Supporting Information

Scalable Synthesis of Bio-Based Functional Styrene: Protected Vinyl Catechol from Caffeic Acid and Controlled Radical and Anionic Polymerizations Thereof

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Experimental Section

Materials. Caffeic acid (KANTO, >98.0%), *sec*-butyllithium (KANTO, 1.0 M solution), *N*,*N*-dimethylformamide (DMF) (KANTO, >99.5%; H_2O <0.001%), triethylamine (Tokyo Kasei, >99.0%), trimethylsilyl chloride (Tokyo Kasei, >98.0%), triethylsilyl chloride (TESCl) (Tokyo Kasei, >97.0%), *tert*-butyldimethylsilyl chloride (TBDMSCl) (KANTO, >98.0%), triisopropylsilyl chloride (TIPSCl) (Aldrich, 97 %), and acetic anhydride (Tokyo Kasei, >99.0%) were used as received. 1,2,3,4-tetrahydronaphthalene (Wako, >97.0%) was distilled over calcium hydride under reduced pressure before use. Toluene (KANTO, >99.5%; H_2O <0.001%), tetrahydrofuran (THF) (KANTO, >99.5%; H_2O <0.001%), and methylcyclohexane (KANTO, >98.0%; H_2O <0.001%) were dried and deoxygenized by passage through columns of Glass Contour Solvent Systems before use. α,α-Azobisisobutyronitrile (AIBN) (Kishida, >99%) was purified by recrystallization from methanol. Cumyl dithiobenzoate (CDB) was synthesized according to the literatures.[1,2]

Synthesis of *O*,*O*-Bis(trimethylsilyl)-4-vinylcatechol (1). Caffeic acid (20.0 g, 111 mmol) was dissolved in DMF (155 mL). Into this solution, triethylamine (46.4 mL, 333 mmol) was added, and then the mixture was heated to 100 °C under stirring. After 1 h, the reaction mixture was cooled to room temperature and the conversion of caffeic acid into 4-vinylcatechol measured by ^{1}H NMR was quantitative (>99%). TMSCl (28.2 mL, 222 mmol) was slowly added at 0 °C. The reaction mixture was stirred at room temperature. After 12 h, the extraction was conducted with *n*-hexane and the organic layer was washed with aqueous HCl, aqueous $NaHCO_3$, and water. The organic layer was concentrated by rotary evaporation. The residue was purified by distillation under reduced pressure. TMS_2VC (**1**) was obtained as colorless liquid (23.6 g, 76%, bp 67 °C/ 36 Pa). ^{1}H NMR ($CDCl_3$, r.t.): δ 0.25 (s, 9H, Si(CH_3)$_3$), 0.26 (s, 9H, Si(CH_3)$_3$), 5.12 (d, 1H, trans, CH_2=CH), 5.57 (d, 1H, cis, CH_2=CH), 6.60 (dd, 1H, CH_2=C*H*), 6.78 (d, 1H, Ar*H*), 6.90 (d, 1H, Ar*H*), 6.91 (s, 1H, Ar*H*). ^{13}C NMR ($CDCl_3$, r.t.): ($CDCl_3$, r.t.): δ 0.46, 0.48 (Si(*C*H_3)$_3$), 112.0 (*C*H_2=CH), 136.5 (CH_2=*C*H), 118.8, 120.2, 121.0, 131.9, 146.7 (phenyl).

Synthesis of *O*,*O*-Bis(triethylsilyl)-4-vinylcatechol (2). Caffeic acid (10.0 g, 55.5 mmol) was dissolved in DMF (77 mL). Into this solution, triethylamine (23.2 mL, 167 mmol) was added, and then the mixture was heated to 100 °C under stirring. After 1 h, the reaction mixture was cooled to room temperature and the conversion of caffeic acid into 4-vinylcatechol measured by ^{1}H NMR was quantitative (>99%). TESCl (18.6 mL, 111 mmol) was slowly added at 0 °C.

The reaction mixture was stirred at room temperature. After 12 h, the extraction was conducted with *n*-hexane and the organic layer was washed with aqueous HCl, aqueous $NaHCO_3$, and water. The organic layer was concentrated by rotary evaporation. The residue was purified by silica gel column chromatography (Silica Gel 60 N, *n*-hexane) and then evaporated to yield TES_2VC (**2**) as colorless liquid (18.4 g, 91%).

^{1}H NMR ($CDCl_3$, r.t.): δ 0.76 (m, 12H, Si$CH_2$$CH_3$), 0.99 (m, 18H, $SiCH_2CH_3$), 5.10 (d, 1H, trans, CH_2=CH), 5.55 (d, 1H, cis, CH_2=CH), 6.58 (dd, 1H, CH_2=C*H*), 6.76 (d, 1H, Ar*H*), 6.85 (dd, 1H, Ar*H*), 6.90 (d, 1H, Ar*H*). ^{13}C NMR ($CDCl_3$, r.t.): δ 5.2 (Si*C*H_2CH_3), 6.8 ($SiCH_2$*C*H_3), 111.6 (*C*H_2=CH), 136.6 (CH_2=*C*H), 118.3, 119.9, 120.5, 131.5, 146.96, 147.01 (phenyl).

