Reactive & Functional Polymers 72 (2012) 407–413

Contents lists available at SciVerse ScienceDirect

Reactive & Functional Polymers

journal homepage: www.elsevier.com/locate/react

RAFT polymerization of *N*-vinylcaprolactam and effects of the end group on the thermal response of poly(*N*-vinylcaprolactam)

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ARTICLE INFO

Article history:
Received 26 January 2012
Received in revised form 2 April 2012
Accepted 3 April 2012
Available online 11 April 2012

Keywords:
RAFT polymerization
Poly(*N*-vinylcaprolactam)
End groups
Thermoresponsive polymer

ABSTRACT

The reversible addition–fragmentation chain transfer (RAFT) radical polymerization of *N*-vinylcaprolactam (NVCL) was performed using either *S*-benzyl-*S*-(benzyl propionate) trithiocarbonate (**CTA 1**) or *N*, *N*-diethyl-*S*-(α,α′- dimethyl-α″-acetic acid) dithiocarbamate (**CTA 2**) as a chain transfer agent (CTA). The polymerizations were controlled processes that yielded polymers with high conversion (>60%), controlled molecular weights that were close to the theoretical values and a narrow molecular weight distribution (minimal value: 1.13). The cloud point temperatures of poly(*N*-vinylcaprolactam) (PNVCL) were measured by turbidimetry and shifted to lower temperature and concentrations as the hydrophobicity of the end groups and the molecular weights of the polymers increased.

1. Introduction

During the past decade, controlled radical polymerization (CRP) techniques have been widely used for the preparation of various polymers that have controlled molecular weight, narrow polydispersity, and well-defined architecture. The most useful CRP techniques include nitroxide-mediated polymerization (NMP) [1], atom transfer radical polymerization (ATRP) [2], reversible addition-fragmentation chain transfer polymerization (RAFT) [3–7], and macromolecular design via the interchange of xanthates (MADIX) [8]. CRP techniques require less strict polymerization conditions than living anionic and cationic polymerization. Therefore, these techniques have been used to synthesize a wide range of conjugated monomers. A variety of thermosensitive water-soluble polymers have been synthesized using CRP [9–14].

Poly(*N*-vinylcaprolactam) (PNVCL) is one of several well-known synthetic thermoresponsive polymers, and it exhibits a dissolution/precipitation transition in aqueous solution at temperatures close to physiological temperatures. PNVCL is non-toxic [15,16] and biocompatible [17,18], and the hydrolysis of the amide group does not produce small amine compounds. These properties make PNVCL an important polymer for use in biomedical applications [19,20]. It has been reported that the lower critical solution temperature (LCST) of PNVCL and its copolymers was sensitive to changes in their molecular weights [21–23]. Research examining the cytotoxicity of PNVCLs having different molecular weights has shown that the lower molecular weight polymers were well tolerated [15]. Therefore, the ability to control the molecule weights of these polymers is desirable. Additionally, controlling the polymerization will contribute to the development of more sophisticated PNVCL-based materials. However, *N*-vinylcaprolactam (NVCL) is representative of the unconjugated monomers that can only be polymerized into high molecular weight polymers through a radical mechanism similar to that of *N*-vinylpyrrolidone (NVP) because the vinyl Π-electron is not conjugated with the C=O functional group. It has been known that the CRP of unconjugated monomers is not an easy task because of the highly reactive radical species that are derived from the monomers and because of the lack of suitable reagents or catalysts that can induce fast interconversion between the highly reactive radical and the dormant species. The CRP of NVCL has only recently been reported. Devasia et al. [24] reported the first RAFT polymerization of NVCL using methyl 2-(ethoxycarbonothioylthio)propanoate as a chain transfer agent (CTA), but no details were included. Later, Wan et al. [25] described the RAFT polymerization of NVCL, which was mediated by 2-diphenylthiocarbamoylsulfanyl-2-methylpropionic acid, ((*O*-ethylxanthyl)methyl) benzene, and (1-(*O*-ethylxanthyl) ethyl) benzene. However, the polymerization of NVCL did not proceed in a strictly living manner. Tebaldi et al. [26] reported the synthesis of a triblock copolymer that consisted of poly(*t*-butylacrylate) and poly(*N*-vinylcaprolactam) by sequential RAFT polymerization, but the CTA (dibenzyltrithiocarbonate) used during the synthesis was not the most suitable for polymerizing NVCL. Negru et al.

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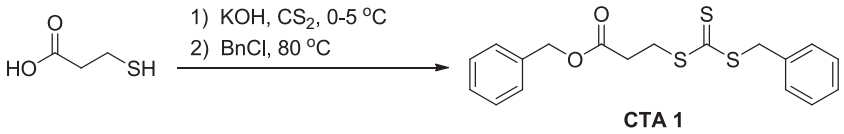
http://dx.doi.org/10.1016/j.reactfunctpolym.2012.04.002



Scheme 1. Synthesis of **CTA 1**.

