Synthesis of Polypropylene via Catalytic Deoxygenation of Poly(methyl acrylate)

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S *Supporting Information*

ABSTRACT: We propose the defunctionalization of vinyl polymers as a strategy to access previously inaccessible polyolefin materials. By utilizing $B(C_6F_5)_3$-catalyzed deoxygenation in the presence of silane, we demonstrate that eliminating the pendent ester in poly(methyl acrylate) effectively leaves a linear hydrocarbon polymer with methyl pendants, which is polypropylene. We further show that a polypropylene-*b*-polystyrene diblock copolymer and a polystyrene-*b*-polypropylene-*b*-polystyrene triblock copolymer can be successfully derived from the poly(methyl acrylate)-containing block polymer precursors and exhibit quite distinct

materials properties due to their chemical transformation. This unique postpolymerization modification methodology, which goes beyond the typical functional group conversion, can offer access to a diverse range of unprecedented polyolefin block polymers with a variable degree of functional groups.
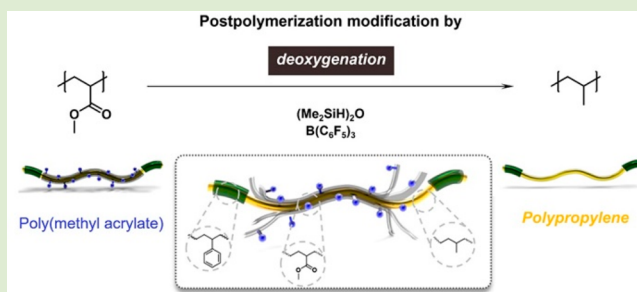
Polyolefins, representatively polyethylene (PE) and polypropylene (PP), are the most widely used commodity plastics in modern life. The majority of polyolefins are commercially produced by metal-catalyzed coordination polymerization that was initially developed by Ziegler and Natta.[1] Significant progress in the design of polymerization catalysts has been made, which allows for the control of molar mass, branching, and the tacticity of polyolefins.[2,3] Most catalysts, however, do not exhibit living/controlled polymerization behavior, mainly due to the undesired irreversible chain transfer and β-elimination paths. Recent years have witnessed a number of alkene polymerization catalysts showing living/controlled characteristics, thus enabling their use in the synthesis of polyolefins with complex macromolecular architectures such as block copolymers.[4−6] Nonetheless, the scope has been largely restricted to a few attainable architectures,[7−13] particularly when compared to the extraordinary architecture control and vast compositional freedom offered by other living/controlled polymerization systems, including anionic[14] and controlled radical polymerization.[14−16] However, controlled radical polymerization of ethylene and propylene is inherently difficult, mainly due to lack of radical-stabilizing pendent groups.[13]
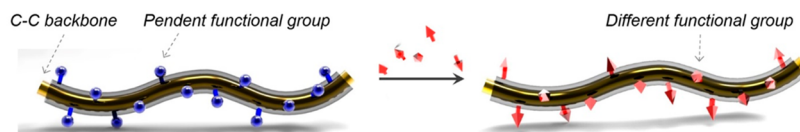
We envisioned developing a postpolymerization modification route for the synthesis of polyolefins by using well-defined vinyl polymers as precursors, wherein a readily obtainable parent polymer is chemically transformed to produce the target polymer, retaining its chain length and architecture.[17] Vinyl polymer precursors with desired architectures were planned by the preparation of reversible addition−fragmentation chain transfer (RAFT) polymerization, which is a well-developed controlled radical polymerization technique.[16,18] Then, we hypothesized that the target polyolefins could be obtained by removing the oxygen-containing pendent groups via a deoxygenation reaction.