Synthesis of *O*,*O*-Bis(*tert*-butyldimethylsilyl)-4-vinylcatechol (3). Caffeic acid (25.6 g, 142 mmol) was dissolved in DMF (199 mL). Into this solution, triethylamine (59.0 mL, 423 mmol) was added, and then the mixture was heated to 100 °C under stirring. After 1 h, the reaction mixture was cooled to room temperature and the conversion of caffeic acid into 4-vinylcatechol measured by ^{1}H NMR was quantitative (>99%). TBDMSCl (42.8 g, 284 mmol in toluene solution) was slowly added at 0 °C. The reaction mixture was stirred at room temperature. After 24 h, ice water was added into the mixture to stop the reaction. The extraction was conducted with *n*-hexane and the organic layer was washed with aqueous HCl, aqueous $NaHCO_3$, and water. The organic layer was concentrated by rotary evaporation. The residue was purified by silica gel column chromatography (Silica Gel 60 N, *n*-hexane) and then evaporated to yield $TBDMS_2VC$ (**3**) as colorless liquid (50.8 g, 98%). ^{1}H NMR ($CDCl_3$, r.t.): δ 0.197 (s, 6H, SiCH_3), 0.204 (s, 6H, SiCH_3), 0.98 (s, 9H, $SiC(CH_3)_3$), 0.99 (s, 9H, $SiC(CH_3)_3$), 5.10 (d, 1H, trans, CH_2=CH), 5.54 (d, 1H, cis, CH_2=CH), 6.58 (dd, 1H, CH_2=C*H*), 6.77 (d, 1H, Ar*H*), 6.86 (dd, 1H, Ar*H*), 6.90 (d, 1H, Ar*H*). ^{13}C NMR ($CDCl_3$, r.t.): δ –3.9 (Si*C*H_3), 18.6 (Si*C*$(CH_3)_3$), 26.1 ($SiC(CH_3)_3$), 111.8 (*C*H_2=CH), 136.6 (CH_2=*C*H), 118.9, 119.8, 121.1, 131.5, 146.98, 147.04 (phenyl).

Synthesis of *O*,*O*-Bis(triisopropylsilyl)-4-vinylcatechol (4). Caffeic acid (14.7 g, 81.7 mmol) was dissolved in DMF (70 mL). Into this solution, triethylamine (35.0 mL, 251 mmol) was added, and then the mixture was heated to 100 °C under stirring. After 1 h, the reaction mixture was cooled to room temperature and the conversion of caffeic acid into 4-vinylcatechol measured by ^{1}H NMR was quantitative (>99%). TIPSCl (35.0 mL, 164 mmol) was slowly added at 0 °C. The reaction mixture was stirred at room temperature. After 24 h, ice water was added into the mixture to stop the reaction. The extraction was conducted with *n*-hexane

and the organic layer was washed with aqueous citric acid and water. The organic layer was concentrated by rotary evaporation. The residue was purified by silica gel column chromatography (Silica Gel 60 N, *n*-hexane) and then evaporated to yield $TIPS_2VC$ (**4**) as colorless viscous liquid (33.8 g, 92%). ^{1}H NMR ($CDCl_3$, r.t.): δ 1.11 (d, 18H, SiCH(CH_3)$_2$), 1.12 (d, 18H, SiCH(CH_3)$_2$), 1.29 (m, 6H, SiC*H*(CH_3)$_2$), 5.07 (d, 1H, trans, CH_2=CH), 5.51 (d, 1H, cis, CH_2=CH), 6.57 (dd, 1H, CH_2=C*H*), 6.76 (d, 1H, Ar*H*), 6.80 (dd, 1H, Ar*H*), 6.92 (d, 1H, Ar*H*). ^{13}C NMR ($CDCl_3$, r.t.): δ 13.3 (Si*C*H(CH_3)$_2$), 18.1 (SiCH(*C*H_3)$_2$), 111.3 (*C*H_2=CH), 136.7 (CH_2=*C*H), 117.5, 119.4, 119.8, 130.8, 147.1, 147.2 (phenyl).

Synthesis of 3,4-Diacetoxystyrene (5). Caffeic acid (25.0 g, 139 mmol) was dissolved in DMF (194 mL). Into this solution, triethylamine (58.0 mL, 416 mmol) was added, and then the mixture was heated to 100 °C under stirring. After 1 h, the reaction mixture was cooled to room temperature and the conversion of caffeic acid into 4-vinylcatechol measured by ^{1}H NMR was quantitative (>99%). Acetic anhydride (26.4 mL, 279 mmol) was slowly added at 0 °C. The reaction mixture was stirred at room temperature. After 2 h, aqueous HCl was added into the mixture to stop the reaction. The extraction was conducted with diethyl ether and the organic layer was washed with aqueous HCl, aqueous $NaHCO_3$, and water. The organic layer was concentrated by rotary evaporation. The residue was purified by distillation under reduced pressure. Ac_2VC (**5**) was obtained as colorless viscous liquid (22.7 g, 74%, bp 80 °C/ 5 Pa). ^{1}H NMR ($CDCl_3$, r.t.): δ 2.28 (s, 3H, OCOCH_3), 2.29 (s, 3H, OCOCH_3), 5.28 (d, 1H, trans, CH_2=CH), 5.69 (d, 1H, cis, CH_2=CH), 6.66 (dd, 1H, CH_2=C*H*), 7.14 (d, 1H, Ar*H*), 7.22 (d, 1H, Ar*H*), 7.27 (d, 1H, Ar*H*). ^{13}C NMR ($CDCl_3$, r.t.): δ 20.8 (OCO*C*H_3), 115.2 (*C*H_2=CH), 135.4 (CH_2=*C*H), 121.0, 123.5, 124.6, 136.8, 141.6, and 142.3 (phenyl), 168.4 (O*C*OCH_3).

RAFT Radical Polymerization. RAFT polymerization was carried out by syringe technique under dry nitrogen in sealed glass tubes. A typical example for polymerization of TES_2VC (**2**) with CDB as RAFT agent in the presence of AIBN is given below: **2** (2.36 mL, 6.0 mmol), CDB (0.147 mL of 408 mM solution in toluene, 0.060 mmol), AIBN (0.10 mL of 150 mM solution in toluene, 0.015 mmol), 1,2,3,4-tetrahydronaphthalene (0.19 mL) as an internal standard and toluene were placed in a 25 mL round-bottomed flask equipped with a three-way stopcock at room temperature. The total volume of the reaction mixture was 3.0 mL. Immediately after mixing, the solution was evenly charged in six glass tubes, and the tubes were sealed by flame under a nitrogen atmosphere. The tubes were immersed in thermostatic oil bath at 60 °C. In predetermined intervals, the polymerization was terminated by cooling the reaction

mixtures to –78 °C. 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., 36 h, 95%). The quenched reaction solutions were evaporated to dryness to give poly(**2**) (M_n = 20800, M_w/M_n = 1.08). The obtained polymer was purified by preparative size-exclusion chromatography (SEC) for the ^{1}H NMR analysis.

