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A Facile Synthesis of Cleavable Block Copolymers via Tandem Polymerizations of NMRP and ATRP

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A functionalized compound, 4-(2-bromoisobutyryl)-2,2,6,6-tetra-methylpiperidine-1-oxyl (Br-TEMPO), was synthesized and used to synthesize block copolymers through tandem nitroxide-mediated radical polymerization (NMRP) and atom transfer radical polymerization (ATRP). First, Br-TEMPO was used to mediate the polymerization of styrene. The kinetics of polymerization proved a typical "living" nature of the reaction and the effectiveness in the mediation of polymerization of Br-TEMPO. Then the PS-Br macroinitiator was used to initiate atom transfer radical polymerization (ATRP). A series of acrylates were initiated by PS-Br macroinitiators in typical ATRP processes at various conditions. The controlled polymerization of ATRP was also confirmed by molecular weight and kinetic analysis. Several cleavable block copolymers of PS-b-P(t-BA), PS-b-P(n-BA), and PS-b-PMA, with different molecular weights, were synthesized via this strategy. Relatively low polydispersities (<1.5) were observed and the molecular weights were in agreement with the theoretical ones. Hydrolysis of PS-b-P(t-BA) was carried out, giving amphiphilic block copolymer PS-b-PAA without the cleavage of C-ON bond or ester bond. All the block copolymers have two T_gs as demonstrated by DSC. A typical cleavable block copolymer of PS-b-PMA was cleaved by adding phenylhydrazine at 120°C to produce homopolymers in situ.

Keywords nitroxide-mediated radical polymerization (NMRP), atom transfer radical polymerization (ATRP), amphiphilic block copolymers, tandem polymerization, cleavable block copolymers

Introduction

Recent decades have witnessed dramatic developments in the design and synthesis of block copolymers. Besides their use as thermoplastic elastomers and high-impact plastics, additives, foams or pressure-sensitive adhesives, block copolymers are potential drug delivery, photonic crystals and information storage materials (1). Among them, cleavable block copolymers should be given a great deal of emphasis for their cleavages under external stimuli, rendering great potentials in controlled drug delivery

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(2–4), commercial materials with abilities to control domain sizes (5, 6), low surface energy surfaces with tunable surface functionalities (7), and covalently bound neutral polymer chains to permanently reduce interactions with other materials (8).

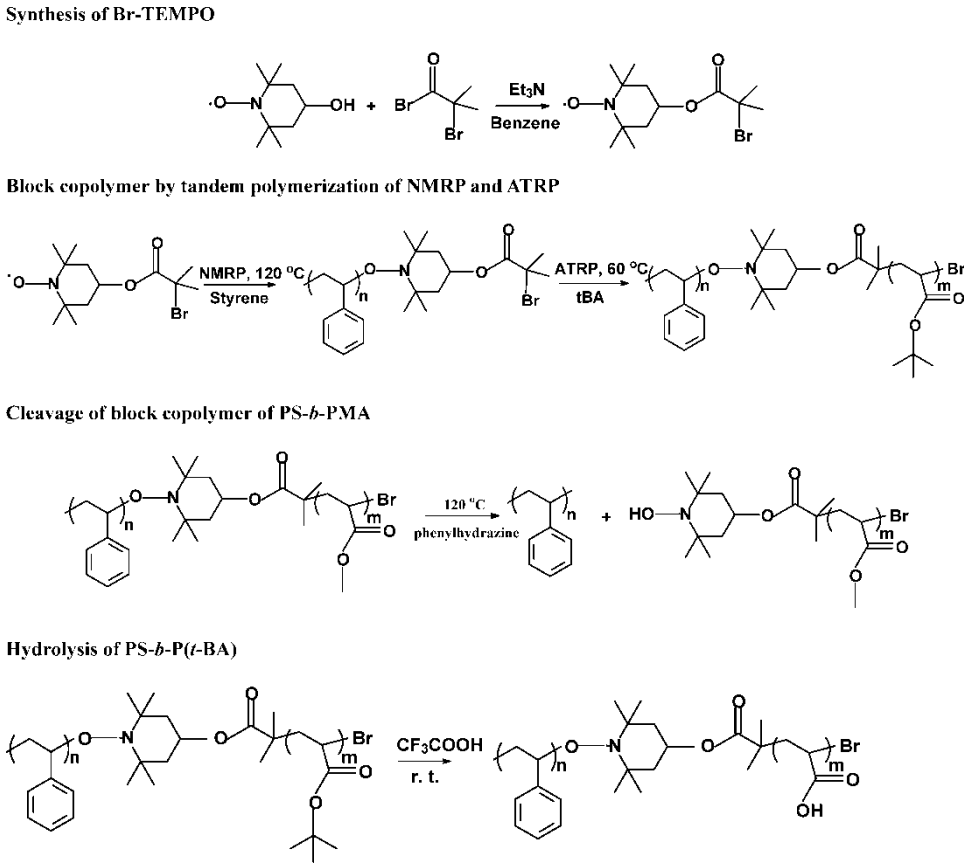
Cleavable polymers require a complex route for synthesis. Polymers of this type cannot be fabricated by a single mechanism of polymerization, because only C-C bonds are located between segments of block copolymers and the high C-C bond energy makes the cleavage of block polymers nearly impossible. Generally speaking, there are three strategies for the synthesis of cleavable polymers. The first strategy entails an end-coupling of telechelic homopolymers (5, 6). The second alternative is the modification of existing block copolymers (4, 7). The third strategy of tandem polymerization, compared to the above-mentioned ones, is more universal and facile. In tandem polymerization, a mechanism transformation is required to produce a labile bond between blocks. Examples of a combination of anionic polymerization and nitroxide-mediated radical polymerization (NMRP) (9), atom transfer radical polymerization (ATRP) and anionic polymerization (10–12), ATRP and living ring opening polymerization (ROP) (3, 13–15), ATRP, and NMRP (2, 16–19), ATRP, NMRP and ROP (20), cationic polymerization and ATRP (21), cationic polymerization and NMRP (22), NMRP and ROP (23–25) have been reported, respectively. Among them, controlled/"living" radical polymerization should be given significant emphasis for it is amenable to molecular design and modification (2, 3, 23–28). One great limitation in such cases is the complex and multiple synthesis of the agents functioning in mechanism transformations. Therefore, the facile synthesis of such agents is vital to the application of cleavable polymers.

