Well-Controlled Polymerization of 2-Azidoethyl Methacrylate at Near Room Temperature and Click Functionalization

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ABSTRACT: A functional monomer with a pendant azide moiety, 2-azidoethyl methacrylate (AzMA), was polymerized via reversible addition-fragmentation chain transfer (RAFT) polymerization with excellent control over the molecular weight distribution (PDI = 1.05–1.15). The subsequent copper-catalyzed Huisgen 1,3-dipolar cycloadditions of phenyl acetylene with polyAzMA was achieved at room temperature with high conversion. The resulting functional polymer exhibited identical ^{1}H NMR and IR spectra with the polymer of the same molecular structure but prepared by a pre-functionalization approach, confirming the retention of the azide side chains during the RAFT polymerization of AzMA. © 2007 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 45: 4300–4308, 2007

Keywords: block copolymers; click chemistry; controlled radical polymerization; cycloadditions; living polymerization; reversible addition fragmentation chain transfer (RAFT)

INTRODUCTION

Click chemistry has been used to describe a group of reactions that have modularity, stereospecificity, give high yields, and generate no offensive byproducts.[1] As one of the most powerful reactions in this family, the copper-catalyzed Huisgen dipolar cycloaddition of a terminal alkyne and an azide[2,3] has drawn much attention because of its high efficiency, technical simplicity, and high specificity. This click reaction has found wide applications in various research areas including chemical synthesis,[4–7] bioconjugation,[8–11] drug discovery,[12] combinatorial chemistry,[13] and materials science.[14–16]

Recently, increasing research efforts have been focused on preparing functional polymers by combining the copper-catalyzed Huisgen dipolar cycloaddition with controlled radical polymerization (CRP) techniques.[17–40] Of the various CRP techniques, atom transfer radical polymerization (ATRP) is so far the most widely used polymerization method to involve this click reaction. The homopolymers with terminal alkynyl or azido functionalities prepared by ATRP have been successfully used to synthesize block copolymers,[31] star polymers,[17,20,37] and macrocyclic polymers.[24] Direct polymerization of the monomer with "clickable" functionality is another promising technique that may provide for the development of new functional polymers. Generally, either the alkyne monomer or the azide monomer can be polymerized, and the resulting polymer can be postfunctionalized by reacting with an azido-containing or alkynyl-containing compound, respectively. Benefiting from the high efficiency of click reaction, this postfunctionalization strategy may provide a

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versatile route to design novel functional polymers by incorporating functionality that is incompatible with the polymerization conditions.[30,38] For the CRP of an alkyne monomer, usually a protecting-deprotecting process is necessary to achieve a well controlled polymer structure.[23] As an alternate approach, direct controlled polymerization of the azide monomer is difficult because the azido group is often unstable under conditions normally used for radical polymerizations. Sumerlin et al. reported the polymerization of 3-azidopropyl methacrylate by ATRP and observed that the molecular weight distributions (M_w/M_n = 1.3–1.5) were broader than typical for ATRP.[38]

As a relatively newer CRP technique, reversible addition-fragmentation chain transfer (RAFT) polymerization has also been successfully applied to the controlled polymerization of various monomers under a wide range of conditions to prepare polymer materials with predetermined molecular weights, narrow polydispersities, and advanced architectures.[41,42] The RAFT technique is performed under mild conditions, is applicable to a wide range of monomers, and does not require a catalyst. Recently, a few reports have demonstrated the capability of using this versatile RAFT technique to prepare functional polymers with clickable acetylene functionalities.[39,40] In this paper, we report the direct homopolymerization of AzMA at near room temperature RAFT polymerization conditions. Click functionalization of the resulting azido-containing polymer was demonstrated by reacting with phenyl acetylene.

EXPERIMENTAL

Materials

Unless otherwise specified, all chemicals were purchased from Acros and used as received. Tetrahydrofuran (THF) was dried over CaH_2 overnight and distilled before use. α-Cyanobenzyl dithionaphthalate (CBDN) was prepared according to the literature.[43] 2,2′-Azoisobutyronitrile (AIBN) was used after recrystallization in ethanol. 2,2′-Azobis (4-methoxy-2,4-dimethyl valeronitrile) (V-70) was purchased from Wako and used as received. Styrene was passed through a neutral alumina column to remove the inhibitor before use.

Instrumentation

NMR spectra were recorded on a Varian 500 spectrometer using $CDCl_3$ and deuterated DMSO as solvents. FTIR spectra were recorded using a BioRad Excalibur FTS3000. Molecular weights and molecular weight distributions were determined using a Waters gel-permeation chromatograph equipped with a 515 HPLC pump, 2410 refractive index detector, three Styragel columns (HR1, HR3, HR4 in the effective molecular weight range of 100–5000, 500–30,000, and 5000–500,000, respectively) with THF as eluent at 30 °C and a flow rate of 1.0 mL/min. The GPC system was calibrated with poly(methyl methacrylate) standards obtained from Polymer Labs. Elemental analyses were conducted by Midwest Microlab (Indianapolis, IN). Copper analysis was conducted by ACS Labs (Houston, TX).

