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Supplementary Information

Synthesis of a Well-Defined Alternating Copolymer of 1,1-Diphenylethylene and *tert*-Butyldimethylsilyloxymethyl Substitduted Styrene by Anionic Copolymerization: Toward Tailored Graft Copolymers with Controlled Side Chain Densities

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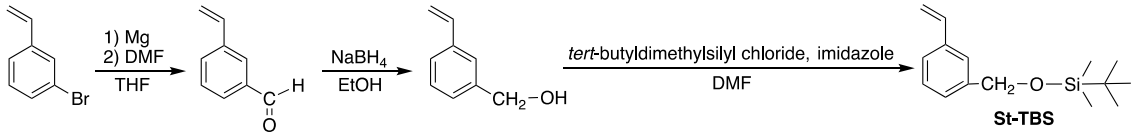
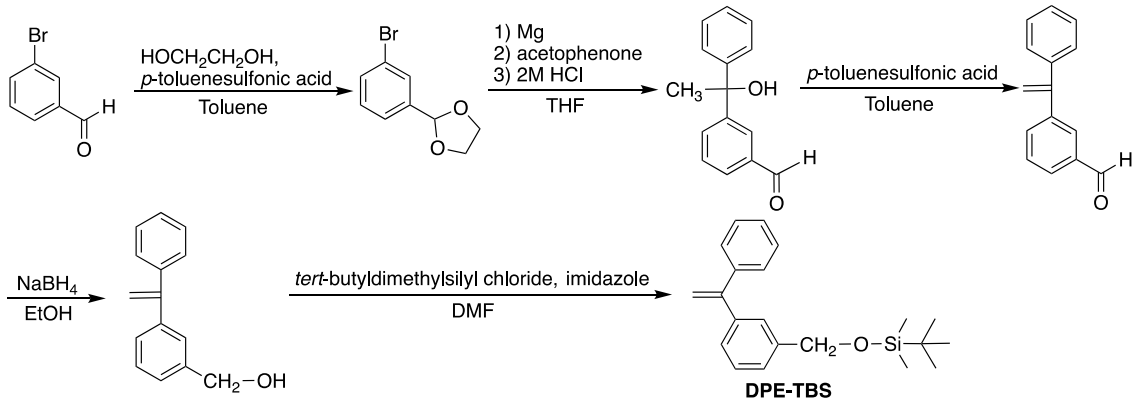
MALDI-TOF-MS was performed on an AXIMA-CFR (Shimadzu/Kratos) equipped with a 337 nm N_2 laser in the linear mode and 20 kV acceleration voltage. 2,5-Dihydroxybenzoic acid (Tokyo Kasei, 97%) was used as matrix, and no ioni

Synthesis of *m*-(*tert*-butyldimethylsilyloxy)methylstyrene (St-TBS)



To synthesize St-TBS, (3-vinylphenyl)methanol was at first synthesized. To a solution of the Grignard reagent from 3-bromostyrene (6.57 g, 35.9 mmol) and Mg (1.40 g, 57.8 mmol) in THF (40 mL) was added carefully dropwise during 30 min a solution of DMF (3.93 g, 53.9 mmol) in THF (10 mL) at 0 °C. The solution was allowed to warm to room temperature and stirred for additional 1 h. After that, addition of a NH_4Cl saturated solution and extraction with diethyl ether, and dried over $MgSO_4$. After removal of solvent under reduced pressure, the residual oil was reacted with $NaBH_4$ (2.03 g, 53.85 mmol) in ethanol (100 mL) to give crude (3-vinylphenyl)methanol (3.35 g, 24.9 mmol). (3-Vinylphenyl)methanol (3.35 g, 24.9 mmol) and imidazole (5.11 g, 75.2 mmol) were weighed into a predried 100 mL flask under an atmosphere of nitrogen. Anhydrous DMF (30 mL) was added to dissolve them. A solution of *tert*-butyldimethylsilyl chloride (6.96 g, 49.8 mmol) in dry DMF (30 mL) was added dropwise during 30 min at 0 °C. After addition, the solution was allowed to warm at room temperature and stirred for 10 h. Aqueous 5% NaOH was carefully added. The mixture was extracted with diethyl ether, and the organic layer was washed with 5% NaOH and water and dried over $MgSO_4$. After filtration and removal of the solvent, distillation of the resulting liquid under reduced pressure gave a colorless liquid of St-TBS (5.78 g, 23.3 mmol, 64%).

