Facile One-Pot/One-Step Technique for Preparation of Side-Chain Functionalized Polymers: Combination of SET-RAFT Polymerization of Azide Vinyl Monomer and Click Chemistry

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ABSTRACT: An azido-containing functional monomer, 11-azidoundecanoyl methacrylate, was successfully polymerized via ambient temperature single electron transfer initiation and propagation through the reversible addition–fragmentation chain transfer (SET-RAFT) method. The polymerization behavior possessed the characteristics of "living"/controlled radical polymerization. The kinetic plot was first order, and the molecular weight of the polymer increased linearly with the monomer conversion while keeping the relatively narrow molecular weight distribution ($M_w/M_n \leq 1.22$). The complete retention of azido group of the resulting polymer was confirmed by ^{1}H NMR and FTIR analysis. Retention of chain functionality was confirmed by chain extension with methyl methacrylate to yield a diblock copolymer. Furthermore, the side-chain functionalized polymer could be prepared by one-pot/one-step technique, which is combination of SET-RAFT and "click chemistry" methods. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 1120–1126, 2012

KEYWORDS: azide polymer; click chemistry; living polymerization; radical polymerization; reversible addition-fragmentation chain transfer (SET-RAFT)

INTRODUCTION "Click chemistry" is a group of chemical reactions, which have modularity, high efficiency, simple reaction conditions, stereospecificity, give high yields, and produce no by-products.[1] As a member of the family of click reaction, copper-catalyzed azide-alkyne cycloaddition (CuAAC) has attracted much attention due to its wide application in various research areas, including bioconjugation,[2] chemical synthesis,[3] materials science,[4] and so on. Many researchers reported the application of click chemistry in polymer design since it was introduced into polymer science area in 2004.[5]

"Living"/controlled radical polymerization (CRP) methods are powerful techniques to prepare polymers with controllable architectures and properties, which include nitroxide-mediated radical polymerization,[6] atom transfer radical polymerization (ATRP),[7] reversible addition–fragmentation chain transfer (RAFT) polymerization,[8] and single electron transfer–living radical polymerization (SET–LRP).[9] As a relatively newer CRP method, SET–LRP has many advantages such as relatively low polymerization temperature (room temperature), ultrahigh polymerization rate, easy removal of the catalyst from reaction mixtures, and decreasing chance of side reactions. Most recently, SET-RAFT, a combination of ambient temperature SET initiation propagation through the RAFT method, was reported.[10] In SET-RAFT system, the controllability of polymerization should be improved due to the coexistence of SET–LRP and RAFT processes, even its mechanism need further deep understanding. Till now, nearly all vinyl monomers except the vinyl alkyne and azide monomer, which can be polymerized by common free-radical polymerization method, were suitable to above CRP methods. The difficulty in controlling polymerizations of vinyl alkyne and azide monomers stems from their sensitivities to heat and UV light (azide monomer) or other side reactions.[11] Recently, our group reported the successful controlled polymerization of an alkyne-containing monomers, propargyl methacrylate (PgMA), via SET-RAFT technique.[11] As for the preparation of azide polymers, chemical modification was often used.[12] However, the azide content in the polymer chain produced by this technique is difficult to be controlled. Living cationic ring-opening polymerization was reported to synthesize azide polymers,[13] but it required stringent reaction

conditions, such as high-vacuum technique and high purities of reagents. According to the literature, the polymerizations of azide monomers should be conducted in the absence of UV light and at low temperature, because the azide group is very sensitive to heat and UV light. Moreover, the side reaction (cycloaddition between azide group and carbon double bond) is prone to take place, especially at relatively high temperature. Fortunately, Bai and coworkers[14] reported several successful low temperature systems for the controlled free-radical polymerizations of azide monomers, including γ-ray irradiation (0 °C) and redox initiator techniques.[15] Bai successfully prepared the side-chain functionalized polymers via click chemistry based on the azide polymers; however, two-step and two-pot reactions should be used.

Modular processes combining CuAAC and CRP techniques have been considered to be a powerful technique to produce functional polymers. Among the CRP techniques reported, ATRP and SET–LRP are the best choice because CuAAC and CRP can share the same Cu(I) catalytic system. Haddleton and coworkers[16] reported the simultaneous CuAAC and CRP techniques to synthesize the functional polymer using PgMA as an alkyne monomer, and the mechanism was studied in detail. We also successfully used PgMA as the alkyne monomer to prepare side-chain functional polymers via combination of SET-RAFT and click chemistry techniques.[11] Drockenmuller and coworkers[17] reported preparation of functionalized random copolymers via one-pot click chemistry/ATRP tandems approaches. However, the polymerization became uncontrollable when the ratio of azide monomer [11-azido-undecanoyl methacrylate (AzUMA)]/methyl methacrylate (MMA) increased from 1:4 to 3:7. The main reason may be due to the relatively high polymerization temperature (90 °C). So, the direct CRP of azide monomer in the presence of Cu(I) catalytic system at low temperature should provide the chance for the one-pot/one-step preparation of functionalized polymers.

