependent^[29], or independent^[30] on the molecular weight. However, polydisperse polymers were used in most of these studies, which may have precluded precise examination of the MW effects. We have reported an inverse relationship between the cloud point and the molecular weight of poly(*N*,*N*-diethylacrylamide) (PDEA) using fractionated samples^[6]. Stöver's group also reported an inverse dependence of the cloud point of PiPA on its molecular weight using narrow-dispersed PiPA prepared with ATRP^[7, 15].

We reported here the successful synthesis of PnPA by ATRP in a DMF-water mixture (50 vol%) at room temperature, with methyl 2-chloropropionate (MCP)/CuCl/Me₆TREN (1:1:1) as the initiating system (Scheme 1). We also investigated the molecular weight dependence on the LCST of the aqueous solutions of PnPA by turbidimetry and differential scanning calorimetry, respectively.



Scheme 1. The schematic illustration of ATRP of *N*-*n*-propylacrylamide

EXPERIMENTAL

Materials

Triethylamine, *n*-propylamine, dichloromethane, DMF and tetrahydrofuran (THF) were purchased from Tianjin Chemicals Co., China and dried with CaH₂ then purified by distillation. MCP (from Tokyo Chemical Industry Co., LTD) and tris(2-aminoethyl)amine (TREN) (from Aldrich) was used as received. Me₆TREN was synthesized as described previously^[31]. CuCl (Aldrich) was purified according to a published procedure^[31]. 2,2'-Azobisisobutyronitrile (AIBN) was purchased from Aldrich and recrystallized from methanol before use. Other chemicals such as HCHO (37%) and HCOOH (88%) were purchased from Tianjin Chemicals Co., China and used as received. *N*-*n*-propylacrylamide (*n*PA) was prepared by reacting acryloyl chloride with *n*-propylamine at *ca.* 0°C in the presence of triethylamine in dichloromethane, to obtain a clear liquid product upon vacuum distillation, which was kept in a freezer until use^[23].

Preparation of PnPA

To prepare PnPA with target degree of polymerization of 50 ($X_n = 50$), a mixture of CuCl (12.0 mg, 0.12 mmol), Me₆TREN (32 μL, 0.12 mmol), water (0.5 mL) and DMF (0.5 mL) was first introduced in a nitrogen-purged 25 mL Schlenk tube. After stirring the mixture for about 10 min to form the Cu-Me₆TREN complex, a mixture of *n*PA (0.68 g, 6 mmol), water (1.5 mL) and DMF (1.5 mL) was added, and then the system was degassed by four freeze-pump-thaw cycles and back-filled with nitrogen again. The solution was stirred for at least 0.5 h to reach room temperature, and a small initial sample was taken to measure the concentration of initial monomers. Finally, MCP (13.5 μL, 0.12 mmol) was added to begin the polymerization.

Aliquots (200 μL) of the reaction solution were removed from the polymerization system at suitable time

periods. A part of the samples was dissolved in DMSO- d_6 for ^1H -NMR spectroscopy to calculate the monomer conversion with DMF as internal standard. The remaining aliquots were dried, re-dissolved in THF, then passed through a short neutral alumina column to remove the catalyst and used for gel permeation chromatography (GPC) analysis.

The polymerization was stopped by opening the flask and exposing the catalysts to air. The reaction mixture was diluted in THF and passed through a column filled with neutral alumina, and then the solvent was removed by rotary evaporation. After precipitation from cold ether and hexane, the polymer was dried under vacuum at 60°C to a constant weight.

Self-blocking Experiment

The first *n*PA block was synthesized as described above with a [*n*PA]:[MCP]:[CuCl]:[Me₆TREN] ratio of 50:1:1:1. When the *n*PA conversion of the first block was approximately 90%, a fresh feed of *n*PA (0.68 g, 6.0 mmol) dissolved in a DMF-water mixture (50 vol%) (0.5 mL) was added. The polymerization was allowed for another 120 min at room temperature.