A few postpolymerization modification approaches have been reported to lead to polyolefins via the hydrogenation of unsaturated hydrocarbon polymers synthesized by anionic polymerization[19] or olefin metathesis polymerization.[20] On the other hand, a deoxygenation route is quite distinct, because oxygen-containing vinyl monomers, such as vinyl esters, vinyl ethers, acrylates, and methacrylates, may be utilized in principle as precursors to produce PE, PP, and polyisobutylene
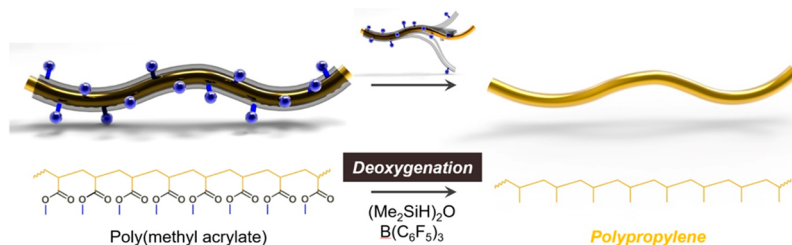
Figure 1. Synthesis of PP by the postpolymerization deoxygenation of PMA. The $B(C_6F_5)_3$-catalyzed deoxygenation of PMA in the presence of 1,1,3,3-tetramethyldisiloxane produces PP by eliminating the oxygens in the pendent group.
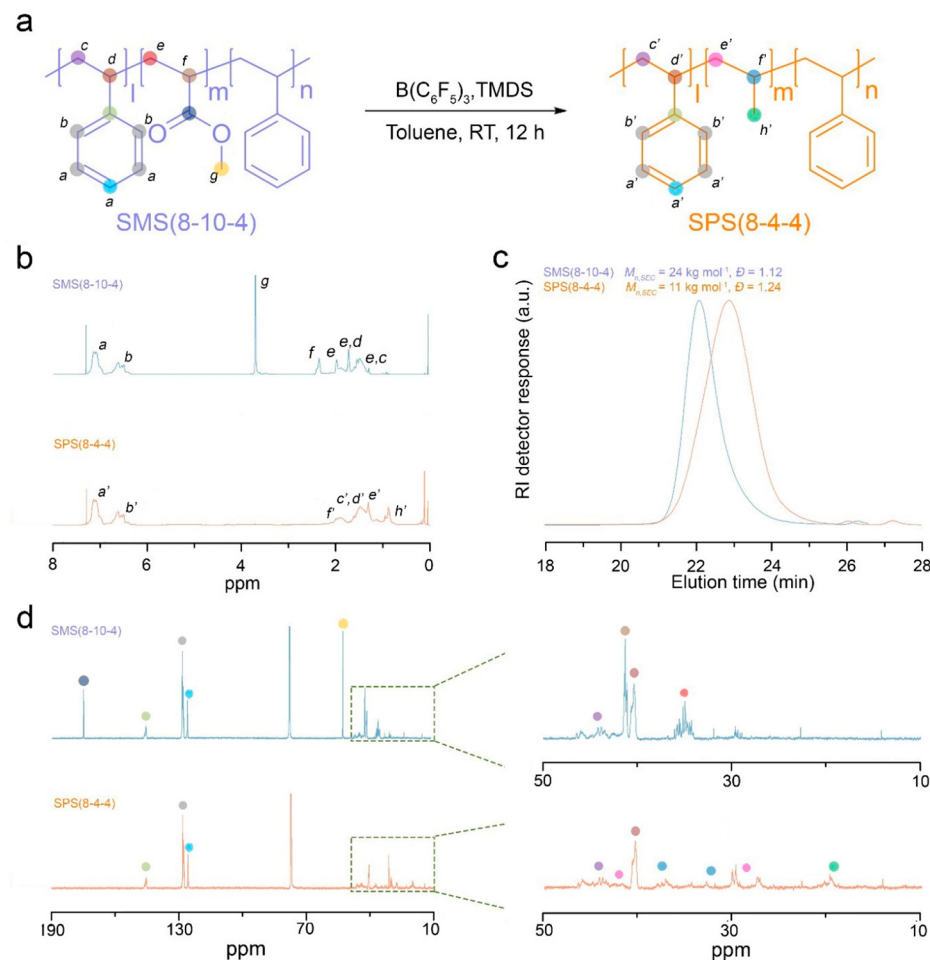

Figure 2. Synthesis of PS-*b*-PP-*b*-PS by the deoxygenation of PS-*b*-PMA-*b*-PS. (a) Reaction scheme. (b–d) ^{1}H NMR (b), SEC (c), and ^{13}C NMR (d) data of SPS(8−4−4) (orange) compared with the parent SMS(8−10−4) (blue). The NMR spectra were recorded using CDCl$_3$ as a solvent.

