

# Synthesis of Well-Defined $(AB)_n$ Multiblock Copolymers Composed of Polystyrene and Poly(methyl methacrylate) Segments Using Specially Designed Living AB Diblock Copolymer Anion

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ABSTRACT: We have developed a new iterative methodology using  $\alpha$ -chain-end-functionalized living AB diblock copolymer anion as a key building block in order to synthesize a series of well-defined (AB)<sub>n</sub> multiblock copolymers composed of polystyrene (PS) and poly(methyl methacrylate) (PMMA). The methodology involves the following three reaction steps in the entire iterative synthetic sequence: (1) a sequential living anionic block copolymerization to prepare  $\alpha$ -chain-end-functionalized living AB diblock copolymer anion with the 3-*tert*-butyldimethylsilyloxypropyl (SiOP) group, (2) an introduction of  $\alpha$ -phenyl acrylate function (PA) via the SiOP group by deprotection followed by Mitsunobu esterification, and (3) a linking reaction of  $\alpha$ -chain-end-PA-functionalized AB diblock copolymer with  $\alpha$ -chain-end-SiOP-functionalized living AB diblock copolymer anion. The same iterative synthetic sequence involving the three reaction steps was repeated several times to successively synthesize a series of (AB)<sub>n</sub> multiblock copolymers (n = 2, 3, 4, and 5) with precisely controlled molecular weights and compositions and very narrow molecular weight distributions ( $M_w/M_n \leq 1.06$ ). Furthermore, different two series of (AB)<sub>n</sub> multiblock copolymers (n = 2 and 3) composed of PS and either poly(*tert*-butyl methacrylate) or poly(2-vinylpyridine) blocks were successfully synthesized by the same methodology using the corresponding  $\alpha$ -chain-end-SiOP-functionalized living AB block copolymer anions.

### Introduction

Recent development of living/controlled polymerization systems has allowed to synthesize a variety of architectural polymers, such as block copolymers, star-branched polymers, graft copolymers, comb-like polymers, dendrimer-like star-branched polymers, and other branched polymers with complex structures.<sup>1-14</sup> Among them, block copolymers have been widely investigated for a long time from the viewpoints of both syntheses and physical proper-ties as well as practical applications.<sup>1,15–20</sup> Since block segments are generally thermodynamically incompatible in almost all block copolymers, they are phase-separated at molecular level, followed by self-organizing, to form composition-sensitive morphological nanostructures. Morphologies of AB diblock copolymers composed of amorphous segments are now well-established as the Molau rule.<sup>21</sup> Very recently, novel characteristic morphological behaviors have been observed in the three-component ABC terpolymers, although they are more complicated due to many variables originated from the three components such as the Flory parameters between A–B, B–C, and C–A interfaces and the unit numbers of A, B, and C segments.<sup>22-32</sup> In addition to AB diblock copolymers, several two-component multiblock copolymers composed of perfectly-(AB) alternating blocks and  $(AB)_n$  blocks with additional longer blocks have been synthesized.<sup>31,33–45</sup> Although the morphological parameters of such block copolymers are limited similar to those of AB diblock copolymers, these block copolymers also show unique and interesting morphologies with ordered nanophase structures originated from the twocomponent segments connected by covalent bonds.

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In order to synthesize block copolymers with well-defined structures, the use of living polymerization is essential. Although many living/controlled polymerization systems have been developed especially in recent 25 years, the living anionic polymerization of styrene, 1,3-butadiene, isoprene, 2-vinylpyridine, and alkyl methacrylates and their derivatives with certain functional groups is still the best living polymerization system from the following features:<sup>1,46-50</sup> First, molecular weights can be precisely controlled in a wide range from  $10^3$  to even  $10^6$ . Second, extremely narrow molecular weight distributions are realized,  $M_{\rm w}/M_{\rm n}$  values being less than 1.05 or even smaller. Moreover, the resulting living polymers from these monomers have active chainend anions that are highly reactive but stable under appropriate conditions. These characteristics are ideally suited for the synthesis of well-defined block copolymers. In fact, most of welldefined AB diblock copolymers, ABC triblock terpolymers, and two-component multiblock copolymers have been successfully synthesized by using this living anionic polymerization system where the corresponding monomers are sequentially added.

A further consideration for successful design and synthesis of block copolymers is the order of monomer addition in the sequential living anionic block copolymerization mentioned above.<sup>1</sup> There is no limitation of the addition order among the monomers with similar reactivities. For instance, styrene and the structural analogous derivatives like  $\alpha$ -methylstyrene and 4-methoxystyrene, styrene and 1,3-diene monomers, 2-vinylpyridine and 4-vinylpyridine, and methyl methacrylate (MMA) and alkyl methacrylates. On the other hand, the order of monomer addition must be considered among the monomers with different reactivities. In the case to synthesize a block copolymer of styrene and MMA, for example, it is necessary first to polymerize styrene and then add MMA to polymerize to result in the block

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copolymer. As is known, MMA is much higher than styrene in reactivity in anionic polymerization because of strong electronwithdrawing effect of the carbonyl group and, on the other hand, the resulting poly(methyl methacrylate) (PMMA) chain-end enolate anion is less reactive than polystyrene (PS) chain-end anion because of the same reason. As a result, PMMA chain-end enolate anion cannot initiate the polymerization of less reactive styrene under normal conditions. This means that the synthesis of PS-*block*-PMMA is possible, but PMMA-*block*-PS cannot be synthesized by the living anionic block copolymerization with sequential monomer addition, *i.e.*, MMA first followed by addition of styrene. Accordingly, the synthesis of triblock copollymer, PS-*block*-PMMA-*block*-PS, and the multiblock copolymers composed of PS and PMMA blocks is not possible by this polymerization technique.