Herein, we reported a strategy for the synthesis of the well-defined azide polymers via SET-RAFT polymerization technique at room temperature. Furthermore, a one-pot/one-step technique combining SET-RAFT and click chemistry techniques has been successfully used to synthesize the side-chain functionalized polymers, and functionalization content of the polymer chains was also controlled by changing the molar ratio of azide monomer and alkyne component.

EXPERIMENTAL

Materials

11-Bromoundecanol (98%, Acros), propargyl bromide (80 wt % solution in toluene, Acros), ethyl-2-bromoisobutyrate (EBiB; 98%, Acros), sodium azide (≥99.5%; Aldrich), and copper powder (Cu(0), <75 μm, 98%, Aldrich) were used as received. Tetrahydrofuran (THF) was dried over sodium overnight and distilled before use. Pentamethyldiethylenetriamine (PMDETA; Jiangsu Liyang Jiangdian Chemical Factory, Liyang, China, 98%) was dried with 4 Å molecular sieve and distilled in vacuum. 2-Cyanoprop-2-yl 1-dithionaphthalate (CPDN) was synthesized according to the references.[18] Dimethyl sulphoxide (DMSO) and triethylamine (analytical reagent, Shanghai Chemical Reagent) were dried by 4 Å molecular sieve before use. All other chemical agents were purchased from Shanghai Chemical Reagent and used as received.

Synthesis of 11-Azido Undecanol

In a 250-mL round-bottomed flask, a solution of 11-bromoundecanol (12.55 g, 50 mmol) in dimethylformamide (DMF) (150 mL) was added an another solution of sodium azide (9.75 g, 150 mmol) in water (50 mL), and the reaction mixture was stirred for 24 h at 80 °C. Then methylene chloride (150 mL) was added, and the solution was washed with water (3 × 150 mL). The organic phase was dried in anhydrous $MgSO_4$ overnight, filtered, and concentrated. The obtained product was a colorless liquid (9.37 g, 88%).

^{1}H NMR ($CDCl_3$): δ (ppm) 3.64 (t, C***H***$_2$—OH, 2H), 3.25 (t, C***H***$_2$—N_3, 2H), 1.71–1.17 (m,C***H***$_2$, 18H), and the appearance of azide signals in FTIR spectra was in 2090 cm^{-1}.

Synthesis of AzUMA

A solution of 11-azido undecanol (8.50 g, 40 mmol), triethylamine (4.85 g, 48 mmol), and anhydrous THF (100 mL) was cooled in an ice water bath. Methacryloyl chloride (5.06 g, 48 mmol) diluted by a small amount of anhydrous THF (15 mL) was added dropwise over a period of 20 min, and the mixture was stirred in the cooling bath for 1 h and then for 24 h at room temperature. Then water (100 mL) was added, and the mixture was extracted with methylene chloride (3 × 100 mL). The organic layer was dried by anhydrous $MgSO_4$, filtered, and concentrated. The obtained crude product was purified by flash chromatography and eluted with the mixture of hexane/ethyl acetate (from 50:1 gradually increasing to 20:1). After eluent was removed, 4.72 g (yield: 42%) of AzUMA was obtained as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ (ppm) 6.06 (d, C***H***H=C(CH_3), 1H), 5.51 (s, CH***H***=C(CH_3), 1H), 4.10 (t, OC***H***$_2$, 2H), 3.25 (t, C***H***$_2N_3$, 2H), 1.91 (s, CH_2=C(C***H***$_3$), 3H), 1.71–1.17 (m, C***H***$_2$, 18H). ^{13}C NMR ($CDCl_3$): δ (ppm) 166.99 (**C**OO, 1C), 136.59 (**C**H_2=CCH_3, 1C), 124.79 (**C**H_2=CCH_3, 1C), 64.60 (O**C**H_2, 1C), 51.37 (**C**H_2N_3, 1C), 29.90–25.90 ((**C**H_2)$_9$, 9C), 18.21 (CH_2=C(**C**H_3), 1C). The appearance of azide signals in FTIR spectra was in 2090 cm^{-1}.

