Supporting Information

An Efficient Avenue for Polybutadiene Functionalization

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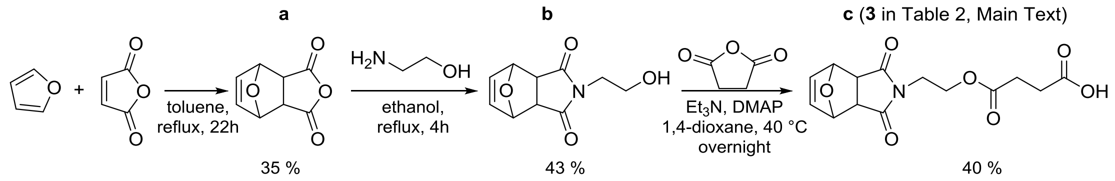
Content:

A. Experimental Procedures:

A.1. Chemicals: The polybutadiene (PBD, LBR-307B) employed in the experiments was kindly supplied by Kuraray Kashima Plant and used without further purification. Tetrahydrofuran (THF, Acros Organics, 99.5%, extra dry, over molecular sieves), toluene (VWR, normapur), toluene (Acros, 99.85 %, extra dry, over molecular sieves), 1,4-dioxane (Acros, 99+% extra pure), 2,3,4,5,6-pentafluorobenzoic acid (Alfa Aesar, 99 %), anthraquinone-2-carboxylic acid (TCI, > 99.0 %), 1-pyrenecarboxylic acid (TCI, > 97.0 %), methanol (MeOH, VWR, normapur), hexane (VWR, normapur), *N*-bromosuccinimide (NBS, Merck, ≥ 99.0 %), *N*-chlorosuccinimide (NCS, Acros, 97 %), ethanol (VWR, normapur), ethanolamine (Acros, 99 %), dichloromethane (DCM, VWR, 99.8 %, stabilized with 0.2 % of ethanol), 4-(dimethylamino)pyridine (DMAP; Sigma Aldrich, 99%), triethylamine (Merck, 99%), furane (Acros, 99+ %, stabilized), maleic anhydride (Acros, 99 %), succinic anhydride (Acros, 99 %), chloroform-d$_1$ ($CDCl_3$, Sigma Aldrich, 99.8% D), dimethyl sulfoxide (DMSO-d$_6$, eurisotop, 99.8% D), 3,6,9-trioxadecanoic acid (TODA, Iris Biotech), sodium azide (Sigma Aldrich, 99.5%), *N*,*N*-dimethylformamide (DMF, Acros organics, 99.8%, extra dry, over molecular sieves) were used as received. 4-(2-(4-methoxyphenyl)-2H-tetrazol-5-yl)benzoic acid (**2** in Scheme 2 in the main text) was synthesized by Vincent Schüller according to a previously reported procedure.[1]

A.2. Synthesis of 4-(2-(1,3-dioxohexahydro-1*H*-4,7-epoxyisoindol-2(3*H*)-yl)ethoxy)-4-oxo-butanoic acid (3 in Scheme 2 in the main text).



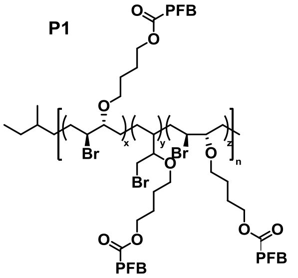
The synthesis of **a** was performed according to literature.[2] 15.0 g maleic anhydride (153 mmol, 1.0 eq.) was dissolved in 75mL toluene which was heated to 45 °C. Subsequently, 16.7mL furane (15.6 g, 231 mmol, 1.5 eq.) was added to the solution and the reaction mixture was stirred under reflux for 22 h. After cooling to 0 °C, the white precipitate was filtered off and washed with 120 mL cold diethyl ether yielding the product as white powder (8.89 g, 53.5 mmol, 35 %). ^{1}H NMR (500 MHz, $CDCl_3$, δ in ppm): 6.58 (2 H, s), 5.45 (2 H, s), 3.17 (2 H, s).

The synthesis of **b** was performed according to literature.[3] 8.89 g of compound **a** (53.5 mmol, 1.0 eq.) was suspended in 15 mL ethanol and cooled down to 0 °C. A solution of 3.34 mL ethanolamine (3.27 g, 53.5 mmol, 1.0 eq.) in 2.7 mL ethanol was added dropwise to the suspension. The reaction mixture was stirred for 10 min at 0 °C. At ambient temperature 10 mL ethanol was added and the solution was stirred at reflux for 4 h. The resulting yellow reaction mixture was left at -7 °C overnight. The product was obtained as white crystals after filtration (4.83 g, 23.1 mmol, 43 %). ^{1}H NMR (500 MHz, DMSO-d_6, δ in ppm): 6.55 (2 H, s), 5.12 (2 H, s), 4.77 (1 H, s, *-OH*), 3.42 (4 H, m, $-NC\underline{H}_2C\underline{H}_2OH$), 2.92 (2 H, s).

The synthesis of **c** (**3** in Table 2) was performed according to literature.[4] 4.83 g of compound **b** (23.1 mmol, 1.0 eq.) was solved in 160 mL 1,4-dioxane. Subsequently, 23.7 mL triethylamine (17.3 g, 170.9 mmol, 7.4 eq.), 6.21 g DMAP (50.8 mmol, 2.2 eq.) and 9.24 g succinic anhydride (92.4 mmol, 4.0 eq.) were added to the colorless solution and the reaction mixture was stirred at 40 °C overnight. The brown solution was poured into ice-cold 250 mL 1M HCl, extracted with DCM (3 × 100 mL) and dried over MgSO4. The solvent was removed under reduced pressure and the residue was recrystallized from ethanol, filtered off and washed with cold ethanol. The product was obtained as white crystals (2.84 g, 9.18 mmol, 40 %). ^{1}H NMR (500 MHz, DMSO-d_6, δ in ppm): 12.20 (1 H, s, $-COO\underline{H}$), 6.55 (2 H, s), 5.12 (2 H, s), 4.10 (2 H, t, J = 6.0 Hz, $-NCH_2C\underline{H}_2OCO$), 3.60 (2 H, t, J = 6.0 Hz, $-NC\underline{H}_2CH_2OCO$), 2.94 (2 H, s), 2.42 (4 H, s,$COC\underline{H}_2C\underline{H}_2COOH$).

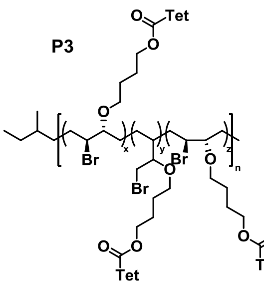
A.3. Example of Post-Polymerization Modification of Polybutadiene (PBD). The post-polymerization modification of polybutadiene with different carboxylic acid derivatives (shown in Scheme 2 in the main text) was performed in the following manner unless otherwise stated. The typical procedure is illustrated here for the post-polymerization modification corresponding to **P1** in Scheme 2, Table 1. Under anhydrous conditions, 0.10 g **PBD** ($M_{\text{n, SEC}}$ = 9 200 g mol^{-1}, 1.85 mmol of the double bond, 1.0 eq.) and 0.4068 g pentafluorobenzoic acid (**1**, 1.85 mmol, 1.0 eq. with respect to the double bonds of the polymer backbone) were dissolved in 11 mL dry THF. The reaction mixture was cooled to 0°C and 1.97 g NBS (11.09 mmol, 6.0 eq. with respect to the double bonds of the polymer backbone) were added. After stirring for 1 h at 0°C, the colorless reaction mixture was stirred for further 22h at ambient temperature (23°C). The residue was filtered off and the solution was concentrated under reduced pressure. Subsequently, the polymer was precipitated into ice cold MeOH and the mixture was centrifuged for 30 min. The liquid was decanted and the isolated residue was dried under high vacuum overnight, yielding an orange, rubber-like polymer. The purified polymer was characterized by NMR and SEC analysis.

P1 (Table 1, Scheme 2): ^{1}H NMR (500 MHz, $CDCl_3$, δ in ppm): 4.41 (s, 2H, $-CO-O-C\underline{H}_2-(CH_2)_2-CH_2-O-$), 4.16 (m, 1H, $-CH_2-CHO-C\underline{H}Br-CH_2-$), 3.74 (s, 1H, $-CO-O-CH_2-(CH_2)_2-C\underline{H}_2-O-$), 3.53 (m, 1H, $-CH_2-C\underline{H}O-CHBr-CH_2-$), 2.26 – 1.37 (m, 8H, $-CO-O-CH_2-(C\underline{H}_2)_2-CH_2-O-$, $-C\underline{H}_2-CHO-CHBr-C\underline{H}_2-$

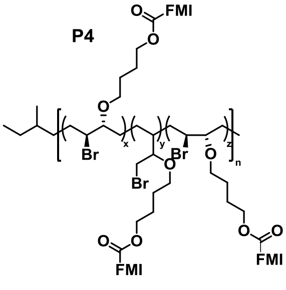

P1

).^{13}C NMR (125 MHz, CDCl$_3$, δ in ppm) 159.16 (1C, *-O-$\underline{C}$O-C$_{arom.}$-*), 146.48 (1C, *-$\underline{C}_{arom.}$-*), 144.43 (2C, *-$\underline{C}_{arom.}$-*), 136.81 (2C, *-$\underline{C}_{arom.}$-*), 108.46 (1C, *-O-CO-$\underline{C}_{arom.}$-*), 82.43 (1C, *CH$_2$-$\underline{C}$HO-CHBr-CH$_2$-*), 70.00 (1C, *-CH$_2$-$\underline{C}$HO-CHBr-CH$_2$-*), 68.11 (1C, *-CO-O-CH$_2$-(CH$_2$)$_2$-$\underline{C}$H$_2$-O-*), 66.75 (1C, *-CO-O-$\underline{C}$H$_2$-(CH$_2$)$_2$-CH$_2$-O-*), 58.90 (1C, *-CH$_2$-CHO-$\underline{C}$HBr-CH$_2$-*), 29.71 (1C, *-CH$_2$-CHO-$\underline{C}$HBr-CH$_2$-*), 26.75 (2C, *-CO-O-CH$_2$-($\underline{C}$H$_2$)$_2$-CH$_2$-O-*), 25.61 (2C, *-$\underline{C}$H$_2$-CHO-CHBr-$\underline{C}$H$_2$-*). ^{19}F NMR (471 MHz, CDCl$_3$, δ in ppm) -138.24 (s, 2F, *$\underline{F}_{ortho}$*), -148.65 (s, 1F, *$\underline{F}_{para}$*), -160.32 (s, 2F, *$\underline{F}_{meta}$*). SEC (THF): M_n = 19 000 g·mol^{-1}, $Đ$ = 1.09.

