Bio-Based Vinylphenol Family: Synthesis via Decarboxylation of Naturally Occurring Cinnamic Acids and Living Radical Polymerization for Functionalized Polystyrenes

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ABSTRACT: A series of bio-based vinylphenols or hydroxystyrenes is prepared by simple decarboxylation of various naturally occurring cinnamic acids such as *o*-, *m*-, and *p*-coumaric; caffeic; ferulic; and sinapinic acids, which possess hydroxy groups and other substituents at different positions on the aromatic ring. After protection of the phenolic moieties with trialkylsilyl groups, reversible addition–fragmentation chain-transfer polymerization is accomplished with cumyl dithiobenzoate to afford various bio-based hydroxyl-protected polystyrenes with controlled molecular weights and narrow molecular weight distributions. Subsequent deprotection of the silyl groups under mild conditions results in a series of well-defined functionalized polystyrenes possessing different numbers (mono-, di-, tri-) of hydroxy groups at different positions (*o*, *m*, *p*). The obtained functionalized polystyrenes show unique thermal properties depending on the substituents, and those with phenol and catechol groups serve as reducing agents for silver ions. © 2019 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2019**

KEYWORDS: bio-based polymer; cinnamic acid; hydroxystyrene; catechol; functionalization of polymers; gallol; guaiacol; living polymerization; phenol; RAFT; radical polymerization; syringol

INTRODUCTION Renewable resources are now receiving attention as raw materials for polymers, mainly from the viewpoint of sustainability.[1–6] In addition, their characteristic structures often lead to unique bio-based polymers with unique properties, which are difficult to realize by simple petroleum-based compounds and are attractive in view of new high-performance or functional polymers. Furthermore, special functions can be added by controlling the polymer structure using precision polymerization.[7]

A family of cinnamic acids widely and abundantly seen in nature is the series of (*E*)-3-phenyl-2-propenoic acids differing in their ring substituents, such as hydroxy and methoxy groups.[8–10] A series of these compounds, which belong to the family of phenylpropanoids, are biologically synthesized via step-by-step enzymatic reactions mediated by various enzymes in plants, whereas most of them are finally converted into lignin, that is, the second largest natural polymer product, via natural polymerization using the phenolic and vinylic groups for the linking reactions. The phenol, catechol, and other related phenolic hydroxy groups in these natural compounds can be used as functional parts for adhesion, reduction, curing, and so forth. Indeed, the catechol contained in natural proteins is a key component for adhesion, as observed in mussel adhesive proteins.[11–16] However, in lignin, many of the hydroxy groups are consumed when linking the components.

The cinnamic acid family has a common structure, namely, (*E*)-3-phenyl-2-propenoic acid, which has phenyl and carboxylic acid groups attached to the 1,2-position of the vinyl group and thus can be regarded as a vinyl compound possessing both styrenic and acrylic structures.[17] However, due to steric hindrance around the 1,2-disubstituted vinyl group, cinnamic acids rarely homopolymerize.[18] Although they are copolymerized with styrene and acrylate, their incorporation into the resulting copolymers is relatively low.[17,19] Alternatively, hydroxy-functionalized cinnamic acids such as ferulic acid are polymerized via condensation polymerization into bio-based polyesters and polycarbonates using the hydroxy and carboxylic groups,[20–23] though they lose the hydroxy functional groups upon polymerization.

Additional supporting information may be found in the online version of this article.

Recently, we reported a facile synthesis of hydroxy-functionalized styrenes, such as 4-vinylguaiacol (4VG) and 4-vinylcatechol (4VC), via decarboxylation of naturally occurring ferulic and caffeic acids, which both belong to the cinnamic acid family, upon heating to 100°C just in the presence of triethylamine.[24–26] Furthermore, after protection of the phenolic functional groups with trialkylsilyl groups, the protected 4VG and 4VC were polymerized via reversible addition–fragmentation chain-transfer (RAFT) polymerization[27] to result in hydroxy-functionalized polystyrenes, that is, poly(4VG) and poly(4VC), with controlled molecular weights after deprotection of the silyl groups.

In this article, we applied this approach to a series of naturally occurring cinnamic acids, including not only ferulic and caffeic acids but also *o*-, *m*-, and *p*-coumaric and sinapinic acids, to synthesize an array of bio-based hydroxy-functionalized polystyrenes with controlled molecular weights (Scheme 1). We thus investigated the synthesis of a series of hydroxystyrenes with different numbers of hydroxy and methoxy substituents at various positions of the aromatic ring via decarboxylation of the cinnamic acids and then the preparation of well-defined functionalized bio-based polystyrenes via RAFT polymerization of the silyl-protected monomers, followed by deprotection. Furthermore, the effects of the substituents on the thermal properties and reducing abilities of the polystyrenes were evaluated.