Synthesis of 2-Azidoethanol

2-Azidoethanol was prepared by a modification of the method of Hooper et al.[44] To a 250 mL round bottom flask was added 2-bromoethanol (37.5 g, 0.3 mol) and sodium azide (32.5 g, 0.5 mol) in 100 mL of water. The mixture was stirred at 80 °C for 8 h and then cooled to room temperature. The solution was extracted with ether (3 × 100 mL), dried with sodium sulfate overnight, and filtered. After the removal of the solvent under vacuum, 2-azidoethanol was obtained as a colorless liquid (90% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 3.43 (t, 2H, CH_2N_3), 3.77 (t, 2H, CH_2O). IR (NaCl disc): 3370 cm^{-1} (broad, O—H) and 2100 cm^{-1} (N_3).

Caution: special care should be taken to minimize the possible explosion in the preparation and handling of the azide compound.

Synthesis of AzMA

To a 250 mL round bottom flask, a solution of 2-azidoethanol (3.915 g, 45 mmol), methacrylic acid (3.44 g, 40 mmol), and 4-dimethylaminopyridine (DMAP) (1.65 g, 13.5 mmol) in 80 mL of methylene chloride was cooled to 0 °C. Dicyclohexylcarbodiimide (DCC) (9.28 g, 45 mmol) was dissolved in 30 mL methylene chloride and added slowly to the solution. The resulting mixture was warmed to room temperature and stirred overnight. The precipitate was removed by filtration. After removal of solvent and silica

gel column chromatography (9:1 mixture of hexane and ethyl acetate), the product was obtained as a colorless liquid (70% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.95 (s, 3H, CH_3C), 3.50 (t, 2H, CH_2N_3), 4.29 (t, 2H, CH_2O), 5.62 (s, 1H, =CH), 6.15 (s, 1H, =CH). ^{13}C NMR (500 MHz, $CDCl_3$): 18.52, 50.10, 63.69, 126.75, 135.95, 166.74. IR (NaCl disc): 1720 cm^{-1} (C=O) and 2100 cm^{-1} (N_3).

Synthesis of 2-Azidoethyl 1-(2-(Methacryloyloxy)ethyl)-4-methyl-4,5-dihydro-1H-1,2,3-triazole-4-carboxylate (TriazolineMA)

A solution of AzMA (0.5 g, 3.23 mmol) and THF (0.5 mL) was prepared in a dried Schlenk tube. The mixture was degassed by three freeze-pump-thaw cycles, back filled with nitrogen, and then placed in an oil bath at 50 °C overnight. After removal of solvent and silica gel column chromatography (2:1 mixture of hexane and ethyl acetate), the product was obtained as a colorless liquid (20% yield). ^{1}H NMR (500 MHz, d^6-DMSO): δ (ppm) 1.37 (s, 3H, $CH_3C^{Triazoline}$), 1.87 (s, 3H, CH_3C), 3.2 (d, 1H, $H^{Triazoline}$), 3.53 (d, 1H, $H^{Triazoline}$), 3.56 (t, 2H, $OCH_2C\mathbf{H}_2N_3$), 3.85–3.94 (m, 2H, $OCH_2C\mathbf{H}_2N^{Triazoline}$), 4.3 (t, 2H, $OC\mathbf{H}_2CH_2N_3$), 4.37 (m, 2H, $OC\mathbf{H}_2CH_2N^{Triazoline}$), 5.7 (s, 1H, =$CH_2$), 6 (s, 1H, =$CH_2$). ^{13}C NMR (500 MHz, $CDCl_3$): 17.94, 21.05, 48.17, 49.17, 53.64, 61.65, 64.3, 83.2, 126.1, 135.6, 166.28, 170.18.

Synthesis of 2-(4-Phenyl-1H-1,2,3-triazol-1-yl)ethyl Methacrylate (TriazoleMA)

