Electronic Supplementary Material (ESI) for Polymer Chemistry.

Synthesis of Well-Defined Di- and Triblock Acrylic Copolymers Consisting of Hard Poly(dicyclopentanyl acrylate) and Soft Poly(alkyl acrylate) Segments by Organocatalyzed Group Transfer Polymerization and Their Glass Transition Behavior

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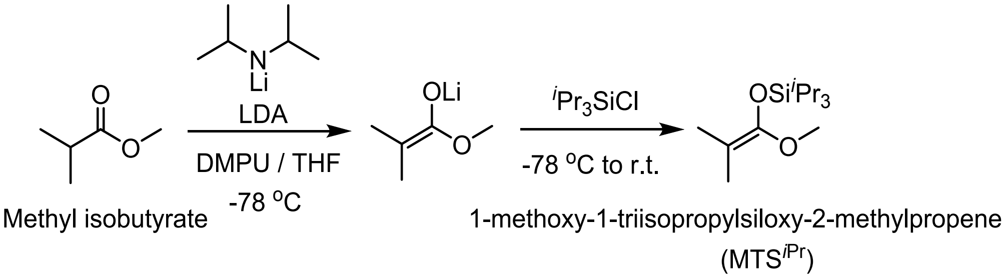
1. Synthesis of 1-methoxy-1-triisopropylsiloxy-2-methylpropene (MTS^{iPr}).



To a solution of DMPU (10.2 mL, 84 mmol) in dry THF (ca.200 mL) in a 500 mL three-necked flask, LDA (42.0 mL, 84.0 mmol, 2.0 mol L^{-1} in hexane) was added dropwise at −78 °C under an argon atmosphere. After stirring for 0.5 h, methyl isobutyrate was slowly added. The reaction mixture was stirred at −78 °C for 0.5 h, and then chlorotriisopropylsilane (18.0 mL, 84.0 mmol) was added. The entire mixture was warmed to r.t. and stirred for 2 h. The solvent was removed under reduced pressure, and impurities with lower boiling temperatures were removed under reduced pressure (55°C, 0.016 mmHg) to give MTS^{iPr} as a colorless liquid. Yield, 12.5 g (69 %). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 0.19 (s, 36H, $(CH_3)_3Si$-), 1.52 (d, 24H, $(CH_3)_2CH$-), 3.87 (s, 8H, -CH_2O-). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 0.3 (12C, $(CH_3)_3Si$-), 16.9 (d, 8C, $(CH_3)_2C{=}C$), 44.9 (1C, $C(CH_2O\text{-})_4$), 67.7 (4C, -CH_2O-), 89.9 (4C, $(CH_3)_2C{=}$)), 148.5 (4C, $(CH_3)_3SiOC{=}$).

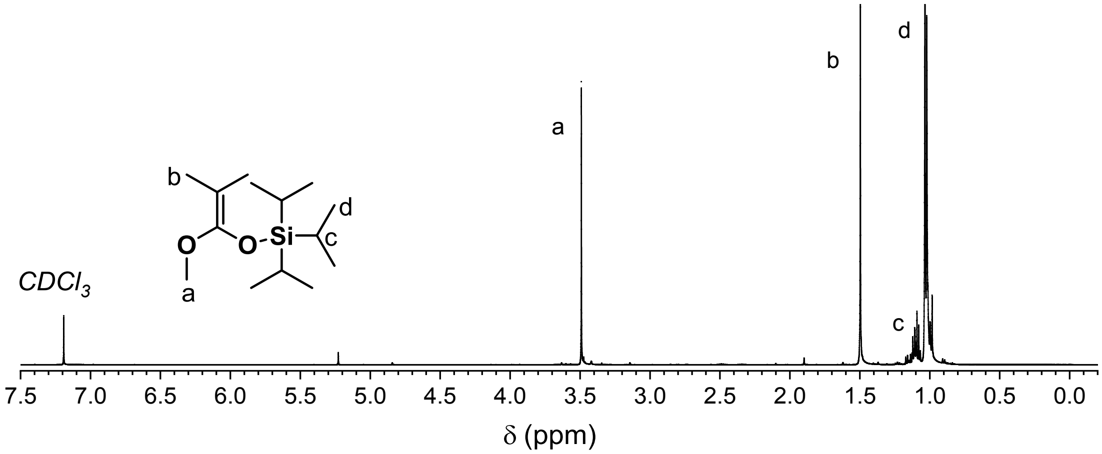
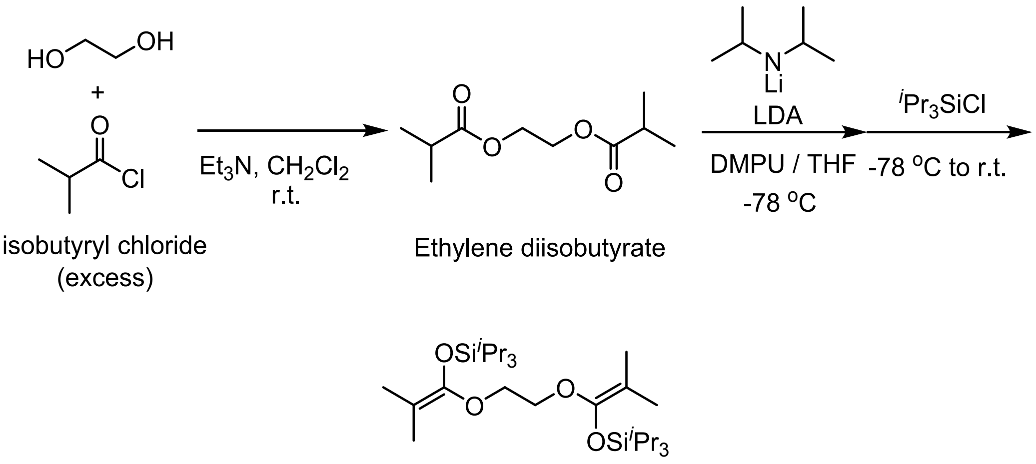


Figure S1. ^{1}H NMR spectrum of MTS^{iPr} in $CDCl_3$.

2. Synthesis of 1,2-bis[2-methyl-1-(triisopropylsiloxy)prop-1-enyloxy]ethane (MTS$^{i\mathrm{Pr}}_2$)



1,2-Bis[2-methyl-1-(triisopropylsiloxy)prop-1-enyloxy]ethane

(MTS$^{i\mathrm{Pr}}_2$)

Synthesis of ethylene diisobutyrate. To a mixture of ethylene glycol (4.66 g, 75.0 mmol), DMAP (0.92 g, 7.5 mmol) and triethylamine (18.21 g, 180.0 mmol) in dry dichloromethane 200 mL, isobutyryl chloride (19.18 g, 180.0 mmol) in dichloromethane 50 mL was slowly added at 0 °C under a nitrogen atmosphere. After the reaction mixture was stirred at room temperature for 12 h, the resultant salt was removed by filtration and the filtered organic layer was washed with saturated aqueous NaHCO$_3$, aqueous NaCl, and distilled water. The organic layer was dried over anhydrous Na$_2$SO$_4$ and then evaporated to remove the solvent. The residue was distilled under reduced pressure (90 °C, 3 mmHg) to give ethylene diisobutyrate as a colorless liquid. Yield, 13.66 g (90 %). ^{1}H NMR (500 MHz, CDCl$_3$, δ): 0.19 (s, 36H, $(\mathrm{C}\mathit{H}_3)_3$Si-), 1.52 (d, 24H, $(\mathrm{C}\mathit{H}_3)_2$CH-), 3.87 (s, 8H, -C$\mathit{H}_2$O-). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 0.3 (12C, $(\mathit{C}\mathrm{H}_3)_3$Si-), 16.9 (d, 8C, $(\mathit{C}\mathrm{H}_3)_2$C=C), 44.9 (1C, $\mathit{C}(\mathrm{CH_2O}\text{-})_4$), 67.7 (4C, -$\mathit{C}H_2$O-), 89.9 (4C, $(\mathrm{CH}_3)_2\mathit{C}$=)), 148.5 (4C, $(\mathrm{CH}_3)_3$SiOC=).