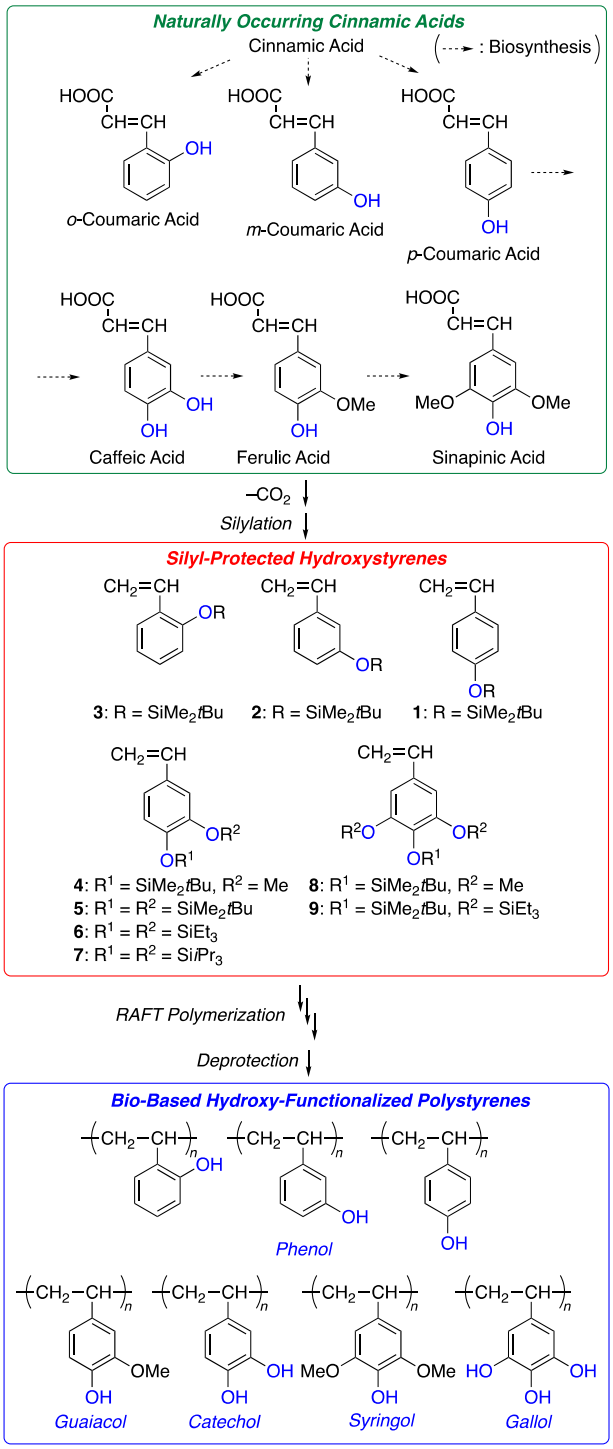
EXPERIMENTAL

Materials

p-Coumaric acid (TCI, Tokyo, Japan, >98.0%), *m*-coumaric acid (TCI, >99.0%), *o*-coumaric acid (Sigma-Aldrich, St. Louis, MO, USA, >97%), ferulic acid (Sigma-Aldrich, >99%), caffeic acid (Kanto Chemical, Tokyo, Japan, >98.0%), sinapinic acid (TCI, >98.0%), triethylamine (Et_3N: TCI, >99.0%), *N*,*N*-dimethylformamide (DMF: Kanto Chemical, >99.5%; H_2O < 0.001%), copper(II) hydroxide (FUJIFILM Wako Chemical, Osaka, Japan, >90.0%), 1,10-phenanthroline monohydrate (TCI, >99.0%), *tert*-butyldimethylsilyl chloride (TBDMSCl: TCI, >98%), imidazole (Kishida Chemical, Osaka, Japan, 99%), triethylsilane (Sigma-Aldrich, 99%), and tris(pentafluorophenyl)borane [$B(C_6F_5)_3$: TCI, >97%] were used as received. 1,2,3,4-Tetrahydronaphthalene (FUJIFILM Wako Chemical, 97%) was distilled over calcium hydride under reduced pressure before use. Toluene (Kanto Chemical, >99.5%; H_2O < 10 ppm) and tetrahydrofuran (THF: Kanto Chemical, >99.5%; H_2O < 0.001%) were dried and deoxygenized by passage through columns of Glass Contour Solvent Systems before use. α,α-4,4′-Azobisisobutyronitrile (AIBN) (Kishida Chemical, >99%) was purified by recrystallization from methanol. Cumyl dithiobenzoate (CDB) was synthesized according to the literature.[28,29]

Synthesis of TBDMS4VP (1)

p-Coumaric acid (25.0 g, 152.4 mmol), triethylamine (43.0 mL, 308.5 mmol), and DMF (86 mL) were placed in a three-necked round-bottom flask equipped with a Dimroth condenser at room temperature. The flask was put into an oil bath and heated to 100°C with stirring. The conversion of *p*-coumaric acid was calculated from the concentration of residual *p*-coumaric acid measured by proton nuclear magnetic resonance (^1H NMR). After 24 h, *p*-coumaric acid was completely consumed (>99.9%) and converted into *p*-hydroxystyrene or 4-vinylphenol (4VP). The flask was cooled to 0°C, and



SCHEME 1 Synthesis of bio-based hydroxyl-functionalized polystyrenes via decarboxylation of naturally occurring cinnamic acids followed by silylation, RAFT polymerization, and deprotection. [Color figure can be viewed at wileyonlinelibrary.com]

TBDMSCl (25.2 g, 167.5 mmol) was slowly added to the mixture. The reaction mixture was stirred at 20°C. After 24 h, ice water was slowly added to stop the reaction. The reaction mixture was diluted with *n*-hexane and washed with water. The organic layer was concentrated by rotary evaporation. The residue was purified by distillation under reduced pressure (62°C/16 Pa). TBDMS4VP (**1**) was obtained as a colorless liquid (34.0 g, 95%). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, δ) [Fig. S1(A)]: 0.20 (s, 6H, SiCH_3), 0.98 (s, 9H, SiC(CH_3)$_3$), 5.12 (d, 1H, trans, CH_2=CH), 5.60 (d, 1H, cis, CH_2=CH), 6.65 (dd, 1H, CH$_2$=CH), 6.79 (d, 2H, ArH), 7.28 (d, 2H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$, 25°C, δ) [Fig. S2(A)]: −4.3 (SiCH$_3$), 18.4 (SiC(CH$_3$)$_3$), 25.8 (SiC(CH$_3$)$_3$), 111.8 (CH$_2$=CH), 136.5 (CH$_2$=CH), 120.3, 127.5, 131.1, 155.6 (phenyl).

Synthesis of TBDMS3VP (2)

m-Coumaric acid (20.5 g, 124.7 mmol), 1,10-phenanthrioline (2.3 g, 12.7 mmol), $Cu(OH)_2$ (1.22 g, 12.5 mmol), and DMF (275 mL) were placed in a three-necked round-bottom flask equipped with a Dimroth condenser at room temperature.[30] The flask was put into an oil bath and heated to 150°C with stirring. The conversion of *m*-coumaric acid was calculated from the concentration of residual *m*-coumaric acid measured by ^{1}H NMR. After 66 h, the conversion of *m*-coumaric acid reached 89%. The reaction mixture was diluted with diethyl ether and washed with aqueous citric acid and water. After drying with Na_2SO_4, the solvents were removed by rotary evaporator to yield *m*-hydroxystyrene or 3-vinylphenol (3VP) as a liquid (13.3 g, 88%).

The obtained 3VP (7.9 g, 66.0 mmol) and imidazole (10.0 g, 146.7 mmol) were dissolved in DMF (37 mL) in a three-necked round-bottom flask. The flask was cooled to 0°C, and TBDMSCl (11.0 g, 73.0 mmol) was slowly added to the mixture. The reaction mixture was stirred at 20°C. After 12 h, ice water was slowly added to stop the reaction. The reaction mixture was diluted with toluene and washed with water. The organic layer was concentrated by rotary evaporation. The residue was purified by silica gel column chromatography (Silica Gel 60N, *n*-hexane). TBDMS3VP (**2**) was obtained as a colorless liquid (14.6 g, 94%). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, δ) [Fig. S1(B)]: 0.20 (s, 6H, SiCH_3), 0.99 (s, 9H, SiC(CH_3)$_3$), 5.23 (d, 1H, trans, CH_2=CH), 5.71 (d, 1H, cis, CH_2=CH), 6.66 (dd, 1H, CH$_2$=CH), 6.74 (dd, 1H, ArH), 6.88 (s, 1H, ArH), 7.00 (d, 1H, ArH), 7.17 (dd, 1H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$, 25°C, δ) [Fig. S2(B)]: −4.2 (SiCH$_3$), 18.4 (SiC(CH$_3$)$_3$), 25.8 (SiC(CH$_3$)$_3$), 114.0 (CH$_2$=CH), 136.9 (CH$_2$=CH), 117.9, 119.6, 119.7, 129.5, 139.2, 156.0 (phenyl).

Synthesis of TBDMS2VP (3)

o-Coumaric acid (25.4 g, 154.7 mmol), triethylamine (43.0 mL, 308.5 mmol), and DMF (85 mL) were placed in a three-necked round-bottom flask equipped with a Dimroth condenser at room temperature. The flask was put into an oil bath and heated to 120°C with stirring. The conversion of *o*-coumaric acid was calculated from the concentration of residual *o*-coumaric acid measured by ^{1}H NMR. After 37 h, *o*-coumaric acid was almost completely consumed (>99.9%) and converted into *o*-hydroxystyrene or 2-vinylphenol (2VP). The flask was cooled to 0°C, and TBDMSCl (23.3 g, 154.7 mmol) was slowly added to the mixture. The reaction mixture was stirred at 20°C. After 12 h, ice water was slowly added to stop the reaction. The reaction mixture was diluted with *n*-hexane and washed with aqueous HCl, aqueous $NaHCO_3$, and water. The organic layer was dried with Na_2SO_4 and concentrated by rotary evaporation. The residue was purified by distillation under reduced pressure (67°C/31 Pa). TBDMS2VP (**3**) was obtained as a colorless liquid (33.1 g, 91%). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, δ) [Fig. S1(C)]: 0.21 (s, 6H, SiCH_3), 1.02 (s, 9H, SiC(CH_3)$_3$), 5.22 (d, 1H, trans, CH_2=CH), 5.67 (d, 1H, cis, CH_2=CH), 7.05 (dd, 1H, CH$_2$=CH), 6.79 (d, 1H, ArH), 6.93 (dd, 1H, ArH), 7.13 (dd, 1H, ArH), 7.50 (d, 1H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$, 25°C, δ) [Fig. S2(C)]: −4.0 (SiCH$_3$), 18.5 (SiC(CH$_3$)$_3$), 26.0 (SiC(CH$_3$)$_3$), 113.7 (CH$_2$=CH), 132.1 (CH$_2$=CH), 119.8, 121.5, 126.2, 128.8, 129.2, 153.0 (phenyl).

