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Design and synthesis of star polymers with hetero-arms by the combination of controlled radical polymerizations and click chemistry

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Abstract

An alternative approach to the synthesis of well-defined star polymers with hetero-arms was described. An azide-functionalized dithioester chain transfer agent (CTA-N_3) was designed and synthesized. Using CTA-N_3 as the reversible addition–fragmentation chain transfer (RAFT) agent, styrene was polymerized in a controlled manner. The so-obtained polystyrene showed a high proportion of azide-functionalized chains (PS-N_3, about 92%). The azide end-capped PS-N_3 could be assembled, via click reaction with a bromide-containing trialkyne coupling agent, to form a 3-arm star polystyrene (PS_3-Br) with a narrow molecular weight distribution. PS_3-Br could further serve as a macro-initiator for the atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA). Accordingly, well-defined star polymers containing three polystyrene and one poly(methyl methacrylate) (PMMA) arms, and with a narrow molecular weight distribution, were successfully prepared.

Keywords: RAFT polymerization; ATRP; Click reaction

1. Introduction

Star-branched polymers have been widely studied for a long time from both synthetic and theoretical viewpoints [1]. Among them, well-defined and asymmetric type stars with arms differing in chemical composition and hetero-arms have recently received much attention. Their arm segments may phase-separate at the molecular level, followed by self-organization to form periodically ordered nanoscopic objects and potentially useful nano-patterned devices [2–5]. Living anionic polymerization has been the main approach to the preparation of hetero-arm star polymers [6].

In recent years, the use of controlled/living free radical polymerization (LRP) techniques in the synthesis of complex macromolecules (star and dendrimeric type polymers) has increased rapidly because of the applicability of the techniques for a variety of monomers and their tolerance of less stringent experimental conditions [7,8]. The most versatile LRP methods have included nitroxide-mediated polymerization (NMP) [9], atom transfer radical polymerization (ATRP) [10,11] and reversible addition–fragmentation chain transfer (RAFT) polymerization [12,13].

Several approaches to the synthesis of hetero-arm star polymers by combination of various LRP techniques, including the LRP technique with ring opening polymerization (ROP), have been developed [3,14]. The preparation of AB_2, A_3B_3 hetero-arm star polymers via the combination of NMP and ATRP polymerization techniques has been reported [15,16]. A common route for the preparation of A_2B and A_3B star block copolymers via combined LRP and ROP has also been reported [14]. Comprehensive reviews of the synthesis routes to form hetero-arm star polymers are available [17,18].

"Click" reaction, which was named by Sharpless et al. [19,20], has been proven to be an efficient and versatile tool in synthesizing functional polymers [21–25]. The most

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popular reaction involving click chemistry is the copper-catalyzed Huisgen dipolar cycloaddition reaction between an azide and an alkyne leading to 1,4-substituted triazole [26,27]. In recent years, the synthetic methodology of a wide range of functional polymers, such as molecularly imprinted polymers [28], dendritic polymer [29,30], block polymers [31], and hetero-armed star polymers [32,33] via a combination of LRP and click method has been described. ATRP is the most commonly used LRP technique in this method for the reason of easy transformation of the ω-bromine chain-ends of polymers prepared by ATRP into azides via nucleophilic substitution and subsequent reaction with functional alkynes [34–36]. By introducing the azide or acetylene functional groups into the chain transfer agent, well-defined block copolymers of styrene and vinylacetate have been prepared via a combination of RAFT polymerization and click chemistry [37]. RAFT polymerization is rather versatile as most of the vinyl monomers can be polymerized in a controlled manner [38]. The versatile post-functionalization method of styrene and *N*,*N*-dimethylacrylamide (DMA) block copolymer, which was obtained from well designed RAFT polymerization, via click chemistry has been demonstrated recently [39].

In the present work, we have designed and synthesized an azide-functionalized dithioester. Using this azide-functionalized dithioester as the chain transfer agent, RAFT polymerization of styrene was carried out. The azide-functionalized polystyrene was obtained with controlled molecular weight and narrow molecular weight distribution. A 3-arm star polymer of polystyrene was then prepared via click reaction with a bromide-containing trialkyne coupling agent. A hetero-arm star polymer was subsequently prepared by using the 3-arm star polymer of polystyrene as the macro-initiator for ATRP. The versatile control properties of RAFT and ATRP polymerization combined with the click method offered a powerful technique for design and preparation of hetero-arm star polymers.

2. Experimental

2.1. Materials

All reagents were purchased from Aldrich Chemical Co. and were used as-received, unless stated otherwise. All solvents were dehydrated using standard methods and distilled under an inert atmosphere before use. Styrene (99%) and methyl methacrylate (MMA, 99%) were passed through individual columns with inhibitor-remover packing (Aldrich Chemical Co.) and then stored at −10 °C. 2,2′-Azo-bis(isobutyronitrile) (AIBN, 99%) was recrystallized from ethanol and stored at −10 °C.