Synthesis of MTS$^{i\mathrm{Pr}}_2$. To a solution of DMPU (7.81 g, 61.0 mmol) in dry THF (ca. 200 mL) in a 500mL three-necked flask, LDA (42.0 mL, 62.0 mmol; 2 molL^{-1} in *n*-hexane) was added dropwise at −78 °C under an argon atmosphere. After stirring for 0.5 h, ethylene diisobutyrate (5.11 g, 25.3 mmol) in dryTHF was slowly added. The reaction mixture was stirred at −78 °C for 0.5 h, and then chlorotriisopropylsilane (11.8 g, 61.0 mmol) was added. The entire mixture was warmed to room temperature and stirred for 2 h. The solvent was removed under reduced pressure, and the residue was distilled (120 °C, 0.016 mmHg) to give MTS$^{i\text{Pr}}{}_2$ as a colorless liquid. Yield, 7.7 g (59 %). ^{1}H NMR (500 MHz, CDCl$_3$, δ): 0.19 (s, 36H, (CH_3)$_3$Si-), 1.52 (d, 24H, (CH_3)$_2$CH-), 3.87 (s, 8H, -CH_2O-). ^{13}C NMR (125 MHz, CDCl$_3$, δ): 0.3 (12C, (CH$_3$)$_3$Si-), 16.9 (d, 8C, (CH$_3$)$_2$C=C), 44.9 (1C, C(CH$_2$O-)$_4$), 67.7 (4C, -CH$_2$O-), 89.9 (4C, (CH$_3$)$_2$$C$=)), 148.5 (4C, (CH$_3$)$_3SiOC$=).

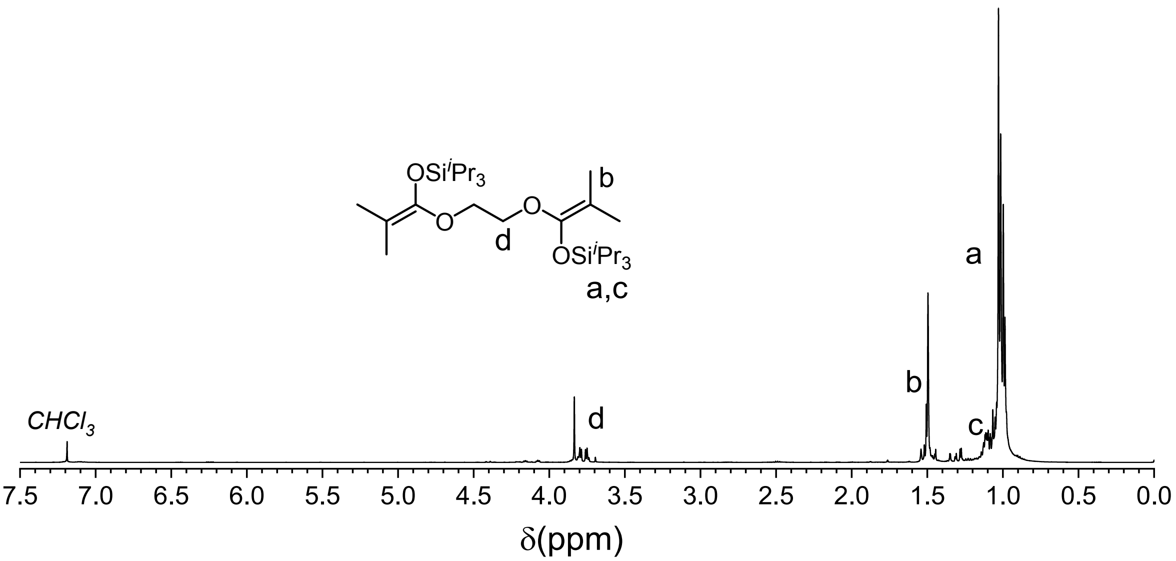


Figure S2. ^{1}H NMR spectrum of MTS$^{i\text{Pr}}{}_2$ in CDCl$_3$.

Table S1. Syntheses of P*dc*PAs and other poly(alkyl acrylate)s by Me_3SiNTf_2-catalyzed GTP ^{a}

Run	Polymer	AA	$[AA]_0$/ $[MTS^{iPr}]_0$	$M_{n,calcd.}$ (g mol^{-1})	$M_{n,NMR}$ (g mol^{-1})	$M_{n,SEC}$ ^{b} (g mol^{-1})	M_w/M_n^{b}	T_g (°C)
S1	P*dc*PA$_{10}$	*dc*PA	10	2,200	2,300	2,300	1.14	--^{c}
S2	P*dc*PA$_{20}$		20	4,200	4,700	5,200	1.11	60.4
S3	P*dc*PA$_{30}$		30	6,300	5,900	9,200	1.08	70.7
S4	P*dc*PA$_{40}$		40	8,400	8,400	15,700	1.11	85.8
S5	P*dc*PA$_{50}$		50	10,400	10,200	23,300	1.08	95.2
S6	P*dc*PA$_{60}$		60	12,500	--	46,700	1.18	--
S7	P*n*BA$_{100}$	*n*BA	100	12,900	--	15,000	1.13	-44.4
S8	P*n*OA$_{100}$	*n*OA	100	18,600	--	18,300	1.13	-32.1
S9	PEHA$_{100}$	EHA	100	18,600	--	19,300	1.12	-63.6
S10	P*n*DA$_{50}$	*n*DA	50	12,100	--	11,200	1.11	--

^{a} $[AA]_0$ = 1.0 mol L^{-1}; $[MTS^{iPr}]_0/[Me_3SiNTf_2]_0$ = 0.02; solvent, CH_2Cl_2; reaction time, 1 h; monomer conversions were >99% determined by ^{1}H NMR in $CDCl_3$. ^{b} Determined by SEC equipped with a RI detector in THF using PS standards. ^{c} No T_g peak was detected.

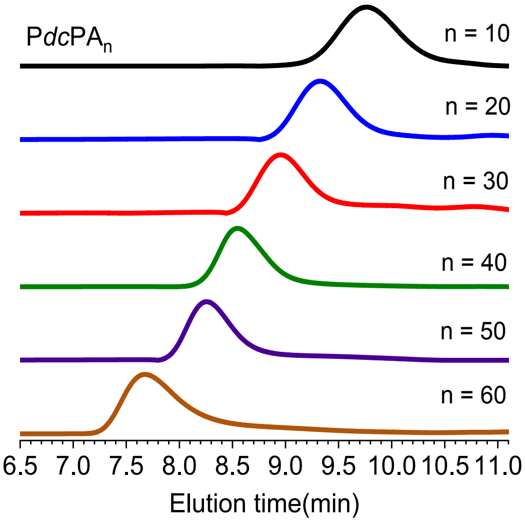


Figure S3. SEC(RI) traces of P*dc*PAs (eluent, THF flowrate, 0.35 mL min^{-1}).