Synthesis of 4-Propargyloxy-4′-Methoxy Azobenzene

In a 250-mL round-bottomed flask, 4-methoxy aniline (2.0 g, 16.3 mmol) was added to a solution of concentrated HCl (37.0%, 4.05 g, 48.9 mmol) in water (80 mL). The mixture was stirred in an ice bath to keep the reaction temperature at 0–5 °C. Then a water solution (10 mL) of sodium nitrite (1.34 g, 19.4 mmol) was added dropwise within 10 min. A brown transparent diazonium salt solution was obtained, after reacted for 60 min at 0–5 °C. Meanwhile, a coupling solution was prepared as follows: phenol (1.68 g, 17.9 mmol), sodium hydroxide (NaOH; 0.70 g, 17.9 mmol), and $NaHCO_3$ (3.0 g, 35.8 mmol) were dissolved in 150 mL of water under vigorous stirring at 0–5 °C. Then the diazonium salt solution was added dropwise to the coupling solution within 20 min

at 0–5 °C. The final mixture was reacted at 5 °C for 3 h. The precipitate was collected by filtration, washed with deionized water three times, and dried under vacuum. The crude product (4-methoxy-4′-hydroxy azobenzene) was obtained as yellow solid (3.21 g, yield 86.7%).

A solution of 4-methoxy-4′-hydroxy azobenzene (1.50 g, 6.57 mmol), propargyl bromide (0.94 g, 7.88 mmol), NaOH (0.31 g, 7.88 mmol), a catalytic amount of potassium iodide, and 50 mL of acetone were prepared in a 100-mL round-bottomed flask under vigorous stirring. After stirring under reflux for 12 h at 45 °C, the solution was concentrated by rotary evaporator. The final crude product was purified by recrystallization from ethanol to yield pure compound 4-propargyloxy-4′-methoxy azobenzene (PMA) as yellow solid (1.42 g, 81.1%).

^{1}H NMR ($CDCl_3$): δ (ppm) 7.87 (d, Ar***H***, 4H), 7.10–6.95 (m, Ar***H***, 4H), 4.77 (s, OC***H***$_2$C≡CH, 2H), 3.89 (s, OC***H***$_3$, 3H), 2.55 (s, C≡C***H***, 1H). ^{13}C NMR (DMSO-d_6), δ (ppm): 162.11, 159.85, 147.19, 146.47, 124.77, 124.55, 115.97, 115.09, 79.43, 79.20, 56.37, 56.15.

Typical Procedures for SET-RAFT Polymerization of AzUMA

AzUMA (0.5 mL, 1.72 mmol), EBiB (2.54 μL, 0.0172 mmol), Cu(0) (3.3 mg, 0.0516 mmol), CPDN (4.7 mg, 0.0516 mmol), and solvent DMSO (0.5 mL) were added to a 5-mL ampoule with a magnetic bar. The reaction mixture was bubbled with argon for ~10 min, and then PMDETA (10.8 μL, 0.0516 mmol) was added to the mixture. The solution was deoxygenated by bubbling with argon for 5 min, and then the ampoule was flame sealed under argon atmosphere and placed in the water bath at 25 °C. At the designed time, the ampoule was opened, and the contents were diluted with about 3.0 mL THF and passed through a small neutral Al_2O_3 chromatographic column to remove any unreacted Cu(0) catalyst and Cu(II) compounds. The resulting solution was precipitated in 200 mL of methanol. The polymers were obtained by filtration and dried to constant weight under vacuum at room temperature. The conversion of the monomer was determined by gravimetry.

Chain Extension of PAzUMA Using PAzUMA as a Macroinitiator

Poly(AzUMA) (PAzUMA; $M_{n(GPC)}$ = 7680 g/mol, M_w/M_n = 1.20) was used as a macroinitiator to synthesize PAzUMA-*b*-poly(MMA) (PMMA) block copolymer with MMA as the second monomer in DMF solution. The reaction was also carried out at 25 °C ($[MMA]_0$:$[EBiB]_0$:$[PAzUMA]_0$:$[Cu(0)]_0$:$[PMDETA]_0$ = 200:1:3:3:3, MMA/DMF = 1/5, v/v). The reaction was stopped after 20 h, and the other procedures were similar to those mentioned above.