In order to overcome such a synthetic limitation and realize the facile synthesis of multiblock copolymers, we have herein developed a new iterative methodology using  $\alpha$ -chain-end-functionalized living AB diblock copolymer anion specially designed for the synthesis of well-defined multiblock copolymers composed of PS and PMMA blocks. As mentioned above, such multiblock copolymers cannot be synthesized by the sequential living anionic block copolymerization. Furthermore, the synthesis of different two series of multiblock copolymers composed of PS with poly-(*tert*-butyl methacrylate) (P<sup>t</sup>BMA) or poly(2-vinylpyridine) (P2VP) blocks are performed in order to demonstrate the generality and versatility of this iterative methodology. Recently, Eastwood and Dadmun have reported the possible synthesis of multiblock copolymers composed of PS and PMMA blocks by the living/controlled radical polymerization with sequential monomer addition.<sup>51,52</sup> Although the resulting polymers were undoubtedly penta- and heptablock copolymers, their molecular weight distributions were broad, the  $M_w/M_n$  values being 1.5 or even higher.

#### **Experimental Section**

Materials. All reagents were purchased from Aldrich, Japan and used as received, unless otherwise stated. Tetrahydrofuran (THF) was refluxed over sodium wire, distilled over LiAlH<sub>4</sub> under nitrogen, and then distilled from its sodium naphthalenide solution under high vacuum conditions ( $10^{-6}$  Torr). Heptane and tert-butylbenzene were washed with concentrated H<sub>2</sub>SO<sub>4</sub>, water, and aqueous NaHCO<sub>3</sub>, dried over P<sub>2</sub>O<sub>5</sub>, and finally distilled in the presence of 1,1-diphenylhexyllithium. Styrene, MMA, and *tert*-butyl methacrylate (<sup>t</sup>BMA) were washed with aqueous NaOH (10 wt %) and water, and dried over MgSO<sub>4</sub>. After filtration, they were distilled twice over CaH<sub>2</sub> under reduced pressures. Finally, styrene was distilled over Bu<sub>2</sub>Mg and dissolved in *tert*-butylbenzene under high vacuum conditions. Both MMA and <sup>t</sup>BMA were distilled over trioctylaluminum and dissolved in THF under high vacuum conditions. 2-Vinylpyridine (2 VP) was distilled over CaH2 twice under reduced pressures, finally under high vacuum, and dissolved in THF under high vacuum conditions. 1,1-Diphenylethylene (DPE) was distilled over butyllithium and dissolved in THF under high vacuum conditions. N, N, N', N'-Tetramethylethylenediamine (TMEDA) was distilled over Bu2Mg and dissolved in heptane under high vacuum conditions. LiCl was dried under high vacuum conditions for 3 days with heating and dissolved in THF. 3-tert-Butyldimethylsilyloxy-1-proxylithium (SiOPLi, in cyclohexane, FMC Corporation Lithium Division) was diluted in an appropriate concentration with heptane under high vacuum conditions.

**Measurements.** Size exclusion chromatography (SEC) was performed on a Viscotek GPC max equipped with a Viscotek TDA 302 triple detector array using THF as a carrier solvent at a flow rate of 1.0 mL/min at 30 °C. Three polystyrene gel columns were used, where pore size/bead size = 650/9, 200/5, and 75/5

 $(\text{\AA}/\mu\text{m})$ . The relative molecular weight of polymer  $(M_{n,\text{SEC}})$  was calculated by RI detection using standard polystyrene calibration. The combination of viscometer, right angle laser light scattering detection (RALLS), and RI detection was applied for the online SEC system in order to determine the absolute molecular weight of block copolymers  $(M_{n,\text{RALLS}})$ . Both <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a Bruker DPX300 in CDCl<sub>3</sub>. Chemical shifts were recorded in ppm downfield relative to CHCl<sub>3</sub> ( $\delta$  7.26) and CDCl<sub>3</sub> ( $\delta$  77.1) for <sup>1</sup>H and <sup>13</sup>C NMR as standards, respectively.

Synthesis of α-Phenylacrylic Acid.<sup>53</sup> 3-Hydroxy-2-phenylpropanoic acid (31.3 g, 188 mmol) was dissolved in 10% potassium hydroxide solution (350 mL) and refluxed for 10 h. After cooling down to room temperature, concentrated 2N HCl (45 mL) was carefully added to quench the reaction. The organic layer was extracted with chloroform, washed with water, and dried over MgSO<sub>4</sub>. Removal of chloroform under reduced pressure gave the object compound (17.9 g, 121 mmol) in 64% yield as a yellowish solid: <sup>1</sup>H NMR (300 MHz):  $\delta = 10.3-9.0$  (broad, 1H, COO*H*), 7.6–7.3 (m, 5H, Ar), 6.52 and 6.01 (d, 2H, C=CH<sub>2</sub>). <sup>13</sup>C NMR (75 MHz):  $\delta = 172.1$  (COOH), 140.8 (C=CH<sub>2</sub>), 136.2 (C=CH<sub>2</sub>), 129.4, 128.5, 128.4, 128.2 (Ar).

Preparation of α-Chain-End-3-(tert-Butyldimethylsilyloxy)propyl (SiOP) Functionalized Living AB Diblock Copolymer (PS-block-PMMA) Anion. All of the polymerizations and reactions were carried out under high-vacuum conditions (10<sup>-6</sup> Torr) in handmade sealed glass reactors. The reactors were always prewashed with a heptane solution of 1,1-diphenylhexyllithium prior to the polymerizations and reactions. α-Chainend-SiOP-functionalized polystyryllithium (PSLi) was prepared by the polymerization of styrene (19.9 mmol) in tert-butylbenzene (15.0 mL) initiated with SiOPLi (0.394 mmol) in the presence of TMEDA (1.40 mmol) at 0 °C for 30 min. THF solutions (10.0 mL, 4.00 mL) containing DPE (0.778 mmol) and LiCl (1.55 mmol) were sequentially added to the PSLi solution at -78 °C, and the reaction mixture was allowed to stand for additional 15 min at -78 °C. Then, a THF solution (22.3 mL) of MMA (20.0 mmol) was added at -78 °C with vigorous shaking, and the reaction mixture was allowed to stand for 30 min.