In our work on NMRP, we synthesized highly branched polystyrene using nitroxyl stable radicals possessing a polymerizable vinyl group (29, 30). The branch point was formed by a labile -C-ON bond. The resulting branched polystyrene was easily cleaved into linear polymers by heating with ascorbic acid (29) and phenylhydrazine (30). In this paper, we report the synthesis and characterization of polystyrene-*b*-polybutylacrylates block copolymers, denoted as PS-*b*-PBA, using a bromo-functionalized nitroxyl stable radical, 4-(2-bromoisobutyryl)-2,2,6,6-tetramethylpiperidine-1-oxyl (Br-TEMPO). The block copolymers were prepared in two tandem steps (Scheme 1), i.e., the polymerization of styrene mediated by the TEMPO moiety followed by ATRP of the acrylates initiated by alkylbromide in the presence of CuBr/PMDETA. These two steps, although both involve a radical process, do not interfere with each other due to the difference in the performing temperature. The methodology is highly effective and pervasive. Such strategy avoids complicated synthesis of agents acting in the transformation of mechanisms, while providing good perspectives for the synthesis and application of cleavable polymers.

Experimental

Materials

Styrene (Yonghua, 99%), methyl methacrylate (Sinopharm, 99%), *tert*-butyl acrylate (Fluka, 99%), methyl acrylate and *n*-butyl acrylate (Sinopharm, 99%) were distilled under vacuum over CaH_2. AIBN (Shanghai 4th Factory of Chemicals, 99%) was recrystallized from absolute ethanol. 4-Hydroxy-2,2,6,6–tetramethylpiperidine-1-oxy (HO-TEMPO) was purchased from Aldrich and used as received. Copper(I) bromide and Copper(I) chloride (Runjie, both 99%) were purified by washing with glacial acetic acid, followed by absolute ethanol and ethyl ether, and then dried under vacuum.



Scheme 1. Synthesis of Br-TEMPO, block copolymers through tandem polymerizations of NMRP and ATRP, cleavage of block copolymers and hydrolysis of PS-*b*-P(*t*-BA).

N,N,N′,N″,N″-Pentamethyldiethyl-enetriamine (PMDETA, Aldrich, 99%) was used as received. Triethylamine (Sinopharm, 99%) was used as received. Benzene was dried with Na and benzophenone and then distilled under N_2. Acetone (Shanghai 4th Factory of Chemicals, 99%) was dried with anhydrous $CaSO_4$ and then distilled. Anisole (Sinopharm, 99%) was distilled under vacuum over CaH_2. Acetonitrile (Lingfeng, HPLC grade), 2-bromoisobutyryl bromide (Lancaster, 99%), trifluoroacetic acid and phenylhydrazine (Sinopharm, both 99%) were used as received.

Characterization

FT-IR spectra were obtained on a Nicolet Magna-550 FT-IR instrument using a KBr pellet of fixed thickness. ^{1}H-NMR spectra were carried out on a Bruker (500 MHz) NMR instrument using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the reference. M_n and M_w/M_n of all samples were measured by gel permeation chromatography (GPC) through three Waters Styragel columns (pore size: 10^2, 10^3, and 10^4 Å in series) in a Waters 2010 system equipped with a Waters 410 RI detector. THF was used as eluent at a flow rate of 1 mL/min at 40°C. The columns were calibrated by narrow polystyrene

standards. ESR measurements were carried out on a Bruker ER 200DSRC spectrometer. Instrument parameters: modulation frequency: 100 kHz; modulation amplitude: 1.25 G; microwave power: 20 mW. UV spectra were carried out on Perkin-Elmer Lambda 35 UV-Vis instrument. Monomer conversions were determined by thermogravimetric analysis (TGA) on a NETZSCH TG209 instrument. The temperature was elevated from 25 to 550°C at a rate of 20 K min^{-1}. The weight loss above 275°C gave the polymer content. GC-MS was measured on a Finnigan Voyager GC-MS instrument. Element analysis of Br was carried out on a Heraeus 1106 instrument; C, H, N was carried out on an ELEMENTAR VARIO EL III instrument. Differential scanning calorimetry (DSC) analyses were performed on a NETZSCH DSC204 instrument, over the temperature range −110 to 150°C, under nitrogen, with a scan rate of 10°C/min.

