

Supporting Information

Precise Synthesis of Structural Possible All Tetrablock Quarterpolymers by Methodology Combining Living Anionic Polymerization with Linking Chemistry Using 1:1 Addition Reaction

Raita Goseki^{*a,b}, Yuri Matsuo^b, and Akira Hirao^{b,c,d}

^aDepartment of Chemical Science and Engineering, Graduate School of Materials and Chemical Technology, Tokyo Institute of Technology, 2-12-1-S1-13, O-okayama, Meguro-ku, Tokyo 152-8552, Japan

^bDepartment of Organic and Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1-S1-13, O-okayama, Meguro-ku, Tokyo 152-8552, Japan

^cDepartment of Chemical Engineering, National Taiwan University, No. 1, Sec. 4, Roosevelt Road, Taipei 10617, Taiwan

^dDepartment of Applied Chemistry, National Chiao Tung University, 1001 University Road, Hsinchu 30010, Taiwan

Corresponding author: R. Goseki, E-mail: rgoseki@polymer.titech.ac.jp

Experimental Details

Materials

All reagents were purchased from Aldrich Japan, and used as received unless otherwise stated. 1,2-butylene oxide (BO) was distilled over fine powder CaH_2 under reduced pressures. Finally, BO was distilled over fine powder CaH_2 under high-vacuum conditions (10^{-6} Torr) and diluted with dry THF, and then divided into ampules equipped with break-seals under high-vacuum conditions.

Analytical Measurement.

Both ^1H and ^{13}C NMR spectra were recorded on a BRUKER DPX-300 spectrometer at 300 MHz and 75 MHz, respectively. Molecular weights (M_n) and molecular weight distributions (M_w/M_n) were measured on an Asahi Technion AT-2002 equipped with a Viscotek TDA model 302 triple detector array using THF as a carrier solvent at a flow rate of 1.0 mL min^{-1} at $40 \text{ }^\circ\text{C}$. Three PS gel column (pore size (bead size)) were used: 650 \AA ($5 \text{ }\mu\text{m}$), 200 \AA ($5 \text{ }\mu\text{m}$), 75 \AA ($5 \text{ }\mu\text{m}$). The relative molecular weights were determined by SEC with RI detection using standard PS calibration curve. The absolute molecular weights were determined by SEC with RI, viscometer, and right angle laser light scattering (RALLS) detectors. The polymer mixtures after the linking reactions were separated by preparative SEC (KNAUER, Smart-line) equipped with four columns (TOSOH TSKgel G5000H_{HRX2}, G4000H_{HRX2}) and RI detector using THF as an eluent at a flow rate of 5.0 mL min^{-1} at room temperature.

Synthesis of ADCB tetrablock quarterpolymer; A: PSt, B: P2VPy, C: PTBMA, D: PBO

The title tetrablock quarterpolymer was synthesized by the linking reaction of a living P2VPy-*block*-PTBMA (BC) with the ω -PA-functionalized PSt-*block*-PBO (AD-PA). The living P2VPy-*block*-PTBMA was prepared by the sequential polymerization of 2VPy (9.36 mmol) and TBMA (6.63 mmol) with 3-methyl-1,1-diphenylpentyllithium from *sec*-BuLi (0.0987 mmol) and DPE (0.114 mmol) in the presence of LiCl (0.220 mmol) at $-78 \text{ }^\circ\text{C}$ in THF solution (17.1 mL) for 30 min and 2 h, respectively. After a small amount of the resulting living P2VPy-*block*-PTBMA was taken for analytical purpose, the residual living polymer (0.0651 mmol) reacted *in situ* with the ω -terminal

PA-functionalized PSt-*block*-PBO (0.0217 mmol, $M_n = 19\,700\text{ g mol}^{-1}$) in dry THF (5.29 mL) at $-25\text{ }^\circ\text{C}$ for 24 h. The reaction was quenched with methanol, and the solution mixture was evaporated and freeze-dried from its benzene solution. The target P2VPy-*block*-PTBMA-*block*-PBO-*block*-PSt was isolated by SEC fractionation. It was purified by reprecipitation twice and freeze-drying from its benzene solution for 24 h (0.40 g, 46% yield). $^1\text{H NMR}$ (300 MHz, CDCl_3 , ref. CHCl_3 ($\delta = 7.26\text{ ppm}$)); $\delta = 8.48\text{--}8.08$ (m, $-\text{N}=\text{CH}-$), $7.26\text{--}6.05$ (m, Aromatic), $3.72\text{--}3.40$ (m, $-\text{O}-\text{CH}_2-\text{CH}-$), $3.40\text{--}3.25$ (m, $-\text{O}-\text{CH}_2-\text{CH}-$), $2.40\text{--}1.30$ (m, $-\text{CH}_2-\text{CH}-$, $-\text{CH}_2-\text{C}(\text{CH}_3)-$, $-\text{O}-\text{CH}(\text{CH}_2-\text{CH}_3)$, $\text{O}-\text{C}(\text{CH}_3)_3$), $1.30\text{--}0.85$ (m, $\text{CH}_2-\text{C}(\text{CH}_3)-$, $-\text{O}-\text{CH}(\text{CH}_2-\text{CH}_3)$).

Synthesis of ADBC tetrablock quarterpolymer

The title ADBC tetrablock quarterpolymer was synthesized by twice repeating the linking reactions starting from the ω -PA-functionalized AD. As the first linking reaction, the ω -PA-functionalized AD (0.0340 mmol, $M_n = 12\,100\text{ g mol}^{-1}$) in THF (10.0 mL), precooled at $-78\text{ }^\circ\text{C}$, was reacted with a separately prepared living α -(TBDMS ether)-functionalized P2VPy (B)^[1] (0.0497 mmol, $M_n = 5\,200\text{ g mol}^{-1}$) at $-78\text{ }^\circ\text{C}$ for 1 h. The polymerization reaction was then terminated with a few drops of degassed methanol, evaporated, and freeze-dried from its absolute benzene solution. The obtained ω -(TBDMS ether)-functionalized ADB was isolated in 69% by SEC fractionation. $^1\text{H NMR}$ (300 MHz, CDCl_3 , ref. CHCl_3 ($\delta = 7.26\text{ ppm}$)); $\delta = 8.45\text{--}8.00$ (m, $-\text{N}=\text{CH}-$), $7.25\text{--}6.05$ (m, Aromatic), $3.70\text{--}3.40$ (m, $-\text{O}-\text{CH}_2-\text{CH}-$), $3.40\text{--}3.05$ (m, $-\text{O}-\text{CH}_2-\text{CH}-$), $2.50\text{--}1.10$ (m, $-\text{CH}_2-\text{CH}-$, $-\text{O}-\text{CH}(\text{CH}_2-\text{CH}_3)$), $1.10\text{--}0.65$ (m, $-\text{O}-\text{CH}(\text{CH}_2-\text{CH}_3)$, $-\text{Si}-\text{C}(\text{CH}_3)_3$), 0.03 (s, $-\text{Si}(\text{CH}_3)_2-$).