Conventional Free Radical Polymerization of *n*PA

*n*PA (0.68 g, 6 mmol), AIBN (4.9 mg, 0.03 mmol), and THF (3 mL) were placed in a 25 mL Schlenk tube. After four freeze-pump-thaw cycles and back-filling with nitrogen, the tube was heated at 60°C for 7 h in an water bath. The polymer was isolated and purified by precipitation from THF into cold hexane twice, and then dried to constant weight in a vacuum oven to afford 0.58 g (85% yield) of PnPA as a white powder, $M_{n,\text{GPC}} = 1.2 \times 10^4$, PDI = 1.75.

Polymer Characterization

The molar masses and their distribution for the polymer samples were determined by GPC on a Waters system equipped with a set of three Ultrastaygel columns (HT2, HT3, and HT4; 30 cm $\times$ 7.8 mm; 10 μm particles; exclusion limits: 100–10000, 500–30000, and 5000–600000 g/mol, respectively), Waters 515 HPLC pump, Waters 717plus Autosampler and an online Waters 2414 refractive index detector maintained at 35°C. THF was used as the mobile phase (1 mL/min), and polystyrene samples as the standards in the calibration of the molar masses.

Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) of the polymers was performed on a BiFlex III MALDI TOF (Bruker Daltonics) equipped with a nitrogen laser (337 nm) and an accelerating potential of 20 kV. Samples were prepared by mixing a solution of the polymer in THF (10 mg/mL) and a solution of 2-cyano-4-hydroxycinnamic acid (CCA) matrix in THF (10 mg/mL) with a ratio of 1:20. Then, the resulting mixture (1 μL) was deposited onto the sample plate and the solvent was evaporated at room temperature. Spectra were recorded in the reflector mode with external calibration.

^1H -NMR spectra were recorded in DMSO- d_6 on Varian UNITY-plus 400 operating for proton at 400 MHz. DMF was used as internal standard.

The cloud point of PnPA in water was set as the temperature at the 50% transmittance of the curve obtained by turbidimetry with a concentration of 1 wt%. A Cary 100 Conc UV-Vis spectrophotometer coupled with an external water bath (Julabo F12) with a precision of $\pm 0.1^\circ\text{C}$ was used in the transmittance mode at a wavelength of 500 nm against deionized water as the reference. Data were recorded after the samples were equilibrated for 30 min at each temperature. Differential scanning calorimetry (DSC) was also used to determine the LCST of PnPA aqueous solutions. The endothermic signal at its maximum (corresponding to the LCST) was recorded for each sample on a DSC 2910 differential scanning calorimeter (TA Instruments, New Castle, DE, USA) with a flow of nitrogen at 50 cm^3/min . The samples (*ca.* 8–10 mg) with a concentration of 10 wt% were placed in sealed capsules and scanned at 5 K/min from 5°C to 50°C against an empty reference pan.

RESULTS AND DISCUSSION

Homopolymerization of *n*PA

The controlled polymerization of (meth)acrylamides by ATRP was challenging and much effort has been made to improve the conditions. To date, the best initializing system reported for ATRP of (meth)acrylamides uses CuCl/Me₆TREN as catalyst and MCP as initiator^[7, 13–17]. It was also reported that solvents have special effects on the polymerization. Therefore, our initial studies focused on searching for a suitable solvent system for the ATRP of *n*PA. Toluene^[10, 13] and 2-propanol^[7], reported to be good solvents for the ATRP of DMA or *i*PA, were tried for the ATRP of *n*PA ($X_n = 50$) with MCP/CuCl/Me₆TREN in a ratio of 1:1:1 at 40°C for more than 48 h, but no polymer was obtained after purification. Masci *et al.*^[16] reported the successful ATRP of *i*PA in a DMF-water mixture (50 vol%), which showed a conversion of 92% in 35 min and linear first order kinetic plot. We opted for this solvent system for the ATRP of *n*PA. When the polymerization was carried out in a DMF-water mixture (50 vol%) (No. 1 in Table 1), upon initiation, the reacted solution changed from dark green to light blue and turbid immediately. The polymerization of *n*PA reached 91% conversion in only 15 min, and the first-order kinetic plot was initially curved which may be attributed to the lower deactivator concentration due to the coordination between Cu(II) and water at the early stage^[32] (Fig. 1a). The polymer (P*n*PA) showed a controlled molecular weight ($M_{n, GPC} = 5500$, $M_{n, th} = 5200$) and a low PDI of 1.09. MALDI-TOF MS analysis of this sample provided similar result ($M_{n, MALDI} = 5100$, PDI = 1.11), which also confirmed the validity of the GPC data for P*n*PA.