[27] synthesized PNVCL-*b*-PEG-*b*-PNVCL triblock copolymers by the ATRP of NVCL using poly(ethylene glycol) that contained a chloride end group (PEG-Cl) as the initiator and CuCl/5, 7, 7, 12, 14, 14-hexamethyl-1, 4, 8, 11-tetraazacyclotetradecane (Me_6Cyclam) as the catalyzed system. However, these reported polymerizations of NVCL did not proceed in a strictly living manner or at least in a lower control degree of the process. Thus, the living and controlled radical polymerization of NVCL has not yet been completely established.

The use of a CTA is crucial for successful RAFT polymerization. It has been reported that the use of *N*, *N*-dialkyl dithiocarbamate was effective for controlling the polymerization of unconjugated monomers [28–31]. Additionally, trithiocarbonate belongs to a family of CTAs (Scheme 2), which contain an S atom connected to a Z group. Compared to other CTAs (dithiobenzoates, dithiocarbamates and xanthates), trithiocarbonates can be employed for the RAFT polymerization of more monomers because of their moderate C_{tr}, which results in less retardation of the polymerization and imparts hydrolytic stability [32]. Moreover, a CTA that has a large Z group can cause retardation of the polymerization process, whereas a CTA with a small or flexible Z group may be helpful for controlling the polymerization. Based on these observations, we have designed *S*-benzyl-*S*-(benzyl propionate) trithiocarbonate (**CTA 1**), which is a new nonsymmetrical trithiocarbonate containing a flexible Z group of $SCH_2CH_2COOCH_2Ph$ and *N*, *N*-diethyl-*S*-(α, α′-dimethyl-α″-actetic acid) dithiocarbamate (**CTA 2**), which belongs to a low C_{tr} family of dithiocarbamates and has a smaller Z group of $N(Et)_2$, to be used as CTAs for mediating the RAFT polymerization of NVCL (Scheme 1). Kinetic studies were used to compare the effectiveness of **CTA 1** and **CTA 2**. The phase separation behavior of thermoresponsive polymer solutions has been reported to be dependent on the physical properties and structure of the polymer, such as the concentration, molecular weight (MW) and end groups [33–38]. It has been demonstrated that the end groups have a significant effect on the cloud point of low-MW poly(*N*-isopropylacrylamide) (PIPAAm) [39]. However, the effect of the end groups on the phase separation behavior of PNVCL is unknown, largely due to the lack of control over both the MW and the end group chemistry for PNVCL. In this study, the effect of the end groups, MW and concentration on the cloud point temperatures (T_{CP}) of PNVCL were also investigated.

2. Experimental

2.1. Materials

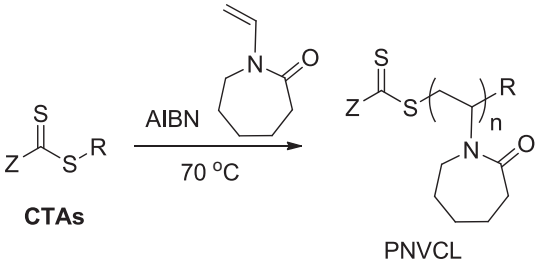
N-vinylcaprolactam (98%, Sigma Aldrich, St. Louis, Missouri, USA) was distilled under reduced pressure to remove the inhibitor and then stored at 4 °C. α, α-azobisisobutyronitrile (AIBN) (98%, Shanghai Chemical Reagents Co., Shanghai, China) was purified by recrystallizing from methanol two times. 3-mercaptopropionic acid (99%, Alfa Aesar, Ward Hill, Massachusetts, USA), benzyl chloride (BnCl) (98%) and carbon disulfide (99%, The Shanghai Chemical Reagents Co., Shanghai, China) were used as received. *N*, *N*-diethyl-*S*-(α, α′-dimethyl-α″-actetic acid)dithiocarbamate (**CTA 2**) was prepared according to the method described in the literature [40].

2.2. Characterizations

^{1}H and ^{13}C NMR spectra were obtained using a Bruker DRX-500 spectrometer with either $CDCl_3$ or D_2O as the solvent. The chemical shifts were calculated relative to tetramethylsilane. Infrared spectra were collected using potassium bromide pellets on a Nicolet AVATAR 360 spectrometer. ESI–MS analyses were performed using a Finnigan LCQ-Advantage Mass Spectrometer. The molecular weight and the polydispersity of the polymers were determined using gel permeation chromatography with multi-angle laser light scattering (GPC/MALLS). The GPC/MALLS system consisted of a Waters 2690D separations module, a Waters 2414 refractive index detector (RI), and a Wyatt DAWN EOS MALLS detector. Styragel HR1 THF and HR2 THF columns (Waters) were used at 40 °C with polystyrene as standards and DMF as a mobile phase at a flow rate of 0.3 ml/min.