The TBDMS protective group was removed in the same manner as that reported in our previous paper^[2]. $^1\text{H NMR}$ (300 MHz, CDCl_3 , ref. CHCl_3 ($\delta = 7.26\text{ ppm}$)); $\delta = 8.45\text{--}8.05$ (m, $-\text{N}=\text{CH}-$), $7.25\text{--}6.15$ (m, Aromatic), $3.70\text{--}3.40$ (m, $-\text{O}-\text{CH}_2-\text{CH}-$), $3.40\text{--}3.15$ (m, $-\text{O}-\text{CH}_2-\text{CH}-$), $2.45\text{--}1.20$ (m, $-\text{CH}_2-\text{CH}-$, $-\text{O}-\text{CH}(\text{CH}_2-\text{CH}_3)$), $1.05\text{--}0.80$ (m, $-\text{O}-\text{CH}(\text{CH}_2-\text{CH}_3)$).

The resulting ω -HO-functionalized ADB (0.0155 mmol) was esterified with α -phenylacrylic acid (0.123 g, 0.831 mmol), triphenylphosphine (0.218 g, 0.829 mmol), and diisopropylazodicarboxylate (0.150 mL, 0.822 mmol) in dry THF (5.0 mL) at $25\text{ }^\circ\text{C}$ for 20 h. The resulting polymer was purified by dialysis membrane cut off 1000 Da in a mixed solvent of chloroform and methanol. The obtained polymer was freeze-dried

from its absolute benzene solution (77% yield). ^1H NMR (300 MHz, CDCl_3 , ref. CHCl_3 ($\delta = 7.26$ ppm)); $\delta = 8.45\text{-}8.05$ (m, $-\text{N}=\text{CH}-$), $7.40\text{-}6.15$ (m, Aromatic), 5.85 (d, $\text{C}=\text{CH}_2$), $3.70\text{-}3.40$ (m, $-\text{O}-\text{CH}_2-\text{CH}-$), $3.40\text{-}3.20$ (m, $-\text{O}-\text{CH}_2-\text{CH}-$), $2.45\text{-}1.20$ (m, $-\text{CH}_2-\text{CH}-$, $-\text{O}-\text{CH}(\text{CH}_2-\text{CH}_3)$), $1.00\text{-}0.80$ (m, $-\text{O}-\text{CH}(\text{CH}_2-\text{CH}_3)$).

The living PTBMA (C^-) was prepared by the polymerization of TBMA (3.84 mmol) with 3-methyl-1,1-diphenylpentyllithium (0.0577 mmol) in the presence of LiCl (0.340 mmol) in THF (8.21 mL) at -78 °C for 2 h and *in-situ* reacted with the ω -PA-functionalized ADB (0.00995 mmol, $M_n = 19\ 100$ g mol $^{-1}$) in the second linking reaction under the conditions in THF (5.29 mL) at -25 °C for 11 h. The reaction was terminated with a few drops of degassed methanol, evaporated, and freeze-dried from its absolute benzene solution. The ADBC tetrablock quarterpolymer was isolated in 30% by SEC fractionation. ^1H NMR (300 MHz, CDCl_3 , ref. CHCl_3 ($\delta = 7.26$ ppm)); $\delta = 8.20\text{-}7.90$ (m, $-\text{N}=\text{CH}-$), $7.25\text{-}6.35$ (m, Aromatic), $3.85\text{-}3.40$ (m, $-\text{O}-\text{CH}_2-\text{CH}-$), $3.40\text{-}3.20$ (m, $-\text{O}-\text{CH}_2-\text{CH}-$), $2.40\text{-}1.30$ (m, $-\text{CH}_2-\text{CH}-$, $-\text{CH}_2-\text{C}(\text{CH}_3)-$, $-\text{O}-\text{CH}(\text{CH}_2-\text{CH}_3)$, $\text{O}-\text{C}(\text{CH}_3)_3$), $1.30\text{-}0.85$ (m, $\text{CH}_2-\text{C}(\text{CH}_3)-$, $-\text{O}-\text{CH}(\text{CH}_2-\text{CH}_3)$).

Synthesis of ABC'D tetrablock quarterpolymer

St (0.913 M, 11.2 mmol) in THF (12.3 mL) was polymerized with *sec*-BuLi (0.124 mmol) at -78 °C. After 10 min, DPE (0.164 mmol) in THF (3.21 mL) and LiCl (0.351 mmol) in THF (3.22 mL) were sequentially added at -78 °C and the reaction mixture was allowed to stand for additional 30 min. 2VPy (10.7 mmol) in THF (11.07 mL) was then added to the reaction mixture to be polymerized. The reaction mixture was allowed to stand at -78 °C for 30 min and MMA (10.7 mmol) in THF (10.8 mL) was added at -78 °C and the mixture was again allowed to stand at -78 °C for 30 min. Finally, the living PSt-*block*-P2VPy-*block*-PMMA thus prepared reacted *in situ* with the ω -termini PA-functionalized PBO (0.0359 mmol) at -40 °C for 17 h. The usual work-up and subsequent SEC fractionation gave a target ABC'D tetrablock quarterpolymer in 57% yield. ^1H NMR (300 MHz, CDCl_3 , ref. CHCl_3 ($\delta = 7.26$ ppm)), $\delta = 8.40\text{-}8.10$ (m, $-\text{N}=\text{CH}-$), $7.25\text{-}6.25$ (m, Aromatic), $3.65\text{-}3.45$ (m, $-\text{O}-\text{CH}_2-\text{CH}-$, $-\text{O}-\text{CH}_3$), $3.45\text{-}3.20$ (m, $-\text{O}-\text{CH}_2-\text{CH}-$), $2.50\text{-}1.10$ (m, $-\text{CH}_2-\text{CH}-$, $-\text{CH}_2-\text{C}(\text{CH}_3)-$, $-\text{O}-\text{CH}(\text{CH}_2-\text{CH}_3)$), $1.10\text{-}0.75$ (m, $\text{CH}_2-\text{C}(\text{CH}_3)-$, $-\text{O}-\text{CH}(\text{CH}_2-\text{CH}_3)$).

