Biocompatible Two-Dimensional Platelets with Tunable Sizes from Polycarbonate-Based Block Copolymers

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Supporting information

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1. General Information

1.1 Materials and methods

THF and methylene chloride (DCM) solvents were dried by a standard "Grubbs" drying system and were stored over 4 Å molecular sieves. Methoxy PEG (5 kDa) was purchased from Polymer Source. All other commercial reagents were purchased from Sigma-Aldrich, Combi-Blocks, and TCI. They were used without further purification unless noted. Trimethylene carbonate was purchased from Combi-Blocks and dried in the oven for 48 h before use in the nitrogen-filled glovebox. 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) was dried by stirring over CaH_2 and vacuum distillation. N-(3,5-trifluoromethyl)phenyl-N-cyclohexyl- thiourea (TU) was prepared according to reported procedures.[1]

1.2 Instrumentation

NMR spectroscopy

^{1}H NMR spectra were recorded on Bruker 500 (500 MHz) or Bruker 300 (300 MHz) at the University of Victoria. The peaks were internally referenced to TMS (0.00 ppm) or residual undeuterated solvent signal. Chemical shifts are quoted in parts per million, while the spectra are referenced to the residual solvent peak. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad.

Ultrasonication

Micelle sonication was carried out using an ultrasonic processor, UP100H. The instrument was operated at an amplitude of 90% at 0 °C.

Gel permeation chromatography (GPC).

GPC measurements were carried out with the Malvern chromatography system equipped with a refractive index (RI), UV/Vis photodiode detector array, and viscometer. Bu_4NBr/THF (1 wt %) was used as the eluent (flow rate = 1 mL/min). Results were calibrated against polystyrene standards (Viscotek). Samples were prepared at 1 mg/mL in the eluent.

Differential scanning calorimetry (DSC)

DSC analysis was performed on a TA Instruments Q100 coupled to a RCS90 refrigerated cooling system with scan rates of 10 °C/min. DSC samples of each homopolymer (5-8 mg) were placed in hermetic aluminium pans The DSC scan was recorded by heating from -60 ℃ to 180 ℃, followed by annealing at 180 ℃ for 4 min, and subsequently cooling to -60 ℃.

UV–vis spectroscopy

UV–vis measurements were performed on an Agilent Cary 60 UV-vis spectrophotometer Xenon flash lamp (80 Hz).

Laser scanning confocal microscopy (LSCM).

Confocal imaging was performed using the ZEISS LSM 880 Axio Observer. Nanoplatelet solutions were aliquoted onto glass coverslips and dried before imaging. Fluorophores were excited using an argon laser operating at 488 nm. Confocal images were obtained using digital detectors with observation windows of 500 – 620 nm. The resulting images were obtained as digital false-color images and then color-coded as green.

Atomic force microscopy (AFM)

AFM analysis was obtained using a 5500 Atomic Force Microscope (Agilent Technologies). The images were recorded in AC mode with a scanning speed of 1.0 μm/s in an area of 4.0 μm^2 at 1024×1024 resolution. The samples for AFM were prepared on a silicon wafer by casting a nanoplatelet solution (in ~ 100% MeOH, 10 μL, 0.05 mg/mL) onto the silicon wafer.

The X-ray diffraction (XRD)

XRD data was taken using an EMPYREAN diffractometer system. The instrument uses copper Kα radiation (1.5 Å). The measurements were performed on thin films cast from nanoplatelet colloidal dispersions.

Transmission electron microscopy (TEM).

TEM measurements were performed on a JEOL 1011 microscope with a CCD camera, operating at an accelerating voltage of 80 kV. Samples were prepared by drop-casting 9 μL of nanoplatelet solutions onto a carbon-coated copper grid, followed by drop-casting 9 μL of uranyl acetate in MeOH (3 wt %) to negatively stain the samples. The sample concentration for TEM analysis was about 0.5 mg/mL based on nanoplatelet concentration. Copper grids (400 mesh) were purchased from Ted Pella, and carbon films of about 8 nm were prepared on mica by carbon sputtering with a Leica ACE 600 carbon coater. Then, the carbon films were deposited onto the copper grids by floatation on water. Images were analyzed with the software Image J (NIH, USA). For the statistical analyses, more than 100 nanoplatelets in several images were traced by the

software to obtain the area or other information. The number average micelle areas (A_n) and weight average micelle areas (A_w) were calculated as shown below from measurements of the contour areas (A). (A, area of the object; n, number).

The distribution of micelle sizes was characterized by $Đ_A = A_w/A_n$.

$$A_n = \frac{\sum_{i=1}^{n} N_i A_i}{\sum_{i=1}^{n} A_i}$$

$$A_w = \frac{\sum_{i=1}^{n} N_i A_i^2}{\sum_{i=1}^{n} N_i A_i}$$

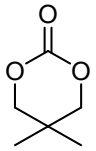
Values of the standard deviation of the size distribution σ were determined.

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n} (A_i - A_n)^2}{n}}$$

2. Synthetic Procedures

2.1 Monomer syntheses

Synthesis of 2,2-dimethyltrimethylene carbonate (DTC)



2,2-dimethyl-1,3-propanediol (4.16 g, 1 equiv) was dissolved in 100 mL of THF and cooled to 0 ℃. Ethyl chloroformate (10 mL,10.8 g, 2.5 equiv) was added in one portion, while Et_3N (13.3 mL, 10.1 g, 2.5 equiv) was added dropwise at 0 ℃. After stirring at 0 ℃ for 1 h, the reaction mixture was warmed up to room temperature and stirred overnight. Ethyl acetate and water were added. The organic layer was separated, dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. After recrystallization in Et_2O, DTC was obtained as a white solid (3.9 g, 75%).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 4.10 (s, 4H, Ha), 1.15 (s, 6H, Hb).