Synthesis of TBDMS4VG (4), (TBDMS)$_2$VC (5), (TES)$_2$VC (6), and (TIPS)$_2$VC (7)

According to the literature, TBDMS4VG (**4**) was synthesized from ferulic acid,[24] and (TBDMS)$_2$VC (**5**), (TES)$_2$VC (**6**), and (TIPS)$_2$VC (**7**) were synthesized from caffeic acid[25] [total yield: 98% (**4**), 98% (**5**), 91% (**6**), and 92% (**7**)].

Synthesis of TBDMS4VS (8)

Sinapinic acid (24.9 g, 111.1 mmol), triethylamine (31.0 mL, 222.4 mmol), and DMF (56 mL) were placed in a three-necked round-bottom flask equipped with a Dimroth condenser at room temperature. The flask was put into an oil bath and heated to 100°C under stirring. The conversion of sinapinic acid was calculated from the concentration of residual sinapinic acid measured by ^{1}H NMR. After 2 h, sinapinic acid was completely consumed (>99.9%) and converted into 4-vinylsyringol (4VS). The flask was cooled to 0°C, and TBDMSCl (16.8 g, 111.7 mmol) was slowly added to the mixture. The reaction mixture was stirred at 20°C. After 14 h, ice water was slowly added to stop the reaction. The reaction mixture was diluted with *n*-hexane and washed with aqueous HCl, aqueous $NaHCO_3$, and water. The organic layer was dried with Na_2SO_4 and concentrated by rotary evaporation. The residue was purified by silica gel column chromatography (Silica Gel 60N, *n*-hexane ~ *n*-hexane/ethyl acetate = 97/3). TBDMS4VS (**8**) was obtained as a white solid (30.4 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, δ) [Fig. S1(D)]: 0.13 (s, 6H, SiCH_3), 1.00 (s, 9H, SiC(CH_3)$_3$), 3.81 (s, 6H, OCH_3), 5.15 (d, 1H, trans, CH_2=CH), 5.61 (d, 1H, cis, CH_2=CH), 6.62 (dd, 1H, CH$_2$=CH), 6.61 (s, 2H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$, 25°C, δ) [Fig. S2(D)]: −4.5 (SiCH$_3$), 18.9 (SiC(CH$_3$)$_3$), 25.9 (SiC(CH$_3$)$_3$), 55.9 (OCH$_3$), 112.0 (CH$_2$=CH), 137.2 (CH$_2$=CH), 103.6, 130.5, 134.7, 151.8 (phenyl).

Synthesis of TBDMS(TES)$_2$4VGa (9)

n-Hexane (32 mL), Et_3SiH (6.0 mL, 37.7 mmol), and $B(C_6F_5)_3$ solution in toluene (0.80 mL, 50 mM), which was prepared in another flask by solubilizing $B(C_6F_5)_3$ (39.8 mg, 0.08 mmol) with toluene (1.5 mL), were placed in a three-necked round-bottom flask equipped with a dropping funnel at room

temperature. TBDMS4VS (**8**) (10.0 mL of 1.89 M solution in *n*-hexane, 18.9 mmol) was put in the dropping funnel. The flask was cooled to 10°C, and then TBDMS4VS (**8**) was slowly dropped into the mixture at 10°C. After the addition of TBDMS4VS (**8**), the reaction mixture was stirred at 20°C. The conversion of TBDMS4VS (**8**) was calculated from the concentration of the methoxy group measured by ^{1}H NMR. After 20 h, the methoxy group was quantitatively consumed to yield TBDMS(TES)$_2$4VGa (**9**), although it contained a small amount of the hydrosilylated product (olefin/hydrosilylated form = 1/0.05, reaction yield = 95%). The reaction mixture was diluted with *n*-hexane and washed with water. After concentration by rotary evaporation, the residue was purified by silica gel column chromatography (Silica Gel 60N, *n*-hexane) to yield TBDMS(TES)$_2$4VGa (**9**) as a colorless viscous liquid (6.31 g, 68%). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, δ) [Fig. S1(E)]: 0.12 (s, 6H, SiCH_3), 0.76 (q, 12H, SiCH_2CH$_3$), 0.97 (t, 18H, SiCH$_2$CH_3), 1.00 (s, 9H, SiC(CH_3)$_3$), 5.09 (d, 1H, trans, CH_2=CH), 5.50 (d, 1H, cis, CH_2=CH), 6.52 (dd, 1H, CH$_2$=CH), 6.54 (s, 2H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$, 25°C, δ) [Fig. S2 (E)]: −4.0 (SiCH_3), 5.2 (SiCH_2CH$_3$), 6.8 (SiCH$_2$$CH_3$), 18.6 (Si$C$(CH$_3$)$_3$), 25.9 (SiC(C$H_3$)$_3$), 111.7 (C$H_2$=CH), 136.8 (CH$_2$=C$H$), 111.3, 130.0, 138.4, 148.5 (phenyl).

RAFT Polymerization

RAFT polymerization was conducted by syringe under dry nitrogen in sealed glass tubes. A representative example of the polymerization of TBDMS4VP (**1**) with CDB as the RAFT agent in the presence of AIBN is given below. **1** (2.58 mL, 10.0 mmol), CDB (0.45 mL of 222 mM solution in toluene, 0.10 mmol), AIBN (0.25 mL of 100 mM solution in toluene, 0.025 mmol), 1,2,3,4-tetrahydronaphthalene (0.22 mL) as an internal standard, and toluene (1.5 mL) were placed in a 25 mL glass tube equipped with a three-way stopcock at room temperature. The total volume of the reaction mixture was 5.0 mL. After mixing, the mixture was aliquoted into six baked glass tubes, and the tubes were sealed by flame under a nitrogen atmosphere. The tubes were immersed in a thermostatic oil bath at 60°C. At certain intervals, the reaction tubes were cooled to −78°C to terminate the polymerization. Monomer conversion was determined from the concentration of residual monomer measured by ^{1}H NMR, with 1,2,3,4-tetrahydronaphthalene as an internal standard (e.g., 48 h, 53%). The quenched reaction solutions were evaporated to dryness to give poly(**1**) (M_n = 12,000, M_w/M_n = 1.10). The obtained polymer was purified by preparative size exclusion chromatography (SEC) for ^{1}H NMR analysis.

