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Synthesis of AB_2 miktoarm star-shaped copolymers by combining stable free radical polymerization and atom transfer radical polymerization

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Abstract

A stable nitroxyl radical functionalized with two initiating groups for atom transfer radical polymerization (ATRP), 4-(2,2-bis-(methyl 2-bromo isobutyrate)-propionyloxy)-2,2,6,6-tetramethyl-1-piperidinyloxy (Br_2-TEMPO), was synthesized by reacting 4-hydroxyl-2,2,6,6-tetramethyl-1-piperidinyloxy with 2,2-bis-(methyl 2-bromo isobutyrate) propanoic acid. Stable free radical polymerization of styrene was then carried out using a conventional thermal initiator, dibenzoyl peroxide, along with Br_2-TEMPO. The obtained polystyrene had two active bromine atoms for ATRP at the ω-end of the chain and was further used as the macroinitiator for ATRP of methyl acrylate and ethyl acrylate to prepare AB_2-type miktoarm star-shaped copolymers. The molecular weights of the resulting miktoarm star-shaped copolymers at different monomer conversions shifted to higher molecular weights without any trace of the macroinitiator, and increased with monomer conversion.

Keywords: Miktoarm star-shaped copolymers; Stable free radical polymerization (SFRP); Atom transfer radical polymerization (ATRP); Functionalized nitroxyl radical

1. Introduction

Increasing attention has been paid to the synthesis of miktoarm star-shaped polymers in recent years because of their unique properties both in solid state and in solution. Three reviews have been published by Hadjichristidis recently [1–3]. One general strategy for the synthesis of miktoarm star-shaped copolymers is through the use of anionic polymerization technique where the living chain ends are consecutively grafted onto a multifunctional chlorosilane [4–12]. Another approach utilizes the addition of anionically or cationically derived living polymers to a small amount of a difunctional monomer, such as divinylbenzene. This leads to the formation of a star molecule with additional sites in the polymerizable core. Subsequent addition of another monomer yields the miktoarm

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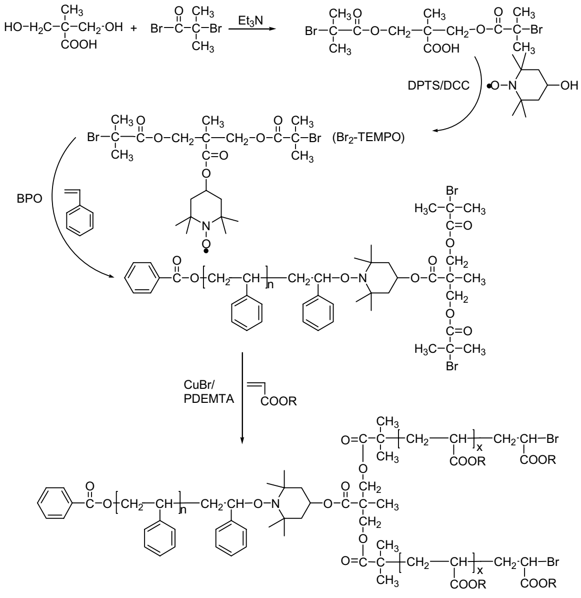
star-shaped polymers [13–17]. This approach has been extended to controlled radical polymerization techniques [18–21]. The third method is based on macromonomer technique [22–35]. In this method, a nonhomopolymerizable macromonomer bearing a 1,4-bis(1-phenylethenyl) benzene or a 1,1-diphenylethylene group at one chain end is incorporated at the junction of two polymer blocks.