Table 1. Reaction conditions and results of the ATRP of *n*PA*

No.	DMF:Water (V/V)	[M] ₀ : [I] ₀	<i>t</i> (min)	Conv. (%)	<i>M</i> _{n, th}	<i>M</i> _n (GPC)	<i>M</i> _w / <i>M</i> _n (GPC)
1**	50:50	50:1 ^a	15	91	5200	5500	1.09
2	75:25	50:1 ^a	90	60	3400	4200	1.05
3	25:75	50:1 ^a	40	97	5500	5600	1.16
4	50:50	100:1 ^b	15	90	10200	9700	1.11
5	50:50	200:1 ^b	60	87	22600	20000	1.20
6	50:50	400:1 ^c	240	80	37200	33100	1.16

* Polymerization condition: room temperature, $[I]_0/[CuCl]_0/[L]_0 = 1/1/1$, while I, L, and M referred to initiator, ligand and monomer, respectively; $[M]_0 = 1.5$ mol/L (a), 3 mol/L (b), 6 mol/L (c);

** *M*_n and *M*_w/*M*_n of this sample have also been measured to be 5100 and 1.11, respectively, by MALDI-TOF MS

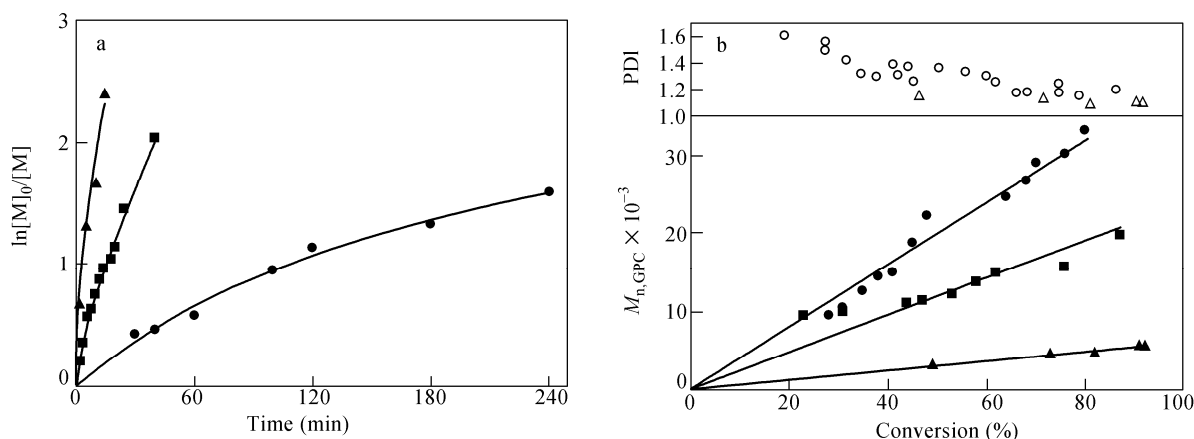


Fig. 1 (a) Kinetic plot for the ATRP of *n*PA in DMF-water mixture (50 vol%) at room temperature; (b) Dependence of molecular weight ($M_{n, GPC}$) and molecular weight distribution (M_w/M_n) on monomer conversion $[MCP]:[CuCl]:[Me_6TREN] = 1:1:1$; Triangles: $[M]_0:[I] = 50:1$, $[M]_0 = 1.5$ mol/L; Squares: $[M]_0:[I] = 200:1$, $[M]_0 = 3$ mol/L; Circles: $[M]_0:[I] = 400:1$, $[M]_0 = 6$ mol/L; All the lines are the best-fit lines.

