Preparation of Amphiphilic PS-*b*-PMAA Diblock Copolymer by Means of Atom Transfer Radical Polymerization

GUOJIAN WANG, DEYUE YAN

College of Chemistry and Chemical Technology, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, People's Republic of China

ABSTRACT: Amphiphilic diblock copolymers of polystyrene-*b*-poly(methacrylic acid) were synthesized by means of atom transfer radical polymerization. First, the polystyrene with a bromine atom at the chain end (PS-Br) was prepared using styrene as the monomer, 1-bromoethyl benzene as the initiator, and CuCl/2,2′-bipyridyl (bpy) as the catalyst ([1-bromoethyl benzene]/[CuCl]/[bpy] = 1:1:3). The polymerization was well controlled. Second, the diblock copolymer of polystyrene-*b*-poly(*tert*-butyl methacrylate) was synthesized also by atom transfer radical polymerization using PS-Br as the macro-initiator, CuCl/bpy as the catalyst, and *tert*-butyl methacrylate (tBMA) as the monomer. Finally, the amphiphilic diblock copolymer, PS-*b*-PMAA, was obtained by hydrolysis of PS-*b*-PtBMA under the acid condition. The molecular weight and the structure of aforementioned copolymers were characterized with gel permeation chromatography, infrared, and nuclear magnetic resonance. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 2381–2386, 2001

Key words: *tert*-butyl methacrylate; amphipathy; diblock copolymer; atom transfer radical polymerization; block copolymerization

INTRODUCTION

Block copolymers in which one or both blocks are hydrophilic have become a field of considerable scientific and industrial interest. Some important uses, such as emulsifiers,[1] crystallization modifier,[2–4] and templates for metal colloids,[5] have been reported. Block copolymers are generally prepared by living (anionic, cationic, group transfer, and controlled radical) polymerization using consecutive monomer additions; a multitude of block copolymers have been manufactured in this way.[6–9] However, this method is handicapped by the fact that many desirable monomer combinations are not possible because the monomers need to be polymerized by different mechanisms. In our case, we desired to synthesize amphiphilic block copolymer of styrene with methacrylic acid. The former monomer can be polymerized by living cationic or anionic polymerization, but the latter one cannot be polymerized by living polymerization. One solution to this kind of problem is the "site transformation" of the polymer chain end after synthesis of the first block, e.g., from cationic to anionic (or radical) or vice versa.[10–14] However, in many cases, this is not easily possible or the initiating efficiency of the macro-initiator formed is poor. In 1995, a sort of novel living radical polymerization, so-called atom transfer radical polymerization (ATRP) was developed by Wang and Matyjaszewski.[15] It provided many potential advantages in the macromolecular design. The proposed mechanism for a typical ATRP is a reversible redox in which a carbon-centered rad-
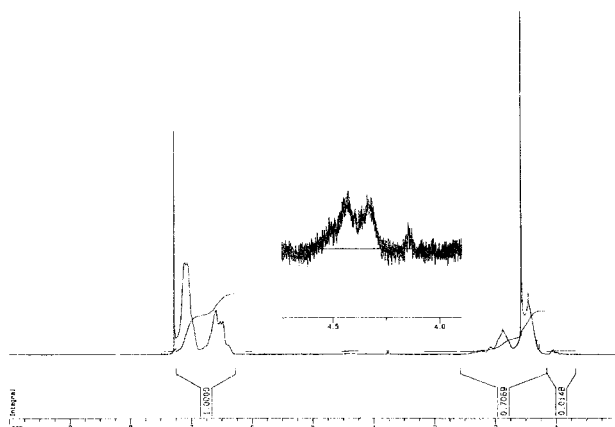
Figure 1 ^{1}H-NMR spectrum of PS obtained by the bulk ATRP.

ical (R·) is formed by reversible reaction of the Cu^I with a moiety such as a benzylic halide containing a labile carbon-halogen bone and in the meantime a Cu^{II} halide is formed. The carbon-centered radical (R·) undergoes addition reaction with an olefinic monomer or reacts with Cu^{II} halide to regenerate Cu^I while a carbon-halogen bond is re-formed. The 2,2′-bipyridyl ligands are needed to solubilize and to selectively stabilize the Cu^I. If the equilibrium constant for the redox is sufficiently small and the reduction of Cu^{II} is sufficiently fast, the concentration of radicals will retain very low and the transfer reactions normally associated with classical free radical polymerization is negligible. We noticed that each of the polystyrene (PS) macromolecules made from ATRP is capped with a halogen terminal group; it can be further used as the macro-initiator to prepare block copolymers.