AzMA (0.93 g, 6 mmol), phenyl acetylene (1.02 g, 10 mmol), anhydrous $CuSO_4$ (0.096 g, 0.6 mmol), and sodium ascorbate (0.198 g, 1 mmol) were added to 20 mL of a 1/2 (v/v) mixture of water and *tert*-butyl alcohol. The solution was degassed by bubbling nitrogen for 10 min and stirred at room temperature overnight. Methylene chloride (20 mL) was added, and the solution was extracted with water (2 × 40 mL). The methylene chloride solution was dried with sodium sulfate overnight, and filtered. After removal of solvent and silica gel column chromatography (1:1 mixture of hexane and ethyl acetate), the product was obtained as a white solid (75% yield). mp: 90 °C (capillary uncorrected). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.9 (s, 3H, CH_3C), 4.6 (t, 2H, CH_2O), 4.7 (t, 2H, CH_2N), 5.6 (s, 1H, =CH_2), 6.1 (s, 1H, =CH_2), 7.3 (m, 1H, H^{Ar}), 7.42 (m, 2H, H^{Ar}), 7.78 (d, 2H, H^{Ar}), 7.82 (s, 1H, $H^{Triazole}$). ^{13}C NMR (500 MHz, $CDCl_3$): 18.5, 49.43, 62.95, 120.31, 125.98, 127.03, 128.53, 129.14, 130.65, 135.73, 148.31, 166.95. ELEM. ANAL. Calcd.: C, 65.4%; H, 5.8%; N, 16.3%; O, 12.5%. Found: C, 65.34%; H, 5.84%; N, 16.15%; O, 12.72%.

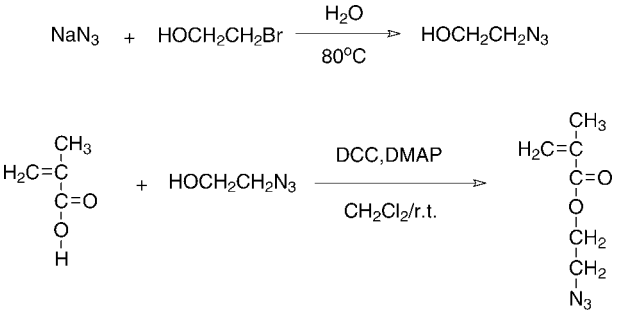
RAFT Polymerization

PolyAzMA

A solution of AzMA (0.5 g, 3.23 mmol), CBDN (3 mg, 9.4 μmol), initiator (0.94 μmol), and THF (0.5 mL) was prepared in a dried Schlenk tube. The mixture was degassed by three freeze–pump–thaw cycles, back filled with nitrogen, and then placed in an oil bath at a preset temperature for various intervals. The polymerization solution was quenched in ice water and poured into an aluminum boat. The solvent and monomer were removed by evaporation in a fume hood overnight and then 2 days under vacuum. Monomer conversion was determined by gravimetric analysis, and molecular weight characteristics were analyzed by GPC. ELEM. ANAL. Calcd.: C, 46.45%; H, 5.8%; N, 27.1%; O, 20.65%. Found for polyAzMA (20% conversion at 50 °C): C, 46.32%; H, 5.81%; N, 26.88%; O, 20.43%. Found for polyAzMA (50% conversion at 50 °C): C, 47.82%; H, 6.04%; N, 24.8%; O, 21.09%. Found for polyAzMA (75% conversion at 40 °C): C, 46.69%; H, 5.77%; N, 26.85%; O, 20.64%.

PolyAzMA-b-Poly(methyl methacrylate)

A solution of PolyAzMA (M_n = 21,500, PDI = 1.08) (100 mg, 4.65 μmol), methyl methacrylate (0.22 mL, 2 mmol), V-70 (0.143 mg, 0.465 μmol), and THF (0.5 mL) was prepared in a dried Schlenk tube. The mixture was degassed by three freeze–pump–thaw cycles, back filled with nitrogen, and then placed in a 40 °C oil bath. After 4 h, the polymerization solution was quenched in ice water and poured into an aluminum boat. The solvent and monomer were removed by evaporation in a fume hood overnight and then two days under vacuum. Monomer conversion was determined by gravimetric analysis, and molecular weight characteristics were analyzed by GPC (conversion = 20%, M_n = 30,000, PDI = 1.12).



Scheme 1. Synthesis of AzMA.

PolyTriazoleMA

A solution of TriazoleMA (0.2 g, 780 μmol), CBDN (1.5 mg, 4.7 μmol), AIBN (0.25 mg, 1.5 μmol), and 1 mL DMSO was prepared in a dried Schlenk tube. The mixture was degassed by three freeze–pump–thaw cycles, back filled with nitrogen, and then placed in a 70 °C oil bath for 7 h. The polymer solution was precipitated into methanol, filtered, washed with methanol (2 × 10 mL), and dried under vacuum. The product was obtained as a pink solid (0.1 g, 50% yield). GPC: M_n = 27,000, PDI = 1.15.

Click Chemistry on PolyAzMA

PolyAzMA (M_n = 14,633, PDI = 1.09) (50 mg, 1 equiv. of $-N_3$), phenyl acetylene (1.1 equiv.), and CuI (0.1 equiv.) were added to DMSO (3 mL). The solution was degassed by bubbling nitrogen for 10 min and stirred at room temperature overnight. To remove the remaining copper after reaction, methylene chloride (20 mL) was added, and the solution was extracted with ammonium hydroxide (30% solution in water) (2 × 20 mL) and then water (3 × 20 mL). The methylene chloride solution was dried with sodium sulfate overnight, and filtered. After the removal of the solvent under vacuum, the crude product was dissolved in DMSO and then precipitated from diethyl ether twice. The product was obtained as a pink solid (45 mg, 54% yield). GPC: M_n = 12,451, PDI = 1.15. Copper analysis by Inductively Coupled Plasma Mass Spectrometry (ICP-MS): 32.35 ppm.

