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Precise Synthesis of New Triblock Co- and Terpolymers by a Methodology Combining Living Anionic Polymers with a Specially Designed Linking Reaction

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Summary: Five A-B-A′, A-C-A′, B-A-B′, C-A-C′, and C-B-C′ triblock terpolymers with block orders difficult to synthesize by sequential polymerization have been successfully synthesized by a new methodology combining living anionic polymers with a specially designed linking reaction using α-phenylacrylate as the reaction site. Here, A(A′), B(B′), and C(C′) represent groups of polymers (having chain-end anions with different nucleophilicities), which are only polymerizable from A(A′) to B(B′) to C(C′) via sequential polymerization. The corresponding polymers are polystyrene (A) and poly(α-methylstyrene) (A′), poly(2-vinylpyridine) (B) and poly(4-vinylpyridine) (B′) and polymers from methacrylate type monomers like poly(methyl methacrylate) (C), poly(*tert*-butyl methacrylate) (C′), poly(2-hydroxyethyl methacrylate) (C′), poly(2,3-dihydroxypropyl methacrylate) (C′), and poly(ferrocenylmethyl methacrylate) (C′). Furthermore, three synthetically difficult B-A-B, C-A-C, and C-B-C triblock copolymers with molecular asymmetry in both side blocks have also been synthesized by the developed methodology. All of the polymers thus synthesized are quite new triblock terpolymers and copolymers with well-defined structures, i.e., precisely controlled molecular weights, compositions and narrow molecular weight distributions ($M_w/M_n \leq 1.05$).

Keywords: linking reaction; living anionic polymers, triblock copolymers, triblock terpolymers

Introduction

Block polymers with a high degree of molecular and compositional homogeneity are very important model polymers to elucidate properties and behavior in solution, bulk, and melt states.[1,2] Moreover, their morphologies and molecular assemblies have been widely studied and the resulting ordered nanostructures and self-organizing assemblies have been employed as nano-scale devices with many potential applications in the fields of nanoscience and nanotechnology.[3–9] Most of the block polymers used for such purposes are usually limited to AB-type diblock copolymers. Recently, alternate $(A\text{-}B)_n$ multiblock copolymers[10–19] and A-B-C triblock terpolymers[20–25] have attracted increasing interest due to their unique morphologies and molecular assemblies which are quite different from those of A-B diblock copolymers.

Such well-defined block polymers are generally synthesized by living anionic polymerization, where two or more monomers are sequentially added to an appropriate initiator, so-called "sequential

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polymerization". With the use of monomers having similar reactivities, almost all block polymers can be synthesized because crossover polymerization is possible among such monomers. For example, A-B, A-B-A, B-A-B, and (A-B)$_n$ multiblock copolymers have been synthesized by sequential polymerization. When three monomers are used, three A-B-C, A-C-B, and B-A-C triblock terpolymers are synthesized.

In order to further design and synthesize block polymers, it is necessary to use a variety of monomers having different reactivities. In this case, the sequential order of monomer addition becomes critical, because the reactivities of monomers and their growing chain-end anions are not similar to each other.[26] In general, a less reactive growing chain-end anion is produced by a more reactive monomer and *vice versa*. This causes a serious problem in that less reactive growing chain-end anions cannot often initiate the polymerization of less reactive monomers. Accordingly, a less reactive monomer should first be polymerized, followed by the polymerization of a more reactive monomer.

Considering the block copolymerization of styrene and 2-vinylpyridine (2VP) by sequential living anionic polymerization, it is known that 2VP is higher than styrene in anionic reactivity and, on the other hand, the growing chain-end anion of living poly(2-vinylpyridine) (P2VP) is less reactive than that of living polystyrene (PS). More seriously, living P2VP cannot initiate the polymerization of styrene with quantitative efficiency and the polymerization is always stopped in the course of the process. Therefore, styrene should first be polymerized and 2VP is subsequently polymerized as the second monomer, resulting in a PS-*b*-P2VP (A-B) diblock copolymer. In a case where 2VP is first polymerized, followed by the polymerization of styrene, the 2VP homopolymer and a P2VP-*b*-PS diblock copolymer with a very broad molecular weight distribution are obtained. In addition, the unreacted styrene monomer is recovered to some extent. This means that the synthesis of well-defined P2VP-*b*-PS (B-A) diblock, PS-*b*-P2VP-*b*-PS (A-B-A) triblock, P2VP-*b*-PS-*b*-P2VP (B-A-B) triblock copolymers, and alternate (PS-*b*-P2VP)$_n$ (A-B)$_n$ multiblock copolymers is not possible by means of living anionic polymerization where 2VP and styrene are sequentially added.