2.3. Synthesis of S-benzyl-S-(benzyl propionate) trithiocarbonate (CTA 1)

The synthesis of *S*-benzyl-*S*-(benzyl propionate) trithiocarbonate (**CTA 1**) was described in Scheme 1. 3-mercaptopropionic acid (4 ml, 46 mmol) was added to a solution of KOH (5.2 g, 93 mmol) in water (50 ml) and cooled in an ice-water bath. Carbon disulfide (6 ml, 100 mmol) was added to the solution dropwise, and then the resulting orange solution was stirred for 5 h. BnCl (5.5 ml, 46 mmol) was added to the mixture, which was then heated for 16 h at 80 °C. The mixture was cooled and $CHCl_3$ (60 ml) was added, the reaction mixture was acidified with hydrochloric acid until the organic layer became yellow. The water phase was extracted using $CHCl_3$ (2 × 60 ml). The combined organic layers were washed with 10% Na_2CO_3 (aq) (2 × 100 ml) and then dried over anhydrous $MgSO_4$. After the solvent had evaporated, the remaining product was purified using flash gel column chromatography with petroleum ether as an eluent, which yielded a yellow oil (14.5 g, 87%). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 7.28–7.41 (m, 10H), 5.17 (s, 2H), 4.63 (s, 2H), 3.68 (t, *J* = 7 Hz, 2H), 2.84 (t, *J* = 7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 223.32, 171.62, 136.01, 135.29, 129.66, 129.13 × 2, 129.02 × 2, 128.78 × 2, 128.69 × 2, 128.22, 67.16, 41.93, 33.61, 31.76. IR (cm^{-1}): 3029 (Ar—H), 2919 (CH_2CH_2), 1733 (C=O), 1499, 1453 (Ar), 1064 (C=S), 840 (C—S). ESI–MS(m/z): calculated for $C_{18}H_{18}O_2S_3$, 362.53; found, 385.37 $[M + Na]^+$.



Z = $SCH_2CH_2COOCH_2Ph$, R = CH_2Ph (**CTA 1**)

Z = $N(Et)_2$, R = $C(CH_3)_2COOH$ (**CTA 2**)

Scheme 2. RAFT polymerization of NVCL mediated by CTAs.

Table 1
RAFT polymerization of NVCL in presence of **CTA 1** and **CTA 2**.

Polymers	CTA	Time (h)	Conv. (%)	Yield (%)	M_nth (g/mol)	M_n[d] (g/mol)	PDI[d]
PNVCL1-1[a]	CTA1	8	18.0	16.1	5373	6800	1.29
PNVCL1-2[a]	CTA1	16	24.1	21.3	7071	7900	1.13
PNVCL1-3[a]	CTA1	24	45.3	44.2	12946	13600	1.42
PNVCL1-4[a]	CTA1	40	52.0	49.7	14834	15700	1.28
PNVCL1-5[a]	CTA1	60	64.4	63.9	18290	20600	1.33
PNVCL2-1[b]	CTA 2	12	43.9	43.4	3290	3840	1.21
PNVCL2-2[b]	CTA 2	42	51.3	50.8	3805	4030	1.32
PNVCL2-3[c]	CTA 2	6	21.3	18.6	3199	3720	1.28
PNVCL2-4[c]	CTA 2	21	33.0	31.7	4828	5710	1.16
PNVCL2-5[c]	CTA 2	25	47.1	46.4	6791	7200	1.15
PNVCL	None	4	51.8	50.2	–	7357	2.75

[a] The theoretic molecular weight was calculated by the formula: M_nth = 200 × 139.2 × conv. + molecular weight of **CTA 1**. which [monomer]:[CTA]:[AIBN] = 200:1:0.25.
[b] The theoretic molecular weight was calculated by the formula: M_nth = 50 × 139.2 × conv. + molecular weight of **CTA 2**. which [monomer]:[CTA]:[AIBN] = 50:1:0.25.
[c] The theoretic molecular weight was calculated by the formula: M_nth = 100 × 139.2 × conv. + molecular weight of **CTA 2**. which [monomer]:[CTA]:[AIBN] = 100:1:0.25.
[d] M_n and PDI were determined by GPC/MALLS.

2.4. RAFT polymerization of NVCL

A round-bottom flask was charged with **CTA 1** (0.016 g, 0.044 mmol) or **CTA 2** (0.016 g, 0.0688 mmol), AIBN (3 mg, 0.018 mmol), NVCL (1.22 g, 8.8 mmol) or (0.971 g, 7.00 mmol); then, the flask was degassed using three freeze-evacuate-thaw cycles, followed by sealing under vacuum. The polymerization was carried out at 70 °C for a predetermined time (Scheme 2). The polymer was purified by precipitating from THF into petroleum ether (b.p. 30–60 °C) three times to remove unreacted NVCL, filtered, and then dried under vacuum at 40 °C for 24 h. The conversion was determined using the gravimetric method. The results are listed in Table 1.

2.5. Transmittance measurements

The PNVCL polymer (Table 1, **PNVCL1-1**, M_n = 6800 g/mol, **PNVCL1-2**, M_n = 20,600 g/mol, **PNVCL2-1**, M_n = 3840 g/mol or **PNVCL2-5**, M_n = 7200 g/mol) was dissolved in deionized water at different concentrations (0.01 mg/ml-6.00 mg/ml). The solutions were maintained at room temperature for 12 h to reach equilibrium. The optical transmittance at 500 nm of each polymer solution was monitored as a function of temperature using a UV–vis spectrometer (CARY UV-50, VARIAN) equipped with a water-circulation heating stage. The heating rate was 1 °C/5 min. The T_{CP} was defined as the temperature that corresponded to the initial break points in the resulting transmittance versus temperature curve.