RESULTS AND DISCUSSION

RAFT Polymerization of AzMA

AzMA monomer was prepared by DCC/DMAP mediated coupling of methacrylic acid and 2-azidoethanol which gave the product in good yield under mild reaction conditions (Scheme 1). Considering the instability of the azide monomer at elevated temperatures, the polymerization was first conducted at the relatively low temperature of 50 °C in the presence of AIBN. CBDN was chosen as the chain transfer reagent (CTA), which has been demonstrated to be very effective for the controlled polymerization of various monomers including methyl methacrylate.[43] Organic azides have been widely used for cross-linking because azido groups can easily decompose under thermal or photochemical conditions to nitrogen gas and reactive nitrenes that undergo insertion reactions.[45–48] Azides can also cycloadd to methacrylate derivatives to give triazolines, which are usually thermally unstable and decompose to aziridines or other products.[49,50] In this work, if the azido groups on the side chains of PolyAzMA are unstable at the 50 °C polymerization conditions, they may either decompose to nitrenes or react with AzMA monomers via cycloaddition, which can cause the coupling or branching of polymer chains. Figure 1(a) shows the GPC traces recorded at 20 and 50% conversions for the polymerization of AzMA at 50 °C. Although the polydispersity was 1.17 at 20% monomer conversion, a high molecular weight shoulder was observed at 50% monomer conversion, suggesting the coupling or branching of polymer chains. Comparison of the ^{1}H NMR spectrum of polyAzMA obtained at

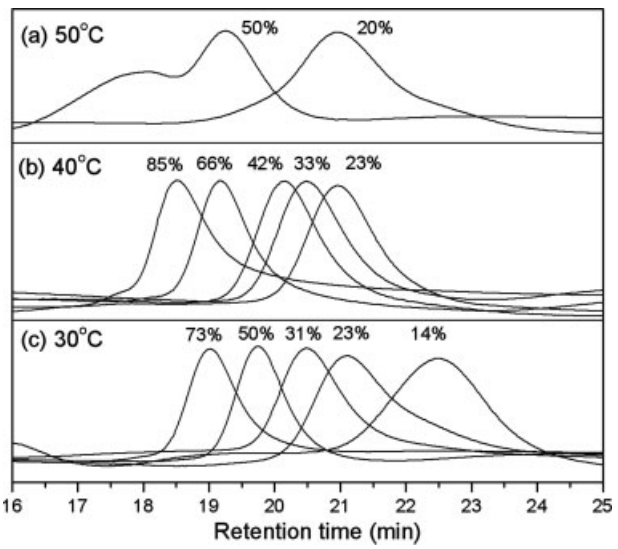


Figure 1. GPC traces for the RAFT polymerization of AzMA with (a) [AzMA]:[CPDN]:[AIBN] = 344:1:0.1, 50 °C; (b) [AzMA]:[CPDN]:[V-70] = 344:1:0.1, 40 °C; and (c) [AzMA]:[CPDN]:[V-70] = 344:1:0.1, 30 °C.

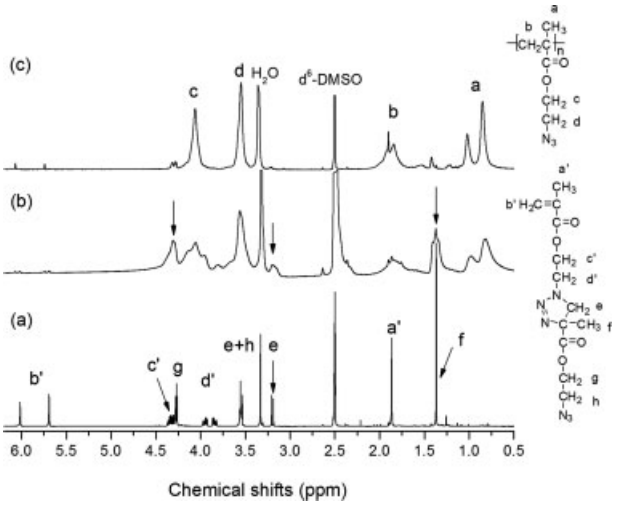


Figure 2. ^{1}H NMR spectra of (a) TriazolineMA and polyAzMAs prepared by the RAFT polymerization at 50 °C; (b) conversion = 50% and (c) conversion = 20%.

