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Facile Synthesis of Triblock Co- and Terpolymers of Styrene, 2-Vinylpyridine, and Methyl Methacrylate by a New Methodology Combining Living Anionic Diblock Copolymers with a Specially Designed Linking Reaction

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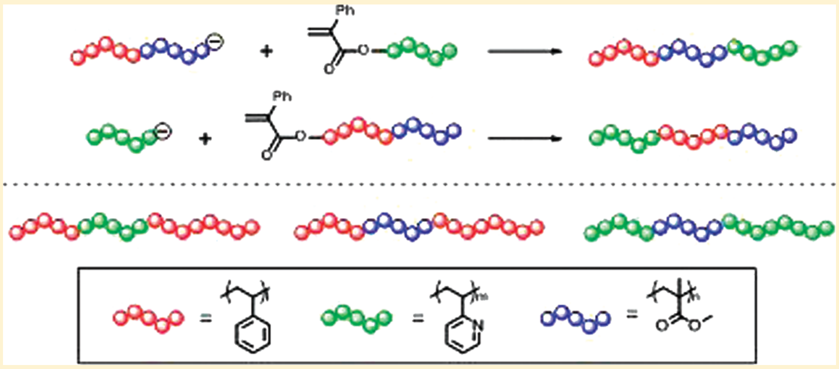
ABSTRACT:



Triblock co- and terpolymers with orders of blocks synthetically difficult to be obtained by means of sequential living anionic polymerization were successfully synthesized by developing a new methodology combining living anionic block copolymers with a specially designed linking reaction. The synthesized polymers involve ACB and BAC triblock terpolymers and ABA′, ACA′, and BCB′ triblock copolymers, where A, B, and C are polystyrene, poly(2-vinylpyridine), and poly(methyl methacrylate) segments, respectively. The A′, A as well as B, B′ are identical in polymer structure but different in molecular weight. All of them are new type triblock ter- and copolymers with well-defined structures, i.e., predictable molecular weights, compositions, and narrow molecular weight distributions. Transmission electron microscopic studies were performed on bulk morphologies of ACB and BAC triblock terpolymers to exemplarily investigate the influence of changing block sequence and thus changing interfaces. Although both terpolymers showed the tendency to form a lamella−lamella morphology, ACB revealed unusually strongly curved lamellae and BAC even undulated lamellae.

INTRODUCTION

Block polymers with a high degree of molecular and compositional homogeneity have attracted increasing interest as model polymers to elucidate interesting properties and behavior in combination with morphologies and molecular assemblies.[1−9] Such well-defined block polymers are usually synthesized by means of living anionic polymerization where two or more monomers are sequentially added to appropriate anionic initiators.[10] In fact, well-defined AB diblock copolymers, ABC triblock terpolymers, and $(AB)_n$ multiblock copolymers have been successfully synthesized.

In order to achieve further design and synthesis of well-defined block polymers by using living anionic polymerization, it is

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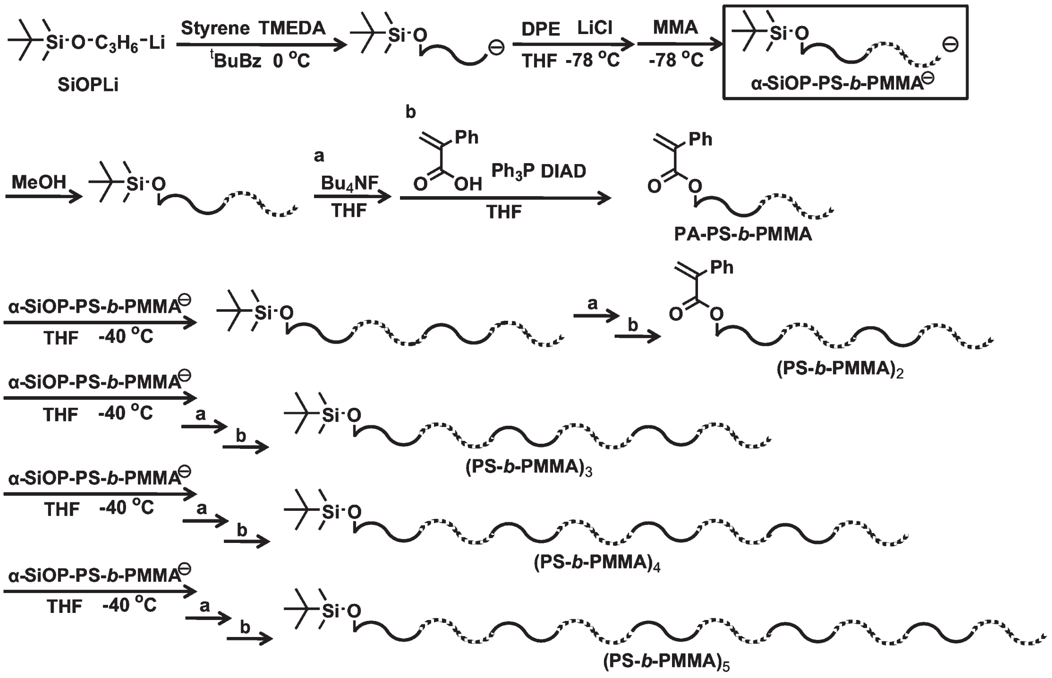
Scheme 1. Synthesis of (PS-*b*-PMMA)$_n$ Multiblock Copolymers



necessary to consider the order of monomer addition because reactivities of monomers and their growing chain-end anions are not always similar to each other. Among the monomers with similar reactivities, a growing chain-end anion formed from the first monomer initiates the second added monomer and *vice versa*. Accordingly, crossover occurs to such monomers, and therefore, not only AB and BA diblock but also ABA, ABAB, and even (AB)$_n$ multiblock copolymers can be synthesized by the sequential addition of A, B, A, B, and so on.[11−24] With the use of third monomer, ABC as well as ACB and BAC triblock terpolymers can readily be synthesized without difficulty. This is indeed true among the following combinations: styrene and their derivatives like α-methylstyrene and 4-methoxystyrene, styrene and 1,3-diene monomers, or methyl methacrylate (MMA) and other alkyl methacrylate monomers.[24−34]

In contrast, the order of monomer addition is very critical and important among monomers with different reactivities. In general, a more reactive growing chain-end anion is produced by a less reactive monomer and *vice versa* because the electron-withdrawing effect of the substituent influences both reactivities of the monomer and the growing chain-end anion. This often causes a serious problem in block copolymerization that less reactive growing chain-end anions cannot initiate the polymerization of less reactive monomers.[35] Accordingly, less reactive monomers should first be polymerized, followed by the polymerization of more reactive monomers. In the block copolymerization of styrene and MMA, for instance, it is necessary first to polymerize styrene and then MMA to synthesize a block copolymer of PS-*b*-PMMA. The reverse addition gives only a MMA homopolymer because the growing chain-end anion formed from MMA cannot initiate the polymerization of styrene at all under normal conditions. This means that the synthesis of PMMA-*b*-PS diblock, PS-*b*-PMMA-*b*-PS triblock, and, as a matter of fact, alternate (PS-*b*-PMMA)$_n$ multiblock copolymers is not possible by means of the living anionic polymerization where styrene and MMA are sequentially added.

Well-defined triblock terpolymers, PS-*b*-poly(2-vinylpyridine) (P2VP)-*b*-poly(*tert*-butyl methacrylate) (P^{t}BMA) and poly(1,3-butadiene) (PB)-*b*-P2VP-*b*-P^{t}BMA, could be synthesized by the living anionic polymerization where styrene or 1,3-butadiene, 2VP, and ^{t}BMA were sequentially added in this order to *sec*-BuLi.[27,36−41] Furthermore, the synthesis of polyisoprene (PI)-*b*-P2VP-*b*-poly(ethylene oxide) (PEO), PI-*b*-P2VP-*b*-P^{t}BMA, and even a particular PI-*b*-P2VP-*b*-P^{t}BMA-*b*-PEO was reported by Hadjichristidis et al.[42,43] Needless to say, the corresponding triblock and tetrablock polymers having block segments different in sequential order cannot be synthesized by changing the sequential addition order of monomers.