The  $\alpha$ -chain-end-SiOP-functionalized living PS-*block*-PMMA anion thus prepared is used for the linking reaction in the iterative synthetic sequence as mentioned below. In order to carry out the chain-end modification reactions in the first reaction step, the living PS-*block*-PMMA anion was quenched with degassed methanol and precipitated in methanol by pouring into a large excess of methanol. The resulting polymer was reprecipitated twice from THF to methanol and freeze-dried from its absolute benzene solution for 48 h. The resulting PS*block*-PMMA obtained in 95% yield was characterized by SEC, RALLS, and <sup>1</sup>H NMR, respectively.  $M_{n,RALLS} = 11400$ ,  $M_w/$  $M_n = 1.03$ . <sup>1</sup>H NMR (300 MHz):  $\delta = 7.24-6.26$  (m, 289H, Ar), 3.63-3.58 (m, 182H, O-CH<sub>3</sub>), 2.01-1.76 (m, 157H, main chain), 0.88 (s, 144H, C-CH<sub>3</sub>), 0.90 (s, 9H, C (CH<sub>3</sub>)<sub>3</sub>), -0.02 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>).

Preparation of  $\alpha$ -Chain-End-( $\alpha$ -Phenyl Acrylate) (PA) Functionalized PS-block-PMMA. The  $\alpha$ -chain-end-SiOP-functionalized PS-block-PMMA ( $M_n = 11 400, 3.89 \text{ g}, 0.341 \text{ mmol for}$ SiOP terminus) was carefully treated with Bu<sub>4</sub>NF (11.2 mmol) in absolute THF (45 mL) at 0 °C for 6 h to remove the silyl protective group and regenerate hydroxyl group. The reaction was repeated two or even three times until the disappearance of methyl protons of the Si-CH<sub>3</sub> group by <sup>1</sup>H NMR. It should be noted that raising the reaction temperature and longer reaction times than 24 h caused undesirable side reactions such as ester hydrolysis. After quenching the reaction with a small amount of methanol and removing the solvent, the polymer dissolved in THF was poured into a large excess of methanol to precipitate. The polymer was purified by reprecipitation twice and freeze-drying from its absolute benzene solution under vacuum. The polymer was obtained in 95% yield.  $M_{n,RALLS} = 12000$ ,  $M_{\rm w}/M_{\rm n} = 1.03$ . <sup>1</sup>H NMR (300 MHz):  $\delta = 7.24-6.26$  (m, 289H, Ar), 3.63-3.58 (m, 174H, O-CH<sub>3</sub>), 2.03-1.72 (m, 155H, main chain), 0.88 (s, 132H, C-CH<sub>3</sub>).

Under a nitrogen atmosphere, the hydroxyl-terminated PS*block*-PMMA ( $M_n = 12000, 3.62 \text{ g}, 0.302 \text{ mmol for hydroxyl}$ terminus),  $\alpha$ -phenylacrylic acid (2.31 g, 15.6 mmol), and PPh<sub>3</sub> (4.12 g, 15.6 mmol) were dissolved in THF (50 mL). Diisopropylazodicarboxylate (DIAD, 3.50 g, 17.3 mmol) was added dropwise at 0 °C and the reaction mixture was allowed to stir at 20 °C for 24 h. After quenching the reaction with a small amount of methanol and removing the solvent, the polymer dissolved in THF was poured into a large excess of methanol to precipitate. The resulting block copolymer was purified by the reprecipitation twice with THF/methanol and once with THF/ hexane and then freeze-dried from its absolute benzene solution under vacuum. Yield of the polymer was quantitative (3.59 g). The <sup>1</sup>H NMR analysis showed that the PA function was introduced quantitatively.  $M_{n,RALLS} = 11~900, M_w/M_n =$ 1.03. <sup>1</sup>H NMR (300 MHz):  $\delta = 7.24-6.26$  (m, 287H, Ar), 6.32 (s, 1H,  $C = CH_2$ ), 5.88 (s, 1H,  $C=CH_2$ ), 3.63–3.58 (m, 174H, O-CH<sub>3</sub>), 2.02-1.73 (m, 158H, main chain), 0.88 (s, 147H, C-CH<sub>3</sub>).

Synthesis of ABAB Tetrablock Copolymers Composed of PS and PMMA Blocks. α-Chain-end-SiOP-functionalized living PS-block-PMMA anion ( $M_n = 14500$ ) was first prepared by the block copolymerization of MMA (24.3 mmol) with  $\alpha$ -chainend-SiOP-functionalized PSLi ( $M_n = 5870, 0.281 \text{ mmol}, \omega$ -chainend-capped with DPE) in THF at -78 °C for 30 min in the presence of LiCl (1.44 mmol). To this solution, a THF solution (25.4 mL) of a-chain-end-PA-functionalized PS-block-PMMA  $(M_{\rm n} = 11\,900, 2.23$  g, 0.187 mmol for PA moiety) was slowly added at -78 °C and the reaction mixture was allowed to stand at -40 °C for 48 h. The reaction was terminated with degassed methanol and the polymers were precipitated by pouring a large excess of methanol. The ABAB tetrablock copolymer was isolated in 85% yield by the fractional precipitation mentioned below, reprecipitated from THF solution to methanol, and freeze-dried from its absolute benzene solution.  $M_{n,RALLS} = 28\,200$ ,  $M_{\rm w}/M_{\rm n}$  = 1.03. <sup>1</sup>H NMR (300 MHz):  $\delta$  = 7.23 – 6.28 (m, 625H, Ar), 3.64-3.55 (m, 429H, O-CH<sub>3</sub>), 1.93-1.62 (m, 333H, main chain), 0.78 (s, 299H, C-CH<sub>3</sub>), 0.90 (s, 9H, C (CH<sub>3</sub>)<sub>3</sub>), -0.02 (s, 6H, Si  $(CH_3)_2).$ 