Preparation of Functional PAzUMA Via One-Pot and One-Step Technique

A typical procedure for the preparation of functional PAzUMA (P1) via one-pot and one-step technique is as follows: AzUMA (0.25 mL, 4.19 mmol), PMA (0.115 g, 2.09 mmol), EBiB (1.27 mL, 0.0172 mmol), Cu(0) (2.8 mg, 0.086 mmol), CPDN (7.1 mg, 0.0516 mmol), and solvent DMF (1.5 mL) were added to a dry glass ampoule with a magnetic bar. The reaction mixture was bubbled with argon for 10 min, and then PMDETA (9.0 μL, 0.086 mmol) was added to the mixture. The solution was bubbled with argon for another 5 min to eliminate the oxygen, and then the ampoule was flame sealed under argon atmosphere and placed in the water bath at 25 °C. After 30 h, the mixture was diluted by 5-mL THF and precipitated in 200-mL methanol. The sample was obtained by filtration and dried to constant weight under vacuum at room temperature. The functional PAzUMA (P2) was also prepared by similar procedures to those described above except that the molar ratio of $[AzUMA]_0$:$[PMA]_0$:$[EBiB]_0$:$[CPDN]_0$:$[Cu(0)]_0$:$[PMDETA]_0$ was 100:110:1:3:5:5, and polymerization time is 30 h.

Characterization

^{1}H and ^{13}C NMR spectra were recorded on an INOVA 400 MHz NMR instrument using $CDCl_3$ as solvent and tetramethylsilane as the internal standard. The molecular weights and molecular weight distributions of the polymers were determined using a Waters 1515 gel permeation chromatograph (GPC) equipped with a refractive-index detector (Waters 2414) using HR 1 (pore size: 100 Å, 100–5000 Da), HR 2 (pore size: 500 Å, 500–20,000 Da), and HR 4 (pore size 10,000 Å, 50–100,000 Da) columns (7.8 × 300 mm^2, 5-μm bead size) with molecular weights ranging from 10^2 to 5 × 10^5 g/mol. THF was used as the eluent at a flow rate of 1.0 mL/min at 30 °C. GPC samples were injected using a Waters 717 plus autosampler and calibrated with PMMA standards purchased from Waters. FTIR spectra were recorded on a Nicolette-6700 FTIR spectrometer.

RESULTS AND DISCUSSION

SET-RAFT Polymerization of AzUMA

According to Refs. [14] and [15], temperature is considered as a crucial factor to decide whether the polymerization of vinyl azide monomer proceeds successfully, because azido group is prone to undergo cycloaddition to carbon double bond at high temperature. The low temperature (room temperature or lower than room temperature) used in SET–LRP system fits the requirement; therefore, we used it to conduct the polymerization of azide monomer, AzUMA.

SET-RAFT polymerization of AzUMA was carried out at room temperature using EBiB as the initiator, CPDN as the chain transfer agent (CTA), and Cu(0)/PMDETA as the catalyst system. The effects of three factors (the concentrations of monomer, CPDN, and solvent) on the polymerization were investigated as presented in Table 1. From Table 1 (entry 1), we can see that the polymerization was uncontrollable, and the molecular weight distribution (M_w/M_n) of the obtained azide polymer reached 1.92 after 3 h in the absence of CPDN. Most interestingly, the polymerization of AzUMA can be well controlled when CPDN, the CTA, was added. With the increase of ratios of CPDN (keeping molar ratio of monomer and catalyst system constant), the M_w/M_n of the obtained polymers decreased from 1.36 to 1.19, which demonstrated the improvement of controllability of the polymerization.

TABLE 1 The SET-RAFT Polymerization Results of AzUMA at 25 °C Under Various Conditions

Entry	Polymerization Ratio[a]	Solvent	Time (h)	Conv. (%)	$M_{n(th)}$ (g/mol)	$M_{n(GPC)}$ (g/mol)	M_w/M_n
1	100:1:0:3:3	DMSO	3	94.3	26,490	38,190	1.92
2	100:1:1:3:3	DMSO	3	59.7	8,390	20,690	1.36
3	100:1:3:3:3	DMSO	3	70.9	4,980	10,390	1.21
4	100:1:5:3:3	DMSO	3	75.2	3,520	6,680	1.19
5	50:1:3:3:3	DMSO	3	84.9	2,980	7,130	1.19
6	100:1:3:3:3	DMF	3	52.5	3,680	8,530	1.18
7	100:0:3:3:3	DMSO	4	70.2	6,570	9,260	1.21

[a] Polymerization ratio: $[AzUMA]_0:[EBiB]_0:[CPDN]_0:[Cu(0)]_0:[PMDETA]_0$.