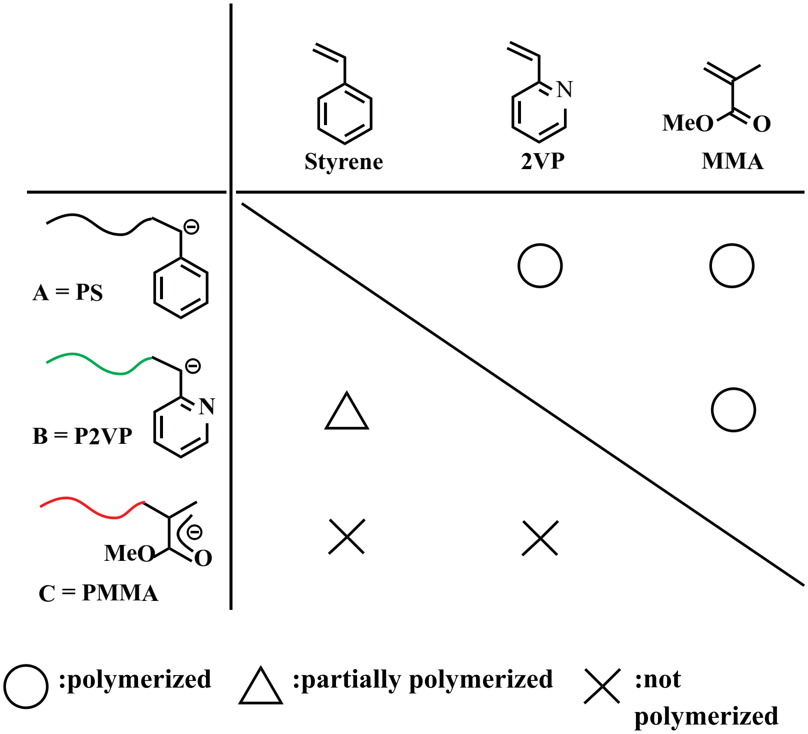
With the use of three monomers having different reactivities, such as styrene, 2VP, and methyl methacrylate (MMA), a PS-*b*-P2VP-*b*-PMMA (A-B-C) type is the only triblock terpolymer synthesized by sequential polymerization based on the reactivities of the monomers and chain-end anions, as shown in Table 1.[27]

Two other possible triblock terpolymers, PS-*b*-PMMA-*b*-P2VP (A-C-B) and P2VP-*b*-PS-*b*-PMMA (B-A-C), cannot be synthesized because 2VP is not polymerized with living PMMA and the polymerization of styrene with living P2VP is problematic, as mentioned above. Thus, the synthesis of block polymers is quite limited in the sequential polymerization using monomers with different reactivities and, therefore, a new methodology is needed in order to synthesize the plural of block copolymer and terpolymer.

Recently, we successfully synthesized a series of alternate (PS-*b*-P2VP)$_n$ (A-B)$_n$ multiblock copolymers by developing a new methodology combining an α-terminal-functionalized living anionic diblock copolymer of PS-*b*-P2VP with a specially designed linking reaction.[28] The synthetic outline is illustrated in Scheme 1.

In the first step, an α-terminal 3-*tert*-butyldimethylsilyloxypropyl (SiOP)-functionalized living PS-*b*-P2VP was prepared by the living anionic polymerization where styrene, 1,1-diphenylethylene (DPE) (used only for end-capping) and 2VP were sequentially polymerized with 3-*tert*-butyldimethylsilyloxy-1-propyllithium (SiOPLi). The α-SiOP terminus of the resulting polymer was then quantitatively converted to an α-phenylacrylate (PA) reaction site by deprotection of the α-SiOP terminus with $(C_4H_9)_4NF$, followed by treatment with α-phenylacrylic acid under the conditions of the Mitsunobu esterification reac-

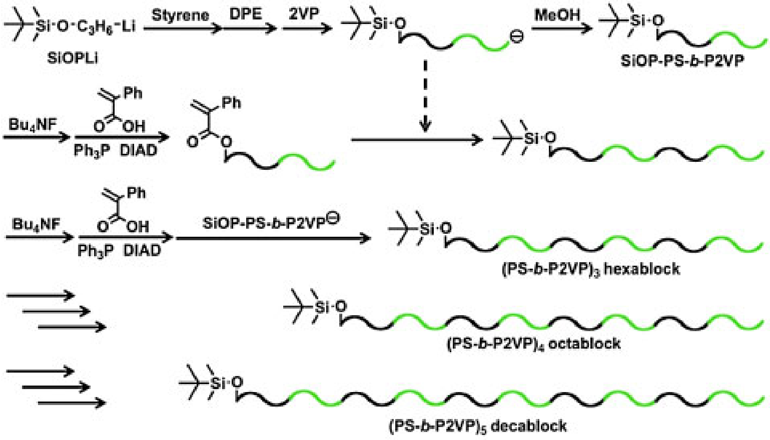
Table 1.
Polymerizability of styrene, 2-vinylpyridine, methyl methacrylate toward their living polymers.



	Styrene	2VP	MMA
A = PS		○	○
B = P2VP	△		○
C = PMMA	×	×	

○ :polymerized △ :partially polymerized × :not polymerized

tion. In the second step, the α-terminal-PA-functionalized PS-*b*-P2VP thus prepared was reacted with the α-terminal-SiOP-functionalized living PS-*b*-P2VP prepared in advance in the same manner, resulting in an α-terminal SiOP-functionalized (PS-*b*-P2VP)$_2$ tetrablock copolymer. Since the two reaction steps proceeded virtually



Scheme 1.
Synthesis of (PS-*b*-P2VP)$_n$ multiblock copolymers.

quantitatively, the same reaction sequence could be repeated three more times to synthesize (PS-*b*-P2VP)$_3$ hexablock, (PS-*b*-P2VP)$_4$ octablock, and even (PS-*b*-P2VP)$_5$ 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, the linking reaction satisfactorily works to connect the P2VP chain with the PS chain-end in ca. 100% yield. This chain connection from P2VP to PS is difficult by sequential block copolymerization, as mentioned above. The linking reaction was also effective for the connection from either the PMMA or P^{t}BMA segment to the PS chain. Thus, other multiblock copolymers of (PS-*b*-PMMA)$_5$ and (PS-*b*-P^{t}BMA)$_3$ were successfully synthesized.