Synthesis of 4-(2-Bromoisobutyryl)-2,2,6,6-tetramethylpiperidine-1-oxyl (Br-TEMPO)

To a benzene solution (28 mL) of 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxy (2 g, 0.0116 mol) and triethylamine (1.6 g, 0.0158 mol), 2-bromoisobutyryl bromide (2.56 mL, 0.0207 mol) was added under vigorous stirring at 5°C. After the addition was finished, the reaction was continued for 1 h at room temperature and 2 h at 70°C. After filtration of the precipitate, the red colored benzene solution was condensed on a rotary evaporator. The obtained red solid was purified by flash column chromatography (Al_2O_3, ethyl acetate/petroleum ether = 1/8 v/v) and then recrystallization from hexane to afford pure Br-TEMPO as a red colored crystal, yield: 73%; purity: 98.76% (GC); mp: 70–71°C. UV max (benzene): 285 and 468 nm. IR: ν [cm^{-1}] = 1732 (C═O), 1373 (N-O·). ESR: $g = 2.0063$, a = 15.33 G, MS (EI): $m/e = 322$, 211, 154, 139, 124, 109. Calcd. for $C_{13}H_{23}NO_3Br$: C, 48.61; H, 7.22; N, 4.36; Br, 24.87. Found: C, 48.41; H, 7.20; N, 4.18; Br, 24.40.

Synthesis of PS-Br Macroinitiator via Nitroxide-Mediated Radical Polymerization of Styrene

The Br-TEMPO-mediated styrene polymerization ([Styrene]/[AIBN]/[Br-TEMPO] = 200/1/1.5) (Entry 3 in Table 1) is used as an example. A solution of styrene (20 mL, 0.174 mol), AIBN (0.14 g, 0.85 mmol), and Br-TEMPO (0.42 g, 1.31 mmol) was degassed through three freeze-pump-thaw cycles. The mixture was thermostated at 120°C

Table 1
Bulk polymerization of styrene mediated by Br-TEMPO at 120°C

Entry	$[St]_0/[AIBN]/[Br\text{-}TEMPO]$	Time (h)	Conv.[a] (%)	$M_{n,calc}$[b] (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n
1	400/1/1.3	24	78.1	16635	15800	1.42
2	250/1/1.3	24	79.0	10660	11500	1.24
3	200/1/1.5	8	35.6	4077	4100	1.28
4	200/1/1.5	24	74.3	6185	6000	1.23

[a]Conversion determined from TGA.
[b]$([St]_0/[Initiator]_0) \times (\%conversion) \times 104 + M_{Br\text{-}TEMPO.}$

under a nitrogen atmosphere. The samples were taken from the system at prescribed intervals for the analysis of molecular weight and conversion. The reaction was stopped by immersing the flask into liquid nitrogen. The final product was dissolved in THF and precipitated into methanol three times to yield the PS-Br macroinitiator. It was then dried under vacuum at 60°C for two days and analyzed by GPC and FT-IR.

Synthesis of PS-b-P(t-BA) via Atom Transfer Radical Polymerization

Entry 1 in Table 2 is used as an example. PS-Br (0.50 g, 0.120 mmol, $M_n = 4100$ g/mol, $M_w/M_n = 1.28$) was added to a dry round-bottom flask. Deoxygenated acetone (2 mL) was added, after which *t*-BA (6 mL, 0.410 mmol) was added via syringes. After the PS-Br powder was dissolved in the solution, CuBr (59 mg, 0.410 mmol) was added. The flask was sealed with a rubber septum, and degassed through three freeze-thaw cycles. PMDETA (86 μL, 0.410 mmol) was added via a syringe and the solution was stirred until the Cu complex had formed as indicated by the appearance of a light green color. After that, the flask was placed in an oil bath thermostated at 60°C. At specific intervals, samples (0.3 mL) were removed for analysis of molecular weight and conversion. After 9.5 h, the reaction was stopped by immersing the flask into liquid nitrogen. The final polymers were dissolved in THF and the mixture was filtered through neutral alumina. The filtered solution was concentrated in a rotary evaporator and then precipitated into 50/50 (v/v) H_2O/methanol twice. It was then dried under vacuum at 40°C for two days and analyzed by ^{1}H NMR, GPC, and FT-IR.

Synthesis of PS-b-PMA via Atom Transfer Radical Polymerization

Entry 7 in Table 2 is described as an example. PS-Br ($M_n = 4100$ g/mol, $M_w/M_n = 1.28$; 0.40 g, 0.0965 mmol) was added to a dry round-bottom flask. Deoxygenated anisole (0.9 mL) was added, after which MA (3.5 mL, 0.0388 mol) was added via syringes. After the powder of PS-Br was dissolved in the solution, CuBr (42 mg, 0.289 mmol) was added. The flask was sealed with a rubber septum, and degassed through three freeze-thaw cycles. PMDETA (60 μL, 0.289 mmol) was added via a syringe and the solution was stirred until the Cu complex had formed. This was visible from the color change of the solution to a green color. After that, the flask was placed in an oil bath thermostated at 70°C. At specific intervals, samples (0.2 mL) were removed for the analysis of molecular weight and conversion. After 12 h, the reaction was stopped by immersing the flask into liquid nitrogen. The final polymers were dissolved in THF and the mixture was filtered through neutral alumina. The filtered solution was concentrated in a rotary evaporator and then precipitated into methanol twice. It was then dried under vacuum at room temperature for two days and analyzed by ^{1}H NMR, GPC, and FT-IR.