(PIB). The synthetic parameter space can be further enriched, considering that polyolefins are produced from their copolymers and functional polyolefins are obtained by partially deoxygenated precursors. From the postpolymerization mod-

ification standpoint, the elimination of functional groups to produce hydrocarbon polymers is quite unique compared to the typical postpolymerization modification reactions forming new covalent bonds with the installation of additional

segments.[17,21−27] Nonetheless, we note that the acetyl group removal is commercially used in the synthesis of poly(vinyl alcohol) from poly(vinyl acetate) with control of the hydrolysis degree. Thus, we believe that the deoxygenation route can be particularly well suited for the synthesis of functional polyolefins, considering that the coordination copolymerization of olefinic monomers with polar monomers has been challenging, mainly because of catalyst poisoning.[28]

As the key deoxygenation reaction, we focused on the borane-catalyzed deoxygenation of acrylates by using hydrosilanes as a reducing reagent.[29] Yamamoto and co-workers discovered an intriguing catalytic reactivity of tris-(pentafluorophenyl) borane $B(C_6F_5)_3$ with excess hydrosilanes,[30] which can cleave a carbon−oxygen bond under mild conditions without requiring transition metals. Alcohols, esters, carboxylic acids, and ethers can be reduced to hydrocarbons with high efficiency by the reductive $B(C_6F_5)_3$ catalysis.[31−34] This finding has been extended to several interesting chemical transformations, including the reduction of CO_2 to methane,[35] the deoxygenation of carbohydrate into hydrocarbons,[36] and the depolymerizations of lignins, polyesters, and polyethers.[37] We anticipated that the highly reductive nature of the $B(C_6F_5)_3$ catalysis[38] would be suitable for the conversion of polyacrylates to PP in a controlled manner.

In this contribution, we have disclosed the synthesis of PP and PP-containing block polymers via the $B(C_6F_5)_3$-catalyzed deoxygenation of poly(methyl acrylate) (PMA) and PMA-containing copolymers, as schematically shown in Figure 1. By combining these with deoxygenation-inert polystyrene (PS), we successfully derived PP and PP-containing diblock and triblock copolymers from PMA, a PS-*b*-PMA diblock copolymer, and a PS-*b*-PMA-*b*-PS triblock copolymer as precursors in the deoxygenation transformations. We have also proven that functional PP containing pendent hydroxyl groups can be prepared by adjusting the relative amounts of hydrosilane to the PMA repeating units. The PS-*b*-PP-*b*-PS triblock copolymers obtained through the presently developed approach exhibited elastic behavior as a thermoplastic elastomer due to the microphase separation between PS and PP, thereby suggesting that these materials have a promising use as additives and compatibilizers.

We investigated the deoxygenation reaction of methyl 2-methyl-3-phenylpropanoate (**1**)[39] as a model substrate containing methyl acrylate and styrene functionalities (Figure S1). The screening of hydrosilanes and solvents revealed that the use of 1,1,3,3-tetramethyldisiloxane (TMDS) in chloroform and toluene at room temperature (RT) was the most effective (Table S1).[40] The ^1H NMR spectra shown in Figure S2 clearly demonstrate that using more than 4 equiv of TMDS in the presence of $B(C_6F_5)_3$ (5 mol %) in $CDCl_3$ effectively cleaved the methyl ester moiety, as evidenced by the complete disappearance of the methyl ester protons. The $B(C_6F_5)_3$-activated addition of the silane to the carbonyl oxygen initiates the deoxygenation to initially produce the methyl ether,[32] which is subsequently deoxygenated to leave the methyl group in the presence of excessive TMDS. As a result, isobutylbenzene (**4**) was formed in a ≥95% yield determined by the ^1H NMR spectrum (Figures S3 and S4). This result indicates that the methyl ester in the methyl acrylate unit is highly reactive to the deoxygenation, while the styrene unit is fully intact. We also noticed that a small amount of *n*-butylbenzene (**5**; ≤5%)

was also concurrently formed, which may be produced through a methyl shift in the carbocation intermediate.

Based on the promise of the model compound, we tested the deoxygenation reaction of PMA using a PS-*b*-PMA-*b*-PS triblock copolymer to see whether the corresponding PS-*b*-PP-*b*-PS can also be produced (Figure 2). The parent PS-*b*-PMA-*b*-PS was synthesized by the sequential RAFT polymerizations of styrene, methyl acrylate, and styrene using *S*-1-dodecyl-*S′*-(*R,R′*-dimethyl-*R″*-acetic acid) trithiocarbonate[41] as a chain transfer agent (CTA; Figures S5 and S6a). We denote the sample according to the constituting blocks in the polymer (S for PS, M for PMA, and P for PP) and the molar mass (kg mol^{-1}) in the parentheses.