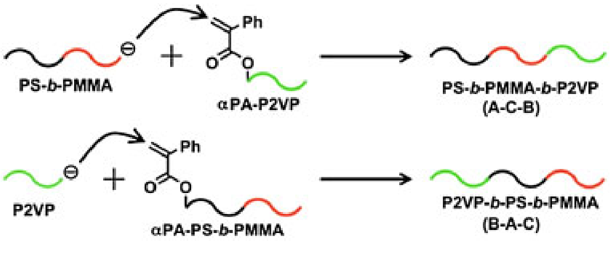
The linking reaction could be applied to the synthesis of both PS-*b*-PMMA-*b*-P2VP (A-C-B) and P2VP-*b*-PS-*b*-PMMA (B-A-C) triblock terpolymers, synthetically difficult by sequential polymerization.[27] As shown in Scheme 2, these polymers were successfully synthesized by the linking reactions of living PS-*b*-PMMA with α-terminal-PA-functionalized P2VP and living P2VP with α-terminal-PA-functionalized PS-*b*-PMMA.

Herein, we report on the successful extension of the methodology using such an effective linking reaction for the synthesis of five A-B-A′, A-C-A′, B-A-B′, C-A-C′, and C-B-C′ triblock terpolymers. In these polymers, A and A′ correspond to polymers of styrene and its derivative α-methylstyrene, B and B′ to polymers of 2-vinylpyridine and 4-vinylpyridine and C and C′ are polymers of the methacrylate monomers, methyl methacrylate (C), *tert*-butyl methacrylate (C′). In addition, poly(2-hydroxyethyl methacrylate) (PHEMA), poly(2,3-dihydroxypropyl methacrylate) (PDIMA), and poly(ferrocenylmethyl methacrylate) (PFMMA) segments are also used as C′ blocks. A′ (or B′ and C′) are similar to A (or B and C) in the reactivities of monomer and chain-end anion, but different from A (or B and C) in polymer structure. Furthermore, the successful synthesis of three B-A-B, C-A-C, and C-B-C triblock copolymers with molecular asymmetry in both side blocks by the methodology using the linking reaction is also described.

Experimental Part

General Procedure of Triblock Terpolymers and Copolymers

The materials and measurements herein used are reported in our previous papers.[27–30] Except for deprotection and the Mitsunobu esterification reaction, all of the polymerization and linking reactions were carried out in THF 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 red-colored 1,1-diphenylhexyllithium (ca. 0.05 M) in a heptane solution prior to the polymerization and linking reactions. All operations were performed according to



Scheme 2.
Synthesis of A-C-B and B-A-C triblock terpolymers.

the usual high-vacuum technique with break-seals. The detailed synthetic procedures are the same as those reported in our previous papers.[27,28] In general, a 2-fold (or more) excess of living P2VP or living PS-*b*-P2VP diblock copolymer was reacted with an α-terminal-PA-functionalized polymer at −78 °C for 15 h. On the other hand, a 3-fold (or more) excess of living PMMA, living PS-*b*-PMMA diblock copolymer, or living P2VP-*b*-PMMA diblock copolymer was reacted with an α-terminal-PA-functionalized polymer at −40 °C for 20 h. The degree of PA-functionalization is estimated by ^{1}H NMR to be ca. 100% in each of all cases. The linking reactions were all complete under such conditions. The requisite block polymers were isolated in 40–88% yield by fractional precipitation using appropriate mixed solvents or fractionated by SEC.

Results and Discussion

In our previous paper,[27] we chose three representative monomers, styrene, 2VP, and MMA, all of which are capable of undergoing living anionic polymerization, to afford stable living polymers. However, only a PS-*b*-P2VP-*b*-PMMA (A-B-C) triblock terpolymer could be synthesized by sequential polymerization, while the synthesis of two other triblock terpolymers, PS-*b*-PMMA-*b*-P2VP (A-C-B) and P2VP-*b*-PS-*b*-PMMA (B-A-C), was not possible, due to the reactivities of the monomers and their chain-end anions, as listed in Table 1. By developing the linking reaction shown in Schemes 1 and 2, the above A-C-B and B-A-C triblock terpolymers were successfully synthesized by connecting PMMA to P2VP and P2VP to PS in the linking reaction.

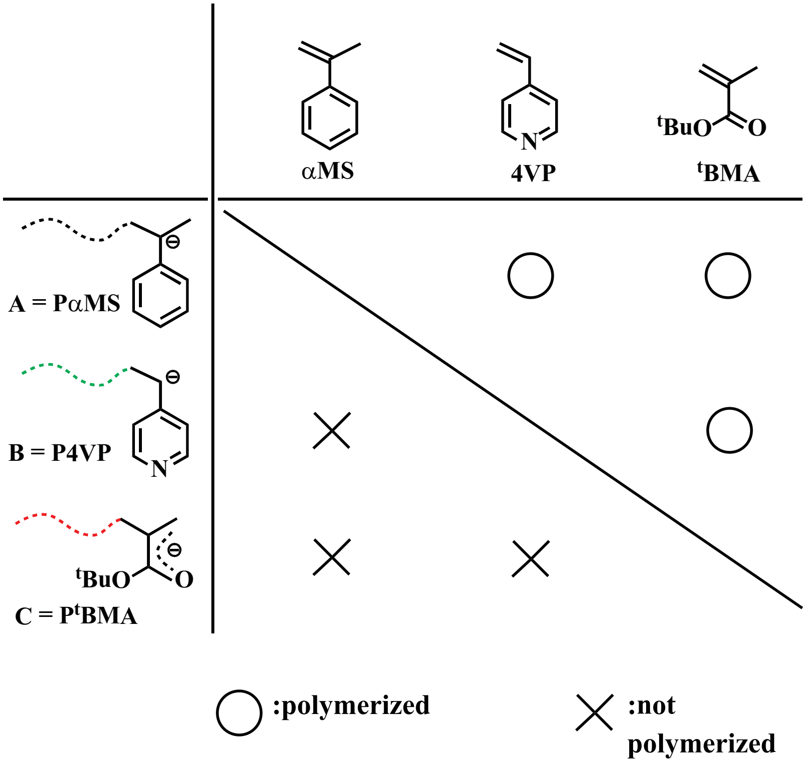
For investigating the more general and versatile aspects of the linking reaction, we will synthesize five different triblock terpolymers, represented as A-B-A′, A-C-A′, B-A-B′, C-A-C′, and C-B-C′. The A′, B′, and C′ blocks are PαMS, P4VP, and P^{t}BMA segments, respectively. In addition, PHEMA, PDIMA, and PFMMA segments are also used as C′ blocks. Based on the monomer structure and the crossover polymerization results summarized in Table 2,[31] the A′ (or B′ and C′) block is found to be similar to the A (or B and C) block in reactivities of monomer and chain-end anion, but different from A (or B and C) block in polymer structure.