General Procedure for Synthesis of (AB)<sub>n</sub> Multiblock Copoly**mers.** A series of (AB)<sub>n</sub> multiblock copolymers (n = 2, 3, 4, and 5)were synthesized by repeating the iterative synthetic sequence involving the three reaction steps mentioned in the Introduction. In the first reaction step of the iterative synthetic sequence, a 1.5-fold excess of α-chain-end-SiOP-functionalized living PS-block-PMMA anion was reacted with the  $\alpha$ -chain-end-PA-functionalized PS-block-PMMA at -40 °C for 48 h. The molar ratio of living polymer to PA-functionalized polymer increased gradually from 1.5 to 5.0 as the iteration proceeded. After quenching the reaction with a small amount of degassed methanol, the reaction mixture was poured into a large excess of methanol to precipitate the polymers. The objective coupled polymer was isolated by fractional precipitation using mixed solvents of THF, ether, and hexane as follows: The polymer (1 g) was dissolved in THF (10 mL) and ether (ca. 100 mL) was added at 0 °C where the solution became cloudy. Then, hexane (10-40 mL) was added and the reaction mixture was kept at 0 °C for 30 min with stirring. With this treatment, higher molecular weight multiblock copolymers were precipitated, while the diblock copolymer remained in the solution. The multiblock copolymers were isolated in  $\geq$ 85% yields by repeating the same treatment. In some cases, the sampling by SEC fractionation was carried out to completely remove very small amounts of high and low molecular weight polymers for the characterization. The isolated polymer was reprecipitated from THF solution to methanol twice and freezedried from its absolute benzene solution for 48 h. The resulting multiblock copolymers were characterized by SEC, RALLS and

<sup>1</sup>H NMR to determine the absolute molecular weights, molecular weight distributions, composition ratios, and degree of SiOP-chain-end-functionalities.

Synthesis of ABABAB Hexa-, ABABABAB Octa-, and ABA-**BABABAB Decablock Copolymers Composed of PS and PMMA Blocks.** The title multiblock copolymers were synthesized by repeating the same iterative synthetic sequence as that employed for the synthesis of tetrablock copolymer mentioned above. The characterization results of these polymers are as follows: ABA-BAB hexablock copolymer (2.21 g, 0.0545 mmol, 92% yield),  $M_{n,RALLS} = 40500, M_w/M_n = 1.03.$ <sup>1</sup>H NMR (300 MHz):  $\delta = 7.23-6.23$  (m, 860H, Ar), 3.67–3.54 (m, 677H, O–CH<sub>3</sub>), 2.02-1.72 (m, 562H, main chain), 0.87 (s, 528H, C-CH<sub>3</sub>), 0.90 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), -0.02 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>). ABABABAB octablock copolymer (1.16 g, 0.0216 mmol, 88% yield),  $M_{\rm n, RALLS} = 53\,600, M_{\rm w}/M_{\rm n} = 1.04.$ <sup>1</sup>H NMR (300 MHz):  $\delta = 7.21 - 6.31 \text{ (m, 1129H, Ar)}, 3.71 - 3.51 \text{ (m, 894H, O} - CH_3),$ 2.01-1.72 (m, 745H, main chain), 0.88 (s, 713H, C-CH<sub>3</sub>), 0.90 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), -0.02 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>). ABABABABABA decablock copolymer (0.501 g, 0.00755 mmol, 90% yield),  $M_{n,RALLS} = 66400, M_w/M_n = 1.06.$ <sup>1</sup>H NMR (300 MHz):  $\delta = 7.22 - 6.33 \text{ (m, 1491H, Ar)}, 3.66 - 3.58 \text{ (m, 1079H, O} - CH_3),$ 1.98-1.74 (m, 1013H, main chain), 0.89 (s, 1060H, C-CH<sub>3</sub>),  $0.90 (s, 9H, C(CH_3)_3), -0.02 (s, 6H, Si(CH_3)_2).$ 

Synthesis of  $\alpha$ -Chain-End-SiOP-Functionalized Di-, Tetra-, and Hexablock Copolymers Composed of PS and P<sup>t</sup>BMA Blocks. The title multiblock copolymers were synthesized in a similar manner by developing the same iterative methodology using α-chain-end-SiOP-functionalized living PS-block-P<sup>t</sup>BMA anion as a key building block. In the synthesis of the block copolymer anion, the polymerization time of <sup>t</sup>BMA was 2 h. The introduction of PA function via the SiOP group and the coupling reactions were carried out under the identical conditions mentioned above. These reactions proceeded cleanly and essentially quantitative in all cases. The linking reactions were carried out in mixtures of *tert*-butylbenzene and THF (1/4, v/v)with use of a 1.5-fold excess, followed by a 3-fold excess of living PS-block-P<sup>t</sup>BMA anion with the progress of the iteration. The objective multiblock copolymers were always isolated in ca. 60% yields by fractional precipitation with use of acetone/ methanol system. The resulting multiblock copolymers were characterized by SEC, RALLS, and <sup>1</sup>H NMR. The details of the synthesis are given in the Supporting Information. AB diblock copolymer:  $M_{n,RALLS} = 12700$ ,  $\overline{M}_w/M_n = 1.04$ . <sup>1</sup>H NMR (300 MHz):  $\delta = 7.2-6.3$  (broad, 320H, Ar), 0.80-2.27 (broad, 417H, main chain and  $C(CH_3)_3$ ), -0.01 (s, 6H, Si- $(CH_3)_2$ ). ABAB tetrablock copolymer:  $M_{n,RALLS} = 25300$ ,  $M_{\rm w}/M_{\rm n} = 1.04$ . <sup>1</sup>H NMR (300 MHz):  $\delta = 7.2-6.3$  (broad, 618H, Ar), 2.68–0.80 (s, 802H, main chain and C(CH<sub>3</sub>)<sub>3</sub>), -0.03 (s, 6H, Si( $CH_3$ )<sub>2</sub>). ABABAB hexablock copolymer:  $M_{n,RALLS} =$ 38 300,  $M_{\rm w}/M_{\rm n} = 1.04$ . <sup>1</sup>H NMR (300 MHz):  $\delta = 7.2-6.3$ (broad, 854H, Ar), 2.40-0.80 (broad, 1201H, C(CH<sub>3</sub>)<sub>3</sub>), -0.03  $(s, 6H, Si(CH_3)_2).$ 

