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Synthesis of polystyrene-*block*-polycarbonate-*block*-polystyrene and polycarbonate-*graft*-polystyrene using tandem condensation polymerization and atom transfer radical polymerization

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Summary

Polystyrene-*block*-polycarbonate-*block*-polystyrene was synthesized by atom transfer radical polymerization of styrene using polycarbonate having two 2-bromoisobutyryloxy end groups as the macroinitiator, which was prepared by condensation polymerization of bisphenol A with triphosgene in the presence of chain-stopper, 2-(4-hydroxyphenyl)-2-(4-(2-bromoisobutyryloxy)phenyl)propane. While polycarbonate-*graft*-polystyrene was synthesized by atom transfer radical polymerization of styrene using polycarbonate having 2-bromoisobutyryloxy side groups as the macroinitiator, which was prepared by condensation of bisphenol A and 1,1-bis(4-hydroxyphenyl)-1-(4-(2-bromoisobutyryloxy)phenyl)ethane with triphosgene. The molecular weights of polystyrene block or graft chains increased linearly with monomer conversion, and their polydispersities were low throughout the blocking or grafting polymerization process.

Introduction

Block and graft copolymers containing sequences of styrene and bisphenol-A carbonate have gained some interests as materials for optical data storage [1] or as compatibilizers in polycarbonate (PC)/polystyrene (PS) blends. In the literature, several methods about the synthesis of PC/PS block and graft copolymers have been reported. For example, Polowinska and Berti *et al.* prepared PC-b-PS by treating polycarbonate with living polystyryllithium [2,3]. Dems *et al.* prepared PC-b-PS multiblock copolymers by condensation polymerization of prepolymer of PC having hydroxyl end groups with prepolymers of PS having reactive chloroformyl (-COCl) end groups [4]. Doi *et al.* used photochemical technique to synthesize block copolymers of PC and polymers of vinyl monomers by the incorporation of benzoin methyl ether in the PC main chain [5]. Bohrbach *et al.* prepared PC-g-PS using the macromonomer technique, i. e., copolymerization of polystyrene macromonomer carrying aromatic hydroxyl functions with bisphenol-A and triphosgene [6]. Pu *et al.*

prepared PC-g-PS by radiation grafting of styrene onto PC [7]. The other methods include using polycarbonate macroinitiators containing azo or peroxy groups to initiate conventional free radical polymerization. However, in the above examples, the reaction conditions were stringent, or the copolymer architectures were not well controlled.

Living free radical polymerization techniques provide a convenient way to prepare block copolymers with well-defined structures by combining living free radical polymerization with condensation polymerization [8-11]. For example, Matyjaszewski *et al.* prepared well-defined ABA block copolymers of styrene with polysulfone and polyester by atom transfer radical polymerization through attachment of the reactive initiating species to the ends of step growth polymers [9]. Knauss *et al.* studied the synthesis of nitroxyl-functionlized phenols which may function as chain-stoppers during the preparation of polycarbonates [10,11]. Korn *et al.* synthesized telechelic polycarbonates as precursors to ABA triblock copolymers via living free radical polymerization by carbonate-corbonate interchange reaction between polycarbonates and functional low molecular weight diarylcarbonates [12]. In this paper we report the synthesis of block and graft copolymers of polycarbonate and polystyrene through the combination of condensation polymerization between bisphenol A and triphosgene and living free radical polymerization of styrene via ATRP.

Experimental

Materials

Bisphenol A (Tianjing Chemical Regent Center) was recrystallized from toluene and dried under vacuum. Styrene (Yanshan Petrochemical Co.) was dried over anhydrous magnesium sulfate, then distilled under reduced pressure and stored at –15°C. Copper(I) bromide (CuBr) (Shanghai Zhenxing Chemical Regent Factory) was stirred in glacial acetic acid, filtered, and washed with acetone. The solid was dried under vacuum at room temperature overnight. Pyridine was stirred over anhydrous magnesium sulfate and filtered just prior to use. All solvents were dried over anhydrous magnesium sulfate. 1,1,1-tris(4-hydroxyphenyl)ethane (Aldrich), triphosgene (Huangshan Chemical Plant), 2-bromoisobutyryl bromide (Aldrich), and N,N,N',N",N"-pentamethyldiethylenetriamine (PMDETA) (Aldrich) were used without any further purification.