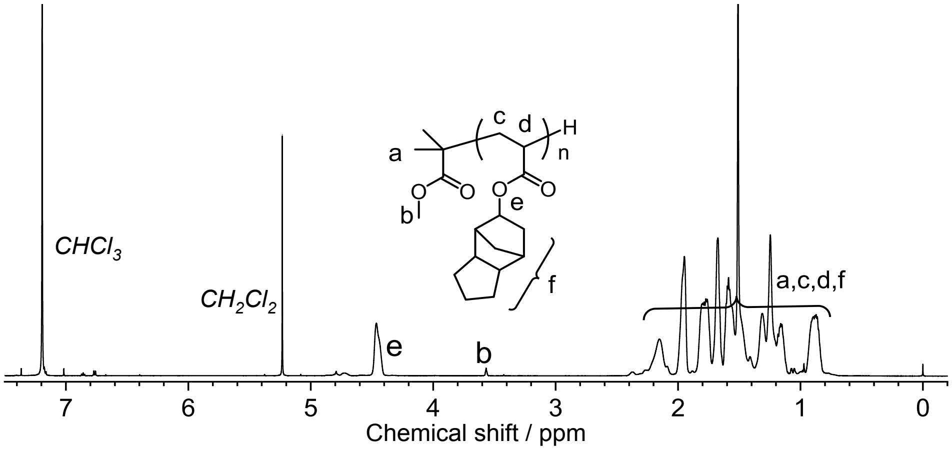


Figure S4. The typical ^{1}H NMR spectrum of P*dc*PA$_{50}$ (Run S5) in CDCl$_3$.

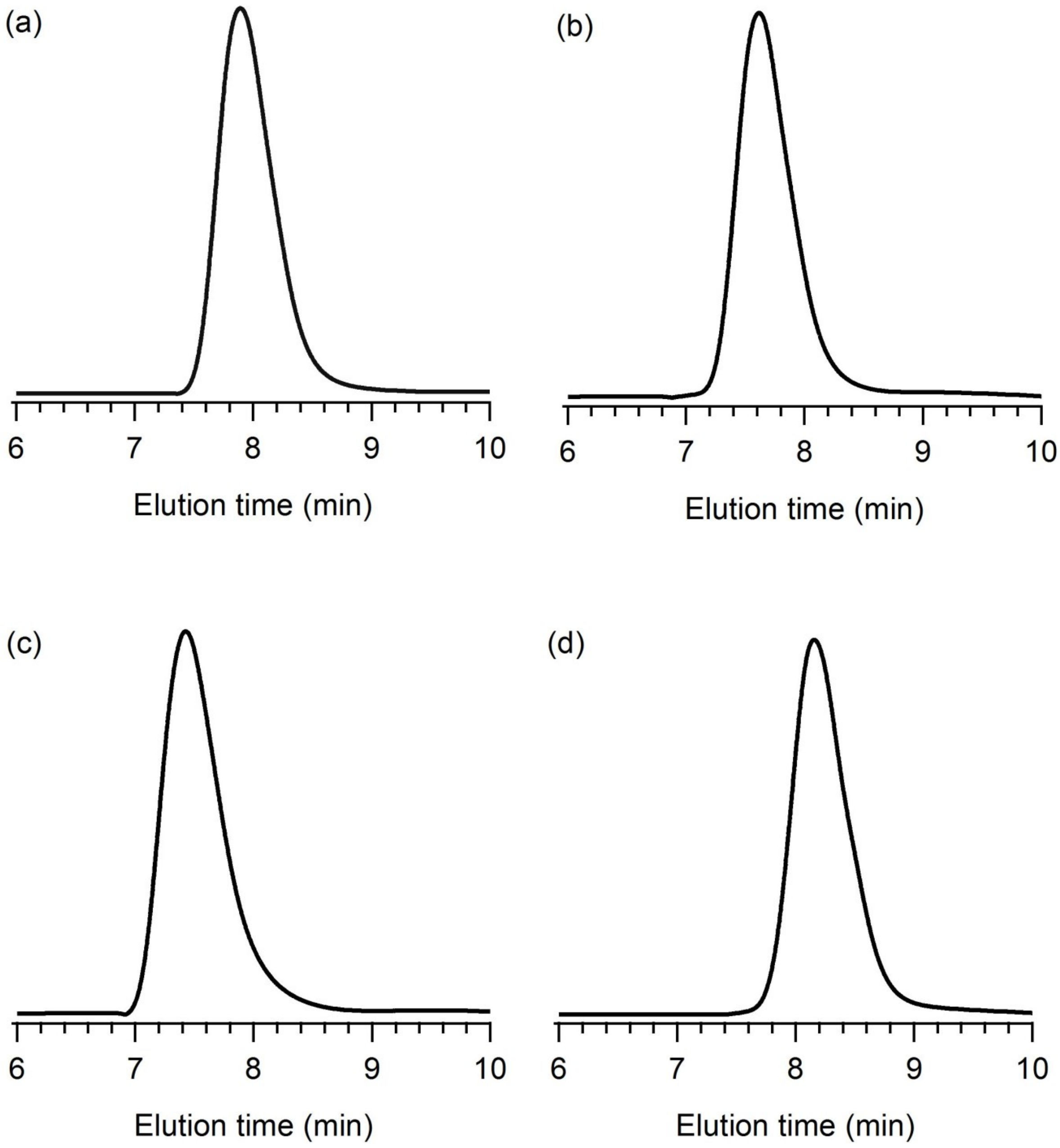


Figure S5. SEC traces of (a) poly(nBA$_{100}$-*stat*-*dc*PA$_{20}$), (b) poly(nOA$_{100}$-*stat*-*dc*PA$_{30}$), (c) poly(EHA$_{100}$-*stat*-*dc*PA$_{30}$), and (d) poly(nDA$_{50}$-*stat*-*dc*PA$_{20}$) (eluent, THF; flow rate, 0.35 mL min^{-1}).

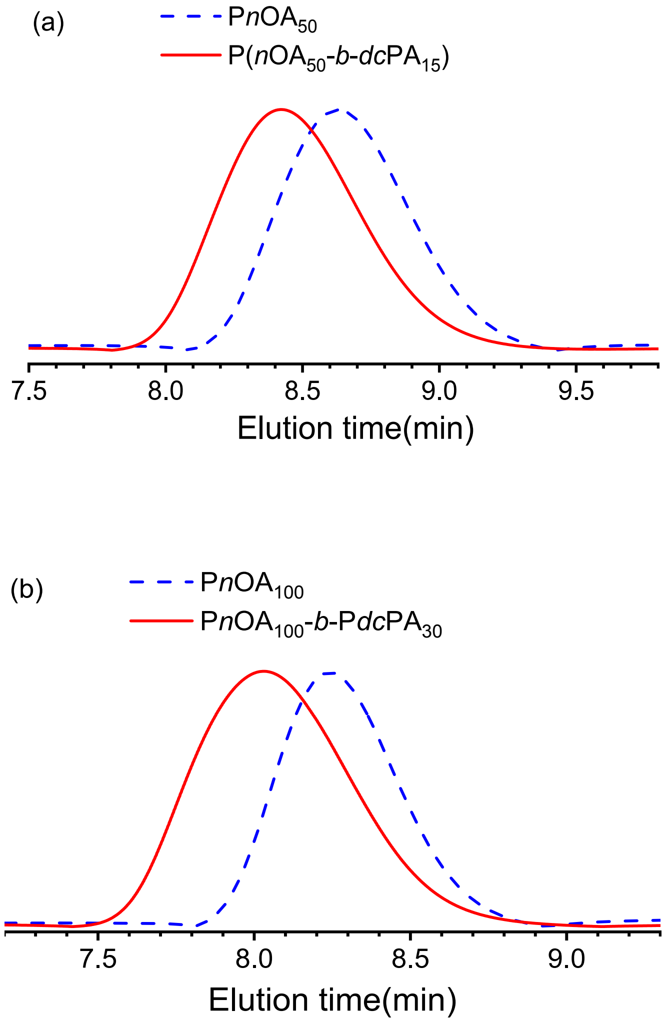


Figure S6. SEC traces of (a) P*n*OA$_{50}$ and P*n*OA$_{50}$-*b*-P*dc*PA$_{15}$ and (b) P*n*OA$_{100}$ and P*n*OA$_{100}$-*b*-P*dc*PA$_{30}$ (eluent, THF; flow rate, 0.35 mL min^{-1}).