Synthesis of Di-, Tetra-, and Hexablock Copolymers Composed of PS and P2VP Blocks. The title multiblock copolymers were synthesized in a similar manner by developing the same iterative methodology using  $\alpha$ -chain-end-SiOP-functionalized living PS-block-P2VP anion as a key building block. The α-chain-end-SiOP-functionalized living PS-block-P2VP anion was prepared by the sequential block copolymerization of styrene, DPE, and 2 VP with SiOPLi at 0 °C for 30 min, -78 °C for 10 min, and -78 °C for 30 min, respectively. The polymerization was quenched with a small amount of degassed methanol. The polymer solution was then concentrated followed by pouring into a large excess of hexane to precipitate the polymer. The block copolymer was purified by reprecipitation from THF to hexanes twice, freeze-dried from its absolute benzene solution for 48 h, and characterized by SEC, RALLS, and <sup>1</sup>H NMR measurements.  $M_{n,RALLS} = 13\ 100, M_w/M_n = 1.03.\ 300\ MHz$ <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):  $\delta = 8.4-8.1$  (broad, 61H, *N*=CH),





7.4–6.2 (broad, 460H, Ar), 5.81 (d, 2H,  $C=CH_2$ ), 2.3–1.6 (broad, 337H, main chain).

Both the introduction of PA function via the SiOP group and the linking reactions were carried out under the identical conditions mentioned above. These reactions proceeded cleanly and essentially quantitative in all cases. The linking reactions were carried out in a mixture of tert-butylbenzene and THF (1/4, v/v) at -78 °C for 24 h with the use of a 1.5-fold (or more) excess of PS-block-P2VP anion. The objective multiblock copolymers were always isolated in ca. 60% yields by fractional precipitation with use of acetone/methanol system. In some cases, the sampling by SEC fractionation was carried out to completely remove very small amounts of high and low polymers for the characterization. The resulting multiblock copolymers were characterized by <sup>1</sup>H NMR, SEC, and RALLS. (Figures S3 and S4). ABAB tetrablock copolymer,  $M_{n,RALLS} = 25\,800, M_w/$  $M_{\rm n} = 1.03.300 \text{ MHz}^{-1} \text{H NMR}$  (CDCl<sub>3</sub>, ppm): 8.4–8.1 (broad, 115H, N=CH), 7.4-6.2 (broad, 847H, Ar), 2.3-1.4 (broad, 832H, main chain), 0.84 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), -0.028 (s, 6H, Si- $(CH_3)_2$ ). ABABAB hexablock copolymer,  $M_{n,RALLS} = 46\,600$ ,  $M_{\rm w}/M_{\rm n} = 1.03.300 \text{ MHz}^{1}\text{H NMR} \text{ (CDCl}_3, \text{ppm)}; \delta = 8.4-8.1$ 

(broad, 191H, *N*=CH), 7.4–6.2 (broad, 1707H, Ar), 2.3–1.4 (broad, 1679H, main chain), 0.84 (s, 9H,  $C(CH_3)_3$ ), -0.03 (s, 6H, Si(*CH*<sub>3</sub>)<sub>2</sub>). The details of the synthesis are given in the Supporting Information.

# **Results and Discussion**

We have herein proposed a new iterative methodology, in which  $\alpha$ -chain-end-SiOP-functionalized living AB diblock copolymer anion is employed as a key building block specially designed for the synthesis of well-defined (AB)<sub>n</sub> multiblock copolymers composed of PS and PMMA blocks. The synthetic outline is illustrated in Scheme 1. As can be seen, the living AB diblock copolymer anion is designed in order to simultaneously introduce both A and B blocks. Furthermore, the SiOP  $\alpha$ -terminus is also designed to link two block copolymer chains by converting the SiOP group to a  $\alpha$ -phenyl acrylate function capable of reacting with the  $\omega$ -chain-end enolate anion in a 1:1 addition manner. The following three reaction steps are used for the entire iterative synthetic sequence: (1) a sequential living anionic block copolymerization with SiOPLi to prepare  $\alpha$ -chain-end-SiOP-functionalized living AB diblock copolymer anion, (2) an introduction of  $\alpha$ -phenyl acrylate (PA) function via the SiOP group by deprotection of the silyl group of the SiOP  $\alpha$ -terminus followed by Mitsunobu esterification reaction, and (3) a linking reaction of the  $\alpha$ -chain-end-PA-functionalized AB block copolymer prepared in step 2 with the  $\alpha$ -chain-end-SiOP-functionalized living AB block copolymer anion prepared in step 1. Since the polymer obtained in step 3 possesses the same SiOP  $\alpha$ -terminus as the starting material prepared in step 1, the same reaction sequence involving the above three reaction steps can be repeated to result in a series of multiblock copolymers.