2.2. Synthesis of 2-azidoethanol (AzEA) [40]

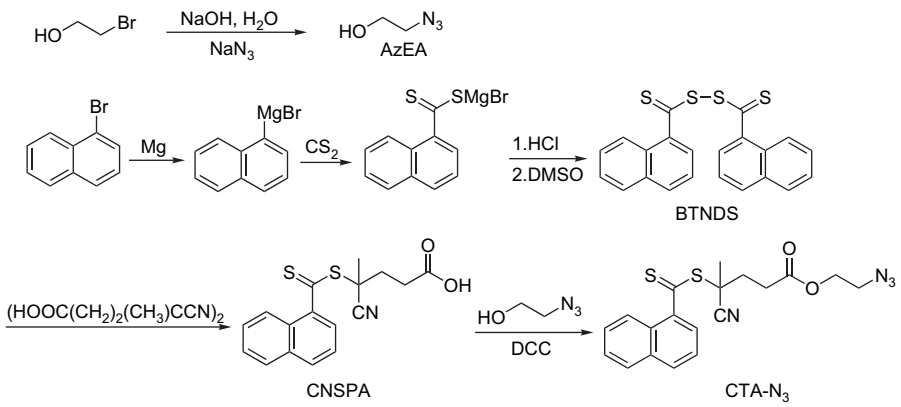
2-Bromoethanol (12.5 g, 0.1 mol) was added to an aqueous solution (20 mL) of sodium azide (99%, 13 g, 0.2 mol) and tetrabutylammonium hydrogen sulfate (99%, 0.5 g). The mixture was stirred at 80 °C for 24 h and then at room temperature for 15 h. The product was extracted with diethyl ether (30 mL × 3). The ether layer was dried with magnesium sulfate overnight. The solvent was removed in a rotary evaporator. The so-obtained 2-azidoethanol was purified by vacuum distillation. Yield: 6.9 g, 80%. ^{1}H NMR in $CDCl_3$ (δ, ppm): 3.82 (t, 2H, CH_2O), 3.51 (t, 2H, CH_2N_3).

2.3. Synthesis of 4-cyano-4-((thionaphthoyl)sulfanyl)pentanoic acid (CNSPA)

Bis(thionaphthoyl) disulfide (BTNDS) was synthesized according to the reported method [41]. BTNDS (4.06 g, 10 mmol) and 4,4′-azo-bis(4-cyanopentanoic acid) (ACP, 75%, 3.74 g, 10 mmol) were dissolved in 50 mL of ethyl acetate. The mixture was brought to reflux under an argon atmosphere for 30 min. The solution was then stirred for 24 h at 70 °C. Ethyl acetate was removed under reduced pressure. The resulting product was dissolved in a small quantity of dichloromethane and subjected to silica gel column chromatography, using a mixture of ethyl acetate:heptane:hexane (2:2:1) as eluent. Removal of the eluent from the product yielded a dark red oil. Yield: 2.68 g, 41%. ^{1}H NMR in $CDCl_3$ (δ, ppm): 7.40–8.31 (m, 7H, proton at naphthalene), 2.62 (t, 2H, $C(CH_3)CNCH_2CH_2$), 2.33 (t, 2H, $C(CH_3)CNCH_2CH_2$), 1.86 (s, 3H, $C(CH_3)CN$). Element. Anal. Calcd for $C_{17}H_{15}NO_2S_2$: C, 61.98; H, 4.59; N, 4.25. Found: C, 62.61; H, 4.44; N, 4.32.

2.4. Synthesis of azide-functionalized chain transfer agent (CTA-N_3)

About 0.53 g of AzEA (6.1 mmol), 2.68 g of dicyclohexylcarbodiimide (DCC, 99%, 12 mmol), 1.2 g of 4-dimethylaminopyridine (DMP, 98%, 10 mmol) and 20 mL of dry dichloromethane were introduced into 50-mL, one-necked flask equipped with a calcium chloride drying tube. The solution was stirred and cooled in an ice bath to 0 °C. A solution of 2 g CNSPA (6 mmol) in 10 mL of dry dichloromethane was added over a 15-min period. After an additional 10 min at 0 °C, the ice bath was removed and the mixture was stirred overnight at room temperature. The mixture was filtered and the filtrate was washed with 0.5 M hydrochloric acid (10 mL × 3) and saturated sodium bicarbonate aqueous solution (10 mL × 3). The organic solution was dried over anhydrous magnesium sulfate and concentrated in a rotary evaporator. The resulting product was purified by silica gel column chromatography, using a mixture of ethyl acetate:hexane (3:1) as eluent. The final azide-functionalized chain transfer agent was obtained as a red oil (Scheme 1). Yield: 0.70 g, 29%. ^{1}H NMR in $CDCl_3$ (δ, ppm): 7.41–8.28 (m, 7H, proton at naphthalene), 4.31 (t, 2H, $CH_2CH_2N_3$), 2.67 (t, 2H, $C(CH_3)CNCH_2CH_2$), 2.21 (t, 2H, $C(CH_3)CNCH_2CH_2$), 1.86 (s, 3H, $C(CH_3)CN$), 1.58 (t, 2H, $CH_2CH_2N_3$). Element. Anal. Calcd for $C_{19}H_{18}N_4O_2S_2$: C, 57.27; H, 4.55; N, 14.06. Found: C, 57.87; H, 4.46; N, 13.76.

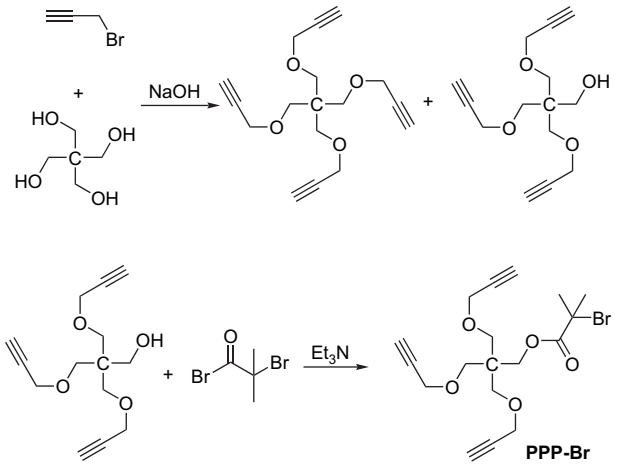


Scheme 1. Synthesis route of the azide-functionalized chain transfer agent (CTA-N_3).