Synthesis of CABD tetrablock quarterpolymer

The title CABD tetrablock quarterpolymer was synthesized by twice repeating the linking reaction starting from the ω -PA-functionalized D. An α -(TBDMS ether)-functionalized ABD was prepared by the first linking reaction of the ω -PA-functionalized D with a living α -(TBDMS ether)-functionalized PSt-*block*-P2VPy. The latter polymer was prepared as follows: St (5.81 mmol) in 4-*tert*-butylbenzene (4.31 mL) was polymerized with **3** (0.0510 mmol) in the presence of TMEDA (0.124 mmol) at 0 °C for 30 min. The resulting living PSt was cooled to -78 °C and THF (10.2 mL) precooled at -78 °C was added. Then, DPE (0.0710 mmol) and LiCl (0.145 mmol) in THF (2.21 mL) were added to the living polymer solution at -78 °C and the mixture was allowed to react at -78 °C for 1 h, followed by the polymerization of 2VPy (2.51 mmol) in THF (5.25 mL) at -78 °C for 1 h. The living α -(TBDMS ether)-functionalized PSt-*block*-P2VPy reacted *in situ* with the ω -termini PA-functionalized PBO (0.0340 mmol, $M_n = 5\,860\text{ g mol}^{-1}$) at -78 °C for 15 h. The reaction was terminated with a few drops of degassed methanol, evaporated, and freeze-dried from its absolute benzene solution. The usual work-up and SEC fractionation gave a α -(TBDMS ether)-functionalized PSt-*block*-P2VPy-*block*-PBO in 67% yield. $^1\text{H NMR}$ (300 MHz, CDCl_3 , ref. CHCl_3 ($\delta = 7.26\text{ ppm}$)); $\delta = 8.50\text{--}8.05$ (m, $-\text{N}=\text{CH}-$), $7.40\text{--}6.20$ (m, Aromatic), $3.75\text{--}3.40$ (m, $-\text{O}-\text{CH}_2-\text{CH}-$), $3.40\text{--}3.25$ (m, $-\text{O}-\text{CH}_2-\text{CH}-$), $2.50\text{--}1.15$ (m, $-\text{CH}_2-\text{CH}-$, $-\text{O}-\text{CH}(\text{CH}_2-\text{CH}_3)$), $1.10\text{--}0.85$ (m, $-\text{O}-\text{CH}(\text{CH}_2-\text{CH}_3)$, $-\text{Si}-\text{C}(\text{CH}_3)_3$), -0.03 (s, $-\text{Si}(\text{CH}_3)_2-$).

Deprotection of the TBDMS group and the esterification reaction were performed in the same manners as those mentioned above. HO-ABD: $^1\text{H NMR}$ (300 MHz, CDCl_3 , ref. CHCl_3 ($\delta = 7.26\text{ ppm}$)), $\delta = 8.50\text{--}8.05$ (m, $-\text{N}=\text{CH}-$), $7.40\text{--}6.20$ (m, Aromatic), $3.80\text{--}3.40$ (m, $-\text{O}-\text{CH}_2-\text{CH}-$), $3.40\text{--}3.25$ (m, $-\text{O}-\text{CH}_2-\text{CH}-$), $2.50\text{--}1.20$ (m, $-\text{CH}_2-\text{CH}-$, $-\text{O}-\text{CH}(\text{CH}_2-\text{CH}_3)$), $1.10\text{--}0.80$ (m, $-\text{O}-\text{CH}(\text{CH}_2-\text{CH}_3)$). PA-ABD: $^1\text{H NMR}$ (300 MHz, CDCl_3 , ref. CHCl_3 ($\delta = 7.26\text{ ppm}$)); $\delta = 8.45\text{--}8.05$ (m, $-\text{N}=\text{CH}-$), $7.40\text{--}6.20$ (m, Aromatic), 5.85 (s, $\text{C}=\text{CH}_2$), $3.70\text{--}3.40$ (m, $-\text{O}-\text{CH}_2-\text{CH}-$), $3.40\text{--}3.20$ (m, $-\text{O}-\text{CH}_2-\text{CH}-$), $2.50\text{--}1.20$ (m, $-\text{CH}_2-\text{CH}-$, $-\text{O}-\text{CH}(\text{CH}_2-\text{CH}_3)$), $1.10\text{--}0.80$ (m, $-\text{O}-\text{CH}(\text{CH}_2-\text{CH}_3)$).

In the second linking reaction, a separately prepared living PTBMA (C^-) (0.0424 mmol) reacted *in situ* with the PA-ABD (0.00772 mmol, $M_n = 25\,900\text{ g mol}^{-1}$) in THF (4.55 mL) at -25 °C for 20 h. The reaction was terminated with a few drops of degassed methanol, evaporated, and freeze-dried from its absolute benzene solution. The usual work-up and SEC fractionation gave a CABD tetrablock quarterpolymer in 58% yield. $^1\text{H NMR}$ (300 MHz, CDCl_3 , ref. CHCl_3 ($\delta = 7.26\text{ ppm}$)); $\delta = 8.50\text{--}8.05$ (m, $-\text{N}=\text{CH}-$),

7.40-6.20 (m, Aromatic), 3.70-3.40 (m, -O-CH₂-CH-), 3.40-3.25 (m, -O-CH₂-CH-), 2.60-1.20 (m, -CH₂-C(CH₃)-, -O-CH(CH₂-CH₃), O-C(CH₃)₃), 1.20-0.85 (m, CH₂-C(CH₃)-, -O-CH(CH₂-CH₃)).

