

## SYNTHESIS OF BLOCK COPOLYMER BY INTEGRATED LIVING ANIONIC POLYMERIZATION-ATOM TRANSFER RADICAL POLYMERIZATION (ATRP)\*

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**Abstract** Alpha-trichloroacetoxy terminated polystyrene oligomer ( $\text{PS-CH}_2\text{CH}_2\text{OCOCCL}_3$ ) and poly-(styrene-*b*-butadiene) oligomer [ $\text{P(S-}b\text{-B)-CH}_2\text{CH}_2\text{OCOCCL}_3$ ] were synthesized by living anionic polymerization using *n*-butyllithium as initiator. Then the  $\text{PS-CH}_2\text{CH}_2\text{OCOCCL}_3$  ( $\text{PS-Cl}_3$ ) or  $\text{P(S-}b\text{-B)-CH}_2\text{CH}_2\text{O-COCCL}_3$  ( $\text{PSB-Cl}_3$ ) was used as the macroinitiator in the polymerization of (meth)acrylates in the presence of  $\text{CuX/bpy}$ . AB diblock and ABC triblock copolymers were prepared by the integrated living anionic polymerization (LAP)-atom transfer radical polymerization (ATRP). The structures of the  $\text{PSB-Cl}_3$  and the  $\text{P(S-}b\text{-MMA)}$  were identified by FTIR and  $^1\text{H-NMR}$  spectrum, respectively. A new way to design block copolymers (the combination of LAP and ATRP) was developed.

**Keywords** Living anionic polymerization, Atom transfer radical polymerization, Block copolymer

### INTRODUCTION

Although living anionic polymerization (LAP) provides a methodology for the controlled polymerization of styrene and dienes, the polymerization of acrylic monomers still has to be carried out under strict conditions such as at very low temperature or in the presence of ligands<sup>[1]</sup>. In order to obtain the block copolymers containing the polar monomer units, many researchers have tried to combine two different polymerization mechanisms. For example, Hazer and his coworkers<sup>[2]</sup> synthesized poly(styrene-*b*-methyl methacrylate) [ $\text{P(S-}b\text{-MMA)}$ ] by using anion-to-radical transformation, but the polydispersity of the second block polymer can not be well controlled. Huang and his coworkers reported<sup>[3, 4, 5]</sup> the syntheses of poly(ethylene oxide-*b*-styrene) and poly(ethylene oxide-*b*-acrylonitrile) by the transformation of living anionic polymerization (LAP) to charge transfer polymerization (CTP).

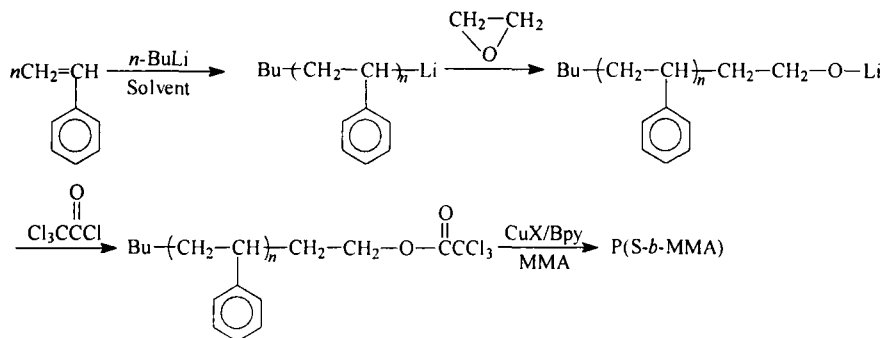
Recently, the extension of atom transfer radical addition to ATRP has allowed us to perform the "living"/controlled radical polymerization<sup>[6]</sup>. By ATRP, using  $\text{RX/CuX/2,2'-bipyridine}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) as the initiating system, the polymerization of vinyl monomers, such as (meth)acrylates, proceeds in a "living" fashion and the resulting polymers have low polydispersity ( $1.05 < M_w/M_n < 1.5$ ). Coca<sup>[7]</sup> and Chen<sup>[8]</sup> reported the syntheses of block copolymers by the combination of "living" carbocationic polymerization with ATRP.