The polymerization was also carried out with different solvent compositions. In a 3:1 (V/V) DMF-water mixture, the polymerization was slower and reached only 60% conversion of *n*PA after 90 min (No. 2 in Table 1), and the first order kinetic plot showed significant curvature. However, the molecular weight increased linearly with conversion and the PDI was low (1.05), indicating that the growing centers were not lost, as it would have led to a broader molecular weight distribution^[7, 9]. When a 1:3 (V/V) DMF-water mixture was used (No. 3 in Table 1), the polymerization proceeded very fast and reached a final monomer conversion of 97% in 40 min, and the molecular weight measured by GPC was in good agreement with the theoretical value ($M_{n, \text{GPC}} = 5600$, $M_{n, \text{th}} = 5500$). The PDI was still low (1.16), but slightly higher than those of the polymers obtained under the other conditions. The PDI may be larger when higher molecular weights were targeted^[7, 16]. The 1:1 (V/V) DMF-water mixture was used in the following experiments for the homopolymerization of *n*PA aiming for higher molecular weights.

At a higher ratio of monomer to initiator (higher target degrees of polymerization, No. 4–6 in Table 1), the polymerization slowed down and the PDIs of the polymers increased somewhat but are still kept less than 1.20. The polymerization gave a monomer conversion of 90% in 15 min for $X_n = 100$ ($[\text{monomer}]_0 = 3 \text{ mol/L}$), which is similar to the obtained conversion for $X_n = 50$ with a more diluted system ($[\text{monomer}]_0 = 1.5 \text{ mol/L}$). Further increases in monomer/initiator ratio (200:1 and 400:1) produced polymers with higher molecular weight but with lower conversions (87% in 60 min and 80% in 240 min, respectively). The first order kinetic plots also showed a small initial curvature, but the molecular weights increased almost linearly with conversion, showing a well-controlled process (Fig. 1). In addition, the GPC traces (Fig. 2) for the homopolymerization of *n*PA with $X_n = 400$ obtained at different times and conversions illustrated a clear evolution of molar mass with time, as well as symmetrical unimodal GPC traces without shoulders and tailings. The polydispersity had a maximum value of $M_w/M_n = 1.50$ at 31% conversion in 5 min, which then decreased with conversion, reaching a final value of 1.16 at 80% in 240 min. Masci *et al.*^[14] reported that the polymerization of *i*PA with $X_n = 200$ required higher catalyst/initiator ratio (2:1), which was thought to be the effect of extensive catalyst deactivation. We have prepared PnPAs of high molecular weights in a fast way without increasing the catalyst/initiator ratio, and this result is likely due to reduced deactivation of the copper catalyst through complexation with the amide group of *n*PA, or to the different polymerization rate between *n*PA and *i*PA.

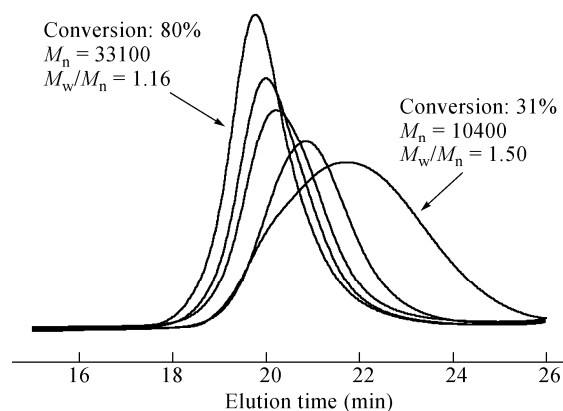


Fig. 2 GPC traces for the homopolymerization of *n*PA (target $X_n = 400$) showing the evolution of the molar mass with conversion

Self-blocking Experiment

The living nature of the ATRP of *n*PA was further demonstrated by self-blocking experiment. In 0.5 mL of DMF-water mixture (50 vol%), a fresh feed of an equal amount of *n*PA (0.68 g, 6.0 mmol) was directly added to the polymerization mixture when the first block polymerization ($X_n = 50$) reached about 91% conversion. The polymerization was left to continue long enough (120 min) to obtain a final monomer conversion of 69% for the chain extension. The relative lower monomer conversion may be caused by catalyst deactivation over time. The final polymer also showed a predictable molecular weight ($M_{n, \text{GPC}} = 9300$, $M_{n, \text{th}} = 9400$) and a low PDI (1.15), as well as reasonably unimodal GPC trace without shoulders (Fig. 3).