^1H NMR ($CDCl_3$, 300 MHz): δ = 7.37 (s, 1H, Ar), 7.25 (d, 1H, J = 4.2 Hz, Ar), 7.24 (s, 1H, Ar), 7.17 (d, 1H, J = 4.2 Hz, Ar), 6.83 (dd, 1H, *J* = 17.6 and 10.8 Hz, CH=), 5.73, 5.21 (dd, 2H, *J* = 17.6 and 10.8 Hz, CH_2=), 4.75 (s, 2H, –OCH_2–), 0.94 (s, 9H, $SiCCH_3$), –0.02 (s, 6H, $SiCH_3$).



Synthesis of 1-(3-bromophenyl)-1,3-dioxolane

3-Bromobenzaldehyde (38.8 g, 210 mmol), ethylene glycol (20.3 g, 320 mmol), and catalytic amount of *p*-toluenesulfonic acid were added in 500 mL two-necked flask equipped with Dean-Stark head, dissolved in toluene (200 mL), and refluxed for 2.5 h. During refluxing, water was removed several times to shift the equilibrium. The reaction was quenched with aqueous $NaHCO_3$. Then, the organic layer was washed with water and dried over $MgSO_4$ in the presence of K_2CO_3 in order to keep alkalescent conditions. After filteration, the organic layer was concentrated, and the residue was

distilled over CaH_2 under reduced pressure (bp : 82 °C/2 mmHg) to yield 1-(3-bromophenyl)-1,3-dioxolane (38.6 g, 168 mmol, 80%) as a colorless liquid.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.65–7.25 (m, 4H, Ar), 5.78 (s, 1H, -O–CH–O-), 4.07 (m, 4H, OCH_2CH_2O).

Synthesis of 1-(3-formylphenyl)-1-phenylethanol

To a Grignard reagent prepared from 1-(3-bromophenyl)-1,3-dioxolane (38.6 g, 168 mmol) and Mg (6.13 g, 252 mmol) in THF (200 mL), THF solution (10 mL) of acetophenone (28.3 g, 235 mmol) was added dropwise at 0 °C under nitrogen. The resulting mixture was stirred at 25 °C for 18 h. It was acidified with 2 M HCl at 0 °C, extracted with ether, and dried over $MgSO_4$. Removal of the solvent under reduced pressure followed by flash column chromatography (hexane/ethyl acetate = 6/1-0/1, v/v) yielded 1-(3-folmylphenyl)-1-phenylethanol (20.9 g, 92.9 mmol, 55%) as a colorless liquid.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.99 (s, 1H, CHO), 7.96–7.26 (m, 9H, Ar), 2.33 (s, 3H, CH_3).

Synthesis of 1-(3-formylphenyl)-1-phenylethylene

1-(3-Formylphenyl)-1-phenylethanol (20.9 g, 92.9 mmol) and *p*-toluenesulfonic acid (0.16 g, 0.82 mmol) were placed in 500 mL two-necked flask equipped with Dean-Stark head, dissolved in toluene (100 mL) and refluxed for 1.5 h. During refluxing, water was removed to shift the equilibrium. The reaction was quenched with aqueous $NaHCO_3$. Then, the organic layer was washed with water and dried over $MgSO_4$. After filtration, the organic layer was concentrated under reduced pressure to yield 1-(3-formylphenyl)-1-phenylethylene (18.9 g, 91.0 mmol, 98%) as a colorless liquid. It was used without purification.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 10.0 (s, 1H, CHO), 7.87–7.25 (m, 9H, Ar), 5.55 (s, 2H, CH_2=).