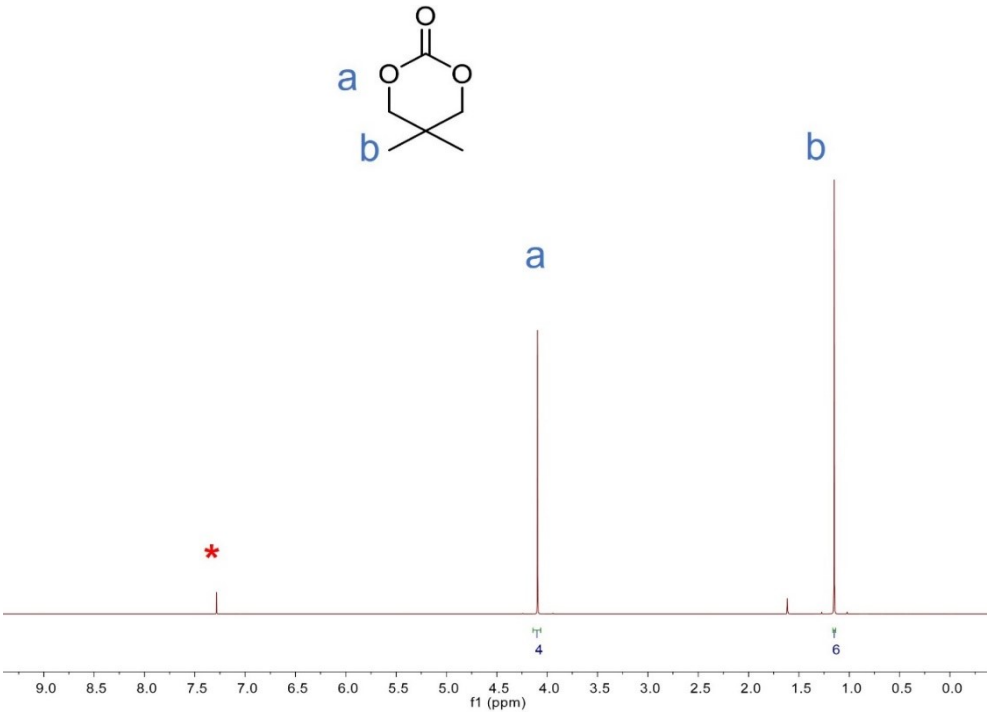
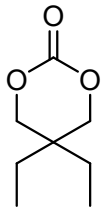


Figure S1: ^{1}H NMR spectra (500 MHz, $CDCl_3$) of 2,2-dimethyltrimethylene carbonate (DTC). Deuterated solvent residual signal denoted by *.

Synthesis of 2,2-diethyltrimethylene carbonate (DEC)



2,2-diethyl-1,3-propanediol (5.28 g, 1 equiv) was dissolved in 100 mL of THF and cooled to 0 °C. Ethyl chloroformate (10 mL,10.8 g, 2.5 equiv) was added in one portion, while Et_3N (13.3 mL, 10.1 g, 2.5 equiv) was added dropwise at 0 °C. After stirring at 0 °C for 1 h, the reaction mixture was warmed up to room temperature and stirred overnight. Ethyl acetate and water were added. The organic layer was separated, dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. After recrystallization in Et_2O, DEC was obtained as a white solid (4.5 g, 71%).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 4.13 (s, 4H, H_a), 1.53 – 1.42 (m, 4H, H_b), 0.90 (t, 6H, H_c)

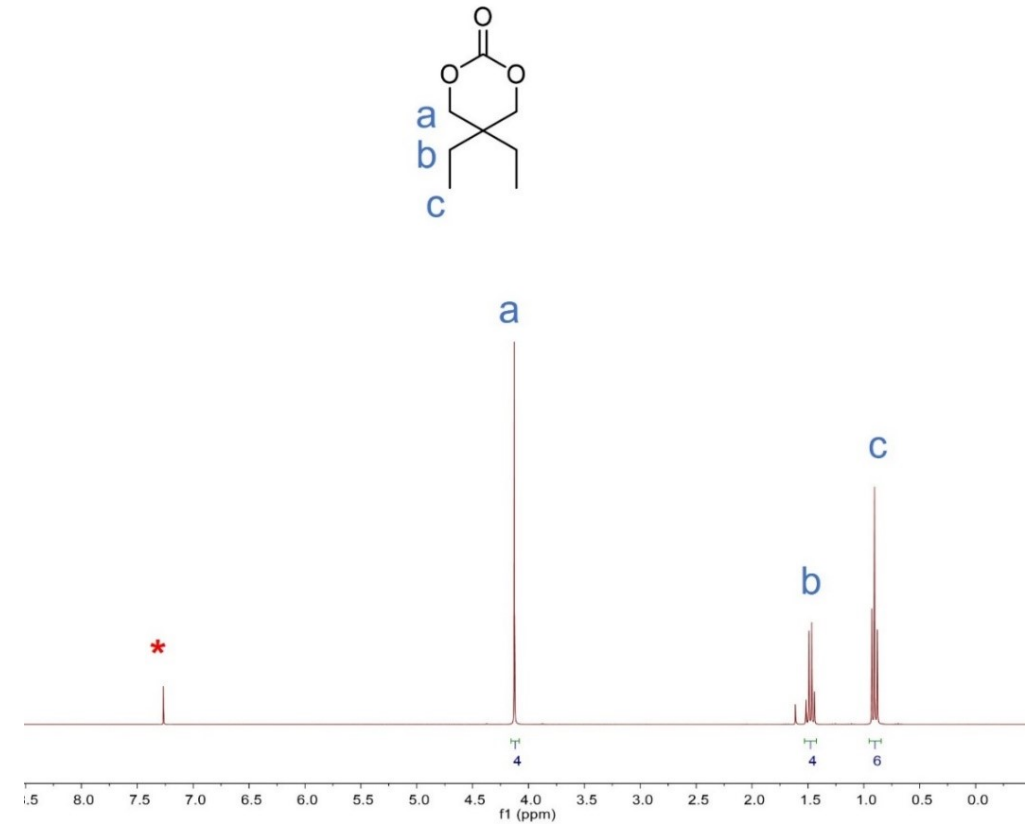
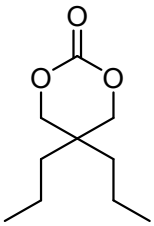


Figure S2: ^{1}H NMR spectra (300 MHz, $CDCl_3$) of 2,2-diethyltrimethylene carbonate (DEC). Deuterated solvent residual signal denoted by *.