In the first step of the iterative synthetic sequence,  $\alpha$ -chainend-SiOP-functionalized living PS-*block*-PMMA anion was prepared as follows: The living anionic polymerization of styrene was first carried out with SiOPLi in *tert*-butylbenzene at 0 °C for 30 min in the presence of a 3-fold excess of TMEDA.<sup>54</sup> The resulting  $\alpha$ -chain-end-SiOP-functionalized PSLi was end-capped with DPE in a 1:1 mixture of *tert*-butylbenzene and THF at -78 °C followed by the polymerization of MMA at -78 °C for 30 min to result in the objective  $\alpha$ -chain-end-SiOP-functionalized living PS*block*-PMMA anion. Prior to the polymerization of MMA, a 3-fold excess of LiCl toward the PSLi was added to narrow the molecular weight distribution of PMMA block.

The resulting living PS-*block*-PMMA anion was quenched with a small amount of degassed methanol. The silyl protective group of the SiOP  $\alpha$ -terminus was completely removed by treatment with Bu<sub>4</sub>NF and the regenerated hydroxyl group





converted to a PA function by reacting with  $\alpha$ -phenyl acrylic acid, DIAD, and Ph<sub>3</sub>P (the so-called Mitsunobu reaction). These end-group modification reactions were followed by <sup>1</sup>H NMR and found to be virtually quantitative by <sup>1</sup>H NMR analyses. It can be observed that the signal corresponding to the silvl methyl protons at -0.02 ppm was completely disappeared after deprotection and the PA vinyl proton signals at 5.88 and 6.32 ppm were subsequently emerged by the esterification as shown in Figure 1. As can be seen in Table 1, the resulting polymer possesses a predictable molecular weight and a narrow molecular weight distribution. Moreover, the composition observed by <sup>1</sup>H NMR was consistent with that calculated from the feed ratio. These results clearly indicate that the resulting polymer is the objective  $\alpha$ -chain-end-PA-functionalized PS-block-PMMA with well-defined and expected structures. Unless otherwise stated, molecular weight of the block copolymer was adjusted to be around 10 000 g/mol and the composition (w/w) of A/B was ca. 50/50.

In the final step, the  $\alpha$ -chain-end-PA-functionalized PS-block-PMMA thus prepared was reacted with a 1.5-fold excess of α-chain-end-SiOP-functionalized living PS-block-PMMA anion separately prepared. The linking reaction was carried out under the conditions in a 1:4 mixture of tert-butylbenzene and THF at -40 °C for 48 h. As shown in Figure 2, the SEC profile of the reaction mixture exhibits only two distinct sharp peaks corresponding to the objective linked product and the deactivated block copolymer anion used in excess in the reaction. No higher molecular weight peak was observed, indicating that the linking reaction between the living chain-end anion and the PA terminus undergoes in a 1:1 addition manner and no more addition of the PA terminus occurs at all under such conditions.<sup>53</sup> The linking efficiency was found to be virtually quantitative by comparing the two peak areas. The linked product was isolated in 85% yield by fractional precipitation. The results are also summarized in Table 1.



**Figure 2.** SEC profiles of ABAB tetrablock copolymer (a) before and (b) after fractional precipitation.

Table 1. Synthesis of a Series of Multiblock Copolymers Composed of PS (A) and PMMA (B) Blocks

code	type	$M_{ m n}  imes 10^{-3}$ (g/mol)			$M_{ m w}/M_{ m n}$	composition (PS/PMMA, w/w)	
		calcd	RALLS <sup>a</sup>	$NMR^{b}$	SEC <sup>a</sup>	calcd	obsd <sup>b</sup>
AB	diblock	10.5	11.4	12.2	1.03	51/49	48/52
$(AB)_2$	tetrablock	26.4	28.2	27.5	1.03	48/52	47/53
$(AB)_3$	hexablock	37.0	40.5	40.7	1.03	45/55	43/57
$(AB)_4$	octablock	51.0	53.6	53.6	1.04	45/55	43/57
$(AB)_5$	decablock	64.5	66.4	67.6	1.06	45/55	45/55
<i>a</i> <b>=</b>			h = .	11 1 1 2 2 2 2 2 2 2			

<sup>a</sup> Determined by SEC equipped with triple detectors. <sup>b</sup> Determined by <sup>1</sup>H NMR.



**Figure 3.** SEC profiles for a series of multiblock copolymers: (a)  $(AB)_5$  decablock, (b)  $(AB)_4$  octablock, (c)  $(AB)_3$  hexablock, (d)  $(AB)_2$  tetrablock, and (e) AB diblock copolymers.

The molecular weight calculated was in good agreement with that determined by either RALLS or <sup>1</sup>H NMR and a narrow molecular weight distribution was attained. The composition observed by <sup>1</sup>H NMR was very close to the calculated value. Thus, obviously, the linking reaction proceeds quantitatively to result in the object tetrablock copolymer composed of two PS and two PMMA blocks referred to as ABAB or (AB)<sub>2</sub>.

Similarly, an ABABAB hexablock copolymer was synthesized by repeating the same reaction sequence (the second iterative process), which involved the chain-end modification of the SiOP group into PA function of the ABAB tetrablock copolymer obtained by the first iterative process, the preparation of an  $\alpha$ -chain-end-SiOP-functionalized living (PS-*block*-PMMA) anion, and the linking reaction between  $\alpha$ -chain-end-PA-functionalized ABAB tetrablock copolymer and  $\alpha$ -chain-end-SiOPfunctionalized living (PS-*block*-PMMA) anion. All these three reaction steps were observed to effectively proceed with nearly quantitative efficiencies under the same conditions. The characterization results listed in Table 1 clearly show that the expected and well-defined ABABAB hexablock copolymer was successfully synthesized.