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However, the preparation of block copolymers by the integrated LAP-ATRP has not yet been reported. This technique allows us to combine the advantages of LAP and ATRP. It has the potential to synthesize some block copolymers with extraordinary structure and performance such as ABC triblock copolymers containing polyether. The present paper reports the synthesis of block copolymers with the  $\alpha$ -trichloroacetoxy terminated polystyrene oligomer [PS-CH<sub>2</sub>CH<sub>2</sub>OCOCCl<sub>3</sub>] (PS-Cl<sub>3</sub>) or poly(styrene-*b*-butadiene) oligomer [P(S-*b*-B)-CH<sub>2</sub>CH<sub>2</sub>OCOCCl<sub>3</sub>] (PSB-Cl<sub>3</sub>) as macroinitiator in an ATRP process. The PS-Cl<sub>3</sub> and PSB-Cl<sub>3</sub> were synthesized by LAP and preconcerted with  $\alpha$ -trichloroacetoxy at their chain end. The detailed steps are shown in Scheme 1.



Scheme 1

## EXPERIMENTAL

### Chemical Reagents and Their Purification

Ethylene oxide (EO) (Shanghai Gaoqiao No. 3 Petroleum Chemical Factory) was treated with KOH for 24 h, then distilled to an ampoule under nitrogen with CaH<sub>2</sub> and stored in a refrigerator for 4 weeks. It was redistilled just before polymerization. Ligand 2,2'-bipyridine (bpy) was purified by recrystallization from *n*-hexane (A.R.). Styrene (S), Methyl methacrylate (MMA), butyl acrylate (BA) (Shanghai No. 1 Reagent Factory) were treated with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for 3 days, then distilled under reduced pressure to an ampoule under nitrogen over CaH<sub>2</sub> and stored in a refrigerator till use. Butadiene was dried over CaH<sub>2</sub> for two weeks and then purified by the addition of *n*-butyllithium. All other solvents and solid reagents were purified by conventional drying and distillation procedures. *n*-Butyllithium (*n*-BuLi) was prepared and analyzed by a known method<sup>[9]</sup>. The preparation of trichloroacetyl chloride (TCAC) was conducted according to the literature<sup>[10]</sup>.

### Preparation of PS-Cl<sub>3</sub> and PSB-Cl<sub>3</sub>

All polymerizations were carried out in a previously flamed glass reactor under a highly pure argon atmosphere. *n*-BuLi was used as initiator and benzene or cyclohexane was used as solvent. Tetrahydrofuran (THF) was used as an ether additive to speed the reaction. First, styrene was polymerized at 10°C for 1 h, and (or without) butadiene was added to the polymerization vessel at 25°C. After 2 h, the polymerization of butadiene was completed. Then, cyclohexane solutions of ethylene oxide and trichloroacetyl chloride were successively added to deactivate and to acylate the living end-group of anionic polymerization. The resulted oligomers were purified by redissolving them in toluene and reprecipitating from ethyl alcohol. They were dried under vacuum at 50°C for 72 h.

### Preparation of Block Copolymer

The polymerization was carried out in a pre-flamed flask fitted with a magnetic stirrer. The following reagents, CuCl, bpy or 1,10-phenanthroline, solvent and macroinitiator, were added to the reaction flask. The reaction solution was purged with argon for 30 min. The flask was tightly sealed with a rubber septum and the monomer was injected in by a syringe. Then the flask containing the reaction mixture was immersed with vigorous stirring in an oil thermostat. After a definite time, the flask was cooled, opened and the polymer was precipitated by adding ethyl alcohol. The resulted polymer was purified by redissolving it in toluene and reprecipitating from ethyl alcohol. It was dried under vacuum at 50°C for 72 h.

### Characterization

The raw copolymer P(S-*b*-MMA) of ATRP was purified by extraction with cyclohexane to remove PS oligomer. The  $M_n$  and polydispersity of the purified P(S-*b*-MMA) were determined with a Waters 150C gel permeation chromatograph (GPC) equipped with styragel columns and calibrated by the standard method with THF as eluant. The structure of PSB-Cl<sub>3</sub> was determined by Magna-FTIR550 and that of the purified P(S-*b*-MMA) was determined by a JEOL FX-90Q <sup>1</sup>H-NMR spectrometer with CDCl<sub>3</sub> as solvent and TMS as internal standard. The conversion of the monomer was determined gravimetrically. The chlorine content of the oligomer was determined by the sodium-naphthalene method<sup>[11]</sup>.