Synthesis of BAC'D tetrablock quarterpolymer

The title BAC'D tetrablock quarterpolymer was synthesized by twice repeating the linking reaction starting from the ω-PA-functionalized D. The reaction steps were described in the manuscript. The ¹H NMR spectra of all the synthesized polymers were as follows: ¹H NMR; α-(TBDMS ether)-functionalized-AC'D: 7.30-6.30 (m, Aromatic), 3.80-3.40 (m, -O-CH₂-CH-, -OCH₃), 3.40-3.30 (m, -O-CH₂-CH-), 2.30-1.20 (m, -CH₂-CH-, -CH₂-C(CH₃)-, -O-CH(CH₂-CH₃)), 1.20-0.85 (m, CH₂-C(CH₃), -O-CH(CH₂-CH₃), -Si-C(CH₃)₃), 0.03 (s, -Si(CH₃)₂-). HO-AC'D: 7.30-6.30 (m, Aromatic), 3.80-3.40 (m, -O-CH₂-CH-, -OCH₃), 3.40-3.30 (m, -O-CH₂-CH-), 2.30-1.20 (m, -CH₂-CH-, -CH₂-C(CH₃)-, -O-CH(CH₂-CH₃)), 1.20-0.85 (m, CH₂-C(CH₃), -O-CH(CH₂-CH₃)). PA-AC'D: 7.30-6.30 (m, Aromatic), 6.22,5.83 (d, C=CH₂), 3.70-3.35 (m, -O-CH₂-CH-, -OCH₃), 3.40-3.25 (m, -O-CH₂-CH-), 2.30-1.20 (m, -CH₂-CH-, -CH₂-C(CH₃)-, -O-CH(CH₂-CH₃)), 1.20-0.85 (m, CH₂-C(CH₃), -O-CH(CH₂-CH₃)). BAC'D: 8.40-8.10 (m, -N=CH-), 7.30-6.30 (m, Aromatic), 3.70-3.35 (m, -O-CH₂-CH-, -O-CH₃), 3.35-3.20 (m, -O-CH₂-CH-), 2.50-1.20 (m, -CH₂-CH-, -CH₂-C(CH₃)-, -O-CH(CH₂-CH₃)), 1.10-0.80 (m, CH₂-C(CH₃)-, -O-CH(CH₂-CH₃)).

Synthesis of BC'AD tetrablock quarterpolymer

The title BC'AD tetrablock quarterpolymer was synthesized by twice repeating the linking reaction starting from the ω-PA-functionalized D. The reaction steps were described in the manuscript. The ¹H NMR spectra of all the synthesized polymers were as follows: ¹H NMR; α-(TBDMS ether)-functionalized AD: 7.20-6.30 (m, Aromatic), 3.70-3.40 (m, -O-CH₂-CH-), 3.40-3.20 (m, -O-CH₂-CH-), 2.30-1.25 (m, -CH₂-CH-, -O-CH(CH₂-CH₃)), 1.00-0.85 (m, -O-CH(CH₂-CH₃), -Si-C(CH₃)₃), -0.03 (s, -Si(CH₃)₂-). HO-AD: 7.20-6.30 (m, Aromatic), 3.70-3.40 (m, -O-CH₂-CH-), 3.40-3.20 (m, -O-CH₂-CH-), 2.40-1.25 (m, -CH₂-CH-, -O-CH(CH₂-CH₃)), 1.10-0.85 (m, -O-CH(CH₂-CH₃)). PA-AD: 7.20-6.30 (m, Aromatic), 6.23,5.81 (d, C=CH₂), 3.70-3.40 (m, -O-CH₂-CH-), 3.40-3.20 (m, -O-CH₂-CH-), 2.30-1.25 (m, -CH₂-CH-, -O-CH(CH₂-CH₃)), 1.00-0.85 (m, -O-CH(CH₂-CH₃)). BC'AD: 8.60-8.10 (m, -N=CH-), 7.35-6.10 (m, Aromatic), 3.70-

3.35 (m, -O-CH₂-CH-, -O-CH₃), 3.35-3.25 (m, -O-CH₂-CH-), 2.45-1.20 (m, -CH₂-CH-, -CH₂-C(CH₃)-, -O-CH(CH₂-CH₃)), 1.30-0.85 (m, CH₂-C(CH₃)-, -O-CH(CH₂-CH₃)).

Synthesis of C'BAD tetrablock quarterpolymer

The title C'BAD tetrablock quarterpolymer was synthesized by repeating thrice the linking reaction starting from the ω-PA-functionalized AD. The reaction steps were described in the manuscript. The ¹H NMR spectra of all the synthesized polymers were as follows: ¹H NMR; (TBDMS ether)-BAD: 8.45-8.05 (m, -N=CH-), 7.30-6.10 (m, Aromatic), 3.70-3.40 (m, -O-CH₂-CH-), 3.40-3.25 (m, -O-CH₂-CH-), 2.40-1.15 (m, -CH₂-CH-, -O-CH(CH₂-CH₃)), 1.00-0.75 (m, -O-CH(CH₂-CH₃), -Si-C(CH₃)₃), 0.00 (s, -Si(CH₃)₂-). HO-BAD: 8.40-8.00 (m, -N=CH-), 7.25-6.15 (m, Aromatic), 3.70-3.40 (m, -O-CH₂-CH-), 3.40-3.20 (m, -O-CH₂-CH-), 2.30-1.15 (m, -CH₂-CH-, -O-CH(CH₂-CH₃)), 1.00-0.80 (m, -O-CH(CH₂-CH₃)). PA-BAD: 8.45-8.05 (m, -N=CH-), 7.25-6.15 (m, Aromatic), 5.85 (d, C=CH₂), 3.70-3.40 (m, -O-CH₂-CH-), 3.40-3.25 (m, -O-CH₂-CH-), 2.40-1.20 (m, -CH₂-CH-, -O-CH(CH₂-CH₃)), 1.00-0.85 (m, -O-CH(CH₂-CH₃)). C'BAD: 8.40-8.10 (m, -N=CH-), 7.35-6.30 (m, Aromatic), 3.70-3.40 (m, -O-CH₂-CH-, -O-CH₃), 3.40-3.25 (m, -O-CH₂-CH-), 2.45-1.20 (m, -CH₂-CH-, -CH₂-C(CH₃)-, -O-CH(CH₂-CH₃)), 1.20-0.85 (m, CH₂-C(CH₃)-, -O-CH(CH₂-CH₃)).