Figure 2 depicts the ^1H and ^{13}C NMR spectroscopy and size exclusion chromatography (SEC) data of SPS(8−4−4) that were obtained upon the deoxygenation of SMS(8−10−4). The reaction was conducted in toluene at room temperature for 12 h in the presence of 5 mol % $B(C_6F_5)_3$ and 10 equiv TMDS relative to the PMA repeating unit (Figure 2a) for complete reduction. A ^1H NMR spectrum of SPS(8−4−4) in Figure 2b clearly indicates that the methyl ester proton in the PMA repeating unit at 3.7 ppm completely disappeared. Instead, a new peak corresponding to the methyl proton in the PP repeating unit at 1.2 ppm emerges, corroborating the formation of PP from PMA. We note that the aliphatic protons corresponding to atactic PMA backbone at 2.1 and 2.4 ppm also completely disappear after the reaction, and new protons corresponding to PP backbone appear upfield at 1.3 ppm. PS aromatic protons at 6.0−7.2 ppm and aliphatic protons appearing as broad peaks at 1−2 ppm were entirely intact. An increase in the integral value of the aliphatic region (0.5−2.5 ppm) due to formation of methyl protons was well consistent with the theoretically expected value at full conversion, supporting that the reaction was nearly quantitative (Figure S7). The SEC trace of the resulting polymer indicated a clear shift to a lower molar mass from 24 to 11 kg mol^{-1} while retaining relatively narrow molar mass distribution, thereby supporting a reduction in mass by the removal of the ester groups (Figure 2c). Peaks corresponding to protons in the CTA moiety were not discernible in the ^1H NMR spectrum of SPS(8−4−4), presumably due to simultaneous removal of the trithiocarbonate group during the deoxygenation reaction.[42]

A ^{13}C NMR spectrum of SPS(8−4−4) supported the formation of PP (Figure 2d). All peaks were assigned on the basis of the distortionless enhancement by the polarization transfer (DEPT) spectra (Figure S8). Peaks corresponding to the carbonyl (178 ppm) and methyl (52 ppm) carbons in the methyl ester of the PMA repeating unit were again completely absent, and PP carbons appeared in the 15−45 ppm range. On the other hand, no change was observed from the peaks corresponding to PS. Based on the assignment given in the literature,[43] we determined that atactic PP with <7% of defects, such as ethylene (E) and propylene repeating units with the head-to-head configuration (P*), was obtained (Figure S9). We mainly attribute the ethylene defects to the alkyl shift during the reaction, as we observed from the model reaction study (Figure S2). Because we did not observe head-to-head defects from the NMR data of SMS(8−10−4), formation of the head-to-head defects appears to involve complex rearrangement reactions but the mechanism is not clear at this moment.

We applied the established reaction conditions to the conversion of PS-*b*-PMA and PMA to derive PS-*b*-PP and PP,
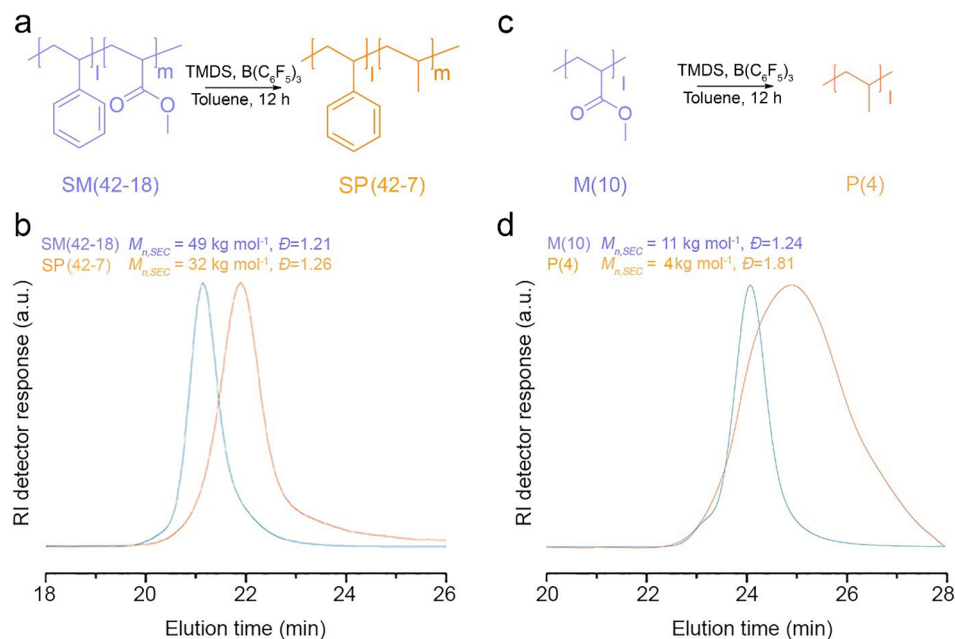
Figure 3. Synthesis of PS-*b*-PP and PP (orange) by the deoxygenation of parent PS-*b*-PMA and PMA (blue). (a, b) Reaction scheme (a), and SEC traces (b) of SP(42−7) compared to SM(42−18). (c, d) Reaction scheme (c) and SEC traces (d) of P(4) compared to M(10).