50% monomer conversion to that of 20% monomer conversion, as shown in Figure 2(b,c), shows several strong proton signals observed at 1.37, 3.2, and 4.37 ppm, suggesting substantial side reactions. To identify the possible side reactions, a control reaction was set up at 50 °C without the addition of radical initiator and RAFT agent. After 20 h, a triazoline formed from the cycloaddition of two AzMA monomers was successfully isolated with 20% yield. By comparing the ^{1}H NMR spectrum of TriazolineMA and that of polyAzMA obtained at 50% monomer conversion, as shown in Figure 2(a,b), it was concluded that the side reactions at 50 °C polymerization of AzMA could be ascribed to either the copolymerization of newly formed TriazolineMA and AzMA or the cycloaddition between the side-chain azido groups of polyAzMA and AzMA monomer. The results of elemental analyses also showed an obvious decrease of N/C ratio for the polyAzMA prepared at 50 °C with the increase of monomer conversion from 20 to 50%, further suggesting decomposition of either the azido groups or newly formed triazolines accompanied by nitrogen elimination, which may cause the coupling of polymer chains. Actually, crosslinked products were obtained with the further increase in monomer conversion (>60%). In a similar report of using ATRP to prepare poly(2-azidopropyl methacrylate) at 50 °C, an obvious increase of PDI was also observed at higher monomer conversion, which was attributed to the potential side reactions involved azide moieties.[38] Since the controlled radical copolymerizations of azide monomers with methyl acrylate, styrene, and methyl methacrylate have been achieved at 0 °C under γ-ray irradiation,[51,52] temperature may play a key role in the success of applying the RAFT technique to the polymerization of azide monomers. To test this hypothesis for the RAFT polymerization of AzMA, polymerizations were also conducted at 40 and 30 °C. Considering the long half-life of AIBN below 50 °C, V-70 was used as the initiator to shorten the induction time of the polymerization. Figure 1(b,c) shows the GPC traces for the polymerizations conducted at 40 and 30 °C, respectively. Compared with the results at 50 °C the GPC traces for the polymerizations at 40 and 30 °C were observed to be narrow and unimodal at low-to-high conversions. Additionally, the NMR spectra of polyAzMA prepared at 40 and 30 °C at high conversions were similar to that shown in Figure 2(c), with mini-

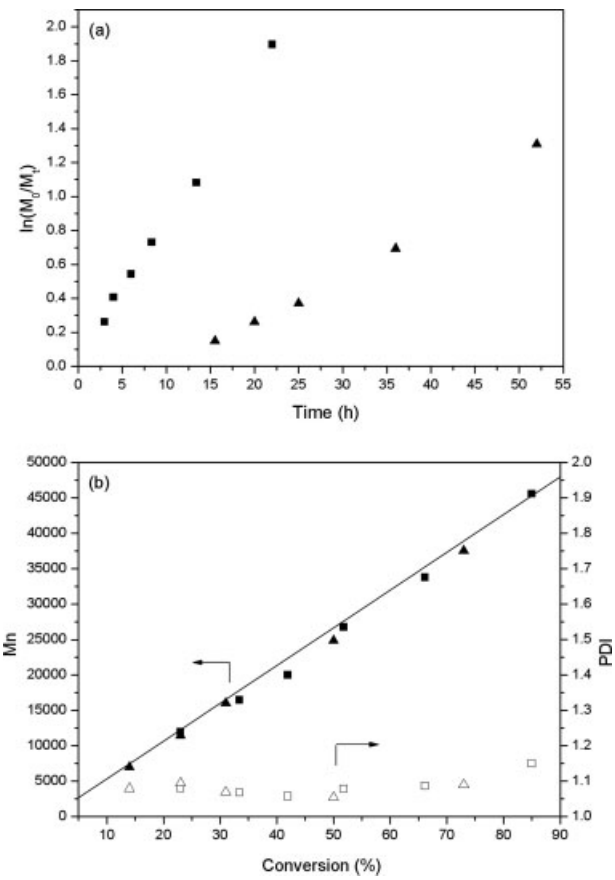


Figure 3. (a) Kinetic plots and (b) dependence of the molecular weight and polydispersity on the conversion for the RAFT polymerization of AzMA ([AzMA]:[CPDN]:[V-70] = 344:1:0.1): (squares) 40 °C and (triangles) 30 °C.