## RESULTS AND DISCUSSION

### Syntheses of $\alpha$ -Trichloroacetoxy Terminated PS and P(S-*b*-B) Oligomers

The  $\alpha$ -trichloroacetoxy terminated oligomers with narrow polydispersity were prepared by anionic polymerization. The results of the preparation are shown in Table 1.

**Table 1.** The results of the preparation of  $\alpha$ -trichloroacetoxy terminated oligomers<sup>a</sup>

| No. | Monomer | TCAC/ <i>n</i> -BuLi (mole ratio) | $T_a^b$ (°C) | $M_n (\times 10^{-3})$ | $M_w/M_n$ | AE (%) <sup>c</sup> |
|-----|---------|-----------------------------------|--------------|------------------------|-----------|---------------------|
| 1   | S       | 2                                 | 40           | 4.51                   | 1.14      | 62.3                |
| 2   | S       | 2                                 | 60           | 4.44                   | 1.15      | 75.8                |
| 3   | S       | 20                                | 60           | 5.44                   | 1.23      | 90.7                |
| 4   | S,B     | 20                                | 60           | 6.61                   | 1.18      | 93.2                |

a) experimental condition: Ben/Chex = 10/20 (mL/mL); [THF]/[*n*-BuLi] = 0.5 (mol/mol); [EO]/[*n*-BuLi] = 10 (mol/mol);  $V_{n\text{-BuLi}}$  = 5 mL; S:B = 5:2 (g/g); acylating time: 8 h; b)  $T_a$ : acylating temperature; c) AE:

acylating efficiency,  $AE = \frac{\text{the measured chlorine content}}{\text{the chlorine content by theory calculation}} \times 100\%$

Table 1 shows that a high acylating efficiency (AE) can be achieved when an excess amount of TCAC and an acylating temperature ( $T_a$ ) of 60°C were employed. The No. 4 experiment in Table 1 shows that the  $\alpha$ -trichloroacetoxy terminated block copolymer PSB-Cl<sub>3</sub> can also be synthesized with AE higher than 90%.

### Characterization of the $\alpha$ -Trichloroacetoxy Terminated Oligomer

Figure 1 is the FTIR spectrum of PSB-Cl<sub>3</sub> (No. 4 sample in Table 1). Compared with the standard IR spectrum of conventional PS, three characteristic bands appeared at 1740 cm<sup>-1</sup> (C=O stretching vibration), 1640 cm<sup>-1</sup> (C=C) and 680 cm<sup>-1</sup> (C—Cl of —CCl<sub>3</sub>). However, it is difficult to distinguish the characteristic C—O—C bands near 1100 cm<sup>-1</sup> because these bands are overlapped by the bands of C—H (C—H of benzene ring and the backbone of PS). Nevertheless, the bands near 1100 cm<sup>-1</sup> in Fig. 1 are different from that of the standard IR spectrum of conventional PS. Therefore, the structure of the  $\alpha$ -trichloroacetoxy terminated oligomer can be assigned to P(S-*b*-B)-CH<sub>2</sub>CH<sub>2</sub>OCOCCL<sub>3</sub>.

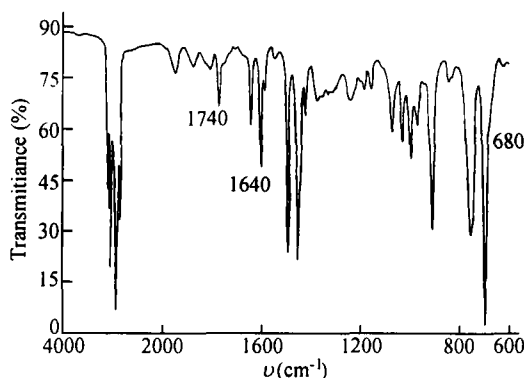


**Fig. 1** FTIR spectrum of P(S-*b*-B)-CH<sub>2</sub>CH<sub>2</sub>OCOCCL<sub>3</sub> (No. 4 sample in Table 1)

### Syntheses of Block Copolymers

In order to synthesize AB diblock and ABC triblock copolymers, ATRP was carried out with PS-Cl<sub>3</sub> or PSB-Cl<sub>3</sub> as macroinitiators. The results of the preparation are shown in Table 2.