In the last decade, there has been rapid growth in the area of living radical polymerization, where stable free radical polymerization (SFRP), atom transfer radical polymerization (ATRP), and reversible addition-fragmentation transfer polymerization (RAFT) are the most successful methods which allow molecular weight, polydispersity, and chain-end functionality to be controlled accurately. Thus, miktoarm star-shaped copolymers can be prepared with the use of miktofunctional initiators by combining SFRP, RAFT, ATRP and ROP. For example, Hedrick et al. [36] obtained the A_3B_3-type miktoarm star-shaped copolymers using a unique miktofunctional initiator containing initiating sites for both ROP and ATRP. Miura et al. [37] prepared AB_2- and AB_3-type miktoarm star copolymers by combination of ROP and SFRP using dendritic tri- and penta-functional initiators. Zhao et al. [38] synthesized ABC tri-miktoarm star-shaped terpolymers by combing ROP, ATRP, and SFRP with a trifunctional initiator bearing a hydroxyl group, an ATRP initiator and a SFRP initiator. Chenet al. [39] prepared AB_2 miktoarm star-shaped polymers via combination of ATRP and ROP using 1,1-dihydroxymethyl-1-(2-bromoisobutyryloxy) methyl ethane as a miktofuntional initiator. Tunca et al. prepared AB_2- and other types miktoarm star polymers using miktofunctional initiators through the combination of ATRP and SFRP [40–42], ATRP and ROP [43], or ROP, SFRP and ATRP [44]. Gnanou [45], Tsukruk [46] and Kakuchi [47] synthesized miktoarm star-shaped polymers by the combination of ROP, ATRP and functional group transformation technique. Gnanou [48] prepared AB_2-type miktoarm star-shaped polymers via ATRP and chemical modification of the termini of ATRP-derived polymers. Chen et al. [49] prepared miktoarm star-shaped rod-coil block copolymers with the same method. Pan's group prepared various miktoarm star-shaped polymers by combination of ATRP or RAFT with ROP [50–56].

In our previous work [57], we reported the successful synthesis of polystyrene-*b*-polyacrylate diblock copolymers via a combination of SFRP and ATRP, with the use of a functionalized nitroxyl radical, 4-(2-bromo-2-methylpropionyloxy)-2,2,6,6-tetramethyl-1-piperidinyloxy. In this work, we extended this concept in order to prepare well-defined AB_2-type miktoarm star-shaped copolymers via a combination of SFRP and ATRP with a trifunctionalized stable nitroxyl radical (Scheme 1). To our knowledge, although polymeric stable nitroxyl radicals have been used in SFRP of styrene to prepare diblock copolymers [58,59], it is the first time to use a stable nitroxyl radical functionalized with two ATRP initiating groups for the synthesis of AB_2-type miktoarm star-shaped copolymers via combination of ATRP and SFRP processes. It should be stressed that our method is different from that reported by Tunca et al., in which a functionalized alkoxyamine (not a functionalized stable nitroxy radical), 2-phenyl-2-[(2,2,6,6-tetramethyl)-1-piperidinyloxy] ethyl 2,2-bis[methyl(2-bromopropionato)] propionate, was used [40]. It was synthesized from 2,2-bis[methyl(2-bromopropionato)] propionyl chloride and 2-phenyl-2-[(2,2,6,6-tetramethylpiperidino)-oxy]-1-ethanol. The later was obtained according to the complicated procedure of Hawker et al. with lower yield [60]. As shown in Scheme 1, the trifunctionalized stable nitroxyl radical used in the present work could be directly synthesized from 2,2-bis-(methyl 2-bromoisobutyrate) propanoic acid and a cheap and commercial



Scheme 1.

chemical, 4-hydroxyl-2,2,6,6-tetramethyl-1-piperidinyloxy (4-HO-TEMPO).

2. Experimental

2.1. Materials

Styrene (99%, Beijing Yanshan Petrochemical Co.) and ethyl acrylate (EA) (99%, Beijing Dongfang Chemical Plant) were dried over anhydrous magnesium sulfate and distilled under reduced pressure prior to use. Methyl acrylate (MA) (99%, Beijing Dongfang Chemical Plant) and toluene were dried over anhydrous magnesium sulfate and distilled prior to use. Tetrahydrofuran (THF) was dried over CaH_2 and distilled prior to use. Copper bromide (CuBr) (Shanghai Zhenxing Chemical Reagent Factory) was stirred in glacial acetic acid, filtered, washed with acetone and dried under vacuum at room temperature overnight. Dibenzoyl peroxide (BPO) (99%, Changzhong Yuanda Chemical Plant) was dissolved in methylene chloride, recrystallized from methanol and dried under vacuum at room temperature. 2,2-Bishydroxymethyl propanoic acid (99%, Aldrich), 2-bromo-2-methylpropionyl bromide (99%, Aldrich), 4-hydroxyl-2,2,6,6-tetramethyl-1-piperidinyloxy (4-HO-TEMPO) (99%, Beijing Huashang Assistant Reagent Plant), *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylene-triamine (PMDETA) (99%, Aldrich), *N*,*N*′-dicylohexylcarbodiimide (DCC) (99%, Shanghai Haiqu Chemical Ltd. Co.) and all other reagents were used without any further purification.