We herein present a route to diblock copolymer PS-*b*-poly(*tert*-butyl methacrylate) (PS-*b*-PtBMA) by means of ATRP, in which styrene (St) was used as the first monomer to prepare the macro-initiator with halogen terminal group (PS-Br) and *tert*-butyl mathacrylate (tBMA) as the second monomer. Then the amphiphilic diblock copolymer, PS-*b*-PMAA, can be obtained by means of the hydrolysis of aforementioned copolymer under acid condition.

EXPERIMENTAL

Materials

St was distilled in high vacuum and stored in a brown glass bottle under 5°C. tBMA (BASF, un-

stabilized) was fractionated from CaH_2 over a 1-m column with Sulzer packing at 45 mbar. After degassing, the distillate was stirred over CaH_2, degassed, and distilled in high vacuum before use. 1-Bromoethyl benzene (1-PEBr) (ACROS) was distilled and stored in a brown glass bottle under 5°C. CuCl was washed with acetone several times until it became light yellow, and was stored in a brown glass bottle. 2,2′-Bipyridyl (bpy) (99%), tetrahydrofuran (THF) (99.9%), cyclohexanone (99.5%), methanol (99.5%), and petroleum ether (b.p. 90°C, 99%) were used directly without further purification.

Polymerization

Synthesis of Macroinitiator PS-Br

The polymerization of styrene was performed by the following typical procedures: 1-PEBr, CuCl, and bpy ([1-PEBr]/[CuCl]/[bpy] = 1:1:3) were added to a reactor. Then the reactor was sealed and purged with N_2 and vacuumized; after three repetitions, a predetermined amount of St was added with syringe under N_2. The reactor was placed in a preheated and thermally regulated oil bath at 120°C. After 16 h, the reactor was removed from the oil bath and allowed to cool to room temperature. About 50 mL THF was added. The mixture was stirred at room temperature for several hours to complete the dissolution of the polymer. The resulting solution was filtered to remove the insoluble salts. The light yellow solution was concentrated and precipitated into a solution of methanol/water (v/v = 1:1). The light
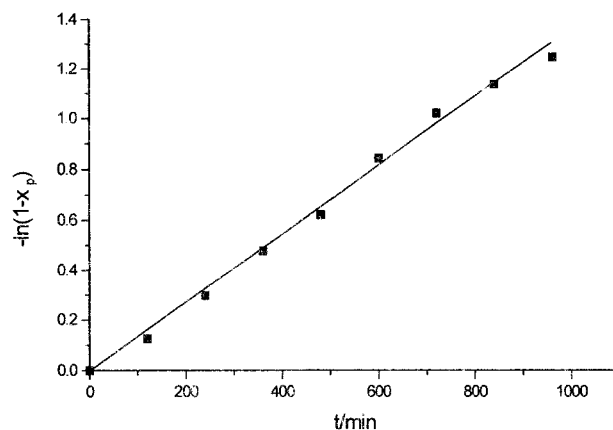
Figure 2 First-order time-conversion plot in the bulk ATRP of St initiated by 1-PEBr/CuCl/bpy at 135°C. Polymerization conditions: [St] = 48 mmol; [1-PEBr] = 0.3 mmol; [1-PEBr]/[CuCl]/[bpy] = 1:1:3.

Table I   Average Molecular Weight and Br Contents of PS-Br

	Entry No.				
	1	2	3	4	5
$\overline{M}_{n,\,\text{th}}$	5000	10,000	15,000	20,000	25,000
$\overline{M}_{n,\,\text{GPC}}$	3533	6740	10,660	15,268	19,638
$\overline{M}_w/\overline{M}_n$	1.24	1.13	1.12	1.15	1.19
Theoretical Br content (%)	2.262	1.185	0.750	0.523	0.407
Br content (%)	2.31	1.22	0.78	0.50	0.41

brown precipitate was reprecipitated. The resulting white powder was dried in vacuum at 40°C for about 24 h.

Synthesis of Diblock Copolymer PS-*b*-PtBMA

To a reactor, the macro-initiator PS-Br, CuCl, and bpy ([PS-Br]/[CuCl]/[bpy] = 1:1:3) were added. Then the reactor was purged with N_2 and vacuumized. After three repetitions, a predetermined amount of tBMA and 20 mL cyclohexanone were added with an injector under N_2. The reactor was placed in a preheated and thermally regulated oil bath at 85°C. After 24 h, the reactor was removed from the oil bath and allowed to cool to room temperature. Twenty milliliters of cyclohexanone was added. The solution was filtered to remove the insoluble salts. The light yellow solution was concentrated and precipitated into methanol. The light brown precipitate was reprecipitated. The resulting white powder was dried in vacuum at 40°C for about 24 h.

