Controlled Synthesis of Poly(vinyl ether)-Grafted Poly(phenylacetylene)s by a Combination of Living Coordination Polymerization and Living Cationic Polymerization

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ABSTRACT: We newly designed a functionalized monomer (PhAVE-AcOH) containing a phenylacetylene (PhA) group and a 1-(acetoxy)ethoxy group, the latter of which is expected to act as an initiator moiety in combination with Lewis acid-based activators under living cationic polymerization conditions. A polyPhA-based multifunctional initiator poly(PhAVE-AcOH) with a narrow molecular weight distribution ($M_w/M_n = 1.02$) was synthesized by Rh complex-mediated living coordination polymerization of PhAVE-AcOH. Then, living cationic graft polymerization of isobutyl vinyl ether (IBVE) was performed employing the pendant 1-(acetoxy) ethoxy initiating moiety of poly(PhAVE-AcOH) to form polyIBVE-grafted polyPhA (polyPhA-g-polyIBVE), where both the main chain and side chains possessed well-controlled structures ($M_w/M_n = 1.05$–1.10). We found that UV–vis absorption spectra of polyPhA-g-polyIBVE were progressively redshifted with increasing molecular weights of the graft chain.

INTRODUCTION

The precision synthesis of graft polymers has been of considerable interest following the discovery of the living polymerization technique.$^{1–6}$ Compared to linear polymers, densely grafted polymers having corresponding molar masses generally show smaller hydrodynamic radii, lower melt and solution viscosities, lower glass transition temperatures, lower crystallinities, and higher solubilities that arise from their compact structures and flexible graft chains.$^{7–12}$ Synthesis of brush-shaped polymers has been mainly achieved by the following three methodologies: (1) the “grafting-onto” method where separately synthesized end-functionalized polymers are attached onto a multifunctional linear backbone polymer,$^{13–15}$ (2) the “grafting-from” method involving the graft polymerization of monomers from a linear macromolecular initiator having multiple initiating sites,$^{16–18}$ and (3) the “grafting-through” method (so-called macromonomer methodology) in which macromonomers are polymerized to form grafted polymers.$^{19–21}$ Thus, for the synthesis of well-defined macromonomers and multi-functionalized macromolecular initiators, not only the molecular design of multi-functionalized monomers containing functional groups of different reaction characteristics but also their selective reactions are important.

Poly(phenylacetylene)s (polyPhAs) have attracted much attention because of their interesting physical and physico-chemical properties.$^{22–26}$ Recently, external stimuli-responsive properties of a series of polyPhA-bearing functionalized side chains have been investigated experimentally and theoretically.$^{27–29}$ In addition, it has already been recognized that the side chain structures of polyPhAs play important roles not only to enhance their solubility but also to affect conjugation lengths in the main chain. Thus, the optical properties of such polyPhA-based materials can be controlled by the total
molecular design of the side chain structure or the graft copolymer structure. Synthesis of well-defined graft polymers based on the polyPhA main chain has been studied extensively. Miura and Okada developed a series of grafted polyPhAs bearing polystyrene branches by living radical polymerization with a polyPhA-based initiator having multiple initiating sites via the “grafting-from” methodology. On the other hand, homo- and copolymerization of PhA-end-capped macromonomers using Rh-based catalysts via the “grafting-through” methodology has been well investigated to yield various functionalized grafted polyPhAs. Recently, we have reported that PhA-end-capped poly(vinyl ether) (polyVE)-based macromonomers can produce a brush-shaped polyPhA bearing polyVE side chains via Rh complex-mediated homopolymerization. However, with this methodology, graft polymers having a main chain structure with a high degree of polymerization (DP) were difficult to synthesize due to steric hindrance of the macromonomers for living coordination homopolymerization (Scheme 1, route A).