Deprotection of Silyl Groups

Deprotection of the TBDMS groups was performed according to previous papers.[24,25] Representative examples are given below. Poly(**1**) (140 mg, M_n = 9900, M_w/M_n = 1.10) was dissolved in THF (7.7 mL), followed by the addition of hydrochloric acid (0.70 mL, 12 M) at room temperature. After stirring for 48 h, the solution was diluted with ethyl acetate and washed with aqueous $NaHCO_3$ and water. The organic layer was evaporated to remove the solvents. The residue was dissolved in acetone and purified by precipitation into *n*-hexane three times to give poly(4VP) (75.2 mg, 100%). For poly(**3**) (170 mg in 5.6 mL of THF, M_n = 12,600, M_w/M_n = 1.08), the TBDMS group was deprotected using acetic acid (0.09 mL) and tetrabutylammonium fluoride (TBAF) (1.45 mL of 1.0 M solution in THF) at 40°C. After stirring for 36 h, the reaction mixture was diluted with ethyl acetate and washed with aqueous HCl and water. After removing the solvent, precipitation was conducted for purification to give poly (2VP) (65.0 mg, 75%).

Reduction of Silver Ions

A representative example of poly(4VC) is given below. Poly (4VC) was dissolved in dried and deoxygenated THF by the syringe technique under dry argon to prepare the polymer solution ([catechol group]$_0$ = 200 mM). $AgNO_3$ was dissolved in degassed and distilled water by the syringe technique under dry argon to prepare the solution ([$AgNO_3$]$_0$ = 2.0 mM). The polymer solution (2.6 mL) was placed in a quartz cell under dry argon, and then $AgNO_3$ solution (0.13 mL) was added to the polymer solution under vigorous stirring at 25°C. The cell was immediately capped, and ultraviolet–visible (UV–vis) measurements were started. The color of the solution changed to yellow, and a peak attributed to Ag nanoparticles (~400 nm) gradually appeared.

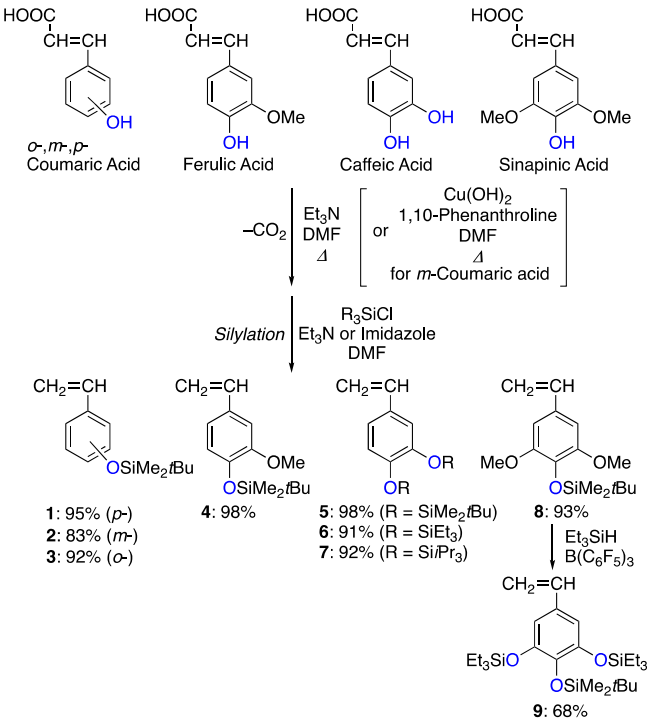
Measurements

^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECS-400 spectrometer operating at 400 and 125 MHz, respectively. The number-average molecular weight (M_n) and molecular weight distribution (MWD; M_w/M_n) of the product polymers were determined by SEC in THF at 40°C on two polystyrene gel columns (Tosoh Multipore H_{XL}-M [7.8 mm i.d. × 30 cm] × 2; flow rate 1.0 mL min^{-1}) or in DMF containing 100 mM LiCl at 40°C on two hydrophilic polymer gel columns (Tosoh α-M + α-3000 [7.8 mm i.d. × 30 cm]; flow rate 1.0 mL min^{-1}) (for polymers after deprotection) connected to a JASCO PU-2080 precision pump and a JASCO RI-2031 detector. The columns were calibrated against standard polystyrene samples (Varian; M_p = 580–3053000, M_w/M_n = 1.02–1.23). The glass transition temperature (T_g) of the polymers was recorded on a Q200 differential scanning calorimeter (TA Instruments Inc.). The sample was first heated to 210°C at 10°C min^{-1}, then equilibrated at this temperature for 10 min, and finally cooled to −10°C at 5°C min^{-1}. After being held at this temperature for 5 min, the sample was then heated to 260°C at 10°C min^{-1}. All T_g values were obtained from the second scan after removing the thermal history. UV–vis absorption spectra were recorded on a JASCO V-550 spectrometer.

RESULTS AND DISCUSSION

Synthesis of Various Bio-Based Functionalized Styrenes from Cinnamic Acids: Decarboxylation and Silylation

A series of hydroxystyrenes with different numbers of substituents at different positions on the aromatic ring were first synthesized by decarboxylation of naturally occurring cinnamic acids, such as *o*-, *m*-, and *p*-coumaric; ferulic; caffeic; and sinapinic acids (Scheme 2). According to our previous reports on the synthesis starting from ferulic and caffeic acids, the



SCHEME 2 Synthesis and total yield of silyl-protected hydroxystyrenes via decarboxylation of cinnamic acids followed by silylation. [Color figure can be viewed at wileyonlinelibrary.com]

decarboxylation of *o*-, *m*-, and *p*-coumaric acids and sinapinic acid was similarly investigated upon heating in the presence of triethylamine in DMF at 100–120°C. *o*- and *p*-Coumaric acids and sinapinic acid were quantitatively converted into *o*-hydroxystyrene (2VP), *p*-hydroxystyrene (4VP), and 4-hydroxy-3,5-dimethoxystyrene (4VS), respectively, without any spontaneous thermal polymerizations. However, almost no decarboxylation occurred for *m*-coumaric acid with triethylamine upon heating. These results suggest that the *o*- and *p*-hydroxy groups work efficiently for the simple base-induced decarboxylation of cinnamic acids due to the resonance effects. However, decarboxylation of *m*-coumaric acid into *m*-hydroxystyrene (3VP) was successfully achieved by the other common method using a copper catalyst.[30]

After decarboxylation, the hydroxy groups were protected with various trialkylsilyl groups via reactions with trialkylsilyl chloride in the presence of appropriate bases. Notably, *in situ* direct silylation of the obtained hydroxystyrenes was achieved not only for 4VG and 4VC but also for 2VP, 4VP, and 4VS upon simple addition of the silyl chloride in the presence of pre-existing triethylamine, which was used for the decarboxylation, in high yields. The total yields were thus very high (>90%). The isolated 3VP, which was prepared by decarboxylation using the copper catalyst, was similarly converted into the silyl-protected form in the presence of imidazole as another base. Even for the two-step reactions, the total yield was 83%. Furthermore, two methoxy groups in the TBDMS-protected 4VS (**8**) derived from sinapinic acid were converted into two