Anionic Polymerization. Anionic polymerization was carried out by syringe technique under dry argon in sealed glassware equipped with a three-way stopcock. A typical example for polymerization of $TBDMS_2VC$ (**3**) with *sec*-butyllithium (*sec*-BuLi) as an initiator is given below: **3** (1.99 mL, 5.00 mmol) and THF (7.51 mL) were placed in a 25 mL glass tube. Then, the monomer solution was cooled at –78 °C. The polymerization was initiated by adding the prechilled initiator solution, containing *sec*-BuLi (0.50 mL of 200 mM solution in methylcyclohexane, 0.10 mmol). The total volume of the reaction solution was 10.0 mL. After stirring for 3 h, the reaction was quenched by argon-bubbled methanol (1.0 mL). Monomer conversion was determined from the concentration of residual monomer measured by ^{1}H NMR using intensity ratios of the peaks around 5.5–7.0 ppm (A: the aromatic protons of monomer and polymer and the methine protons of the vinyl group in monomer) and those at 5.1 ppm (B: the methylene protons of the vinyl group in monomer): conversion (%) = $(1–[B/(A–B)]/[B_0/(A_0–B_0)]) \times 100$. The quenched solution was diluted with *n*-hexane and washed with water, evaporated to dryness under reduced pressure, and vacuum-dried to give poly(**3**) (M_n = 14100, M_w/M_n = 1.04). The obtained polymer was purified by preparative SEC for the ^{1}H NMR analysis.

Deprotection. The deprotection of TMS and TES groups were performed according to the previous paper.[3] Typical examples are given below: poly(**3**) (732.0 mg, M_n = 14100, M_w/M_n = 1.04) was dissolved in THF (16 mL) followed by addition of hydrochloric acid (1.46 mL, 12 M) at 60 °C. 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(VC) (277.0 mg, 100 %). For poly(**4**) (890.5 mg in 13.8 mL THF, M_n = 11000, M_w/M_n = 1.08), the bulky TIPS was deprotected using acetic acid (0.45 mL) and tetrabutylammonium fluoride (TBAF) (7.92 mL of 1.0 M solution in THF) at room temperature. After stirring for 36 h, the similar procedure gave poly(VC) (258.7 mg, 96 %). The acetate group in poly(**5**) (74.4 mg 2.0 mL THF, M_n = 7200, M_w/M_n = 1.07) was hydrolyzed using KOH (0.254 g) in ethanol (6.1

mL) for 12 h to give poly(VC) (44.3 mg, 96%).

Measurements. ^{1}H NMR spectra were recorded on a JEOL ECS-400 spectrometer, operating at 400 MHz. The number-average molecular weight (M_n) and molecular weight distribution (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] or in DMF containing 100 mM LiCl at 40 °C on two hydrophilic polymer gel columns [Tosoh a-M + a-3000 (7.8 mm i.d. × 30 cm); flow rate 1.0 mL/min] (for poly(VC)) 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).

References

(1) Moad, G.; Chiefari, J.; Chong, Y. K.; Krstina, J.; Mayadunne, R. T. A.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polym. Int.* **2000**, *49*, 993–1001.

(2) Thang, S. H.; Chong, Y. K.; Mayadunne, R. T. A.; Moad, G.; Rizzardo, E. *Tetrahedron Lett.* **1999**, *40*, 2435–2438.

(3) Takeshima, H.; Satoh, K.; Kamigaito, M. *Macromolecules* **2017**, *50*, 4206–4216.