In order to synthesize such block polymers difficult to be obtained by the sequential polymerization, Hadjichristidis et al. reported a quite effective methodology using a new heterofunctional agent having benzyl chloride (BnCl) and silyl chloride moieties, 2-(chloromethylphenyl)ethyldimethylchlorosilane. This agent is designed to selectively react with the terminal silanolate anion of poly(dimethylsiloxane) (PDMS) or its block polymer to introduce the BnCl function at the ω-chain end. The resulting ω-terminal BnCl-functionalized PDMS or block polymer is readily reacted with living anionic homopolymer or block polymer to result in a variety of new PDMS-containing block polymers such as PDMS-*b*-P2VP, PDMS-*b*-P^{t}BMA, PS-*b*-PDMS-*b*-PS, PS-*b*-PI-*b*-PDMS-*b*-P2VP, and PS-*b*-PI-*b*-PDMS-*b*-P^{t}BMA-*b*-P2VP.[44−47] Such block polymers are not synthesized by the polymerization where the corresponding monomers are sequentially added.

Recently, we have successfully synthesized a series of multiblock copolymers consisting of several PS-*b*-PMMA blocks by developing a new methodology which combines an α-terminal functionalized living PS-*b*-PMMA as the building block with a specially designed linking reaction. The synthetic outline is illustrated in Scheme 1.[48] In the first step, an α-terminal 3-*tert*-butyldimethylsilyloxypropyl (SiOP)-functionalized living anionic

PS-*b*-PMMA was prepared by the living anionic polymerization where styrene and MMA were sequentially polymerized with 3-*tert*-butyldimethylsilyloxy-1-propyllithium (SiOPLi). The α-SiOP terminus was then converted to an α-phenyl acrylate (PA) reaction site. In the second step, the resulting α-terminal PA-functionalized PS-*b*-PMMA was reacted with the α-terminal SiOP-functionalized living PS-*b*-PMMA prepared in advance by the same manner, resulting in an α-terminal SiOP-functionalized (PS-*b*-PMMA)$_2$ tetrablock copolymer. Since the two reaction steps proceeded virtually quantitatively, the same reaction sequence could be repeated to successfully synthesize (PS-*b*-PMMA)$_3$ hexablock, (PS-*b*-PMMA)$_4$ octablock, and even (PS-*b*-PMMA)$_5$ decablock copolymers. These multiblock copolymers were all new and well-defined in structure, i.e., predictable molecular weights, compositions, and narrow molecular weight distributions. Thus, a satisfactory linking reaction occurred between the PMMA chain-end enolate anion and the PA α-terminus of PS to connect the PMMA chain to the PS segment which is not possible by sequential block copolymerization. It is therefore expected that the connection between other polymer chains difficult by the sequential polymerization is achieved by means of this linking reaction.

Herein, we report on the successful development of the methodology combining living anionic diblock copolymers with a specially designed linking reaction for the synthesis of new triblock co- and terpolymers of styrene, 2-vinylpyridine (2VP), and MMA, which are not obtained by the sequential living anionic polymerization.

■ EXPERIMENTAL SECTION

Materials. The reagents (>98% purities) were purchased from Aldrich Japan and used as received unless otherwise stated. Styrene, 1,1-diphenylethylene (DPE), 2VP, MMA, THF, heptane, *tert*-butylbenzene, *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), and LiCl were purified by usual manners. Bu_2Mg, BuLi, *sec*-BuLi, and 3-(*tert*-butyldimethylsilyloxy)-1-propyllithium (SiOPLi) purchased from FMC Corp., Lithium Division, were diluted with heptane in appropriate concentrations under high-vacuum conditions (10^{-6} Torr) and used. Styrene, DPE, MMA, and 2VP were distilled over CaH_2 twice under reduced pressures. Styrene was finally distilled from its Bu_2Mg (ca. 3 mol %) solution on the vacuum line. DPE were finally distilled from their ca. 3 mol % 1,1-diphenylhexyllithium (BuLi and DPE) solutions on the vacuum line. MMA was finally distilled from its $(C_8H_{17})_3Al$ solution on the vacuum line. 2VP was finally distilled over fine powder CaH_2 twice on the vacuum line. Ph_3P, diisopropyl azodicarboxylate (DIAD), and $(C_4H_9)_4NF$ in THF solution (1 M) was purchased from Tokyo Kasei Kogyo Co., Ltd., Japan, and used as received. α-Phenyacrylic acid was synthesized by the procedure previously reported.[49] 1-(3-*tert*-Butyldimethylsilyloxymethylphenyl)-1-phenylethylene (**1**) was synthesized by our procedure previously reported.[50]

Measurements. Both ^{1}H and ^{13}C NMR spectra were measured on a Bruker DPX300 in $CDCl_3$. Chemical shifts were recorded in ppm downfield relative to $CHCl_3$ (δ 7.26) and $CDCl_3$ (δ 77.1) for ^{1}H and ^{13}C NMR as standard, respectively. Molecular weights and polydispersity indices were measured on an Asahi Techneion AT-2002 equipped with a Viscotek TDA model 302 triple detector array using THF as a carrier solvent at a flow rate of 1.0 mL/min at 30 °C. Three PS gel column (pore size (bead size)) were used: 650 Å (9 μm), 200 Å (5 μm), and 75 Å (5 μm). The relative molecular weights were determined by SEC with RI detection using standard polystyrene or poly(methyl methacrylate) calibration curve. 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 weights of homopolymers, in-chain-functionalized polymers, and exact graft (co)polymers. For transmission electron microscopic studies 100 mg of terpolymer was dissolved in 2 mL of THF, and the solvent was allowed to evaporate over a period of 1 week. The as-prepared thin films were cut on an ultramicrotome into sheets with a thickness of 60 nm and were deposited on carbon-coated copper grids. All cuts were selectively stained with iodine for 3 h to improve the contrast of P2VP. Bright-field TEM was performed on a Zeiss CEM 902 electron microscope operated at 80 kV.

General Procedure of Triblock Co- and Terpolymer Synthesis. Except for deprotection and the Mitsunobu esterification reaction, all of the polymerizations and linking reactions were carried out under high-vacuum conditions (10^{-6} Torr) in sealed handmade glass reactors equipped with break-seals. The reactors were sealed off from the vacuum line and prewashed with a red 1,1-diphenylhexyllithium (ca. 0.05 M) in heptane solution prior to the polymerizations and reactions. All operations were performed according to the usual high-vacuum technique with break-seals.

Synthesis of ACB (or BCA) Triblock Terpolymer: PS-*b*-PMMA-*b*-P2VP (or P2VP-*b*-PMMA-*b*-PS). The title triblock terpolymer was synthesized by the linking reaction of living PS-*b*-PMMA (AC block copolymer) with α-terminal PA-functionalized P2VP (B). 2VP (21.5 mmol) in THF solution (1.08 M, 19.9 mL) was polymerized at −78 °C for 1 h with the initiator prepared from *sec*-BuLi (0.125 mmol), **1** (0.212 mmol), and LiCl (0.492 mmol) in THF solution (10.0 mL). After quenching the reaction with degassed methanol, the polymer was precipitated in hexane and reprecipitated twice from the ethanol solution to hexane. α-Terminal SiOP-functionalized P2VP (2.07 g) was obtained in 91% yield. ^{1}H NMR ($CDCl_3$): δ 8.3−8.1 (m, $-N{=}CH-$), 7.4−6.2 (m, aromatic), 3.5 (t, Si $-O-CH_2-$), 2.5−1.3 (m, $-CH_2-CH-$), 0.89 (m, $-C(CH_3)_3$), 0.04 (m, $-Si(CH_3)_2-$).

Under an atmosphere of nitrogen, the α-SiOP-functionalized P2VP (1.95 g, 0.104 mmol for SiOP α-terminus) dissolved in dry THF (13.5 mL) was mixed with $(C_4H_9)_4NF$ (6.50 mmol) in THF solution (6.50 mL), and the reaction mixture was allowed to stir at 25 °C for 16 h. The reaction mixture was poured into hexane to precipitate the polymer. The polymer was purified by reprecipitation twice from the ethanol solution to hexane and dried in vacuo for 24 h (1.72 g, 88%). ^{1}H NMR ($CDCl_3$): δ 8.3−8.1 (m, $-N{=}CH-$), 7.4−6.1 (m, aromatic), 3.5 (t, $HO-CH_2-$), 2.5−1.4 (m, $-CH_2-CH-$).