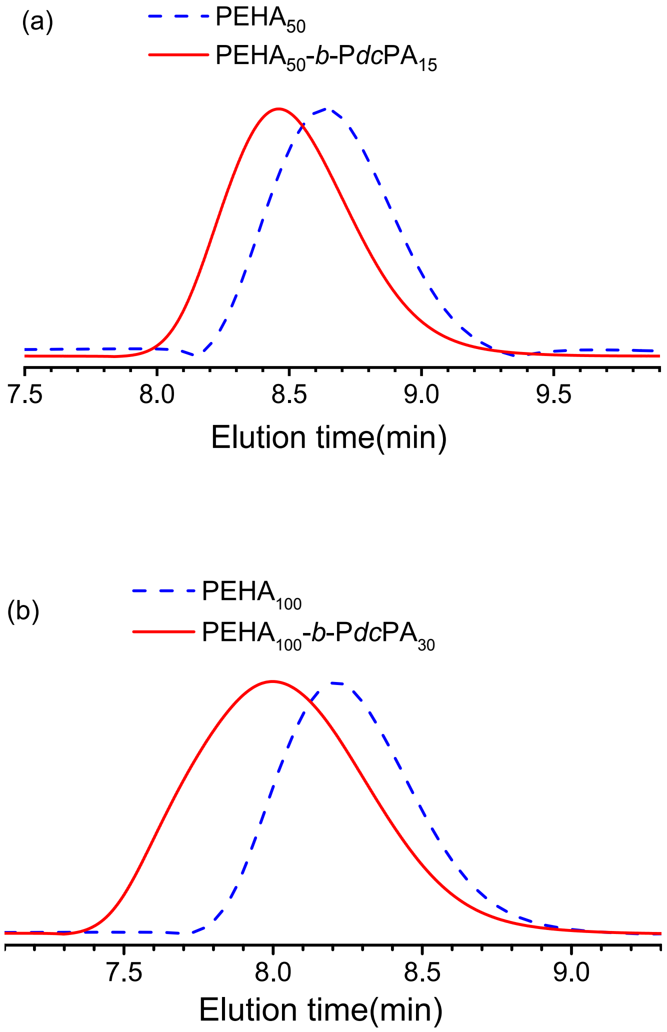


Figure S7. SEC traces of (a) $PEHA_{50}$ and $PEHA_{50}$-*b*-P*dc*PA_{15} and (b) $PEHA_{100}$ and $PEHA_{100}$-*b*-P*dc*PA_{30} (eluent, THF flow rate, 0.35 mL min^{-1}).

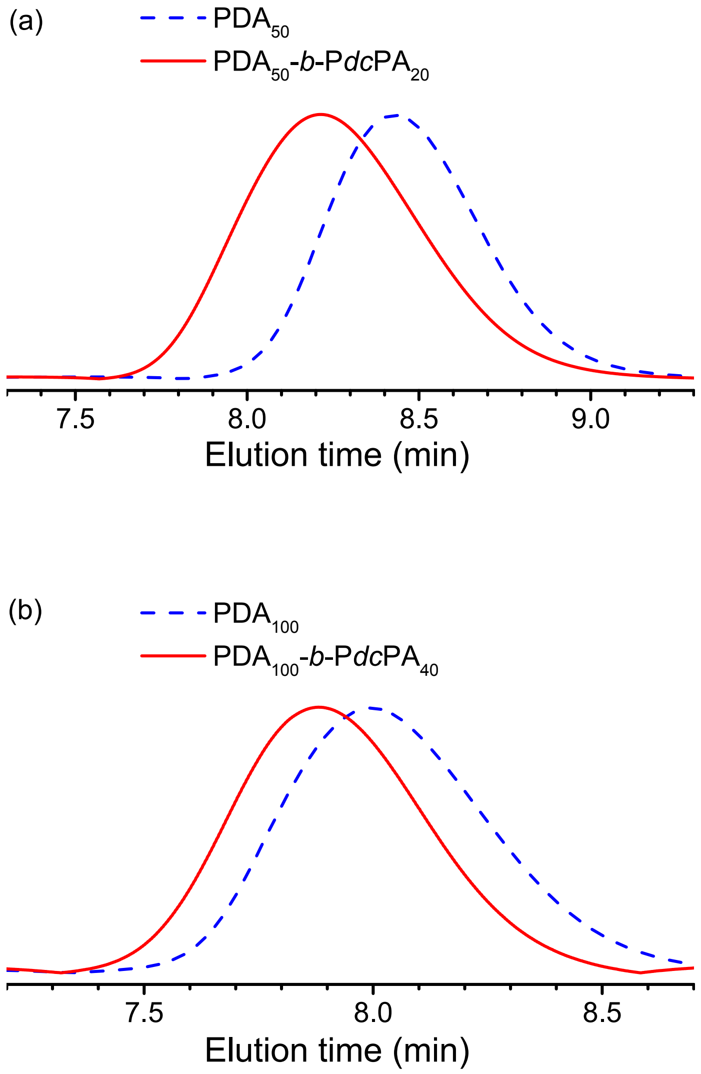


Figure S8. SEC traces of (a) P*n*DA$_{50}$ and P*n*DA$_{50}$-*b*-P*dc*PA$_{20}$ and (b) P*n*DA$_{100}$ and P*n*DA$_{100}$-*b*-P*dc*PA$_{20}$ (eluent, THF; flow rate, 0.35 mL min^{-1}).

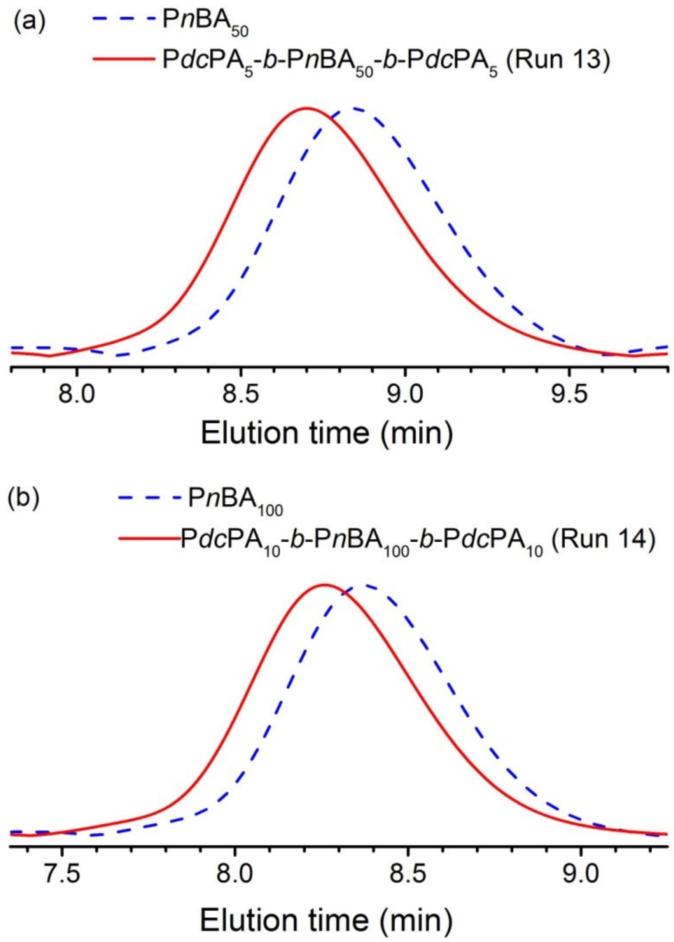
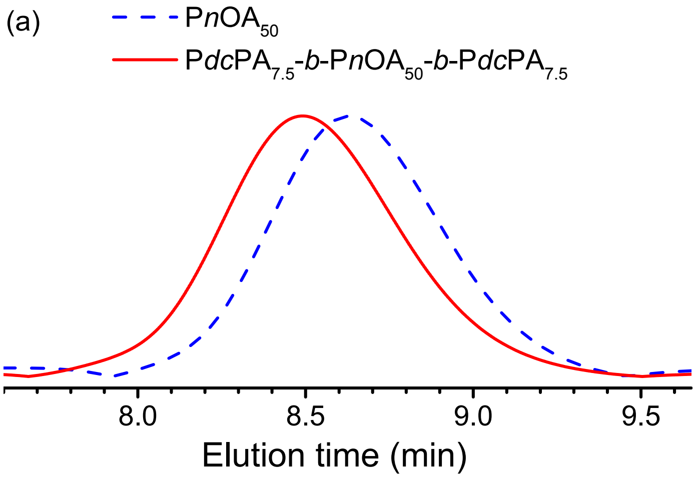