Previously, Hadjichristidis and his coworkers reported a quite effective methodology for the synthesis of block polymers difficult to be obtained by sequential polymerization.[32–35] In this methodology, they prepared 2-(chloromethylphenyl)ethyldimethylchlorosilane of a new heterofunctional terminator having benzyl chloride (BnCl) and silyl chloride moieties. This terminator is designed to selectively react with the terminal silanolate anion of poly(dimethylsiloxane) (PDMS) or its block polymers to introduce the BnCl function at the ω-chain-end. The ω-terminal BnCl-functionalized PDMS or block polymers thus prepared were reacted with living anionic polymers to result in a variety of new PDMS-containing block polymers. Very unfortunately, this terminator cannot be utilized for our synthetic purpose, because all living polymers employed in this study do not selectively react with the silyl chloride moiety of the terminator.

Synthesis of PS-*b*-P2VP-*b*-PαMS (A-B-A′) and PS-*b*-PMMA-*b*-PαMS (A-C-A′) Triblock Terpolymers

Because of the reactivities of styrene, αMS (similar to styrene in reactivity), 2VP, and MMA and their chain-end anions, the title triblock terpolymers cannot be synthesized by sequential polymerization. However, the PS-*b*-P2VP-*b*-PαMS (A-B-A′) triblock terpolymer may be synthesized by the linking reaction of a living A-B diblock copolymer with an α-terminal-PA-functionalized A′ polymer. From the viewpoint of block sequential order, a PαMS-*b*-P2VP-*b*-PS. (A′-B-A) triblock copolymer is the same as the above A-B-A′ polymer, although the order is exactly opposite. Interestingly, this A′-B-A triblock terpolymer can be synthesized by using a different combination of a

Table 2.
Polymerizabilities of α-methylstyrene, 4-vinylpyridine, and *tert*-butyl methacrylate toward their living polymers.

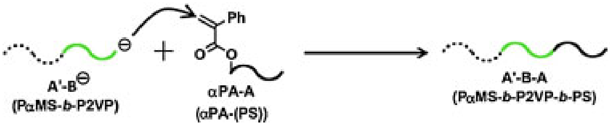


	αMS	4VP	ᵗBMA
A = PαMS		○	○
B = P4VP	×		○
C = PᵗBMA	×	×	

○ :polymerized × :not polymerized

living A′-B diblock copolymer with an α-terminal-PA-functionalized A polymer in the linking reaction, as shown in Scheme 3. Similarly, the A-C-A′ (or A′-C-A) triblock terpolymer may be synthesized by the linking reaction of living A-C (or A′-C) diblock copolymer with α-terminal-PA-functionalized A′ (or A) polymer.

For experimental convenience, both A′-B-A and A′-C-A polymers are herein synthesized because the same α-terminal-PA-functionalized A polymer is usable in each reaction. A typical synthetic procedure of the A′-B-A triblock terpolymer is as follows: First, an α-chain-end-PA-functionalized PS was prepared by the living anionic polymerization of styrene with 3-*tert*-butyldimethylsilyloxy-1-propyllithium (SiOPLi), followed by conversion of the α-SiOP terminus to a PA reaction site via deprotection of the silyl group and subsequent esterification with α-phenylacrylic acid under the conditions of the Mitsunobu reaction.[27] In the second step, the α-chain-end-PA-functionalized PS ($M_n = 11\,000$ g/mol) thus prepared was used in the linking



Scheme 3.
Synthesis of A′-B-A triblock terpolymer.

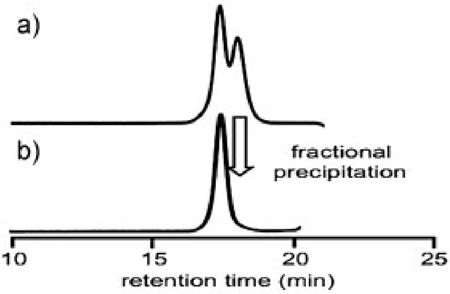


Figure 1.
SEC profiles of the reaction mixture (a) and A′-B-A triblock terpolymer (b) isolated by fractional precipitation.