3. Results and discussion

3.1. RAFT polymerization of NVCL mediated by CTA 1 and CTA 2

The RAFT polymerization of NVCL was performed using **CTA 1** and the AIBN initiator by maintaining the molar ratio $[NVCL]_0$:$[CTA\ 1]_0$:$[AIBN]_0$ = 200:1:0.4 in the bulk solution at 70 °C. The presence of the R-group in the trithiocarbonate moiety at the ends of the polymer chain (Scheme 2) could be observed in the IR and ^{1}H NMR spectra of PNVCL (Fig. 1a). The strong, broad peak at 2926 cm^{-1} corresponds to the absorption of the PNVCL backbone and caprolactam ring because of the polymerization. The intense absorption peak at 1634 cm^{-1} was assigned to the C=O band of PNVCL. The characteristic bands of the **CTA 1** moiety (C=S, 1083 cm^{-1}; C—S, 842 cm^{-1}) appeared, which demonstrates that the resulting PNVCL has a trithiocarbonate end group. The ^{1}H NMR spectrum of PNVCL is shown in Fig. 2a. Compared with the ^{1}H NMR of **CTA 1**, the peaks assigned to the aromatic protons (at 7.4 ppm), benzyl methylene protons (at 5.2 ppm), methylene protons (at 3.7 ppm) and benzyl methylene protons (at 2.4 ppm) appeared, indicating that the trithiocarbonate **CTA 1** participated in the polymerization and yielded the corresponding PNVCL that contained a trithiocarbonate end group.

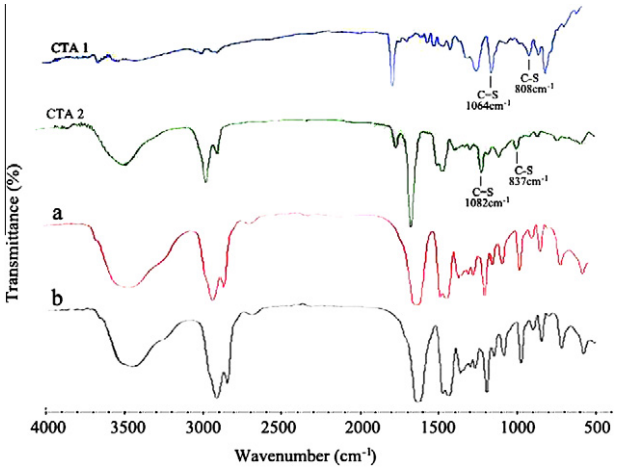


Fig. 1. IR spectra of **CTA 1**, **CTA 2** and PNVCL prepared via RAFT polymerization mediated by **CTA 1** (a) and **CTA 2** (b).

Similarly, we examined the bulk radical polymerization of NVCL by using **CTA 2** at two different concentrations ($[NVCL]_0$:$[CTA\ 2]_0$:$[AIBN]_0$ = 100:1:0.25 or $[NVCL]_0$:$[CTA\ 2]_0$:$[AIBN]_0$ = 50:1:0.25). The presence of the R-group of the trithiocarbonate moiety at the ends of the polymer chain (Scheme 2) could also be observed in the IR and ^{1}H NMR spectra of PNVCL. Fig. 2b shows a ^{1}H NMR spectrum of PNVCL obtained from the **CTA 2** system, from which chemical shifts at 4.40 ppm (NCH), 3.22 ppm (NCH_2), 2.33–2.50 ppm ($COCH_2$), 1.45–1.75 ppm ($NCCH_2CH_2CH_2$ of caprolactam ring and CH_2 of backbone) due to the PNVCL chain were observed. Specifically, the quartet signal at 3.71 ppm (CH_2NCH_2) and the triplet signal at 1.22 ppm (CH_3) were assigned to the **CTA 2** moiety. In addition, from the IR spectrum of PNVCL (Fig. 1b), the bands at 2925 cm^{-1} (—$CH_2CH_2CH_2$— of the caprolactam ring and —CH_2— of the backbone) and 1640 cm^{-1} were assigned to the carbonyl band of PNVCL. The characteristic bands of the **CTA 2** moiety (C=S, 1084 cm^{-1}; C—S, 842 cm^{-1}) appeared, indicating that the synthesized PNVCL contained a dithiocarbamate end group.