Synthesis of 2,2-dipropyltrimethylene carbonate (DPC)



2,2-dipropyl-1,3-propanediol (4.2 g, 1.0 equiv) was dissolved in 100 mL of THF and cooled to 0 °C. Ethyl chloroformate (7.3 mL,7.9 g, 2.5 equiv) was added in one portion, while Et_3N (9.8 mL, 7.4 g, 2.5 equiv) was added dropwise at 0 °C. After stirring at 0 °C for 1 h, the reaction mixture was warmed up to room temperature and stirred overnight. Ethyl acetate and water were added. The organic layer was separated, dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The product was purified by column chromatography using petroleum and ethyl acetate as the eluent. Compound DPC was obtained as a colorless oil (4.7 g, 96%).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 4.12 (s, 4H, H_a), 1.40 – 1.20 (m, 8H, H_b), 1.03 – 0.81 (t, 6H, H_c).

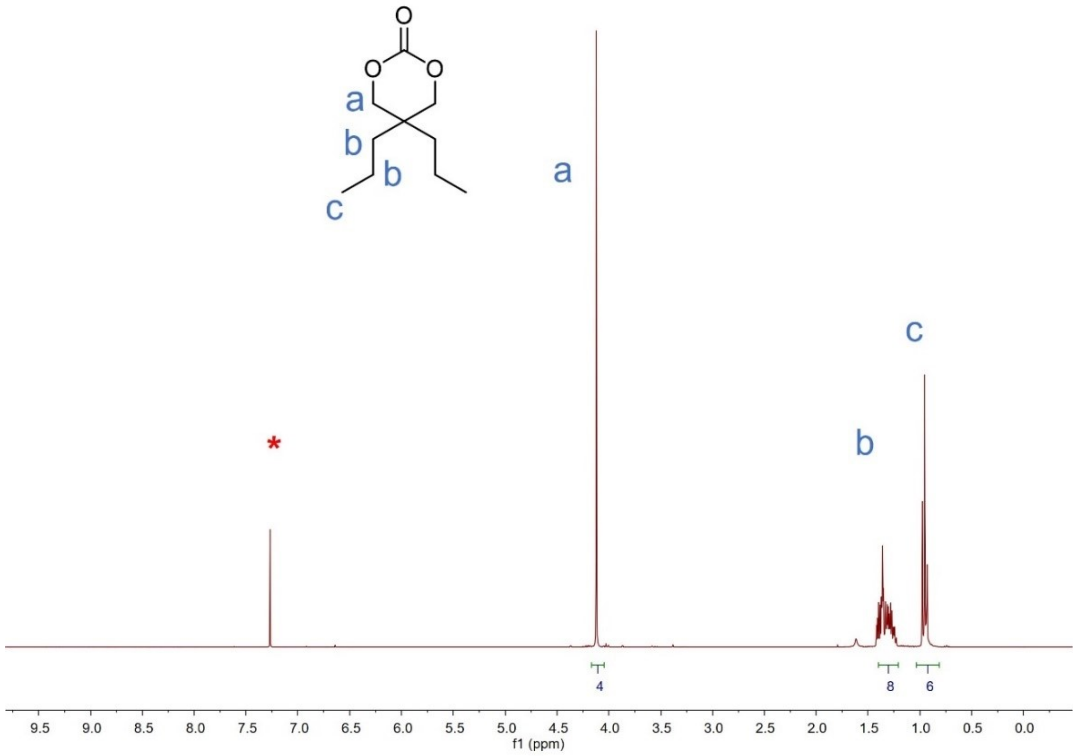
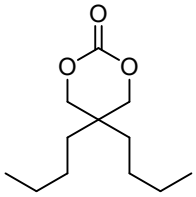


Figure S3: ^{1}H NMR spectra (300 MHz, $CDCl_3$) of 2,2-dipropyltrimethylene carbonate (DPC). Deuterated solvent residual signal denoted by *.

Synthesis of 2,2-dibutyltrimethylene carbonate (DBC)



2,2-dibutyl-1,3-propanediol (4.0 g, 1.0 equiv) was dissolved in 100 mL of THF and cooled to 0 °C. Ethyl chloroformate (6.2 mL, 6.9 g, 2.5 equiv) was added in one portion, while Et_3N (8.8 mL, 6.4 g, 2.5 equiv) was added dropwise at 0 °C. After stirring at 0 °C for 1 h, the reaction mixture was warmed up to room temperature and stirred overnight. Ethyl acetate and water was added. The organic layer was separated, dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The product was purified by column chromatography using petroleum and ethyl acetate as the eluent. Compound DBC was obtained as a colorless oil (3.7 g, 81%).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 4.12 (s, 4H, H_a), 1.45 – 1.15 (m, 12H, H_b), 0.93 (t, 6H, H_c).