Scheme 1. Two Routes for the Synthesis of Poly(vinyl ether)-Grafted Poly(phenylacetylene)s by a Combination of Living Coordination Polymerization and Living Cationic Polymerization

Here, we propose a synthetic strategy combining two types of controlled polymerizations to design well-defined grafted polymers consisting of a polyPhA backbone and polyVE pendants via the “grafting-from” methodology. In this study, we first synthesized a PhA derivative (PhAVE-AcOH) bearing a 1-(acetoxy)ethoxy group, which is an initiating site for living cationic polymerization. Next, we synthesized a polyPhA-based multifunctional initiator [poly(PhAVE-AcOH)] by Rh complex-mediated living coordination polymerization of PhAVE-AcOH. The resulting poly(PhAVE-AcOH) was then employed as a macromolecular multifunctional initiator in living cationic polymerization of isobutyl vinyl ether (IBVE) to afford the target polyPhA having both well-defined main chain and the side chains structures (Scheme 1; route B). Solutions of the resulting graft polymers showed intriguing changes in color depending on the side chain lengths, i.e., molecular weight of polyIBVE. Our strategy to combine two types of living polymerization techniques thus will enable the design of a wide variety of polyPhA-based graft polymers, where the length and type of pendant polyVEs can be modified concurrently.

RESULTS AND DISCUSSION

In our previous report, we presented the synthesis of a novel bifunctional compound having both phenylacetylene and VE moieties, revealed that its trifluoroacetic acid adduct with 1-(trifluoroacetoxy)ethoxy group can act as novel initiators for living cationic polymerization of VE, and then succeeded in the controlled synthesis of a novel PhA-end-capped polyVE macromonomer. Moreover, we described that the polymerization of the PhA-end-capped polyVE-based macromonomer using Rh catalysts ([nbdbRhCl]3 (nbdb = 2,5-norbornadiene)) allowed the synthesis of graft copolymers consisting of a polyPhA main chain and well-defined polyVE side chains. We initially attempted to synthesize a graft copolymer with well-defined main chain and side chains using the “grafting-through” strategy by living coordination polymerization with the Rh catalyst system [1/(Ph-F)]3P; 1 = R(CPh=CPh-F)2(nbd)](Ph-F)]3P; (Ph-F)P = tris(4-fluorophenyl)phosphine), which is an effective catalyst for the living polymerization of PhA derivatives in toluene at 25 °C (Scheme 1; route A). However, size exclusion chromatography (SEC) analysis indicated that the polymerization failed because no molecular weight increase was observed. The elution peak of the major compound in the reaction mixture did not shift to a higher-molecular-weight region as compared to the corresponding macromonomer. The graft copolymer synthesis was then attempted by the “grafting-from” methodology, that is, graft polymerization of VE was carried out with a macromolecular multifunctional initiator bearing pendant 1-(acetoxy)ethoxy groups. As shown in Scheme 1 route B, the synthesis of graft copolymer polyPhA-g-polyIBVE was based on a two-step synthetic strategy: (1) synthesis of the macromolecular initiator [poly(PhAVE-AcOH)] by living coordination polymerization and (2) synthesis of the graft copolymer of IBVE with poly(PhAVE-AcOH) by living cationic polymerization. It should be noted that the combination of the two types of controlled polymerization techniques allows multiple means to control the structure of the graft copolymers, where the lengths of the pendant polyIBVEs and the backbone polyPhA can be concurrently regulated.

Synthesis of PhAVE-AcOH. Recently, we have focused on the 1-(trifluoroacetoxy)ethoxy group, which can act as an initiator for living cationic polymerization of VE, and succeeded in the synthesis of various types of end-functionalized polyVEs. However, introduction of the 1-(trifluoroacetoxy)ethoxy group to polymer side chains as a macromolecular initiator is difficult due to its moisture sensitivity. To attain an effective macromolecular initiator, we instead focus on the 1-(acetoxy)ethoxy group, which can be prepared by the addition of acetic acid and has already been recognized as an initiator moiety in combination with Lewis acid-based activators under living cationic polymerization conditions. As depicted in Scheme 1, PhA reacted with 2 eqs of acetic acid at 60 °C for 4 h to give PhA-AcOH in 97% yield. The structure of PhA-AcOH was characterized by 1H and 13C NMR. As shown in Figure 1a, 1H NMR analysis of PhA-AcOH showed a series of characteristic resonances, including those of the phenyl protons (peak c at δ 8.0 and peak b at δ 7.6 ppm), the 1-(acetoxy)ethoxy group...
protons (peak f at $\delta$ 6.0, peak h at $\delta$ 2.1, and peak g at $\delta$ 1.4 ppm), and the ethynyl protons (peak a at $\delta$ 3.2 ppm). The integration area ratios of a:c:f are 1.00:2.00:1.00, which were in good agreement with the proton number ratios of the proposed structure.