Hydrolysis[16]

One gram PS-*b*-PtBMA was dissolved into the solution of 10 mL HCl in 90 mL methanol, and heated under reflux for 24 h. The resulting solution was filtered to remove the insoluble impurities. The light yellow solution was concentrated and precipitated into petroleum ether. The resulting white powder was dried in vacuum at 40°C for about 24 h. The hydrolytic degree of ester groups was determined by the titration of carboxyl with tetramethylammonium hydroxide as titrant.

Characterization

Gas permeation chromatography (GPC) measurements were performed at room temperature in THF using PE Series 200 GPC meter with 5-μm PSt-gel columns (column set: 100 Å, 10^4 Å linear,

60 cm each) at a flow rate of 1.0 mL/min. Detectors: RI (Bischoff 8110). The column set was calibrated with PS standards.

Infrared (IR) measurements were performed at room temperature using a PE Pargon 1000 infrared spectrophotometer. Nuclear magnetic resonance (NMR) measurements were performed using the BRUKER AVANCE 500 NMR spectrometer.

Br content was measured by the oxygen flask method.[17]

RESULTS AND DISCUSSION

The ATRP of St using organic halide as initiator has been reported by Wang and Matyjaszewski.[15] Our experimental data also verify that this polymerization can be well controlled. So every resulting macromolecule possesses a halogen group (Cl or Br) at the chain end. This conclusion can be verified by the ^{1}H-NMR spectrum of the prepolymer. In Figure 1, signals were observed at 1.3 ~ 1.9 ppm, originating from the methene and methine protons of the main chain. The signals at
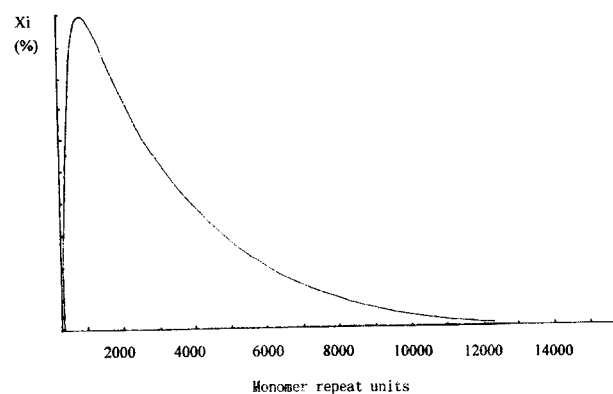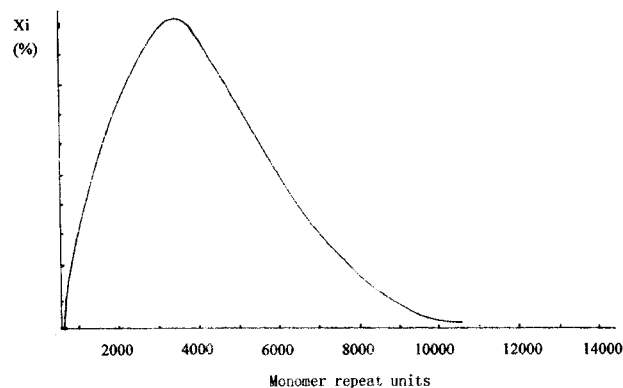
Figure 3   GPC curve of PS-Br (Sample 1 of Table I).
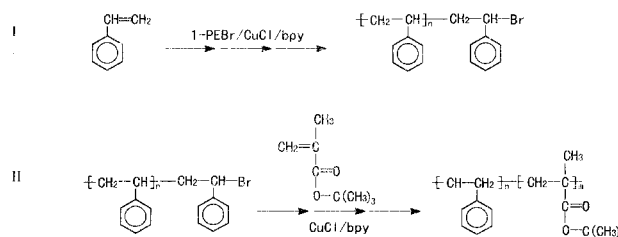
Scheme 1 Synthesis procedure of PS-*b*-PtBMA.

Figure 4 GPC curve of PS-*b*-PtBMA (Sample 6 of Table II).