reaction with a 2.7-fold excess of living PαMS-*b*-P2VP (M_n = 10 000 g/mol (4 600 g/mol (PαMS) and 5 400 g/mol (P2VP)) prepared in advance by the sequential polymerization of αMS, DPE (used for end-capping), and 2VP with *sec*-BuLi in THF at −78 °C. The reaction was carried out in THF at −78 °C for 15 h. As can be seen in Figure 1, the SEC profile exhibits only two distinct peaks for the requisite triblock terpolymer and the unreacted PS-*b*-P2VP used in excess in the reaction. The linking efficiency was estimated to be almost quantitative by comparing the ratio of two peak areas. The polymer, isolated in 50% yield by fractional precipitation using THF, ethanol, and hexane, exhibits a sharp monomodal distribution. The isolated polymer was 20 600 g/mol in M_n value determined by SEC-LS, which is in good agreement with that calculated (M_n = 21 000 g/mol). Furthermore, the composition observed by ^{1}H NMR agreed well with the calculated value. All of these analytical results, listed in Table 3, clearly indicate the successful formation of the expected PαMS-*b*-P2VP-*b*-PS (A′-B-A) triblock terpolymer with well-defined structures.

Similarly, the PαMS-*b*-PMMA-*b*-PS (A′-C-A) triblock terpolymer was synthesized by the linking reaction of living PαMS-*b*-PMMA (M_n = 9 000 g/mol (4 400 g/mol (PS) and 4 600 g/mol (PMMA)) with the same α-chain-end-PA-functionalized PS (M_n = 11 000 g/mol). The living diblock copolymer was prepared by the sequential polymerization of αMS, DPE (used only for end-capping), and MMA in THF at −78 °C with *sec*-BuLi. Prior to the polymerization of MMA, a 5-fold excess of LiCl to *sec*-BuLi was added to narrow the molecular weight distribution of the PMMA segment. In order to complete the reaction, a 3-fold excess of the living diblock copolymer for the PA functionality was needed in the linking reaction under slightly different conditions at −40 °C for 20 h. The triblock terpolymer was isolated in 50% yield by fractional precipitation with chloroform, ether, and hexane and characterized by SEC, SEC-LS, and ^{1}H NMR. As expected, the resulting polymer was the target A′-C-A triblock terpolymer with predictable molecular weight and composition as well as a narrow molecular weight distribution (see also Table 3).

The B-C-B′ (or B′-C-B) triblock terpolymer is one of the same series of triblock terpolymers and may be synthesized by the linking reaction of a living B-C (or B′-C) diblock copolymer with an α-terminal-PA-functionalized B′ (or B) polymer. However, the P4VP used as the B′ segment in this study was readily precipitated at an early

Table 3.
Synthesis of A′-B-A and A′-C-A triblock terpolymers.

Polymers	M_n (kg/mol)			M_w/M_n[b]	composition of A′/B or C/A (wt/wt/wt)	
	calcd	^{1}H NMR	SEC-LS[a]		calcd	^{1}H NMR
(A′-B-A) PαMS-*b*-P2VP-*b*-PS	21.0	25.6	20.6	1.05	22/26/52	26/31/43
(A′-C-A) PαMS-*b*-PMMA-*b*-PS	20.6	22.4	20.6	1.04	21/23/56	23/25/52

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

stage of the polymerization in THF at −78 °C and the resulting P4VP was observed to be totally insoluble in THF. Accordingly, neither of the precursory polymers of α-terminal-PA-functionalized P4VP nor living P4VP-*b*-PMMA could be prepared. Thus, the synthetic attempt of P2VP-*b*-PMMA-*b*-P4VP (or P4VP-*b*-PMMA-*b*-P2VP) triblock terpolymer was not successful due to the insolubility of P4VP.

Synthesis of P2VP-*b*-PS-*b*-P4VP (B-A-B′), PMMA-*b*-PS-*b*-P^{t}BMA (C-A-C′), and PMMA-*b*-P2VP-*b*-P^{t}BMA (C-B-C′) Triblock Terpolymers

Similar to the A-B-A′ and A-C-A′ triblock terpolymers, the synthesis of B-A-B′, C-A-C′, and C-B-C′ triblock terpolymers is not possible by sequential polymerization, but may be synthesized by the linking methodology.

The P2VP-*b*-PS-*b*-P4VP (B-A-B′) triblock terpolymer was synthesized by the linking reaction of a 2-fold excess of living P2VP with α-terminal-PA-functionalized PS-*b*-P4VP in THF at −78 °C for 15 h. As mentioned above, P4VP was totally insoluble in THF, while living PS-*b*-P4VP ($M_n = 15\,000$ g/mol (10 000 g/mol (PS) and 4 340 g/mol (P4VP)) was completely soluble in THF even at −78 °C. Therefore, the linking reaction could be carried out under an identical condition in THF. From the SEC profile of the reaction mixture, there were two peaks for the triblock terpolymer and the deactivated living P2VP used in excess in the reaction. Based on the two peak areas, the linking reaction was estimated to be almost quantitative. The isolated polymer exhibited a monomodal sharp distribution and possessed predictable molecular weight and composition, as listed in Table 4.

We next tried to synthesize a series of C-A-C′ triblock terpolymers consisting of the following functional poly(alkyl methacrylate)s as C′ blocks: P^{t}BMA convertible to poly(methacrylic acid), hydrophilic PHEMA and water-soluble PDIMA having hydroxyl groups, and PFMMA having a ferrocenyl function. For the polymer synthesis, hydroxyl groups of HEMA and DIMA were protected as *tert*-butlydimethylsilyl ether and acetal forms during the living anionic polymerization, followed by deprotection after the linking reaction.