Polymerization of PhAVE-AcOH with the Rh Catalyst.
Polymerization of PhAVE-AcOH was investigated in toluene at 25 °C for 1.5 h using a binary Rh catalyst system $[1/(Ph-F)_{3}P]$ ($[PhAVE-AcOH]_{0}/[1]_{0}/[(Ph-F)_{3}P]_{0} = 250/1/5$, $[PhAVE-AcOH]_{0} = 50$ mmol L$^{-1}$). The reaction was quenched with acetic acid through hydrogenation of the $\omega$-terminal.45 The resulting polymer [poly(PhAVE-AcOH)] was analyzed by refractive index (RI)-detected SEC in THF. The SEC curve of the obtained poly(PhAVE-AcOH) shows a unimodal peak with relatively broad molecular weight distribution (MWD) ($M_n = 15,000$, $M_w/M_n = 1.43$, as estimated using polystyrene standards). However, we found that the present polymerization proceeded in a controlled manner at 0 °C. As shown in Figure 2a, the recorded SEC chromatogram of the poly(PhAVE-AcOH) showed a unimodal and narrow elution peak ($M_n = 42,000$, $M_w/M_n = 1.02$). The $^1$H NMR spectrum of the isolated poly(PhAVE-AcOH) is depicted in Figure 1b. The signals of phenyl and $-CH=\text{C}-$ protons (peaks c’, b’, and a’) coming from the polyPhA repeating units appeared at $\delta$ 7.6, 6.7, and 5.7 ppm, respectively. The ratio of the resonance intensities of the methine proton versus aromatic protons in poly(PhAVE-AcOH) (peaks f’ and c’) was 0.998:2.00, indicating that the pendant 1-(acetoxy)ethoxy group was intact under the living coordination polymerization conditions. In addition, a clear signal at $\delta$ 5.7 ppm (peak a’) was assigned to the cis olefinic proton, indicating that the backbone of polyPhA possessed a cis-tranoidal structure. The cis content of poly(PhAVE-AcOH) was estimated to be 92%. The cis content is nearly identical to those of the polyPhA derivatives synthesized by using the same Rh catalyst system $[1/(Ph-F)_{3}P]$.46 All the resonances are relatively broad due the rigid conformation of the main chain that restricted the motion of the backbone. These results clearly indicate that the controlled coordination polymerization of PhAVE-AcOH resulted in the successful synthesis of a well-defined macromolecular multifunctional initiator [poly(PhAVE-AcOH)].

Cationic Polymerization of IBVE with Poly(PhAVE-AcOH).
There have been reports about living cationic polymerization of a number of vinyl monomers, such as alkyl vinyl ether, isobutylene, and styrene-type monomers.47 Among them, the adducts with a 1-(acetoxy)ethoxy group, which are prepared from acetic acid and alkyl vinyl ethers, can induce living cationic polymerization of VEs in the presence of an activator, such as ZnCl$_2$ or EtAlCl$_2$.43,44 In the present paper, pendant 1-(acetoxy)ethoxy groups were employed as initiating sites for cationic polymerization of IBVE. The cationic polymerization of IBVE was carried out with poly(PhAVE-AcOH) as a macromolecular multifunctional initiator, EtAlCl$_2$.
as an activator, and dioxane as an added base at −35 °C in toluene under dry nitrogen for 1−12 h ([PhAVE-AcOH]*/IBVE]0/[EtAlCl2]/[dioxane]0 = 1/100/5/200; [PhAVE-AcOH]*], concentration based on repeating units). The reaction was quenched by using sodiomalonic ester as an end-capping agent.28 The polymerization product was obtained as a reddish yellow sticky solid that is soluble in common organic solvents such as toluene, CHCl3, and THF.