2.5. Synthesis of 3-(prop-2-ynyloxy)-2,2-bis((prop-2-ynyloxy)methyl)propyl 2-bromo-2-methylpropanoate (PPP-Br)

An aqueous solution of NaOH (40 wt%, 10 mL) was added to a solution of pentaerythritol (99%, 2 g, 14.7 mmol) in 15 mL of dimethylsulfoxide (DMSO). The solution was kept under magnetic stirring at room temperature for 30 min. Propargyl bromide (97%, 9.8 mL, 110.4 mmol) was then added and the solution was kept at room temperature for an additional 10 h. Ethyl ether (100 mL) was added to the reaction mixture. The reaction mixture was washed with water (50 mL × 2). The organic layer was dried with Na_2SO_4 and purified by column chromatography, using a mixture of hexane:ethyl ether (1:3) as the eluent to yield 0.76 g of tetrapropargylpentaerythritol (18%) and 2.6 g of tripropargylpentaerythritol (71%) (Scheme 2). Tetrapropargylpentaerythritol: ^{1}H NMR in $CDCl_3$: 4.11 (d, 2H, *J* 2.4 Hz, OCH_2CCH), 3.50 (s, 8H, CH_2OCH_2CCH), 2.46 (t, 4H, *J* 2.3 Hz, OCH2CCH). Tripropargylpentaerythritol: ^{1}H NMR in $CDCl_3$: 4.15 (d, 6H, OCH_2CCH), 3.71 (d, 2H, *J* 6.4 Hz, CH_2OH) 3.58 (s, 6H, CH_2OCH_2CCH), 2.44 (t, 3H, *J* 2.2 Hz, CCH).

Tripropargylpentaerythritol (1.25 g, 5 mmol), triethylamine (99%, 0.55 g, 5.5 mmol) and 20 mL of dry chloroform were introduced into a three-necked flask equipped with a drop funnel. The solution was cooled in an ice salt bath. A solution of 2-bromoisobutanoyl bromide (97%, 0.13 g, 5.5 mmol) in 5 mL of dry chloroform was added drop-wise into the flask under vigorous stirring at 0 °C. The reaction mixture was stirred at 0 °C for 4 h and at room temperature overnight. After that the solution was washed with 5% $NaHCO_3$ (10 mL × 3) and de-ionized water (10 mL × 4). The solution mixture was dried over anhydrous magnesium sulfate and concentrated in a rotary evaporator. The resulting product was purified by silica gel column chromatography, using a mixture of ethyl acetate:hexane (1:4) as eluent. Removal of the eluent from the product yielded a clear liquid (PPP-Br). Yield: 0.98 g, 49%. ^{1}H NMR in $CDCl_3$ (δ, ppm): 4.20 (d, 6H, $CHCCH_2O$), 4.08 (s, 2H, CCH_2OOC), 3.36 (t, 3H, $CHCCH_2O$), 3.82 (s, 6H, CCH_2OCH_2CCH), 2.06 (s, 6H, $(CH_3)_2CBr$).



Scheme 2. Synthesis route of 3-(prop-2-ynyloxy)-2,2-bis((prop-2-ynyloxy) methyl)propyl 2-bromo-2-methylpropanoate (PPP-Br).

2.6. Reversible addition–fragmentation chain transfer (RAFT) polymerization

A mixture of styrene (10 mL, 87 mmol), AIBN (23.8 mg, 0.145 mmol) and CTA-N_3 (288.6 mg, 0.725 mmol) was introduced into a Schlenk tube. The system was sealed after three freeze–evacuate–thaw cycles. After a pre-determined polymerization time (between 6 and 48 h) at 80 °C, 2 mL of the reaction mixture was extracted with a syringe, diluted with 2 mL of THF, and then precipitated in 200 mL of methanol. The polymer was filtered and dried at 40 °C in a vacuum oven for 48 h. Conversion was determined gravimetrically.

2.7. Click reaction

Azide end-capped polystyrene (PS-N_3) from 6 h of RAFT polymerization (number-average molecular weight (M_n) = 2450, polydispersity index (PDI) = 1.05, 294 mg, 0.12 mmol) was dissolved in 3 mL of dimethylsulfoxide (DMSO). PPP-Br (40 μL, 0.04 mmol), copper(II) sulfate pentahydrate (1.2 mg, 0.0049 mmol, in 0.5 mL of water) and sodium ascorbate (1.9 mg, 0.0098 mmol, in 0.5 mL of water) were then added. After the mixture was stirred at 70 °C for 24 h, it was precipitated in 75 mL of methanol. The polymer was collected by

centrifugation. The polymer was washed three times with 20 mL of methanol and dried under reduced pressure to yield the product, PS_3-Br.