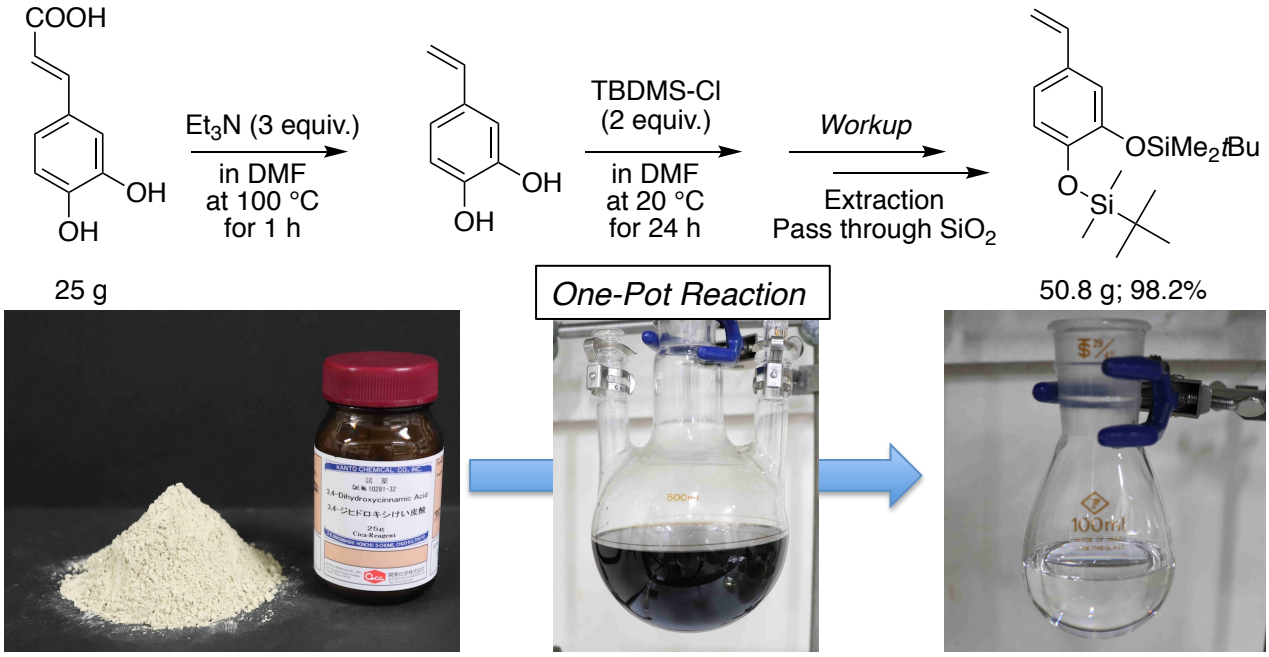


Figure S1. One-pot scalable synthesis of $TBDMS_2VC$ (**3**) via deacarboxylation of caffeic acid followed by protection of catechol groups with *tert*-butyldimethylsilyl (TBDMS) chloride

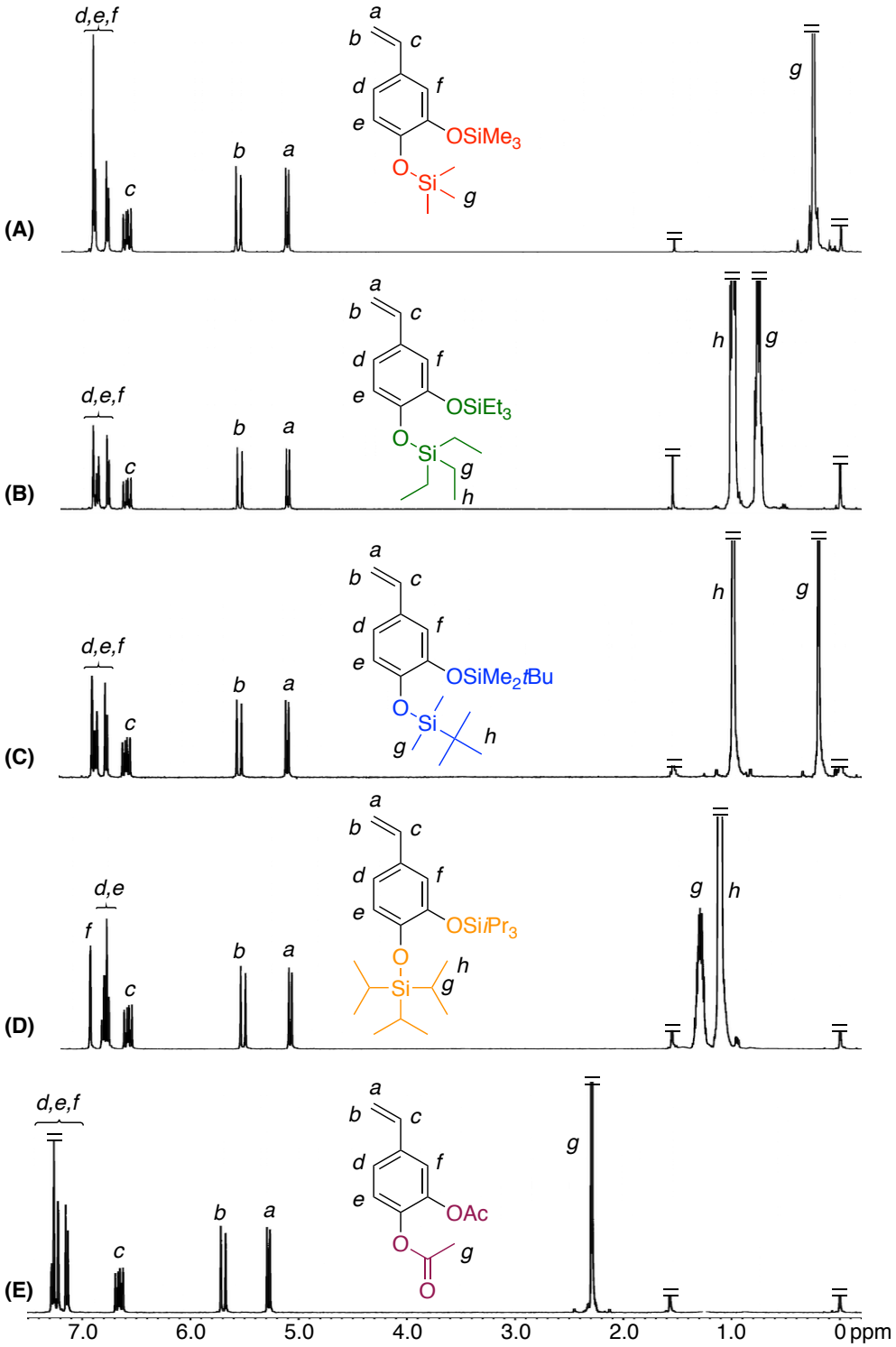


Figure S2. ^{1}H NMR spectra ($CDCl_3$, r.t.) of monomer **1**–**5**: TMS_2VC (**1**) (A), TES_2VC (**2**) (B), $TBDMS_2VC$ (**3**) (C), $TIPS_2VC$ (**4**) (D), Ac_2VC (**5**) (E).