Under an atmosphere of nitrogen, the resulting polymer (1.60 g, 0.0851 mmol for 3-hydroxypropyl α-terminus) dissolved in dry THF (20.0 mL) was mixed with PPh_3 (5.36 mmol) and α-phenylacrylic acid (5.61 mmol), followed by the subsequent addition of DIAB (5.89 mmol) to the mixture at 0 °C. The reaction mixture was allowed to stir at 25 °C for 12 h. Usual work-up gave the α-terminal PA-functionalized P2VP (1.35 g, 84%). ^{1}H NMR ($CDCl_3$): δ 8.3−8.0 (m, $-N{=}CH-$), 7.4−6.2 (m, aromatic), 5.84 (d, $-C{=}CHH$), 2.4−1.4 (m, $-CH_2-CH-$). $M_{n,RALLS}$ = 18 800 g/mol, M_w/M_n = 1.03.

A living PS-*b*-PMMA (1.51 g, $M_{n,RALLS}$ = 15 800 g/mol, 0.0956 mmol) was prepared at −78 °C in the same manner reported by our previous paper.[48] A small amount (ca. 10% in volume) was taken for analytical purposes, and the residual living polymer (0.0872 mmol) solution was mixed with the α-terminal PA-functionalized P2VP (0.413 g, M_n = 18 800 g/mol, 0.0220 mmol for PA α-terminus) prepared above. The reaction mixture was allowed to react at −40 °C for 17 h. The reaction was quenched with degassed methanol, and the polymers were precipitated in hexane. The target ACB triblock copolymer, PS-*b*-PMMA-*b*-P2VP, was isolated in 50% yield by fractional precipitation using THF/diethyl ether/hexane. The isolated polymer was reprecipitated twice and freeze-dried from its benzene solution for 48 h. ^{1}H NMR ($CDCl_3$): δ 8.5−8.1 (m, $-N{=}CH-$), 7.2−6.2 (m, aromatics), 3.8−3.5

(m, $-\mathrm{O}-\mathit{CH}_3$), 2.5−1.4 (m, $-\mathit{CH}_2-\mathit{CH}-$ and $-\mathit{CH}_2-\mathrm{C}(\mathrm{CH}_3)-$), 0.95 (s, $-\mathrm{CH}_2-\mathrm{C}(\mathit{CH}_3)-$). $M_{\mathrm{n,RALLS}}$ = 34 600 g/mol, M_w/M_n = 1.04.

A BCA triblock terpolymer, P2VP-*b*-PMMA-*b*-PS, possesses the same block sequence as that of the above ACB triblock terpolymer, PS-*b*-PMMA-*b*-P2VP. However, it was synthesized by the linking reaction of living P2VP-*b*-PMMA with α-terminal PA-functionalized PS as follows: Styrene (38.0 mmol) in *tert*-butylbenzene solution (2.48 M, 15.3 mL) was polymerized with SiOPLi (0.431 mmol) in the presence of TMEDA (1.52 mmol) at 0 °C for 30 min. After quenching the reaction with degassed methanol, the polymer was precipitated in methanol, reprecipitated from the THF solution to methanol twice, and freeze-dried from its absolute benzene solution (3.76 g, 95%). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 7.2−6.4 (m, aromatic), 3.5 (t, $\mathrm{Si}-\mathrm{O}-\mathrm{CH}_2-$), 2.2−1.2 (m, $-\mathit{CH}_2-\mathit{CH}-$), 0.91 (s, $-\mathrm{C}(\mathit{CH}_3)_3$), 0.01 (s, $-\mathrm{Si}(\mathrm{CH}_3)_2-$).

The SiOP α-terminus was deprotected with $(\mathrm{C_4H_9})_4\mathrm{NF}$, followed by conversion to a PA function in similar manners to those in the preparation of α-terminal PA-functionalized P2VP mentioned above. α-Terminal (3-hydroxypropyl)-functionalized PS (3.76 g, 100%). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 7.2−6.5 (m, aromatic), 3.4 (t, $\mathrm{HO}-\mathit{CH}_2-$), 2.2−1.2 (m, $-\mathit{CH}_2-\mathit{CH}-$). α-Terminal PA-functionalized PS (3.65 g, 97%). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 7.2−6.5 (m, aromatic), 6.14 and 5.74 (d, $\mathrm{C}{=}\mathit{CH}_2$), 2.2−1.2 (m, $-\mathit{CH}_2-\mathit{CH}-$). $M_{\mathrm{n,RALLS}}$ = 9190 g/mol, M_w/M_n = 1.03.

A living P2VP-*b*-PMMA was prepared as follows: 2VP (10.8 mmol) in THF solution (1.13 M, 9.56 mL) was polymerized with the initiator from *sec*-BuLi (0.116 mmol), DPE (0.205 mmol), and LiCl (0.432 mmol) in THF solution (5.05 mL) at −78 °C for 1 h. Then, ^{t}BMA (0.437 mmol) in THF solution (5.20 mL) was added *in situ* to end-cap the P2VP chain-end anion at −78 °C for 40 min, and subsequently MMA (10.6 mmol) in THF solution (1.07 M, 9.89 mL) was added to polymerize at −78 °C for 30 min. A small amount (10% in volume) of the resulting living P2VP-*b*-PMMA was taken for analytical purposes, and the residual living polymer (0.104 mmol) reacted *in situ* with the α-terminal PA-functionalized PS (0.299 g, M_n = 9190 g/mol, 0.0326 mmol for PA α-terminus) dissolved in THF (7.20 mL) at −40 °C for 24 h. The reaction was quenched with methanol, and the polymers were precipitated in methanol. The target P2VP-*b*-PMMA-*b*-PS was isolated by SEC fractionation. It was purified by reprecipitation twice and freeze-dried from its benzene solution for 24 h. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 8.2−8.0 (m, $-\mathrm{N}{=}\mathrm{CH}-$), 7.2−6.3 (m, aromatics), 3.7−3.3 (m, $-\mathrm{O}-\mathit{CH}_3$), 2.2−1.4 (m, $-\mathit{CH}_2-\mathit{CH}-$ and $-\mathit{CH}_2-\mathrm{C}(\mathrm{CH}_3)-$), 0.95 (s, $-\mathrm{CH}_2-\mathrm{C}(\mathit{CH}_3)-$). $M_{\mathrm{n,RALLS}}$ = 30 100 g/mol, M_w/M_n = 1.05.

Synthesis of BAC (or CAB) Triblock Terpolymer: P2VP-*b*-PS-*b*-PMMA (or PMMA-*b*-PS-*b*-P2VP). The title triblock terpolymer was synthesized by the linking reaction of living P2VP with α-terminal PA-functionalized PS-*b*-PMMA. The α-terminal PA-functionalized PS-*b*-PMMA was prepared in similar manners previously reported.[48] The resulting polymer (3.33 g) was characterized by SEC-RALLS and ^{1}H NMR, respectively. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 7.3−6.4 (m, aromatic), 6.13 and 5.72 (d, $\mathrm{C}{=}\mathit{CH}_2$), 3.6−3.3 (m, $-\mathrm{O}-\mathit{CH}_3$), 1.9−1.4 (m, $-\mathit{CH}_2-\mathit{CH}-$ and $-\mathit{CH}_2-\mathrm{C}(\mathrm{CH}_3)-$), 0.95 (s, $-\mathrm{CH}_2-\mathrm{C}(\mathit{CH}_3)-$). $M_{\mathrm{n,RALLS}}$ = 24 300 g/mol, M_w/M_n = 1.03.