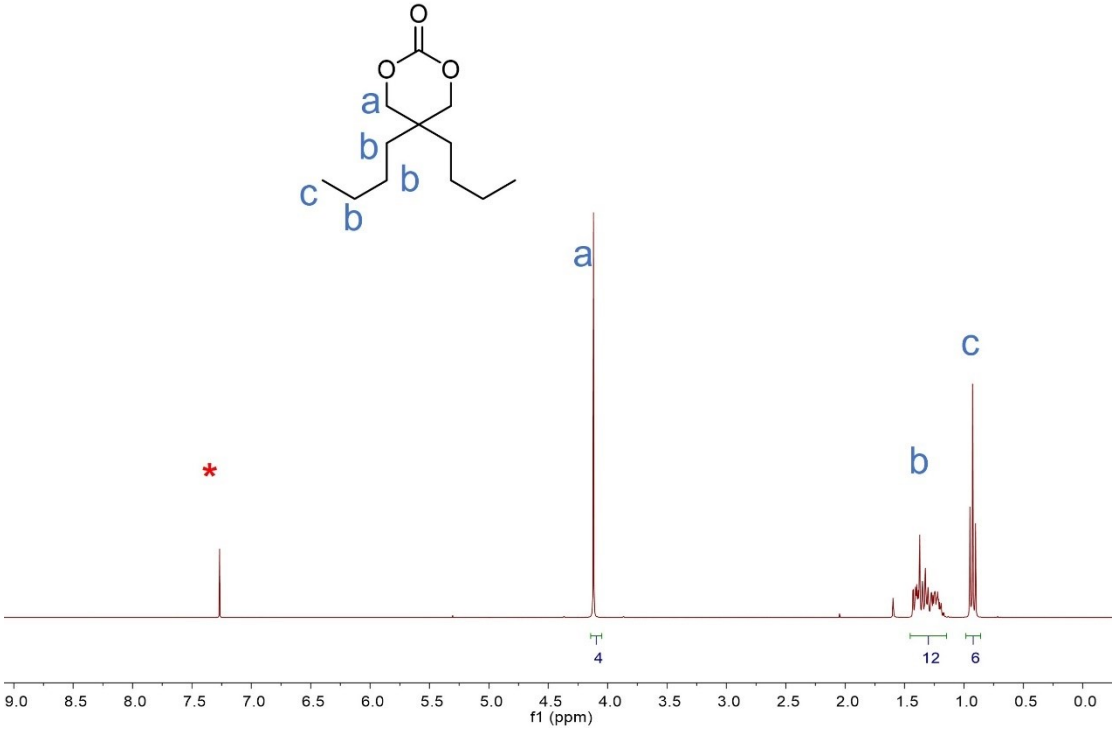
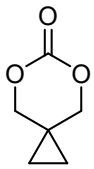


Figure S4: ^{1}H NMR spectra (300 MHz, $CDCl_3$) of 2,2-dibutyltrimethylene carbonate (DBC). Deuterated solvent residual signal denoted by *.

Synthesis of cyclopropane-trimethylene carbonate (CPC)



The synthesis of cyclopropane-trimethylene carbonate (CPC) was adapted from the synthesis of DTC.

Cyclopropane-1,3-propanediol (4.0 g, 1 equiv) was dissolved in 100 mL of THF and cooled to 0 °C. Ethyl chloroformate (9.3 mL,10.6 g, 2.5 equiv) was added in one portion, while Et_3N (13.6 mL, 9.9 g, 2.5 equiv) was added dropwise at 0 °C. After stirring at 0 °C for 1 h, the reaction mixture was warmed up to room temperature and stirred overnight. Ethyl acetate and water were added. The organic layer was separated, dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. After recrystallization in Et_2O, CPC was obtained as a white solid (3.8 g, 76%).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 4.13 (s, 4H, H_a), 0.75 (s, 4H, H_b).

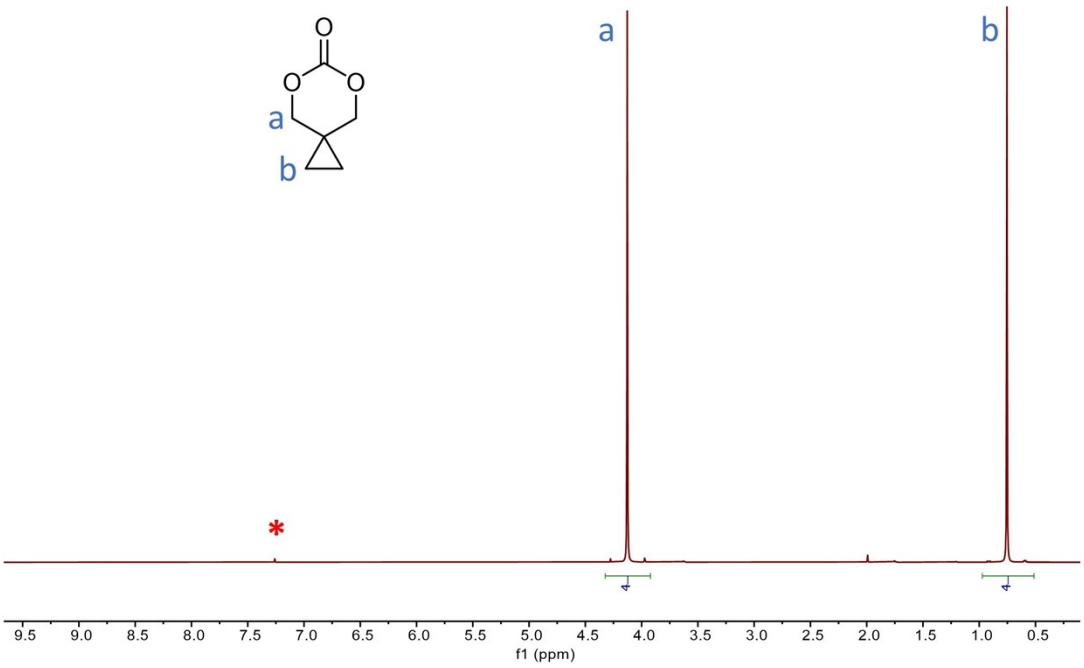
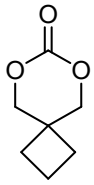


Figure S5: ^{1}H NMR spectra (500 MHz, $CDCl_3$) of cyclopentenetrimethylene carbonate (CPC). Deuterated solvent residual signal denoted by *.