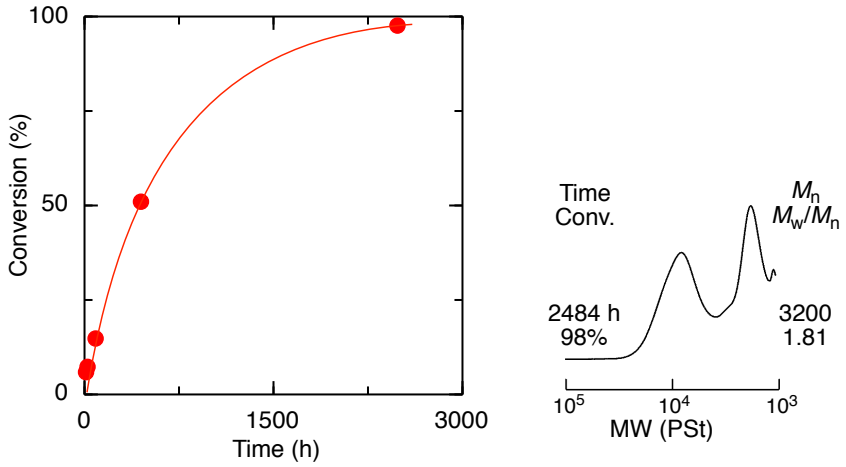


Figure S3. Time-conversion and SEC curves for free radical polymerization of unprotected VC: $[VC]_0/[AIBN]_0$ = 1000/10 mM in CH_3OH at 60 °C.

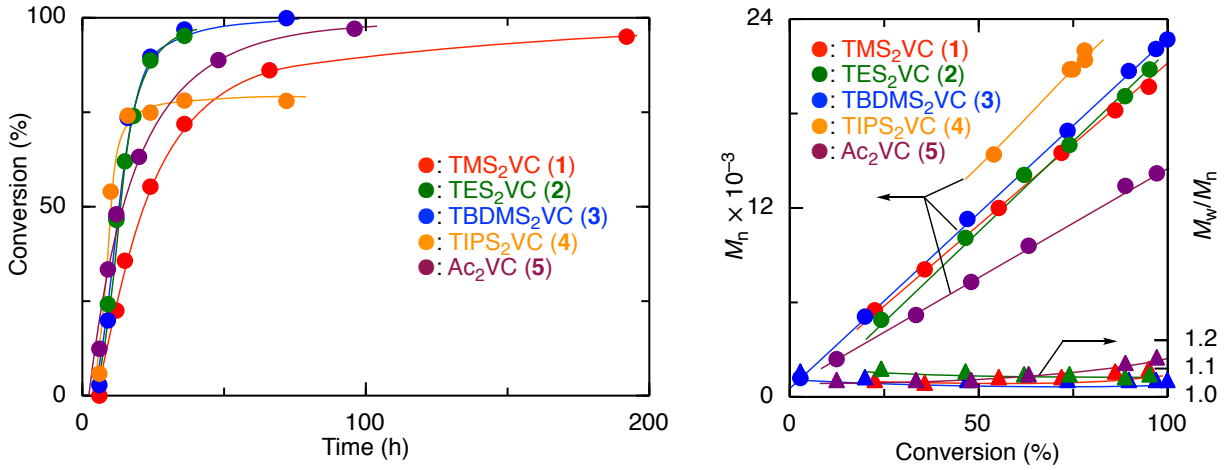


Figure S4. Time-conversion curves, M_n, and M_w/M_n for RAFT polymerization of protected VCs: $[monomer]_0/[CDB]_0/[AIBN]_0$ = 2000/20/5.0 mM in toluene (**1**–**3**), bulk (**4**), or ethyl acetate (**5**) at 60 °C.

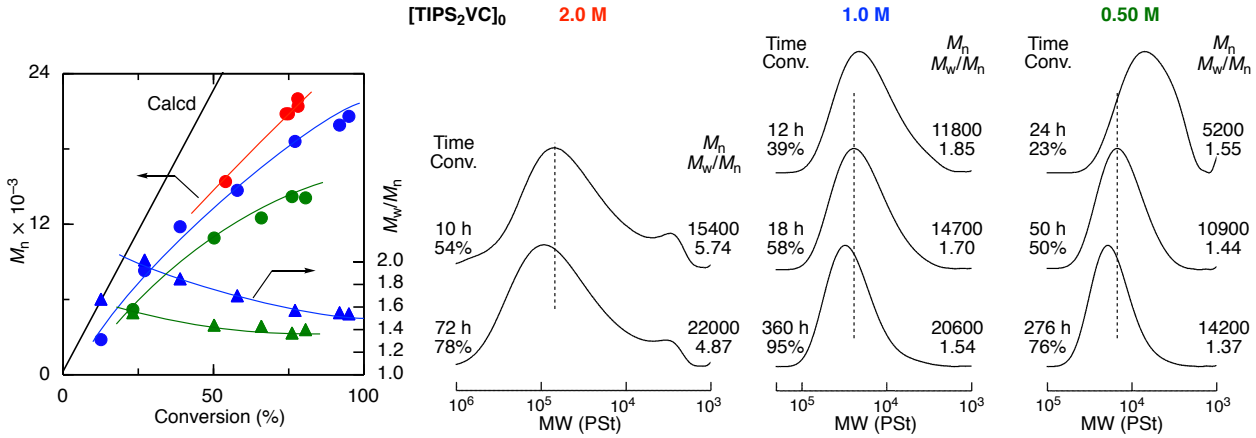


Figure S5. M_n, M_w/M_n, and SEC curves for RAFT polymerization of $TIPS_2VC$ (**4**): $[\mathbf{4}]_0/[CDB]_0/[AIBN]_0 = 100/1.0/0.25$ at 60 °C, $[\mathbf{4}]_0 = 2.0$ M (in bulk), 1.0 M (in toluene), 0.50 M (in toluene).