Furthermore, the molecular weight of the polymer can also be adjusted by changing the amount of CPDN in this system. The similar polymerization behavior was also observed in our previous reported system.[11] In addition, the polymerization rate increased when we changed the molar ratios of monomer and CPDN from 100:1 to 100:5 (entries 2–4), which was opposite to the RAFT mechanism. The reason may be due to conjunction of retardation effect[19] and the increase of initiator concentration. The retardation effect means that the increase of CTA agent concentration would cause the decrease of polymerization rate. On the contrary, the increase of initiator concentration will cause the rate enhancement. In the current system, the increase of initiator concentration is dominant when compared with the retardation effect. Furthermore, the polymerization rate decreased when the molar ratios of monomer and CPDN were changed from 50:3 to 100:3 (entries 3 and 5). Klumperman and coworkers[20] and our group[21] also reported the similar results. The polymerization of AzUMA in DMF (another classical solvent for SET–LRP) was also investigated, and the result was favorable (Table 1, entry 6, $M_w/M_n = 1.18$). Interestingly, the living/controlled nature of polymerization was still observed even in the absence of EBiB (Table 1, entry 7, $M_w/M_n = 1.21$). We reported the similar results previously.[22] From these results, we considered that CPDN may play two roles simultaneously in the polymerization approach, a pseudohalide alkyl initiator and a CTA, which was identical to our previous results.[21]

The kinetic plot for the SET-RAFT polymerization of AzUMA was shown in Figure 1(a). A linear relationship between $\ln([M]_0/[M])$ and polymerization time was observed, indicating a constant radical concentration throughout the polymerization process. As given in Figure 1(b), the molecular weight of the obtained PAzUMA measured by GPC ($M_{n(GPC)}$) increased linearly with monomer conversion, while keeping the relatively low molecular weight distributions ($M_w/M_n \leq 1.22$) even up to relatively high monomer conversion (88.3%). Moreover, GPC curves of PAzUMAs also showed unimodal and normal distributions as presented in Figure 2. However, the molecular weight ($M_{n(GPC)}$) was higher than the theoretical value ($M_{n(th)}$), which indicated the initiator efficiency was not high. $M_{n(th)}$ was calculated from the following equation, $M_{n(th)} = [M]_0/([CTA]_0 + [RX]_0) \times M_M \times$ Conversion, where $[M]_0$, $[CTA]_0$, and $[RX]_0$ are the initial concentration of AzUMA, CPDN, and EBiB, respectively. M_M is the molecular weight of AzUMA and Conversion is the AzUMA conversion. All of the above results indicated that SET-RAFT polymerization of AzUMA showed the nature of CRP.

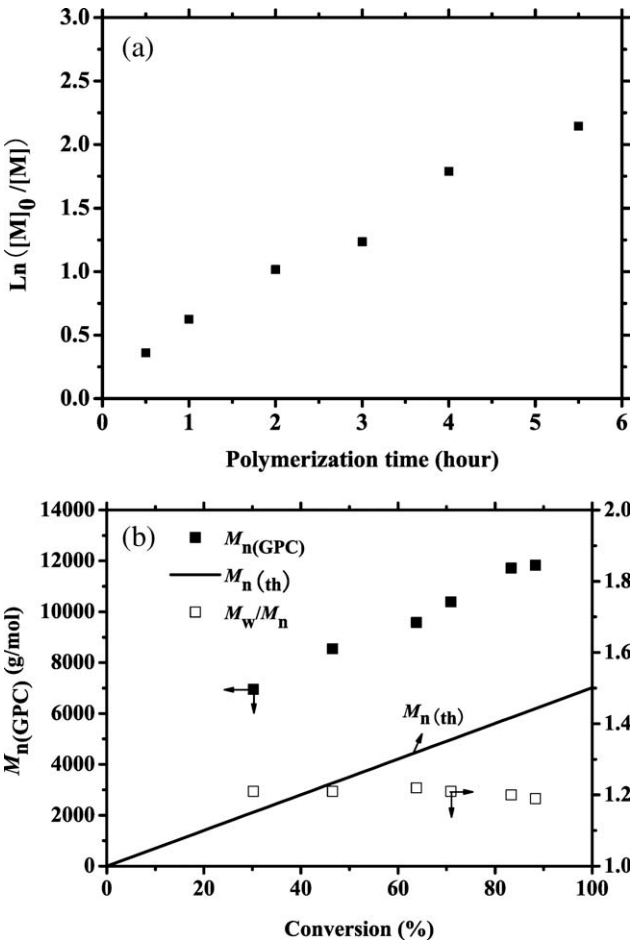

FIGURE 1 (a) Kinetic plots of SET-RAFT polymerization of AzUMA in DMSO solution at 25 °C. Polymerization conditions: $[AzUMA]_0:[EBiB]_0:[CPDN]_0:[Cu(0)]_0:[PMDETA]_0 = 100:1:3:3:3$ and AzUMA/DMSO = 1/1 (v/v); (b) the dependence of the molecular weights and molecular weight distributions on the monomer conversions for the SET-RAFT polymerization of AzUMA. Polymerization conditions are the same as in (a).