Figure S9. SEC traces of the prepolymer P*n*BA obtained in the first polymerization and the ABA-type triblock P*dc*PA-*b*-P*n*BA-*b*-P*dc*PA in the tiiblock copolymerization: (a) P*n*BA$_{50}$ and P*dc*PA$_5$-*b*-P*n*BA$_{50}$-*b*-P*dc*PA$_5$ (Run 13), and (b) P*n*BA$_{100}$ and P*dc*PA$_{10}$-*b*-P*n*BA$_{100}$-*b*-P*dc*PA$_{10}$ (Run 14) (eluent, THF; flow rate, 0.35 mL min^{-1}).



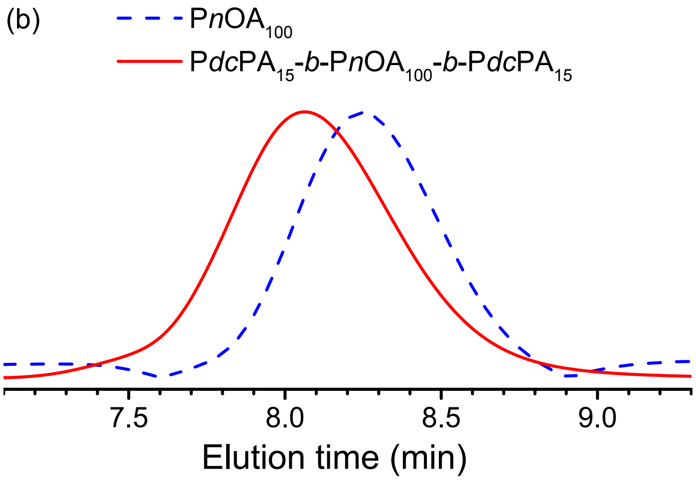


Figure S10. SEC traces of (a) P*n*OA$_{50}$ and P*dc*PA$_{7.5}$-*b*-P*n*OA$_{50}$-*b*-P*dc*PA$_{7.5}$ and (b) P*n*OA$_{100}$ and P*dc*PA$_{15}$-*b*-P*n*OA$_{100}$-*b*-P*dc*PA$_{15}$ (eluent, THF; flow rate, 0.35 mL min^{-1}).

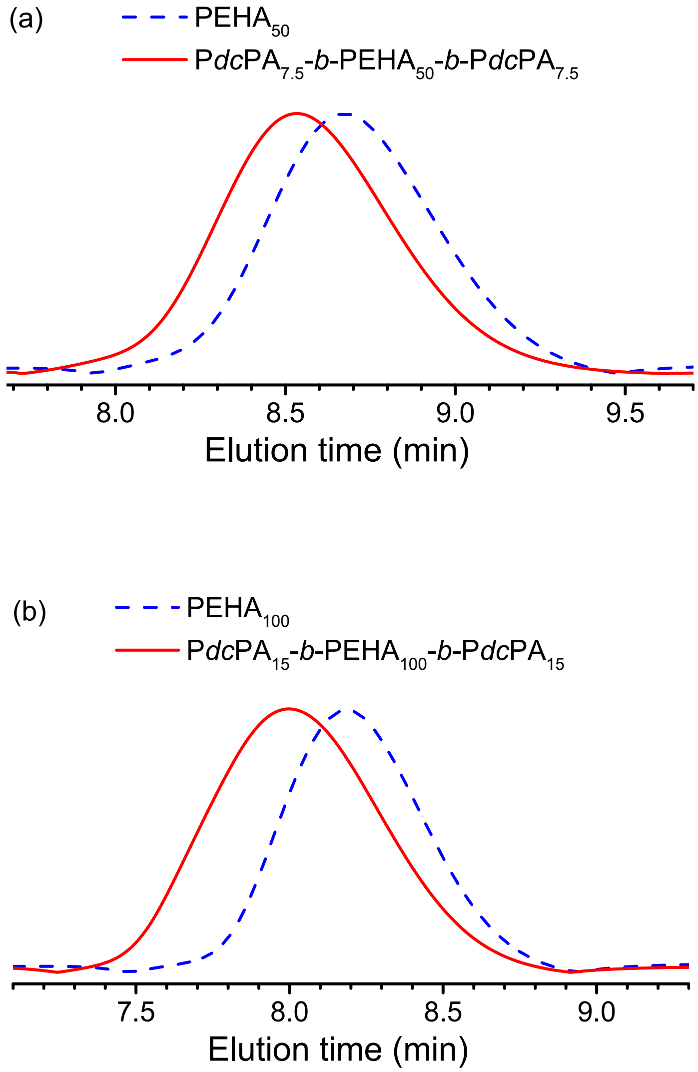


Figure S11. SEC traces of (a) $PEHA_{50}$ and P*dc*$PA_{7.5}$-*b*-$PEHA_{50}$-*b*-P*dc*$PA_{7.5}$ and (b) $PEHA_{100}$ and P*dc*PA_{15}-*b*-$PEHA_{100}$-*b*-P*dc*PA_{15} (eluent, THF; flow rate, 0.35 mL min^{-1}).