*2-(4-hydroxyphenyl)-2-(4-(2-bromoisobutyryloxy)phenyl)propane (**1**)*

A 500 mL three-neck round-bottom flask equipped with a magnetic stirrer was charged with 80.15 g (0.35 mol) of bisphenol A, 40 mL of pyridine and 240 mL of methlene chloride. The flask was fitted with a pressure equalizing addition funnel, which itself was charged with 23 g (0.10 mol) of 2-bromoisobutyryl bromide and 30 mL of methlene chloride. The reactor was cooled to 0°C in an ice/water bath and 2-bromoisobutyryl bromide solution was added dropwise under argon. The reaction mixture was stirred at room temperature overnight, 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 hexane, acetone and methlene chloride (5/3/2, volume ratio) and passed through a silica gel column prepared with the same solvent, collecting the first fraction. The solvent was removed by rotary evaporation, and the white solid was dried under vacuum overnight at 35°C. Yield = 25.5g.

*1,1-bis(4-hydroxyphenyl)-1-(4-(2-bromoisobutyryloxy)phenyl)ethane (**2**)*

A 500 mL three-neck round-bottom flask was charged with 23 g (75 mmol) of 1,1,1-tris(4-hydroxyphenyl)ethane, 35 mL of pyridine and 170 mL of methlene chloride. 7.2 g (75 mmol) of 2-bromoisobutyryl bromide and 30mL of methlene chloride were added dropwise through a pressure equalizing addition funnel under argon at 0°C in an ice/water bath. The reaction mixture was stirred at room temperature overnight, washed first with 0.1 N hydrochloric acid and then with distilled water. The organic phase was dried with anhydrous magnesium sulfate overnight. After the solvent was removed by rotary evaporation, the crude product was dissolved in a mixture of hexane and ethyl acetate (5/4, volume ratio) and passed through a silica gel column prepared with the same solvent, collecting the third fraction. The solvent was removed, and the white solid was dried under vacuum overnight. Yield = 20.5 g.

Synthesis of PC macroinitiator with two 2-bromoisobutyryloxy end groups

To a 500 mL three-neck round-bottom flask was added 0.68 g (1.8 mmol) of **1**, 9.27 g (40.5 mmol) of bisphenol A, 10 mL of pyridine, 170 mL of methlene chloride, and a magnetic stirrer. To the magnetically stirred mixture cooled to 0°C in an ice/water bath was added dropwise 4.46 g (15 mmol) of triphosgene in 30 mL of methlene chloride, and stirring was continued for 24 hours at room temperature. The salt was removed by filtration, and the PC macroinitiator with 2-bromoisobutyryloxy end groups at both ends was precipitated into a large amount of cold methanol and dried under vacuum.

Synthesis of PC macroinitiator with 2-bromoisobutyryloxy side groups

To a 100 mL three-neck round-bottom flask was added 1.36 g (3 mmol) of **2**, 2.75 g (12 mmol) of bisphenol A, 5 mL of pyridine, 50 mL of methlene chloride, and a magnetic stirrer. To the magnetically stirred mixture cooled to 0°C in an ice/water bath was added dropwise 1.48 g (5 mmol) of triphosgene in 15 mL of methlene chloride, and stirring was continued for 24 hours at room temperature. The salt was removed by filtration, and the PC macroinitiator with 2-bromoisobutyryloxy side groups was precipitated into a large amount of cold methanol and dried under vacuum for 24h.