Likewise, the same reaction sequence was repeated two more times in order to synthesize ABABABAB octa- and ABABA-BABAB decablock copolymers. The SEC profiles always showed two distinct peaks corresponding to the object linked products and the block copolymer anions used in excess in the reactions. Higher molecular weight products were not observed at all in both cases. After isolation of the object products by fractional precipitation (>85% yields), they were characterized by SEC, <sup>1</sup>H NMR, and RALLS, respectively. It can be seen from the results listed in Table 1 that the agreement of the molecular weights between calculated and observed by both RALLS and <sup>1</sup>H NMR is quite satisfactory in each of both cases and the narrow molecular weight distributions are attained. The resulting block polymers possessed the expected compositions close to 50/50 (w/w). The SEC peaks of all the isolated multiblock copolymers shown in Figure 3 clearly exhibit that all of the multiblock copolymers herein synthesized possess sharp monomodal peaks. These results strongly support the conclusion that the first, second, third, and fourth iterative processes proceeded satisfactory as desired to result in a series of well-defined  $(AB)_n$  multiblock copolymers, (n = 2, 3, 4, and 5), composed of PS and PMMA blocks. Since the ABABABABAB decablock copolymer possesses the same SiOP  $\alpha$ -terminus, the same reaction sequence can be repeated to result in multiblock copolymers composed of more blocks. Once again, it should be noted that such multiblock copolymers are not synthesized by the sequential living anionic block copolymerization of styrene with MMA.

Synthesis of ABAB Tetra- and ABABAB Hexablock Copolymers Composed of PS Blocks and Either P<sup>t</sup>BMA or P2VP Blocks. In order to demonstrate the generality and versatility of the iterative methodology developed in this study, the synthesis of other two series of multiblock copolymers composed of PS blocks and either P<sup>t</sup>BMA or P2VP blocks were carried out by using the corresponding  $\alpha$ -chain-endfunctionalized living AB diblock copolymer anions. The choice of P<sup>t</sup>BMA and P2VP segments is to be expected that they can be transformed into poly(methacrylic acid) and poly(2-vinylpyridinium salt) by hydrolysis and quaternization with either HX or RX, respectively. As is known, poly(methacrylic acid) is a typical weak polyelectrolyte and soluble in water depending on pH. On the other hand, poly(2-vinylpyridinium salt) is a cationic polyelectrolyte and soluble in water. Accordingly, the resulting multiblock copolymers may be amphiphilic in character with many potential applications.

Synthesis of the multiblock copolymers composed of PS blocks and either P<sup>t</sup>BMA or P2VP blocks followed essentially the same iterative methodology as that employed for the synthesis of the multiblock copolymers composed of PS and PMMA blocks. The first PS block was prepared by the polymerization of styrene with SiOPLi in *tert*-butylbenzene in the presence of TMEDA at 0 °C as mentioned before. The block copolymer, PS-block-PtBMA, anion was prepared by sequential addition of DPE at first and then <sup>t</sup>BMA to polymerize in a 1:2 mixture of tert-butylbenzene and THF at -78 °C for 2 h. Similar to the polymerization of MMA, the addition of a 3-fold excess of LiCl was essential to narrow the molecular weight distribution of P<sup>t</sup>BMA block prior to the polymerization of <sup>t</sup>BMA. Then, the block copolymer was treated carefully with Bu<sub>4</sub>NF in THF to remove the silyl protective group of the SiOP  $\alpha$ -terminus without affecting ester functionalities. The subsequent Mitsunobu esterification with  $\alpha$ -phenyl acrylic acid was carried out under the same conditions as mentioned above. <sup>1</sup>H NMR analysis confirmed that the silvl protective group was quantitatively removed and the degree of the PA functionalization with a value of almost 100% was achieved (Figure S1). The resulting  $\alpha$ -chain-end-PA-functionalized PS-block-P<sup>t</sup>BMA was reacted with the  $\alpha$ -chain-end-SiOP-functionalized living PS-block-P<sup>t</sup>BMA anion separately prepared. A 1.5-fold excess of the living diblock copolymer anion was used to complete the reaction under the conditions in a 1:4 mixture of *tert*butylbenzene and THF at -40 °C for 48 h.

The SEC curve of the crude product showed two peaks corresponding to the object tetrablock copolymer and the deactivated diblock copolymer anion used in excess in the reaction. The linking efficiency was observed to be essentially quantitative by comparing the two peak areas. The objective polymer isolated in 60% yield by fractional precipitation showed a sharp monomodal distribution. It can be seen in Table 2 that the resulting polymer is confirmed to be the expected ABAB tetrablock copolymer by good agreement of the molecular weight as well as composition between calculated and observed.

Deprotection of silyl group of the SiOP  $\alpha$ -terminus with Bu<sub>4</sub>NF followed by esterification yielded the  $\alpha$ -chain-end-PA-functionalized tetrablock copolymer. The chain-end modification reactions were observed by <sup>1</sup>H NMR to be quantitative. The second iteration was performed by the linking reaction of the PA-functionalized tetrablock copolymer with a 3-fold excess of  $\alpha$ -chain-end-SiOP-functionalized living PS-*block*-P<sup>t</sup>BMA anion under the identical

Table 2. Synthesis of Multiblock Copolymers Composed of PS Blocks and P<sup>t</sup>BMA or P2VP Blocks

polymer				$M_{ m n}  imes 10^{-3}  ( m g/mol)$			composition (A/B, wt/wt)	
А	В	type	calcd	RALLS <sup>a</sup>	NMR <sup>b</sup>	SEC <sup>a</sup>	calcd	obsd <sup>b</sup>
PS	<b>P</b> <sup>t</sup> <b>BMA</b>	AB	11.3	12.7	13.4	1.04	52/48	50/50
PS	<b>P</b> <sup>t</sup> <b>BMA</b>	ABAB	24.3	25.3	25.7	1.04	49/51	49/51
PS	<b>P</b> <sup>t</sup> <b>BMA</b>	ABABAB	37.2	38.3	37.6	1.04	49/51	49/51
PS	P2VP	AB	10.4	13.1	11.6	1.03	47/53	46/54
PS	P2VP	ABAB	24.4	25.8	22.5	1.03	47/53	46/54
PS	P2VP	ABABAB	41.5	46.6	43.7	1.06	48/52	46/54

<sup>a</sup> Determined by SEC equipped with triple detectors. <sup>b</sup> Determined by <sup>1</sup>H NMR.

conditions. The characterization results listed in Table 2 clearly indicate the successful formation of the requisite ABABAB hexablock copolymer with well-defined structure. Thus, the synthesis of ABAB tetra- and ABABAB hexablock copolymers composed of PS and PtBMA blocks is realized by developing the same iterative methodology using  $\alpha$ -chainend-SiOP-functionalized living PS-*block*-P<sup>t</sup>BMA anion (Figure S2).