2.2. Synthesis of Br_2-TEMPO

Br_2-TEMPO was synthesized in two steps. Firstly, 2,2-bis-(methyl 2-bromo isobutyrate) propanoic acid was synthesized as follows: a 250 mL three-neck round-bottom flask equipped with a magnetic stirrer was charged with 6.71 g (50 mmol) of 2,2-bishydroxymethyl propanoic acid, 9.50 g (120 mmol) of bipyridine and 100 mL of tetrahydrofuran; the flask was fitted with a pressure equalizing addition funnel, which was charged with 28.80 g (120 mmol) of 2-bromo-2-methylpropionyl bromide and 50 mL of methylene chloride; the flask was cooled to 0 °C in an ice/water bath and 2-bromo-2-methylpropionyl bromide solution was added dropwise under argon over a period of 2.5 h, then the reaction mixture was stirred at room temperature overnight; the salt was removed by filtration and after THF evaporation, the crude product was dissolved in ethyl ether; the salt was removed by filtration and washed first with 0.1 N hydrochloric acid and then with distilled water; the organic phase was dried with anhydrous magnesium sulfate overnight; after magnesium sulfate was filtered off, the solvent was removed by rotary evaporation; the crude product was recrystallized from hexane. Yield: 10.0 g. ^{1}H NMR ($CDCl_3$): $\delta = 4.35$ ppm (2H, $(CH_3)_2CBrCOOC\mathbf{H}_2$–), 1.89 ppm (6H, $(\mathbf{CH}_3)_2CBrCOOCH_2$–), 1.35 ppm (3H, $(CH_3)_2CBrCOOCH_2)_2$-$C(COOH)\mathbf{CH}_3$. Secondly, the esterification of 4-hydroxyl-2,2,6,6-tetramethyl-1-piperidinyloxy with 2,2-bis-(methyl 2-bromo isobutyrate) propanoic acid was carried out in the presence of (*N*,*N*-dimethylamino) pyridinium tosylate (DPTS) (DPTS was synthesized according to the method of Moore and Stupp [61]) and DCC. A 100 mL three-neck round-bottom flask equipped with a magnetic stirrer was charged with 4.33 g (10 mmol) of 2,2-bis-(methyl 2-bromo isobutyrate) propanoic acid, 3.45 g (20 mmol) of 4-hydroxyl-2,2,6,6- tetramethyl-1-piperidinyloxy, 0.30 g (1 mmol) of DPTS, and 50 mL of methylene chloride. After all the regants were dissolved, 3.12 g (15 mmol) of DCC and 20 mL of methylene chloride were added into the flask. The reaction mixture was stirred at room temperature for 20.0 h. The urea was removed by filtration, and after solvent evaporation the crude product was dissolved in methylene chloride and washed first with 0.1 N hydrochloric acid and then with distilled water. The organic phase was dried with anhydrous magnesium sulfate overnight. After magnesium sulfate was filtered off, the solvent was removed by rotary evaporation. The crude product was dissolved in a mixture of chloroform and ethyl acetate (8/1, volume ratio) and passed through a silica gel column prepared with the same solvent. The first fraction was collected. The solvent was removed by rotary evaporation, and the pink solid was dried under vacuum overnight at 35 °C. Yield: 3.80 g.

2.3. SFRP of styrene in the presence of Br_2-TEMPO

Polystyrene macroinitiators for ATRP were prepared by SFRP of styrene with dibenzoyl peroxide as initiator in the presence of Br_2-TEMPO. In a typical example, 0.24 g (1.0 mmol) of BPO, 1.06 g (1.3 mmol) of Br_2-TEMPO, 15.0 g (14.4 mmol) of styrene and 15.5 g of xylene were added to a 100 mL dry round-bottom flask equipped with a magnetic stirring bar. After sealing it with a rubber septum, the flask was degassed and back-filled with argon three times and then left under argon. The polymerization was carried out at first for 3.5 h at 95 °C, and then continued at 123 °C. At predetermined time, about 2 mL of solution was withdrawn with argon-filled gas-tight syringe to measure monomer conversion and molecular weight. After polymerization, the polymerization mixture was diluted with THF, and the polymer was precipitated into cold methanol, washed with methanol, and purified by reprecipitation from THF solution into methanol. The polymer was dried at 35 °C under vacuum for 48 h.