Synthesis of AC'BD tetrablock quarterpolymer

The title AC'BD tetrablock quarter polymer was synthesized by twice repeating the linking reaction starting from the ω-PA-functionalized D. The reaction steps were described in the manuscript. The ¹H NMR spectra of all the synthesized polymers were as follows: ¹H NMR; (TBDMS ether)-BD: 8.50-8.00 (m, -N=CH-), 7.40-6.15 (m, Aromatic), 3.70-3.40 (m, -O-CH₂-CH-), 3.40-3.25 (m, -O-CH₂-CH-), 2.45-1.20 (m, -CH₂-CH-, -O-CH(CH₂-CH₃)), 1.10-0.85 (m, -O-CH(CH₂-CH₃), -Si-C(CH₃)₃), 0.03 (s, -Si(CH₃)₂-). HO-BD: 8.50-8.00 (m, -N=CH-), 7.40-6.15 (m, Aromatic), 3.70-3.40 (m, -O-CH₂-CH-), 3.40-3.25 (m, -O-CH₂-CH-), 2.45-1.20 (m, -CH₂-CH-, -O-CH(CH₂-CH₃)), 1.10-0.85 (m, -O-CH(CH₂-CH₃)). PA-BD: 8.50-8.05 (m, -N=CH-), 7.25-6.15 (m, Aromatic), 5.85 (d, C=CH₂), 3.70-3.40 (m, -O-CH₂-CH-), 3.40-3.25 (m, -O-CH₂-CH-), 2.40-1.40 (m, -CH₂-CH-, -O-CH(CH₂-CH₃)), 1.00-0.80 (m, -O-CH(CH₂-CH₃)). AC'BD: 8.40-8.05 (m, -N=CH-), 7.30-6.30 (m, Aromatic), 3.65-3.40 (m, -O-CH₂-CH-,

-O-CH₃), 3.35-3.15 (m, -O-CH₂-CH-), 2.40-1.20 (m, -CH₂-CH-, -CH₂-C(CH₃)-, -O-CH(CH₂-CH₃)), 1.10-0.80 (m, CH₂-C(CH₃)-, -O-CH(CH₂-CH₃)).

Synthesis of ABDC tetrablock quarterpolymer

The title tetrablock quarterpolymer was synthesized by twice repeating the linking reactions starting from the α,ω -(THP ether and PA)-functionalized PBO. The α,ω -(THP ether and PA)-functionalized PBO (0.0252 mmol, $M_n = 5\,910\text{ g mol}^{-1}$) was reacted with a living PTBMA (0.0781 mmol, $M_n = 10\,200\text{ g mol}^{-1}$) in the first linking reaction at -25 °C for 10 h, resulting in an α -(THP ether)-functionalized DC. It was obtained in 39% yield by the usual work-up and SEC fractionation. ¹H NMR (CDCl₃); δ 4.79 (s, O-CH-O), 4.75 (s, O-CH₂-Ph), 4.70 (t, O-CH₂-Ph), 4.48 (s, O-CH₂-Ph), 3.99, 3.91 (d, CH-O-CH₂-), 3.70-3.40 (m, -O-CH₂-CH-), 3.40-3.25 (m, -O-CH₂-CH-), 2.60-1.20 (m, CH₂-C(CH₃)-, -O-CH(CH₂-CH₃), O-C(CH₃)₃), 1.20-0.85 (m, CH₂-C(CH₃)-, -O-CH(CH₂-CH₃)).

The resulting α -(THP ether)-functionalized DC (0.0110 mmol) dissolved in THF (5 mL) was mixed with 12N HCl (0.103 mL) at 25 °C and the mixture was allowed to stir for 20 h at 25 °C. After neutralization with NaHCO₃ and washing with H₂O, the polymer was precipitated in water and freeze-dried from its absolute benzene solution. ¹H NMR (CDCl₃); δ 4.70 (t, O-CH₂-Ph), 4.52 (s, O-CH₂-Ph), 3.70-3.40 (m, -O-CH₂-CH-), 3.40-3.25 (m, -O-CH₂-CH-), 2.60-1.20 (m, CH₂-C(CH₃)-, -O-CH(CH₂-CH₃), O-C(CH₃)₃), 1.20-0.85 (m, CH₂-C(CH₃)-, -O-CH(CH₂-CH₃)).

The hydroxyl group was quantitatively converted to PA function in the same manner as that described above. ¹H NMR (CDCl₃); δ 6.36, 5.90 (d, C=CH₂), 5.26 (s, O-CH₂-Ph), 4.53 (s, O-CH₂-Ph), 3.70-3.40 (m, -O-CH₂-CH-), 3.40-3.25 (m, -O-CH₂-CH-), 2.60-1.20 (m, CH₂-C(CH₃)-, -O-CH(CH₂-CH₃), O-C(CH₃)₃), 1.20-0.85 (m, CH₂-C(CH₃)-, -O-CH(CH₂-CH₃)).

Finally, the obtained α -PA-functionalized DC (0.0609 mmol) dissolved in dry THF (4.9 mL) was cooled to -78 °C and reacted with the living PS-*block*-P2VP (0.0945 mmol) in THF (5.20 mL) at -78 °C for 5 h. The usual work-up and SEC fractionation gave an ABDC tetrablock quarter polymer in 20% yield. ¹H NMR (CDCl₃); δ 8.50-8.05 (m, -N=CH-), 7.40-6.15 (m, Aromatic), 3.80-3.40 (m, -O-CH₂-CH-), 3.30-3.20 (m, -O-CH₂-CH-), 2.45-1.20 (m, -CH₂-CH-, CH₂-C(CH₃)-, -O-CH(CH₂-CH₃), O-C(CH₃)₃), 1.20-0.85 (m, CH₂-C(CH₃)-, -O-CH(CH₂-CH₃)).