The molecular weights (MWs) and polydispersities (PDIs) of the obtained polymers were measured using GPC/MALLS and are summarized in Table 1. Although PNVCL has been widely studied,

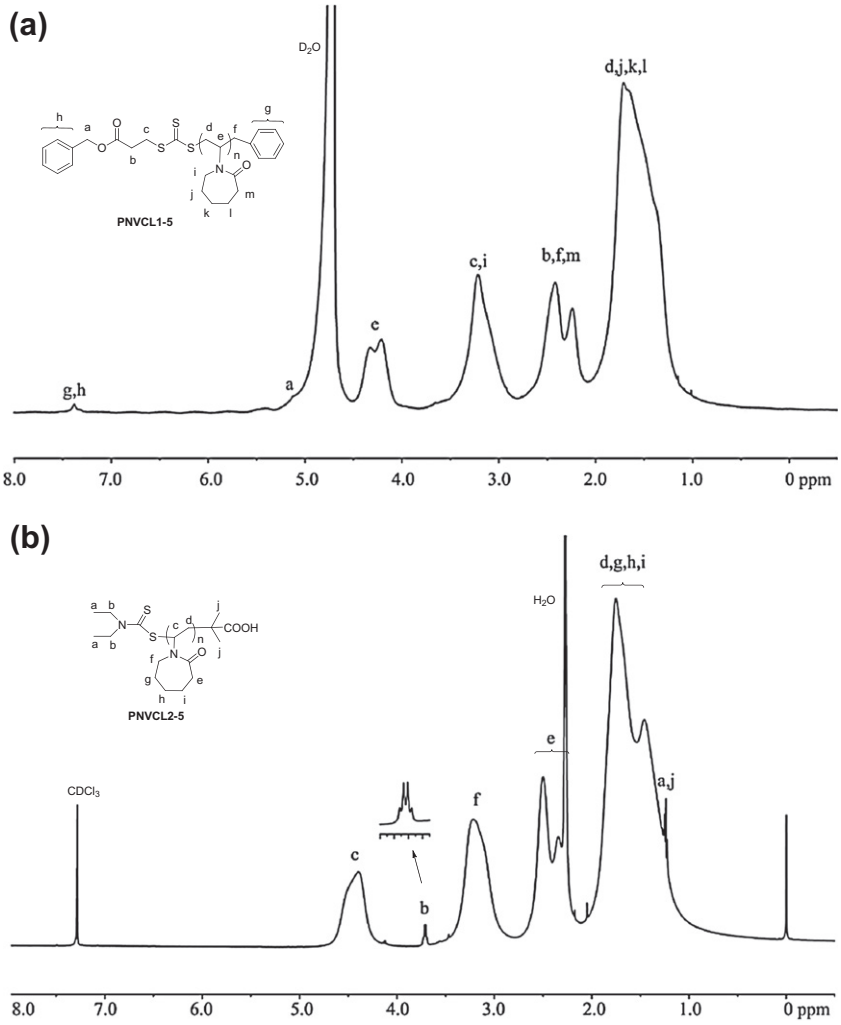


Fig. 2. ^{1}H NMR spectra of PNVCL prepared via RAFT polymerization mediated by **CTA 1** (a) and **CTA 2** (b).

the reports on its GPC data are very limited [22–24]. In our study, we examined the following eluents: THF, THF+*n*-$BuNH_4Br$, H_2O, H_2O + NaCl, and DMF. We found that in all of the solvents, the measured molecular weights were much lower (1×10^2 g/mol with THF system) or much higher (1×10^6 g/mol with H_2O system) than the theoretical values, with the exception of DMF, which resulted in a molecular weight that was closer to the theoretical values than the other solvents. Therefore, DMF was selected as the GPC eluent in our study. As shown in Table 1, in the presence of any of the CTAs, polymers with relatively narrow polydispersities (with PDI $\leqslant$ 1.42) and conversion that was dependent on MW were obtained, whereas in the absence of CTA, the corresponding PDI was wide. This observation indicated that the polymerization was under control.

Kinetic studies of the bulk polymerization of NVCL were performed at 70 °C in the presence of **CTA 1** with the molar ratio $[NVCL]_0:[CTA1]_0:[AIBN]_0 = 200:1:0.4$ or **CTA 2** with $[NVCL]_0:[CTA2]_0:[AIBN]_0 = 100:1:0.25$ or 50:1:0.25 to evaluate the effectiveness of **CTA 1** and **CTA 2**. For the polymerization with **CTA 1**, induction periods of 1 h could be observed in the time-conversion plot (Fig. 3a). The $\ln([M_0]/[M])$ increased with the reaction time in a nearly linear fashion, suggesting that the radical concentration remained essentially constant during the course of the polymerization following the 1 h induction period. Additionally, the GPC/MALLS analysis (Fig. 3a) showed that the MW increased nearly linearly with conversion and that the corresponding PDI varied in a small domain from 1.13 to 1.42 with increasing conversion. Fig. 4 shows the corresponding GPC traces of the polymers from the above-mentioned kinetic study. It is easily observed that the GPC traces are symmetric and unimodal and that no shoulder peak appears at a high MW position, which would be attributed to linear–linear polymer coupling. All of the results indicated that the polymerization of NVCL mediated by **CTA 1** has controlled polymerization characteristics.