2.4. *ATRP of MA and EA with the polystyrenes obtained above as the macroinitiator*

The miktoarm copolymers were prepared through ATRP of MA and EA with the polystyrene obtained above as macroinitiator. The number average molecular weight and the polydispersity of the polystyrene macroinitiator determined by GPC were 3300 and 1.20, respectively. The typical procedure was as follows: 0.99 g (0.3 mmol) of macroinitiator was added to a 100 mL three-neck round-bottom flask equipped with a stirring bar. MA (20.6 g) (240 mmol) or 24.0 g (240 mmol) of EA and the same volume (at 80 °C) of toluene were then added to dissolve the macroinitiator. After the macroinitiator was dissolved completely, 0.0043 g (0.3 mmol) of CuBr and 0.0079 g (0.45 mmol) of PMDETA were added to the flask. After sealed with a rubber septum, the flask was degassed and backfilled with argon three times and then left under argon. The flask was then immersed in an oil bath thermostated at 80 °C. At different time intervals, samples were withdrawn from the flask using degassed syringes to determine monomer conversion and molecular weight.

2.5. *Hydrolysis of miktoarm polystyrene*

The miktoarm polystyrene was hydrolyzed as follows: One gram of miktoarm polystyrene was added to a flask and dissolved in 90 mL of THF, and then about 60 mL of methanol were added slowly under stirring to prevent the precipitation of polystyrene. Finally, 0.2 g of KOH was added to the solution. The solution was refluxed for 4 days. After insoluble impurities were removed by filtration, the solution was concentrated by rotating evaporation of THF and methanol. The polymer was obtained by precipitation from cold methanol and dried under vacuum.

2.6. *Characterization*

Molecular weights and molecular weight distributions of the polymers were measured using gel permeation chromatography (GPC), on a system equipped with a Waters 515 pump, three columns (Styragel HR1, Styragel HR3 and Styragel HT4) and a 2410 differential refractometer detector. The eluent was THF and the flow rate was 1 mL/min. Narrow polystyrene standards were used to generate the calibration curve. ^{1}H NMR spectra were obtained using a Bruker spectrometer (600 MHz) with $CDCl_3$ as solvent at 25 °C. Monomer conversions were determined gravimetrically.

3. Results and discussion

3.1. *Synthesis of Br_2-TEMPO*

Br_2-TEMPO was synthesized in two steps as shown in Scheme 1. It could be subjected to ^{1}H NMR measurement in the presence of phenylhydrazine because nitroxyl moiety was reduced into the corresponding hydroxylamine by this reagent. The ^{1}H NMR spectrum thus obtained is shown in Fig. 1. The methyl protons of 2-bromoisobutyryloxy, $(C\mathbf{H}_3)_2CBrCOO$–, were seen at 1.96 ppm, and the methylene protons of 2-bromoisobutyrylate, $(CH_3)_2CBrCOOC\mathbf{H}_2$–, were seen at 4.36–4.44 ppm. The signal at 5.10 ppm was assigned to the methine proton originated from 4-HO-TEMPO. The singals at 1.24 and 1.27 ppm were assigned to two types of methyl protons from 4-HO-TEMPO, while the singals at 1.71 and 2.00 ppm were assigned to two types of methylene protons from TEMPO. The observed peak intensity ratios of the signals were

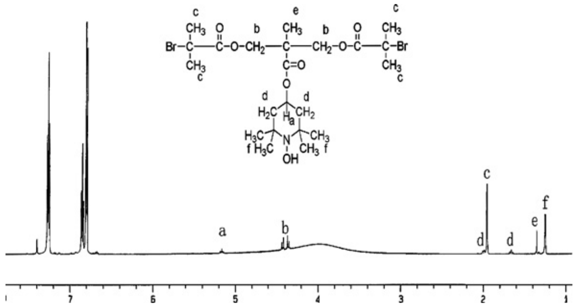


Fig. 1. ^{1}H NMR spectrum of Br_2-TEMPO in the presence of phenylhydrazine (solvent: $CDCl_3$).

in good agreement with the calculated values, confirming the formation of Br_2-TEMPO. To further confirm the formation of Br_2-TEMPO, its chemical composition was determined using elemental analysis. The found values (C, 48.08; H, 6.24; N, 2.25) were also in good agreement with the calculated ones (C, 48.07; H, 6.19; N, 2.39).

3.2. Synthesis of polystyrene macroinitiators via SFRP

The polymerization of styrene was performed with BPO as an initiator in the presence of Br_2-TEMPO in xylene (styrene/xylene = 1, v/v) at 123 °C, after being held at 95 °C for 3.5 h. The number-average molecular weights (M_n) of polystyrenes (PS-TEMPO-Br_2) increased in direct proportional to monomer conversion, and agreed well with the calculated ones, as shown in Fig. 2. In addition, their polydispersities were relatively low throughout the polymerization process. The results showed that the SFRP of styrene in the presence of Br_2-TEMPO had characteristics of living polymerization.