2VP (7.07 mmol) in THF solution (1.00 M, 7.07 mL) was polymerized at −78 °C for 1.5 h with the initiator prepared from *sec*-BuLi (0.0594 mmol), DPE (0.146 mmol), and LiCl (0.339 mmol) in THF solution (9.24 mL). A part of the living P2VP was taken for analytical purposes. Then, the α-terminal PA-functionalized PS-*b*-PMMA (0.598 g, M_n = 24 300 g/mol, 0.0248 mmol for PA α-terminus) dissolved in THF (11.3 mL) was carefully added to the resulting living P2VP (0.0424 mmol) at −78 °C, and the reaction mixture was allowed to react at −78 °C for 15 h. The polymerization was quenched with degassed methanol, and the polymers were precipitated in hexane. The target P2VP-*b*-PS-*b*-PMMA was isolated in 73% yield by fractional precipitation using THF, ethanol, and hexane. Typically, a crude polymer mixture (ca. 1.1 g) was dissolved in THF (500 mL), followed by addition of ethanol (30 mL). Hexane (70 mL) was then gradually added to this solution until the mixed solution became cloudy, and the resulting solution was allowed to stir at 0 °C for 30 min and then stand at 0 °C for an additional 30 min. The target triblock terpolymer was precipitated from the solution. This operation was repeated several times. The isolated polymer (0.660 g, 73%) was purified by reprecipitation, freeze-dried from its absolute benzene solution for 48 h, and characterized. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 8.2−8.0 (m, $-\mathrm{N}{=}\mathrm{CH}-$), 7.2−6.2 (m, aromatics), 3.5−3.3 (m, $-\mathrm{O}-\mathit{CH}_3$), 2.2−1.4 (m, $-\mathit{CH}_2-\mathit{CH}-$ and $-\mathit{CH}_2-\mathrm{C}(\mathrm{CH}_3)-$), 0.95 (s, $-\mathrm{CH}_2-\mathrm{C}(\mathit{CH}_3)-$). $M_{\mathrm{n,RALLS}}$ = 38 200 g/mol, M_w/M_n = 1.04.

A CAB triblock terpolymer, PMMA-*b*-PS-*b*-P2VP, possesses the same block sequence as that of the BAC triblock terpolymer, P2VP-*b*-PS-*b*-PMMA, synthesized above. However, this polymer was synthesized by the linking reaction of living PMMA with α-terminal PA-functionalized PS-*b*-P2VP as follows: Styrene (20.1 mmol) in *tert*-butylbenzene solution (2.72 M, 7.39 mL) was polymerized with SiOPLi (0.190 mmol) in the presence of TMEDA (0.771 mmol) at 0 °C for 30 min. The living PS solution was cooled to −78 °C, and THF (10.5 mL) precooled at −78 °C was added. Then, DPE (0.291 mmol) and LiCl (0.745 mmol) in THF solution (15.0 mL) were added to the above living polymer solution at −78 °C, and the mixture was allowed to react at −78 °C for 1 h, followed by addition of 2VP (21.7 mmol) in THF solution (1.19 M, 18.2 mL) to polymerize 2VP at −78 °C for 1 h. The polymer was precipitated in hexane, reprecipitated from the THF solution to ethanol/hexane twice, and freeze-dried from its absolute benzene solution (4.16 g, 95%). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 8.2−8.0 (m, $-\mathrm{N}{=}\mathrm{CH}-$), 7.2−6.4 (m, aromatics), 3.5 (t, $\mathrm{Si}-\mathrm{O}-\mathrm{CH}_2-$), 2.2−1.2 (m, $-\mathit{CH}_2-\mathit{CH}-$), 0.91 (s, $-\mathrm{C}(\mathit{CH}_3)_3$), 0.01 (s, $-\mathrm{Si}(\mathrm{CH}_3)_2-$).

The SiOP α-terminus was deprotected with $(\mathrm{C_4H_9})_4\mathrm{NF}$, followed by conversion to a PA function in similar manners to those in the preparation of α-terminal PA-functionalized P2VP mentioned above. α-Terminal (3-hydroxypropyl)-functionalized PS-*b*-P2VP (3.95 g, 95%). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 8.2−8.0 (m, $-\mathrm{N}{=}\mathrm{CH}-$), 7.2−6.5 (m, aromatics), 3.4 (t, $\mathrm{HO}-\mathit{CH}_2-$), 2.2−1.2 (m, $-\mathit{CH}_2-\mathit{CH}-$). α-Terminal PA-functionalized PS (3.56 g, 90%). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 8.2−8.0 (m, $-\mathrm{N}{=}\mathrm{CH}-$), 7.2−6.5 (m, aromatics), 6.14 and 5.74 (d, $\mathrm{C}{=}\mathit{CH}_2$), 2.2−1.2 (m, $-\mathit{CH}_2-\mathit{CH}-$). $M_{\mathrm{n,RALLS}}$ = 22 300 g/mol, M_w/M_n = 1.03.

MMA (9.93 mmol) in THF solution (0.951 M, 10.5 mL) was polymerized with the initiator from *sec*-BuLi (0.0877 mmol), DPE (0.188 mmol), and LiCl (0.436 mmol) in THF solution (18.0 mL) at −78 °C for 45 min. A small amount (10% in volume) of the resulting living PMMA was taken for analytical purposes, and the residual living polymer (0.797 mmol) reacted *in situ* with the α-terminal PA-functionalized PS-*b*-P2VP (0.529 g, M_n = 22 300 g/mol, 0.0237 mmol for PA α-terminus) dissolved in THF (11.0 mL) at −40 °C for 21 h. The reaction was quenched with methanol, and the polymers were precipitated in hexane. The target P2VP-*b*-PMMA-*b*-PS was isolated by fractional precipitation using THF/acetone/hexane. It was purified by reprecipitation twice and freeze-dried from its benzene solution for 24 h (0.670 g, 83%). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 8.2−8.0 (m, $-\mathrm{N}{=}\mathrm{CH}-$), 7.2−6.2 (m, aromatics), 3.6−3.3 (m, $-\mathrm{O}-\mathit{CH}_3$), 2.2−1.4 (m, $-\mathit{CH}_2-\mathit{CH}-$ and $-\mathit{CH}_2-\mathrm{C}(\mathrm{CH}_3)-$), 0.95 (s, $-\mathrm{CH}_2-\mathrm{C}(\mathit{CH}_3)-$). $M_{\mathrm{n,RALLS}}$ = 34 300 g/mol, M_w/M_n = 1.04.

Synthesis of ABA′, ACA′, and BCB′ Asymmetric Triblock Copolymers: PS-*b*-P2VP-*b*-PS, PS-*b*-PMMA-*b*-PS, and P2VP-*b*-PMMA-*b*-P2VP. The first two polymers were synthesized by the linking reaction of either living PS-*b*-P2VP or living PS-*b*-PMMA with α-terminal PA-functionalized PS. On the other hand, the third polymer was synthesized by the linking reaction of living P2VP-*b*-PMMA with α-terminal PA-functionalized P2VP. All of the starting living diblock copolymers and α-terminal PA-functionalized polymers were prepared by the same procedures as those described in the preceding sections.

The linking reaction of living PS-*b*-P2VP with α-terminal PA-functionalized PS was carried out at −78 °C for 15 h. A 1.5-fold excess of the living polymer toward the PA reaction site was used. The linking reaction was estimated to be almost quantitative by SEC. The target ABA′ polymer was isolated in 44% yield by fractional precipitation using first THF/ethanol/hexane and then THF/cyclohexane/hexane. On the other hand, a 3-fold excess of living PS-*b*-PMMA or P2VP-*b*-PMMA reacted with the α-terminal PA polymer at −40 °C for 20 h. Under such conditions, the linking reactions quantitatively proceeded. The ACA′ triblock terpolymer was isolated in 54% yield by fractional precipitation using first THF/acetone/methanol and then THF/diethyl ether/hexane. The BCB′ polymer was isolated in 50% yield by fractional precipitation using THF/acetone/hexane.

ABA′ triblock copolymer: ^{1}H NMR ($CDCl_3$): δ 8.2−8.0 (m, $-N{=}CH-$), 7.4−6.2 (m, aromatics), 2.2−1.3 (m, $-CH_2-CH-$). $M_{n,RALLS}$ = 33 000 g/mol, M_w/M_n = 1.04. ACA′ triblock copolymer: ^{1}H NMR ($CDCl_3$): δ 7.2−6.4 (m, aromatic), 3.8−3.3 (m, $-O-CH_3$), 2.3−1.4 (m, $-CH_2-CH-$ and $-CH_2-C(CH_3)-$), 0.95 (s, $-CH_2-C(CH_3)-$). $M_{n,RALLS}$ = 30 800 g/mol, M_w/M_n = 1.02. BCB′ triblock copolymer: ^{1}H NMR ($CDCl_3$): δ 8.5−8.1 (m, $-N{=}CH-$), 7.3−6.2 (m, aromatic), 3.7−3.5 (m, $-O-CH_3$), 2.6−1.4 (m, $-CH_2-CH-$ and $-CH_2-C(CH_3)-$), 0.95 (s, $-CH_2-C(CH_3)-$). $M_{n,RALLS}$ = 39 900 g/mol, M_w/M_n = 1.03.