As shown in Fig. 5, the pseudo-first-order kinetics indicate a constant concentration of radicals, and the experimental MW values that are close to the theoretical values indicate that the polymerizations mediated by **CTA 2** also proceeded in a controlled manner. Although a small shoulder or bump at low retention volumes was present in most of the GPC traces from the polymers, which has been attributed to bimolecular coupling in some studies of RAFT polymerization [12], the PDIs of all polymers throughout the polymerization are constant, in the range of 1.15–1.32. Additionally, Fig. 5 showed that the PDI of the polymers prepared using the ratio of $[NVCL]_0:[CTA2]_0:[AIBN]_0 = 100:1:0.25$ were lower than that of the polymers prepared using the ratio of $[NVCL]_0:[CTA2]_0:[AIBN]_0 = 50:1:0.25$, and the curve obtained from the former ratio was closer to the origin. Such results imply that the polymerization could be better controlled by changing the ratio of $[NVCL]_0:[CTA2]_0:[AIBN]_0$. These results indicate that **CTA 1** and

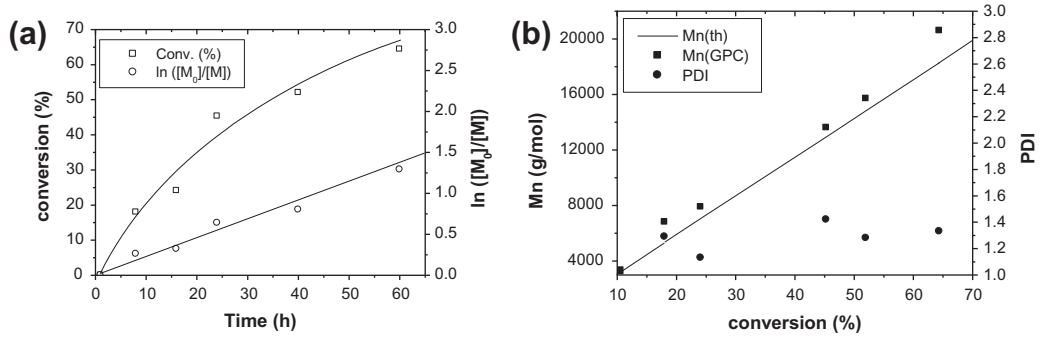


Fig. 3. Trace of time versus monomer conversion and $\ln[M_0]/[M]$ (where $[M_0]$ = concentration of the monomer at time t = 0 h and $[M]$ = concentration of the monomer at the corresponding time) (a); and dependence of MW and PDI on conversion for the RAFT polymerization of NVCL in the presence of **CTA 1** (b).

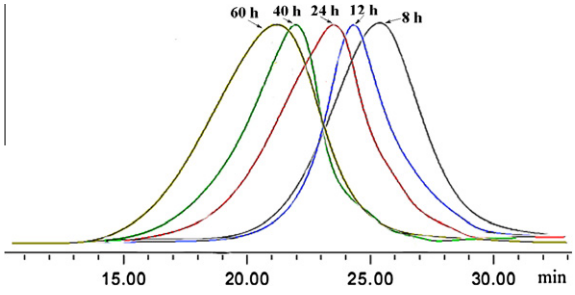


Fig. 4. Gradual traces of GPC in the kinetic study of the bulk polymerization of *N*-vinylcaprolactam mediated by **CTA 1** with the molar ratio of $[NVCL]_0$:$[CTA1]_0$:$[AIBN]_0$ = 200:1:0.4.

CTA 2 are effective chain transfer agents for controlling the radical polymerization of NVCL and that **CTA 1** is more suitable than **CTA 2**, suggesting that the former shows higher chain transfer ability than the latter.

3.2. Thermoresponsive properties

It has been reported that the end groups of polymer molecules may affect the thermal phase transition [38,39]. The NVCL polymer molecules from the **CTA 1** system and the **CTA 2** system have different end groups. To investigate the effects of the end groups on the phase transition, the cloud point temperatures (T_{CP}) of aqueous solutions of **PNVCL1-1** (M_n = 6800 g/mol, Table 1) and **PNVCL2-5** (M_n = 7200 g/mol), which have similar MW, were determined from turbidimetry measurements. Fig. 6a and b shows the transmittance *vs* temperature plots (cloud point curves) for the aqueous solutions of **PNVCL1-1** and **PNVCL2-5** at different concentrations. **PNVCL1-1** exhibited a sharper transition at a lower temperature above a polymer concentration of 0.10 mg/ml than **PNVCL2-5** did. This finding is attributed to **PNVCL1-1** having more hydrophobic end groups. The hydrophobic end groups may associate with each other at temperatures that are close to the transition point and change the hydrophobic–hydrophilic balance, resulting in a lower cloud point [11]. It is known that the phase transition temperature of PNVCL is sensitive to the molecular weight of the polymer [21]. To examine how the molecular weight affected the cloud point of NVCL polymers obtained from the **CTA 1** and **CTA 2** systems, the phase transitions of **PNVCL1**, which had a different MW, and **PNVCL2-1** (M_n = 3840 g/mol) were also studied using T_{CP} measurements. Fig. 7 shows that the T_{CP} of **PNVCL1** solutions with identical concentrations (1 mg/ml and 0.5 mg/ml) decreases with increasing polymer MW. Additionally, the T_{CP} of **PNVCL2-1** and **PNVCL2-5** had an inverse dependence on their MW. This behavior is similar to that observed for solutions of the PNVCL obtained using conventional radical polymerization, where the T_{CP} shifts to a lower temperature and concentration as the molecular weight of the polymer increases [21]. This phenomenon is attributed to the fact that the solution behavior of the PNVCL/water system corresponds to a typical Flory–Huggins (Type I) de-mixing behavior with T_{CP}.