P3 (Table 1, Scheme 2): a beige colored powder (0.20 g). ^{1}H NMR (500 MHz, CDCl$_3$, δ in ppm): 8.32 (m, 2H, H$_{arom.}$), 8.19 (m, 2H, H$_{arom.}$), 8.09 (m, 2H, H$_{arom.}$), 8.07 (m, 2H, H$_{arom.}$), 4.46 (s, 2H, *-CO-O-C$\underline{H_2}$-(CH$_2$)$_2$-CH$_2$-O-*), 4.37 (m, 2H, *-CO-O-CH$_2$-(CH$_2$)$_2$-C$\underline{H_2}$-O-*), 4.07 (m, 1H, *-CH$_2$-CHO-C$\underline{H}$Br-CH$_2$-*), 3.90 (m, 3H, *C$\underline{H_3}$-O-*), 3.48 (m, 1H, *-CH$_2$-C$\underline{H}$O-CHBr-CH$_2$-*), 2.6-1.4 (m, 8H, *-C$\underline{H_2}$-CHO-CHBr-C$\underline{H_2}$-*, *-CO-O-CH$_2$-(C$\underline{H_2}$)$_2$-CH$_2$-O-*). ^{13}C NMR (125 MHz, CDCl$_3$, δ in ppm): 177.23 (1C, *-O-$\underline{C}$O-C-*), 166.15 (1C, *-N-$\underline{C}$-N-*), 165.43 (1C, *CH$_3$-O-$\underline{C}$-CH-*), 164.19 (1C, *-O-CO-$\underline{C}$-CH-*), 160.79 (1C, *-CH-$\underline{C}$-C-N-*), 132.03 (1C, *-N-$\underline{C}$-CH-*), 130.28 (2C, *-CO-C-$\underline{C}$H$_{arom.}$-CH$_{arom.}$-*), 127.02 (2C, *-CH$_{arom.}$-$\underline{C}$H$_{arom.}$-C-*), 121.56 (2C, *-C-$\underline{C}$H$_{arom.}$-CH$_{arom.}$-C-O-*), 114.88 (2C, *-C-CH$_{arom.}$-$\underline{C}$H$_{arom.}$-C-O-*), 69.98 (1C, *-CH$_2$-$\underline{C}$HO-CHBr-CH$_2$-*), 65.14 (1C, *-O-$\underline{C}$H$_2$-(CH$_2$)$_2$-CH$_2$-O-CO-*), 64.86 (1C, *-O-CH$_2$-(CH$_2$)$_2$-$\underline{C}$H$_2$-O-CO-*), 58.02 (1C, *-CH$_2$-CHO-$\underline{C}$HBr-CH$_2$-*), 55.78 (1C, *$\underline{C}$H$_3$-O-*), 45.04 (1C, *-CH$_2$-$\underline{C}$HO-CHBr-CH$_2$-*), 33.44 (1C, *-CH$_2$-CHO-$\underline{C}$HBr-CH$_2$-*), 29.70 (2C, *-O-CH$_2$-($\underline{C}$H$_2$)$_2$-CH$_2$-O-CO-*), 26.74 (1C, *-$\underline{C}$H$_2$-CHO-CHBr-CH$_2$-*), 25.73 (1C, *-CH$_2$-CHO-CHBr-$\underline{C}$H$_2$-*). SEC (THF): M_n = 17 300 g·mol^{-1}, $Đ$ = 1.09.


P3

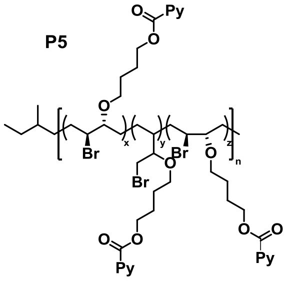
P4 (Table 1, Scheme 2): an orange sticky polymer (0.10 g). ^{1}H NMR (500 MHz, CDCl$_3$, δ in ppm): 6.50 (s, 2H, *-CH-(C$\underline{H}$)$_2$-CH-*), 5.25 (s, 2H, *-CO-CH-C$\underline{H}$-CH-*), 4.34 (t, 2H, *-CO-O-CH$_2$-(CH$_2$)$_2$-C$\underline{H_2}$-O-*), 4.24 (s, 2H, *-O-C$\underline{H_2}$-CH$_2$-N-*), 4.10 (s, 1H, *-CH$_2$-C$\underline{H}$Br-CHO-CH$_2$-*), 3.95 (m, 2H, *-CO-O-C$\underline{H_2}$-(CH$_2$)$_2$-CH$_2$-O-*), 3.74 (s 2H, *-O-CH$_2$-C$\underline{H_2}$-N-*), 3.47 (m, 1H, *-CH$_2$-CHBr-C$\underline{H}$O-CH$_2$-*), 2.88 (s, 1H, *-CO-C$\underline{H}$-CH-*), 2.57 (m, 2H, *-O-CO-(C$\underline{H}$)$_2$-CO-O-*), 2.30-1.61 (m, 8H, *-O-CH$_2$-(C$\underline{H_2}$)$_2$-CH$_2$-O-*, *-C$\underline{H_2}$-CHO-CHBr-C$\underline{H_2}$-*). ^{13}C NMR (125 MHz, CDCl$_3$, δ in ppm): 176.53 (2C, *-N-$\underline{C}$O-CH-*), 175.90 (1C, *-O-$\underline{C}$O-(CH$_2$)$_2$-*), 136.59 (2C, *-CO-CH-CH-$\underline{C}$H-*), 106.29 (2C, *-CO-CH-$\underline{C}$H-CH-*), 80.37 (1C, *-CH$_2$-$\underline{C}$HO-CHBr-CH$_2$-*), 68.47 (1C, *-O-$\underline{C}$H$_2$-(CH$_2$)$_2$-CH$_2$-O-*), 66.91 (1C, *-O-CH$_2$-(CH$_2$)$_2$-$\underline{C}$H$_2$-O-*), 61.55 (1C, *-O-$\underline{C}$H$_2$-CH$_2$-N-*), 57.85 (1C, *-CH$_2$-CHO-$\underline{C}$HBr-CH$_2$-*), 47.23 (2C, *-CO-$\underline{C}$H-CH-CH-*), 37.74 (1C, *-O-CH$_2$-$\underline{C}$H$_2$-N-*), 29.51 (2C, *-O-CO-($\underline{C}$H$_2$)$_2$-CO-O-*


P4

), 27.74 (2C, $-O-CH_2-(\underline{C}H_2)_2-CH_2-O-$), 23.81 (1C, $-CH_2-CHO-CHBr-\underline{C}H_2-$), 22.13 (1C, $-\underline{C}H_2-CHO-CHBr-CH_2-$). SEC (THF): M_n = 17 100 g·mol^{-1}, $Đ$ = 1.24.

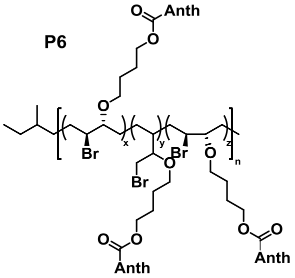
P5 (Table 1, Scheme 2): a beige colored powder (0.10 g). ^{1}H NMR (500 MHz, CDCl$_3$, δ in ppm): 9.26 (m, 1H, $\underline{H}_{arom.}$), 8.63 (m, 1H, $\underline{H}_{arom.}$), 8.25 – 8.06 (m, 7H, $\underline{H}_{arom.}$), 4.53 (s, 2H, $-CO-O-C\underline{H_2}-(CH_2)_2-CH_2-O-$), 4.39 (s, 1H, $-CH_2-CHO-C\underline{H}Br-CH_2-$), 4.11 (m, 1H, $-CH_2-CHO-C\underline{H}Br-CH_2-$), 3.97 (m, 1H, $-C\underline{H_2}-CHO-CHBr-CH_2-$), 3.74 (m, 2H, $-CO-O-CH_2-(CH_2)_2-C\underline{H_2}-O-$), 3.42 (m, 1H, $-CH_2-C\underline{H}O-CHBr-CH_2-$), 2.30 – 1.24 (m, 8H, $-CO-O-CH_2-(CH_2)_2-C\underline{H_2}-O-$, $-CH_2-CHO-C\underline{H}Br-CH_2-$). ^{13}C NMR (125 MHz, CDCl$_3$, δ in ppm): 168.11 (1C, $-O-\underline{C}O-C_{arom.}-$), 131.12 – 124.27 (15C, $-\underline{C}_{arom.}-$), 115.04 (1C, $-O-CO-\underline{C}_{arom.}-$), 83.51 (1C, $-CH_2-\underline{C}HO-CHBr-CH_2-$), 68.10 (1C, $-CO-O-CH_2-(CH_2)_2-\underline{C}H_2-O-$), 65.11 (1C, $-CO-O-\underline{C}H_2-(CH_2)_2-CH_2-O-$), 58.35 (1C, $-CH_2-CHO-\underline{C}HBr-CH_2-$), 56.88 (1C, $-CH_2-\underline{C}HO-CHBr-CH_2-$), 34.21 (1C, $-CH_2-CHO-\underline{C}HBr-CH_2-$), 30.84 (2C, $-CO-O-CH_2-(\underline{C}H_2)_2-CH_2-O-$), 29.06 (1C, $-\underline{C}H_2-CHO-CHBr-CH_2-$), 25.73 (1C, $-CH_2-CHO-CHBr-\underline{C}H_2-$). SEC (THF): M_n = 15 200 g·mol^{-1}, $Đ$ = 1.21.