RESULTS AND DISCUSSION

Reactivities of Monomers and Their Growing Chain-End Anions. In this study, we have chosen three representative monomers—styrene, 2VP, and MMA—which are known to undergo living anionic polymerization to afford stable living polymers. These monomers have, however, different reactivities (or electrophilicities) in anionic polymerization. Among them, MMA is most reactive, while styrene is least reactive. The reactivity of 2VP is positioned between MMA and styrene. Such a reactivity difference can be explained by the order of electron-withdrawing character of the substituent ($-COOMe > -C_5H_5N$ ($-CH{=}N-$) $> -C_6H_5$). Although an electron-donating methyl group is substituted at the α-position in MMA, the electron-withdrawing effect of the ester carbonyl is more influenced on the reactivity.

As mentioned in the Introduction, a more reactive growing chain-end anion is generally produced by a less reactive monomer and *vice versa*. Accordingly, the reactivity (or nuclophilicity) order of growing chain-end anion formed from each of three monomers may be opposite, as compared with the monomer reactivity. Actually, their reactivities can be recognized by the sequential anionic block copolymerization under the conditions in THF at −78 °C. A growing chain-end anion formed from the most reactive MMA cannot initiate the polymerization of either styrene or 2VP at all. On the other hand, a growing chain-end anion formed from styrene of the least reactive monomer readily and quantitatively polymerizes both 2VP and MMA. Since the PS chain end-anion often reacts with the CH═N bond of 2VP or the ester carbonyl of MMA, it is usually end-capped with DPE to convert a less reactive and hindered 1,1-diphenylalkyl anion prior to the polymerization of both monomers in order to avoid such side reactions.

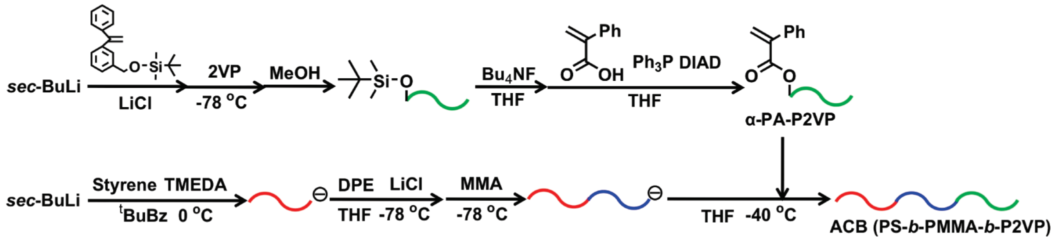
A growing chain-end anion formed from 2VP can initiate the polymerization of styrene. However, the polymerization was not quantitative to give a polymer with a multimodal distribution in molecular weight. This is attributed to the slow initiation of styrene with the P2VP growing chain-end anion and the CH═N bond attack by the resulting PS chain-end anion to disturb the quantitative polymerization. The P2VP chain-end anion can initiate the polymerization of MMA. However, the resulting block copolymer, P2VP-*b*-PMMA, possessed a relatively broad molecular weight distribution (M_w/M_n = 1.3) along with lower-molecular-weight fractions, indicating that the P2VP chain-end anion attacks to some extent the ester carbonyl of MMA as well as PMMA during the polymerization. Under the same conditions, *tert*-butyl methacrylate (^{t}BMA) having a similar reactivity of MMA was smoothly polymerized with the P2VP chain-end anion to afford a well-defined block copolymer, P2VP-*b*-P^{t}BMA.[51] Therefore, the growing chain-end anion of P2VP is first end-capped with a few units of ^{t}BMA, and then MMA is polymerized to successfully synthesize a well-defined P2VP-*b*-PMMA. Thus, the reactivity of growing chain-end anion increases from PMMA anion, P2VP anion, to PS anion in this order and is exactly opposite for the monomer reactivity order decreasing from MMA, 2VP, to styrene.

With these reactivities and limitations in block copolymerization in mind, the methodology combining living anionic diblock copolymers as key building blocks with a specially designed linking reaction has been developed to synthesize special triblock terpolymers which are not obtained by the sequential anionic block terpolymerization. With use of styrene, 2VP, and MMA in anionic block polymerization, the synthesis of three sequentially different triblock terpolymers are considered. These polymers are ABC, ACB, and BAC triblock terpolymers. Although other three CBA, BCA, and CAB triblock terpolymers are also considered, they are identical in block sequence order to the above-mentioned ABC, ACB, and BAC ones. Herein, A, B, and C are corresponding to PS, P2VP, and PMMA segments, respectively. Only an ABC (or CBA) triblock terpolymer, that is, PS-*b*-P2VP-*b*-PMMA (or PMMA-*b*-P2VP-*b*-PS), can be synthesized by the living anionic polymerization where the corresponding monomers are sequentially added. On the other hand, a new methodology is essential to synthesize other two ACB (or BCA) and BAC (or CAB) triblock terpolymers.

Synthesis of ACB (or BCA) Triblock Terpolymer: PS-*b*-PMMA-*b*-P2VP (or P2VP-*b*-PMMA-*b*-PS). The first example synthesized by the proposed methodology is an ACB triblock terpolymer represented as PS-*b*-PMMA-*b*-P2VP. Although a living PS-*b*-PMMA is prepared by the sequential polymerization of styrene followed by MMA, the resulting PMMA chain-end enolate anion cannot initiate the polymerization of 2VP as mentioned in the preceding section. Accordingly, the synthesis of PS-*b*-PMMA-*b*-P2VP triblock terpolymer is not possible by the anionic polymerization using the sequential monomer addition. We have herein proposed a new methodology based on the aforementioned methodology effective for the synthesis of (PS-*b*-PMMA)$_n$ multiblock copolymers previously reported by us.[48] The synthetic design of the ACB triblock terpolymer, PS-*b*-PMMA-*b*-P2VP, is illustrated in Scheme 2. As you can see, the target triblock terpolymer will be synthesized by the linking reaction of a living anionic AC diblock copolymer, PS-*b*-PMMA, with an α-terminal PA-functionalized P2VP (B).

The α-terminal PA-functionalized P2VP was prepared by the living anionic polymerization of 2VP with the initiator from *sec*-BuLi and **1**, followed by the conversion of the 3-(*tert*-butyldimethylsilyloxymethyl)phenyl α-terminus to a PA function by treatment with $(C_4H_9)_4NF$ (deprotection) and subsequently with α-phenylacrylic acid under the conditions of the Mitsunobu esterification reaction. The conversion was confirmed by the

Scheme 2. Synthesis of ACB Triblock Terpolymer



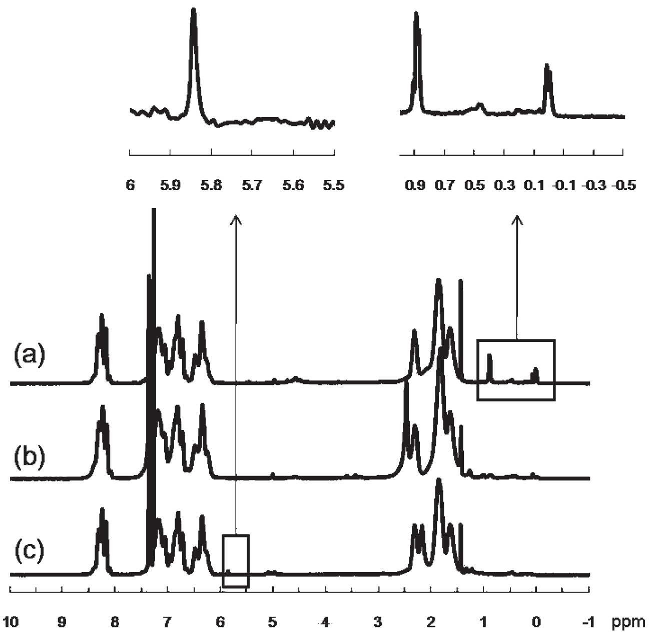


Figure 1. ^{1}H NMR spectra of α-terminal SiOP-functionalized P2VP (a), α-terminal 3-hydroxypropyl-functionalized P2VP (b), and α-terminal PA-functionalized P2VP (c).

analysis of ^{1}H NMR spectra, as shown in Figure 1, to be virtually quantitative. After the above treatment, the signals at 0.89 and 0.04 ppm assigned to *tert*-butyl and silylmethyl protons of the initiator residue completely disappeared, while a new peak at 5.84 ppm corresponding to one of the α-phenyl acrylate vinylene protons appeared. Although a peak of the other proton should be present at 6.14 ppm, it was overlapped with those of the aromatic protons. In a separate experiment, a living anionic PS-*b*-PMMA was prepared by the sequential addition of styrene, DPE (only for the end-capping), and MMA to *sec*-BuLi and reacted *in situ* with the α-terminal PA-functionalized P2VP. In this block copolymerization, a 4-fold excess of LiCl was added prior to the polymerization of MMA in order to narrow the molecular weight distribution. The linking reaction of a 2-fold excess of living PS-*b*-PMMA with α-terminal PA-functionalized P2VP was carried out at −78 °C for 20 h, but the reaction was sluggish and incomplete under the conditions. Therefore, a 4-fold excess of living PS-*b*-PMMA ($M_{n,RALLS}$ = 15 800 g/mol) was added to the same α-terminal PA-functionalized P2VP ($M_{n,RALLS}$ = 18 800 g/mol) at −78 °C, and the polymer mixture was allowed to react at −40 °C for 17 h. The reaction was terminated with degassed methanol, and the polymers were precipitated in hexane.