Figure 2b shows the time−conversion curve obtained for the polymerization of IBVE, showing that the polymerization proceeded smoothly without an induction phase then reaching over 90% conversion within 12 h. The first-order kinetic plot for the polymerizations of IBVE revealed a linear dependence indicating a constant carbocationic species concentration indicative of the absence of significant termination reactions (Figure 2c). The resulting graft copolymer was analyzed in THF using a size exclusion chromatograph equipped with RI and UV (254 nm) dual detectors. The SEC traces for the obtained copolymer are shown in Figure 2a; the peak of the backbone or side chains. Because the graft copolymer has the side chain lengths of the graft copolymer polyPhA-polyIBVE-based side chain formation. To this end, direct analysis of the pendant polyIBVE moieties was performed.52 In the present study, graft copolymers with well-controlled architecture are studied for their side chain lengths. Direct analysis of the pendant polyIBVE moieties was performed.52 In the present study, graft copolymers with well-controlled architecture are studied for their side chain lengths. Direct analysis of the pendant polyIBVE moieties was performed.52 In the present study, graft copolymers with well-controlled architecture are studied for their side chain lengths. Direct analysis of the pendant polyIBVE moieties was performed.52 In the present study, graft copolymers with well-controlled architecture are studied for their side chain lengths. Direct analysis of the pendant polyIBVE moieties was performed.52 In the present study, graft copolymers with well-controlled architecture are studied for their side chain lengths. Direct analysis of the pendant polyIBVE moieties was performed.52 In the present study, graft copolymers with well-controlled architecture are studied for their side chain lengths. Direct analysis of the pendant polyIBVE moieties was performed.52 In the present study, graft copolymers with well-controlled architecture are studied for their side chain lengths. Direct analysis of the pendant polyIBVE moieties was performed.52 In the present study, graft copolymers with well-controlled architecture are studied for their side chain lengths. Direct analysis of the pendant polyIBVE moieties was performed.52 In the present study, graft copolymers with well-controlled architecture are studied for their side chain lengths. Direct analysis of the pendant polyIBVE moieties was performed.52 In the present study, graft copolymers with well-controlled architecture are studied for their side chain lengths. Direct analysis of the pendant polyIBVE moieties was performed.52 In the present study, graft copolymers with well-controlled architecture are studied for their side chain lengths. Direct analysis of the pendant polyIBVE moieties was performed.52 In the present study, graft copolymers with well-controlled architecture are studied for their side chain lengths. Direct analysis of the pendant polyIBVE moieties was performed.52 In the present study, graft copolymers with well-controlled architecture are studied for their side chain lengths. Direct analysis of the pendant polyIBVE moieties was performed.52 In the present study, graft copolymers with well-controlled architecture are studied for their side chain lengths. Direct analysis of the pendant polyIBVE moieties was performed.52 In the present study, graft copolymers with well-controlled architecture are studied for their side chain lengths. Direct analysis of the pendant polyIBVE moieties was performed.52 In the present study, graft copolymers with well-controlled architecture are studied for their side chain lengths. Direct analysis of the pendant polyIBVE moieties was performed.52 In the present study, graft copolymers with well-controlled architecture are studied for their side chain lengths. Direct

**Table 1. Results from Polymerization of IBVE from Poly(PhAVE-AcOH)**

| reaction time (h) | conversion (%) | M<sub>theory</sub> (g mol<sup>−1</sup>) | DP<sub>theory</sub> | M<sub>SEC</sub> (g mol<sup>−1</sup>) | M<sub>n</sub>/M<sub>i0</sub> | M<sub>M</sub>/M<sub>M</sub> | f (%) |
|------------------|----------------|-------------------------------|-------------------|--------------------------|----------------|----------------|------|
| poly(PhAVE-AcOH) | 1              | 69,300                        | 62,000            | 52,000                   | 1.02           | 1.00           | 69,000 |
|                  | 2              | 74,500                        | 52,000            | 52,000                   | 1.05           | 1.00           | 395,000 |
|                  | 4              | 1,071,000                     | 52,000            | 52,000                   | 1.08           | 1.00           | 890,000 |
|                  | 3              | 1,972,000                     | 52,000            | 52,000                   | 1.10           | 1.00           | 1,330,000 |
|                  | 12             | 2,523,000                     | 52,000            | 52,000                   | 1.07           | 1.00           | 1,706,000 |