In order to synthesize such C′-A-C (instead of C-A-C′ due to the synthetic convenience) triblock terpolymers, four different living C′ polymers, prepared in advance, were reacted with the same α-terminal-PA-functionalized A-C diblock copolymers. Living P^{t}BMA, poly(2-*tert*-butyldimethylsilyloxyethyl methacrylate) (P(Si-HEMA)), poly(2,3-dimethyl-1,3-dioxolan-4-yl)methyl methacrylate) (P(acetal-

Table 4.
Synthesis of B′-A-B, C′-A-C and C′-B-C triblock terpolymers.

Polymers	M_n (kg/mol)			M_w/M_n [b)]	composition of B′ or C′/A or B/B or C (wt/wt/wt)	
	calcd	^{1}H NMR	SEC-LS [a)]		calcd	^{1}H NMR
(B′-A-B)						
P2VP-*b*-PS-*b*-P4VP	19.7	20.3	20.8	1.03	25/52/23	24/53/23
(C′-A-C)						
P^{t}BMA-*b*-PS-*b*-PMMA	32.8	38.0	34.5	1.03	35/31/34	35/31/34
P(Si-HEMA)-*b*-PS-*b*-PMMA	32.5	33.4	32.4	1.04	34/32/34	28/35/37
P(acetal-DIMA)-*b*-PS-*b*-PMMA	32.0	36.1	33.3	1.03	33/32/35	33/33/34
PFMMA-*b*-PS-*b*-PMMA	32.5	31.6	29.1	1.03	31/33/36	31/33/36
(C′-B-C)						
P^{t}BMA-*b*-P2VP-*b*-PMMA	37.7	39.5	36.2	1.03	30/27/43	33/26/41
P(acetal-DIMA)-*b*-P2VP-*b*-PMMA	36.3	35.1	34.9	1.05	29/28/43	26/29/45
PFMMA-*b*-P2VP-*b*-PMMA	35.1	35.7	35.4	1.04	26/29/45	27/29/44

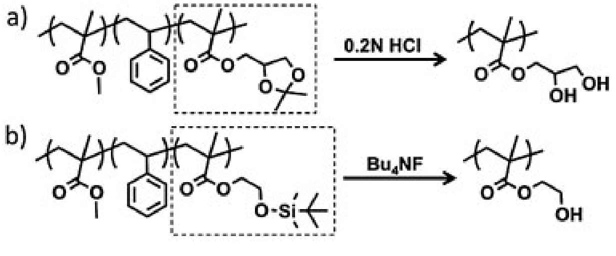
[a)] Determined by SEC equipped with triple detectors. [b)] Estimated by SEC with standard polystyrenes.

DIMA)), and PFMMA were used as living C′ polymers. These linking reactions were observed to be complete under conditions where a 3-fold excess of living C′ polymer for the PA functionality was used in each reaction in THF at −40 °C for 20 h. It should be mentioned, however, that the linking reaction using living P^{t}BMA was not efficient in THF at −40 °C for 20 h, but could proceed to completion by raising the temperature to −25 °C. The resulting polymers, P^{t}BMA-*b*-PS-*b*-PMMA, P(Si-HEMA)-*b*-PS-*b*-PMMA, and P(acetal-DIMA)-*b*-PS-*b*-PMMA, were isolated in 40–70% yields by fractional precipitation, while the isolation of PFMMA-*b*-PS-*b*-PMMA was performed by SEC fractionation. All of the isolated polymers have sharp monomodal distributions ($M_w/M_n \leq 1.05$). Their molecular weights and compositions determined by SEC-LS and ^{1}H NMR agreed with those calculated (see Table 3). The two polymers, P(Si-HEMA)-*b*-PS-*b*-PMMA, and P(acetal-DIMA)-*b*-PS-*b*-PMMA, were treated with $(C_4H_9)_4NF$ and 0.2N HCl, respectively, to regenerate the original hydroxyl groups, converting to PHEMA-*b*-PS-*b*-PMMA and PDIMA-*b*-PS-*b*-PMMA, as shown in Scheme 4. It should be herein mentioned that the combination between PA-functionalized PS-*b*-PMMA (A-C) and living P(Si-HEMA) (C′) is essential in the synthesis of C′-A-C triblock terpolymer. The reason is that a PA-functionalized PS-*b*-P(Si-HEMA) cannot be prepared, because the *tert*-butyldimethylsilyl protecting groups of P(Si-HEMA) are also cleaved with Bu_4NF during the introduction stage of the PA function. Thus, there is a restrain with the use of P(Si-HEMA).

Similarly, a 3-fold excess of living P^{t}BMA (C′), living P(acetal-DIMA) (C′), or living FMMA (C′) was reacted with α-terminal-PA-functionalized P2VP-*b*-PMMA (B-C) to afford three different C′-B-C triblock copolymers. These results are also summarized in Table 4. Thus, the linking methodology was also effective for the synthesis of well-defined B-A-B′, C-A-C′, and C-B-C′ triblock terpolymers.

Synthesis of P2VP-*b*-PS-*b*-P2VP (B-A-B), PMMA-*b*-PS-*b*-PMMA (C-A-C), and PMMA-*b*-P2VP-*b*-PMMA (C-B-C) Triblock Copolymers with Molecular Asymmetry in Both Side Blocks

Not only triblock terpolymers, but also the title triblock copolymers cannot be synthesized by sequential polymerization. On the basis of the successful synthesis of the triblock terpolymers demonstrated in this study and our previous results,[27] these polymers may be synthesized by the linking reactions of a 2-fold excess of living P2VP with an α-terminal-PA-functionalized PS-*b*-P2VP diblock copolymer at −78 °C for 15 h and a 3-fold excess of living PMMA with either an α-terminal-PA-functionalized PS-*b*-PMMA diblock copolymer or α-terminal-PA-functionalized P2VP-*b*-PMMA diblock copolymer at −40 °C for 20 h. As expected, these linking reactions were observed to efficiently proceed under the above-mentioned conditions, resulting in the target triblock copolymers in ca. 100% yields. All



Scheme 4.
Deprotection of P(acetal-DIMA) (a) and P(Si-HEMA) (b).

of the polymers, after isolation in around 60% yields by fractional precipitation or SEC fractionation, were observed to have predictable molecular weights, compositions, and narrow molecular weight distributions, as listed in Table 5.