Synthesis of PS-b-P(n-BA) via Atom Transfer Radical Polymerization

Entry 9 (Table 2) is described as an example. PS-Br ($M_n = 11500$, $M_w/M_n = 1.24$; 0.84 g, 0.0730 mmol) was added to a dry round-bottom flask. Deoxygenated acetonitrile (1.4 mL) was added, after which *n*-BA (4.2 mL, 0.0292 mol) was added via syringes. After the powder of PS-Br was dissolved in the solution, CuBr (32 mg, 0.219 mmol) was added. The flask was sealed with a rubber septum, degassed through three freeze-thaw cycles. PMDETA (46 μL, 0.219 mmol) was added via a syringe and the solution was stirred

Table 2
Polymerization of *t*-BA, MA; and *n*-BA using PS-Br as macroinitiatiors

Entry	Monomer	$M_{n,PS\text{-}Br}$	Solvent (vol %)	[PS-Br][a] (M)	Temp (°C)	Conv.[b] (%)	$M_{n,theo}$[c]	$M_{n,GPC}$	$M_{n,NMR}$	M_w/M_n
1	*t*-BA	4100	Acetone, 25	1.15×10^{-2}	60	78.4	38164	28600	40234	1.27
2	*t*-BA	6000	Acetone, 25	3.35×10^{-2}	60	25.7	11004	6700	11385	1.29
3	*t*-BA	6000	Acetone, 25	3.15×10^{-2}	60	55.7	17477	9700	19537	1.48
4	MA	11500	Anisole, 20	2.22×10^{-2}	70	39.8	25185	27800	24154	1.32
5	MA	11500	Acetonitrile, 20	2.22×10^{-2}	70	36.9	24188	23300	NA	1.28
6	MA	11500	Acetonitrile, 20	2.19×10^{-2}	70	45.7	27223	24800	25097	1.41
7	MA	4100	Anisole, 20	1.30×10^{-2}	70	61.2	25781	26400	25567	1.30
8	*n*-BA	11500	Anisole, 25	1.30×10^{-2}	70	33.8	28803	23600	28180	1.50
9	*n*-BA	11500	Acetonitrile, 25	1.30×10^{-2}	70	52.9	38587	38400	39818	1.49

[a][CuBr] = [PMDETA] = 3[PS-Br].
[b]Conversion determined from TGA.
[c]$M_{n,PS\text{-}Br} + M_{monomer}([M]_0/[I]_0)$.

until the Cu complex had formed. This was visible from the color change of the solution, i.e., colorless to light green. After that, the flask was placed in an oil bath thermostated at 70°C. At specific intervals, samples (0.2 mL) were removed for the analysis of molecular weight and conversion. After 21 h, the reaction was stopped by immersing the flask into liquid nitrogen. The final polymers were dissolved in THF and the mixture was filtered through neutral alumina. The filtered solution was concentrated in a rotary evaporator and then precipitated into 50/50 (v/v) H_2O/methanol twice. It was then dried under vacuum at room temperature for two days and analyzed by ^{1}H NMR, GPC and FT-IR.

Hydrolysis of PS-b-P(t-BA)

PS-*b*-P(*t*-BA) ($M_n = 17800$ g/mol, $M_w/M_n = 1.48$; 0.5 g, 0.0281 mmol,) was added to a round-bottom flask. Ten milliliters dichloromethane was added with a syringe and then 1 mL trifluoroacetic acid (0.0137 mol). After the mixture was dissolved completely, it was allowed to stir at room temperature for 24 h. After that, the solution was precipitated into 100 mL petroleum ether twice, yielding glassy polymer solids. It was then dried under vacuum at 50°C for two days and analyzed by ^{1}H NMR, GPC, and FT-IR.

Cleavage of Block Copolymers

Take the cleavage of the product of Entry 4 in Table 2 as an example. The product (0.3 g, $M_n = 27800$ g/mol, $M_w/M_n = 1.32$) of Entry 4 in Table 2 was dissolved in 3 mL of chlorobenzene before the addition of phenylhydrazine (1.0 g, 9.2 mmol). The mixture was heated at 120°C for 24 h before precipitated into cool cyclohexane (0°C). PMA was obtained as the precipitate and PS (stay in cyclohexane) was obtained after evaporation of cyclohexane. All the products were analyzed by GPC and ^{1}H-NMR.