*Polymerization was conducted with EtAlCl2/dioxane in toluene at −35 °C, [IBVE]0 = 1.0 mol L<sup>−1</sup>; [PhAVE-AcOH]*]/[IBVE]/[EtAlCl2]/[dioxane]0 = 1/100/5/200; [PhAVE-AcOH]*], concentration based on repeating units. The reaction was quenched with a solution of sodiomalonic ester in toluene/dioxane. *Estimated by 1H NMR. Calculated from M<sub>theory</sub> = ([IBVE]0/[PhAVE-AcOH]*) × (molecular weight)IBVE × (conversion)IBVE × DP<sub>theory</sub>poly(PhAVE-AcOH) + (molecular weight)poly(PhAVE-AcOH) × (conversion)poly(PhAVE-AcOH) × (molecular weight)IBVE × (conversion)IBVE. *Estimated by PSt-calibrated SEC in THF. Estimated by SEC in THF with a multi-angle laser light scattering detector.
peaks observed in the lower-molecular-weight region of SEC cleaved polyIBVE side chains agree with those of the small distribution with a polyPhA backbone and polyIBVE side controlled molecular weight and narrow molecular weight measurements indicate that the graft copolymers having UV

In Figure 4, we have discovered a very interesting fact that the polyIBVE obtained by hydrolysis is also 12,000. On the of the small peak observed for the graft copolymer at 98% reaction was nearly quantitative. Because the polyPhA reactions, only a single low-molecular-weight polymer was observed in each experiment, which indicates that the cleavage reaction was nearly quantitative. Because the polyPhA backbone makes up a low percentage of the overall mass of the graft copolymer, it is undetectable after the side chains are removed. MWDs of polyIBVEs obtained from the graft combination of living coordination polymerization and living cationic polymerization. First, living coordination polymerization of PhAVE-AcOH led to the formation of polyPhA-based macromolecular multifunctional initiators [poly(PhAVE-AcOH)] with well-defined structures. Next, these macromolecular initiators are useful for the synthesis of polyPhA-g-polyIBVE via “grafting-from” methodology. Solutions of the resulting polymers showed intriguing changes in absorption color depending on the length of side chains. The conjugation lengths of the polyPhA main chain would be closely related to the pendant polyIBVE structure; we therefore expect to design various polyVEs-grafted conjugated polymers that are capable of responding to external stimuli such as pH, temperature, and addition of metal ions or biomolecules.

**EXPERIMENTAL SECTION**

**Instruments.** 1H and 13C NMR spectra were recorded at 25 °C on a Bruker model AC-500 spectrometer operating at 500 and 125 MHz, respectively, where chemical shifts (δ in ppm) were determined with respect to nondeuterated solvent residues as internal standards. Analytical size exclusion chromatography (SEC) was performed at 40 °C using 8.0 mm × 300 mm polystyrene gel columns (Shodex KF-804 x 2) on a TOSOH model DP-8200 equipped with a UV-8000 variable-wavelength UV–vis detector and a RI-8022 RI detector. The number-average molecular weight (Mn) and polydispersity ratio (Mw/Mn) were calculated from the

**Figure 3.** SEC curves of the cleaved side chains from the graft polymers (polyPhA-g-polyIBVE) obtained at various IBVE conversions.