P5



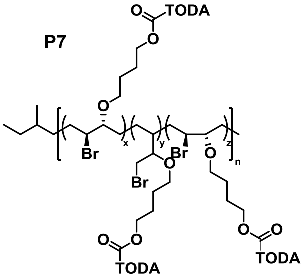
P6 (Table 1, Scheme 2): a beige colored powder (0.33 g). ^{1}H NMR (500 MHz, CDCl$_3$, δ in ppm): 8.92 (m, 1H, $\underline{H}_{arom.}$), 8.39 (m, 2H, $\underline{H}_{arom.}$), 8.31 (m, 2H, $\underline{H}_{arom.}$), 7.81 (m, 2H, $\underline{H}_{arom.}$), 4.51 (s, 2H, $-CO-O-C\underline{H_2}-(CH_2)_2-CH_2-O-$), 4.43 (s, 2H, $-CO-O-CH_2-(CH_2)_2-C\underline{H_2}-O-$), 4.12 (m, 1H, $-CH_2-CHO-C\underline{H}Br-CH_2-$), 3.45 (m, 1H, $-CH_2-C\underline{H}O-CHBr-CH_2-$), 2.46 – 1.36 (m, 8H, $-CO-O-CH_2-(C\underline{H_2})_2-CH_2-O-$, $-C\underline{H_2}-CHO-CHBr-C\underline{H_2}-$).^{13}C NMR (125 MHz, CDCl$_3$, δ in ppm): 182.24 (2C, $-C_{arom.}-\underline{C}O-C_{arom.}-$), 164.97 (1C, $-O-\underline{C}O-C_{arom.}-$), 136.07 (1C, $-O-CO-\underline{C}_{arom.}-$), 135.17 (2C, $-\underline{C}_{arom.}-$), 134.54 (2C, $-\underline{C}_{arom.}-$), 133.34 (2C, $-\underline{C}_{arom.}-$), 128.55 (1C, $-\underline{C}_{arom.}-$), 127.58 (2C, $-\underline{C}_{arom.}-$), 127.41 (2C, $-\underline{C}_{arom.}-$), 81.99 (1C, $-CH_2-CHO-\underline{C}HBr-CH_2-$), 70.02 (1C, $-CH_2-\underline{C}HO-CHBr-CH_2-$), 65.69 (1C, $-CO-O-CH_2-(CH_2)_2-\underline{C}H_2-O-$), 65.24 (1C, $-CO-O-\underline{C}H_2-(CH_2)_2-CH_2-O-$), 58.22(1H, $-CH_2-CHO-\underline{C}HBr-CH_2-$), 33.83 (1H, $-CH_2-\underline{C}HO-CHBr-CH_2-$), 29.66 (2C, $-CO-O-CH_2-(\underline{C}H_2)_2-CH_2-O-$), 25.68 (2C, $-\underline{C}H_2-CHO-CHBr-\underline{C}H_2-$). SEC (THF): M_n = 15 000 g·mol^{-1}, $Đ$ = 1.14.

P6



P7 (Table 1, Scheme 2): black colored, rubberlike polymer (0.25 g). ^{1}H NMR (500 MHz, CDCl$_3$, δ in ppm): 4.35 (m, 2H, $-O-CO-C\underline{H_2}-O-$), 4.15 (m, 2H, $-CO-O-C\underline{H_2}-(CH_2)_2-CH_2-O-$), 4.08 (m, 1H, $-CH_2-CHO-C\underline{H}Br-CH_2-$), 3.70 (m, 8H, $-(O-(C\underline{H_2})_2-O)_2-$), 3.56 (m, 1H, $-CH_2-C\underline{H}O-CHBr-CH_2-$), 3.46 (m, 3H, $-O-C\underline{H_3}$), 3.38 (m, 2H, $-CO-O-CH_2-(CH_2)_2-C\underline{H_2}-O-$), 2.49 – 1.22 (m, 8H, $-CO-O-CH_2-(C\underline{H_2})_2-CH_2-O-$, $-C\underline{H_2}-CHO-CHBr-C\underline{H_2}-$). SEC (THF): M_n = 15 300 g·mol^{-1}, $Đ$ = 1.17.

P7



A.4. Calculation of the Isolated Yield of Modified Polybutadiene (PBD). The calculations of the isolated yield of the modified polybutadiene polymers were adopted and modified accordingly from the literature.[5]

$$\underset{\text{(mmol)}}{\text{mole of modified PBD}} = \frac{\text{A x B}}{\underset{\text{(mg/mmol)}}{\text{C + (D x E x F)}}}$$

A = weight of product polymer (mg)

B = ratio of modification calculated by ^{1}H NMR

C = average molecular weight of PBD (mg/mmol)

D = number of double bonds

E = incorporation ratio of modification calculated by ^{1}H NMR

F = molecular weight of each modification unit

$$\text{yield \%} = \frac{\text{mole of modified PBD (mmol)}}{\text{mole of PBD (mmol)}} \text{ x 100}$$

A.5. A Typical Procedure for the Synthesis of Modified Polybutadiene (PBD) with 1:1 Ratio of Mixed Acid Derivatives (Entry P8.1, Table 1). In a 100 mL two-neck flask under anhydrous conditions 0.20 g **PBD** ($M_{\text{n, SEC}}$ = 9 200 g mol^{-1}, 3.70 mmol of the double bond, 2.0 eq.), 0.55 g tetrazole (**2**) (1.85 mmol, 1.0 eq. with respect to the double bonds of the polymer backbone) and 0.57 g protected maleimide (**3**) (1.85 mmol, 1.0 eq. with respect to the double bonds of the polymer backbone) were dissolved in 22 mL of dry THF. The dark red reaction mixture was cooled to 0°C and 3.95 g NBS (22.18 mmol, 6.00 eq. with respect to the double bonds of the polymer backbone) were added. After stirring for 1h at 0°C the red-orange reaction mixture was stirred for further 22 h at ambient temperature (23°C). The residue was filtered off and the solution was concentrated under reduced pressure. Subsequently, the isolated polymer was precipitated into cold MeOH, filtered off and dried under high vacuum overnight, thus yielding a light orange colored, solid polymer. SEC (THF): M_n = 15 500 g·mol^{-1}, *Đ* = 1.14.

A.6. A Typical Procedure for the Synthesis of Modified Polybutadiene (PBD) with 1.9:1 Ratio of Mixed Acid Derivatives (Entry P8.2, Table 1). In a 100 mL two-neck flask under anhydrous conditions, 0.20 g **PBD** ($M_{\text{n, SEC}}$ = 9 200 g mol$^{-1,}$ 3.70 mmol of the double bond, 2.0 eq.), 0.75 g protected maleimide (**3**) (2.40 mmol, 1.3 eq. with respect to the double bonds of the polymer backbone) and 0.39 g tetrazole (**5**) (1.30 mmol, 0.7 eq. with respect to the double bonds of the polymer backbone) were dissolved in 22 mL of dry THF. The dark red reaction mixture was cooled to 0°C and 3.95 g NBS (22.18 mmol, 6.00 eq. with respect to the double bonds of the polymer backbone) were added. After stirring for 1h at 0°C the red-orange reaction mixture was stirred for further 22 h at ambient temperature (23°C). After the precipitation into cold MeOH, the mixture was centrifuged for 30 min, the liquid part was decanted and the polymer was dried under high vacuum overnight, yielding a light yellow colored, sticky polymer (**P8.2**, m = 0.10 g). ^{1}H NMR (500 MHz, $CDCl_3$, δ in ppm): 8.31 (m, 2H, $\underline{H}_{arom.}$), 8.20 (m, 2H, $\underline{H}_{arom.}$), 8.10 (m, 2H, $\underline{H}_{arom.}$), 7.06 (m, 2H, $\underline{H}_{arom.}$), 6.50 (s, 2H, $-CH-(C\underline{H})_2-CH-$), 5.26 (s, 2H, $-CH-C\underline{H}-CH-CO-$), 4.47 (s, 4H, $-CO-O-C\underline{H}_2-(CH_2)_2-CH_2-O-$), 4.39 (m, 4H, $-CO-O-CH_2-(CH_2)_2-C\underline{H}_2-O-$), 4.24 (m, 2H, $-N-CH_2-C\underline{H}_2-O-CO-$), 4.09 (m, 2C, $-CH_2-CHO-C\underline{H}Br-CH_2-$), 3.90 (s, 3H, $-O-C\underline{H}_3$), 3.74 (m, 2H, $-N-C\underline{H}_2-CH_2-O-CO-$), 3.49 (m, 2H, $-CH_2-C\underline{H}O-CHBr-CH_2-$), 2.96 (s, 2H, $-CH-CH-C\underline{H}-CO-$), 2.87 (s, 4H, $-O-CO-(C\underline{H}_2)_2-CO-O-$), 2.48 – 1.39 (m, 16H, $-CO-O-CH_2-(C\underline{H}_2)_2-CH_2-O-$, $-C\underline{H}_2-CHO-CHBr-C\underline{H}_2-$). SEC (THF): M_n = 18 400 g·mol^{-1}, $Đ$ = 1.17.