Result and Discussion

Synthesis of Br-TEMPO

Br-TEMPO was synthesized by esterification between 4-hydroxy-2,2,6,6-tetramethyl-piperidine-1-oxy (HO-TEMPO) and 2-bromoisobutyryl bromide in the presence of triethylamine, as depicted in Scheme 1. A significantly high yield of 73% was achieved. The product structure was confirmed by UV-vis, IR, MASS, and ESR spectroscopy. The ESR in Figure 1 shows g factor of 2.0062 (a = 15.33 G), in good agreement with the literature value (31) of HO-TEMPO ($g = 2.0070$ and a = 15.88 G for HO- TEMPO).

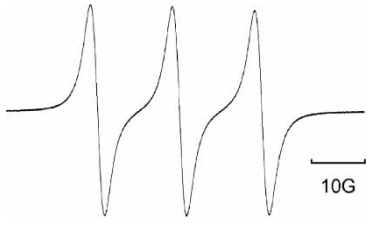


Figure 1. ESR spectrum of Br-TEMPO in benzene solution (10^{-3} M).

Styrene Polymerization Mediated by Br-TEMPO

Although Br-TEMPO has two functionalities to initiate/mediate NMRP and ATRP, the synthesis of the first block was confined to NMRP of styrene. If otherwise, TEMPO moiety may hinder the propagation of radical chains in the process of ATRP. Indeed, we found that Br-TEMPO did not initiate the ATRP of *n*-butyl acrylate in the presence of CuBr/PMDETA even after 24 h.

The polymerization of styrene mediated by Br-TEMPO was performed under the normal conditions for NMRP. For a typical system, Figure 2 shows that GPC curves of the resulting polystyrene shifted stepwise to larger molecular weights with reaction time. Figure 3 shows that the measured molecular weights increased linearly with monomer conversion, while the molecular weight distributions decreased as low as 1.4 for high conversion. Figure 4 shows the kinetic plot is a straight line, indicating a constant number of propagating radicals during the process. All these features meet the criteria for a living polymerization. Four polymerizations with different predetermined molecular weight were listed in Table 1. It is obvious that the measured molecular weights by GPC agree well with the theoretical ones, demonstrating a living polymerization again.

The presence of Br-TEMPO moiety as terminus of the resulting polystyrene was confirmed by IR spectrum that shows a peak at 1736 cm^{-1}(result not given), which was attributed to the stretching of the ester carbonyl.

ATRP of Acrylates using PS-Br as Macroinitiator

The above-synthesized polystyrene with end group of alkylbromide, PS-Br, was used as macroninitiator to initiate the polymerization of acrylates. Following a standard procedure (32, 33), ATRPs of acrylates were performed at 60°C (Scheme 1), a temperature at which alkoxyamine remain dormant. It is important to select an appropriate solvent for each monomer to polymerize, i.e., *t*-BA in acetone, MA, and *n*-BA in acetonitrile or anisole, respectively. The initiation and polymerization went steadily for each polymerization system, as indicated by a change in color from green to brown immediately after mixing the reactants and the ligand.

As an example, the results of polymerizations initiated by macroinitiator PS-Br of $M_n = 4100$ g/mol and $M_w/M_n = 1.28$) were present in Figures 5–8. Figure 5 shows

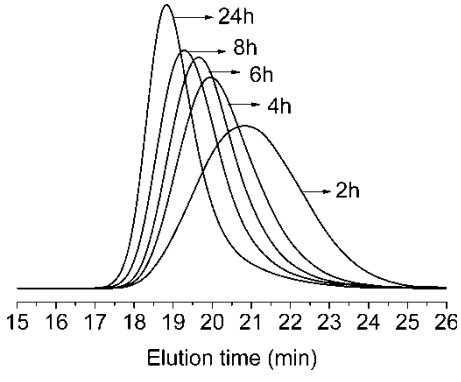


Figure 2. GPC traces of styrene polymerization mediated by Br-TEMPO at 120°C. $[St]_0/[AIBN]_0/[Br\text{-}TEMPO] = 400/1/1.3$ (Entry 1 in Table 1).

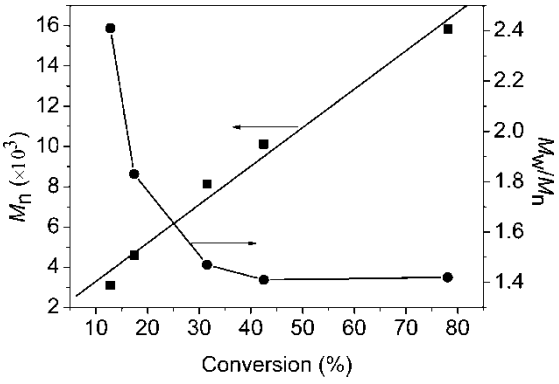


Figure 3. Plots of M_n and M_w/M_n vs. conversion for NMRP of styrene at 120°C in bulk. $[St]_0/[AIBN]_0/[Br\text{-}TEMPO] = 400/1/1.3$.

first-order kinetics for three polymerizations of *t*-BA, MA, and *n*-BA. The linearity indicates a constant concentration of propagating radicals during the polymerization. Figure 6 shows GPC curves of the macroinitiator and the samples taken at different reaction period. While the molecular weight increased with reaction time, the peak for the macroinitiator disappeared, indicating high efficiency of the initiation. The same result was also observed for macroinitiator with higher molecular weight, i.e., $M_{n,PS\text{-}Br} = 11500$ g/mol. Figure 7 shows the measured molecular weights increased linearly with monomer conversions, and Figure 8 shows the polydispersity indices remained lower than 1.5, demonstrating a living character of the polymerization of the second block.