As shown in Fig. 6a and c, the water solubility of the PNVCLs obtained from the **CTA 1** system decreased with increasing MW. For example, at a polymer concentration of 6.0 mg/ml, the transmittance of the **PNVCL1-1** solution at room temperature is approximately 80%, whereas the transmittance of the **PNVCL1-5** solution is only 42%. From visual inspection, the **PNVCL1-5**

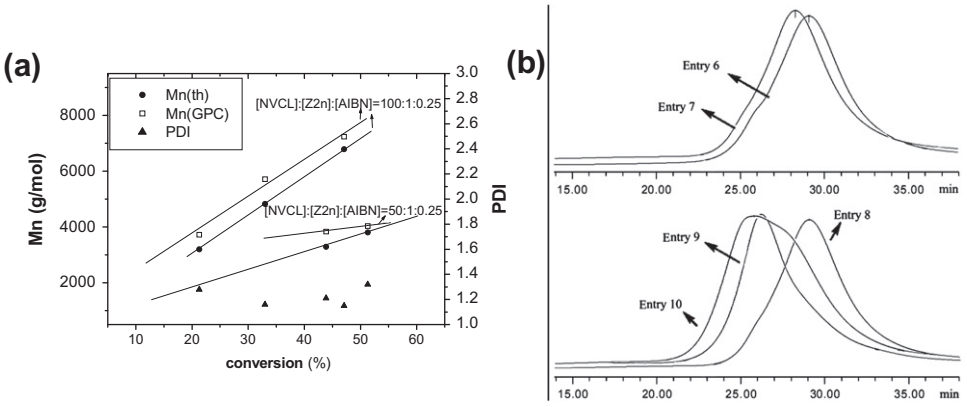


Fig. 5. Dependence of MW and PDI on conversion for the RAFT polymerization of NVCL in the presence of **CTA 2** (a), and GPC traces of PNVCL prepared via RAFT polymerization mediated by **CTA 2** (b).

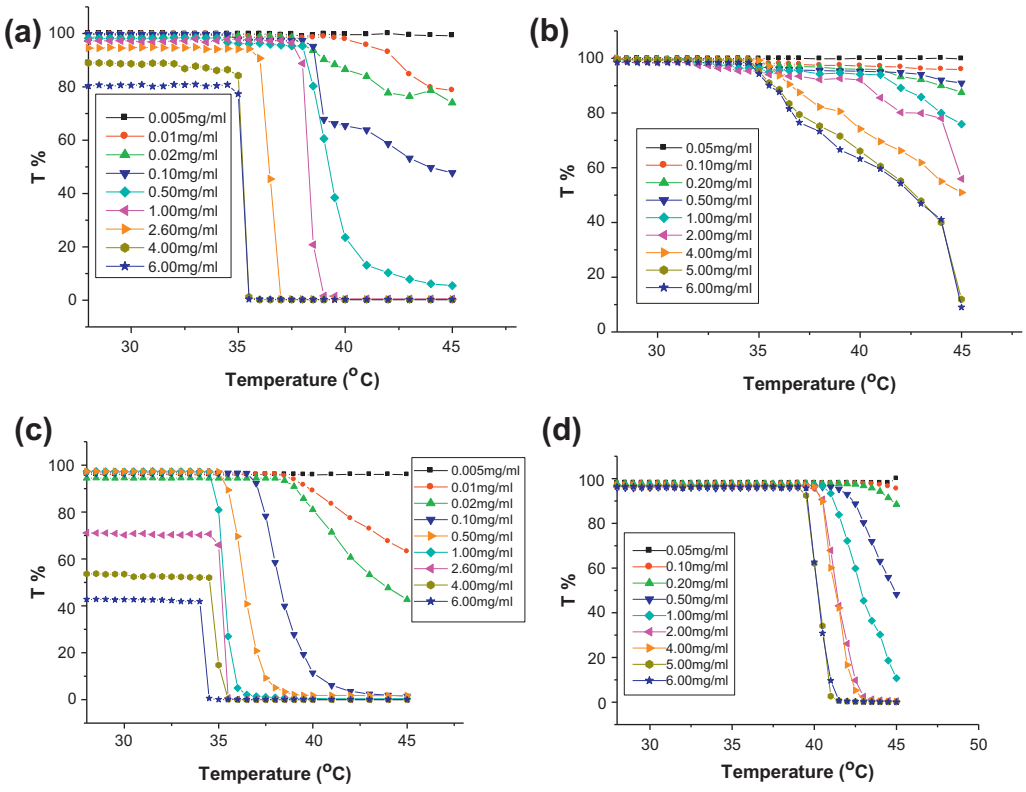


Fig. 6. Transmittance measurements as a function of temperature for different concentrations of **PNVCL1-1** (a), **PNVCL2-5** (b), **PNVCL1-5** (c) and **PNVCL2-1** (d).