The polystyrenes (PS-TEMPO-Br_2) obtained by SFRP of styrene in the presence of Br_2-TEMPO have two 2-bromoisobutyryloxy groups at ω-end as illustrated in Scheme 1. Fig. 3 shows the ^1H NMR spectrum of polystyrene with M_n to be 3300 (determined by GPC). The signal at 4.96 ppm was assigned to the methine proton of Br-TEMPO. The signal around 4.30 ppm was assigned to the methylene protons of styrene unit bonding to the benzoyl group and that of 2-bromoisobutyrylate ($(CH_3)_2CBrCOOCH_2$–). The signal at 3.96 ppm was attributed to the methine proton of styrene unit which was bonded to Br_2-TEMPO. A signal was also discerned at 7.90 ppm, which was assigned to the aromatic protons at ortho position of benzoyl group attached to the other polystyrene terminal. The peaks from 6.20 to 7.30 ppm corresponded to aromatic protons of the main chain. According to the peak intensity ratio of the peak at 4.96 ppm to the peak at 6.20–7.30 ppm, the number average molecular weight was calculated to be 3800. This value was in good agreement with that obtained by GPC.

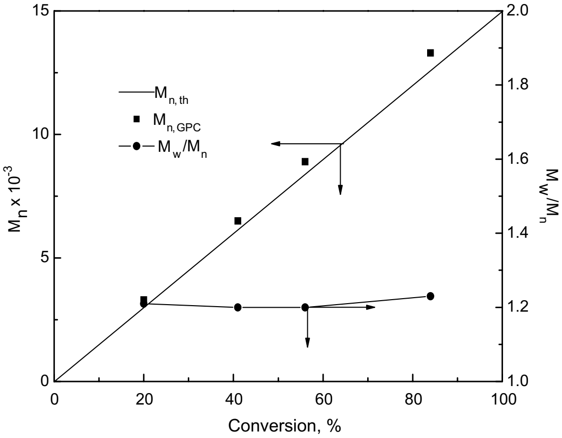


Fig. 2. Conversion dependence of number-average molecular weights and molecular weight distributions of polystyrenes prepared in the presence of Br_2-TEMPO. Conditions: $[BPO]_0$:$[Br_2\text{-TEMPO}]_0$:$[St]_0$ = 1:1.3:144.

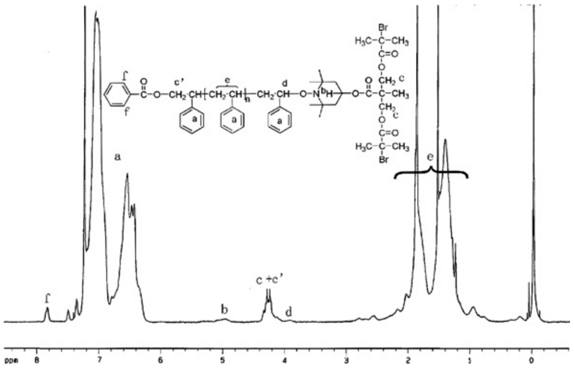


Fig. 3. ^1H NMR spectrum of polystyrene macroinitiator, PS-TEMPO-Br_2.

3.3. Synthesis of AB_2-type miktoarm copolymers by polystyrene macroinitiator via ATRP

It is well known that ethyl 2-bromoisobutyrate is an excellent initiator for ATRP of styrene and acrylates with high initiating efficiency [62]. Therefore, the polystyrenes with 2-bromoisobutyryloxy end groups obtained above can initiate ATRP of acrylates to prepare star-shaped polystyrene/polyacrylate$_2$ copolymers. The polymerization was carried out in toluene (monomer/solvent = 1, v/v) with CuBr/PDEMTA complexes as the catalyst. The number-average molecular weight and the polydispersity of the polystyrene macroinitiator determined by GPC were 3300 and 1.20, respectively. The GPC traces of the macroinitiator and corresponding miktoarm star-shaped copolymers obtained at different monomer conversions are shown in Figs. 4 and 5. It can be seen that the molecular weight shifted to higher molecular weight direction without any trace of the unreacted polystyrene macroinitiator,