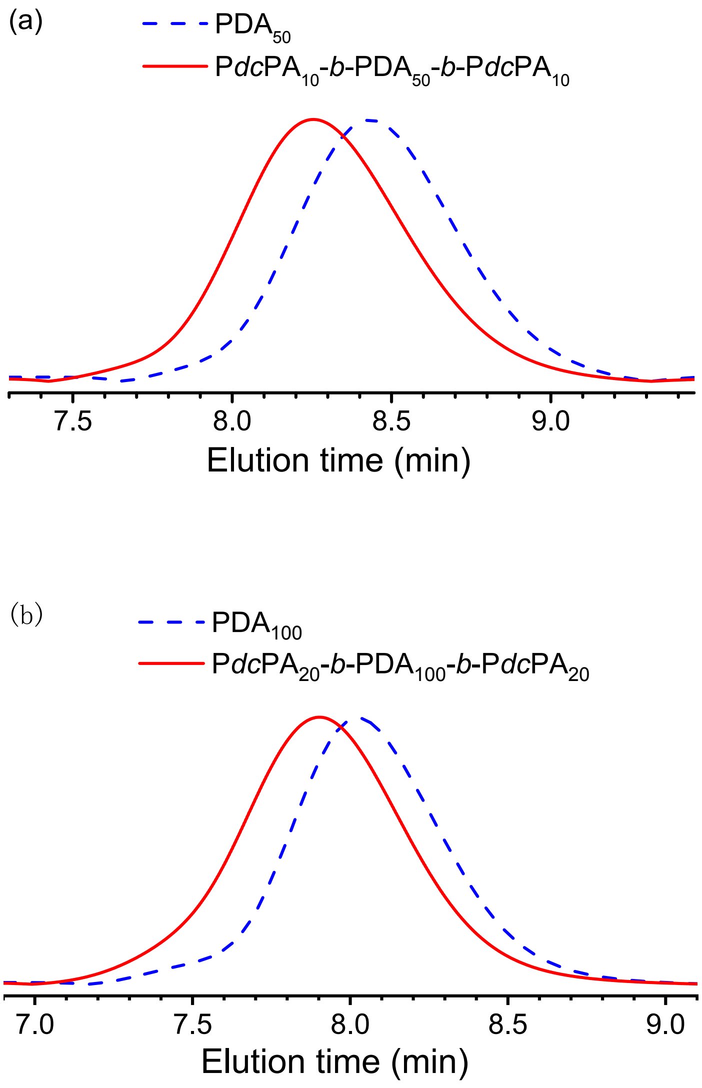


Figure S12. SEC traces of (a) PnDA$_{50}$ and PdcPA$_{10}$-b-PnDA$_{50}$-b-PdcPA$_{10}$ and (b) PnDA$_{100}$ and PdcPA$_{20}$-b-PnDA$_{100}$-b-PdcPA$_{20}$ (eluent, THF; flow rate, 0.35 mL min^{-1}).

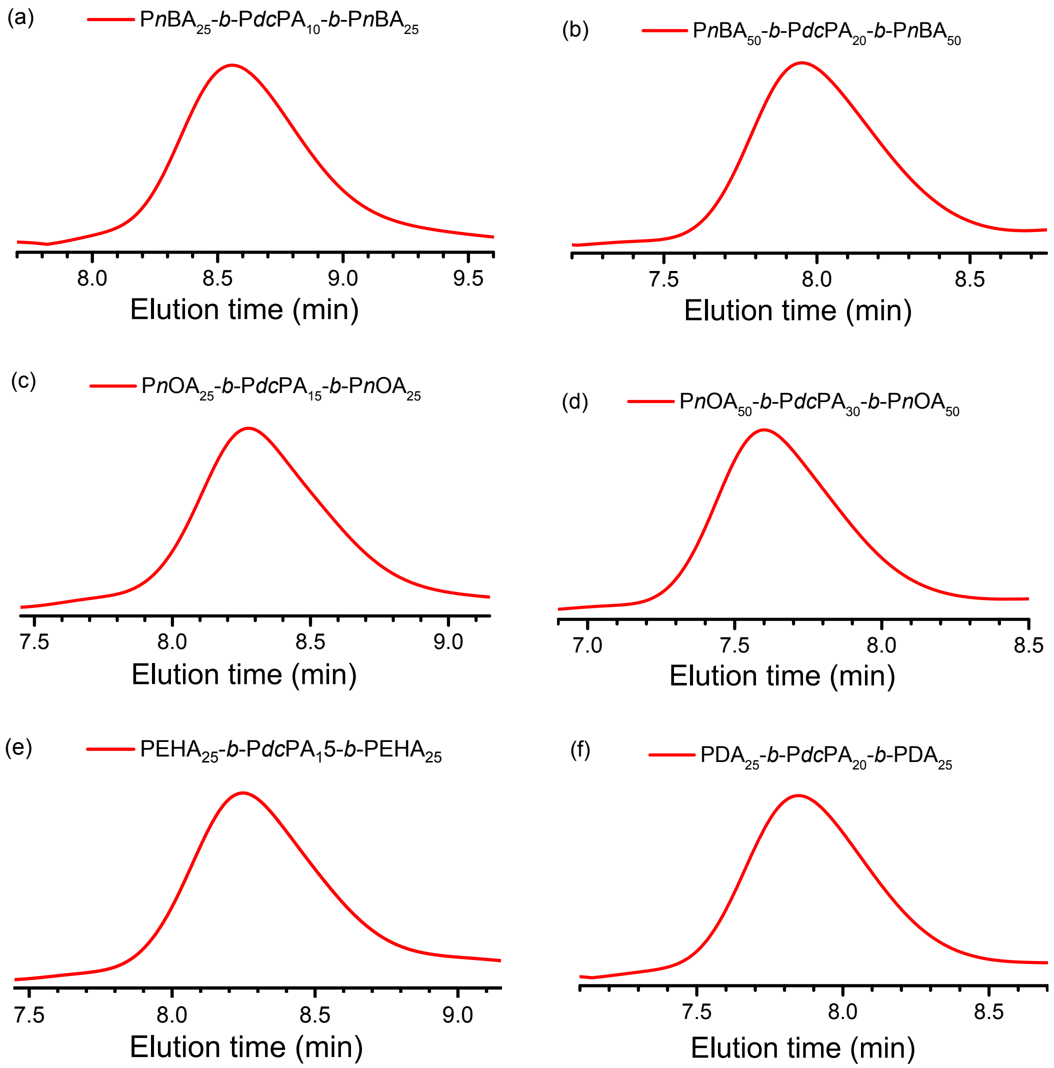


Figure S13. SEC traces of (a) P*n*BA$_{25}$-*b*-P*dc*PA$_{10}$-*b*-P*n*BA$_{25}$, (b) P*n*BA$_{50}$-*b*-P*dc*PA$_{20}$-*b*-P*n*BA$_{50}$, (c) P*n*OA$_{25}$-*b*-P*dc*PA$_{15}$-*b*-P*n*OA$_{25}$, (d) P*n*OA$_{50}$-*b*-P*dc*PA$_{30}$-*b*-P*n*OA$_{50}$, (e) PEHA$_{25}$-*b*-P*dc*PA$_{10}$-*b*-PEHA$_{25}$, and (f) P*n*DA$_{25}$-*b*-P*dc*PA$_{20}$-*b*-P*n*DA$_{25}$ (eluent, THF; flow rate, 0.35 mL min^{-1}).