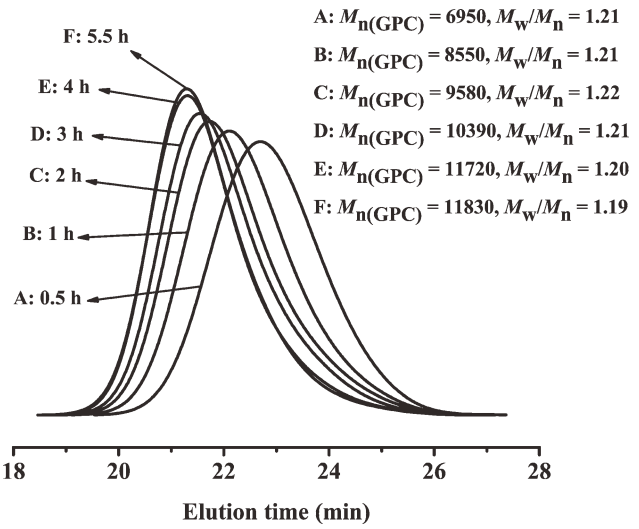

FIGURE 2 GPC traces of PAzUMA prepared by SET-RAFT polymerization at 25 °C. Polymerization conditions: $[PAzUMA]_0$:$[EBiB]_0$:$[CPDN]_0$:$[Cu(0)]_0$:$[PMDETA]_0$ = 100:1:3:3:3 and PAzUMA/DMSO = 1/1 (v/v).

Analysis of Chain-End and Chain-Extension Experiment

The chain end of the PAzUMA sample prepared by SET-RAFT polymerization was analyzed by ^{1}H NMR spectra, and the result was shown in Figure 3. The signals at δ = 3.24 ppm (**a** in Fig. 3) represented the methylene group next to the azido monomer unit, and the signals at δ = 3.90 ppm (**b** in Fig. 3) were assigned to the methylene group next to the oxygen of the ester group. The 1:1 ratio of the corresponding integration values for **a** and **b** peaks in Figure 3 suggested that azido groups were kept intact after polymerization. The peak at δ = 4.12 ppm (**c** in Fig. 3) corresponded to the methylene protons of the ethyl ester unit in the initiator EBiB, which revealed that the initiator EBiB moieties were successfully attached to the polymer chain ends. The signals at δ = 7.35–8.25 ppm (**d, e, f,** and **g** in Fig. 3) were attributed to the aromatic protons of the naphthalene units of CPDN, which showed that the dithiocarbonate moieties in CPDN were also attached to the polymer chain ends. A chain-extension experiment was also conducted to verify the

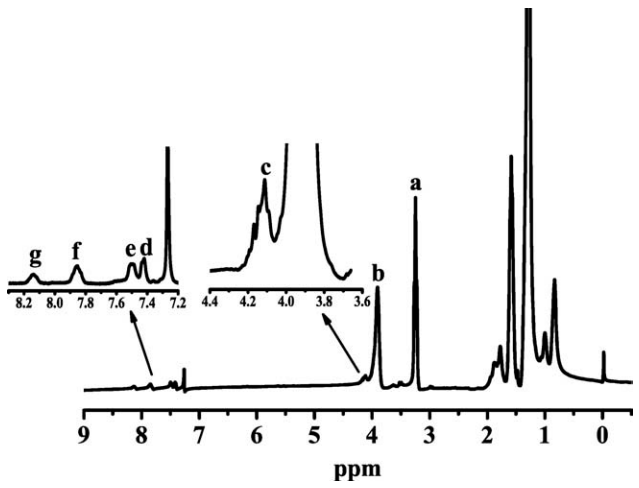

FIGURE 3 ^{1}H NMR spectrum of PAzUMA ($M_{n(GPC)}$ = 8550 g/mol, M_w/M_n = 1.21) prepared via SET-RAFT polymerization with EBiB as the initiator and CPDN as the RAFT agent. Polymerization conditions: $[AzUMA]_0$:$[EBiB]_0$:$[CPDN]_0$:$[Cu(0)]_0$:$[PMDETA]_0$ = 100:1:3:3:3, t = 1 h, T = 25 °C, and AzUMA/DMSO = 1/1 (v/v).