A number of synthesized block copolymers and the polymerization conditions were listed in Table 2. It is noted that, for PS-*b*-P(*t*-BA), the measured M_n by GPC are much lower than theoretical values due to the difference of hydrodynamic volume of P(*t*-BA) and the polystyrene standards. Nevertheless, the M_n estimated from ^{1}H-NMR agrees well with the theoretical values for all three kinds of block copolymers.

Figure 9 shows the ^{1}H-NMR spectra of PS-Br ($M_n = 11500$ g/mol, $M_w/M_n = 1.24$), PS-*b*-PMA ($M_n = 28000$ g/mol, $M_w/M_n = 1.32$), PS-*b*-P(*n*-BA) ($M_n = 23600$ g/mol,

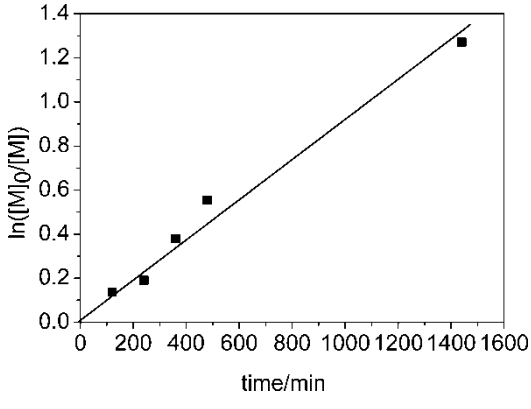


Figure 4. Plot of $\ln([M]_0/[M])$ vs. time for NMRP of styrene at 120°C in bulk. $[St]_0/[AIBN]_0/[Br\text{-}TEMPO] = 400/1/1.3$.

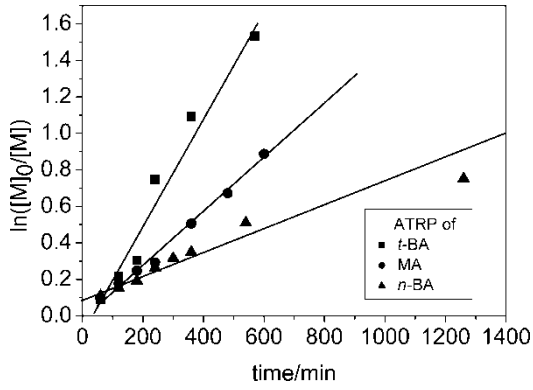


Figure 5. Plot of $\ln([M]_0/[M])$ vs. time for ATRP in solution of *t*-BA (60°C), MA (70°C), and *n*-BA (70°C) initiated by PS-Br.

$M_w/M_n = 1.50$). The composition of the block copolymers, and therefore the block length, can be easily calculated by integration of the alkoxy protons (around 4.0 ppm) and aromatic protons (around 7.0 ppm). The results are listed in Table 2. The molecular weights of the second block, simply calculated by $M_{n,NMR}$ minus $M_{n,PS\text{-}Br}$, are quite large in comparison with the first block. This again implies the efficiency of the block copolymerization.

Hydrolysis of PS-b-P(t-BA)

As precursors, polystyrene-*b*-polyacrylates in Table 2 can be hydrolyzed to prepare amphiphilic cleavable block copolymers. It was reported that both homopolymer and block copolymer of *tert*-butylacrylate were readily hydrolyzed by refluxing with HCl in dioxane(33). However, the process cannot be applied in this work because the prepared block copolymers contain an ester group between the two blocks (see Scheme 1) that can undergo hydrolysis at the same time. To avoid the undesired cleavage at this step, we used a milder process (32) developed by Wooley and coworkers, in which anhydrous trifluoroacetic acid instead of HCl was utilized. The hydrolysis is complete after 24 h, followed by precipitation into methanol. No chain breaking was observed

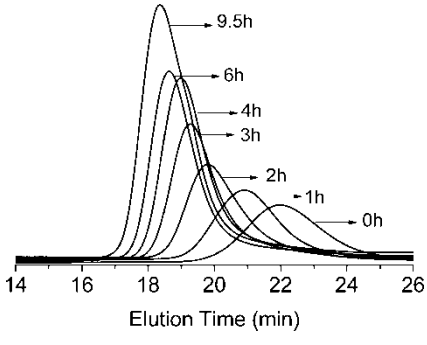


Figure 6. GPC traces for the ATRP of *t*-BA initiated by PS-Br at 60°C in 25% acetone ([PS-Br] = 1.51×10^{-2} M, [CuBr] = 4.53×10^{-2} M,[PMDETA] = 4.53×10^{-2} M, [*t*-BA] = 5.13 M).