Blocking or grafting polymerization of styrene via ATRP with PC macroinitiator

The general procedure is as follows: The macroinitiator, PMDETA and CuBr were added to a 100 mL three-neck round-bottom flask equipped with a stirring bar. After sealing it with rubber stopples, the flask was degassed and back-filled with argon three times and then left under argon. Deoxygenated monomer and solvent were added to dissolve the macroinitiator. After the macroinitiator had been dissolved, the flask was immersed in an oil bath thermostated at 110°C. At timed intervals, samples were withdrawn from the flask using degassed syringes to determine monomer conversion

and molecular weight.

Hydrolysis of block or graft copolymer

The block or graft copolymer was added to a flask and dissolved in THF. Then, a small amount of KOH (ethanol solution) was added. The solution was refluxed for 3 days. The solution was concentrated by rotating evaporation of THF. Then, the polymer was precipitated from pure methanol and dried under vacuum.

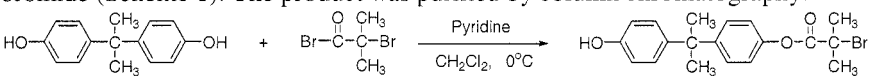
Characterization

Monomer conversion was obtained gravimetrically. Molecular weights and molecular weight distributions of PC macroinitiator, block or graft copolymers, and polystyrene block or graft chains 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 eluant was THF and the flow rate was 1 mL/min. Narrow polystyrene standards were used to generate the calibration curve. Elemental analysis was carried out on Carlo erda 1106 elemental analyzer. ^{1}H NMR spectra were obtained using a Bruker AC 400 NMR spectrometer. $CDCl_3$ was used as solvent.

Results and Discussion

1. Synthesis of functional chain-stopper.

The functional chain-stopper for the condensation polymerization of bisphenol A and triphosgene was prepared by the reaction between bisphenol A and 2-bromoisobutyryl bromide (Scheme 1). The product was purified by column chromatography.



Scheme 1. Synthesis of -(4-hydroxyphenyl)-2-(4-(2-bromoisobutyryloxy)phenyl)propane (**1**).

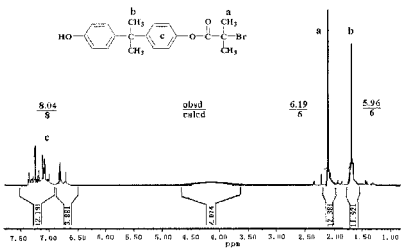


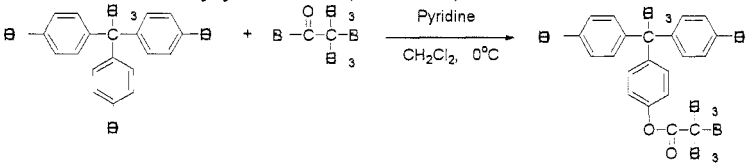
Figure 1. ^{1}H NMR spectrum of 2-(4-hydroxyphenyl)-2-(4-(2-bromoisobutyryloxy) phenyl)propane (**1**).

Figure 1 shows the ^{1}H NMR spectrum of the first fraction. The methyl protons of 2-bromoisobutyryloxy $(CH_3)_2CBrCOO$- and those of bisphenol A $-C(CH_3)_2$- were seen at 2.1 ppm and 1.6 ppm, respectively, while the signal between 6.7 ppm to 7.2 ppm was assigned to the protons of phenyl group of bisphenol A. The observed peak intensity ratios of the signals were in good agreement with the calculated values, confirming the formation of chain-stopper, **1**. To further confirm the formation of **1**, its chemical composition was determined on an elemental analyzer. The found values

(C, 60.42; H, 5.48; O, 12.80.) were also in good agreement with the calculated ones (C, 60.48; H, 5.57; O, 12.73; Br, 21.22.).