2.8. Atom transfer radical polymerization (ATRP)

A mixture of CuBr (99.9%, 1.72 mg, 0.012 mmol), *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA, 99%, 5 μL, 4.16 mg, 0.024 mmol), initiator (PS_3-Br, $M_n = 6980$, PDI = 1.19, 82.4 mg, 0.012 mmol), MMA (0.5 mL, 4.77 mmol) and toluene (0.5 mL) was introduced into a dry Schlenk tube. The reaction tube was sealed, after three freeze–evacuate–thaw cycles, and placed in an 80 °C oil bath to initiate polymerization. After a pre-determined period (2 or 5 h) of reaction, the content was dissolved in 2 mL of THF. The solution was passed through a neutral Al_2O_3 column with THF as eluent to remove the catalyst. The solution was concentrated in a rotary evaporator and the star polymer with three polystyrene (PS) and one poly(methyl methacrylate) (PMMA) arms, or PS_3-*b*-PMMA, was precipitated into 200 mL of methanol. Conversion of the monomer was determined gravimetrically.

2.9. Materials characterization

Fourier transform infrared (FT-IR) spectra were recorded on a Shimadzu FT-IR 8400 spectrophotometer with the sample dispersed in KBr pellets. Elemental analysis was carried out on a Perkin–Elmer Series II CHNS/O Analyzer 2400. ^{1}H NMR spectra were measured in deuterated chloroform ($CDCl_3$) on a Bruker ACF 300 spectrometer at ambient temperature. The M_n and PDI of the polymers were determined using a Waters 1515 gel permeation chromatograph (GPC). The GPC was equipped with a refractive index detector and four Waters Ultrastyragel columns to allow separation of polymers in the molecular weights range of 10^2–5×10^5 g/mol. The columns were calibrated with polystyrene standards. Tetrahydrofuran was used as an eluent at a flow rate of 1.0 mL min^{-1} and temperature of 30 °C.

3. Results and discussion

3.1. RAFT polymerization of styrene using CTA-N_3 as the RAFT agent

An azide-functionalized chain transfer agent (CTA), CTA-N_3, was synthesized according to Scheme 1. The structure of CTA-N_3 was ascertained by ^{1}H NMR and elemental analysis. Using CTA-N_3 as the chain transfer agent, reversible addition–fragmentation chain transfer (RAFT) polymerization of styrene, initiated by 2,2′-azo-bis(isobutyronitrile) (AIBN) at 80 °C, was carried out. The polymerization kinetics are shown in Fig. 1. The linear relationship between ln([M]/[M]$_0$) and reaction time, where [M] is the instantaneous monomer concentration and [M]$_0$ is the initial monomer concentration, indicates that the concentration of propagating chains is almost constant. Chain termination and other side reactions probably did not occur to a significant extent in the polymerization system. Furthermore, the molecular weight evolves linearly with conversion (Fig. 2). The number-average molecular weights (M_ns) determined from gel permeation chromatography (GPC) measurements are consistent with the theoretical values. The polydispersity indices (PDIs) of the polymer samples are narrow, for example, around 1.1. These results indicate that styrene has polymerized in a well controlled manner in the presence of CTA-N_3 as the RAFT agent.

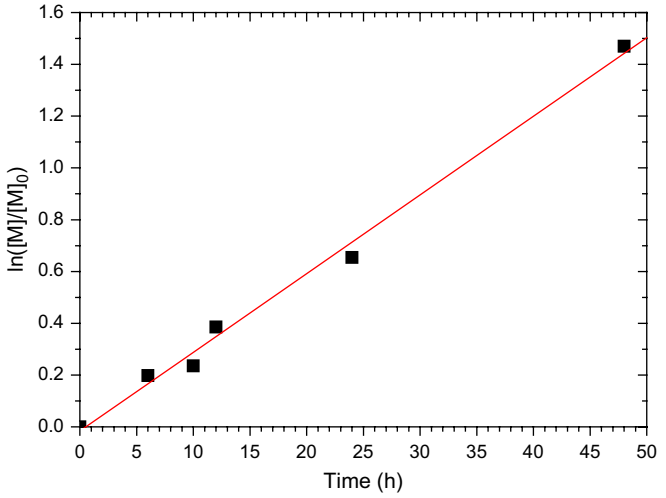


Fig. 1. Plots of reaction time versus ln([M$_0$]/[M]) (where [M]$_0$ = initial monomer concentration and [M] = concentration of the monomer at the corresponding time) in the bulk RAFT polymerization of styrene using the azide-functionalized chain transfer agent (CTA-N_3) as the RAFT agent and AIBN as the initiator at 80 °C. Reactant feed molar ratio: [styrene]:[CTA-N_3]:[AIBN] = 600:5:1.

The structure of azide end-capped polystyrene so-obtained, PS-N_3, was investigated by ^{1}H NMR. Fig. 3 shows the ^{1}H

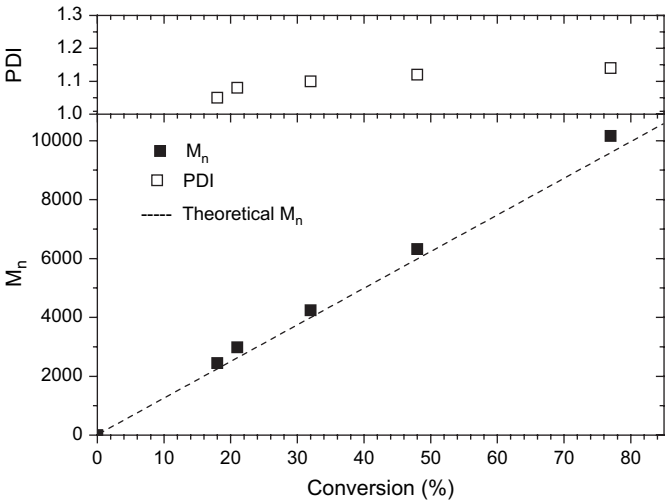


Fig. 2. Plots of number-average molecular weight (M_n) and polydispersity index (PDI) versus conversion in the bulk RAFT polymerization of styrene using the azide-functionalized chain transfer agent (CTA-N_3) as the RAFT agent and AIBN as the initiator at 80 °C. Reactant feed molar ratio: [styrene]:[CTA-N_3]:[AIBN] = 600:5:1.