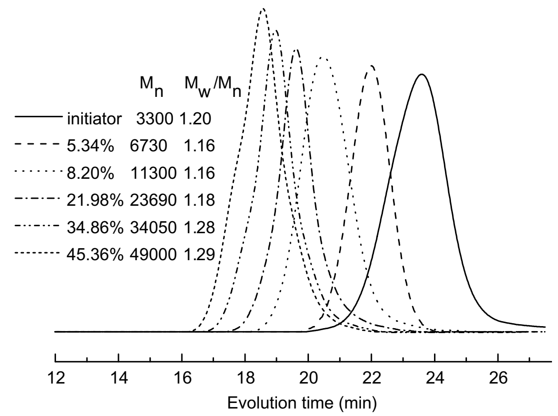


Fig. 4. GPC traces of the polystyrene macroinitiator and corresponding star-shaped PS-PMA$_2$ copolymers obtained at different monomer conversions. Conditions: [PS-TEMPO-Br$_2$]$_0$:[CuBr]$_0$:[PMDETA]$_0$:[MA]$_0$ = 1:1:1.5:800, T = 80 °C.

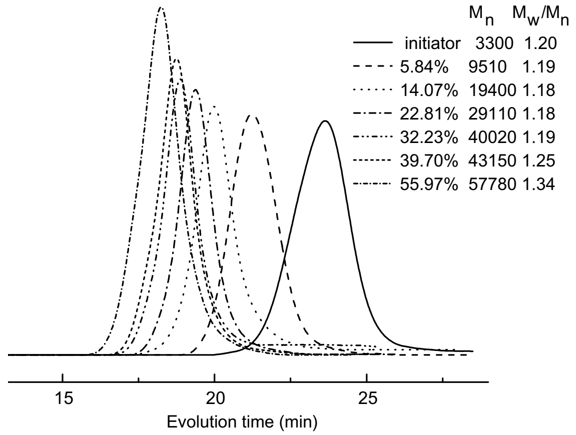
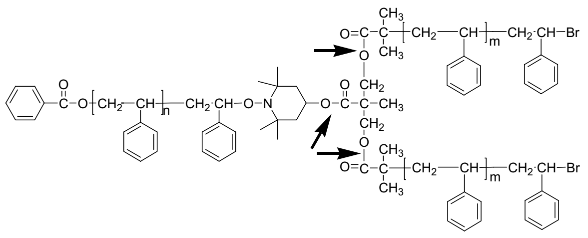


Fig. 5. GPC traces of the polystyrene macroinitiator and corresponding star-shaped PS-PEA$_2$ copolymers obtained at different monomer conversions. Conditions: [PS-TEMPO-Br$_2$]$_0$:[CuBr]$_0$:[PMDETA]$_0$:[EA]$_0$ = 1:1:1.5:800, T = 80 °C.

indicating that almost all the macroinitiator was converted to the miktoarm star-shaped copolymers. The polydispersity was relatively low, especially at lower monomer conversions. However, the molecular weight distributions became broader with the increase of monomer conversion, and high molecular weight shoulder was observed in the synthesis of PS-PMA2 when monomer conversion reached 45% (Fig. 4), indicating that bimolecular termination took place at higher monomer conversions.

To verify the weak C–O bond of between polystyrene and Br$_2$-TEMPO remained intact during the ATRP process of MA and EA, ATRP of styrene was carried out under the same polymerization conditions as that for acrylates, because there are three relatively weak ester bonds between polystyrene in the macroinitiator and those produced via ATRP, which can be cleaved by hydrolysis (Scheme 2).



Scheme 2.

A PS-TEMPO-Br$_2$ with number-average molecular weight to be 8500 (determined by GPC) was used as the macroinitiator of ATRP of styrene. The number-average molecular weight of the obtained PS$_1$–PS$_2$ star-shaped polystyrene was 13900. If the C–O bond between polystyrene and Br$_2$-TEMPO remained intact during the ATRP process, the number-average molecular weight of the polystyrene arm, PS$_1$, formed by SFRP process would remained constant. It can be seen from Fig. 6 that the GPC trace of the hydrolyzed PS$_1$–PS$_2$ was bimodal. The number-average molecular weights of the two peaks after mathematical treatment using the GPC software developed by Longzhida Co. were calculated to be 7930 and 2300, respectively. If two hydrolyzed ATRP initiator species (M_n = 445) were took into consideration, the higher molecular weight peak exactly corresponded to the polystyrene arm, PS$_1$, formed by SFRP process. This result confirmed that the C–O bond between polystyrene and Br$_2$-TEMPO remained intact during the ATRP process. Therefore, well-defined PS-PMA$_2$ and PS-PEA$_2$