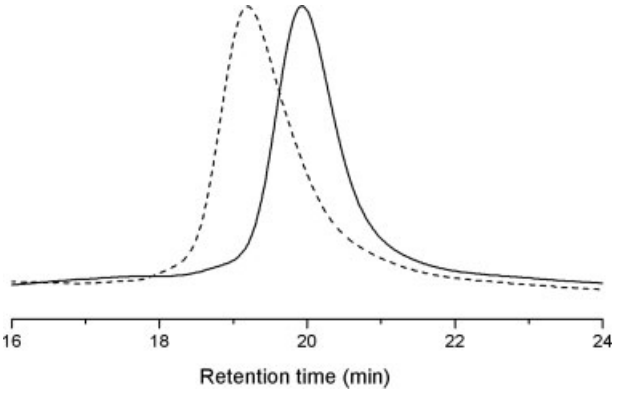


Figure 4. GPC traces for (solid line) polyAzMA (M_n = 21,500; PDI = 1.08) and (dase line) polyAzMA-b-poly(methyl methacrylate) (M_n = 30,000; PDI = 1.12).

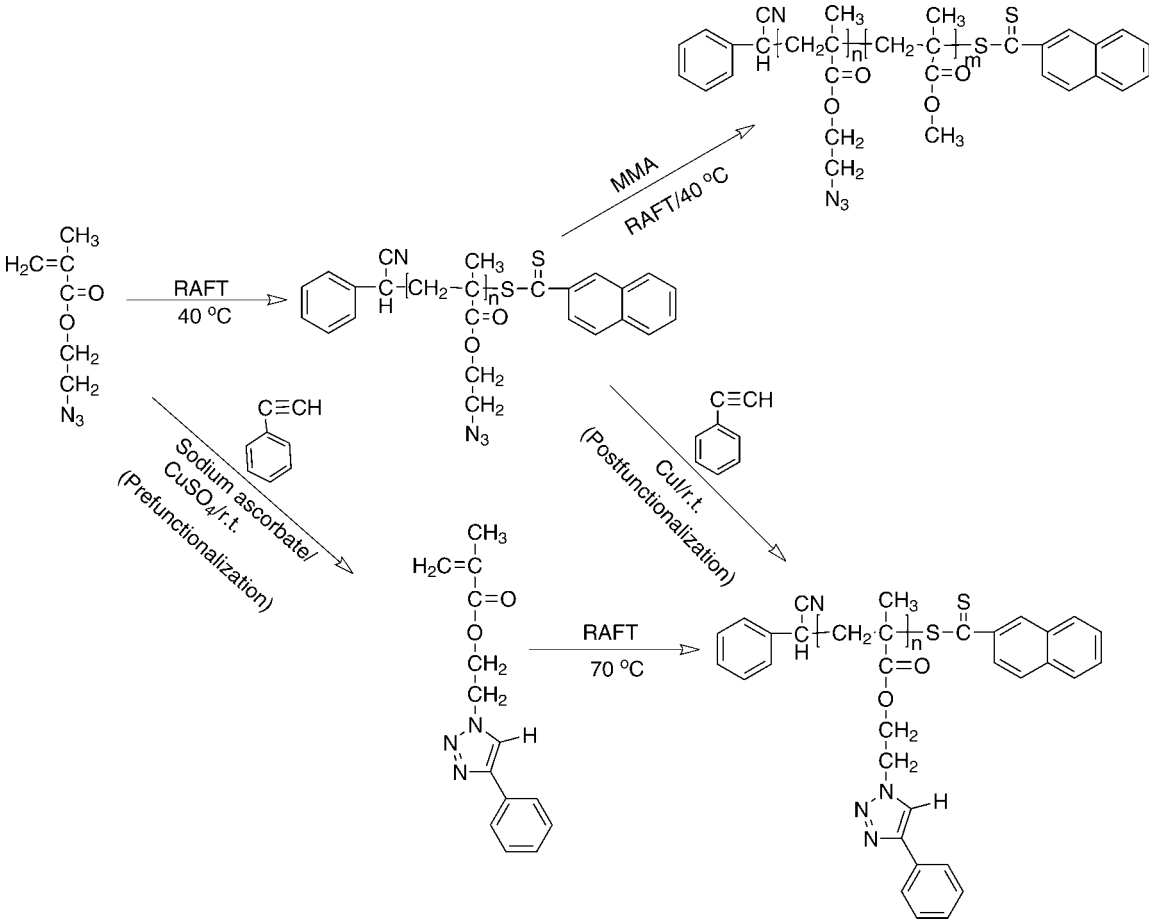
mal extra signals attributed to side reactions. The pseudo-first-order kinetic plots for the polymerization of AzMA at 40 and 30 °C are shown in Figure 3(a). A linear relationship between $\ln([M]_0/[M_t])$ (where $[M]_0$ is the initial monomer concentration and $[M_t]$ is the monomer concentration at time t) and polymerization time was observed indicating a constant radical concentration throughout the polymerization. It was noted that the polymerization at 30 °C had a very long induction period, which is probably due to the fact that the V-70 initiator has a much longer half-life ($\sim$ 10 h) at 30 °C compared to its $\sim$ 2 h half-life at 40 °C. Excellent control over the polymer chain growth was demonstrated by the linear increase in Mn with monomer conversion as shown in Figure 3(b), and the measured molecular weight had a close agreement with the theoretical molecular weight (represented by the solid line in Fig. 3). It is worth noting that the polydispersity index (Mw/Mn) remained less than 1.1 below 75% conversion and was still 1.15 even at the highest monomer conversion (85%) tested in this study, indicating that the azido group on the AzMA is stable under the RAFT conditions at both 40 and 30 °C. In addition to the 344:1 ratio of monomer to CTA, a higher ratio (600:1) was also studied at 40 °C, which still gave predictable molecular weights and narrow polydispersities (M_n = 17,000, PDI = 1.08 at 20% conversion; M_n = 50,000, PDI = 1.13 at 60% conversion). Elemental analysis performed on samples polymerized at 40 °C and 75% conversion showed excellent agreement with calculated values, supporting the earlier discussion of azide or triazoline decomposition at 50 °C that led to complicated side reactions and crosslinking.