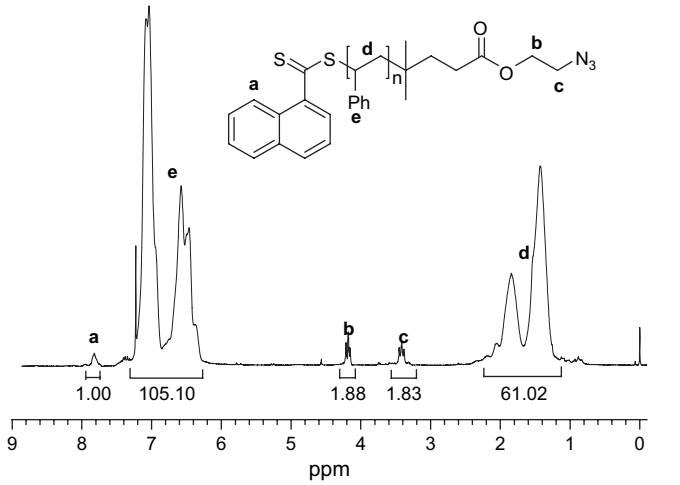


Fig. 3. 300 MHz ^{1}H NMR spectrum of azide end-capped polystyrene (PS-N_3) in $CDCl_3$ with tetramethylsilane (TMS) as the standard at room temperature. The polymer was obtained from 6 h of RAFT polymerization of styrene using the azide-functionalized chain transfer agent (CTA-N_3) as the RAFT agent and AIBN as the initiator at 80 °C. The polymer had a number-average molecular weight of 2450 and a polydispersity index of 1.05, as determined from gel permeation chromatographic measurement.

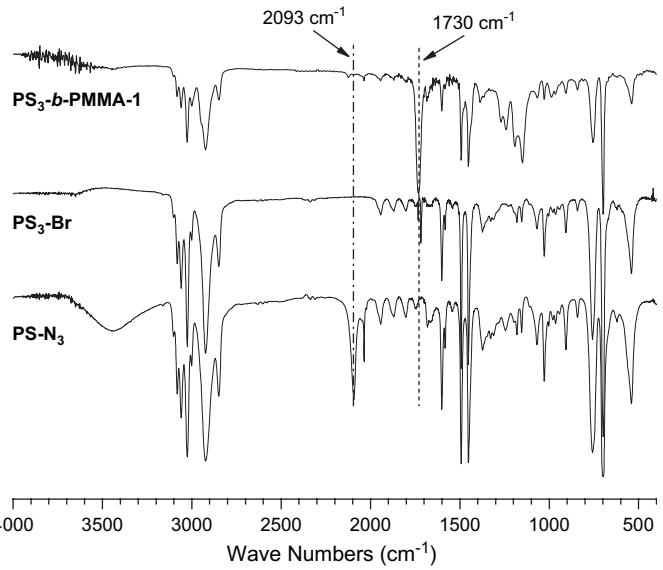


Fig. 4. FT-IR spectra of the linear and star polymers. PS-N_3 with number-average molecular weight (M_n) = 2450, polydispersity index (PDI) = 1.05; PS_3-Br with M_n = 6980, PDI = 1.19; PS_3-*b*-PMMA with M_n = 14 870, PDI = 1.42 (PS-N_3 = azide end-capped polystyrene from 6 h of RAFT polymerization; PS_3-Br = 3-arm star polystyrene from assembly of the azide end-capped polystyrene; PS_3-*b*-PMMA-1 = hetero-arm star polymer containing three polystyrene arms and one poly(methyl methacrylate) arm from 2 h of ATRP of methyl methacrylate (MMA) using PS_3-Br as the macro-initiator).

NMR spectrum of PS-N_3 from 6 h of RAFT polymerization and terminated by dithioester and azide groups. The polymer has an M_n of 2450 and a PDI of 1.05, as determined by GPC. The appearance of a chemical shift at 7.82 ppm (assigned to protons in the naphthalene ring) is consistent with the presence of the dithioester moiety of CTA-N_3 in the PS-N_3 chain. The shifts at 4.19 and 3.41 ppm, which are associated with the proton signals at the α and β positions to the terminal azide groups, suggest the existence of the azide group at the polymer chain end. The FT-IR spectrum of PS-N_3 in Fig. 4 also shows the characteristic peak of the azide group at 2093 cm^{-1}. The FT-IR result, thus, further confirms the existence of azide group in the PS-N_3 chain.

The molecular weight ($M_{n(NMR)}$) of PS-N_3 can be calculated from the ratio of protons in the styrene polymer to protons near the functional azide group at the chain end in the ^{1}H NMR spectrum. The equation is shown below:

$$M_{n(NMR)} = \left(\frac{I_{0.9-2.2}}{3} \Big/ \frac{I_{4.1-4.3}}{2}\right) \times M_{n,St} + M_{n,CTA\text{-}N_3} \quad (1)$$

where $I_{0.9-2.2}$: integral of the signals at 0.9−2.2 ppm, $I_{4.1-4.3}$: integral of the signals at 4.1−4.3 ppm, $M_{n,St}$: molecular weight of styrene, $M_{n,CTA\text{-}N_3}$: molecular weight of CTA-N_3.