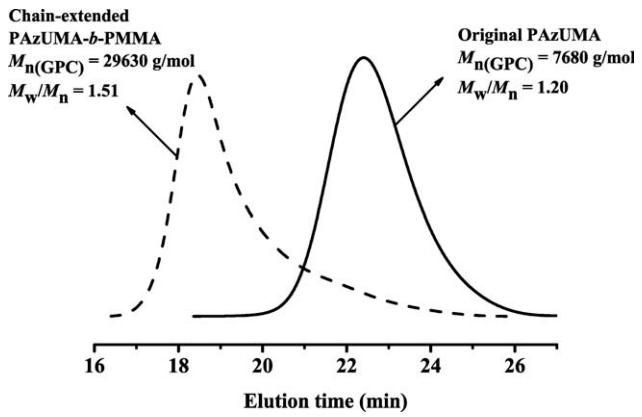

FIGURE 4 GPC curves of polymers before and after chain extension with PAzUMA as the macroinitiators. Conditions: $[MMA]_0$:$[EBiB]_0$:$[PAzUMA]_0$:$[Cu(0)]_0$:$[PMDETA]_0$ = 200:1:3:3:3, MMA/DMF = 1/5 (v/v), t = 20 h, T = 25 °C, and conversion (%) = 99%.

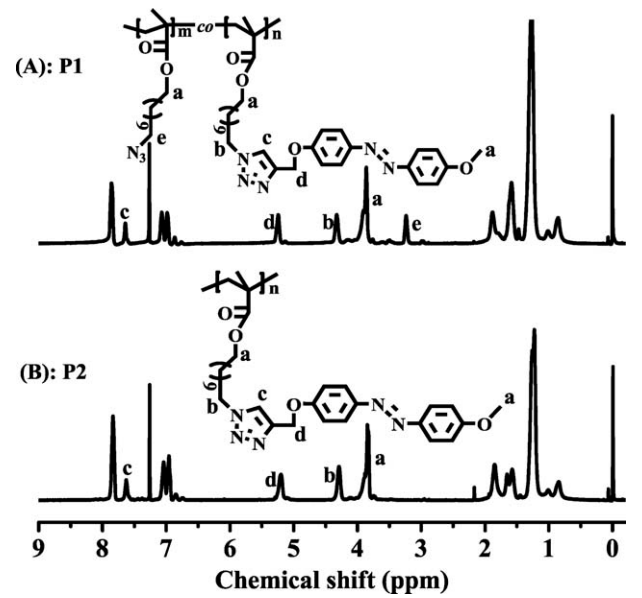

FIGURE 5 ^{1}H NMR spectra of copolymer (P1: $M_{n(GPC)}$ = 21,400 g/mol, M_w/M_n = 1.30) and homopolymer (P2: $M_{n(GPC)}$ = 15,120 g/mol, M_w/M_n = 1.19) synthesized by one-pot and one-step technique. Reaction conditions: P1: $[AzUMA]_0$:$[PMA]_0$:$[EBiB]_0$:$[CPDN]_0$:$[Cu(0)]_0$:$[PMDETA]_0$ = 100:50:1:3:5:5, AzUMA/DMF = 1/6 (v/v), T = 25 °C, and conversion (%) = 97.5%; P2: $[AzUMA]_0$:$[PMA]_0$:$[EBiB]_0$:$[CPDN]_0$:$[Cu(0)]_0$:$[PMDETA]_0$ = 100:110:1:3:5:5, AzUMA/DMF = 1/12 (v/v), T = 25 °C, and conversion (%) = 72.7%.

living nature of obtained polymer (Fig. 3). As presented in Figure 4, there was an apparent peak shift from the macroinitiator with $M_{n(GPC)} = 7680$ g/mol and $M_w/M_n = 1.20$ to the chain-extended PAzUMA-*b*-PMMA with $M_{n(GPC)} = 29{,}630$ g/mol and $M_w/M_n = 1.51$, respectively. All the above results proved the functionality and feature of the living/controlled polymerization of AzUMA.