Synthesis of cyclobutane-trimethylene carbonate (CBC)



The synthesis of cyclobutene-1,3-diol was adapted from a literature procedure.[2]

The synthesis of cyclobutane-trimethylene carbonate (CBC) was adapted from the synthesis of DTC.

Cyclobutane-1,3-propanediol (4.3 g, 1 equiv) was dissolved in 100 mL of THF and cooled to 0 °C. Ethyl chloroformate (8.7 mL,10.0 g, 2.5 equiv) was added in one portion, while Et_3N (12.9 mL, 9.4 g, 2.5 equiv) was added dropwise at 0 °C. After stirring at 0 °C for 1 h, the reaction mixture was warmed up to room temperature and stirred overnight. Ethyl acetate and water were added. The organic layer was separated, dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. After recrystallization in Et_2O, CBC was obtained as a white solid (3.4 g, 65%).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 4.28 (s, 4H, H_a), 2.02 (s, 6H, H_b).

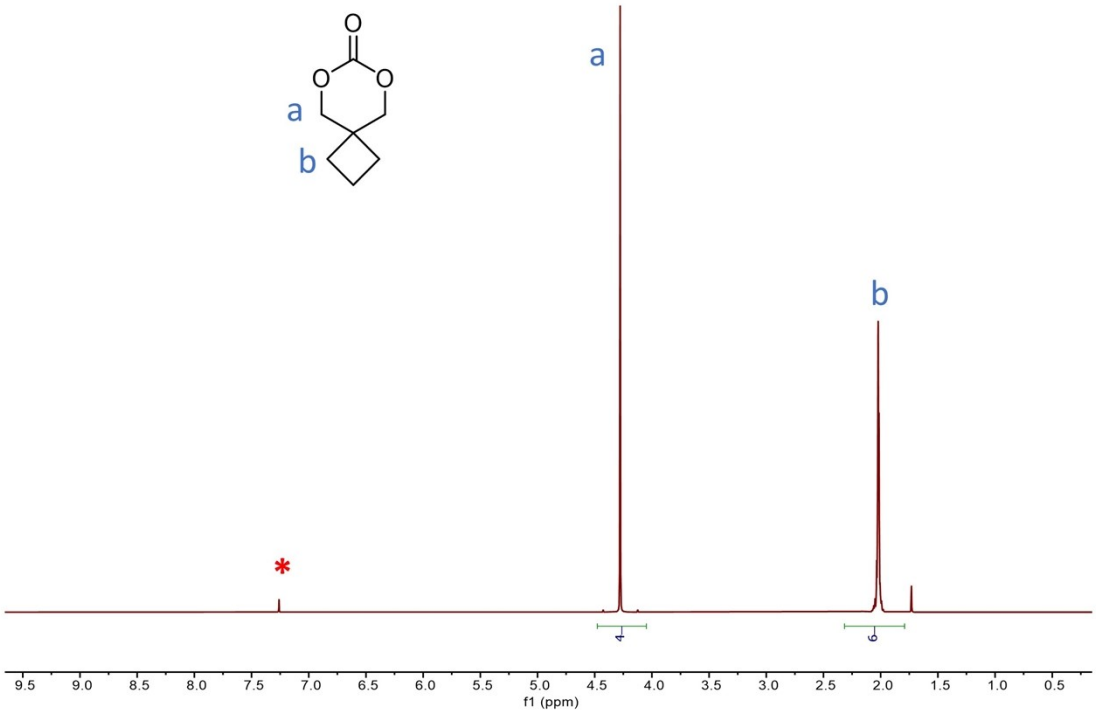
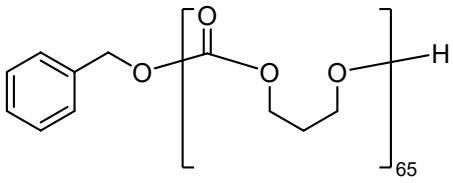


Figure S6: ^{1}H NMR spectra (500 MHz, $CDCl_3$) of cyclobutenetrimethylene carbonate (CBC). Deuterated solvent residual signal denoted by *.

2.2 Synthesis of homopolymers by living ring-opening polymerizations

Synthesis of $PTMC_{65}$



In the nitrogen-filled glovebox, benzyl alcohol (2.2 mg, 1 equiv), TMC (204.0 mg, 100 equiv) and TU (8.9 mg, 1.2 equiv) were added to an oven-dried 2 mL vial equipped with a magnetic bar and dissolved in 150 µL of anhydrous DCM. A solution of DBU in DCM (36 µL, 100 mg/mL, 1.2 equiv) was added via pipette and the reaction mixture was stirred for 2 h at room temperature. The polymerization was quenched with an excess of benzoic acid (20 mg). The reaction mixture was precipitated three times into 45 mL of ice-cold MeOH and collected by centrifugation. After drying in vacuo overnight, PTMC was obtained as a viscous colorless oil (121 mg, 58%).

GPC: M_n = 8,630 gmol^{-1}, $Đ_M$ = 1.16, M_n (^{1}H NMR) = 6,740 gmol^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.43 – 7.32 (m, 5H, H_d), 5.17 (s, 2H, H_a), 4.26 (t, 260H, H_b), 3.76 (t, 2H, H_e), 2.07 (m, 130H, H_c).

The DP_n value of the PTMC block was determined by comparing the relative integration of the methylene moiety of the benzyl end-group (at 5.17 ppm, H_a) with the integration of the methylene protons adjacent to the carbonate carbons (H_b and H_e) in the PTMC segment.