2. Synthesis of functional monomer.

The functional monomer for condensation polymerization of bisphenol A and triphosgene was prepared by the reaction between 1,1,1-tris(4-hydroxyphenyl)ethane and 2-bromoisobutyryl bromide (Scheme 2).



Scheme 2. Synthesis of 1,1-bis(4-hydroxyphenyl)-1-(4-(2-bromoisobutyryloxy)phenyl)ethane(**2**)

The product was purified by column chromatography, and four fractions were collected. Figure 2 compares the GPC curves for the four fractions and the reactant, 1,1,1-tris(4-hydroxyphenyl)ethane. In this experiment, three high-resolution columns Styragel HR0.5, HR1 and HR3 were used. It can be seen that the fourth fraction is nonreacted 1,1,1-tris(4-hydroxyphenyl)ethane, and that the third, second and first fractions should be **2**, 1-(4-hydroxyphenyl)-1,1-bis(4-(2-bromoisobutyryloxy)phenyl) ethane, and 1,1,1-tris(4-(2-bromoisobutyryloxy)phenyl)ethane, respectively.

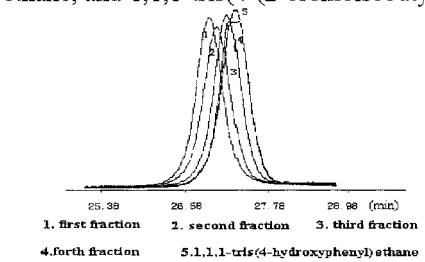


Figure 2. GPC curves for the four fractions and 1,1,1-tris(4-hydroxyphenyl)ethane.

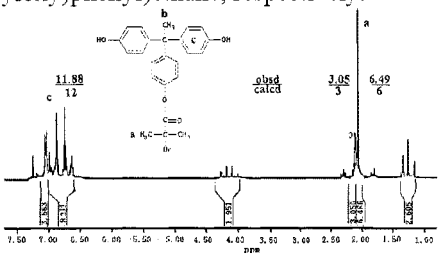


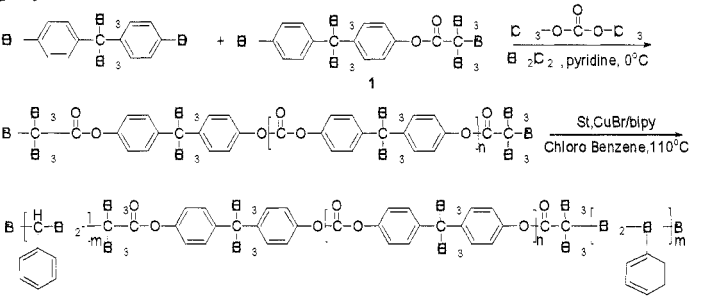
Figure 3. ^{1}H NMR spectrum of **2**.

Figure 3 is the ^{1}H NMR spectrum of the third fraction. The methyl protons of 2-bromoisobutyryloxy $(CH_3)_2CBrCOO$- and those of 1,1,1-tris(4-hydroxyphenyl)ethane $-C(CH_3)$ were seen at 2.04 ppm and 2.08 ppm, respectively, while the signal between 6.7 ppm to 7.2 ppm was assigned to the protons of phenyl group of 1,1,1-tris(4-hydroxyphenyl)ethane. The observed peak intensity ratios of the signals were in good agreement with the calculated values, confirming that the third fraction was **2**. Furthermore, the found chemical composition (C, 63.38; H, 5.12; O, 14.22.) was also in good agreement with the calculated one (C, 63.30; H, 5.05; O, 14.07; Br, 17.58.).

3. Synthesis of PS-b-PC-b-PS triblock copolymers via ATRP by the PC macroinitiator with 2-bromoisobutyryloxy end groups.

The condensation polymerization between bisphenol A and triphosgene in the presence of chain-stopper **1** will generate polycarbonate with two 2-bromoisobutyryloxy end groups at both ends as illustrated in Scheme 3.