The molecular weight of PS-N_3 from 6 h of RAFT polymerization, deduced from the ^{1}H NMR spectroscopy of Fig. 3, was 2648 g/mol. The $M_{n(NMR)}$ was obtained based on the assumption that every polymer chain end was capped with an azide group. The molecular weight determined by GPC was 2450. Thus, about 92% of the PS-N_3 chains was end-functionalized with the azide group.

3.2. Assembly of azide end-capped PS-N_3 via click chemistry

The copper-catalyzed alkyne and azide 1,3-dipolar cycloaddition (CuAAC) has been shown to be a highly efficient green reaction and has been termed "click chemistry". Recently, this reaction has been widely used in the synthesis of well-defined polymers. The CuAAC coupling reaction was carried out using PS-N_3 from RAFT polymerization and 3-(prop-2-ynyloxy)-2,2-bis((prop-2-ynyloxy)methyl)propyl 2-bromo-2-methylpropanoate (PPP-Br) as the trialkyne coupling agent to synthesize the 3-arm star polymer with alkyl-bromide termination, PS_3-Br. In order to ensure an efficient coupling reaction, the ratio of PS-N_3 to PPP-Br was set at 3.26:1 to offset the contribution from about 8% of the azide-free polystyrene chains.

Fig. 4 shows the FT-IR spectra of PS-N_3 from 6 h of RAFT polymerization (M_n = 2450, PDI = 1.05) before and after the click reaction. The strong signal at 2093 cm^{-1}, assigned to the azide group, has disappeared completely in the coupled product of 3-arm star polystyrene (PS_3-Br), consistent with the high efficiency of the click reaction. Furthermore, GPC traces (Fig. 5) show a clear molecular weight shift (increase), which is also an indication of the occurrence of coupling reaction. The molecular weight of the star polymer is measured to be about 6980 by GPC, using linear polystyrene samples as the standards. This value is close to the theoretical value of 7735 (three polystyrene arms + PPP-Br), with the assumption of formation a 3-arm star polymer. The deviation in molecular weight may have been caused, at least in part, by the difference in dynamic radius in solution between linear polystyrene standards and the 3-arm

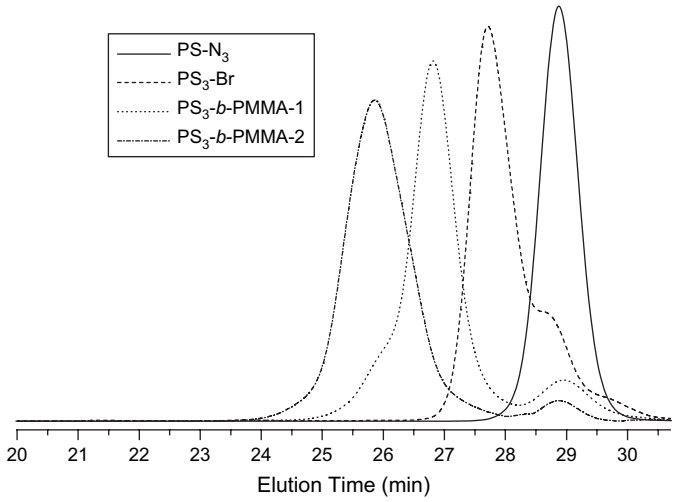


Fig. 5. GPC traces of the PS-N_3, PS_3-Br, PS_3-*b*-PMMA-1 and PS_3-*b*-PMMA-2 polymers. PS-N_3: with $M_n = 2450$, PDI = 1.05; PS_3-Br: $M_n = 6980$, PDI = 1.19; PS_3-*b*-PMMA-1: $M_n = 14\,870$, PDI = 1.42; PS_3-*b*-PMMA-2: $M_n = 33\,720$, PDI = 1.35 (PS-N_3 = azide end-capped polystyrene from 6 h of RAFT polymerization; PS_3-Br = 3-arm star polystyrene from assembly of the azide end-capped polystyrene; PS_3-*b*-PMMA-1 (PS_3-*b*-PMMA-2) = hetero-arm star polymer containing three polystyrene arms and one poly (methyl methacrylate) arm from 2 h (5 h for PS_3-*b*-PMMA-2) of ATRP of MMA using PS_3-Br as the macro-initiator.