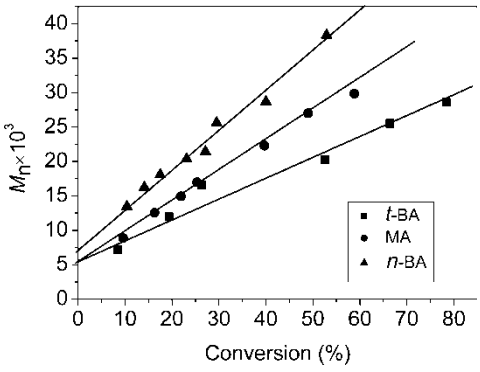


Figure 7. Plot of M_n vs. conversion for ATRP in solution of *t*-BA (60°C), MA (70°C), and *n*-BA (70°C) initiated by PS-Br.

since the GPC (Figure 10) of the precipitated sample showed a monomodal distribution. After hydrolysis, the molecular weight measured by GPC became obviously smaller due to the smaller hydrodynamic volume of the resulting polyacrylic acid block. FT-IR (Figure 11) shows a broad band around 3400 cm^{-1} that is characteristic of carboxylic acid group. In ^{1}H-NMR spectra in Figure 12, the proton signal of carboxylic acid is located at $\delta = 12.20$ ppm. Besides, a broad signal at $\delta = 3.30$ ppm demonstrates the exchange of proton between PAA and undeuterated water in DMSO-d_6. These results demonstrate that hydrolysis took place in the presence of trifluoroacetic acid while it did not destroy the ester group between the two blocks.

DSC Measurement of Block Copolymers

The thermal behavior of the polymers was investigated by DSC measurements (Figure 13). Phase separated block copolymers are expected to display two distinct glass transitions. The PS-*b*-P(*n*-BA) displays the following characteristic temperature: $T_g = -45.8$°C and $T_g = 88.3$°C. These temperatures are consistent with those of the P(*n*-BA) and PS segments. PS-*b*-PMA has two T_gs of 14.4°C for PMA and 92.3°C for

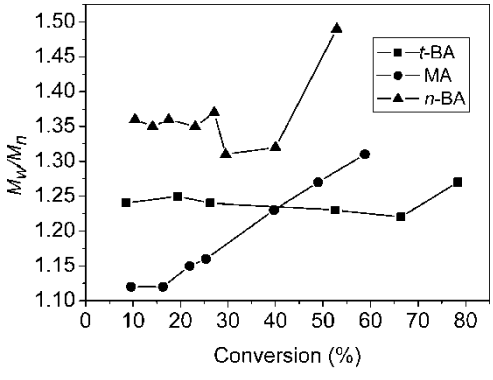


Figure 8. Plot of M_w/M_n vs. conversion for ATRP in solution of *t*-BA (60°C), MA (60°C), and *n*-BA (60°C) initiated by PS-Br.

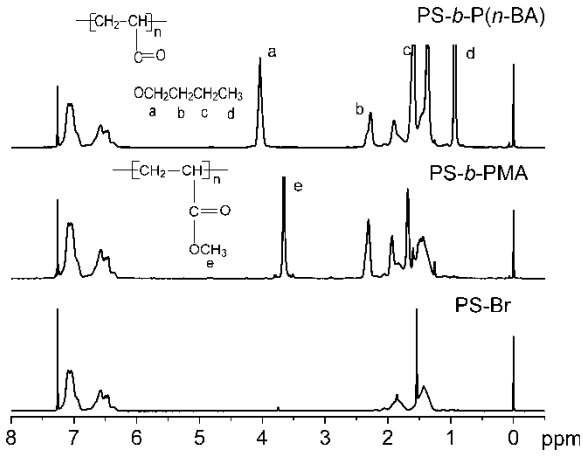


Figure 9. ^{1}H-NMR spectra of PS-Br ($M_n = 11500$ g/mol, $M_w/M_n = 1.24$), PS-*b*-PMA ($M_n = 28000$ g/mol, $M_w/M_n = 1.32$), PS-*b*-P(*n*-BA) ($M_n = 23600$ g/mol, $M_w/M_n = 1.50$) (Solvent: $CDCl_3$).

PS. The first transition was almost identical to that of PMA, whereas the second transition was similar to that of PS. Similarly, two glass transitions were displayed in PS-*b*-P(*t*-BA) and PS-*b*-PAA, as shown in Figure 13.

Cleavage of the Labile C-ON Bond between Two Blocks

The -C-ON- bond between the two segments can be broken by reagents such as ascorbic acid or phenylhydrazine (30). In this work, a block copolymer of PS-*b*-PMA was heated with phenylhydrazine in chlorobenzene at 120°C. After 24 h, the reaction mixture was precipitated into cyclohexane to yield a white powder. From GPC curves in Figure 14, it is clear that the initial block copolymer was completely cleaved into a mixture of two homopolymers, polystyrene, and polymethacrylate, as demonstrated by the bimodal distribution of the final mixture. These two components were isolated by precipitation into cyclohexane, a selective solvent of polystyrene. At 0°C, PMA homopolymers precipitated from cyclohexane and PS homopolymers remained in solution. The isolated polymers showed monomodal GPC

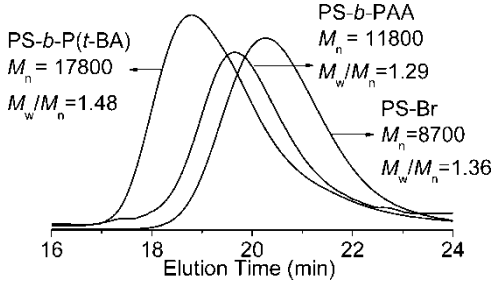


Figure 10. GPC traces of PS-*b*-P(*t*-BA), its precursor PS-Br, and its product after hydrolysis of PS-*b*-P(*t*-BA).