A.7. A Typical Procedure for the Synthesis of (Pro)-Fluorescent Single-Chain Nanoparticles (SCNPs) via Photoinduced Nitrile Imine Intramolecular Cross-Ligation. In a 2 L round bottom flask, 34.5 mg of polymer **P8.2** were dissolved in 1.5 L DCM. The solution was irradiated with UV light (Aramid B6, 290 – 350 nm, maximum 320 nm). After 60 min reaction time, the resulting solution was concentrated, recovered by precipitation with ice cold MeOH, and dried under vacuum at 25 °C for 24 h. ^{1}H NMR (500 MHz, $CDCl_3$, δ in ppm): 8.52 – 8.02 (m, 6H, $\underline{H}_{arom.}$), 7.02 (m, 2H, $\underline{H}_{arom.}$), 6.51 (s, 2H, $-CH-C\underline{H}-C-$), 5.26 (m, 2H, $-C\underline{H}-CH-C-$), 4.37 – 3.08 (m, 19H, $-CH_2-C\underline{H}O-C\underline{H}Br-CH_2-$, $-CO-O-C\underline{H}_2-(CH_2)_2-C\underline{H}_2-O-$, $-O-C\underline{H}_3$, $-CO-O-(C\underline{H}_2)_2-O-CO-$), 2.88 (m, 2H, $-N-CO-C\underline{H}-CH-$), 2.77 (m, 4H, $-O-CO-(C\underline{H}_2)_2-CO-O-$), 2.29 – 0.79 (m, 16H, $-C\underline{H}_2-CHO-CHBr-C\underline{H}_2-$, $-CO-O-CH_2-(C\underline{H}_2)_2-C\underline{H}_2-O-$). SEC (THF): M_n = 10 400 g·mol^{-1}, $Đ$ = 1.34.

A.8. A Typical Procedure for the Substitution of the Pendent Bromine Group in Modified Polymer P6 with Sodium Azide. In a 10 mL round bottom flask equipped with a stir bar, 10.0 mg of **P6** (0.022 mmol) was suspended in 5.0 mL of DMF to which sodium azide (7.15 mg, 0.110 mmol) was added and stirred for 24 h under an N_2 atmosphere. Subsequently, the solution was precipitated in an ice-cold MeOH and the precipitate was washed with methanol and dried under a stream of nitrogen to afford the desired post-modified polymer **P6M.** The purified polymer was characterized by NMR and SEC analysis. Compare Figure S19 for the corresponding ^{1}H NMR characterization data. M_n = 15 900 g·mol^{-1}, $Đ$ = 1.18.

B.Measurements and Analysis

B.1. Nuclear Magnetic Resonance (NMR) Spectroscopy. All 1D and 2D NMR spectra were acquired in $CDCl_3$ or DMSO-d_6 as solvents using a Bruker Avance spectrometer equipped with Ultrashield magnets, and operating at 500 MHz for ^1H NMR and 125 MHz for ^{13}C NMR. The ^1H NMR spectra were referenced to the residual proton impurities at δ H 2.50 ppm and 7.26 ppm in DMSO-d_6 and $CDCl_3$, respectively. The ^{13}C-NMR spectra were referenced at δ C 39.52 and 77.00 ppm to ^{13}DMSO and $^{13}CDCl_3$, respectively. All NMR data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q =quartet), coupling constant(s) in Hertz (Hz) and integration. Multiplets (m) were reported over the range (ppm) where they appeared at the indicated field strength.

B.2. Size Exclusion Spectroscopy (SEC). The apparent number average molar mass (M_n) and the molar mass distribution [$Đ$ (polydispersity index) = M_w/M_n] values of the polymers were determined using SEC measurements which were performed on a TOSOH Eco-SEC HLC-8320 GPC System, comprising an autosampler, a SDV 5 µm bead-size guard column (50 × 8 mm, PSS) followed by three SDV 5 µm columns (300 × 7.5 mm, subsequently 100 Å, 1000 Å and 10^5 Å pore size, PSS), and Waters 2487 dual wavelength absorbance detector (analysis at 254 nm) in series with a refractive index detector using tetrahydrofuran (THF) as the eluent at 30 °C with a flow rate of 1 $mL\cdot min^{-1}$. The SEC system was calibrated using linear polystyrene standards ranging from 266 to $2.52\cdot10^6$ $g\cdot mol^{-1}$. Calculation of the molecular weight proceeded via the Mark-Houwink-Sakurada (MHS) parameters for polystyrene (PS) in THF at 30 °C, i.e., $K = 13.63\cdot10^{-3}$ $mL\cdot g^{-1}$, $\alpha = 0.714$.

B.3. Attenuated Total Reflectance Infrared Spectroscopy (ATR-IR). ATR IR measurements were conducted employing a VERTEX 80 research spectrometer with a PIKE MIRacle ATR unit and a DTGS detector. The spectra were recorded with a resolution of 4 cm^{-1} and 128 scans and underwent baseline correction as well as atmospheric compensation.

B.4. Dynamic Light Scattering (DLS). The apparent hydrodynamic diameters ($D_{h,app}$) were determined at 25 °C by means of a dynamic light scattering (DLS) analysis using a Zetasizer Nano ZS light scattering apparatus (Malvern Instruments, UK) equipped with He-Ne laser (at a wavelength of 633 nm, 4 mW). The Nano ZS instrument incorporates a non-invasive backscattering (NIBS) optic with a detection angle of 173°. The polymer solutions were prepared in THF and were subsequently filtered into quartz cuvettes. The prepared samples were stabilized prior to DLS analysis at ambient temperature. All values of the apparent hydrodynamic diameter for each polymer mixture were averaged over six measurements (60 runs/measurement), and were automatically provided by the instrument using a cumulative analysis.

C. Additional Data and Figures

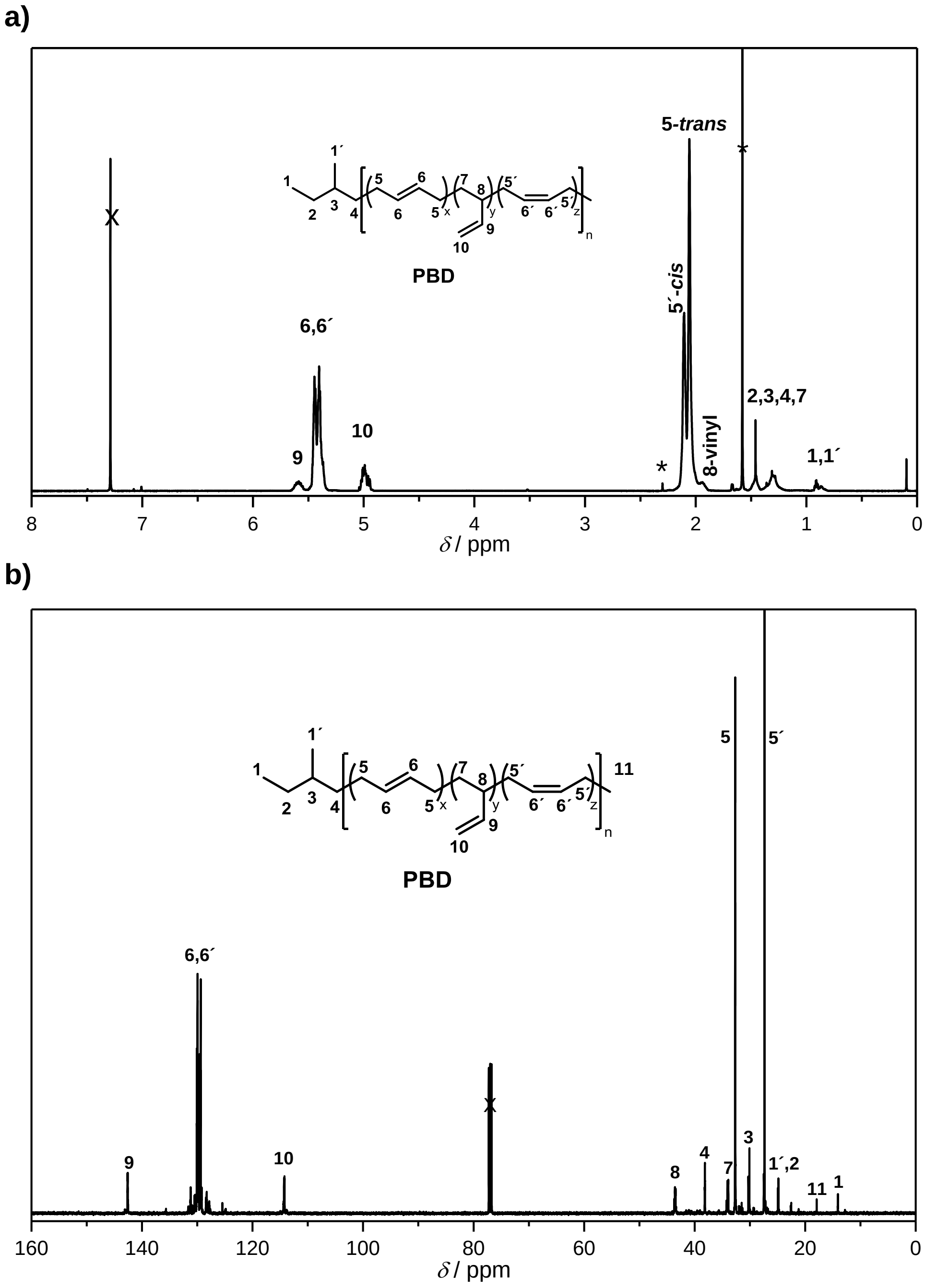


Figure S1. ^{1}H (500 MHz) and ^{13}C (125 MHz) spectra of **PBD**, respectively **(a)** and **(b)**. NMR spectra recorded in $CDCl_3$ at ambient temperature.