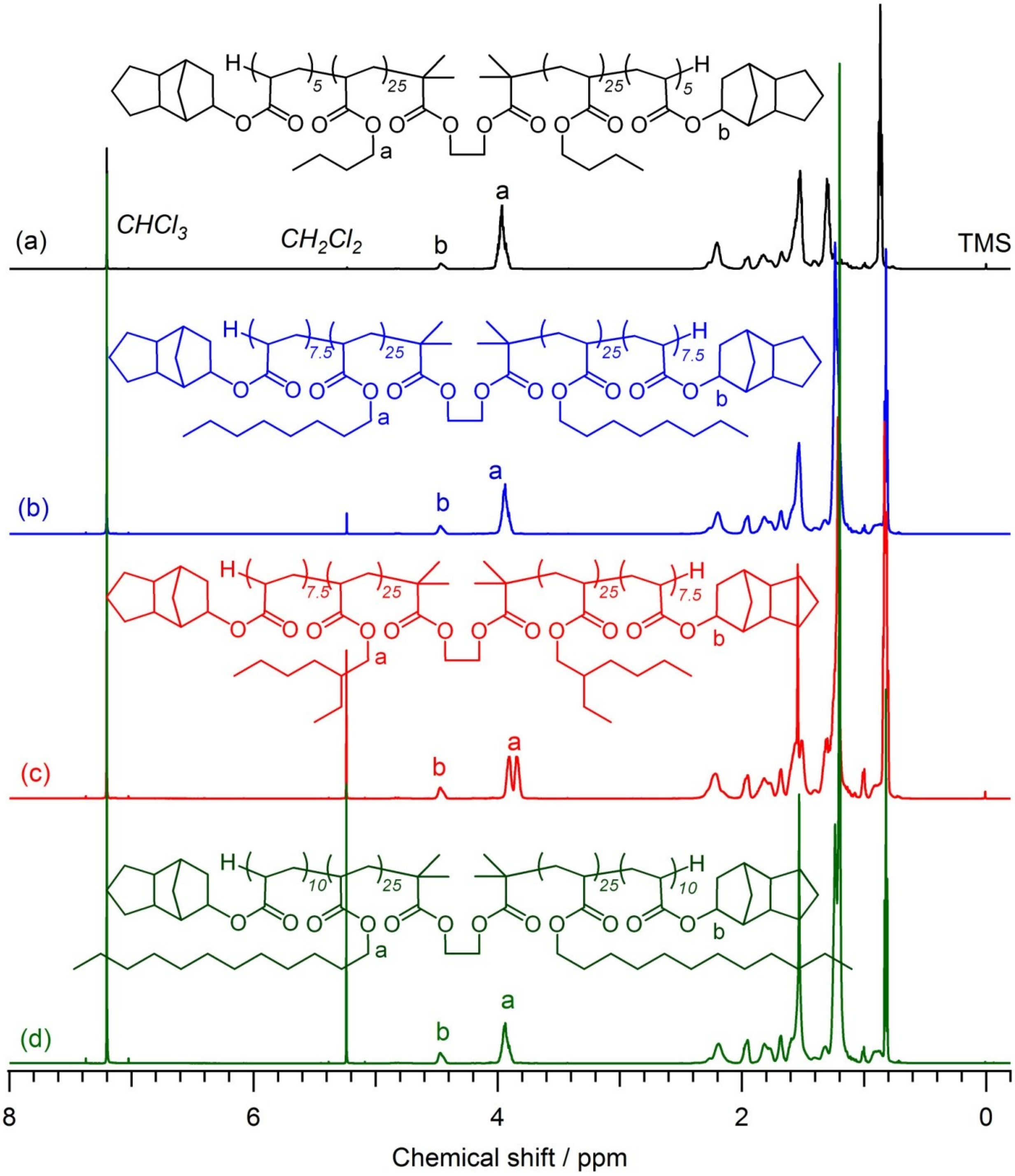


Figure S14. ^{1}H NMR spectra of (a) P*dc*PA$_5$-*b*-P*n*BA$_{50}$-*b*-P*dc*PA$_5$ (Run 13), (b) P*dc*PA$_{7.5}$-*b*-P*n*OA$_{50}$-*b*-P*dc*PA$_{7.5}$ (Run 15), (c) P*dc*PA$_{7.5}$-*b*-PEHA$_{50}$-*b*-P*dc*PA$_{7.5}$ (Run 17), and (d) P*dc*PA$_{10}$-*b*-P*n*DA$_{50}$-*b*-P*dc*PA$_{10}$ (Run 19) in CDCl$_3$.

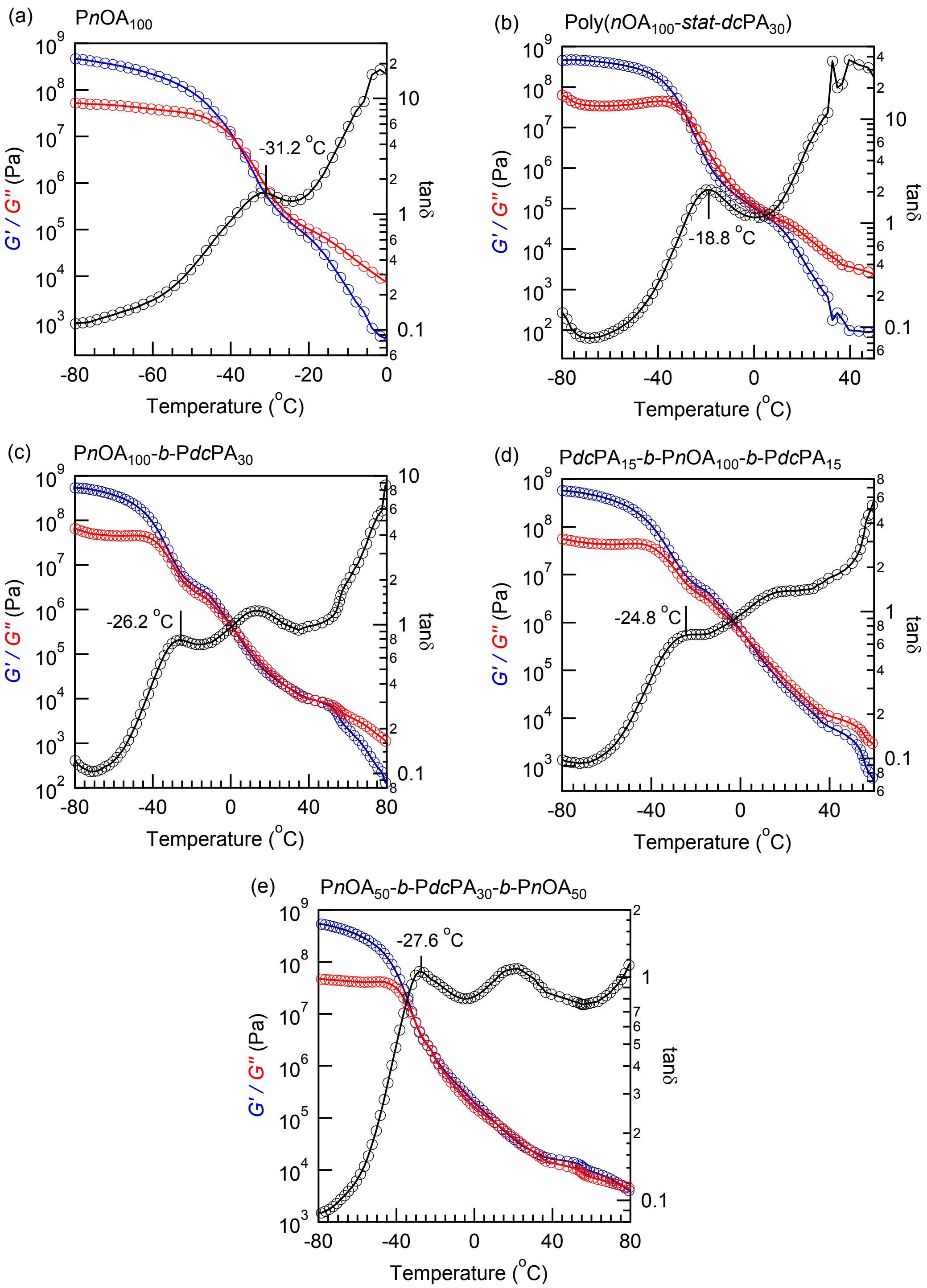


Figure S15. The temperature dependences of storage modulus (G', blue color), loss modulus (G'', red color), and loss factor (tanδ black color at the frequency of 10 rad s^{-1} for (a) P*n*OA$_{100}$, (b) Poly(*n*OA$_{100}$-*stat*-*dc*PA$_{30}$), (c) P*n*OA$_{100}$-*b*-P*dc*PA$_{30}$, (d) P*dc*PA$_{15}$-*b*-P*n*OA$_{100}$-*b*-P*dc*PA$_{15}$, and (e) P*n*OA$_{50}$-*b*-P*dc*PA$_{30}$-*b*-P*n*OA$_{50}$, respectively.