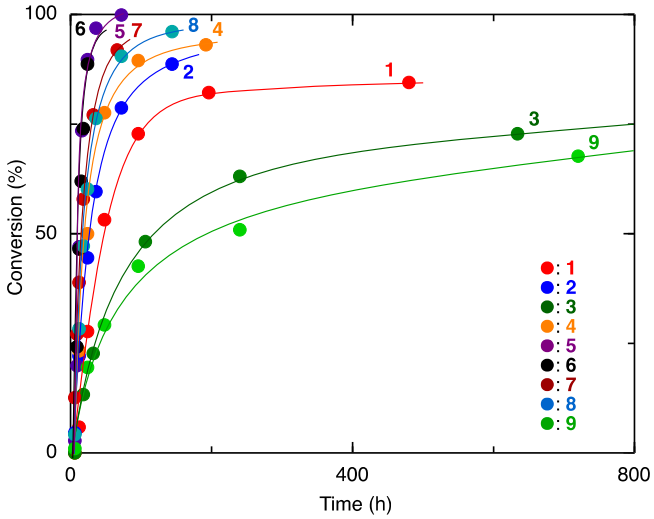


FIGURE 1 Time-conversion curves for RAFT polymerization of a series of silyl-protected hydroxystyrenes: $[M]_0/[CDB]_0/[AIBN]_0$ = 2000/20/5.0 mM (**1**–**6**, **8**) or 1000/10/2.5 mM (**7**, **9**) in toluene at 60°C. [Color figure can be viewed at wileyonlinelibrary.com]

triethylsilyloxy groups via reaction with Et_3SiH in the presence of $B(C_6F_5)_3$[15,24] to result in the silyl-protected 4-vinylgallol (4VGa) (**9**), which has three trialkylsilyl-protected hydroxyl groups at the *m*, *p*, and *m*-positions, in good yield (68%). A series of mono-, di-, and tri-hydroxystyrenes with trialkylsilyl-protected groups were thus prepared from naturally occurring cinnamic acids via successive simple reactions in relatively high yields.

RAFT Polymerization of Bio-Based Silyl-Protected Hydroxystyrenes

RAFT polymerization of a series of bio-based silyl-protected hydroxystyrenes was investigated using CDB as an RAFT agent, which is generally effective for the controlled radical polymerization of styrenes,[27] in the presence of AIBN in toluene at 60°C (Fig. 1). All monomers were consumed up to high conversions, although the polymerization rates depended on the positions, numbers, and bulkiness of the substituents on the aromatic ring. In particular, highly bulky trisubstitutions with all trialkylsilyl groups at the 3,4,5-position (**9**) and one substitution with bulky TBDMS at the 2-position near the vinyl group (**3**) significantly retarded the polymerizations. The first-order plots for the monomers with slow rates gradually deviated from the linearity due to the depletion of AIBN for the long reactions (Fig. S3).

Figure 2 shows the M_n, M_w/M_n, and SEC curves of the polymers obtained from the monosubstituted monomers (**1**–**3**) derived from *o*-, *m*-, and *p*-coumaric acids. M_n values of the obtained polymers all increased in direct proportion to monomer conversion, indicating that all these polymerizations proceeded in living fashion, although the slopes were slightly different, most likely due to the difference in the hydrodynamic volumes of the resulting polymers depending on the substituted positions. The MWDs were narrow for the *p*- and

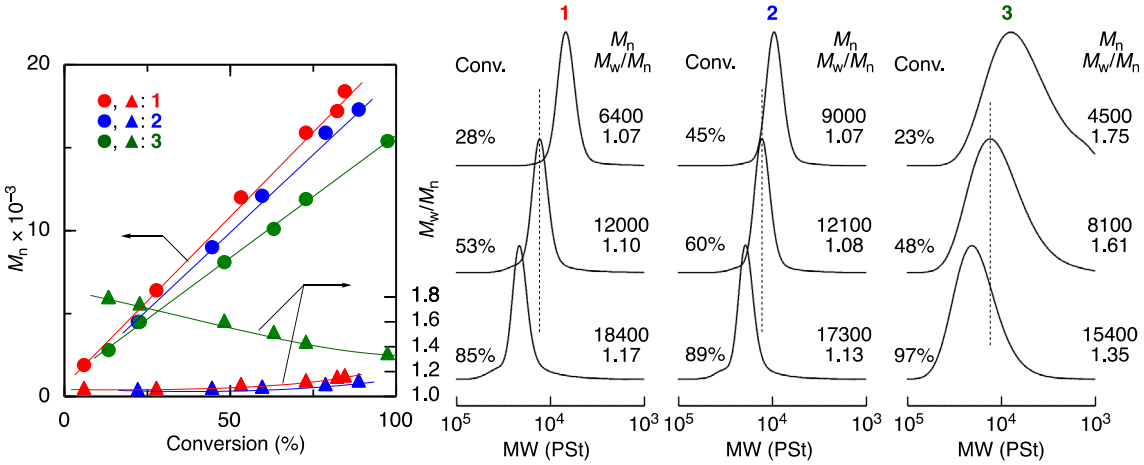


FIGURE 2 M_n, M_w/M_n, and SEC curves of the polymers obtained by RAFT polymerization of monosubstituted silyl-protected hydroxystyrenes derived from *o*-, *m*-, and *p*-coumaric acids: $[M]_0/[CDB]_0/[AIBN]_0$ = 2000/20/5.0 mM in toluene at 60°C. [Color figure can be viewed at wileyonlinelibrary.com]

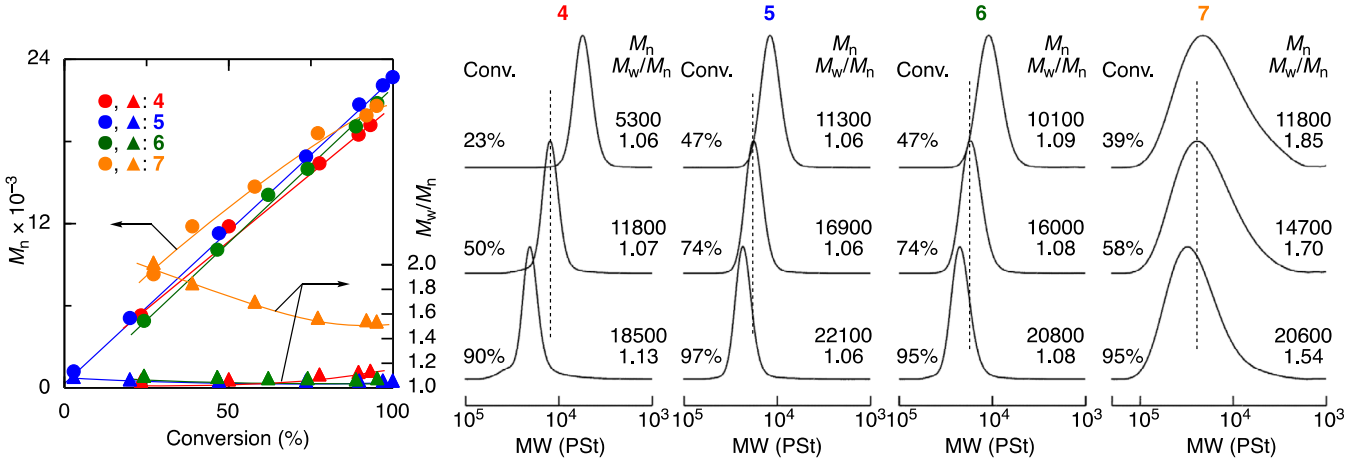


FIGURE 3 M_n, M_w/M_n, and SEC curves of the polymers obtained by RAFT polymerization of di-substituted silyl-protected hydroxystyrenes derived from ferulic and caffeic acids: $[M]_0/[CDB]_0/[AIBN]_0$ = 2000/20/5.0 mM (**4**–**6**) or 1000/10/2.5 (**7**) mM in toluene at 60°C. [Color figure can be viewed at wileyonlinelibrary.com]