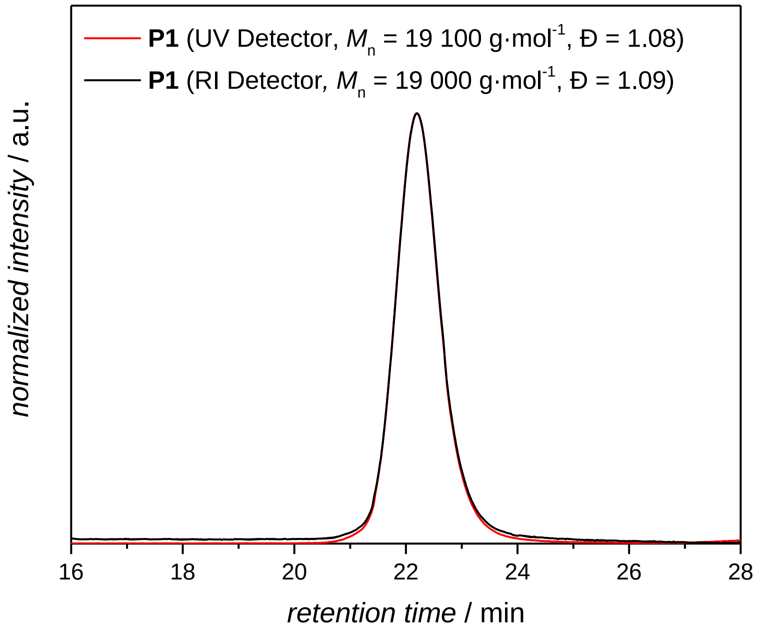


Figure S2. SEC elution traces of the obtained polymer, **P1**, after MCR post-polymerization functionalization of **PBD** with 2,3,4,5,6-pentafluorobenzoic acid (PFB, Table 1, Entry 1) and NBS as halogen source. Red and black traces represent the SEC measurements performed with two different detectors, respectively UV and RI. Determined in THF at 30 °C *vs.* linear PS standards.

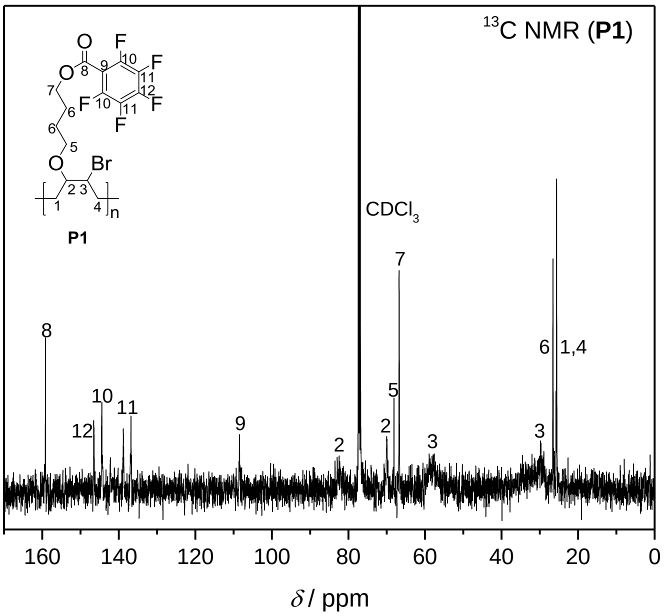


Figure S3. ^{13}C NMR (125 MHz) spectrum of **P1**. The spectrum was recorded in $CDCl_3$ at ambient temperature.

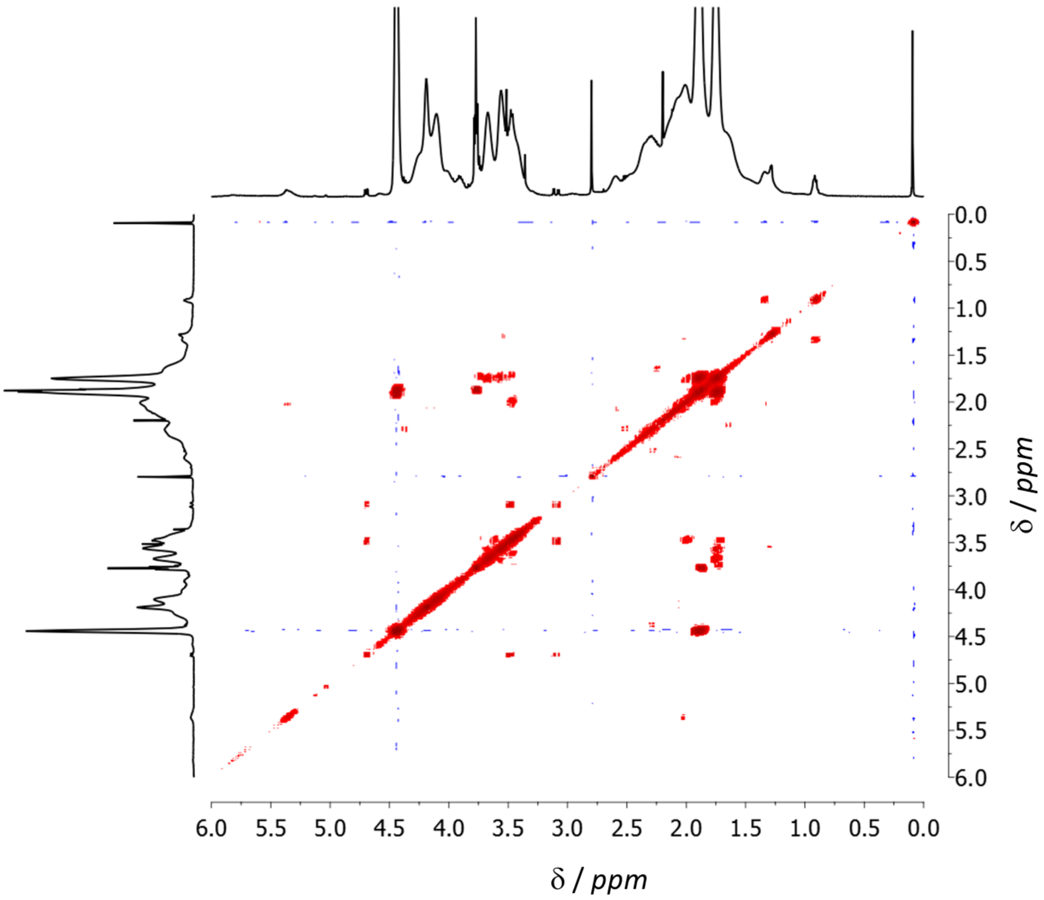


Figure S4. COSY spectrum of **P1** recorded in $CDCl_3$ at ambient temperature.

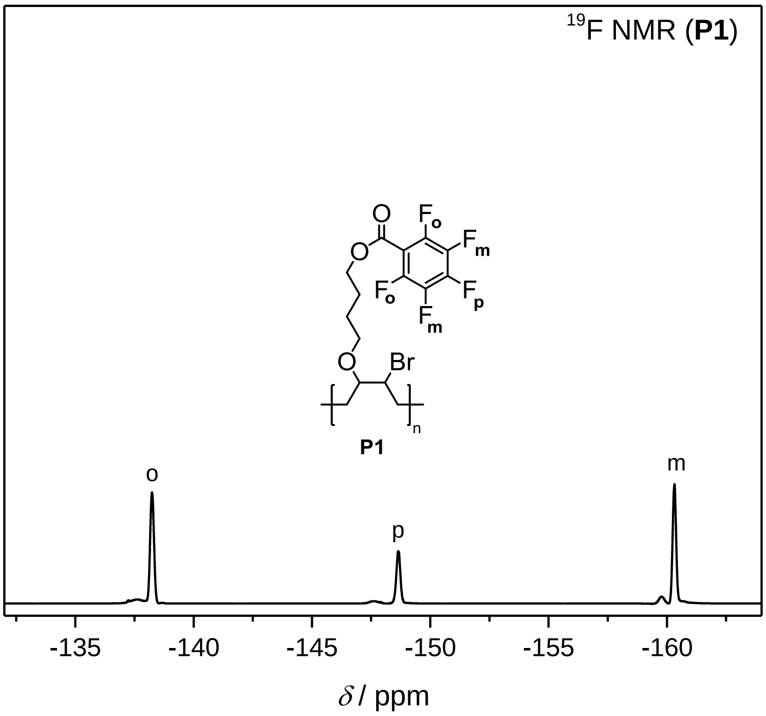


Figure S5. ^{19}F NMR spectrum of **P1** recorded in $CDCl_3$ at ambient temperature.

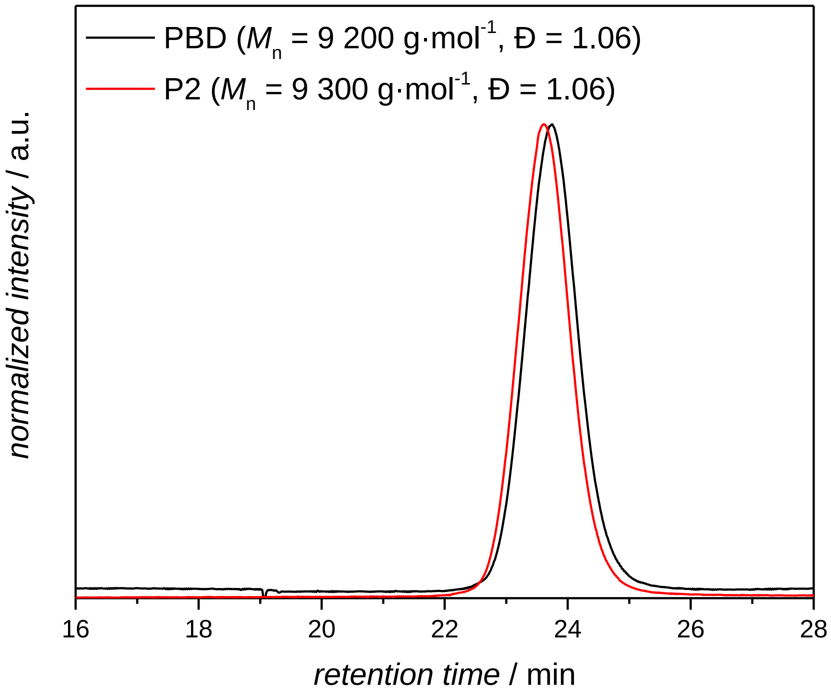


Figure S6: SEC elution traces of **PBD** and the obtained polymer after MCR post-modification functionalization with NBS as halogen source (**P2**). The SEC traces were determined in THF at 30 °C *vs.* linear PS standards.