**Table 2.** The results of ATRP with  $\alpha$ -trichloroacetoxy terminated oligomers as macroinitiators<sup>a</sup>

| No. | Monomer | The GPC results of the resulted polymer |         |                          |         | The yield of block copolymer (%) <sup>b</sup> |
|-----|---------|-----------------------------------------|---------|--------------------------|---------|-----------------------------------------------|
|     |         | $M_{n1}(\times 10^{-3})$                | $D_1^c$ | $M_{n2}(\times 10^{-3})$ | $D_2^c$ |                                               |
| 1   | MMA     | 5.2                                     | 1.25    | 31.5                     | 1.39    | 54.2                                          |
| 2   | St      | —                                       | —       | 6.59                     | 1.31    | >90                                           |
| 3   | BA      | 6.5                                     | 1.21    | 42.7                     | 1.24    | 65.3                                          |
| 4   | BA      | 6.7                                     | 1.23    | 7.94                     | 1.89    | 75.7                                          |
| 5   | BA      | —                                       | —       | 8.64                     | 1.24    | >90                                           |

a) experimental condition: the macroinitiator of No.1 is the PS-Cl<sub>3</sub> (No.3 in Table 1), the macroinitiator of No.2~5 is the PSB-Cl<sub>3</sub> (No.4 in Table 1), No.1 R-Cl<sub>3</sub>/CuCl/Bpy = 1:2:6 (mole ratio),  $T = 15^\circ\text{C}$ ,  $t = 45$  h,  $V_{\text{Xylene}}/V_{\text{MMA}} = 5/5$  (mL/mL), No.2 R-Cl<sub>3</sub>/CuCl/Bpy = 1:1:3 (mole ratio),  $T = 130^\circ\text{C}$ ,  $t = 8.5$  h,  $V_{\text{Xylene}}/V_{\text{S}} = 5/5$  (mL/mL), No.3 R-Cl<sub>3</sub>/CuCl/Bpy = 1:1:3 (mole ratio),  $T = 130^\circ\text{C}$ ,  $t = 4$  h,  $V_{\text{Xylene}}/V_{\text{BA}} = 5/5$  (mL/mL), No. 4 R-Cl<sub>3</sub>/CuCl/1,10-phenanthroline = 1:1:3 (mole ratio),  $T = 130^\circ\text{C}$ ,  $t = 19$  h,  $V_{\text{Xylene}}/V_{\text{BA}} = 20/5$  (mL/mL), No.5 R-Cl<sub>3</sub>/CuCl/Bpy = 1:1:3 (mole ratio),  $V_{\text{Diphenylether}}/V_{\text{BA}} = 20/5$  (mL/mL),  $T = 130^\circ\text{C}$ ,  $t = 10$  h; b) the yield of block copolymer = (the mass of block copolymer  $\div$  the mass of resulted polymer)  $\times 100\%$ ; c)  $D$ : molecular weight distribution

Wang *et al.*<sup>[12]</sup> reported that MMA can be polymerized at  $40^\circ\text{C}$  when acetonitrile is used as the solvent in the presence of R-X/CuCl. However, it has not been reported that the polymerization temperature of MMA in the presence of CuCl/bpy can be dropped to  $15^\circ\text{C}$  with the  $\alpha$ -trichloroacetoxy terminated oligomer as macroinitiator. Table 2 shows that the PS-Cl<sub>3</sub> macroinitiator can initiate MMA even at  $15^\circ\text{C}$  (No.1 in Table 2). When PSB-Cl<sub>3</sub> was used as macroinitiator, ABC triblock copolymer P(S-*b*-B-*b*-BA) was synthesized (No.3~5 in Table 2). When 1,10-phenanthroline was used in place of bpy, the molecular weight distribution ( $D_2$ ) of the block copolymer became wider (No. 4 in Table 2). When diphenyl ether was used as the solvent in place of xylene, there is only one peak in the GPC chromatogram of the resulted polymer and the yield of block copolymer is more than 90% (No.5 in Table 2). When styrene was used, only one peak is shown in the GPC chromatogram of the resulted polymer and the yield of block copolymer is more than 90% (No.2 in Table 2). Some of the GPC chromatograms show two peaks because not all the macroinitiators could initiate the second (or third) monomer. So the yield of the block copolymer is low.