Table 1. Characterization Details of the PP-Containing Block Polymers Synthesized in This Study

	Precursor				Polyolefin		
Entry	$M_{n,NMR}$ (kg mol^{-1})	$M_{n,SEC}$ (kg mol^{-1})	$Đ$	Entry	$M_{n,NMR}$ (kg mol^{-1})	$M_{n,SEC}$ (kg mol^{-1})	$Đ$
SMS	8-10-4	24	1.12	SPS	8-4-4	11	1.24
SM	42-18	49	1.21	SP	42-7	32	1.26
				SP$_{0.47}$	42-13	43	1.22
M	10	11	1.24	P	4	4	1.81

as shown in Figure 3 (see Figure S6b for the synthesis of PS-*b*-PMA). The successful formation of SP(42−7) and P(4) from SM(42−18) and M(10) was verified by ^{1}H NMR (Figure S10) and SEC analysis, supporting the fidelity of the deoxygenation approach. The SEC trace of the PS-*b*-PP diblock copolymer shown in Figure 3b exhibited a clean shift to a higher elution volume without broadening, indicating that the narrow molar mass distribution achieved by the RAFT polymerization was retained during the deoxygenation reaction, as in the case of the PS-*b*-PP-*b*-PS triblock copolymer. We observed significant broadening of the SEC trace of the PP homopolymer, however (Figure 3d). It is not clear what would cause the broadening of the molar mass distribution at this moment. Nonetheless, PP

was successfully produced from the PMA precursor, as evidenced by ^{1}H NMR spectra. Characterization details of synthesized polymers are summarized in Table 1.

We also explored the possibilities of partially deoxygenating PMA by adjusting the ratio of $B(C_6F_5)_3$ and TMDS relative to the PMA repeating unit to afford the functional PP with a controlled density of the pendent functional groups (Figure 4a). While the use of 5 equiv or higher amount of TMDS was sufficient to quantitatively eliminate all of the oxygen in the PMA repeating unit in SM(42−18), about 60% of the methyl ester proton in the PMA repeating unit disappeared after treating it with 1 equiv TMDS, and a new peak emerged at 3.3 ppm (Figure 4b). Based on the observation from the model
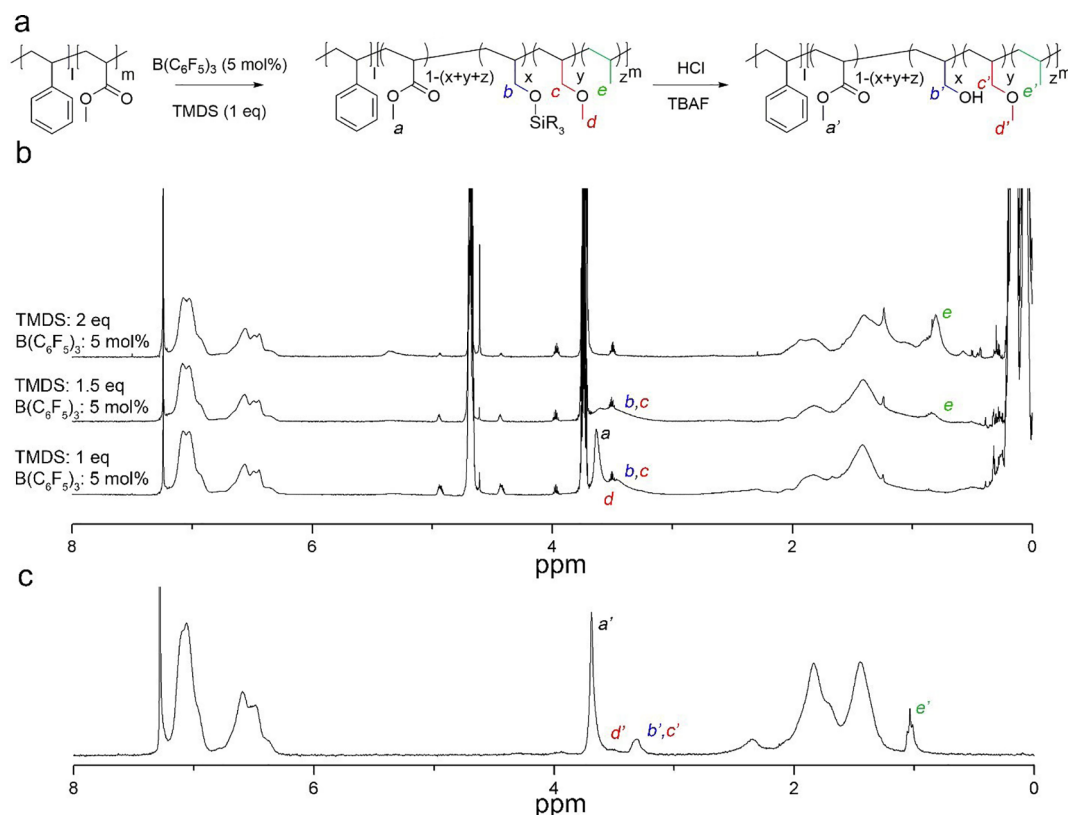
Figure 4. Partial deoxygenation of PS-*b*-PMA to produce PS-*b*-PP bearing functional groups along the PP block. (a) Reaction scheme. (b) ^{1}H NMR spectra of SM(42−18) treated with 1, 1.5, and 2 equiv TMDS. The spectra were recorded in situ after the reaction. (c) ^{1}H NMR spectrum of isolated $SP_{0.47}$(42−13). The NMR spectra were recorded using $CDCl_3$ as a solvent.