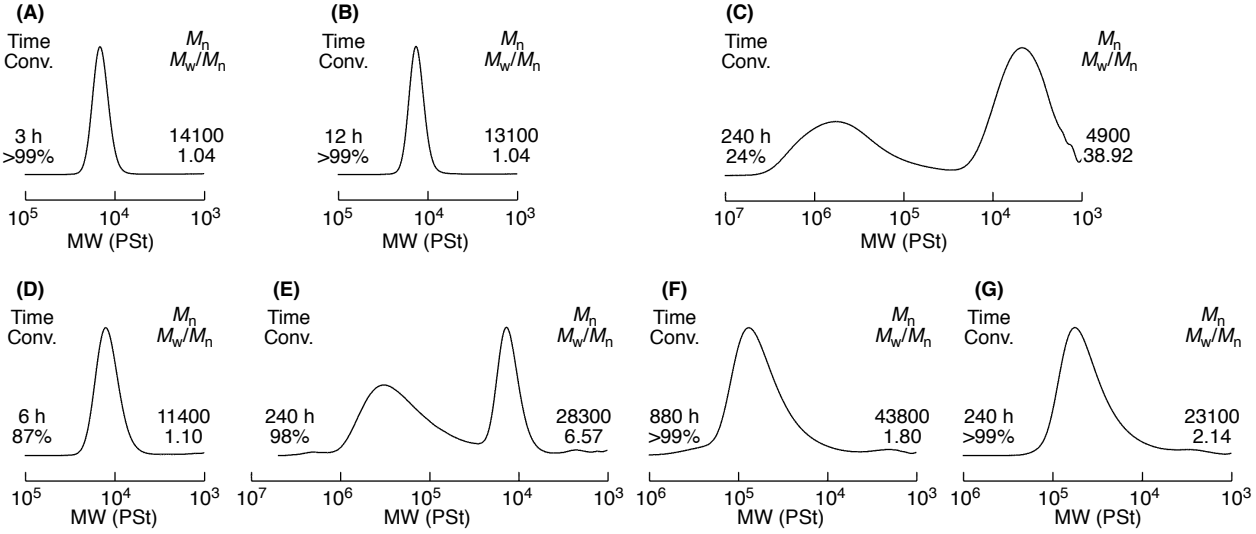


Figure S6. SEC curves for anionic polymerization of $TBDMS_2VC$ (**3**) and $TIPS_2VC$ (**4**): $[\mathbf{3}]_0/[sec\text{-BuLi}]_0 = 500/10$ mM in THF at –78 °C (A), in methylcyclohexane (containing 50 mM or THF) at –40 °C (B), in toluene at –15 °C (C), $[\mathbf{4}]_0/[sec\text{-BuLi}]_0 = 500/10$ mM in THF at –78 °C (D), in methylcyclohexane (containing 50 mM or THF) at –40 °C (E), in toluene at –40 °C (F), in toluene at –15 °C (G).