**Table 2.** Molecular Weights and Dispersity of PolyIBVE Side Chains Cleaved from the Graft Copolymer PolyPhA-g-polyIBVE

| reaction time (h) | IBVE conversion (%) | Mνtheor[b] (g mol⁻¹) | Mνcleav[c] (g mol⁻¹) | Mw/Mn |
|------------------|---------------------|-----------------------|----------------------|-------|
| 1                | 27                  | 2700                  | 3800                 | 1.37  |
| 2                | 40                  | 4000                  | 5000                 | 1.30  |
| 3                | 76                  | 7600                  | 9900                 | 1.16  |
| 12               | 98                  | 9800                  | 12,000               | 1.07  |

* Determined by 1H NMR. b Calculated from Mn,theory = ([IBVE]/[Poly(PhAVE-AcOH)]) × (Molecular weight)IBVE × (conversion)IBVE. c Estimated by PSS-calibrated SEC in THF.

conversion of IBVE were 450, 455, 460, and 470 nm, respectively, This result indicates that the graft copolymer have longer conjugation lengths in the main chain than poly(PhAVE-AcOH). It has been reported that the absorption peak of a polyPhA derivative shifts to a longer wavelength as the steric effect of the substituents increases. For example, poly[(o-methylphenyl)acetylene] exhibits an absorption at 440 nm, while poly[(o-(trimethylsilyl)phenyl]-acetylene], which possesses a bulkier trimethylsilyl substituent, has an absorption at 520 nm. Grubbs and co-workers have proposed an idea that the steric requirements of the substituents impose a planar conformation on the polymer backbone. The bulky polyIBVE side chain of the grafted copolymer should prevent the polyPhA backbone from bending and twisting and force the main chain to take a more planar conformation.

**CONCLUSIONS**

In summary, we have demonstrated an efficient and convenient route to the synthesis of a graft copolymer (polyPhA-g-polyIBVE) containing a well-defined polyPhA backbone and well-defined polyIBVE side chains. This achievement was brought about by a successful combination of living coordination polymerization and living cationic polymerization. First, living coordination polymerization of PhAVE-AcOH led to the formation of polyPhA-based macromolecular multifunctional initiators [poly(PhAVE-AcOH)] with well-defined structures. Next, these macromolecular initiators are useful for the synthesis of polyPhA-g-polyIBVE via “grafting-from” methodology. Solutions of the resulting polymers showed intriguing changes in absorption color depending on the length of side chains. The conjugation lengths of the polyPhA main chain would be closely related to the pendant polyIBVE structure; we therefore expect to design various polyVEs-grafted conjugated polymers that are capable of responding to external stimuli such as pH, temperature, and addition of metal ions or biomolecules.

**Optical Properties of PolyPhA-g-polyIBVE.** As depicted in Figure 4, we have discovered a very interesting fact that the UV–vis absorption maxima of polyPhA-g-polyIBVE were redshifted depending on the polyIBVE side chain length. The normalized UV–vis absorption spectrum of poly(PhAVE-AcOH) in dichloromethane at 25 °C exhibits a peak in the range of 375–550 nm with maximum at 425 nm, while the maxima of polyPhA-g-polyIBVE at 27, 40, 76, and 98%
chromatograms with respect to 15 polystyrene standards (Scientific Polymer Products, Inc.; \(M_n = 580-670,000\) g mol\(^{-1}\), \(M_n/M_w = 1.01-1.07\)). SEC—multi-angle laser light scattering (MALLS) measurements were performed on a TOSOH GPC-8020 system, equipped with a column (Shodex XF-805 L), a Wyatt Technology, DAWN HELEOS multi-angle laser light scattering photometer with a He–Ne laser (\(\lambda = 658\) nm), and a Wyatt Technology Optilab rEX differential refractometer, using CHCl\(_3\) as an eluent at a flow rate of 0.40 mL min\(^{-1}\). The SEC—MALLS profiles were recorded and analyzed using ASTRA software (ver.6.1.1, Wyatt Technology). Differential refractive index increments (dn/dc) for the polymers in CHCl\(_3\) were determined based on the peak area of the refractive index chromatograms and the polymer mass concentration (c) of the injected solutions assuming that all the injected polymers were fully recovered. UV–vis spectra were recorded using a quartz cell of 1 cm path length on a SHIMADZU Type UV-2550 spectrometer.

**Materials.** Unless otherwise stated, all commercial reagents were used as received. Ethyl aluminum dichloride (EtAlCl\(_2\); FUJIFILM Wako Pure Chemical Corporation, 1.0 mol L\(^{-1}\) in n-hexane) was used as received. 2-Vinylxethyl 4-ethynylbenzoate (PhAVE) was prepared according to literature.\(^{39}\) Rh catalyst (1) was prepared according to literature.\(^{40}\) Isobutyl vinyl ether (IBVE; Aldrich, 99\%) was dried overnight over KOH pellets and distilled twice over CaH\(_2\). Anhydrous solvents for reactions were purchased from Kanto Chemicals.