The proton NMR spectrum of this polycarbonate is displayed in Figure 4. According to the peak intensity ratio of the peak at 2.1 ppm and the peak at 1.6 ppm, and assuming that there was one 2-bromoisobutyryloxy end-group at each end of polycarbonate chain, the number average molecular weight was calculated to be 6770. While the number average molecular weight determined by GPC calibrated with narrow polystyrene standards was 10490 (Mw/Mn = 1.77.). After further calibration with the K and α values of the Mark-Houwink equation for polycarbonate in THF [13], the real number average molecular weight for polycarbonate macroinitiator was equal to 6400. This value was in good agreement with that obtained by ^{1}H NMR, showing that there is indeed one 2-bromoisobutyryloxy end-group at each end of polycarbonate chain.



Scheme 3. Synthesis of PC macroinitiator with 2-bromoisobutyryloxy end groups and PS-b-PC-b-PS triblock copolymers.

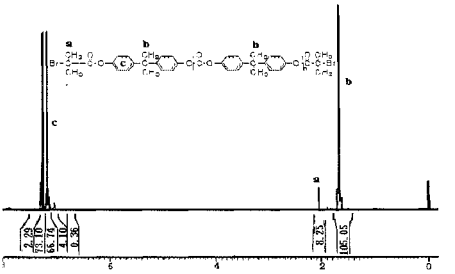


Figure 4. ^{1}H NMR spectrum of PC macroinitiator with 2-bromoisobutyryloxy end groups.

It is well known that ethyl 2-bromoisobutyrate is an excellent initiator for ATRP of styrene with high initiating efficiency, therefore, the polycarbonate with 2-bromoisobutyryloxy end groups obtained above was used to initiate ATRP of styrene in order to prepare PS-b-PC-b-PS triblock copolymers. The molecular weight distributions of the resulting block copolymers at different styrene conversions are shown in Figure 5. It can be seen that the molecular weight distribution shifts to higher molecular weights without any trace of the PC macroinitiator, indicating that efficient initiation has taken place.

In order to show that the blocking polymerization of styrene via ATRP proceeded in a living fashion, the PC central block was hydrolyzed, and the molecular weights of polystyrene outer blocks were determined by GPC. Figure 6 shows that the number average molecular weight increased linearly with monomer conversion and agreed well with the calculated ones based on the assumption that one initiating site generates one polystyrene chain, and that the polydispersity was relatively low throughout the polymerization process. These results showed that the blocking polymerization was

indeed a living or controlled process.

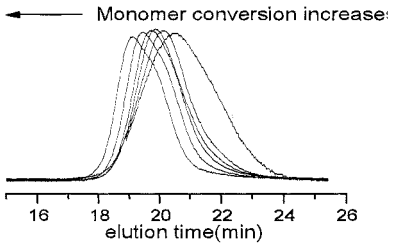


Figure 5. GPC curves of PS-b-PC-b-PS triblock copolymers at different monomer conversions. Reaction conditions: PC macroinitiator, 10.3 g, 1.78 mmol; CuBr, 3 mmol; PMDETA, 4.5 mmol; St, 75 g; chlorobenzene, 75 g; temperature,110°C.

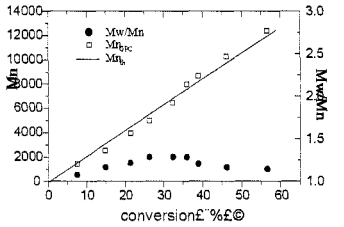
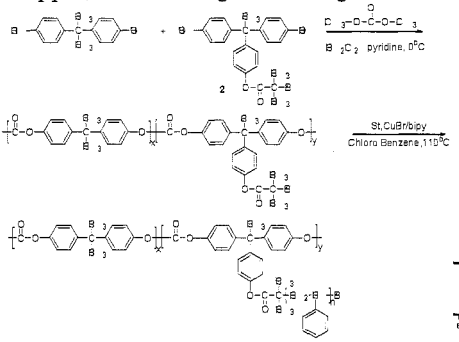


Figure 6. Conversion dependence of Mn and Mw/Mn for polystyrene outer block of PS-b-PC-b-PS.