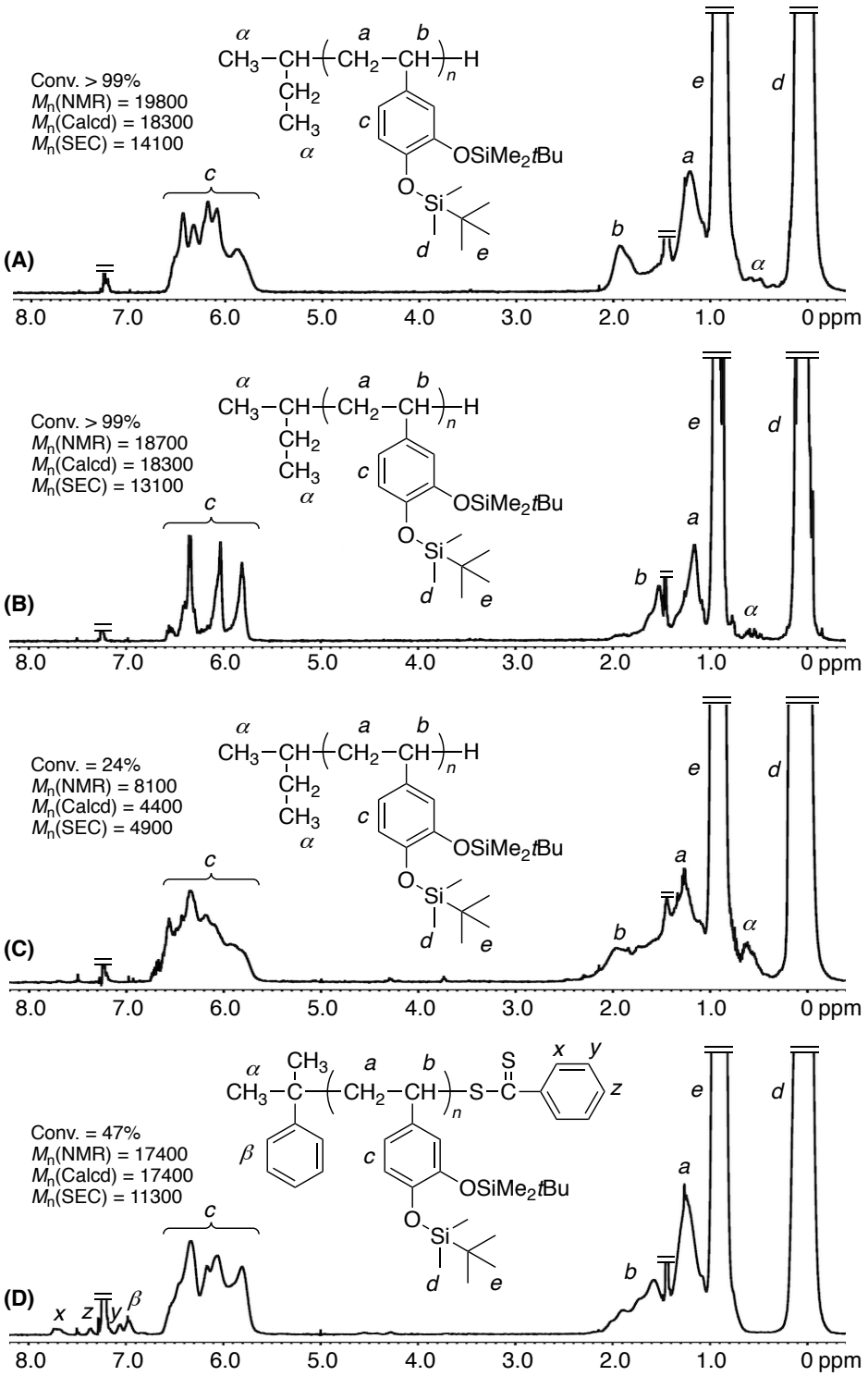
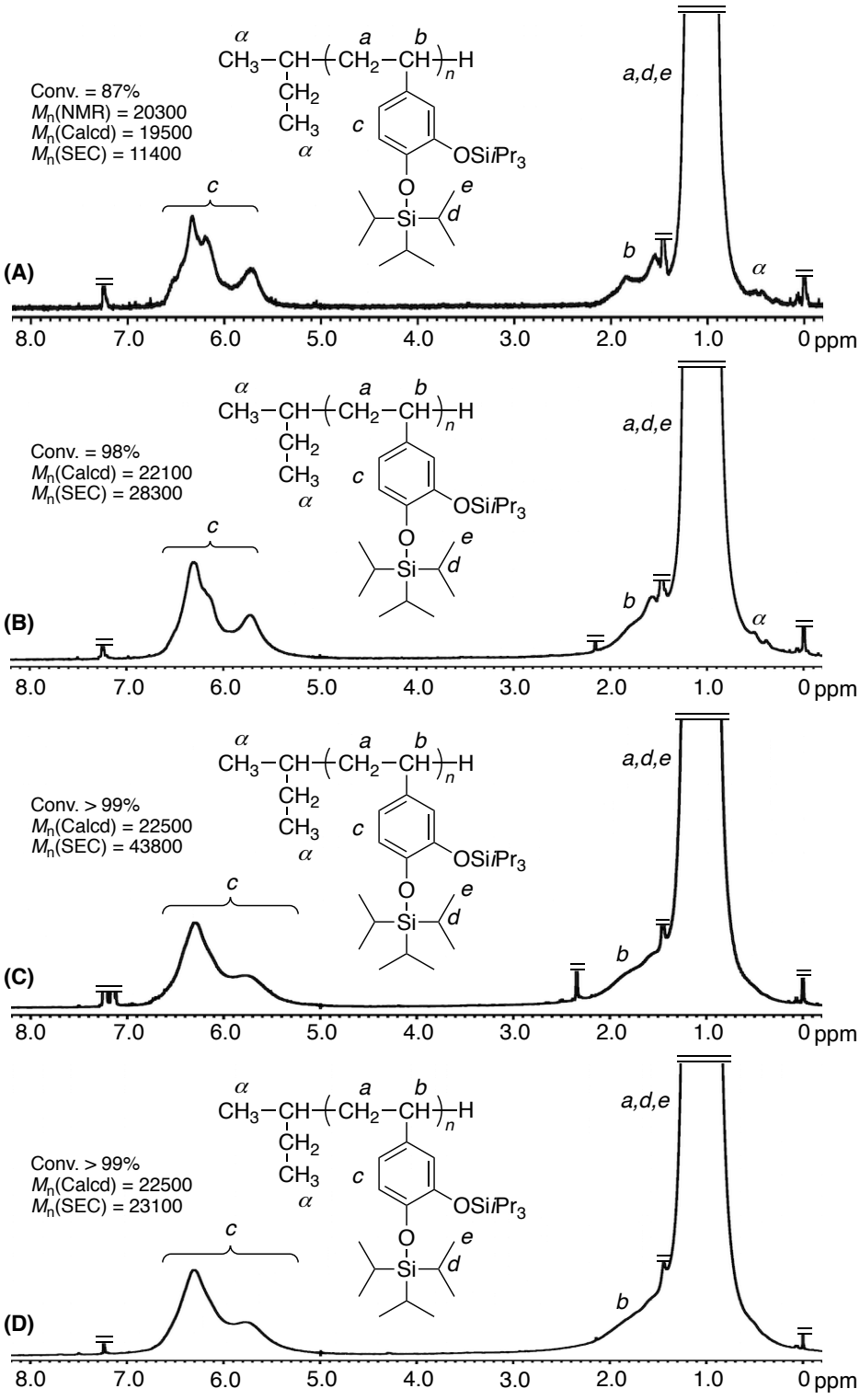


Figure S7. ^{1}H NMR spectra ($CDCl_3$, 55 °C) of poly(**3**) obtained from various conditions: $[\mathbf{3}]_0/[\textit{sec}\text{-BuLi}]_0$ = 500/10 mM in THF at –78 °C (A), in methylcyclohexane (containing 50 mM of THF) at –40 °C (B), in toluene at –15 °C (C), $[\mathbf{3}]_0/[CDB]_0/[AIBN]_0$ = 2000/20/5.0 mM in toluene at 60 °C (D).