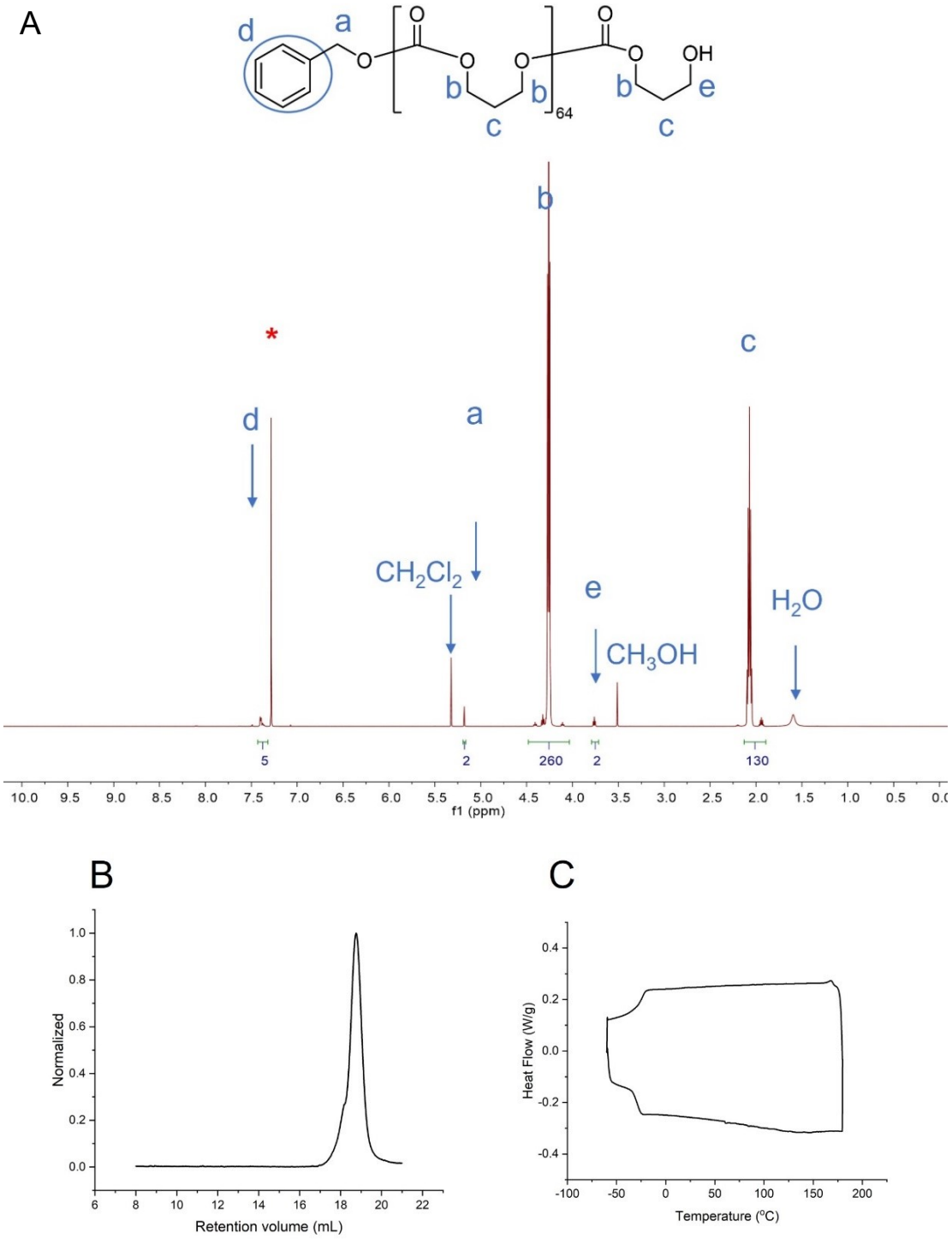
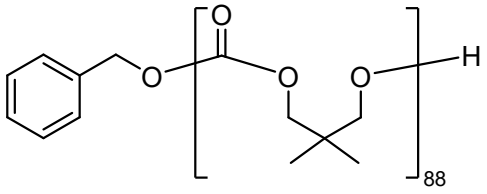


Figure S7: (A) ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of $PTMC_{65}$. Deuterated solvent residual signal denoted by *. (B) GPC chromatogram of $PTMC_{65}$ using Bu_4NBr/THF (1 wt %) as the eluent. (C) DSC thermogram of $PTMC_{65}$ homopolymer. The scan was recorded at a heating and cooling rate of 10 ºC/min.

Synthesis of $PDTC_{88}$



In the nitrogen-filled glovebox, benzyl alcohol (1.1 mg, 1 equiv), DTC (195.0 mg, 150 equiv) and TU (7.4 mg, 2 equiv) were added to an oven-dried 2 mL vial equipped with a magnetic bar and dissolved in 250 µL of anhydrous DCM. A solution of DBU in DCM (152 µL, 100 mg/mL, 1 equiv) was added via pipette and the reaction mixture was stirred for 24 h at room temperature. The polymerization was quenched with an excess of benzoic acid (20 mg). The reaction mixture was precipitated three times into 45 mL of ice-cold MeOH and collected by centrifugation. After drying in vacuo overnight, PDTC was obtained as a white solid (115.0 mg, 59%).

GPC: M_n = 14,550 gmol^{-1}, $Đ_M$ = 1.30, M_n (NMR) = 11,560 gmol^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.40 (m, 5H, H_d), 5.17 (s, 2H, H_a), 3.99 (s, 352H, H_b), 3.38 (d, 2H, H_e), 1.02 (s, 530H, H_c).

The DP_n value of the PDTC block was determined by comparing the relative integration of the methylene moiety of the benzyl end-group (at 5.17 ppm, H_a) with the integration of the methylene protons adjacent to the carbonate carbons (H_b and H_e) in the PDTC segment.