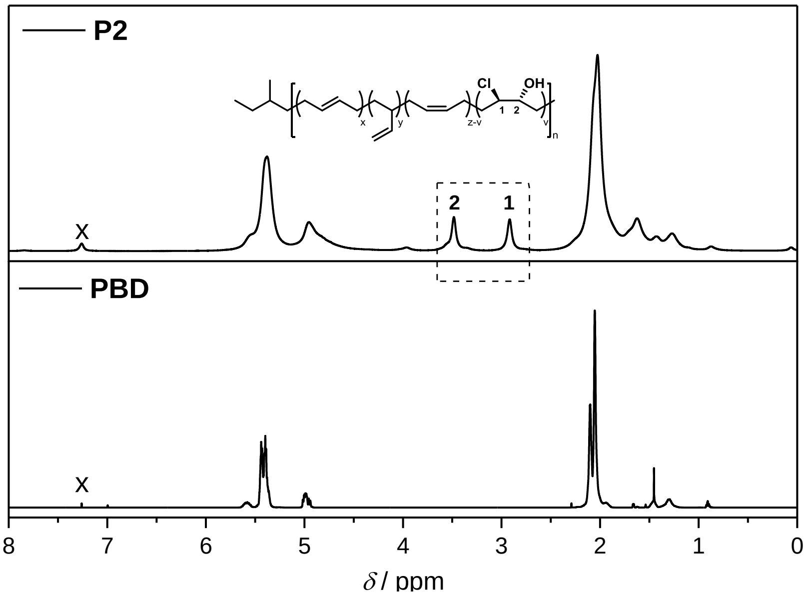


Figure S7. ^{1}H NMR (500 MHz) spectra of **P2** (top) and **PBD** (bottom), respectively. The NMR spectra were recorded in $CDCl_3$ at ambient temperature.

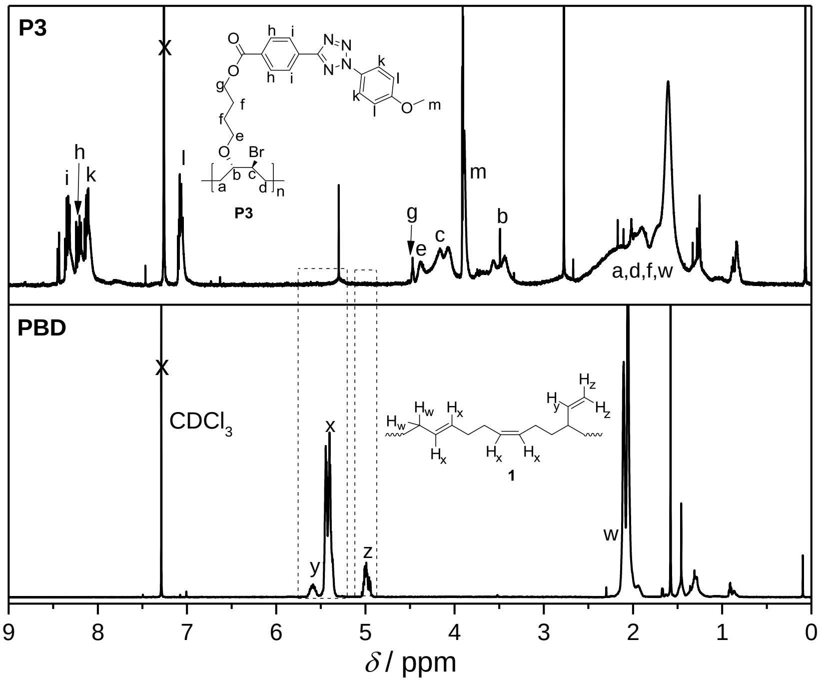


Figure S8. ^{1}H NMR (500 MHz) spectra of **P3** (top) and **PBD** (bottom), respectively. NMR spectra were recorded in CDCl$_3$ at ambient temperature.

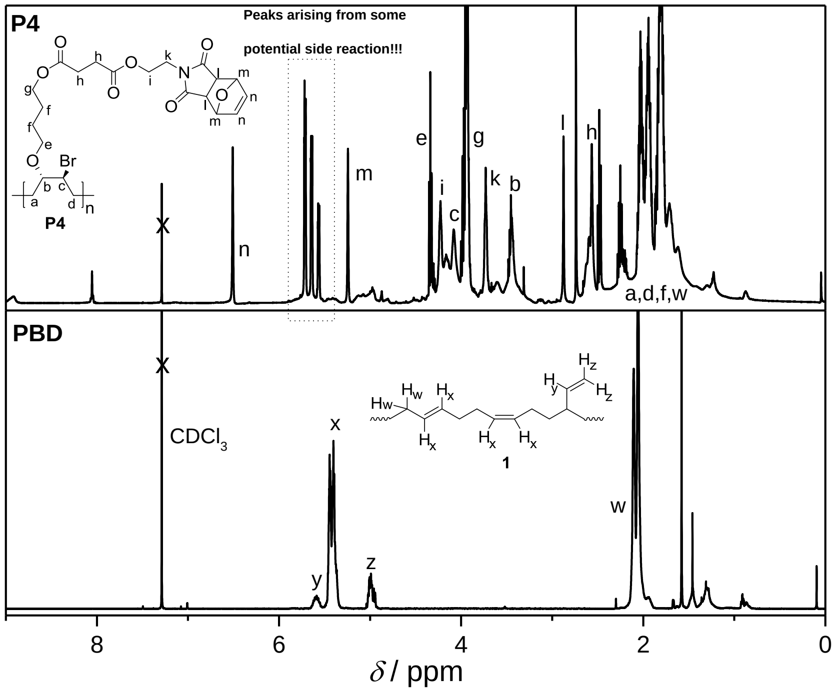


Figure S9. ^{1}H NMR (500 MHz) spectra of **P4** (top) and **PBD** (bottom), respectively. NMR spectra were recorded in CDCl$_3$ at ambient temperature.

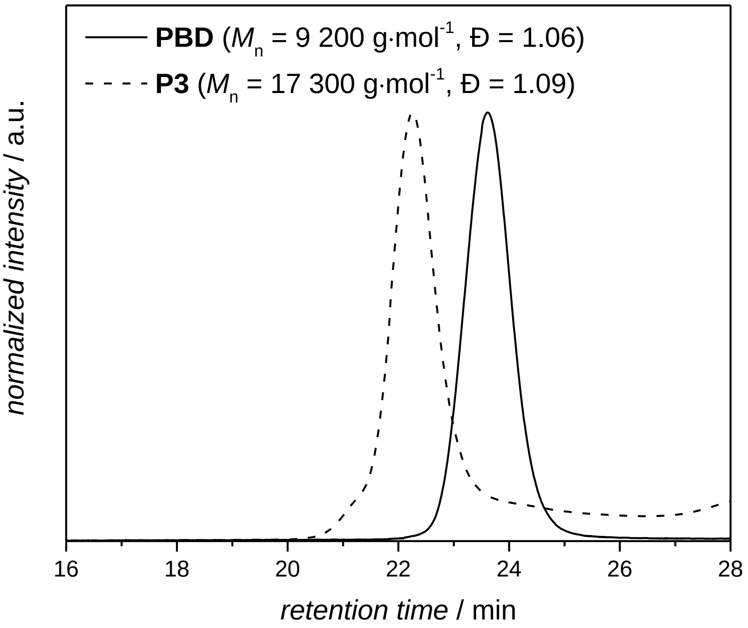


Figure S10. SEC traces of the **P3** and **PBD**. Determined in THF at 30 °C *vs.* linear PS standards.

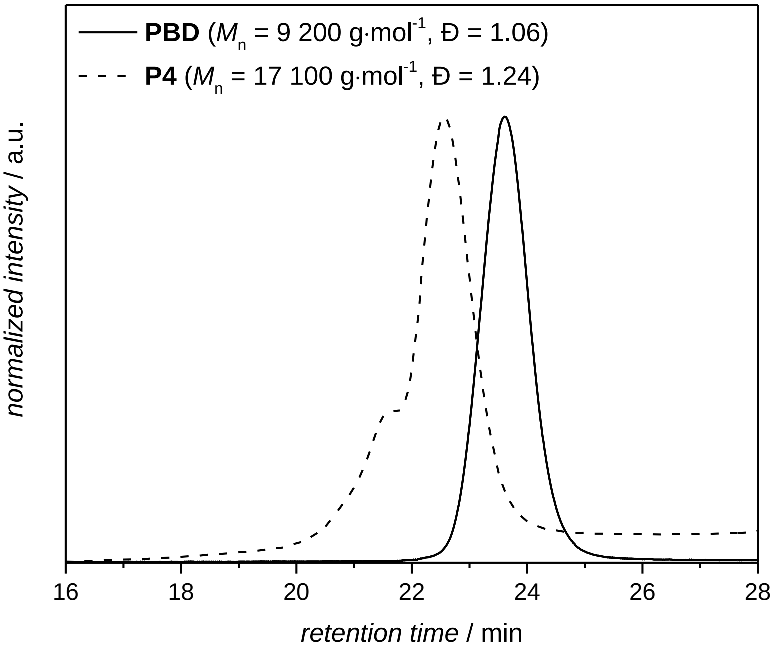


Figure S11. SEC elution traces of the **P4** and **PBD**. Determined in THF at 30 °C *vs.* linear PS standards.