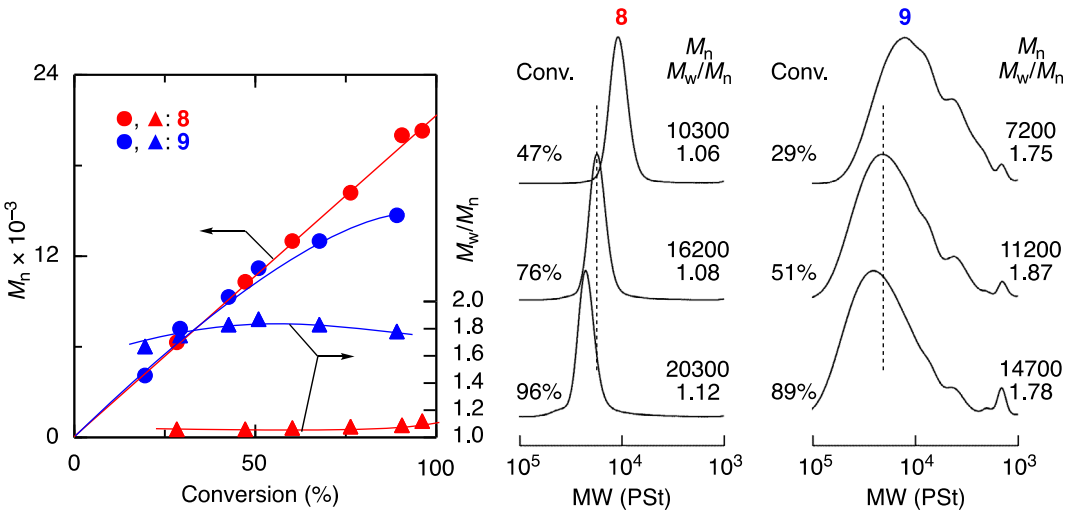


FIGURE 4 M_n, M_w/M_n, and SEC curves of the polymers obtained by RAFT polymerization of tir-substituted silyl-protected hydroxystyrenes derived from sinapinic acid: $[M]_0/[CDB]_0/[AIBN]_0$ = 2000/20/5.0 mM (**8**) or 1000/10/2.5 mM (**9**) in toluene at 60°C. [Color figure can be viewed at wileyonlinelibrary.com]

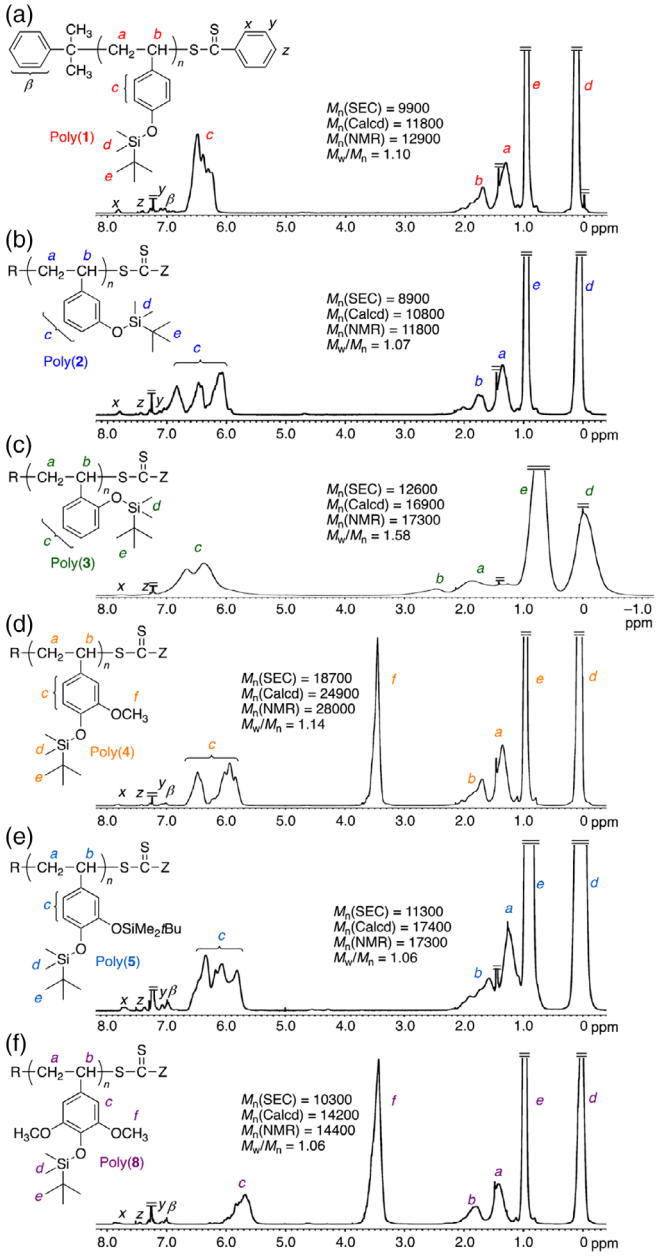


FIGURE 5 ^{1}H NMR spectra ($CDCl_3$, 55°C) of the polymers obtained by RAFT polymerization of **1** (a), **2** (b), **3** (c), **4** (d), **5** (e), and **8** (f). [Color figure can be viewed at wileyonlinelibrary.com]

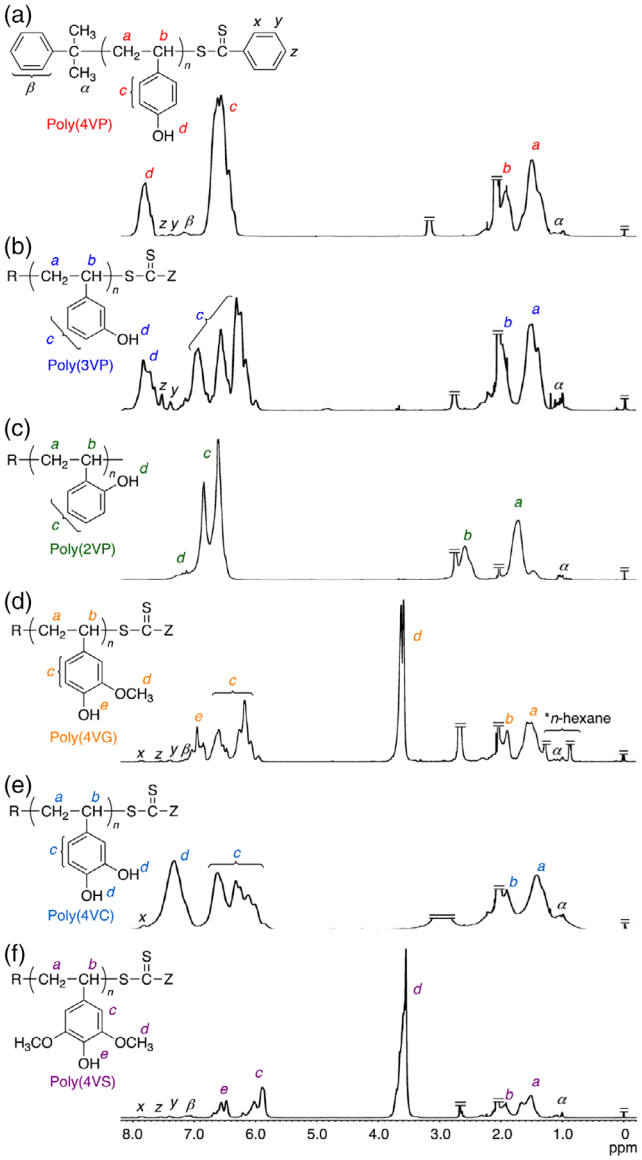


FIGURE 6 ^{1}H NMR spectra [$(CD_3)_2CO$, 50°C] of the polymers obtained after deprotection of poly(**1**) (a), poly(**2**) (b), poly(**3**) (c), poly(**4**) (d), poly(**5**) (e), and poly(**8**) (f). [Color figure can be viewed at wileyonlinelibrary.com]

m-substituted monomers (**1** and **2**) ($M_w/M_n \sim 1.1$). The *o*-substituted monomer (**3**) resulted in relatively broad MWDs, which became narrower ($M_w/M_n = 1.8 \rightarrow 1.3$) as the polymerization proceeded. These results suggest that the steric hindrance around the propagating radical species slowed the interchanging reaction between the propagating radical and the RAFT terminal, as similarly observed in the RAFT polymerization of highly bulky methacryaltes.[31]