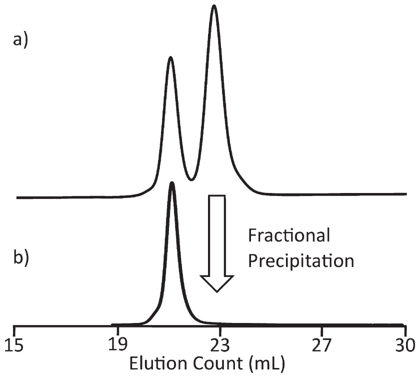


Figure 2. SEC profiles of the reaction mixture (a) and ACB triblock terpolymer isolated by fractional precipitation (b).

The SEC profile of the reaction mixture shown in Figure 2a exhibits two peaks: one for the linked polymer and the other for the deactivated PS-*b*-PMMA used in excess in the reaction. Since both starting polymers (living block copolymer and α-terminal PA-functionalized P2VP) were similar in molecular weight and the two peak area ratio was approximately 2:3, the reaction efficiency was estimated to be nearly quantitative. The target linked polymer was isolated in 50% yield by fractional precipitation using a mixed solvent of THF, diethyl ether, and hexane, reprecipitated twice, and freeze-dried from its absolute benzene solution. The isolated polymer was observed to have a sharp monomodal distribution (M_w/M_n = 1.04) (see Figure 2b). The characterization results are listed in Table 1. The molecular weights observed by SEC-RALLS and ^{1}H NMR ($M_{n,RALLS}$ = 34 600 g/mol and $M_{n,NMR}$ = 35 000 g/mol) were in good agreement with that calculated (M_n = 32 200 g/mol). Moreover, the composition observed by ^{1}H NMR was very close to the calculated value from the feed ratio. All of these analytical results clearly indicate the successful formation of the target ACB triblock terpolymer, PS-*b*-PMMA-*b*-P2VP, with expected and well-controlled structures. Each block length of this terpolymer was 9 300 (PS), 6 600 (PMMA), and 18 700 (P2VP) in M_n value (g/mol).

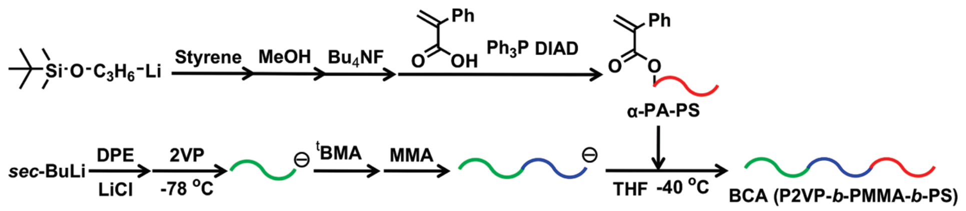
As mentioned above, ACB triblock terpolymer is exactly the same as BCA triblock terpolymer in block structure. However, a different design is possible when one considers the synthetic route of BCA polymer. As illustrated in Scheme 3, this polymer may be synthesized by the linking reaction of a living anionic BC block copolymer, P2VP-*b*-PMMA, with an α-terminal PA-functionalized PS (A). The α-terminal PA-functionalized PS was prepared by the living anionic polymerization of styrene with SiOPLi, followed by conversion of the SiOP α-terminus to the PA reaction site in similar manners as mentioned above. A living

Table 1. Synthesis of ACB and BCA Triblock Copolymers

polymers	$M_n \times 10^{-3}$ (g/mol) calcd	^{1}H NMR	SEC-LS^a	M_w/M_n^{b}	A/B/C (wt/wt/wt) calcd	^{1}H NMR
α-PA-P2VP	18.3	17.7	18.8	1.03	0/100/0	0/100/0
ACB (PS-*b*-PMMA-*b*-P2VP)	32.2	35.0	34.6	1.04	25/58/17	27/54/19
α-PA-PS	9.34	10.7	9.19	1.03	100/0/0	100/0/0
BCA (P2VP-*b*-PMMA-*b*-PS)	28.9	29.7	30.1	1.05	32/34/34	31/34/35

[a] Determined by SEC equipped with triple detectors. [b] Estimated by SEC with standard polystyrenes.

Scheme 3. Synthesis of BCA Triblock Terpolymer



P2VP-*b*-PMMA was prepared by the sequential anionic block copolymerization of 2VP and MMA with the initiator from *sec*-BuLi and DPE in THF at −78 °C. Prior to the polymerization of MMA, the living P2VP was end-capped with a few unit of ^{t}BMA to avoid the ester carbonyl attack, and a 4-fold excess of LiCl was added to narrow the molecular weight distribution of the PMMA block. A 3.2-fold excess of the living P2VP-*b*-PMMA reacted *in situ* with the α-terminal PA-functionalized PS in THF at −40 °C for 24 h.

The SEC profile of the reaction mixture showed two peaks overlapped to each other to a certain extent. A higher peak may correspond to the target linked polymer, while a lower peak is considered to be the excess deactivated living P2VP-*b*-PMMA based on the SEC elution count. The linking reaction was estimated to be nearly quantitative by comparing two peak areas. Since the isolation of the target polymer was not successful by fractional precipitation using various solvent combinations, it was isolated by the SEC fractionation. The isolated polymer was observed to have a sharp monomodal distribution (M_w/M_n = 1.05). The molecular weights observed by SEC-RALLS and ^{1}H NMR agreed with that calculated (see Table 1). Agreement between the composition observed and that calculated was satisfactory. Thus, the target BCA triblock terpolymer, P2VP-*b*-PMMA-*b*-PS (10 200−10 500−9 300 in M_n (g/mol)), was also successfully synthesized.

Synthesis of BAC (or CAB) Triblock Terpolymer: P2VP-*b*-PS-*b*-PMMA (or PMMA-*b*-PS-*b*-P2VP). Another possible triblock terpolymer synthesized by the proposed methodology is a BAC triblock terpolymer, P2VP-*b*-PS-*b*-PMMA. This terpolymer may be synthesized by the linking reaction of a living anionic P2VP (B) with an α-terminal PA-functionalized AC diblock copolymer, PS-*b*-PMMA, as illustrated in Scheme 4.

The α-terminal PA-functionalized PS-*b*-MMA was prepared by the living anionic block copolymerization of styrene, DPE (only for end-capping), and MMA with SiOPLi. A 5-fold excess of LiCl was added prior to the polymerization of MMA in order to narrow the molecular weight distribution. The resulting diblock copolymer was treated first with $(C_4H_9)_4NF$ and then with α-phenylacrylic acid. By this treatment, the α-SiOP terminus was converted to the PA reaction site. The resulting α-terminal PA-functionalized PS-*b*-PMMA was reacted with a 1.7-fold excess of living P2VP at −78 °C for 15 h.

Under the conditions, the linking reaction appeared to be complete on the basis of SEC peak areas. The linked polymer was isolated in 73% yield by fractional precipitation using THF, ethanol, and hexane. The isolated polymer was observed to have a sharp monomodal distribution (M_w/M_n = 1.04) and observed M_n values ($M_{n,RALLS}$ = 38 200 g/mol and $M_{n,NMR}$ = 38 400 g/mol) in agreement with that calculated (M_n = 37 200 g/mol), as listed in Table 2. The composition observed by ^{1}H NMR was quite consistent with that calculated. Thus, the target BAC triblock terpolymer, P2VP-*b*-PS-*b*-PMMA (14 100−11 800−12 200 in M_n (g/mol)), was successfully synthesized.