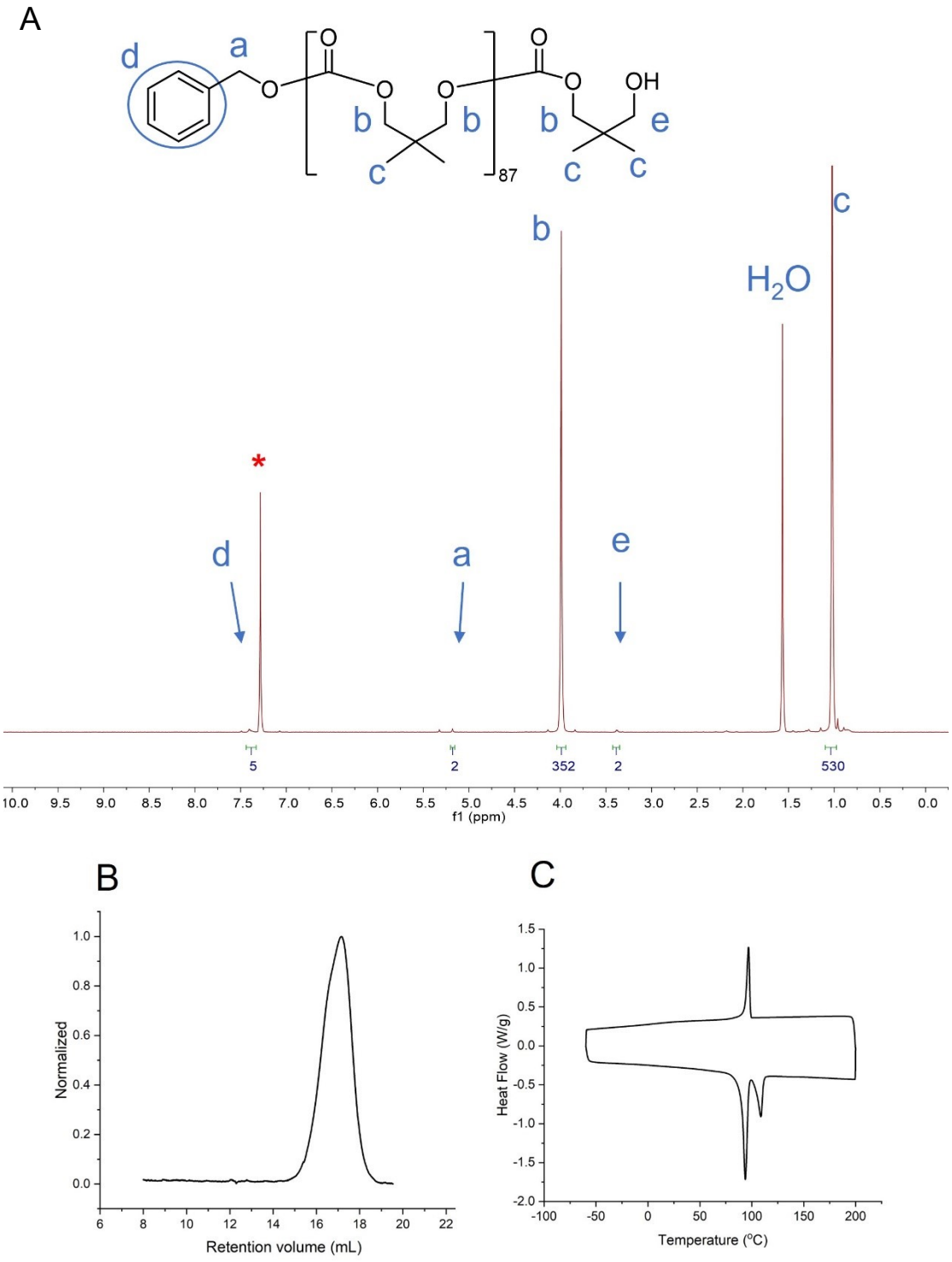
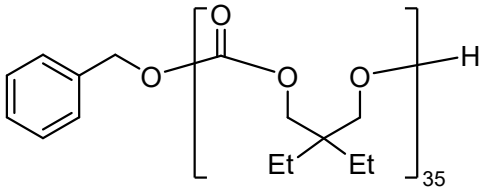


Figure S8: (A) ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of $PDTC_{88.}$ Deuterated solvent residual signal denoted by *. (B) GPC chromatogram of $PDTC_{88}$ using Bu_4NBr/THF (1 wt %) as the eluent. (C) DSC thermogram of $PDTC_{88}$ homopolymer. The scan was recorded at a heating and cooling rate of 10 ºC/min.

Synthesis of $PDEC_{35}$



In the nitrogen-filled glovebox, benzyl alcohol (2 mg, 1 equiv), DEC (180 mg, 150 equiv) and TU (4.22 mg, 1.5 equiv) were added to an oven-dried 2 mL vial equipped with a magnetic bar and dissolved in 50 µL of anhydrous DCM. A solution of DBU in DCM (173 µL, 100 mg/mL, 1.5 equiv) was added via pipette and the reaction mixture was stirred for 24 h at room temperature. The polymerization was quenched with an excess of benzoic acid (20 mg). The reaction mixture was precipitated three times into 45 mL of ice-cold MeOH and collected by centrifugation. After drying in vacuo overnight, the PDEC was obtained as a white solid (42 mg, 23%).

GPC: M_n = 7,780 gmol^{-1}, $Đ_M$ = 1.13, M_n (NMR) = 5,650 gmol^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.46 – 7.31 (m, 5H, H_d), 5.17 (s, 2H, H_a), 4.02 (s, 138H, H_b), 3.38 (d, 2H, H_e), 1.38 (m, 140H, H_f), 0.86 (t, 212H, H_c).

The DP_n value of the PDEC block was determined by comparing the relative integration of the methylene moiety of the benzyl end-group (at 5.17 ppm, H_a) with the integration of the methylene protons adjacent to the carbonate carbons (H_b and H_e) in the PDEC segment.