Synthesis of BADC' tetrablock quarterpolymer

The title BADC' tetrablock quarter polymer was synthesized by thrice repeating the linking reaction starting from the α,ω -(THP ether and PA)-functionalized PBO. The reaction steps were described in the manuscript. The ^1H NMR spectra of all the synthesized polymers were as follows: ^1H NMR (CDCl_3); (THP ether)-DC': 4.79 (s, O-CH-O), 4.75 (s, O-CH₂-Ph), 4.70 (t, O-CH₂-Ph), 4.48 (s, O-CH₂-Ph), 3.75, 3.68 (d, CH-O-CH₂-), 3.80-3.35 (m, -OCH₃, -O-CH₂-CH-), 3.35-3.25 (m, -O-CH₂-CH-), 2.60-1.20 (m, CH₂-C(CH₃)-, -O-CH(CH₂-CH₃)), 1.10-0.85 (m, CH₂-C(CH₃)-, -O-CH(CH₂-CH₃)). HO-DC': 4.68 (t, O-CH₂-Ph), 4.52 (s, O-CH₂-Ph), 3.80-3.35 (m, -OCH₃, -O-CH₂-CH-), 3.35-3.25 (m, -O-CH₂-CH-), 2.60-1.20 (m, CH₂-C(CH₃)-, -O-CH(CH₂-CH₃)), 1.10-0.85 (m, CH₂-C(CH₃)-, -O-CH(CH₂-CH₃)). PA-DC': 6.36, 5.90 (d, C=CH₂), 5.26 (s, O-CH₂-Ph), 4.53 (s, O-CH₂-Ph), 3.80-3.35 (m, -OCH₃, -O-CH₂-CH-), 3.35-3.25 (m, -O-CH₂-CH-), 2.60-1.20 (m, CH₂-C(CH₃)-, -O-CH(CH₂-CH₃)), 1.10-0.85 (m, CH₂-C(CH₃)-, -O-CH(CH₂-CH₃)). (TBDMS ether)-ADC': 7.30-6.30 (m, Aromatic), 3.80-3.40 (m, -O-CH₂-CH-, -OCH₃), 3.40-3.30 (m, -O-CH₂-CH-), 2.30-1.20 (m, -CH₂-CH-, -CH₂-C(CH₃)-, -O-CH(CH₂-CH₃)), 1.20-0.85 (m, CH₂-C(CH₃), -O-CH(CH₂-CH₃), -Si-C(CH₃)₃), 0.03 (s, -Si(CH₃)₂-). HO-ADC': 7.20-6.30 (m, Aromatic), 3.70-3.35 (m, -O-CH₂-CH-, -OCH₃), 3.35-3.25 (m, -O-CH₂-CH-), 2.30-1.20 (m, -CH₂-CH-, -CH₂-C(CH₃)-, -O-CH(CH₂-CH₃)), 1.15-0.80 (m, CH₂-C(CH₃), -O-CH(CH₂-CH₃)). PA-ADC': 7.20-6.40 (m, Aromatic), 6.20, 5.81 (d, C=CH₂), 3.70-3.40 (m, -O-CH₂-CH-, -OCH₃), 3.40-3.20 (m, -O-CH₂-CH-), 2.30-1.10 (m, -CH₂-CH-, -CH₂-C(CH₃)-, -O-CH(CH₂-CH₃)), 1.10-0.80 (m, CH₂-C(CH₃), -O-CH(CH₂-CH₃)). BADC': 8.50-8.10 (m, -N=CH-), 7.35-6.25 (m, Aromatic), 3.70-3.35 (m, -O-CH₂-CH-, -O-CH₃), 3.35-3.20 (m, -O-CH₂-CH-), 2.50-1.20 (m, -CH₂-CH-, -CH₂-C(CH₃)-, -O-CH(CH₂-CH₃)), 1.10-0.80 (m, CH₂-C(CH₃)-, -O-CH(CH₂-CH₃)).

Synthesis of BDAC' tetrablock quarterpolymer

The title BDAC' tetrablock quarter polymer was synthesized by thrice repeating the linking reaction starting from the α,ω -(THP ether and PA)-functionalized PBO. The reaction steps were described in the manuscript. The ^1H NMR spectra of all the synthesized polymers were as follows: ^1H NMR (CDCl_3); (THP ether)-DA-(TBDMS ether): 7.20-6.40 (m, Aromatic), 4.79 (s, O-CH-O), 4.75 (s, O-CH₂-Ph), 4.70 (t, O-CH₂-

Ph), 4.48 (s, O-CH₂-Ph), 3.90 (d, CH-O-CH₂-), 3.70-3.40 (m, -O-CH₂-CH-), 3.40-3.20 (m, -O-CH₂-CH-), 2.30-1.25 (m, -CH₂-CH-, -O-CH(CH₂-CH₃)), 1.10-0.85 (m, -O-CH(CH₂-CH₃), -Si-C(CH₃)₃), -0.03 (s, -Si(CH₃)₂-). (THP ether)-DA-OH: 7.20-6.40 (m, Aromatic), 4.79 (s, O-CH-O), 4.75 (s, O-CH₂-Ph), 4.70 (t, O-CH₂-Ph), 4.48 (s, O-CH₂-Ph), 3.85 (d, CH-O-CH₂-), 3.70-3.40 (m, -O-CH₂-CH-), 3.40-3.20 (m, -O-CH₂-CH-), 2.30-1.25 (m, -CH₂-CH-, -O-CH(CH₂-CH₃)), 1.10-0.85 (m, -O-CH(CH₂-CH₃)). (THP ether)-DA-PA: 7.20-6.40 (m, Aromatic), 6.23, 5.83 (d, C=CH₂), 4.79 (s, O-CH-O), 4.75 (s, O-CH₂-Ph), 4.70 (t, O-CH₂-Ph), 4.48 (s, O-CH₂-Ph), 3.70-3.40 (m, -O-CH₂-CH-), 3.40-3.20 (m, -O-CH₂-CH-), 2.30-1.25 (m, -CH₂-CH-, -O-CH(CH₂-CH₃)), 1.10-0.85 (m, -O-CH(CH₂-CH₃)). (THP ether)-DAC': 7.30-6.30 (m, Aromatic), 4.79 (s, O-CH-O), 4.75 (s, O-CH₂-Ph), 4.70 (t, O-CH₂-Ph), 4.48 (s, O-CH₂-Ph), 3.80-3.40 (m, -O-CH₂-CH-, -OCH₃), 3.40-3.30 (m, -O-CH₂-CH-), 2.30-1.20 (m, -CH₂-CH-, -CH₂-C(CH₃)-, -O-CH(CH₂-CH₃)), 1.20-0.85 (m, CH₂-C(CH₃), -O-CH(CH₂-CH₃)). HO-DAC': 7.30-6.30 (m, Aromatic), 4.68 (s, O-CH₂-Ph), 4.53 (s, O-CH₂-Ph), 3.80-3.40 (m, -O-CH₂-CH-, -OCH₃), 3.40-3.30 (m, -O-CH₂-CH-), 2.30-1.20 (m, -CH₂-CH-, -CH₂-C(CH₃)-, -O-CH(CH₂-CH₃)), 1.20-0.85 (m, CH₂-C(CH₃), -O-CH(CH₂-CH₃)). PA-DAC': 7.30-6.30 (m, Aromatic), 5.90 (d, C=CH₂), 5.26 (s, O-CH₂-Ph), 4.53 (s, O-CH₂-Ph), 3.80-3.40 (m, -O-CH₂-CH-, -OCH₃), 3.40-3.30 (m, -O-CH₂-CH-), 2.30-1.20 (m, -CH₂-CH-, -CH₂-C(CH₃)-, -O-CH(CH₂-CH₃)), 1.20-0.85 (m, CH₂-C(CH₃), -O-CH(CH₂-CH₃)). BDAC': 8.45-8.05 (m, -N=CH-), 7.35-6.15 (m, Aromatic), 3.70-3.35 (m, -O-CH₂-CH-, -O-CH₃), 3.35-3.20 (m, -O-CH₂-CH-), 2.50-1.10 (m, -CH₂-CH-, -CH₂-C(CH₃)-, -O-CH(CH₂-CH₃)), 1.10-0.80 (m, CH₂-C(CH₃)-, -O-CH(CH₂-CH₃)).