One more advantageous point in this synthetic procedure is that both side blocks can be intentionally changed in molecular weight by changing the molecular weights of the precursor polymers. For example, the PMMA-*b*-PS-*b*-PMMA (C-A-C) triblock copolymer was synthesized by the following linking reaction: A 3-fold excess of living PMMA ($M_n = 18\,700$ g/mol) was reacted with α-PA-functionalized PS-*b*-PMMA ($M_n = 22\,800$ g/mol (11 200 g/mol (PS) and 11 600 g/mol (PMMA)) in THF at $-40\,°C$ for 20 h. The SEC profile exhibits two distinct peaks for the requisite triblock copolymer and the deactivated living PMMA used in excess in the reaction. Quantitative linking efficiency was confirmed by comparing the ratio of two peak areas. The polymer, isolated in 88% yield by fractional precipitation using benzene and methanol, exhibits a sharp monomodal distribution. Both side PMMA blocks really possessed different molecular weights, 18 700 g/mol and 11 600 g/mol. Similarly, the molecular weights of both side blocks could be changed in two other triblock copolymers (see Table 5).

Each of the title triblock copolymers could also be synthesized by the polymerization when styrene and 2VP, styrene and MMA, or 2VP and MMA were sequentially added to an appropriate difunctional initiator. However, both side blocks in the resulting polymers were always same and not changeable in molecular weight. The versatility of the methodology using the linking reaction is thus obvious. Such asymmetric triblock copolymers are expected to have unique and interesting morphologies and molecular assemblies which should be different from those of the corresponding symmetric triblock copolymers.

Conclusion

By developing a methodology combining living anionic polymers with a specially designed linking reaction using the PA reaction site, we successfully synthesized a variety of the following triblock terpolymers and triblock copolymers, which are synthetically difficult to obtain by sequential polymerization: PS-*b*-P2VP-*b*-PαMS (A-B-A$'$), PS-*b*-PMMA-*b*-PαMS (A-C-A$'$), P2VP-*b*-PS-*b*-P4VP (B-A-B$'$), PMMA-*b*-PS-*b*-P^{t}BMA (C-A-C$'$), PMMA-*b*-PS-*b*-PHEMA (C-A-C$'$), PMMA-*b*-PS-*b*-PDIMA (C-A-C$'$), PMMA-*b*-PS-*b*-PFMMA (C-A-C$'$), PMMA-*b*-P2VP-*b*-P^{t}BMA (C-B-C$'$), PMMA-*b*-P2VP-*b*-PDMA (C-B-C$'$), and PMMA-*b*-P2VP-*b*-PFMMA (C-B-C$'$) triblock terpolymers, as well as P2VP-*b*-PS-*b*-P2VP (B-A-B), PMMA-*b*-PS-*b*-PMMA (C-A-C), and PMMA-*b*-P2VP-*b*-PMMA (C-B-C) triblock copolymers with molecular weight asymmetry. All of the polymers herein synthesized are quite new in block sequential order and well-defined in chain length and composition. Furthermore, each side block can be intentionally changed in molecular weight to afford triblock copolymers with molecular asymmetry in both side blocks. Thus, the developed methodology using the linking

Table 5.
Synthesis of B-A-B, C-A-C and C-B-C asymmetric triblock terpolymers.

Polymers	M_n (kg/mol)			M_w/M_n[b]	composition (wt)	
	calcd	^{1}H NMR	SEC-LS[a]		calcd	^{1}H NMR
B-A-B (P2VP-*b*-PS-*b*-P2VP)[c]	42.5	40.9	39.9	1.02	49/25/26 (B/A/B)	49/25/26
C-A-C (PMMA-*b*-PS-*b*-PMMA)[d]	42.5	43.8	41.6	1.03	43/28/29 (C/A/C)	45/27/28
C-B-C (PMMA-*b*-P2VP-*b*-PMMA)[e]	40.9	41.2	39.5	1.03	14/29/57(C/B/C)	16/32/52

[a] Determined by SEC equipped with triple detectors. [b] Estimated by SEC with standard polystyrenes. [c] B-A-B (19 500-10 000-10 400). [d] C-A-C (18 700-11 200-11 600). [e] C-B-C (6 300-12 600-20 500).

reaction allows for the general and versatile synthesis of triblock co- and terpolymers of most combinations without consideration of electrophilicity of monomers and nucleophilicity of their living polymers. It should also be mentioned that the PA reaction sites of homopolymers and diblock copolymers, capable of reacting with various living polymers having different nucleophilicities, were and can be used in a modular way to produce a variety of triblock co- and terpolymers. Furthermore, these polymers are expected to be very interesting materials concerning their bulk and self-assembled structures. Since there are many A′, B′, and C′ segments usable in the linking reaction, the synthesis of a wide variety of triblock co- and terpolymers with functional groups is expected in the near future.[36]

[1] H. Watanabe, in: "*Rheology of Multiphase Polymeric Materials. Structure and Properties of Multiphase Polymeric Materials*", T. Araki, T. Qui, M. Shibayama, Eds., Marcel Dekker, New York **1998**, Chapter 9.