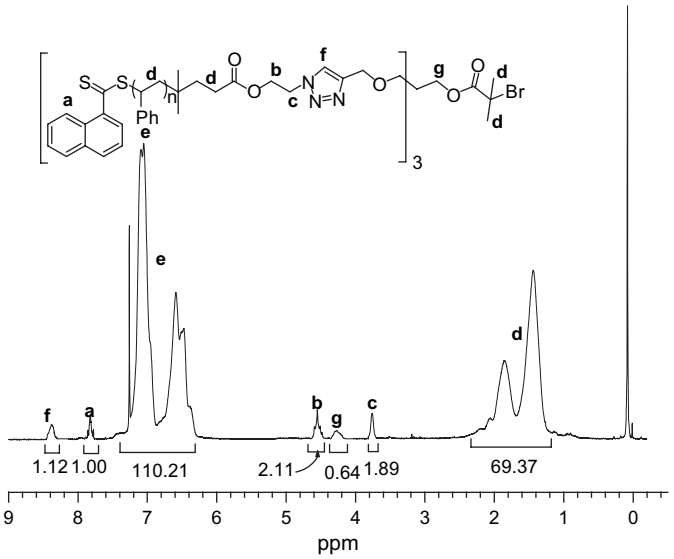


Fig. 6. 300 MHz ^{1}H NMR spectrum of PS_3-Br ($M_n = 6980$, PDI = 1.19) in $CDCl_3$ solution using tetramethylsilane (TMS) as the standard at room temperature. The polymer was obtained from the click reaction between PS-N_3 and PPP-Br (PS-N_3 = azide end-capped polystyrene from 6 h of RAFT polymerization; PS_3-Br = 3-arm star polystyrene from assembly of the azide end-capped polystyrene).

star polymer. The GPC trace of the 3-arm star polymer also shows a shoulder in the low molecular range. This low molecular weight fraction is, nevertheless, consistent with the presence of a small portion of azide-free polystyrene chains (about 8%). The GPC trace also shows that the low molecular weight shoulder in PS_3-Br has a retention time less than that of PS-N_3. This result indicated that there may exist some side reaction to the formation of star polymers with two PS arms. The existence of these chains also account for the increased polydispersity of the star polymer (PDI = 1.19) from that of the original PS-N_3 (PDI = 1.05).

The ^{1}H NMR spectrum of PS_3-Br is shown in Fig. 6. The shift at 8.38 ppm corresponds to the resonance of protons in the 1,2,3-triazole ring, and indicates the occurrence of the CuAAC reaction. The chemical shift of CH_2 near the azide group in PS-N_3 has increased from 3.4 ppm (c in Fig. 3) to 3.7 ppm (c in Fig. 6) due to the formation of the triazole ring. The shift of the CH_2 group (g in Fig. 6) of PPP-Br is also found in the PS_3-Br spectrum. The molecular weight of PS_3-Br can be calculated from the ratio of protons in the PS repeat units to the protons of CH_2 group associated with PPP-Br, using Eq. (2). The equation does not include the value of PPP-Br and CTA-N_3 for the reason of difficult to separate integral value of methenyl and methyl groups in PPP-Br and CTA-N_3 from the polystyrene. The so-obtained $M_{n(NMR)}$ of PS_3-Br is 7475, which is very close to the theoretical value of 7735. This result further testifies to the high efficiency of the CuAAC reaction.

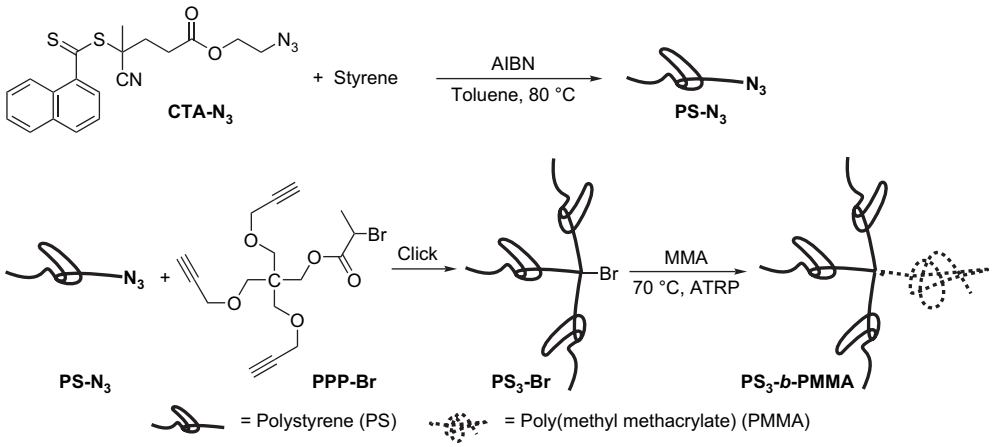
$$M_{n(NMR)} = \left(\frac{I_{0.9-2.2}}{3} \Big/ \frac{I_{4.1-4.4}}{2}\right) \times M_{n,St} \quad (2)$$

where $I_{0.9-2.2}$: integral of the signals at 0.9–2.2 ppm, $I_{4.1-4.4}$: integral of the signals at 4.1–4.4 ppm, $M_{n,St}$: molecular weight of styrene.

3.3. Formation of the hetero-arm star polymer

The bromide-terminated star polymer, PS_3-Br, can act as a macro-initiator for atom transfer radical polymerization (ATRP). Therefore, the ATRP of methyl methacrylate (MMA), initiated by PS_3-Br, was carried out to produce the hetero-arm star polymer (PS_3-*b*-PMMA), consisting of three polystyrene arms and one arm of MMA polymer (PMMA) (Scheme 3). The characteristics of two hetero-arm star polymers from different ATRP times of MMA are summarized in Table 1.

The GPC traces of the two hetero-arm star polymers are shown in Fig. 5. The molecular weights for PS_3-Br have increased from 6980 to 14 870 and 33 720, after 2 and 5 h of MMA polymerization, respectively. The molecular weight distribution of the hetero-arm star polymers is wider than that of the original macro-initiator, albeit it decreases upon prolonging the ATRP time. A low molecular weight fragment was observed in the GPC curves of the final hetero-arm star polymers. The low molecular weight fragment can be attributed to the persistence of a small fraction of azide-free polystyrene, as evidenced by its same retention time as that of PS-N_3. There were another high molecular weight shoulder peak in PS_3-*b*-PMMA-1 GPC trace, which may be resulted from the side reaction in ATRP polymerization in the early stage [11]. Furthermore, the FT-IR spectrum of PS_3-*b*-PMMA (Fig. 4) shows a strong absorption peak at 1730 cm^{-1}, attributable to the carbonyl group of PMMA.