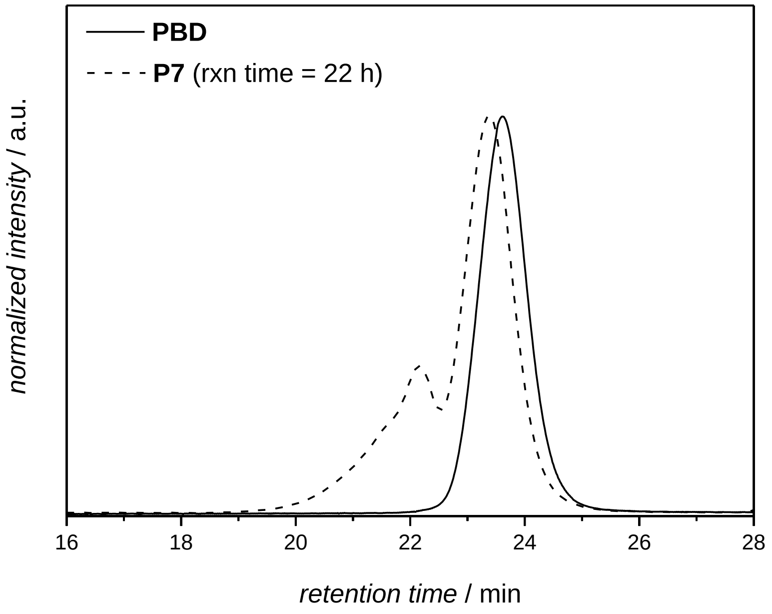


Figure S12. SEC traces of polymer **P7** and **PBD**. The post-polymerization reaction for **P7** was performed for 22 h. Determined in THF at 30 °C *vs.* linear PS standards.

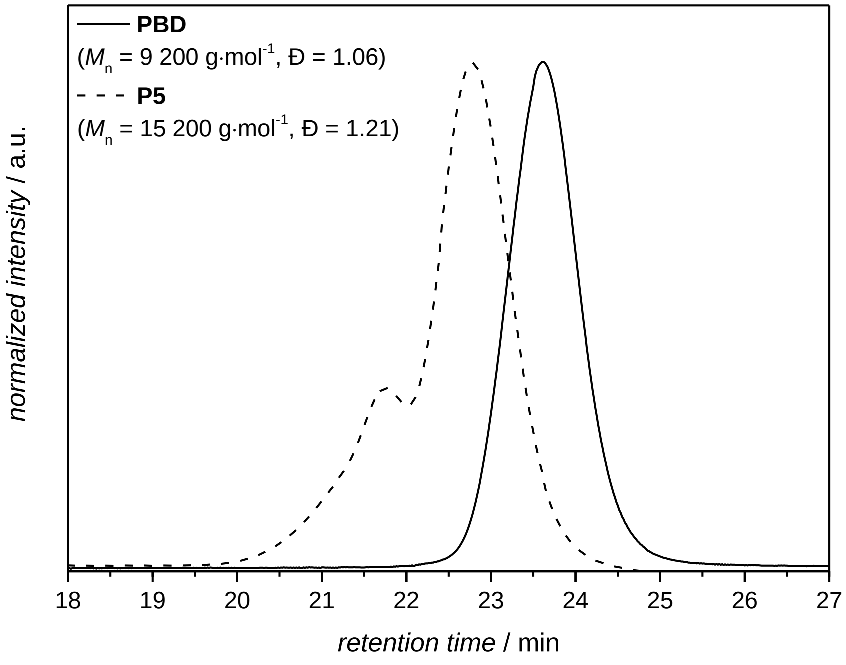


Figure 13. SEC traces of polymer **P5** and **PBD**. The post-polymerization reaction for **P5** was performed for 5 h. Determined in THF at 30 °C *vs.* linear PS standards.

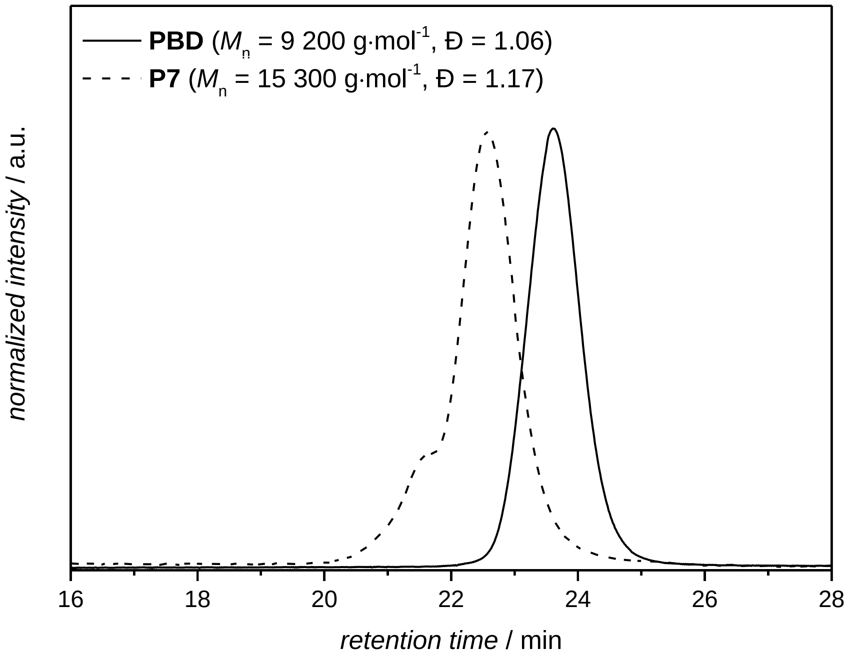


Figure S14. SEC traces of polymer **P7** and **PBD**. The post-polymerization reaction for **P7** was performed for 8 h. Determined in THF at 30 °C *vs.* linear PS standards.

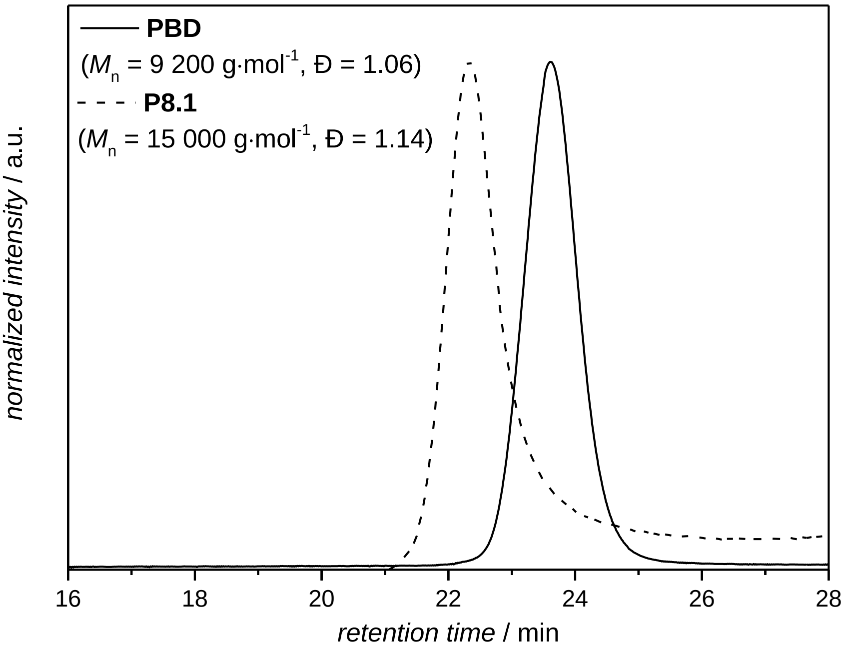


Figure S15. SEC traces of polymer **P8.1** and **PBD**. Determined in THF at 30 °C *vs.* linear PS standards.