In a similar fashion, an  $\alpha$ -chain-end-SiOP-functionalized living PS-block-P2VP anion was prepared by sequential addition of styrene, DPE, and 2-vinylpyridine with SiOPLi as an initiator at 0 °C for 30 min, -78 °C for 10 min, and -78 °C for 30 min, respectively. Then, the SiOP  $\alpha$ -terminus of the resulting AB diblock polymer was deprotected with Bu<sub>4</sub>NF and the subsequent Mitsunobu esterification to introduce PA functionality was carried out under the same conditions. <sup>1</sup>H NMR analysis confirmed that the two end-functionalization reactions proceeded essentially quantitatively (Figure S3). The resulting PAfunctionalized polymer was carefully freeze-dried several times and reacted with a 1.5-fold excess of  $\alpha$ -chain-end-SiOP-functionalized living PS-block-P2VP anion in a 1:4 mixture of tert-butylbenzene and THF at -78 °C for 24 h. The linking reaction was observed by SEC to proceed quantitatively without the formation of any higher molecular weight product than the 1:1 linked product under such conditions. The results are also listed in Table 2. It can be seen that the expected ABAB tetrablock copolymer is successfully obtained with a predictable molecular weight, a controlled composition, and a very narrow molecular weight distribution.

Likewise, the ABABAB hexablock copolymer was synthesized by repeating the same reaction sequence one more time (Figure S4). Generally, a living anionic P2VP potentially initiates the polymerization of styrene under the conditions in THF at -78 °C. However, SEC profile of the resulting polymer showed a multimodal distribution with the residual peak corresponding to the starting P2VP.<sup>55–57</sup> Both of the slow initiation reaction due to rather low nucleophilicity of P2VP anion and the fast propagation reaction of styrene may cause the starting P2VP being left behind, result in failure of the multiblock copolymer synthesis by the living anionic block copolymerization based on sequential addition of the two monomers. Accordingly, the method herein developed is only the procedure for the synthesis of well-defined (AB)<sub>n</sub> multiblock copolymers composed of PS and P2VP.

# Conclusions

Herein, we have developed a new iterative methodology using  $\alpha$ -chain-end-functionalized living AB diblock copolymer anion as a key building block specially designed for the synthesis of a series of well-defined multiblock copolymers copolymer composed of PS and PMMA blocks. The methodology involves the following three reaction steps in the iterative synthetic sequence: (1) a sequential living anionic block copolymerization with

SiOPLi to prepare  $\alpha$ -chain-end-SiOP-functionalized living PSblock-PMMA anion, (2) an introduction of PA function via the SiOP group by deprotection of the silyl protective group followed by esterification with  $\alpha$ -phenyl acrylic acid, and (3) a linking reaction of  $\alpha$ -chain-end-PA-functionalized PS-block-PMMA with  $\alpha$ -chain-end-SiOP-functionalized living PS-block-PMMA anion. Since the three reaction steps proceeded cleanly and quantitatively, the iterative synthetic sequences involving the three reaction steps could be repeated at least four times to successively synthesize a series of multiblock copolymers up to the stage of ABABABABABAB decablock copolymer composed of PS and PMMA blocks.

The resulting multiblock copolymers all possessed precisely controlled molecular weights, compositions, and very narrow molecular weight distributions  $(M_w/M_n \le 1.06)$ . It should be noted that the molecular weight and composition can be readily and intentionally changed by changing the monomers to initiator ratios in this methodology by means of living anionic polymerization. Moreover, it may be possible to synthesize the multiblock copolymers with more blocks, since the final block copolymer has the same SiOP terminus capable of continuing the iterative process. Furthermore, other two series of well-defined multiblock copolymers (up to ABABAB hexablock) composed of PS with either P<sup>t</sup>BMA or P2VP blocks were also successfully synthesized by developing the same iterative methodology using the corresponding a-chain-end-SiOP-functionalized living AB block copolymer anions. The generality and versatility of this iterative methodology is thus obvious. It should be emphasized that the multiblock polymers composed of PS and PMMA, P<sup>t</sup>BMA, or P2VP blocks herein synthesized cannot be synthesized by sequential addition of two monomers in the living anionic polymerization due to a big difference between PS and PMMA, P<sup>t</sup>BMA, or P2VP chainend anions in reactivity.

On the basis of the successful synthesis of well-defined multiblock copolymers, the iterative methodology developed in this study offers the potential of providing a general and versatile procedure for a variety of well-defined multiblock copolymers. Furthermore, this iterative methodology may be applied to the synthesis of a series of multiblock copolymers composed of PS, P2VP, and PMMA blocks refer to as  $(ABC)_n$ , which is now under investigation.

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**Supporting Information Available:** Text giving synthetic details of  $(AB)_n$  multiblock copolymers composed of PS and P<sup>t</sup>BMA and synthetic details of  $(AB)_n$  multiblock copolymers composed of PS and P2VP including figures showing <sup>1</sup>H NMR spectra and SEC curves. This material is available free of charge via the Internet at http://pubs.acs.org.

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