Preparation of Functional Polymer Via One-Pot and One-Step Technique

Because Cu(I) as the catalyst for click chemistry could be generated *in situ* from the Cu(0)/PMDETA system in SET-RAFT system, functional side-chain polymer could be prepared via one-pot and one-step technique in current system. The approaches involved SET-RAFT polymerization of AzUMA and simultaneous coupling of PMA by click chemistry reaction. Two kinds of functional polymers with different functionalities could be obtained by changing the molar ratios of AzUMA and PMA unit. The results were shown in Figures 5 and 6. As represented in Figure 5(a), when $[AzUMA]_0/[PMA]_0$ was 1:0.5, the chemical shifts at 3.23 ppm (**e**) was the characteristic peak of AzUMA unit, and the chemical shifts of PMA at around 5.24 (**d**), 6.98, 7.07, and 7.86 ppm also appeared in P1. In addition, the peak of triazole ring emerged at 7.64 ppm (**c**). These results indicated that P1 still contained the azido group and PMA units also coupled into the polymer backbone successfully via click chemistry. As $[AzUMA]_0/[PMA]_0$ was 1:1.1, the signal at $\delta = 3.23$ ppm [**e** in Fig. 5(a)] disappeared completely in Figure 5(b), but the other signals still existed. This proved that the obtained polymer was a homopolymer and click reaction was successful. Furthermore, in the FTIR spectra (Fig. 6), the strong absorption peak at 2100 cm^{-1} was ascribed to the azido group [Fig. 6(a)], which meant the azido group still existed in P1 chain. However, in Figure 6(b), the absorption peak at 2100 cm^{-1} disappeared completely indicating the completion of the click chemistry reaction.

Therefore, the click reaction was quantitative, and the functional content could be well controlled by adjusting the molar ratios of $[AzUMA]_0$ and $[PMA]_0$. Moreover, the GPC curves of the obtained polymers also showed that these two

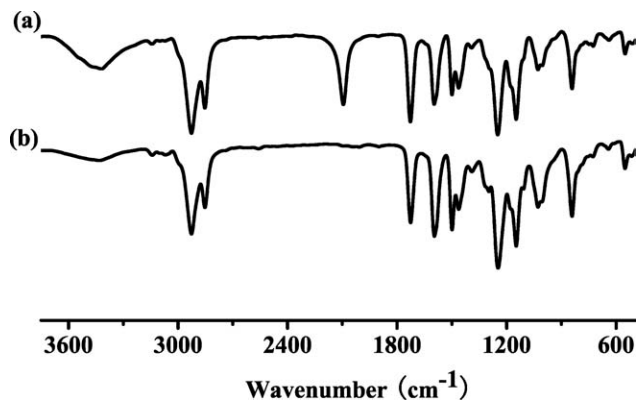

FIGURE 6 FTIR spectra of polymers on KBr tablet: (a) P1 and (b) P2.

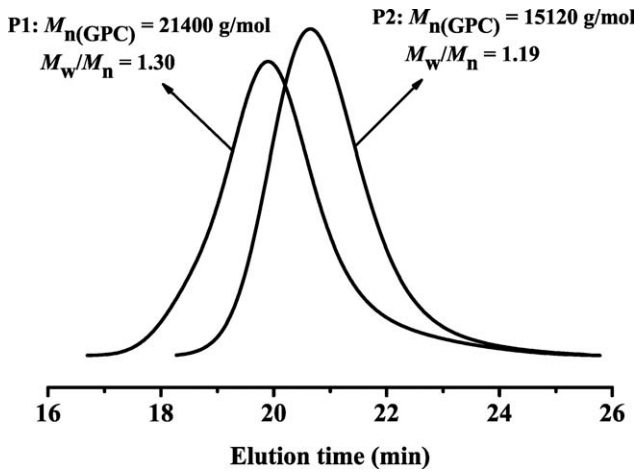

FIGURE 7 GPC curves of polymers (P1 and P2) prepared by one-pot/one-step technique. Reaction conditions: P1: $[AzUMA]_0:[PMA]_0:[EBiB]_0:[CPDN]_0:[Cu(0)]_0:[PMDETA]_0 = 100:50:1:3:5:5$, AzUMA/DMF = 1/6 (v/v), and $T = 25$ °C; P2: $[AzUMA]_0:[PMA]_0:[EBiB]_0:[CPDN]_0:[Cu(0)]_0:[PMDETA]_0 = 100:110:1:3:5:5$, PAzUMA/DMSO = 1/12 (v/v), and $T = 25$ °C.

polymers had monomodal distributions with relatively low molecular weight distributions (P1: $M_{n(GPC)} = 21{,}400$ g/mol, $M_w/M_n = 1.30$; P2: $M_{n(GPC)} = 15{,}120$ g/mol, $M_w/M_n = 1.19$) as given in Figure 7. Hence, the successful one-pot and one-step technique can facilitate the synthesis of side-chain functional polymers and has many advantages, such as avoidance of complex purification of precursors, less synthetic steps, high efficiency, and so on.

CONCLUSIONS

In summary, SET-RAFT polymerization of azide monomer, AzUMA, was achieved at room temperature in the presence of CTA (CPDN). The polymerization was a living/controlled procedure, and azide group can be kept intact after polymerization. The functional polymers with different functional content were also successfully synthesized via one-pot/one-step method, which combined SET-RAFT and click chemistry techniques.

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