**Synthesis of PhAVE-AcOH.** Acetic acid (220 mg, 3.6 mmol) was added to PhAVE (400 mg, 1.8 mmol), and the mixture was stirred for 4 h at 60 °C under dry nitrogen. The reaction mixture was concentrated by evaporating the unreacted acetic acid under reduced pressure. By column chromatography using mixed solvents of ethyl acetate and hexane (1/5 v/v), PhAVE-AcOH was obtained as yellow solids (480 mg, 1.7 mmol) in 97% yield. \(^1\)H NMR (500 MHz, CDCl\(_3\), δ): 8.00 (d, J = 8.5 Hz, 2H, Ar H), 7.55 (d, J = 8.5 Hz, 2H, Ar H), 5.98 (q, J = 5.3 Hz, 1H, OCH(CH\(_3\))OCO), 4.45 (m, 2H, OCH(CH\(_3\))CH\(_2\)), 3.92 (m, OCH\(_2\)CH\(_2\)), 3.23 (s, 1H, CH), 2.06 (s, 3H, COCH\(_3\)), 1.42 (d, d, J = 5.3 Hz, 3H, CHCH\(_3\)); \(^13\)C NMR (125 MHz, CDCl\(_3\), δ): 170.7, 165.8, 132.1, 130.0, 129.9, 126.9, 69.3, 82.8, 80.2, 66.9, 64.0, 21.2, 20.7. The polymerization using [(Ph-F)\(_3\)P] was carried out under dry nitrogen atmosphere in baked glass tubes equipped with a three-way stopcock. A typical example for the polymerization procedure is as follows: to a toluene solution (2.68 mL) of poly(PhAVE-AcOH) (11 mg, 0.04 mmol; the value based on repeating units), IBVE (0.52 mL, 4.0 mmol) and dioxane (0.68 mL, 8 mmol) was added EtAlCl\(_2\) (in hexane, 1.6 mol L\(^{-1}\); 0.12 mL, 0.20 mmol) at −35 °C under a dry nitrogen atmosphere. After the reaction time of 1, 2, 5, and 12 h, each polymerization was quenched with sodiomalonic ester solution (in toluene/dioxane (1.2/1 v/v), 0.23 mol L\(^{-1}\); 5.0 mL, 1.2 mmol). The conversion of IBVE was determined by \(^1\)H NMR analysis. The solution was diluted with toluene, then washed with brine, evaporated under reduced pressure, and then vacuum-dried to yield the target polymer (polyPhA-g-polyIBVE). \(M_n\) and \(M_w/M_n\) of the obtained polymers were determined by analytical SEC in THF. The toluene solution of the reaction mixture was poured into a large amount of EtOH to precipitate the polymers to remove the lower-molecular-weight product. The resultant polymer was collected by centrifugation and dried under reduced pressure. The isolated polymer structure was analyzed by \(^1\)H NMR measurement.

**Hydrolysis of Graft Copolymer.** To a solution of graft copolymer (20 mg) in THF (9 mL) was added a solution of KOH (9 g) in MeOH (18 mL); the resultant mixture was gently refluxed for 2 h. After cooling to room temperature, it was neutralized with a diluted aqueous HCl and the mixture was evaporated under reduced pressure. The residue was dissolved in toluene, washed with water, and evaporated under reduced pressure. The resulting polymer was subjected to SEC analysis.

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Macromolecules Atom Transfer Radical Polymerization. Efficiency in the Synthesis of Molecular Brushes by Grafting from via 702
Chem., Int. Ed. Engl. Polymerizations: Preparation of Star and Graft Polymers. 703
J. Polym. Sci., Part A: Polym. Chem. Poly(Vinyl Ether)s. 6834
Brush-Shaped Conjugated Polymers with Pendant Well-Defined π-shaped γ with Externally Added activity. 6850
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