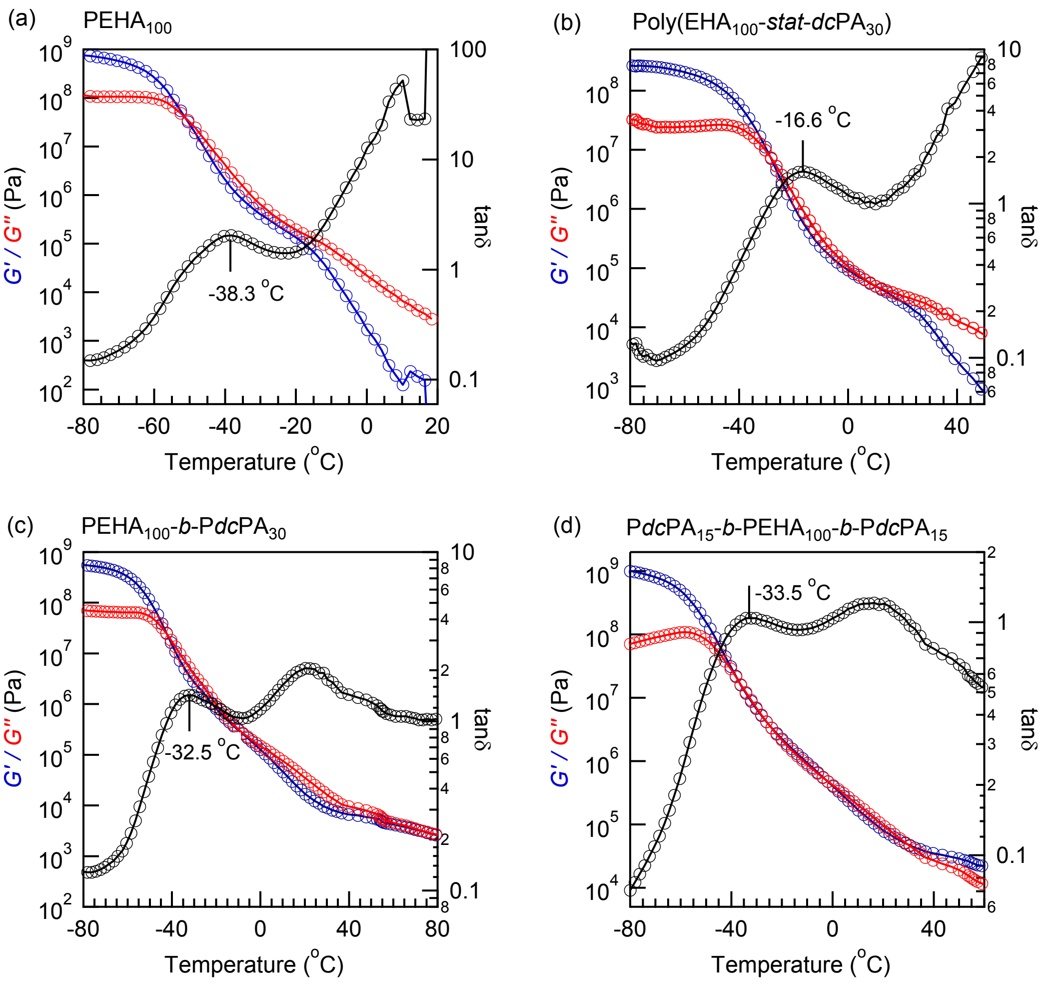


Figure S16. The temperature dependences of storage modulus (*G*′, blue color), loss modulus (*G*′′, red color), and loss factor (tanδ, black color at the frequency of 10 rad s^{-1} for (a) PEHA$_{100}$, (b) poly(EHA$_{100}$-*stat*-*dc*PA$_{30}$), (c) PEHA$_{100}$-*b*-P*dc*PA$_{30}$, and (d) P*dc*PA$_{15}$-*b*-PEHA$_{100}$-*b*-P*dc*PA$_{15}$, respectively.

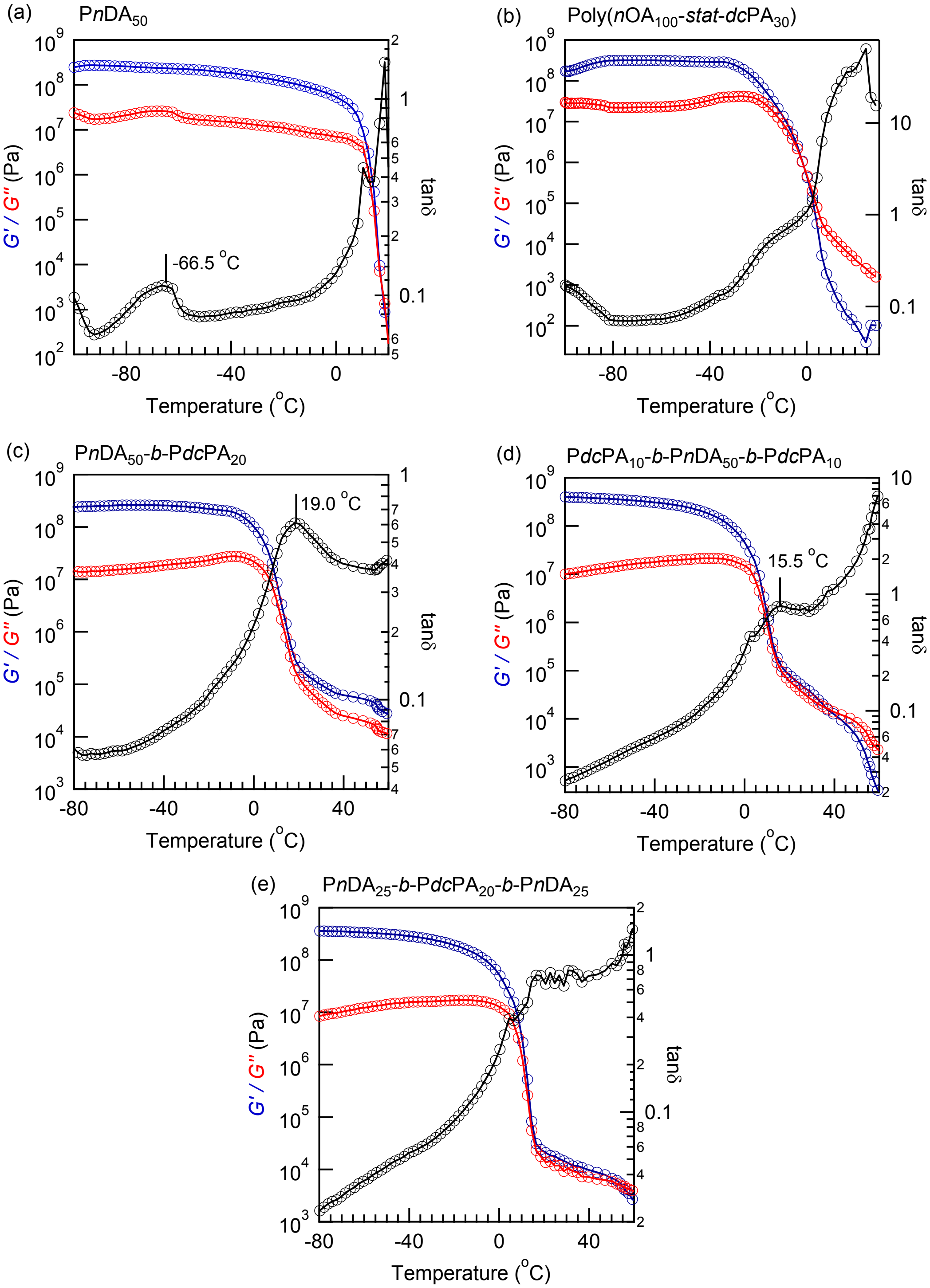


Figure S17. Temperature dependences of storage modulus (G', blue color), loss modulus (G'', red color), and loss factor (tanδ, black color) at the frequency of 10 rad s^{-1} for (a) P*n*DA$_{50}$, (b) P(*n*DA$_{50}$-*stat*-*dc*PA$_{20}$), (c) P*n*DA$_{50}$-*b*-P*dc*PA$_{20}$, (d) P*dc*PA$_{10}$-*b*-P*n*DA$_{50}$-*b*-P*dc*PA$_{10}$, and (e) P*n*DA$_{25}$-*b*-P*dc*PA$_{20}$-*b*-P*n*DA$_{25}$.