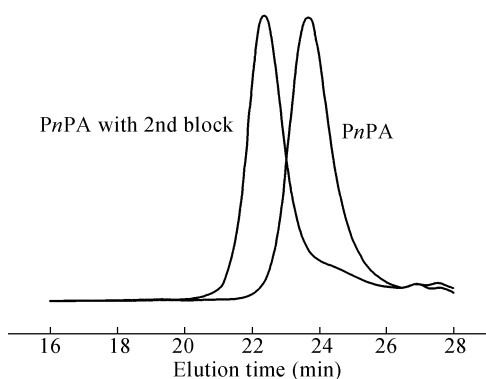


Fig. 3 GPC traces of PnPAs before and after self-chain extension (target $X_n = 50 + 50$)

Effect of Polymer MW on LCST

DSC and turbidimetry were used to measure the cloud points of the aqueous solutions of the narrow-dispersed PnPA samples prepared by ATRP with $M_{n, GPC}$ ranging from 2.4×10^3 to 37.2×10^3 . Figure 4(A) showed endothermic peaks by DSC measurement, while samples at 10 wt% concentration (ca. 8–10 mg) were placed in sealed capsules and scanned at 5 K/min from 5°C to 50°C. The endothermic peaks broadened and became more asymmetrical for lower-MW samples despite similar and low PDIs (less than 1.2). Figure 4(B) showed the transmittance versus temperature plots for 1 wt% solution of PnPAs by ATRP and conventional free radical polymerization. While the transitions are quite sharp for the narrow-dispersed PnPA samples with higher MW ($M_{n, GPC} > 9.3 \times 10^3$), they are broader for the lower-MW samples, and the transition for the lowest-MW sample ($M_{n, GPC} = 2.4 \times 10^3$) occurs over a 10°C range. Interestingly, the PnPA sample made by conventional free radical polymerization with AIBN initiator ($M_{n, GPC} = 1.2 \times 10^4$ and PDI = 1.75) gave a cloud point of 21.5°C which is about 1°C lower than a narrow-disperse sample of similar M_n made by ATRP. This may be attributed to the significant high-MW fraction present in such polydisperse sample, which will have a lower LCST and thus mask the transition of the lower-MW fractions^[7]. Figure 5 showed an inverse dependence of MW on LCST and a more pronounced effect for lower-MW PnPAs, which was similar to the results of PDEA^[6] and PiPA^[7, 15]. The slope was steep for samples with $M_{n, GPC}$ lower than 6.1×10^3 and became more gradual for higher values of MW, and finally reached a plateau after $M_{n, GPC}$ higher than 2×10^4 .