Scheme 3. Synthesis route of the hetero-arm star polymer via controlled free radical polymerization and the click chemistry (AIBN = 2,2′-azo-bis(isobutyronitrile), PS-N_3 = azide end-capped polystyrene, PS_3-Br = 3-arm star polystyrene from assembly of the azide end-capped polystyrene, MMA = methyl methacrylate, PS_3-*b*-PMMA = hetero-arm star polymer with three arms of polystyrene and one arm of poly(methyl methacrylate)).

Table 1
Atom transfer radical polymerization of methyl methacrylate using PS_3-Br as the macro-initiator

Sample	Time (h)	Conv. (%)	$M_{n,GPC}$[a]	PDI[b]
PS_3-*b*-PMMA-1	2	18.9	14 870	1.42
PS_3-*b*-PMMA-2	5	63.6	33 720	1.35

Polymerization conditions: [MMA]:[PS_3-Br]:[CuBr]:[PMDETA] = 393:1:1:2; MMA/toluene = 1/1 (v/v); the polymerization temperature was 80 °C. (MMA = methyl methacrylate, PMDETA = *N*,*N*,*N*′,*N*′,*N*′-pentamethyldiethylenetriamine, PS_3-Br = 3-arm star polystyrene from assembly of the azide end-capped polystyrene of M_n = 6980 and PDI = 1.19, PS_3-*b*-PMMA = hetero-arm star polymer with three polystyrene and one poly(methyl methacrylate) arms).

[a] Number-average molecular weight determined from gel permeation chromatography (GPC) using polystyrene standards as references.

[b] PDI = number-average molecular weight (M_n)/weight-average molecular weight (M_w).

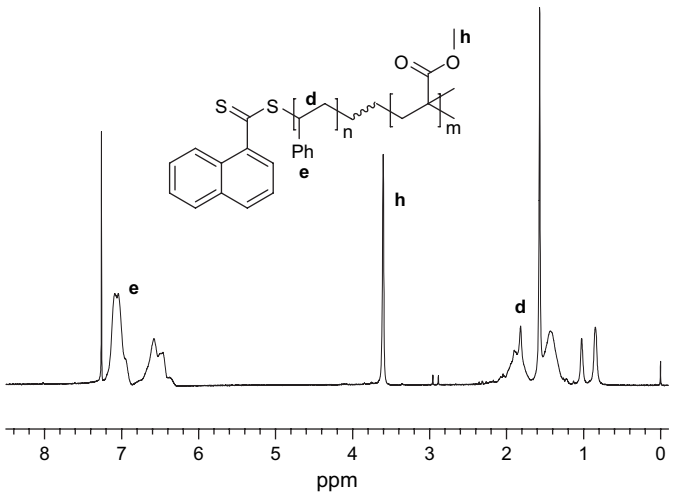


Fig. 7. 300 MHz ^{1}H NMR spectrum of PS_3-*b*-PMMA-2 (M_n = 33 720, PDI = 1.35) in $CDCl_3$ solution using tetramethylsilane (TMS) as the standard at room temperature. The polymer was obtained from ATRP of MMA using PS_3-Br as the macro-initiator (PS-N_3 = azide end-capped polystyrene from 6 h of RAFT polymerization; PS_3-Br = 3-arm star polystyrene from assembly of the azide end-capped polystyrene; PS_3-*b*-PMMA-2 = hetero-arm star polymer containing three polystyrene arms and one poly(methyl methacrylate) arm from 5 h of ATRP of MMA using PS_3-Br as the macro-initiator).

The ^{1}H NMR spectrum of the final hetero-arm star polymer (Fig. 7) also shows the chemical shift of the CH_3 group associated with PMMA.

4. Conclusions

A dithioester chain transfer agent (CTA) containing azide in the R group (CTA-N_3,) was successfully synthesized. Reversible addition–fragmentation chain transfer (RAFT) polymerization of styrene, using CTA-N_3 as the chain transfer agent, exhibited characteristics of living free radical polymerization. As determined from ^{1}H NMR spectroscopic and gel permeation chromatographic (GPC) results, about 92% of the polystyrene chains was functionalized with the azide groups. The azide end-capped polystyrene (PS-N_3) can assemble, via click reaction, with a bromide-containing trialkyne coupling agent to form the 3-arm, bromide-terminated, star polymer, PS_3-Br. The click reaction proceeded with high efficiency and the resulting 3-arm star polymer had a narrow molecular weight distribution. Furthermore, the bromide terminal group of PS_3-Br can be used as the ATRP initiator to initiate the controlled free radical polymerization of methyl methacrylate (MMA). In this manner, two star polymers, one with three polystyrene arms (PS_3-Br) and another one with an additional poly(methyl methacrylate) (PMMA) hetero-arm (PS_3-*b*-PMMA), were successfully prepared. The hetero-arm star polymer also exhibited well-defined structure and controlled molecular weight with narrow distribution. The present work, thus, has illustrated a relatively simple approach to the preparation of well-defined hetero-arm star polymers, via combined living radical polymerizations and click chemistry.

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