Raising the reaction temperature to −40 °C in the linking reaction, a small amount of higher-molecular-weight shoulder was observed in the SEC peak of the target linked polymer. It is most probably caused by the addition reaction of living P2VP to the ester carbonyl of PMMA block. Thus, the temperature of −78 °C is essential in this linking reaction.

A CAB triblock terpolymer, PMMA-*b*-PS-*b*-P2VP, is identical in block sequential order to the above BAC triblock terpolymer. As illustrated in Scheme 5, the CAB terpolymer may be synthesized by the linking reaction of a living PMMA with an α-terminal PA-functionalized PS-*block*-P2VP. The α-terminal PA-functionalized PS-*b*-P2VP was prepared by the living anionic block copolymerization where styrene, DPE (used only for end-capping), and 2VP were sequentially added with SiOPLi, followed by conversion of the SiOP α-terminus to the PA reaction site. Then, the α-terminal PA-functionalized PS-*b*-P2VP thus prepared was reacted with a 3.4-fold excess of living PMMA. The linking reaction was complete at −40 °C for 21 h.

The target polymer was isolated in 83% yield by fractional precipitation using a mixed solvent of THF, acetone, and hexane. It was observed that the isolated polymer possessed a sharp monomodal distribution (M_w/M_n = 1.04). As listed in Table 2, the molecular weights determined by SEC-RALLS and ^{1}H NMR ($M_{n,RALLS}$ = 34 300 g/mol and $M_{n,NMR}$ = 33 600 g/mol) were in good agreement with that calculated (M_n = 34 000 g/mol).

Scheme 4. Synthetic Route of BAC Triblock Terpolymer

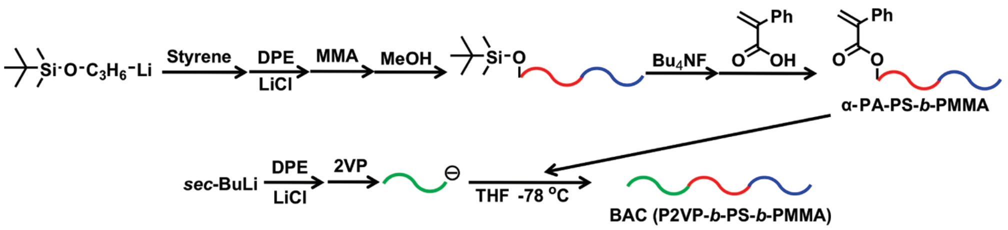
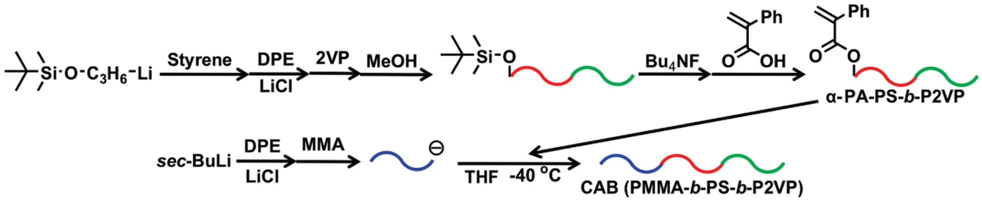


Table 2. Synthesis of BAC and CAB Triblock Terpolymers

	$M_n \times 10^{-3}$ (g/mol)				A/B/C (wt/wt/wt)	
polymers	calcd	^{1}H NMR	SEC-LS[a]	M_w/M_n[b]	calcd	^{1}NMR
α-PA-PS-*b*-PMMA	24.1	24.1	24	1.03	49/0/51	49/0/51
BAC (P2VP-*b*-PS-*b*-PMMA)	37.2	38.4	38.2	1.04	32/35/33	31/37/32
α-PA-PS-*b*-P2VP	23.2	27.0	22.3	1.04	48/52/0	51/49/0
CAB (PMMA-6-PS-6-P2VP)	34.0	33.6	34.3	1.04	31/33/36	29/37/34

[a] Determined by SEC equipped with triple detectors. [b] Estimated by SEC with standard polystyrenes.

Scheme 5. Synthesis of CAB Triblock Terpolymer



Moreover, the composition observed by ^{1}H NMR agreed well with the calculated value from the feed ratio. Thus, the target CAB triblock terpolymer, PMMA-*b*-PS-*b*-P2VP (11 700−9 950−12 700 in M_n (g/mol)), was also successfully synthesized.

Throughout the synthesis of triblock terpolymers, the PA reaction site works satisfactorily in the linking reaction with either living polymer of 2VP or MMA. Neither polymerization nor even oligomerization of the PA reaction site occurred at all under the conditions employed. However, the reaction temperature is critical. The chain-end enolate anion of living PMMA, living PS-*b*-PMMA, or living P2VP-*b*-PMMA reacted quantitatively with the PA reaction site at −40 °C, while the reaction was incomplete at −78 °C. In contrast, the linking reaction between living P2VP and the PA reaction site should be carried out at −78 °C to suppress undesirable side reactions.

Synthesis of ABC Triblock Terpolymer: PS-*b*-P2VP-*b*-PMMA. From a viewpoint of monomer reactivity, it may be possible to synthesize an ABC triblock terpolymer, PS-*b*-P2VP-*b*-PMMA, by the anionic polymerization where styrene, 2VP, and MMA are sequentially added to an anionic initiator. In fact, a similar ABC triblock terpolymer of PS-*b*-P2VP-*b*-P^{t}BMA with well-defined structures was readily synthesized by the procedure using sequential addition of the corresponding monomers.[36] However, the synthesis of a well-defined PS-*b*-P2VP-*b*-PMMA was not straightforward by the same sequential addition procedure. Although the yield of polymer was quantitative, the resulting polymer was observed to possess a trimodal distribution along with a small low-molecular-weight peak, as shown in Figure 3a. As you can see, a higher molecular weight shoulder and a lower molecular weight tail were present in the main peak. These fractions may be formed by the reaction of the P2VP chain-end anion with the ester carbonyl of MMA and PMMA.

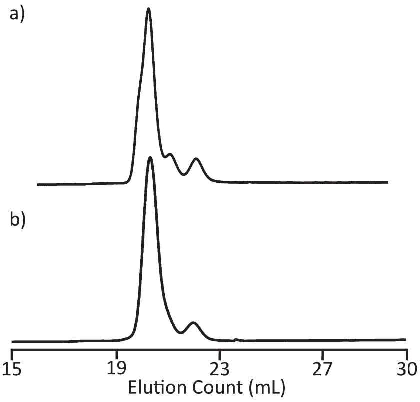


Figure 3. ABC triblock terpolymers synthesized by sequential polymerization without ^{t}BMA end-capping (a) and with end-capping (b).

This was overcome by end-capping the living chain-end anion of P2VP with a few units of ^{t}BMA, resulting in the formation of a well-defined PS-*b*-P2VP-*b*-PMMA triblock terpolymer

Table 3. Synthesis of Asymmetric ABA′, ACA′, and BCB′ Triblock Terpolymers

	$M_n \times 10^{-3}$ (g/mol)				A/B/C (wt/wt/wt)	
polymers	calcd	^{1}H NMR	SEC-LS[a]	M_w/M_n[b]	calcd	^{1}H NMR
α-PA-PS	9.34	10.7	9.19	1.03	100/0/0	100/0/0
ABA′ (PS-*b*-P2VP-*b*-PS)	29.4	32	33.0	1.04	67/33/0	63/37/0
α-PA-PS	9.34	10.7	9.19	1.03	100/0/0	100/0/0
ACA′ (PS-*b*-PMMA-*b*-PS)	27.2	32.3	30.8	1.02	69/0/31	64/0/36
α-PA-P2VP	18.3	17.7	18.8	1.03	0/100/0	0/100/0
BCB′ (P2VP-*b*-PMMA-*b*-P2VP)	39.7	41.1	39.9	1.03	0/75/25	0/74/26

[a] Determined by SEC equipped with triple detectors. [b] Estimated by SEC with standard polystyrenes.