For *m*- and *p*-disubstituted monomers (**4**–**7**), which were derived from ferulic and caffeic acids, all M_n values were controlled and nearly the same, independent of the substituents. All these results for the disubstituted monomers are summarized in Figure 3 for comparison, although some of the results were previously reported elsewhere.[24,25] The MWDs were fairly narrow ($M_w/M_n \sim 1.1$) for **4**–**6**. However, for **7**, which possess two highly bulky TIPS groups at the *m*- and *p*-positions, the MWD was relatively broad. However, these distributions became narrower ($M_w/M_n = 1.8 \rightarrow 1.5$) with monomer conversion, again indicating slow interconversion due to steric hindrance.

m-, *p*-, and *m*-Trisubstituted monomers, that is, 4VS protected with TBDMS (**8**) and 4VGa protected with two TES and one TBDMS (**9**), which were both derived from sinapinic acid as described above, also afforded the polymers with controlled molecular weights (Fig. 4). In particular, the TBDMS-silyl

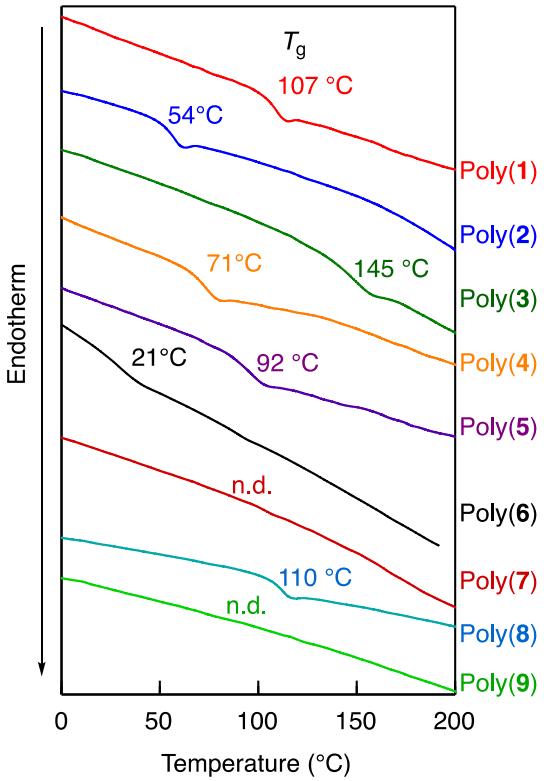


FIGURE 7 DSC curves of the polymers obtained by RAFT polymerization of silyl-protected hydroxyl styrenes. Polymer [M_n(SEC), M_w/M_n]: poly(**1**) (9900; 1.10), poly(**2**) (8900; 1.07), poly(**3**) (12,600; 1.58), poly(**4**) (19,500; 1.13), poly(**5**) (11,300; 1.06), poly(**6**) (21,700; 1.08), poly(**7**) (11,600; 1.86), poly(**8**) (10,300; 1.06), poly(**9**) (6400; 1.88). [Color figure can be viewed at wileyonlinelibrary.com]

protected 4VS (**8**), which possesses two less bulky methoxy groups at the two *m*-positions, resulted in polymers with very narrow MWDs ($M_w/M_n \sim 1.1$) and controlled molecular weights that increased in direct proportion to monomer conversion. In contrast, the three-trialkylsilyl-protected 4VGa (**9**), which has two bulkier TES groups at the two *m*-positions, resulted in polymers with broader MWDs, indicating that two bulkier substituents at both meta-positions prevent efficient reversible chain transfer during the RAFT process.

These results show that a series of mono-, di-, and tri-substituted hydroxystyrenes protected with trialkylsilyl groups were all polymerized in a controlled fashion by RAFT polymerization using CDB as the RAFT agent. However, bulkiness, particularly near the propagating radical species, not only retarded the polymerization but also induced broadening of MWDs.

Figure 5 shows a series of ^{1}H NMR spectra of poly(**1**), poly(**2**), poly(**3**), poly(**4**), poly(**5**), and poly(**8**) obtained by RAFT polymerization using CDB. In all the spectra, small peaks attributed to phenyl protons (β, *x*, *y*, and *z*) of the RAFT groups at both the α- and ω-chain ends were observed in addition to large peaks of the repeating monomer units. M_n values (M_n[NMR]) measured by the peak intensity ratio of aromatic protons (*c*) of

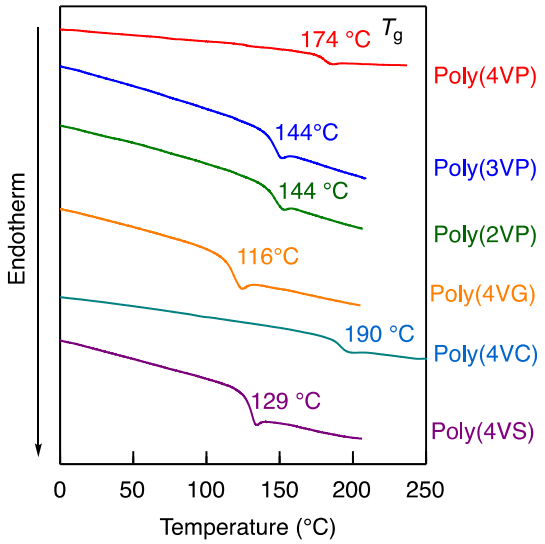


FIGURE 8 DSC curves of the polymers obtained after deprotection of silyl groups. Polymer [M_n(Calcd)]: poly(4VP) (10,400), poly(3VP) (5700), poly(2VP) (8800), poly(4VG) (8200), poly(4VC) (12,900), poly(4VS) (8800). [Color figure can be viewed at wileyonlinelibrary.com]

the repeating monomer units and the RAFT ω-terminal (*x* and *z*) were very close to the calculated values (M_n[calcd]), assuming that one RAFT agent produces one polymer chain. In contrast, M_n(SEC) values based on polystyrene calibration were lower than both M_n(calcd) and M_n(NMR) due to the difference in the hydrodynamic volumes of the polymers.[24,25] Thus, CDB works as an appropriate RAFT agent for controlling the radical polymerizations of a series of silyl-protected hydroxystyrenes regardless of the number of substituents on the aromatic ring, except for excessively bulky ones.