4. Synthesis of PC-g-PS graft copolymers via ATRP by the PC macroinitiator with 2-bromoisobutyryloxy side groups.

PC-g-PS graft copolymers were synthesized via ATRP of styrene using PC with 2-bromoisobutyryloxy side groups as the macroinitiator. This macroinitiator was prepared by condensation polymerization of bisphenol A and **2** with triphosgene as illustrated in Scheme 4.

The number average molecular weight of this macroinitiator determined by GPC after calibrated with Mark-Houwink equation of polycarbonate was 3930, and the polydispersity was 1.68. Figure 7 shows the proton NMR spectrum of this macroinitiator. From the peak intensity ratio of the peak at 2.05 ppm and the peak at 1.6 ppm, the initiating sites along the macroinitiator chain were calculated to be 3.0



Scheme 4. Synthesis of PC macroinitiator having 2-bromoisobutyryloxy side groups and PC-g-PS graft copolymer.

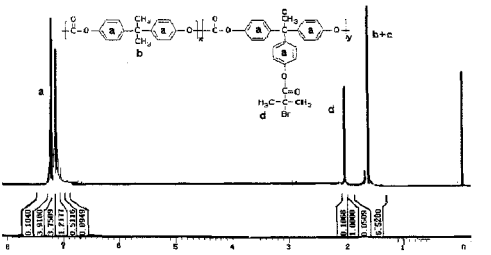


Figure 7. ^{1}H NMR spectrum of PC macroinitiator with 2-bromoisobutyryloxy side groups.

To determine the extent of control for the free radical grafting process by ATRP, the individual grafted polystyrene chains were also cleaved from PC backbones by hydrolysis. Figure 8 shows that the number average molecular weight of grafted

polystyrene chain increased linearly with monomer conversion and agreed well with the calculated ones based on the assumption that one initiating site generates one polystyrene chain, and that the polydispersity was relatively low throughout the polymerization process. These results demonstrate that the synthesized graft copolymer exhibits the expected structure.

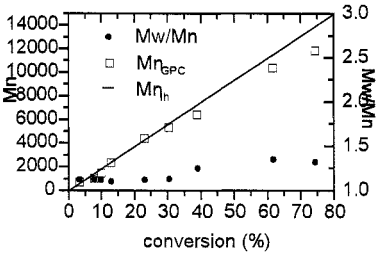


Figure 8. Conversion dependence of Mn and Mw/Mn for polystyrene graft of PC-g-PS. Reaction conditions: PC macroinitiator, 1.86 g, 0.33 mmol; CuBr, 1 mmol; PMDETA, 1.5 mmol; St, 20 g; chlorobenzene, 40 g; temperature,110°C.

Conclusions

Polystyrene-*block*-polycarbonate-*block*-polystyrene and polycarbonate-*graft*-polystyrene with well-defined structures were successfully prepared through atom transfer radical polymerization of styrene using polycarbonate macroinitiators. Polycarbonate macroinitiator having two 2-bromoisobutyryloxy end groups for triblock copolymer synthesis was synthesized by condensation polymerization of bisphenol A with triphosgene in the presence of a chain-stopper, 2-(4-hydroxyphenyl)-2-(4-(2-bromoisobutyryloxy)phenyl)propane. While polycarbonate macroinitiator having 2-bromoisobutyryloxy side groups for graft copolymer synthesis was synthesized by condensation copolymerization of bisphenol A and 1,1-bis(4-hydroxyphenyl)-1-(4-(2-bromoisobutyryloxy)phenyl)ethane with triphosgene.

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