(M_n = 40 000 (12 500–14 000–13 500) g/mol and M_w/M_n = 1.04) (see Figure 3b). Thus, the side reactions mentioned above is completely avoided. The formation of a small amount of low-molecular-weight peak observed in either Figure 3a or Figure 3b is most probably caused by impurities in 2-vinylpyridine which are added in the second step.

Synthesis of ABA′, ACA′, and BCB′ Asymmetric Triblock Copolymers: PS-*b*-P2VP-*b*-PS, PS-*b*-PMMA-*b*-PS, and P2VP-*b*-PMMA-*b*-P2VP. Because of reactivities of styrene, 2VP, and MMA as well as their growing chain-end anions, the triblock copolymers, PS-*b*-P2VP-*b*-PS, PS-*b*-PMMA-*b*-PS, and P2VP-*b*-PMMA-*b*-P2VP, are not obtained by the sequential block copolymerization. However, the former two polymers may be synthesized by the linking reaction of either living PS-*b*-P2VP or PS-*b*-PMMA with α-terminal PA-functionalized PS. The last P2VP-*b*-PMMA-*b*-P2VP may be synthesized by the linking reaction of living P2VP-*b*-PMMA with α-terminal PA-functionalized P2VP. All of such precursor polymers were prepared in similar manners carried out in the preceding sections. In the linking reaction of either living PS-*b*-PMMA or P2VP-*b*-PMMA with the α-PA-functionalized PS, a 3-fold excess of living block copolymer toward the PA reaction site was used, and the linking reaction was carried out at −40 °C for 20 h in each case. On the other hand, a 1.5-fold excess of living PS-*b*-P2VP toward the PA reaction site was used, and the linking reaction was carried out at −78 °C to avoid the ester carbonyl attack.

In the synthesis of all triblock copolymers, the SEC profile of the reaction mixture always exhibited two main peaks. On the basis of two SEC peak areas, the linking efficiency was estimated to be around 100% in each of all cases, similar to the linking reactions under the same conditions. The characterization results are summarized in Table 3. The resulting triblock copolymers isolated by fractional precipitation or the SEC fractionation were all observed to have narrow molecular weight distributions as well as predicable molecular weights and compositions. Thus, the target triblock copolymers were successfully synthesized without difficulty. As expected, the PA reaction site works in these linking reactions.

Similar triblock copolymers can be synthesized by the coupling reaction of living AB, AC, or BC block copolymer with an appropriate difunctional electrophile. In the resulting polymers, both side blocks are always same in molecular weight. However, in the triblock copolymers synthesized by the present methodology, it is possible to intentionally change the molecular weight of each of both side blocks. For instance, the BCB triblock copolymer herein synthesized possessed 10 700 (B), 10 400 (C), and 18 800 (B) in molecular weight (g/mol). Therefore, this polymer is abbreviated as BCB′. Other two polymers are also abbreviated as ABA′ and ACA′, although their both side blocks were similar in molecular weight (11 600–12 200–9 200 (g/mol)) and 10 500–11 100–9 200 (g/mol)). Such asymmetric triblock copolymers are expected to have unique and interesting morphologies which should be different from those of the corresponding symmetric triblock copolymers of ABA, ACA, and BCB types. This is one of the advantages in this linking methodology.

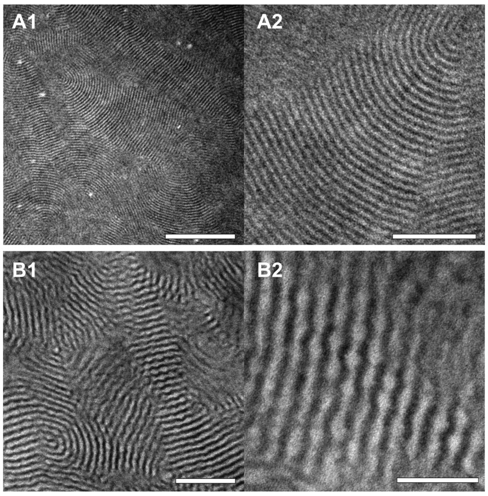


Figure 4. Triblock terpolymer morphologies of BCA (A) and BAC (B) solvent-cast from THF as a nonselective solvent. All samples were stained with iodine (P2VP appears dark), and scale bars correspond to 500, 200, 200, and 100 nm.

Bulk Morphologies of BAC and BCA Triblock Terpolymers P2VP-*b*-PS-*b*-PMMA and P2VP-*b*-PMMA-*b*-PS. Our new synthetic methodology allows the screening of all possible block sequences and, hence, all possible bulk phase interfaces in a combinatorial fashion. Exchanging the middle block with an end block, e.g., from BAC to BCA, will also change the interfaces from B/A and A/C to B/C and C/A. Bulk morphology thin films of both terpolymers were cast from THF to investigate the influence of changing interfaces on the morphology. Thin films were cut on an ultramicrotome into sheets of a thickness of 60 nm, and the P2VP phase was selectively stained with iodine (see Figure 4).

Both terpolymers have equal block weight fractions, and as expected, lamella–lamella morphologies are observed in bulk, but with distinct differences. BCA only has interfaces between the P2VP/PMMA and PMMA/PS phases, whereas BAC has shared interfaces between P2VP/PS and PS/PMMA. Figures 4A1 and 4A2 clearly show lamellae with an unusual directed curvature and a tendency to long-range order. This might be attributed to the moderate Flory–Huggins interaction parameter, $\chi_{\mathrm{P2VP/PMMA}} \approx 0.075$, compared to the lower parameter $\chi_{\mathrm{PMMA/PS}} \approx 0.035$. The equal weight fractions of all blocks still force the morphology into the lamella–lamella regimen. BAC lamellae in Figures 4B1 and 4B2 consist of a periodically undulating P2VP-lamella as a consequence of the very high interaction parameter $\chi_{\mathrm{P2VP/PS}} \approx 0.13$ and the same low parameter $\chi_{\mathrm{PMMA/PS}} \approx 0.035$. Triblock terpolymer bulk morphologies depend not only on synthetically tunable parameters, such as overall molecular weight and block weight fractions, but especially on the interfacial tensions and polymer–polymer interaction parameters. Thus, exchanging blocks in triblock terpolymers while keeping molecular weight and weight fractions constant directly affects the obtained bulk morphology. Here the small effect on the morphology for the presented low-molecular-weight polymers may have a greater impact with increased overall molecular weights and is part of ongoing investigations.

■ CONCLUSIONS

By developing the methodology combining living anionic diblock copolymers as building blocks with a specially designed linking reaction, we have successfully synthesized new triblock terpolymers, PS-*b*-PMMA-*b*-P2VP (and P2VP-*b*-PMMA-*b*-PS) and P2VP-*b*-PS-*b*-PMMA (and PMMA-*b*-PS-*b*-P2VP), and triblock copolymers, PS-*b*-P2VP-*b*-PS, PS-*b*-PMMA-*b*-PS, and P2VP-*b*-PMMA-*b*-P2VP, whose synthesis is not possible by the living anionic block polymerization where the corresponding monomers are sequentially added. The specially designed linking reaction between living anionic polymer (or diblock copolymer) and α-terminal PA-functionalized block copolymer (or homopolymer) is employed in the methodology. In the triblock copolymers synthesized by this linking methodology, each side block was intentionally changed in molecular weight to afford asymmetric triblock copolymers which cannot be synthesized by any other methods. As often mentioned in this study, sequential addition of monomers was important and critical for obtaining well-defined triblock terpolymers of styrene, 2-VP, and MMA due to nucleophilicity of their living anionic polymers. However, well-defined triblock co- and terpolymers of styrene, 2-VP, and MMA could be synthesized without consideration of nucleophilicity of their living polymers by using the methodology herein developed.

It may be also possible to synthesize ABA″ (ACA″ and BCB″) triblock terpolymers whose A (or B) and A″ (or B″) blocks are different in polymer structure, but their growing chain-end anions as well as monomers are similar in reactivity. Typically, A and A″ are PS and polyisoprene (PI), while B and B″ are P2VP and P4VP. The synthesis of such new triblock terpolymers like PS-*b*-P2VP-*b*-PI, PS-*b*-PMMA-*b*-PI, and P2VP-*b*-PMMA-*b*-P4VP is now under investigation. Investigating bulk morphologies obtained from solvent casting, BAC and BCA triblock terpolymers exhibited deviations in the fine structure. Terpolymer specifics were almost identical for both terpolymers, and hence, a direct influence of the block sequence on the morphology was observed.

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