[2] W. Hamly, in "*The Physics of Block Copolymers*", Oxford University Press, New York **1998**.

[3] C. Park, J. Yoon, E. L. Thomas, *Polymer*, **2003**, *44*, 6724.

[4] H. Mori, A. H. E. Müller, *Prog. Polym. Sci.* **2003**, *28*, 1403.

[5] R. Adhikari, G. H. Micher, *Prog. Polym. Sci.* **2004**, *29*, 949.

[6] N. Hadjichristidis, H. Iatrou, M. Pitsikalis, S. Pispas, A. Avgeropoulos, *Prog. Polym. Sci.* **2005**, *30*, 725.

[7] F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer, A. P. J. H. Schenning, *Chem. Rev.* **2005**, *105*, 1491.

[8] V. Abetz, P. F. W. Simon, *Adv. Polym. Sci.* **2005**, *189*, 125.

[9] N. Hadjichristidis, A. Hirao, Y. Tezuka, F. Du Prez, in: "*Complex Macromolecular Architectures: Synthesis, Characterization, and Self-Assembly*", John Wiley & Sons (Asia), Singapore **2011**.

[10] R. I. Spontak, S. D. Smith, *J. Polym. Sci. Part B: Polym. Phys.* **2001**, *39*, 947.

[11] M. E. Vigild, C. Chu, M. Sugiyama, K. A. Chaffin, F. S. Bates, *Macromolecules* **2001**, *34*, 951.

[12] Y. Mori, L. S. Lim, F. S. Bates, *Macromolecules* **2003**, *36*, 9879.

[13] R. Nap, I. Erukhimovich, G. T. Bricke, *Macromolecules* **2004**, *37*, 4296.

[14] Y. Nagata, J. Matsuda, A. Noro, D. Cho, A. Takano, Y. Matsushita, *Macromolecules* **2005**, *38*, 10220.

[15] L. Wu, T. P. Lodge, F. S. Bates, *Macromolecules* **2006**, *39*, 294.

[16] R. Nap, N. Sushko, I. Erukhimovich, G. T. Bricke, *Macromolecules* **2006**, *39*, 6770.

[17] H. Watanabe, Y. Matsumiya, T. Sawada, T. Iwamoto, *Macromolecules* **2007**, *40*, 6885.

[18] Y. Matsushita, *Macromolecules* **2007**, *40*, 771.

[19] R. Stadler, C. Austrra, J. Beckmann, U. Krappe, I. Voit-Martin, L. Leibler, *Macromolecules* **1995**, *28*, 3080.

[20] E. Giebeler, R. Stadler, *Macromol. Chem. Phys.* **1997**, *198*, 3815.

[21] S. Ludwig, A. Böker, V. Abetz, A. H. E. Müller, G. Krausch, *Polymer* **2003**, *44*, 6815.

[22] S. Ludwig, A. Böker, A. Voronov, N. Rehse, R. Magerle, G. Krausch, *Nature Mater.* **2003**, *2*, 744.

[23] F. H. Schacher, A. Walther, M. Ruppel, M. Drechsler, A. H. E. Müller, *Macromolecules* **2009**, *42*, 3540.

[24] F. H. Schacher, J. Yuan, H. J. Schoberth, A. H. E. Müller, *Polymer* **2010**, *51*, 2021.

[25] A. Sperschneider, H. F. Schacher, L. Tsarkova, A. Böker, V. Abetz, A. H. E. Müller, *Macromolecules* **2010**, *43*, 10213.

[26] H. L. Hsieh, R. P. Quirk, in: "*Anionic Polymerization: Principles and Applications*" Marcel Dekker, New York **1996**.

[27] A. Hirao, Y. Matsuo, T. Oie, R. Goseki, T. Ishizone, K. Sugiyama, A. H. Gröschel, A. H. E. Müller, *Macromolecles* **2011**, *44*, 6345.

[28] K. Sugiyama, T. Oie, A. A. El-Magd, A. Hirao, *Macromolecules* **2010**, *43*, 1403.

[29] T. Hirano, H.-S. Yoo, Y. Ozama, A. A. El-Magd, K. Sugiyama, A. Hirao, *J. Inorg. Organomet. Polym. Mater.* **2010**, *20*, 445.

[30] A. Hirao, R. Inushima, T. Nakayama, T. Watanabe, H.-S. Yoo, T. Ishizone, K. Sugiyama, T. Kakuchi, S. Carlotti, A. Deffieux, *Eup. Polym. J.* **2011**, *47*, 713.

[31] The crossover polymerization was examined by the polymerization of either styrene or MMA with a living PS-*b*-P4VP, instead of a living 4VP insoluble in THF.

[32] V. Bellas, H. Iatrou, N. Hadjichristidis, *Macromolecules* **2000**, *33*, 6993.

[33] V. Bellas, H. Iatrou, E. N. Pitsinos, N. Hadjichristidis, *Macromolecules* **2001**, *34*, 5376.

[34] P. G. Fragouli, H. Iatrou, N. Hadjichristidis, *J. Polym. Sci. Part A: Polym. Chem.* **2004**, *42*, 514.

[35] P. G. Fragouli, H. Iatrou, D. J. Lohse, N. Hadjichristidis, *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 3938.

[36] A. Hirao, S. Loykulnant, T. Ishizone, *Prog. Polym. Sci.* **2002**, *27*, 1399.