Deprotection of Silyl Groups into Hydroxy-Functionalized Bio-Based Polystyrenes

Deprotection of the silyl groups was then conducted using hydrochloric acid or TBAF under mild conditions. The trialkylsilyl groups in poly(**1**), poly(**2**), poly(**4**), poly(**5**), and poly(**8**) were quantitatively deprotected by hydrochloric acid in THF at room temperature to afford poly(4VP), poly(3VP), poly(4VG), poly(4VC), and poly(4VS), respectively (Fig. 6), which all possess intact RAFT ω-chain ends even after deprotection due to the mild conditions. In contrast, for poly(**3**), the *o*-silyloxy group was hardly deprotected by hydrochloric acid under the same conditions due to steric hindrance close to the main chain. However, the deprotection of poly(**3**) was successfully achieved with TBAF in THF at 40°C to result in poly(2VP), although the RAFT ω-chain ends were not observed after deprotection. SEC curves of the deprotected polymers were similarly narrow (Fig. S4). In addition, the deprotection of poly(**9**) into poly(4VGa), which has high antioxidant and adsorption properties,[32] was investigated using hydrochloric acid or TBAF, but complete deprotection was difficult. The appropriate deprotection method is still under investigation.

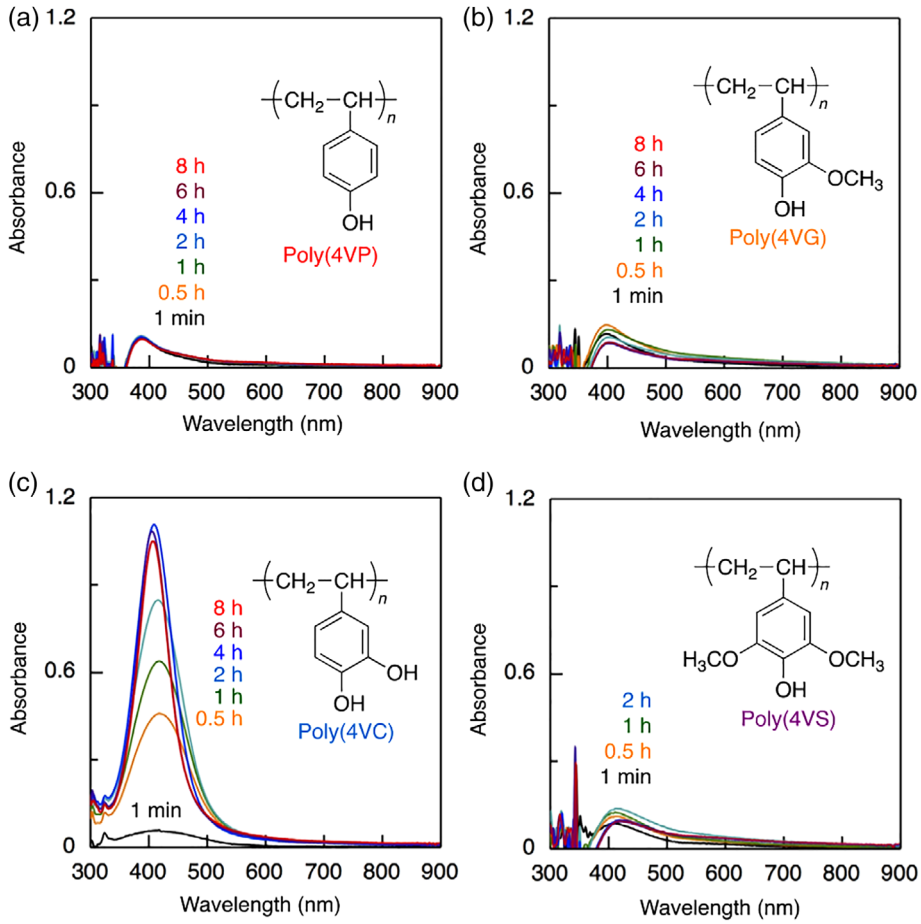


FIGURE 9 UV–vis spectra of mixtures of $AgNO_3$ and hydroxy-functionalized polystyrenes: $[\text{monomer unit}]_0$ = 95 mM, $[AgNO_3]_0$ = 0.095 mM, in THF at 25°C. poly(4VP) (M_n = 10,400) (a), poly(4VG) (M_n = 14,200) (b), poly(4VC) (M_n = 13,500) (c), and poly (4VS) (M_n = 17,600) (d). [Color figure can be viewed at wileyonlinelibrary.com]

These results indicate that a series of well-defined bio-based hydroxy-functionalized polystyrenes with different numbers of substituents at different positions can be obtained by RAFT polymerization of silyl-protected hydroxystyrenes followed by the deprotection of the silyl groups under mild conditions.

Thermal Properties

The thermal properties of the obtained polymers were evaluated using differential scanning calorimetry (DSC).

Almost all the silyl-protected polymers except for poly(**7**) and poly(**9**) showed distinct glass transition temperatures (T_g), varying widely from 20 to 145°C and depending on the substituents (Fig. 7). Poly(**1**), poly(**2**), and poly(**3**), which have the same TBDMS group but at different positions, showed significantly different T_gs depending on the substituted positions. The T_g of poly(**1**) with the *p*-substitution was 107°C, while poly(**2**) with the *m*-substitution showed the lowest T_g (54°C), and poly(**3**) with the *o*-substitution had the highest T_g value (145°C). These results suggest that the molecular motion of the main chain is significantly affected by the positions of TBDMS groups and that substitution nearest the main chain heavily prevents the motion to result in the highest T_g. A similar result was reported for a series of poly(acetoxy-substituted styrene)s with different substituted positions.[33]

After deprotection of the silyl groups, the T_g values of the resulting poly(hydroxystyrene)s increased because of hydrogen bonding between the phenolic hydroxy groups except for poly(2VP) with an *o*-hydroxy substituent (Fig. 8). Among them, poly(4VC) showed the highest T_g value (190°C). The T_g values of poly(4VG) and poly(4VS) were 116 and 129°C, respectively. These values were lower than that of poly(4VP) (174°C) without additional substituents, most likely because the *m*-methoxy groups adjacent to the *p*-hydroxy group prevent hydrogen bonding interactions between the hydroxy groups.[34,35] A similar effect of methoxy substituents on T_gs has been reported for bio-based epoxy resins.[36]

Reducing Properties

The reducing abilities of the obtained phenolic polymers were evaluated by mixing the polymers with silver ions (Ag^+) because catechol groups can reduce Ag ions to form Ag nanoparticles.[37] When the solution of $AgNO_3$ was dropped into poly(4VC) solution in THF, the color of the solution quickly changed to yellow. In the UV–vis spectrum,

a peak at 400 nm, which can be attributed to the plasmon resonance of Ag nanoparticles, appeared and increased in intensity (Fig. 9). This result indicates that Ag ions were reduced by the catechol groups to produce Ag nanoparticles. For other phenolic polymers, such as poly(4VG) and poly (4VS), a similar peak at approximately 400 nm was observed, but the intensity was lower than that for poly(4VC). Thus, poly(4VC) has stronger reducing properties than the other phenolic polymers.

CONCLUSIONS

In conclusion, a series of bio-based hydroxystyrenes were prepared in high yield via simple decarboxylation of various naturally occurring cinnamic acids, such as *o*-, *m*-, and *p*-coumaric; caffeic; ferulic; and sinapinic acids. All the phenolic groups were easily protected with trialkylsilyl groups in high yield. RAFT polymerization of these silyl-protected styrenes afforded the polymers with controlled molecular weights. The silyl groups were easily deprotected to result in an array of bio-based functionalized polystyrenes with different numbers of hydroxy groups at different positions, which affect the thermal and reducing properties of the polymers. Since the synthesis of various hydroxy-functionalized polystyrenes from petroleum-derived compounds is difficult, the utilization of naturally occurring cinnamic acids is attractive and straightforward for functional polymers with various phenolic groups.

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