6.4 ∼ 7.2 ppm were assigned to the aromatic protons on the benzene rings. The broad double peaks at 4.4 ppm are attributed to the bromine end group. Because there is only one bromine atom in a prepolymer chain, the peaks at 4.4 ppm are rather small. Evidently, the prepolymer obtained can be used as the macro-initiator in ATRP, which can initiate the polymerization of the second monomer. Figure 2 shows the first-order kinetic plot for the polymerization of St in bulk initiated with 1-PEBr in the presence of CuCl/bpy at 120°C. The linearity of the first-order kinetic plot indicates that the number of active species in this system remains constant. We designed and synthesized a series of PS-Br with various number average molecular weights. Table I reveals the regular increase of number average molecular weights of PS-Br measured by GPC. From Table I it can be seen that the number average molecular weight of PS-Br varies in accordance with the predetermined design, but lower than the theoretical one because of the incomplete reaction in bulk polymerization. The molecular weight distributions are very narrow ($\bar{M}_w/\bar{M}_n \leq 1.24$; see Table I and Fig. 3).

Because the double peaks of the bromine end group at 4.4 ppm in Figure 1 are too small to calculate the Br contents, we used the chemical analysis to determine the Br contents in the PS-Br. The data determined by chemical analysis are listed in Table I. These data show that there is a

Br end group in every PS-Br macromolecular chain, so it can be further used as the macro-initiator in ATRP. Using tBMA as the second monomer, we synthesized the diblock copolymer, PS-*b*-PtBMA, by means of ATRP. Scheme 1 shows the synthesis procedure of PS-*b*-PtBMA diblock copolymer. Table II lists various average molecular weights of PS-Br used and those of respective diblock copolymers (PS-*b*-PtBMA) formed. The data in Table II show that the number average molecular weight of the diblock copolymer approaches to the designed molecular weight, although the molecular weight distribution becomes slightly broader than the prepolymer. However, we do not find shoulder peaks in the GPC curve of PS-*b*-PtBMA (see Fig. 4). These experimental results indicate that the block copolymerization of tBMA with PS-Br as the macro-initiator has been implemented successfully.

Figure 5 shows the IR spectra of PS-Br and diblock copolymer PS-*b*-PtBMA. In Figure 5(a), it can be found that there are absorption peaks of extension vibration of —C—H on the benzene ring at 3020.2 ∼ 3081.8 cm⁻¹, framework of benzene ring at 1452.0 ∼ 1601.0 cm⁻¹, and absorption peaks of bending vibration of —C—H on the

Table II   Average Molecular Weights of PS-Br and Corresponding Diblock Copolymer PS-*b*-PtBMA

	Entry No.				
	6	7	8	9	10
$\bar{M}_{n,\,\text{GPC}}$ of PS-Br	3533	6740	10,660	15,268	19,638
$\bar{M}_{n,\,\text{th}}$ of diblock copolymer	7100	13,500	21,000	26,720	34,400
$\bar{M}_{n,\,\text{GPC}}$ of diblock copolymer	7937	13,724	21,680	27,219	32,095
$\bar{M}_w/\bar{M}_n$ of diblock copolymer	1.32	1.20	1.15	1.14	1.16

(a)

(b)
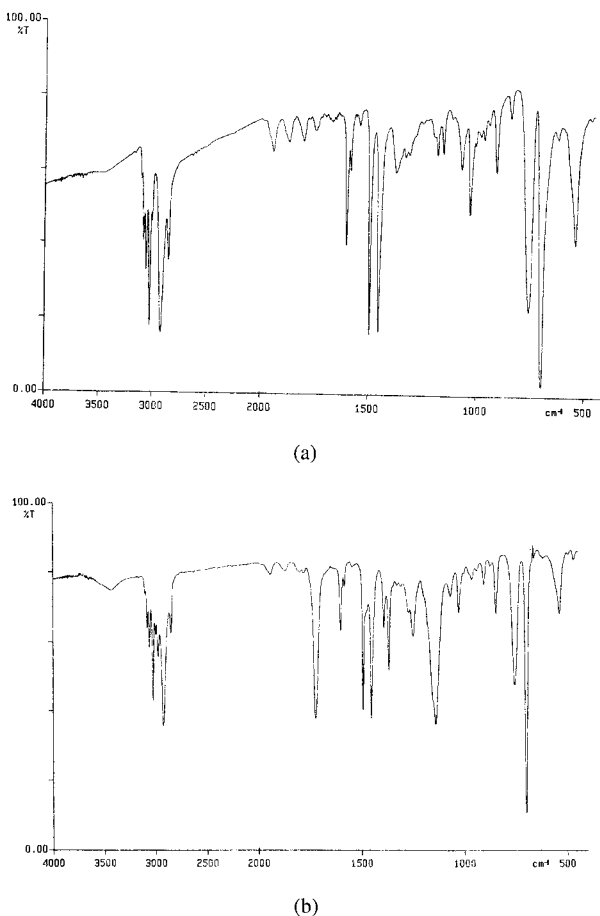
Figure 5 (a) IR spectrum of PS obtained by the bulk ATRP (Sample 1 of Table I). (b) IR spectrum of diblock copolymer PS-*b*-PtBMA obtained by the ATRP (Sample 6 of Table II).