Synthesis of 1-(3-hydroxymethylphenyl)-1-phenylethylene

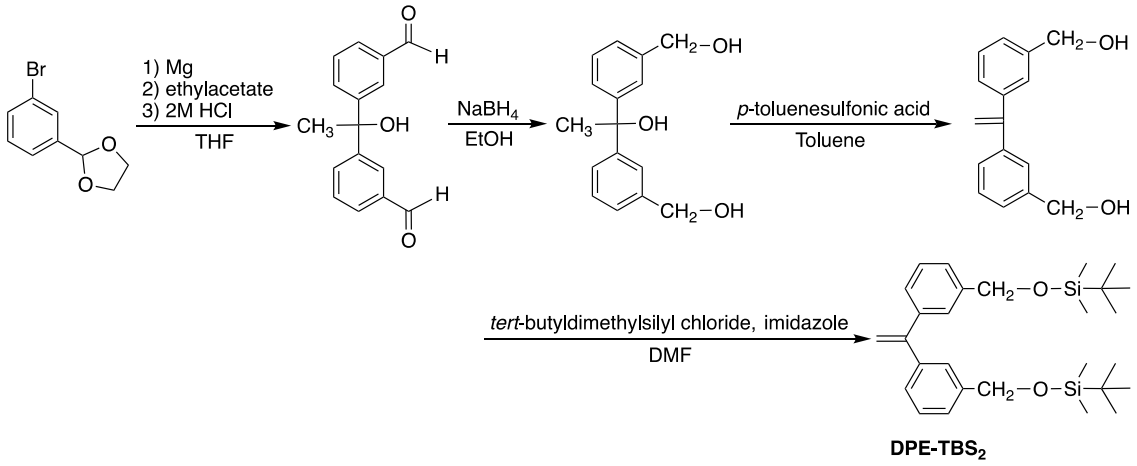
$NaBH_4$ (5.28 g, 138 mmol) was added to ethanol solution (200 mL) of 1-(3-formylphenyl)-1-phenylethylene (18.9 g, 91.0 mmol) at 0 °C and stirred at 25 °C for 1.5 h. The reaction was quenched with 2M HCl, and the resulting solution was concentrated under reduced pressure. The organic layer was extracted with ether, washed with water, and dried over $MgSO_4$. After filtration, the organic layer was concentrated under reduced pressure to yield 1-(3-hydroxymethylphenyl)-1-phenylethylene (11.2 g, 80.1 mmol, 88%) as a viscous brownish liquid.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.40–7.25 (m, 9H, Ar), 5.47 (s, 2H, CH_2=), 4.67 (s, 2H, CH_2O), 1.75 (broad, 1H, OH).

Synthesis of 1-(3-*tert*-butyldimethylsilyloxy)methylphenyl-1-phenylethylene (DPE-TBS)

tert-Butyldimethylsilyl chloride (11.2 g, 80.1 mmol) was slowly added to a DMF solution (100 mL) containing 1-(3-hydroxymethylphenyl)-1-phenylethylene (11.0 g, 53.4 mmol) and imidazole (10.9 g, 161 mmol) at 0 °C and stirred at 25 °C for 14 h. After quenching with aqueous $NaHCO_3$, the organic layer was extracted with hexanes, washed with water, and dried over $MgSO_4$ in the presence of K_2CO_3 in order to keep alkalescent conditions. Removal of the solvent under reduced pressure followed by flash column chromatography (hexane) yielded the DPE-TBS (10.4 g, 32.0 mmol, 60%) as a viscous yellowish liquid. It was finally purified by drying under high-vacuum conditions followed by colorimetric titration with *s*-BuLi from colorless to a very faint pink in order to remove impurities that can react with anionic species.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.28–7.20 (m, 9H, Ar), 5.41 (s, 2H, CH_2=), 4.70 (s, 2H, CH_2O), 0.88 (s, 9H, $SiC(CH_3)_3$), 0.03 (s, 6H, $Si(CH_3)_2$).



Synthesis of 1,1-bis[(3-*tert*-butyldimethylsilyloxy)methylphenyl]-ethylene (DPE-TBS2)

To a stirred solution of the Grignard reagent, prepared from 1-(3-bromophenyl)-1,3-dioxolane (36.1 g, 160 mmol) and Mg (5.76 g, 240 mmol) in THF (300 mL), was added ethyl acetate (7.2 mL, 73.6 mmol) in THF (10 mL) dropwise at 0 °C, and the mixture was stirred at 25 °C for 10 h. The reaction mixture was acidified by 2M HCl to generate the formyl group, extracted with ether, and dried over $MgSO_4$. After removal of solvent under reduced pressure, the residual oil was reacted with $NaBH_4$ (16.0 g, 420 mmol) in ethanol (200 mL) to give crude 1,1-bis-(3-hydroxymethylphenyl)ethanol (35.0 g, 140 mmol). It was then dehydrated with a catalytic amount of *p*-toluenesulfonic acid in $CHCl_3$ (120 mL) at 70 °C for 3 h. After that, extracted with ether, and dried over $MgSO_4$, 1,1-bis(3-hydroxymethylphenyl)ethylene (30.2 g, 130 mmol) was obtained in 90% yield as a pale yellow liquid. The resulting 1,1-bis(3-hydroxymethylphenyl)ethylene was used in the further silylation reaction without purification. To a solution of 1,1-bis(3-hydroxymethylphenyl)ethylene (30.2 g, 130 mmol) and imidazole (21.2 g, 310 mmol) in DMF (200 mL) was added *tert*-butyldimethylsilyl chloride (46.1, 300 mmol) in DMF (100 mL) dropwise at 0 °C. The mixture was