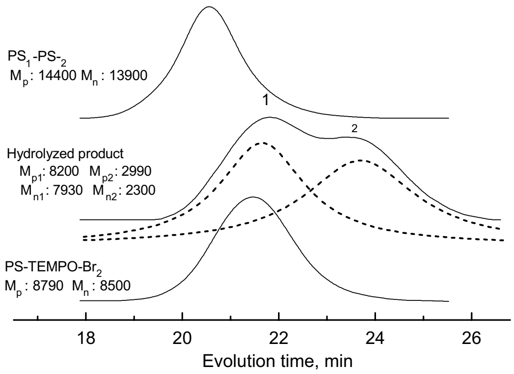


Fig. 6. GPC curves of the PS-TEMPO-Br$_2$ macroinitiator and PS$_1$–PS$_2$ star-shaped polystyrene before and after hydrolysis.

miktoarm star-shaped copolymers were obtained as shown in Scheme 1.

4. Conclusions

The synthesis of miktoarm copolymers has been demonstrated by combination of SFRP and ATRP. SFRP of styrene was carried out using BPO as initiator and Br_2-TEMPO as the stable free radical. With the obtained polystyrenes as macroinitiators and CuBr/PMDETA as catalyst, AB_2-type miktoarm star-shaped copolymers were synthesized successfully by ATRP of MA and EA. The molecular weights of the resulting miktoarm star-shaped copolymers increased with monomer conversions without any trace of the macroinitiator. Furthermore, the C–O bond between polystyrene and Br_2-TEMPO remained intact during the ATRP process, which was confirmed by hydrolysis of star-shaped polystyrene obtained by ATRP of styrene under the same polymerization conditions as those for ATRP of acrylates.

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References

[1] Hadjichristidis N. J Polym Sci Part A: Polym Chem 1999;37:857–71.

[2] Hadjichristidis N, Pitsikalis M, Iatrou H, Pispas S. Macromol Rapid Commun 2003;24:979–1013.

[3] Hadjichristidis N, Iatrou H, Pitsikalis M, Pispas S, Avgeropoulos A. Prog Polym Sci 2005;30:725–82.

[4] Tsoukatos T, Hadjichristidis N. J Polym Sci Part A: Polym Chem 2002;40:2575–82.

[5] Iatrou H, Hadjichristidis N. Macromolecules 1992;25: 4649–4651.

[6] Iatrou H, Hadjichristidis N. Macromolecules 1993;26: 2479–2484.

[7] Avgeropoulos A, Poulos Y, Hadjichristidis N. Macromolecules 1996;29:6076–8.

[8] Sioula S, Tselikas Y, Hadjichristidis N. Macromolecules 1997;30:1518–20.

[9] Iatrou H, Hadjichristidis N. Macromolecules 2000;33: 6993–6997.

[10] Mavroudis A, Avgeropoulos A, Poulos Y, Hadjichristidis N, Thomas EL, Lohse DJ. Chem Mater 2003;15:1976–83.

[11] Wang XS, Mitchell AW, Ian M. Macromol Rapid Commun 2003;24:403–7.

[12] Mavroudis A, Hadjichristidis N. Macromolecules 2006;39: 535–540.

[13] Eschwey H, Hallensleben ML, Burchard W. Makromol Chem Phys 1973;173:235–42.

[14] Kanaoka S, Sawamoto M, Higashimura T. Macromolecules 1991;24:2309–13.

[15] Storey RF, Shoemake KA. J Polym Sci, Part A: Polym Chem 1998;36:471–83.

[16] Kanaoka S, Fujita Y, Higashimura T. Macromol Rapid Commun 2000;21:218–22.

[17] Fazeli N, Taromi FA. J Polym Sci Part A: Polym Chem 2003;41:135–42.

[18] Du JZ, Chen YM. J Polym Sci Part A: Polym Chem 2004;42:2263–71.

[19] Du JZ, Chen YM. Macromolecules 2004;37:3588–94.

[20] Gao HF, Tsarevsk V, Matyjaszewsk K. Macromol Rapid Commun 2003;24:979–1013.

[21] Wu Y, Yan S, Fu ZF. Polymer 2005;46:12722–8.

[22] Quirk RP, Lee B. Pure Appl Chem 1994;A31:911.

[23] Fujimoto T, Zhang H, Kazama T, Isono Y, Hasegawa H, Hashimoto T. Polymer 1992;33:2208.

[24] Huckstadt H, Abetz V, Stadler R. Macromol Rapid Commun 1996;17:599–606.

[25] Bae YC, Faust R. Macromolecules 1998;31:2480–7.

[26] Hayashi M, Kojima K, Hirao A. Macromolecules 1999;32: 2425–2433.