benzene ring at 697.2, 757.0 cm^{-1}. In Figure 5(b), the aforementioned absorption peaks remain. In the meantime, there are absorption peaks of extension vibration of C=O at 1722.8 cm^{-1}, the double absorption peaks of bending vibration of —C(CH$_3$)$_3$ at 1392.1 and 1367.6 cm^{-1}, and the double absorption peaks of extension vibration of C—O—C at 1249.8 and 1139.5cm^{-1}. These experimental results demonstrate that the diblock copolymer of PS-*b*-PtBMA has been actually obtained by way of ATRP.

The hydrolysis of PtBMA chains was performed mildly in the solution of 10 mL HCl (concentration: 35%) in 90 mL methanol. Under given reaction conditions, the conversion of *tert*-butyl groups was more than 95% after reaction for 24 h. PS-*b*-PMAA is a special amphiphilic material, which dissolves neither in organic solvents nor in water. So it is impossible to measure the molecu-

lar weight and its distribution of PS-*b*-PMAA by GPC. Fortunately, the molecular weight and its distribution of the pre-copolymer, PS-*b*-PtBMA, has been carefully determined, from which the molecular weight of PS-*b*-PMAA can be estimated because the main chains do not degrade and only the side ester groups hydrolyze into carboxylic acids during hydrolysis. The conversion of *tert*-butyl groups is more than 95% as mentioned; therefore, the molecular weight of PS-*b*-PMAA (sample 10, for example) mediates between 27,270 ~ 27,510. The molecular weights of other PS-*b*-PMAA samples can be calculated with a similar approach and are omitted here.

Figure 6 shows the IR spectrum of the amphiphilic diblock copolymer PS-*b*-PMAA (the product of hydrolysis of PS-*b*-PtBMA). From Figure 6, we know that the absorption peaks of bending vibration of —C(CH$_3$)$_3$ at 1392.1 cm^{-1} and the double absorption peaks of extension vibration of C—O—C at 1249.8 and 1139.5 cm^{-1} become distinctly weak. Contrarily, the absorption peak of extension vibration of C=O at 1702.7cm^{-1} is strengthened. At 3500 ~ 2500 cm^{-1}, a very strong peak appears, which is caused by the extension vibration of —OH and their hydrogen-bonded effect. These data indicate that most part of *tert*-butyl groups in the copolymer have successfully transformed into the carboxyl groups. Therefore, the structure of amphiphilic diblock copolymer PS-*b*-PMAA can be affirmed.

CONCLUSION

A new approach to amphiphilic diblock copolymers was developed in this work. Using PS-Br
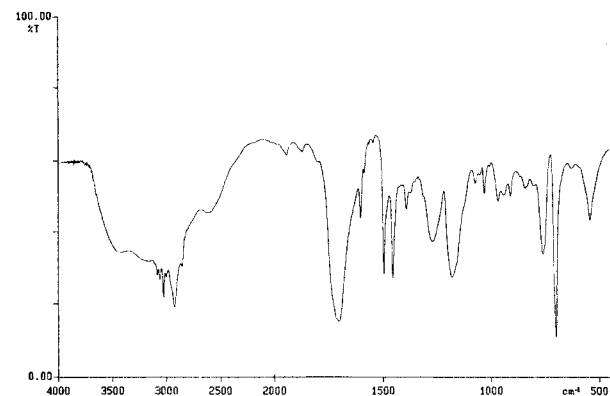
Figure 6 IR spectrum of the amphiphilic diblock copolymer PS-*b*-PMAA.

prepared by ATRP as the macro-initiator, a diblock copolymer PS-*b*-PtBMA has been synthesized by means of ATRP once more. The amphiphilic diblock copolymer PS-*b*-PMAA can be further obtained by hydrolysis of PS-*b*-PtBMA in the acid condition. The number average molecular weight and the structure of the aforementioned copolymers have been characterized with GPC, IR, and NMR.

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