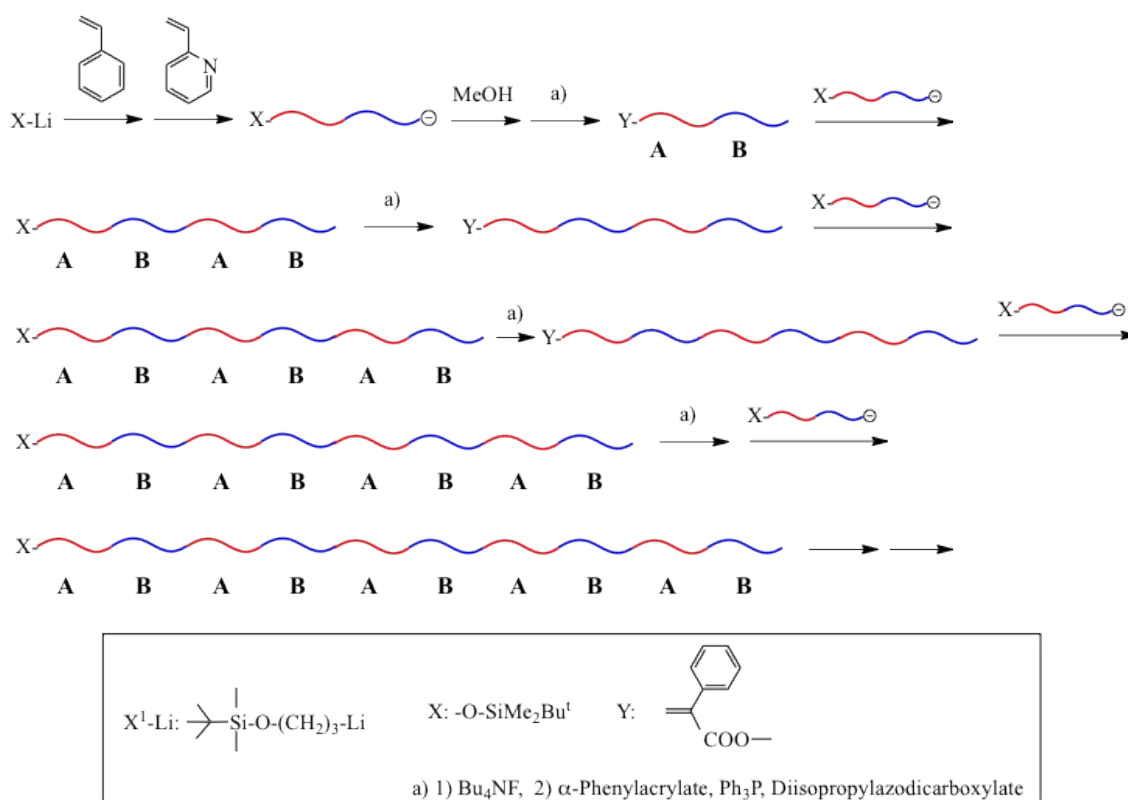
Synthesis of BDC'A tetrablock quarterpolymer

The title BDC'A tetrablock quarterpolymer was synthesized by twice repeating the linking reaction starting from the α,ω -(THP ether and PA)-functionalized-PBO. The reaction steps were described in the manuscript. The ¹H NMR spectra of all the synthesized polymers were as follows: ¹H NMR (CDCl₃), (THP ether)-DC'A: 7.30-6.30 (m, Aromatic), 4.79 (s, O-CH-O), 4.75 (s, O-CH₂-Ph), 4.70 (t, O-CH₂-Ph), 4.48 (s, O-CH₂-Ph), 3.80-3.40 (m, -O-CH₂-CH-, -OCH₃), 3.40-3.30 (m, -O-CH₂-CH-), 2.30-1.20 (m, -CH₂-CH-, -CH₂-C(CH₃)-, -O-CH(CH₂-CH₃)), 1.20-0.85 (m, CH₂-C(CH₃), -O-CH(CH₂-CH₃)). HO-DC'A: 7.30-6.30 (m, Aromatic), 4.70 (t, HO-CH₂-Ph), 4.52 (s, O-CH₂-Ph), 3.80-3.40 (m, -O-CH₂-CH-, -OCH₃), 3.40-3.30 (m, -O-CH₂-CH-), 2.30-1.20

(m, $-CH_2-CH-$, $-CH_2-C(CH_3)-$, $-O-CH(CH_2-CH_3)$), 1.20-0.85 (m, $CH_2-C(CH_3)$, $-O-CH(CH_2-CH_3)$). PA-DC'A: 7.30-6.40 (m, Aromatic), 5.90 (d, $C=CH_2$), 5.26 (s, $O-CH_2-Ph$), 4.52 (s, $O-CH_2-Ph$), 3.80-3.40 (m, $-O-CH_2-CH-$, $-OCH_3$), 3.40-3.25 (m, $-O-CH_2-CH-$), 2.10-1.10 (m, $-CH_2-CH-$, $-CH_2-C(CH_3)-$, $-O-CH(CH_2-CH_3)$), 1.20-0.85 (m, $CH_2-C(CH_3)$, $-O-CH(CH_2-CH_3)$). BDC'A: 8.40-8.10 (m, $-N=CH-$), 7.40-6.30 (m, Aromatic), 3.65-3.40 (m, $-O-CH_2-CH-$, $-O-CH_3$), 3.40-3.25 (m, $-O-CH_2-CH-$), 2.50-1.10 (m, $-CH_2-CH-$, $-CH_2-C(CH_3)-$, $-O-CH(CH_2-CH_3)$), 1.10-0.75 (m, $CH_2-C(CH_3)-$, $-O-CH(CH_2-CH_3)$).