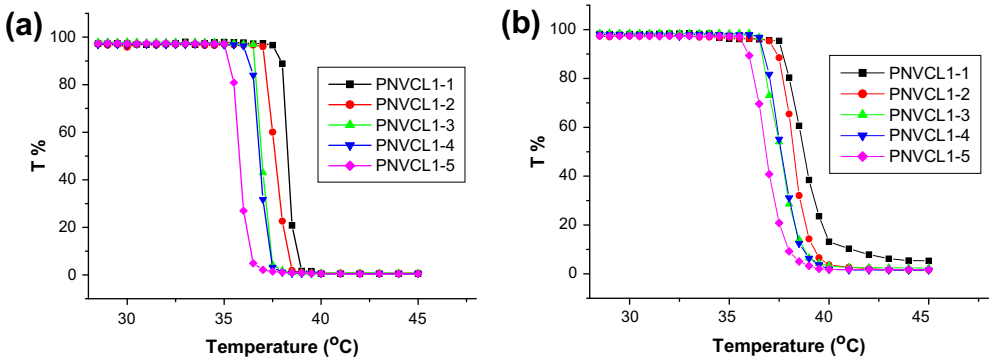


Fig. 7. Transmittance measurements as a function of temperature for 1 mg/ml (a) and 0.5 mg/ml (b) aqueous solutions of **PNVCL1-1**, **PNVCL1-2**, **PNVCL1-3**, **PNVCL1-4** and **PNVCL1-5**.

solution underwent gelation above a polymer concentration of 2.6 mg/ml. The same phenomenon has been observed for telechelic poly(*N*-isopropylacrylamides) (PNIPAMs) that have an *n*-octadecyl group at each chain end [41,42]. In dilute aqueous solutions below the LCST, the telechelic HM-PNIPAMs form flower-like associates consisting of loops of hydrated polymer chains that have both end groups entrapped in the micellar core. At higher concentrations ($c > 20$ g/l), the HM-PNIPAMs chains form bridges between the rosettes, which trigger significant enhancement of the viscosity, and eventually, result in the formation of a gel phase [41]. In our case, the **PNVCL1** that has a hydrophobic benzyl group at each chain end is similar to the telechelic PNIPAM. The gelling behavior of **PNVCL1-5** with the higher MW implies that there is hydrophobic association of the chain ends.

The concentration-dependence in Fig. 6 showed that the solution concentration also affected the phase transition temperature of the PNVCL obtained from the **CTA 1** and **CTA 2** systems in aqueous medium, which decreased with increasing solution concentration, but the T_{CP} was almost independent when the concentration increased to nearly 4.0 mg/ml for **PNVCL1-1** and **PNVCL1-5** and to 5.0 mg/ml for **PNVCL2-1** and **PNVCL2-5**. We can also observe from Fig. 7 that the **PNVCL1** exhibits a sharper decrease in transmittance at 1.0 mg/ml than at 0.5 mg/ml. This finding is consistent with the generally accepted LCST principle for dilute solutions, which states that higher water content enhances the hydrogen-bonding interactions between water and the polymer chain, which requires more thermal energy to break the water structure, thereby resulting in an increase of the LCST [36].

4. Conclusion

The radical polymerization of NVCL using AIBN as an initiator and one of two new compounds, *S*-(benzyl propionate) trithiocarbonate (**CTA 1**) or *N*, *N*-diethyl-*S*- (α,α′-dimethyl-α″-actetic acid)

dithiocarbamate (**CTA 2**), as a chain transfer agent exhibited controlled polymerization characteristics, which was indicated by a well-controlled molecular weight, narrow molecular weight distribution, and linear relationship between the molecular weight and monomer conversion. **CTA 1** was a good mediator for the RAFT polymerization of NVCL, whereas the polymerization of NVCL that was mediated by **CTA 2** was not an ideal RAFT process. However, the polymerization could be better controlled by changing the ratio of $[NVCL]_0$:$[CTA2]_0$:$[AIBN]_0$. With the use of the above mentioned trithiocarbonate and dithiocarbamate, new thiocarbonylthio compounds were applied during the RAFT polymerization of NVCL. The influence of the end groups on the T_{CP} of PNVCL was demonstrated for the first time. The T_{CP} of PNVCL with the more hydrophobic **CTA 1** end groups was lower than that of the PNVCL obtained from the **CTA 2** system in the range of MW studied. Finally, the transition temperatures decreased with increasing MW and concentration for all of the samples studied.

Acknowledgements

The authors gratefully acknowledge the support for this work from the National Natural Foundation of China (No. 20864003), Program for Changjiang Scholars and Innovative Research Team in University, PCSIRT, and the Natural Science Foundation of Yunnan Province (2009ZC064M), PR China.

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