### Characterization of the Block Copolymer Synthesized by ATRP

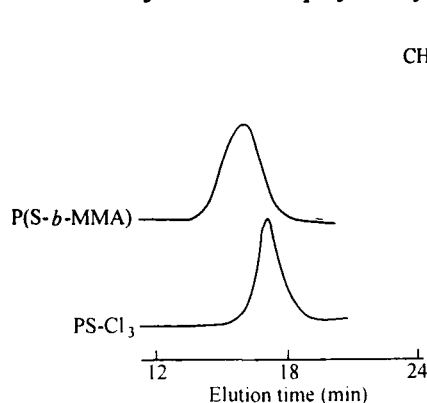


**Fig. 2** The GPC chromatogram of the macroinitiator and the P(S-*b*-MMA)

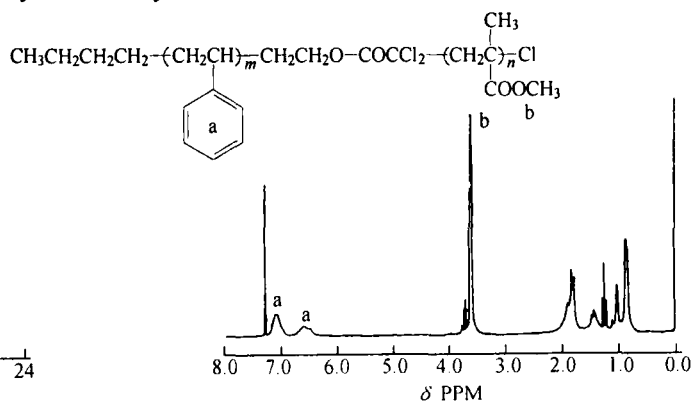


**Fig. 3** <sup>1</sup>H-NMR spectrum of P(S-*b*-MMA)

The resulted P(S-*b*-MMA) (shown in Table 2 (No.1)), which was prepared at 15°C, was chosen to show the typical results of characterization in present work. After extraction, the GPC chromatogram of the purified block copolymer shows a symmetrical peak due to the removal of uninitiated macroinitiator (in Fig. 2). The purified copolymer was characterized by <sup>1</sup>H-NMR.

In the <sup>1</sup>H-NMR spectrum of the purified copolymer (Fig. 3), the values of  $\delta$  at 3.6 (—OCH<sub>3</sub>) and 6.5~7.0 (benzene ring) indicate that the purified copolymer is a diblock copolymer composed of polystyrene and PMMA blocks.

## CONCLUSIONS

Alpha-trichloroacetoxyl terminated polystyrene oligomer (PS-Cl<sub>3</sub>) and poly(styrene-*b*-butadiene) oligomer (PSB-Cl<sub>3</sub>) were synthesized by living anionic polymerization using *n*-butyllithium as initiator. The yield of the oligomer preconverted with  $\alpha$ -trichloroacetoxyl at their chain end was more than 90%. The structure of the PSB-Cl<sub>3</sub> was identified by FTIR spectroscopy. The ATRP of S, BA and MMA can be carried out in the presence of CuX/ligand/ PS-Cl<sub>3</sub> or PSB-Cl<sub>3</sub>. The PS-Cl<sub>3</sub> macroinitiator can initiate MMA even at 15°C and the structure of the purified polymer [P(S-*b*-MMA)] was confirmed by its <sup>1</sup>H-NMR spectrum. The structure of the monomer and the solvent of ATRP have some effects on the yield of block copolymer. The yield of block copolymer can be more than 90% when the structure of monomer is BA with diphenylether as solvent or styrene with xylene as the solvent.

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