allowed to stand at 25 °C for 3 h. After the usual workup, flash column chromatography (hexane/benzene 1/1) afforded 12.1 g (26.1 mmol, 20%) of DBE-TBS2 as a viscous liquid. It was freeze-dried several times to remove water from its benzene solution prior to use.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.28 (m, 8H, Ar), 5.48 (s, 2H, C=CH_2), 4.75 (s, 4H, –CH_2O–), 0.99 (d, 18H, $SiC(CH_3)_3$), 0.02 (d, 12H, $Si(CH_3)_2$).

Synthesis of poly(DPE-*alt*-St)

The typical procedure is as follows; A THF solution of DPE (27.3 mmol, 13.2 mL) was added to the heptane solution of *s*BuLi (0.110 mmol, 2.0 mL) through the break-seal at room temperature. After 15 min, St in THF (3.44 mmol, 3.4 mL) was added to the mixture and reacted for 4 h at 0 °C. The reaction was quenched with degassed methanol. The polymer was precipitated in methanol and purified by reprecipitation from THF to methanol twice and finally freeze-dried from its benzene solution (560 mg, 62%, M_n = 8.74 kg/mol).

^{1}H NMR ($CDCl_3$, 300MHz; ppm): δ -0.1-0.4 (br, -C*H*$_3$ of *s*Bu), 0.4-2.5 (br, main chain and -C*H*$_3$ of *s*Bu), 3.1 (s, terminal methine), 5.3-7.4 (br, aromatic).

Synthesis of alternating polymer using styrene derivatives and DPE derivatives (poly(DPE-TBS-*alt*-St-TBS), poly(DPE-TBS$_2$-*alt*-St-TBS), poly(DPE-TBS-*alt*-St), poly(DPE-TBS$_2$-*alt*-St))

The synthetic procedure is almost same as poly(DPE-*alt*-St-TBS) in experimental section in main article except using each corresponding monomers.

Poly(DPE-TBS-*alt*-St-TBS) : ^{1}H NMR ($CDCl_3$, 300MHz; ppm): δ -0.2-0.2 (br, -C*H*$_3$ of *s*Bu and Si-C*H*$_3$), 0.3-0.4 (br, -C*H*$_3$ of *s*Bu), 0.5-2.1 (br, main chain and C(C*H*$_3$)$_3$), 2.9 (s, terminal end), 4.0-4.7 (br, Ph-C*H*$_2$), 6.0-7.4 (br, aromatic).

Poly(DPE-TBS-*alt*-St) : ^{1}H NMR ($CDCl_3$, 300MHz; ppm): δ -0.1-0.1 (br, -C*H*$_3$ of *s*Bu and Si-C*H*$_3$), 0.3-0.4 (br, -C*H*$_3$ of *s*Bu), 0.8-2.0 (br, main chain and C(C*H*$_3$)$_3$), 2.9 (s, terminal end), 4.2-4.9 (br, Ph-C*H*$_2$), 5.2-7.4 (br, aromatic).

Synthesis of poly(DPE-*alt*-BMS)-*g*-PMMA

Typical synthetic procedure is as follows: A THF solution (2.1 mL) of DPE (0.243 mmol) was added to a heptane solution (1.3 mL) of *s*BuLi (0.0978 mmol) through the break-seal at -78 °C. After 15 min, LiCl (0.467 mmol) in THF (3.9 mL) was added to the mixture at -78 °C, and the initiator system was allowed to stand at -78 °C for 15 min. Then, MMA (5.00 mmol) in THF (5.4 mL), was rapidly added to the initiator system at -78 °C through the break-seal with vigorous shaking of the apparatus. After 15 min, THF solution of poly(DPE-*alt*-BMS) (0.0483 mmol for the benzyl bromide