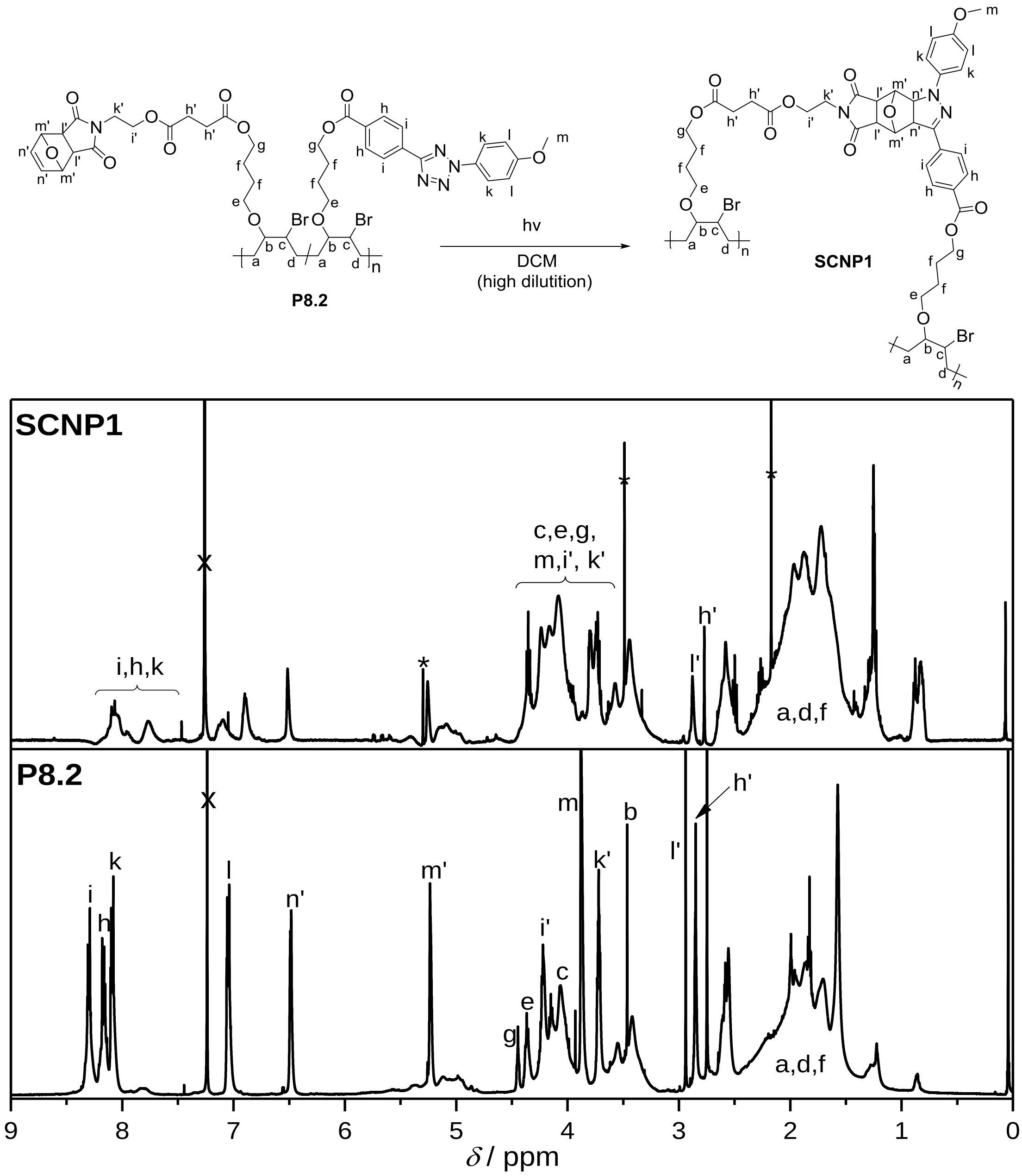


Figure S16. The ^{1}H NMR characterization data of the linear, functional precursor **P8.2** as well as of the **SCNP1**.

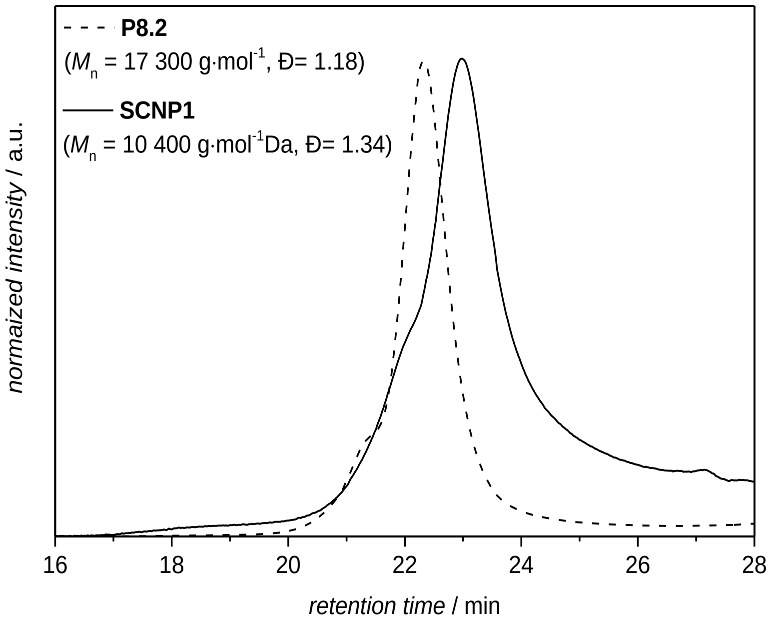


Figure S17. SEC traces of post-polymerization functionalized polymer **P8.2** and **SCNP1**. The SEC traces were measured in THF at 30 °C.

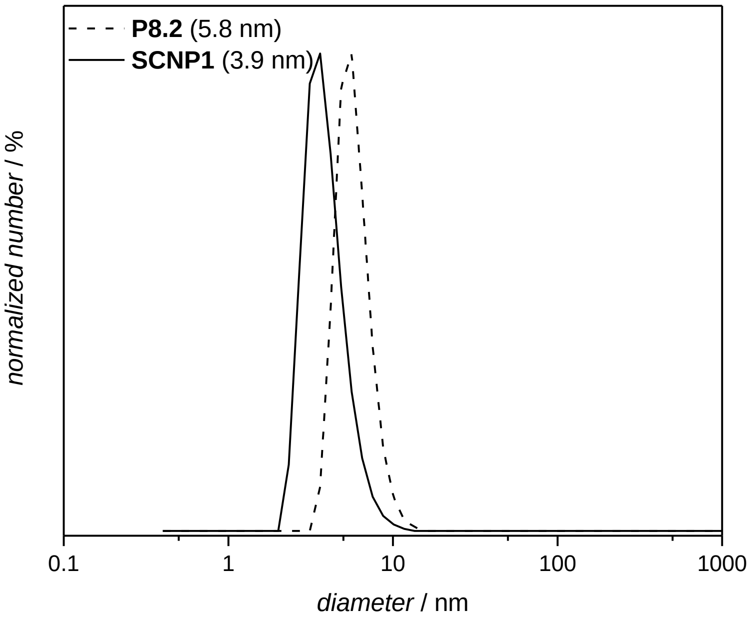


Figure S18. Comparative DLS traces of post-polymerization functionalized polymer **P8.2** and **SCNP1**.

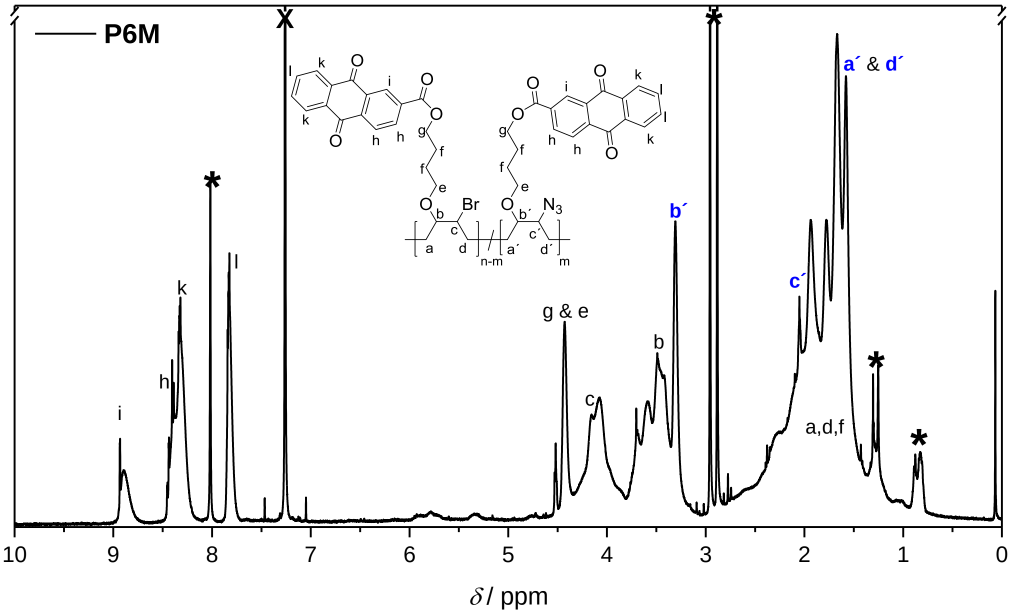


Figure S19. The ^{1}H NMR characterization data of azide-functionalized polymer **P6M**. NMR spectra was recorded in $CDCl_3$ at ambient temperature.

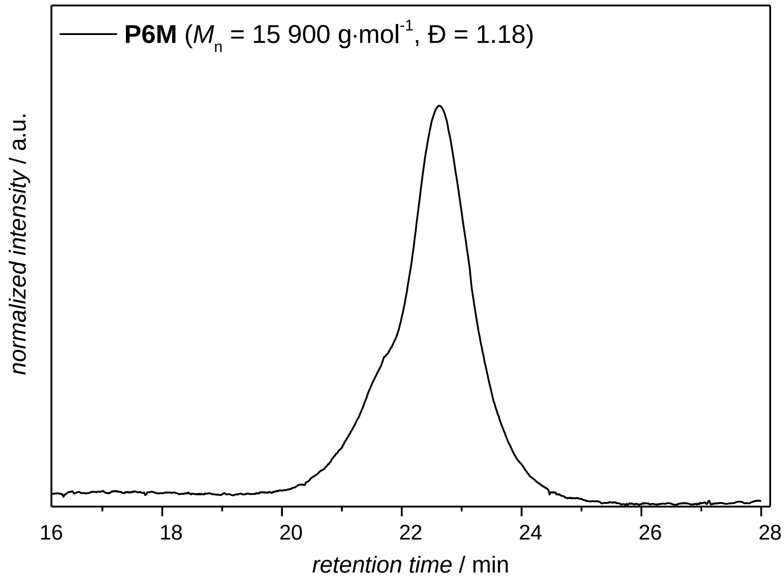


Figure S20. SEC trace of polymer **P6M** obtained via the substitution of the pendent bromine group in polymer **P6** with sodium azide. Determined in THF at 30 °C *vs.* linear PS standards.

D. References

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