[27] Hirao A, Matsuo A, Morifuji K, Tokuda Y, Hayashi M. Polym Adv Technol 2001;12:680–6.

[28] Hirao A, Tokuda Y, Morifuji K, Hayashi M. Macromol Chem Phys 2001;202:1606–13.

[29] Hirao A, Hayashi M, Higashihara T. Macromol Chem Phys 2001;202:3165–73.

[30] Hirao A, Hayashi M, Matsuo A. Polymer 2002;43:7125–31.

[31] Hirao A, Tokuda Y. Macromolecules 2003;36:6081–6.

[32] Hirao A, Hayashi M, Higashihara T. Adv Mater Sci Technol 2004;5:469–77.

[33] Fragouli PG, Iatrou H, Hadjichristidis N, Sakurai T, Hirao A. J Polym Sci Part A: Polym Chem 2006;44:614–9.

[34] Fernyhough CM, Young RN, Tack RD. Macromolecules 1999;32:5760–4.

[35] Reutenauer S, Hurtrez G, Philippe D. Macromolecules 2001;34:755–60.

[36] Heise A, Trollsås M, Magbitang T, Hedrick JL, Frank CR, Miller RD. Macromolecules 2001;34:2798–804.

[37] Miura Y, Sakai Y, Yamaoka K. Macromol Chem Phys 2005;206:504–12.

[38] He T, Li D, Sheng X, Zhao B. Macromolecules 2004; 37:3128–35.

[39] Deng GH, Zhang LW, Liu CD, He LH, Chen YM. Eur Polym J 2005;41:1177–86.

[40] Celik C, Hizal G, Tunca U. J Polym Sci Part A: Polym Chem 2003;41:2542–8.

[41] Erdogan T, Gungor E, Durmaz H, Hizal G, Tunca U. J Polym Sci Part A: Polym Chem 2006;44:1396–403.

[42] Durmaz H, Karatas F, Tunca U, Hizal G. J Polym Sci Part A: Polym Chem 2006;44:499–509.

[43] Erdogan T, Ozyurek Z, Hizal G, Tunca U. J Polym Sci Part A: Polym Chem 2004;42:2313–20.

[44] Tunca U, Ozyurek Z, Erdogan T, Hizal G. J Polym Sci Part A: Polym Chem 2004;42:4228–36.

[45] Angot S, Tato D, Gnanou Y. Macromolecules 2000;33: 5418–5426.

[46] Peleshanko S, Jeong J, Shevchenko VV, Genson KL, Piku Y, Ornatska M, et al. Macromolecules 2004;37:7497–506.

[47] Miura Y, Narumi A, Matsuya S, Satoh T, Duan Q, Kaga H, et al. J Polym Sci Part A: Polym Chem 2005;43:4271–9.

[48] Francis R, Lepoittevin B, Taton D, Gnanou Y. Macromolecules 2002;35:9001–8.

[49] Chen JF, Wang XZ, Liao XJ, Zhang HL, Wang XY, Zhou QF. Macromol Rapid Commun 2006;27:51–6.

[50] Guo YM, Pan CY. Polymer 2001;24:2863–9.

[51] Guo YM, Xu J, Pan CY. J Polym Sci Part A: Polym Chem 2001;39:437–45.

[52] Guo YM, Pan CY, Wang J. J Polym Sci Part A: Polym Chem 2001;39:2134–42.

[53] Feng XS, Pan CY. Macromolecules 2002;35:2084–9.

[54] Feng XS, Pan CY. Macromolecules 2002;35:4888–93.

[55] Li YG, Wang YM, Pan CY. J Polym Sci Part A: Polym Chem 2003;41:1243–50.

[56] Shi PJ, Li YG, Pan CY. Eur Polym J 2004;40:1283–90.

[57] Shi Y, Fu ZF, Li BY, Yang WT. J Polym Sci Part A: Polym Chem 2006;44:2468–75.

[58] Matyjaszewski K, Xia J. Chem Rev 2001;101:2921–90.

[59] Hawker CJ, Hedrick JL, Malmstrom EE, Trollsas M, Mecerreyes D, Moineau G, et al. Macromolecules 1998;27: 213–219.

[60] Hawker CJ, Barclay GG, Orellana A, Dao J, Devonport W. Macromolecules 1996;29:5245–54.

[61] Moore JS, Stupp SI. Macromolecules 1990;23:65–70.

[62] Matujaszewski K, Xia J. Chem Rev 2001;101:2921–90.