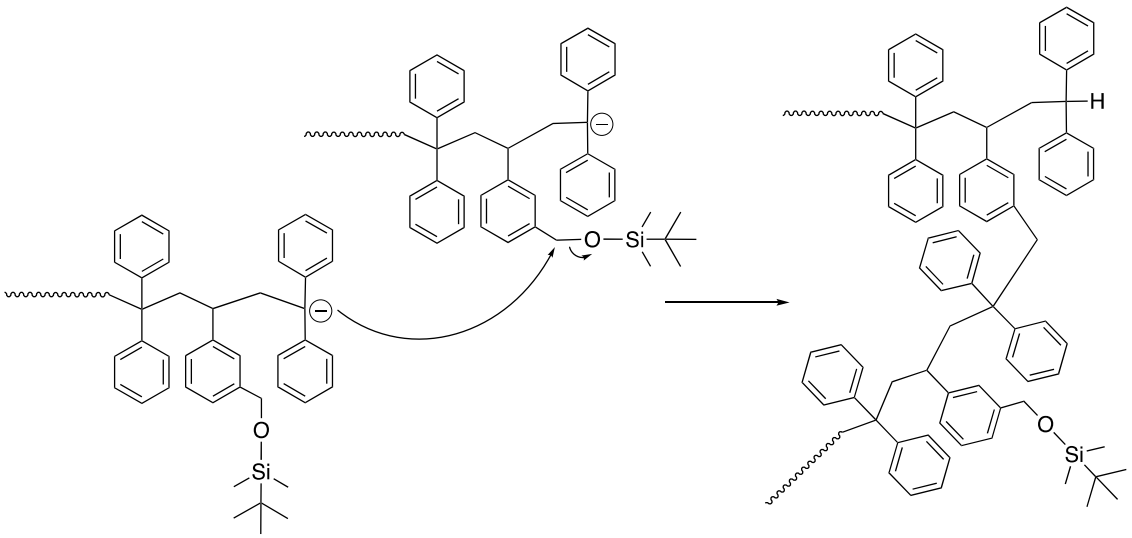
groups, M_n = 7.13 kg/mol, 3.8 mL) was added to the mixture at -78 °C for 24 h. After reacting at -78 °C for 24 h, the reaction was continued at -40 °C for 24 h. The reaction was quenched with degassed methanol. The reaction mixture was poured into large amount of MeOH, and a branched polymer was isolated by fractional reprecipitation using THF/Et_2O/hexane. The isolated polymer was purified by reprecipitation from THF to methanol and finally freeze-dried from its benzene solution (50 mg, 21%). ^{1}H NMR ($CDCl_3$, 300MHz; ppm): δ 0.2 (br, -C*H*$_3$ of *s*Bu), 0.5-1.4 (br, α-C*H*$_3$), 1.4-2.4 (broad, backbone), 3.5-3.7 (br, -OC*H*$_3$), 7.0-7.3 (br, aromatic).

Estimation of the reactivity of St-TBS

The reactivity ratio of St-TBS was calculated by using following equation.

$$\ln[M_2]/[M_2]_0 + 1/(r_{St\text{-}TBS}-1)\ln[[M_1]_0/[M_2]_0(r_{st\text{-}TBS}-1)+1] = 0 \qquad (S1)$$

$[M_1]_0$ and $[M_2]_0$ are the initial monomer concentration of St-TBS and DPE, and $[M_2]$ is the final concentration of DPE. The reaction must have gone to completion, and $r_{st\text{-}TBS} \neq 1$ and $[M_2] \neq 0$. The $[M_2]$ was estimated from the result of ^{1}H NMR spectrum of obtained polymers.



Scheme S1. Plausible mechanism of side reaction.