References

- [1] A. Hirao, Y. Matsuo, T. Oie, R. Goseki, T. Ishizone, K. Sugiyama, A. H. Göschel, A.H.E. Müller, *Macromolecules*, **2011**, 44, 6345-6355.
- [2] K. Sugiyama, T. Oie, A.A. El-Magd, A. Hirao, *Macromolecules*, **2010**, 43, 1403-1410.



Scheme S1. Synthetic scheme of $(AB)_n$ multiblock copolymers ($n = 1 \sim 5$) by the methodology applying in an iterative fashion.

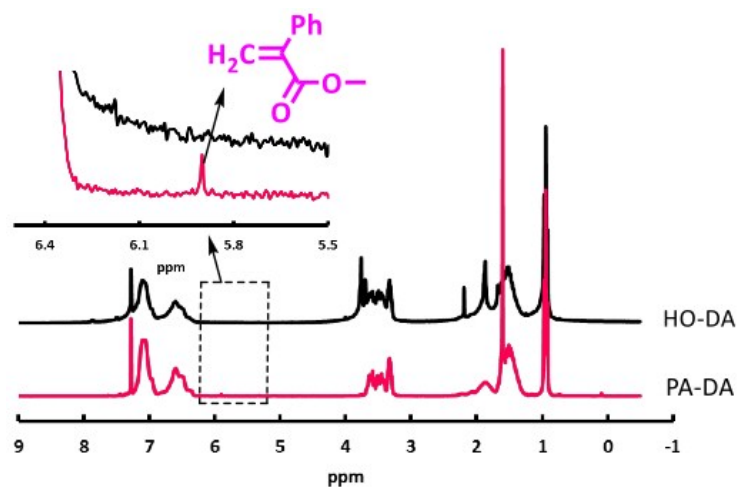


Figure S1. ¹H NMR spectra of ω-OH-functionalized AD (black) and ω-PA-functionalized AD (red).

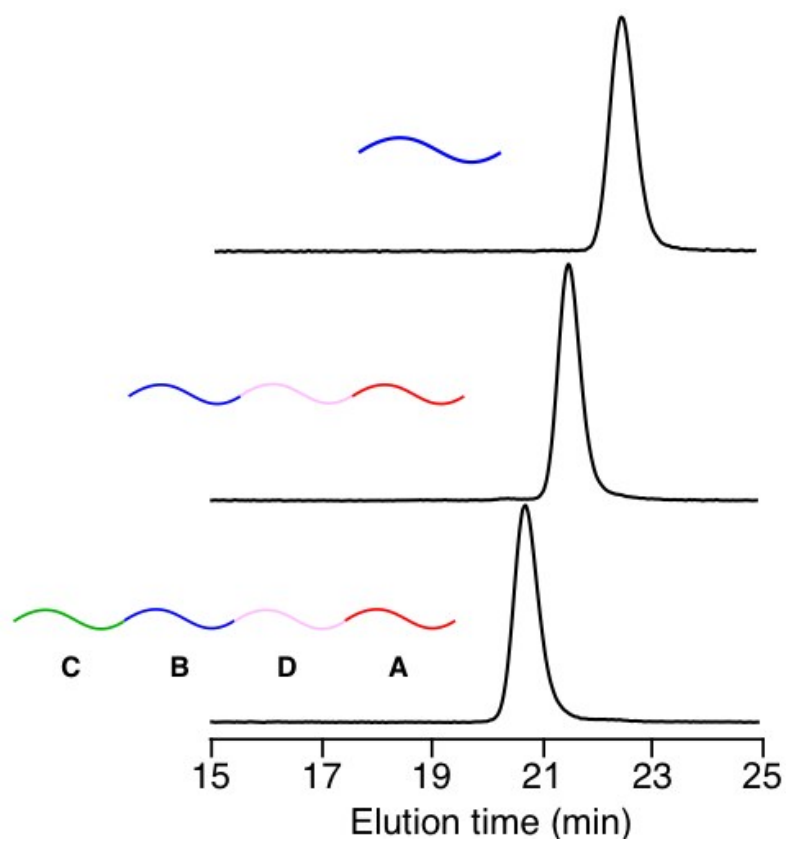


Figure S2. SEC profiles of C, BDA, and CBDA tetrablock quarterpolymer.

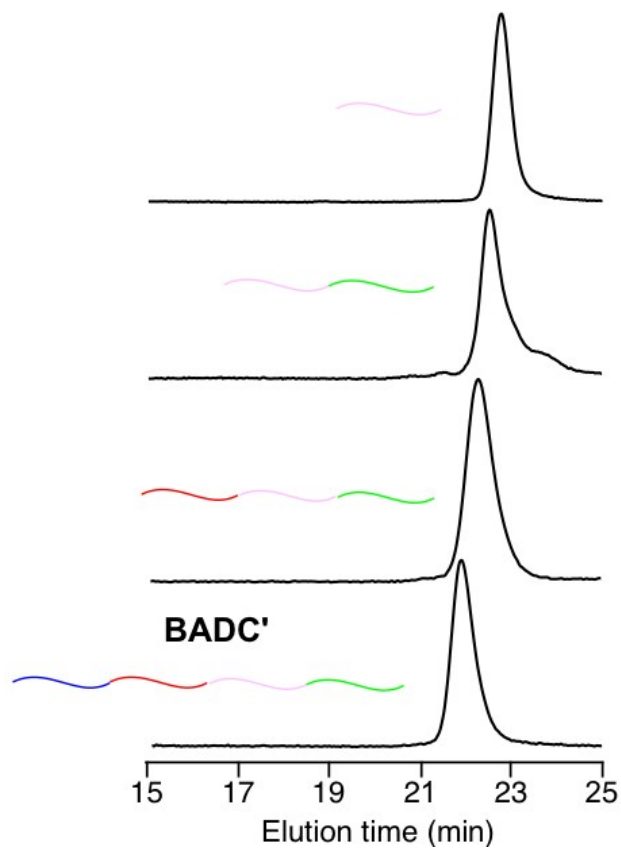


Figure S3. SEC profiles of D, DC', ADC', and BADC' tetrablock quarterpolymer.