The RAFT technique has particular utility in the preparation of controlled-architecture copolymers. A polymer chain bearing a dithioester end group can be considered a macro-CTA capable of reactivation to produce block copolymers in the presence of a second monomer. Herein, an isolated polyAzMA homopolymer was used as a macro-RAFT agent to prepare a block copolymer with methyl methacrylate. As shown in Figure 4, the obvious shift of the GPC trace and the low polydispersity (PDI = 1.12) of the final block copolymer demonstrated the controlled nature of the polymerization and the fidelity of both the side-chain and the end-group functionalities.

Preparation of Click Functionalized PolyAzMA

The copper-mediated azide-alkyne coupling reaction of the polyAzMA homopolymer and a slight excess of phenyl acetylene was performed in DMSO solvent with 0.1 equiv. of copper iodide as catalyst. After completion of the reaction, we found that the copper was not removed from the reaction system by precipitating in methanol, ether, or water. This might be due to the strong coordination between the copper ions and triazoles formed along the polyAzMA backbone, and the resulting white solid had very poor solubility in common organic solvents and could only be dissolved in a few highly polar solvents such as DMSO and DMF. The copper was removed by washing with aqueous ammonium hydroxide, and the resulting pink solid showed good solubility in organic solvents such as THF, CH_2Cl_2 and $CHCl_3$. The copper content determined by ICP-MS decreased from 2.92% to approximately 32 ppm after extraction with aqueous ammonium hydroxide.

To evaluate the efficiency of the click process as a tool to postfunctionalize polyAzMA, a prefunctionalization approach was designed to prepare the polymer with the same structure (Scheme 2). AzMA was first reacted with phenyl acetylene by the click coupling reaction to prepare TriazoleMA, which was then polymerized under RAFT conditions to give polyTriazoleMA with well-controlled structure (M_n = 27,000, PDI = 1.15). The IR spectra and ^{1}H NMR spectra of polyAzMA and polyTriazoleMAs prepared by two different routes are shown in Figures 5 and 6, respectively. The prefunctionalized polyAzMA offered a standard to compare the postfunctionalized polyAzMA. The strong absorption peak at 2100 cm^{-1} ascribed to the —N_3 group in the IR spectrum of polyAzMA completely disappeared after the 1,3-cycloadditon with phenyl



Scheme 2. Preparation of polyAzMA and polyAzMA derivatives by combining RAFT polymerization and click chemistry.

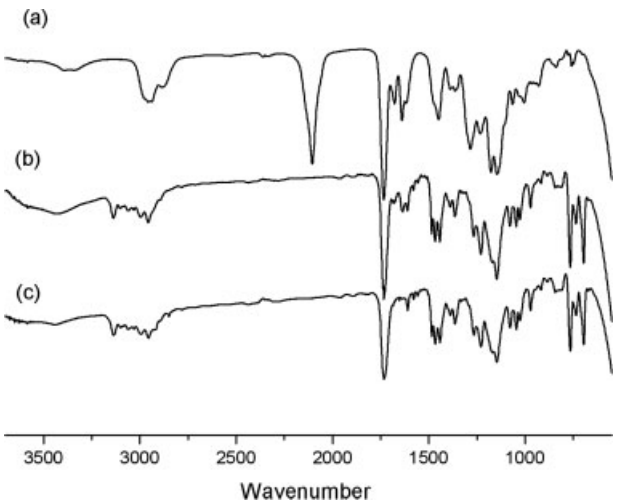


Figure 5. IR spectra of (a) polyAzMA, (b) polyTriazoleMA (postfunctionalization route) and (c) polyTriazoleMA (prefunctionalization route).