reaction, the new peak was assigned to a methylene proton adjacent to a hydroxyl group. Heteronuclear single quantum coherence spectroscopy (HSQC) and ^{1}H−^{1}H correlation spectroscopy (COSY) analysis corroborated the assignment (Figures S11−S12). We estimated the molar fractions of propylene, allyl alcohol, methyl ether, and methyl acrylate repeating units to be 47, 4, 9, and 40%, respectively, by integrating the ^{1}H NMR spectrum (Figure 4c). The appearance of O−H vibrational bands at 3500 cm^{-1} in the FTIR spectrum confirmed the presence of hydroxyl groups (Figure S13). For comparison, vibrational frequencies corresponding to the O−H and the C=O stretching (1740 cm^{-1}) were not observed in the FTIR spectrum of SP(42−7), supporting the complete deoxygenation. The SEC analysis indicated a smaller reduction in the molar mass than in the fully deoxygenated product, which is consistent with the partial deoxygenation (Figure S14). The characterization details are included in Table 1. This result suggests that the synthesis of functional PP with a control of the functional group density can be readily achieved by deoxygenation, compared with the traditional approaches involving the copolymerization of propylene with functional monomers, by taking advantage of PMA as a precursor containing 100% functionality. By further adjusting the amount of TMDS relative to the PMA repeating units, we were able to produce PS-*b*-PPs with different functional group densities, as demonstrated in Figure 4b.

The chemical transformation of PMA into PP has a profound effect on the thermal and mechanical properties of the triblock copolymer. The differential scanning calorimetry (DSC) data of SPS(8−4−4) show two distinct glass transitions at 95 and −8 °C, corresponding to PS and atactic PP,

respectively, suggesting that microphase separation occurs to form PS and PP microdomains (Figure S15). The glass transition of PMA at 20 °C that is observed in SMS(8−10−4) is not discernible in the thermogram of SPS(8−4−4). A significant reduction in glass transition temperature (T_g) of the middle block in the triblock architecture indicates that SPS would behave as a thermoplastic elastomer containing the rubbery PP middle block with low T_g between the glassy PS end blocks.