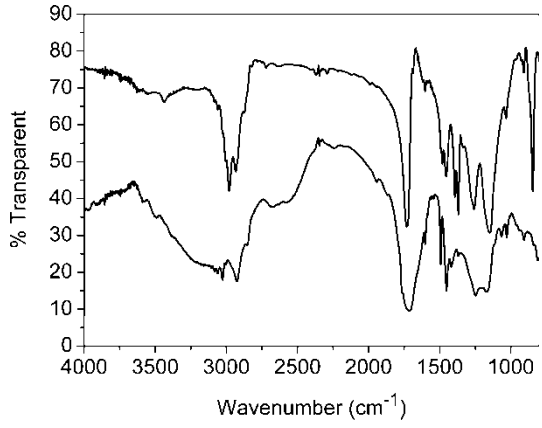


Figure 11. FT-IR of PS-*b*-P(*t*-BA) (upper) and its product of hydrolysis PS-*b*-PAA (lower) (KBr pellet).

curves that corresponded to the homopolymers. For example, the M_n of isolated PS is 11700 g/mol, nearly indentical to 11500 g/mol of PS-Br macroinitiator. The M_n of isolated PMA is 21500 g/mol, $M_w/M_n = 1.10$. The value is higher than the theoretical one from NMR. The discrepancy is due to the different hydrodynamic volume of PMA and PS standards.

Conclusions

A bifunctional compound, Br-TEMPO, was synthesized and applied in the preparation of block copolymers through tandem polymerizations, i.e., NMRP of styrene followed by ATRP of acrylates. Both polymerization processes proceeded in a controlled/"living" fashion. The resulting block copolymers have predetermined block lengths and an incorporated cleavable -C-ON bond. A series of block copolymers, such as

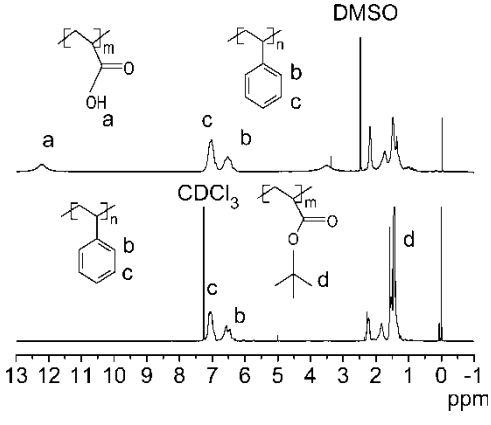


Figure 12. ^{1}H-NMR spectra of PS-*b*-P(*t*-BA) ($M_n = 17700$ g/mol, $M_w/M_n = 1.48$, $CDCl_3$) and PS-*b*-PAA ($M_n = 11800$ g/mol, $M_w/M_n = 1.29$, DMSO-d_6).

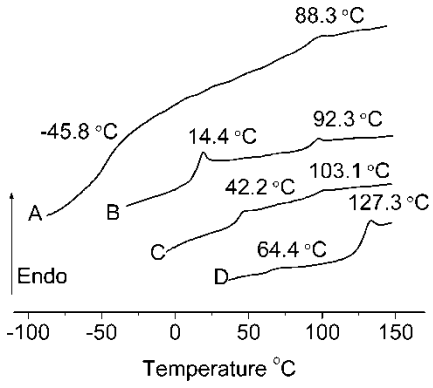


Figure 13. DSC measurements of block copolymers. (A) PS-*b*-P(*n*-BA), (B) PS-*b*-PMA, (C) PS-*b*-P(*t*-BA), (D) PS-*b*-PAA.

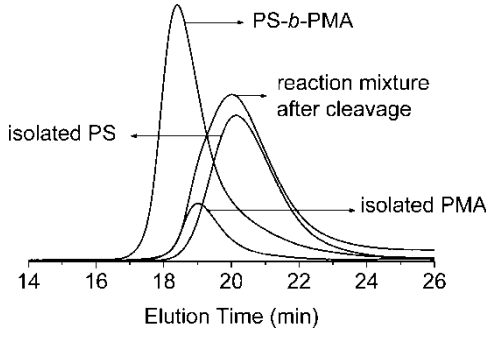


Figure 14. GPC traces of PS-b-PMA (Mn = 27800 g/mol, Mw/Mn = 1.32), the product after treatment with phenylhydrazine (Mn = 15800 g/mol, Mw/Mn =1.60) at 120°C and the isolated PS (Mn =11700, Mw/Mn =1.21) and PMA (21500 g/mol, Mw/Mn = 1.10) homopolymer.

PS-*b*-P(*t*-BA), PS-*b*-PMA and PS-*b*-P(*n*-BA), were prepared. The block copolymers were not only readily hydrolyzed to yield amphiphilic block copolymers, but also cleaved by breaking the -C-ON bond through reaction with phenylhydrazine. DSC measurements detected two T_gs for all block copolymers.

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