(Figure S8. continued)

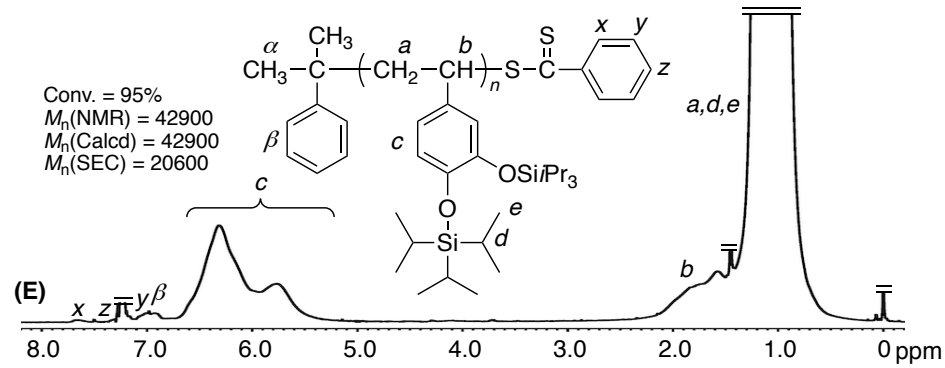


Figure S8. ^{1}H NMR spectra ($CDCl_3$, 55 °C) of poly(**4**) obtained under various conditions: $[\mathbf{4}]_0/[sec\text{-BuLi}]_0$ = 500/10 mM in THF at –78 °C (A), in methylcyclohexane (containing 50 mM of THF) at –40 °C (B), in toluene at –40 °C (C), in toluene at –15 °C (D), $[\mathbf{4}]_0/[CDB]_0/[AIBN]_0$ = 1000/10/2.5 mM at 60 °C in toluene (E).

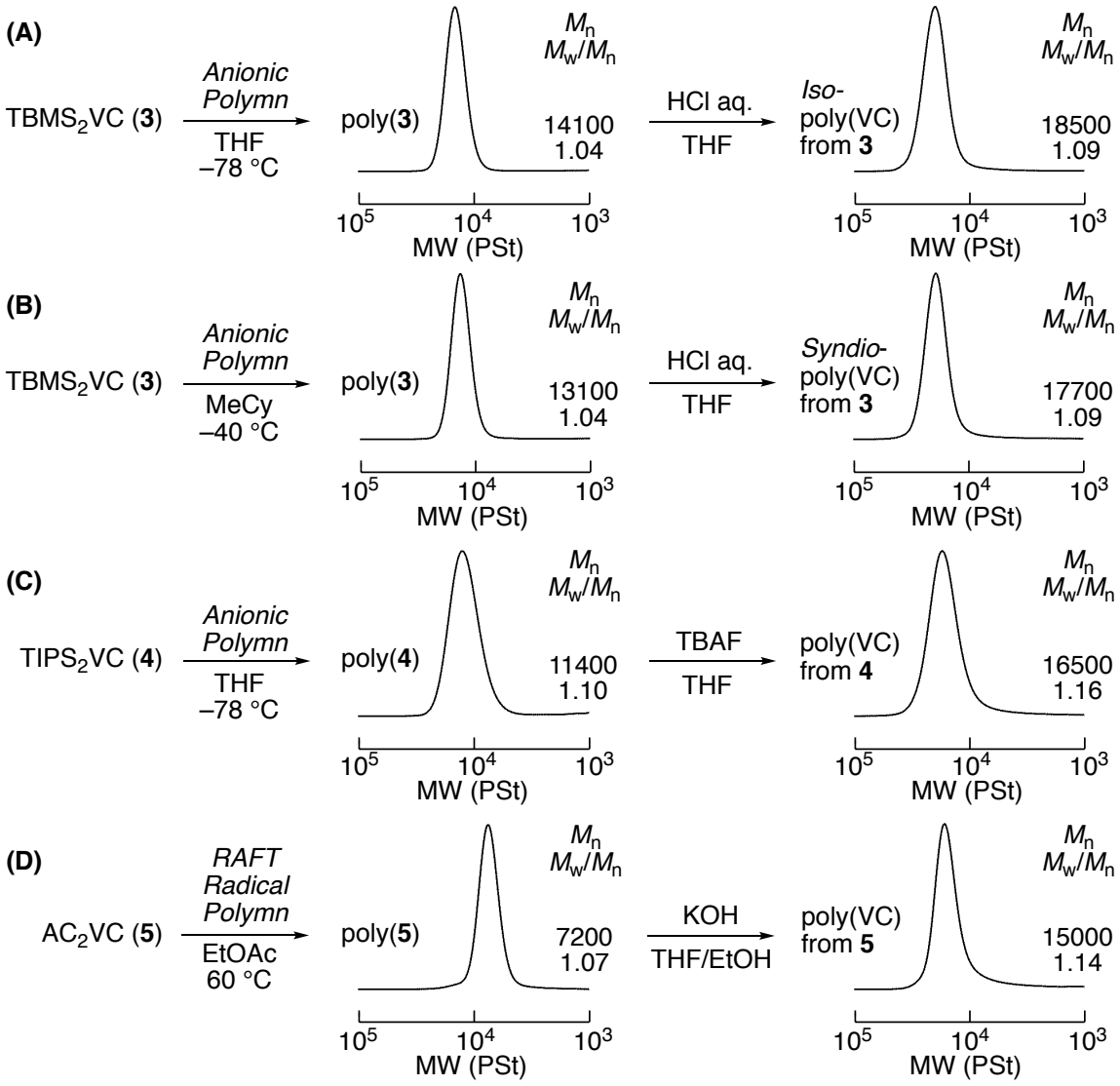


Figure S9. SEC curves for poly(**3**), poly(**4**), poly(**5**) and deprotected polymers: $[\mathbf{3}]_0/[\textit{sec}\text{-BuLi}]_0$ = 500/10 mM in THF at –78 °C (A), in methylcyclohexane (containing 50 mM or THF) at –40 °C (B), $[\mathbf{4}]_0/[\textit{sec}\text{-BuLi}]_0$ = 500/10 mM in THF at –78 °C (C), $[\mathbf{5}]_0/[\text{CDB}]_0/[\text{AIBN}]_0$ = 2000/20/5.0 mM in ethyl acetate at 60 °C (D). The difference in molecular weight was due to the eluent for SEC measurement, i.e., THF (before deprotection) and DMF containing LiCl (after deprotection).