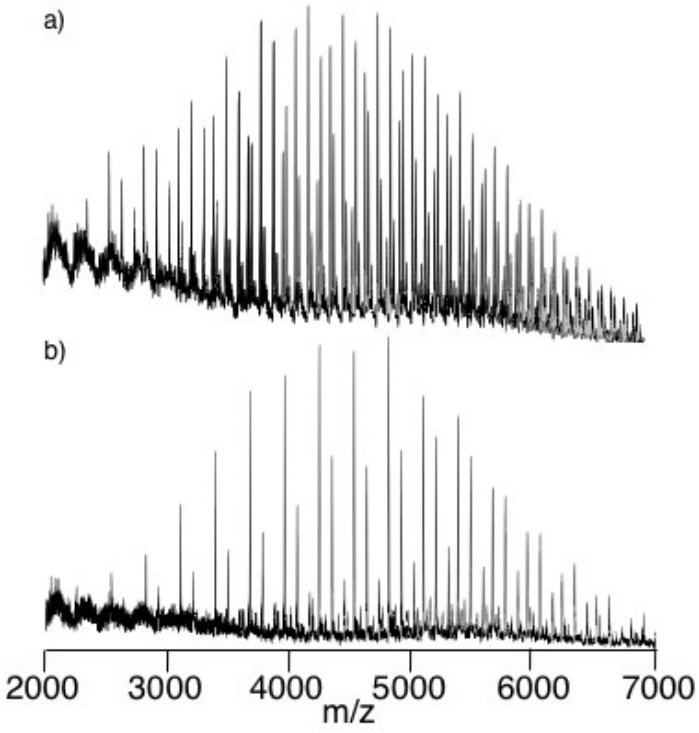


Figure S1. MALDI-TOF-MS spectra of St-DPE copolymer synthesized by anionic copolymerization using *s*-BuLi in cyclohexane at 50 °C with different feed monomer ratio a) DPE/St = 1.47 and b) DPE/St = 5.61.

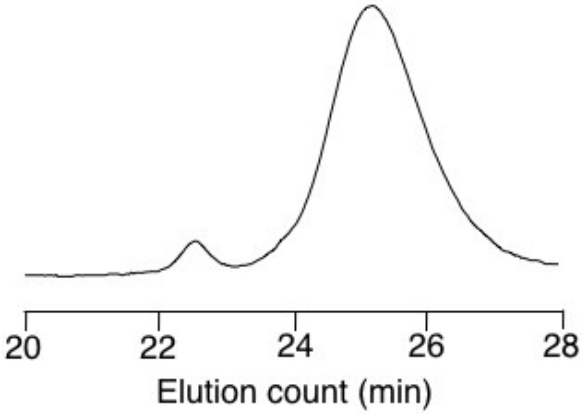


Figure S2. SEC chart of the result of copolymerization of St and DPE-TBS.

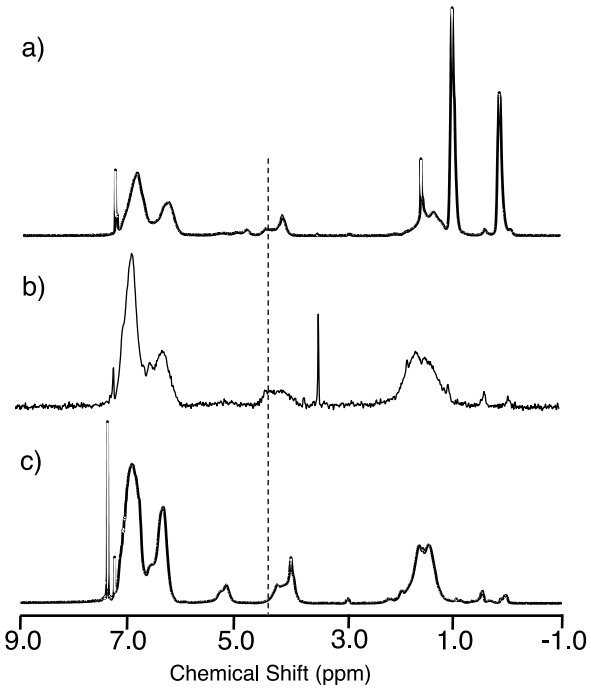


Figure S3. ^{1}H NMR spectra of poly(DPE-*alt*-St-TBS) (a), poly(DPE-*alt*-St-HMS) (b), and poly(DPE-*alt*-St-BMS) (c).