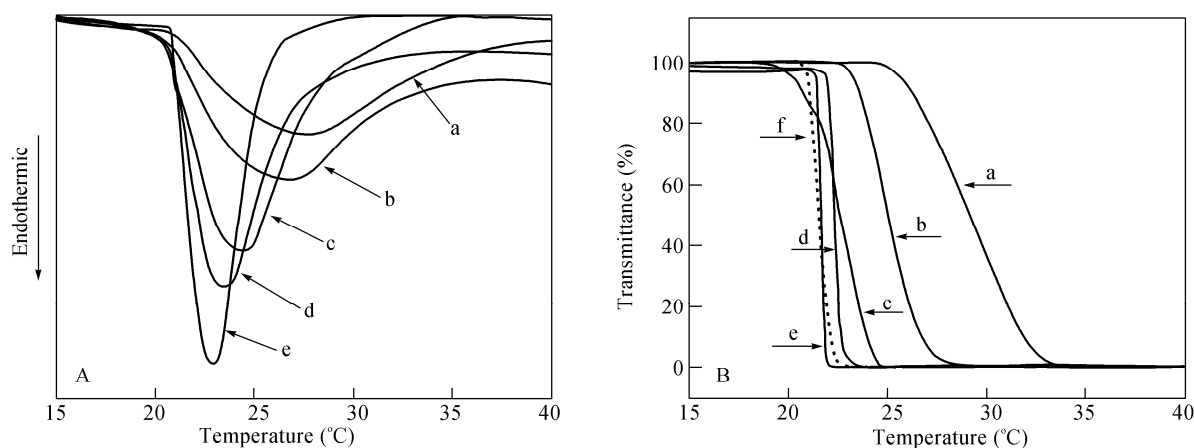


Fig. 4 Cloud points of aqueous solutions of PnPAs prepared by ATRP (a–e, solid line) or conventional free radical polymerization (f, dashed line): $M_{n, GPC} = 2.4 \times 10^3$ (a), 3.4×10^3 (b), 6.1×10^3 (c), 9.3×10^3 (d), 37.2×10^3 (e) and 11.8×10^3 (f)
A) Calorimetry: 10 wt% solution, scanned at a heating rate of 5 K/min; B) Turbidimetry: 1 wt% solution, data were read after thermostated for 20 min at certain temperature.

In a previous study of PDEA, we found that the polydispersity may play an important role in lower-MW samples for the broadening in the transmittance curves and the endothermic peaks^[6]. The polydispersities of the samples used were much broader (more than 1.4). Recently, similar phenomena were reported by Xia *et al.*^[7, 15] in their studies on the thermal response of narrow-dispersed PiPA prepared by ATRP. They thought that the differences in the aggregation rates of PiPAs with different molecular weights (low MW leads to low aggregation rate), rather than the hydrophobic end groups or micellization of low-MW fractions, might be the main factor leading to a broad transition with low-MW PiPAs determined by turbidimetry. In the low-MW region, the slope is very steep indicating that a little change of the molecular weight may lead to a distinct difference of LCST, while the hydrophobic end group may play a minor role. Our results of the thermosensitivity of PnPA aqueous solutions further confirmed the effect of aggregation rate on the turbidity curve. It is unclear why lower-MW polymer samples have a lower aggregation rate. The lack or even absence of chain entanglements of the shorter polymer chains may account for a lower aggregation rate. For the endothermic peaks of DSC in Fig. 4(A), because the PDIs of the low-MW PnPAs in our study were very low (*ca.* 1.05), the broadening for low-MW samples may only be attributed to the lower aggregation rates rather than residual polydispersities.

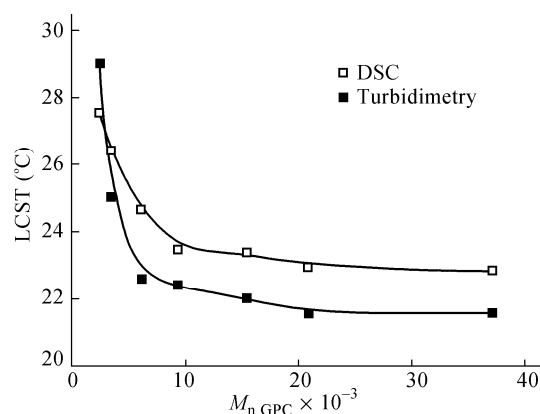


Fig. 5 Effect of the molecular weight on the LCST of narrow-dispersed PnPA samples measured by DSC (open squares) and turbidimetry (closed squares)

CONCLUSIONS

Atom transfer radical polymerization of *n*PA can be performed in a DMF-water mixture at room temperature with linear first order kinetics, controlled molecular weights and low PDIs even when high molecular weights (up to 3.7×10^4) were targeted. The living character of the polymerization was also demonstrated by the chain extension experiment. An inverse dependence of the cloud points on MW was observed, especially with the lower-MW polymers ($< 6.0 \times 10^3$) and became more gradual for samples of higher MW. This, together with results in the literature on PiPA and PDEA, indicates that this dependence is the general trend for all the poly(*N*-alkylacrylamide)s studied. The broadening with the lower-MW samples may be caused by the low aggregation rate. Further experiments with block copolymers with multiple thermosensitivity are being carried out.

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