To investigate the microphase separation behavior and the mechanical properties of SPS, we synthesized SMS(6−70−6) containing a PMA middle block with a much higher molar mass and subsequently converted it to the corresponding SPS(6−28−6) (Figure S16). While the complete deoxygenation of the methyl ester was confirmed even in a reaction with this high molar mass material, SPS(6−28−6) exhibited a broader SEC trace distribution, presumably due to the chain scrambling accompanied by the rearrangement reaction. Nonetheless, SPS(6−28−6) showed a distinct scattering peak at the scattering vector (q^*) = 0.26 nm^{-1} in the small-angle X-ray scattering (SAXS) measurement, indicating that the block polymer architecture was retained to induce microphase separation (Figure 5a). Compared with the SAXS pattern of SMS(6−70−6) showing scattering peaks originating from the hexagonal symmetry, the scattering intensity of SPS(6−28−6) is reduced, probably because of the decrease in the electronic density contrast as a result of the deoxygenation. The increased heterogeneity may be also responsible for the decreased scattering intensity, and a slight increase in the characteristic distance.[44] Consistent with the chemical transformation of PMA into PP, SPS(6−28−6)
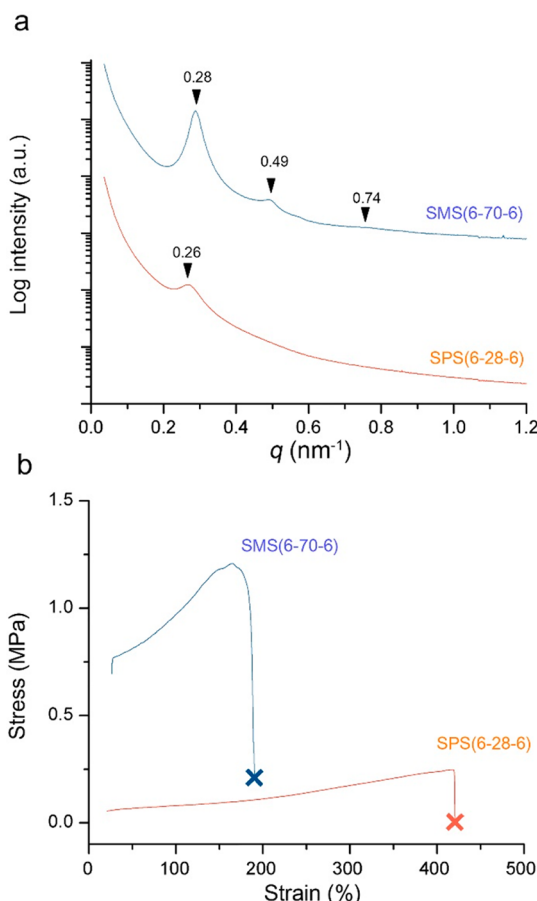
Figure 5. Microphase separation behavior and mechanical properties of PS-*b*-PP-*b*-PS in comparison with PS-*b*-PMA-*b*-PS. (a) SAXS data of SMS(6−70−6) and SPS(6−28−6). The data have been vertically shifted for clarity. (b) Representative strain−stress curves of SMS(6−70−6) and SPS(6−28−6).

showed a much higher ultimate elongation at break (425%) and a lower Young's modulus (0.26 MPa) compared with those of SMS(6−70−6) (Figure 5b).

In conclusion, we have developed the postpolymerization modification route to PP from a PMA precursor by utilizing B(C$_6$F$_5$)$_3$-catalyzed deoxygenation by using hydrosilane. The fidelity and versatility of the deoxygenation approach was demonstrated by the synthesis of PP-containing block polymers, including the PP homopolymer, the PS-*b*-PP diblock copolymer, and the PS-*b*-PP-*b*-PS triblock copolymer from PMA-containing precursors synthesized by RAFT polymerization with a control of the degree of deoxygenation. As precursors composed of a wide range of monomers with diverse architectures and tacticity control[45] are accessible by RAFT polymerization, we envision that this currently developed approach will not only open a new route to polyolefin synthesis but also greatly enrich a pool of polyolefin-containing functional macromolecules with unprecedented combinations, which will lead to the next-generation materials with superior properties.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacro-lett.9b00522.

Experimental details, ^{1}H NMR data on the model reaction, SEC data of the PMA-containing polymer precursors, ^{1}H (with integration), ^{13}C, and ^{13}C DEPT NMR spectra of PS-*b*-PP-*b*-PS, ^{1}H−^{1}H COSY, HSQC, and FTIR spectra of partially deoxygenated PS-*b*-PP, and DSC and SEC data of PS-*b*-PP-*b*-PS (PDF)

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Notes
The authors declare the following competing financial interest(s): The authors are declared to be inventors on a patent filed by KAIST related to the work presented here.

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