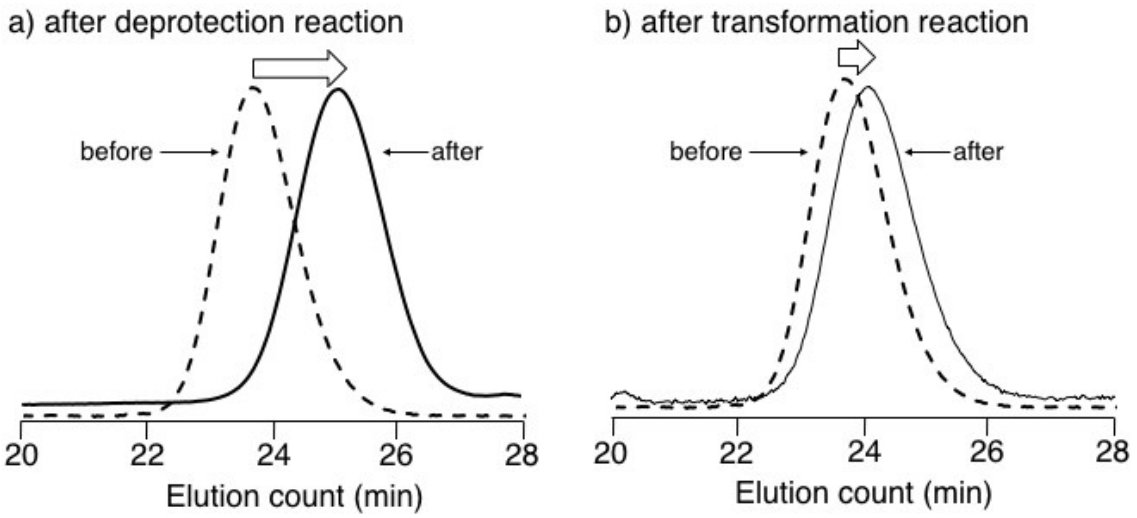


Figure S4. SEC charts of after (a) deprotection reaction and (b) transformation reaction of poly(DPE-*alt*-TBS).

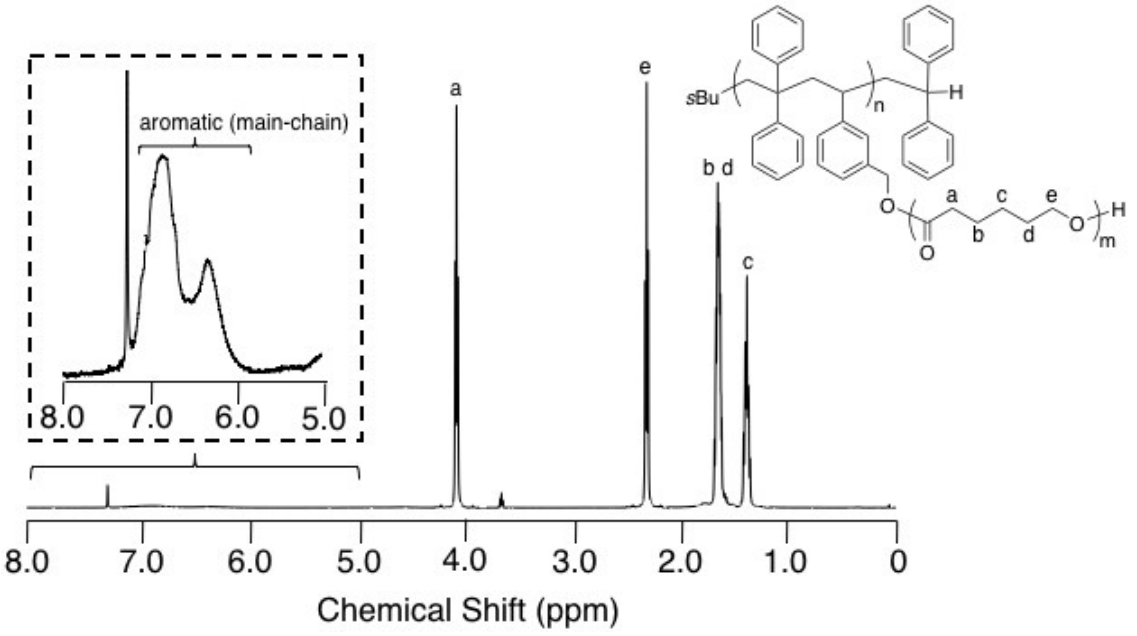


Figure S5. ^{1}H NMR spectrum of poly(DPE-*alt*-HMS)-*g*-PCL.