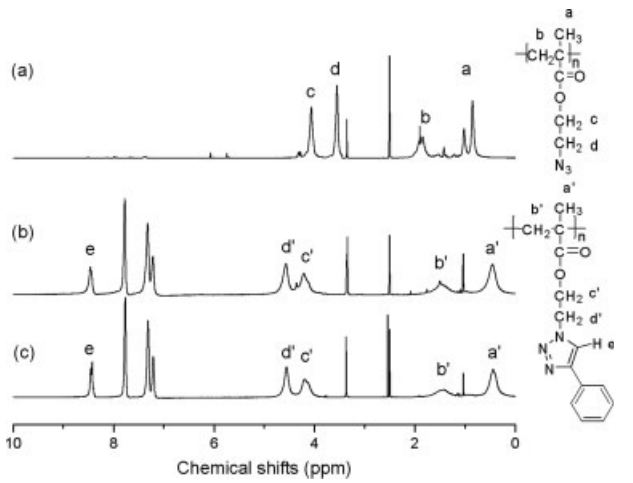


Figure 6. ^{1}H NMR spectra of (a) polyAzMA, (b) polyTriazoleMA (postfunctionalization route) and (c) polyTriazoleMA (prefunctionalization route).

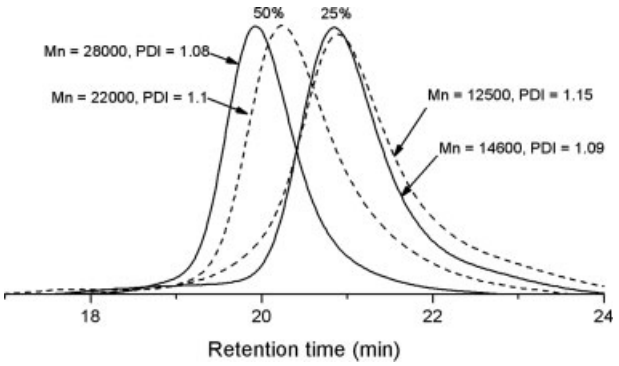


Figure 7. GPC traces for polyTriazoleMAs (dash lines) and their precursory polyAzMAs (solid lines) prepared at 25% and 50% conversions for 40 °C polymerizations.

acetylene, indicating the high conversion of the click reaction. Further information can be obtained from ^{1}H NMR spectra. The signal (d, 3.5 ppm) from $-CH_2N_3$ protons was shifted quantitatively downfield (d′, 4.6 ppm) upon triazole formation. The complete disappearance of the signal at 3.5 ppm and the appearance of a new proton signal originating from the formed triazole ring at 8.5 ppm indicate a complete functionalization of polyAzMA. Furthermore, as shown in Figures 5 and 6, the IR and ^{1}H NMR spectra of the polyTriazoleMA from the postfunctionalization route were substantially identical to those of the prefunctionalization route. Additionally, the integration of the signals in the ^{1}H NMR spectra for these polymers agreed very well with the values expected from the ratio of protons.

The polyTriazoleMAs prepared from the postfunctionalization of polyAzMAs with two different molecular weights were subjected to GPC analysis (Fig. 7). After the click functionalization, a slight broadening of the molecular weight distribution was observed, which might be due to a small amount of the side-chain azido groups that were also involved in side reactions during the polymerization of AzMA at 40 °C. However, this broadening was not enhanced when a polyAzMA with a higher molecular weight was used as a precursor, and the polydispersity indices of polyTriazoleMAs still remained narrow (PDI = 1.1–1.15), further confirming that the polyAzMAs prepared at 40 °C polymerization have well defined structure and the azido groups are well maintained. Although an increase in molecular weight is expected upon functionalization, changes in the interactions between the polymer and solvent when the side chains are functionalized in the click reaction may cause a decrease in the hydrodynamic volume of the polymer chains in solution. This is the likely reason for the lack of the shift to higher molecular weight region in the GPC curve after funtionalization.

CONCLUSIONS

A "clickable" polymer was prepared by the near room temperature RAFT polymerization of AzMA. Initial attempts to conduct the polymerization at 50 °C produced poorly defined products at high monomer conversion due to the involvement of the azido groups in substantial side reactions. The RAFT polymerization of AzMA was successfully achieved at 40 and 30 °C with excellent control over the molecular weight and molecular weight distribution at low-to-high conversions. A narrow-polydispersity block copolymer was also prepared from a poly(2-azidoethyl methacrylate) macro-RAFT agent. The postfunctionalization of poly(2-azidoethyl methacrylate) was successfully performed via a copper-catalyzed Huisgen dipolar cycloaddition with phenyl acetylene without causing the significant change of the molecular weight distribution. Complete conversion of the side-chain azide functionalities to triazoles was confirmed by IR and ^{1}H NMR analysis. An alternative approach which prefunctionalized the monomer via the click reaction, followed by conventional RAFT polymerization, further confirmed the structure of the polymer. The strategy of combining the RAFT technique with click chemistry described in this work could be applied to prepare a wide range of functional polymers, particularly when the pendant moiety may interfere with the polymerization reaction.

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