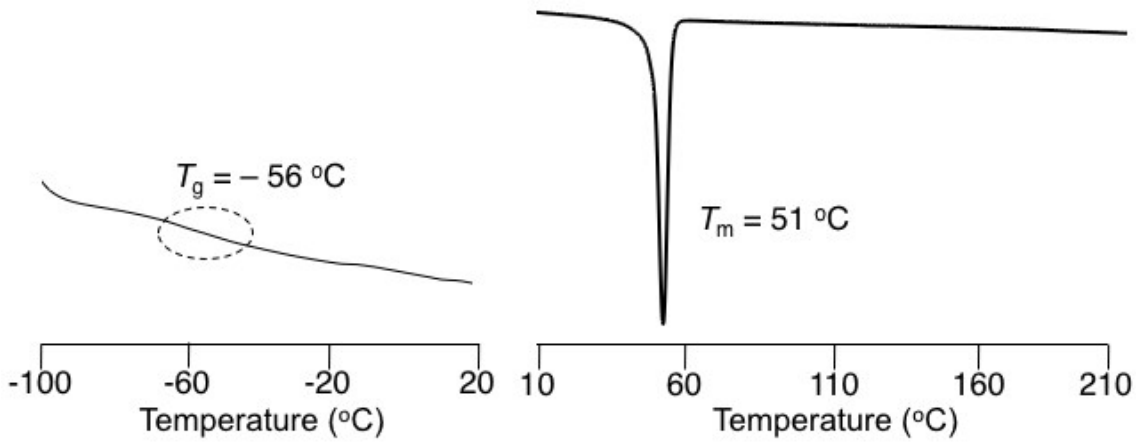


Figure S6. DSC chart of poly(DPE-*alt*-HMS)-*g*-PCL.

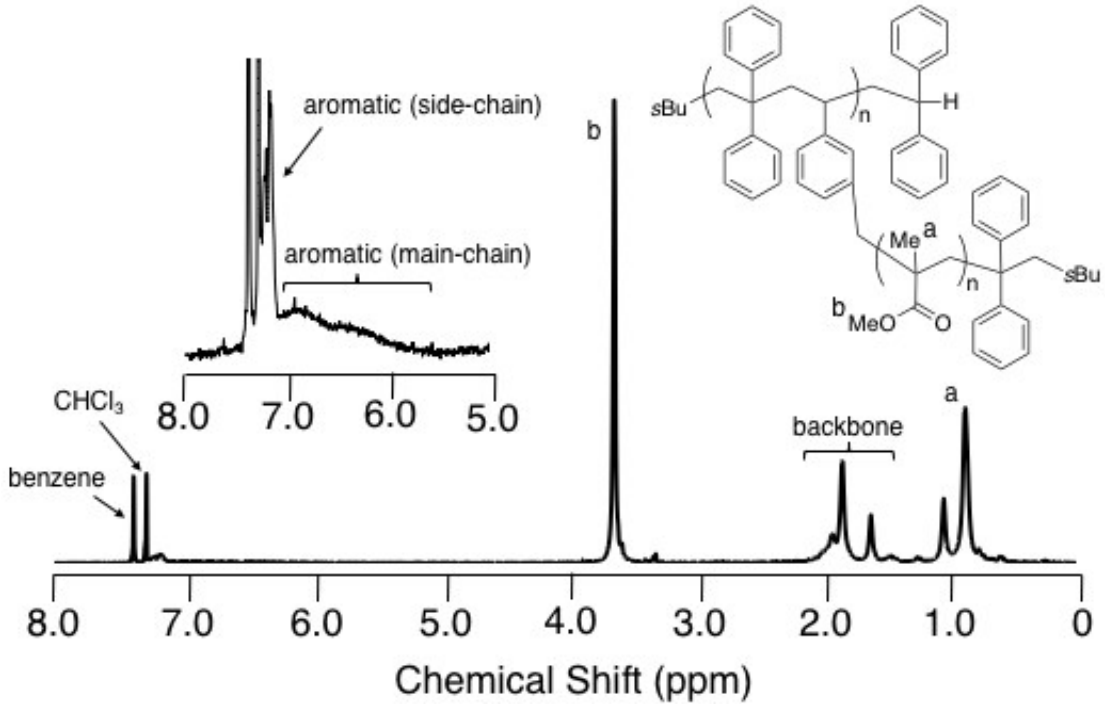


Figure S7. ^{1}H NMR spectrum of poly(DPE-*alt*-BMS)-*g*-PMMA.