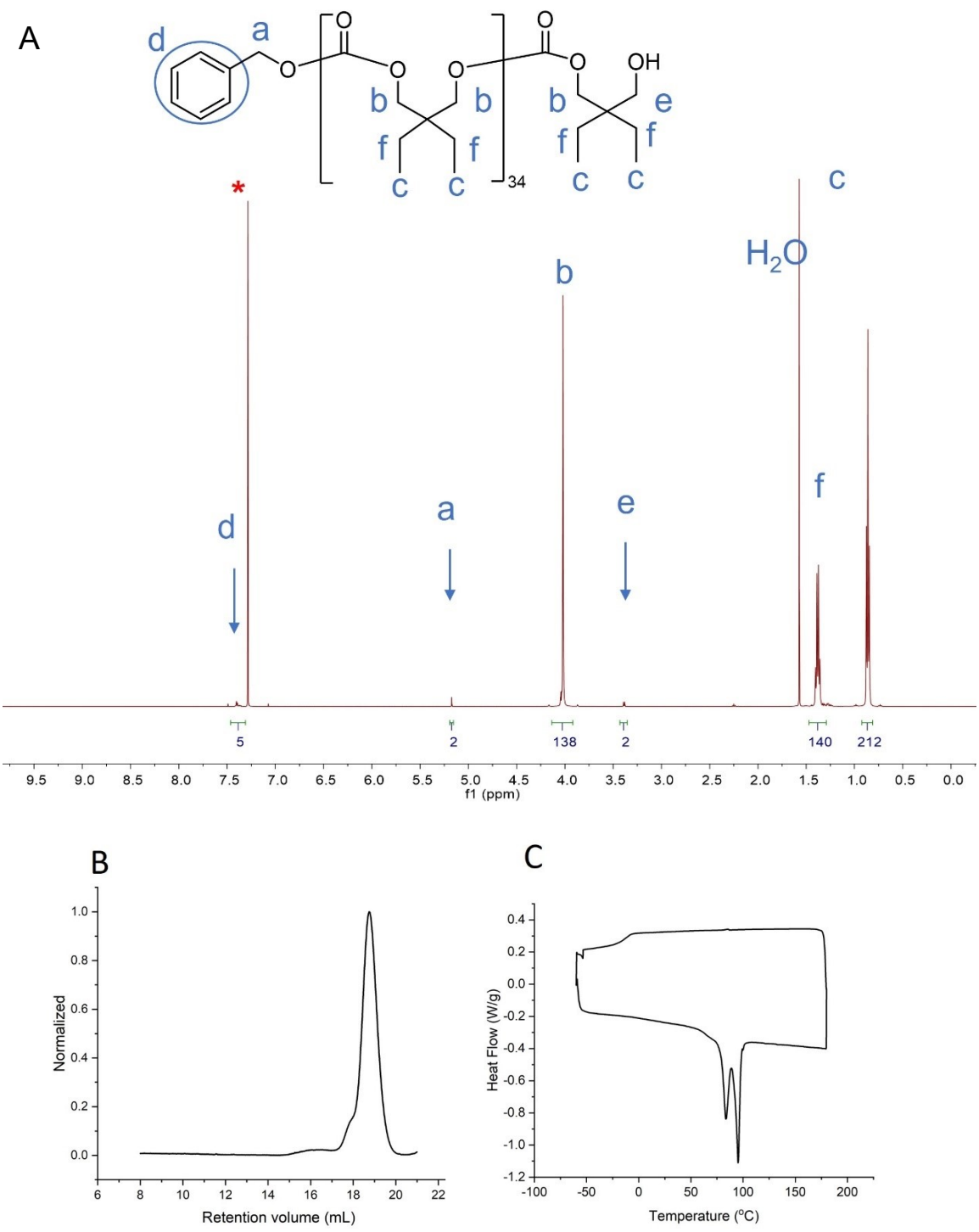
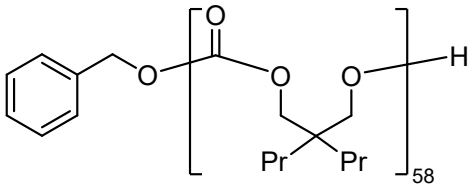


Figure S9: (A) ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of $PDEC_{35}$. Deuterated solvent residual signal denoted by *. (B) GPC chromatogram of $PDEC_{35}$ using Bu_4NBr/THF (1 wt%) as the eluent. (C) DSC thermogram of $PDEC_{35}$ homopolymer. The scan was recorded at a heating and cooling rate of 10 ºC/min.

Synthesis of $PDPC_{58}$



In the nitrogen-filled glovebox, benzyl alcohol (2 mg, 1 equiv) and DPC (344 mg, 100 equiv) were added to an oven-dried 2 mL vial equipped with a magnetic bar and dissolved in 100 µL of anhydrous DCM. Diphenyl phosphate (DPP) (23 mg, 5 equiv) was added in one portion and the reaction mixture was stirred for 24 h at 23 °C. The polymerization was quenched with excess benzoic acid (20 mg). The reaction mixture was precipitated three times into 45 mL of ice-cold MeOH and collected by centrifugation. After drying in vacuo overnight, PDPC was obtained as a white solid (175 mg, 51%).

GPC: M_n = 11,400 gmol^{-1}, $Đ_M$ = 1.16, M_n (NMR) = 10,900 gmol^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.46 – 7.33 (m, 5H, H_d), 5.17 (s, 2H, H_a), 4.02 (s, 230H, H_b), 3.39 (s, 2H, H_e), 1.29 (d, 466H, H_f), 0.96 – 0.87 (m, 350H, H_c).

The DP_n value of the PDPC block was determined by comparing the relative integration of the methylene moiety of the benzyl end-group (at 5.17 ppm, H_a) with the integration of the methylene protons adjacent to the carbonate carbons (H_b and H_e) in the PDPC segment.

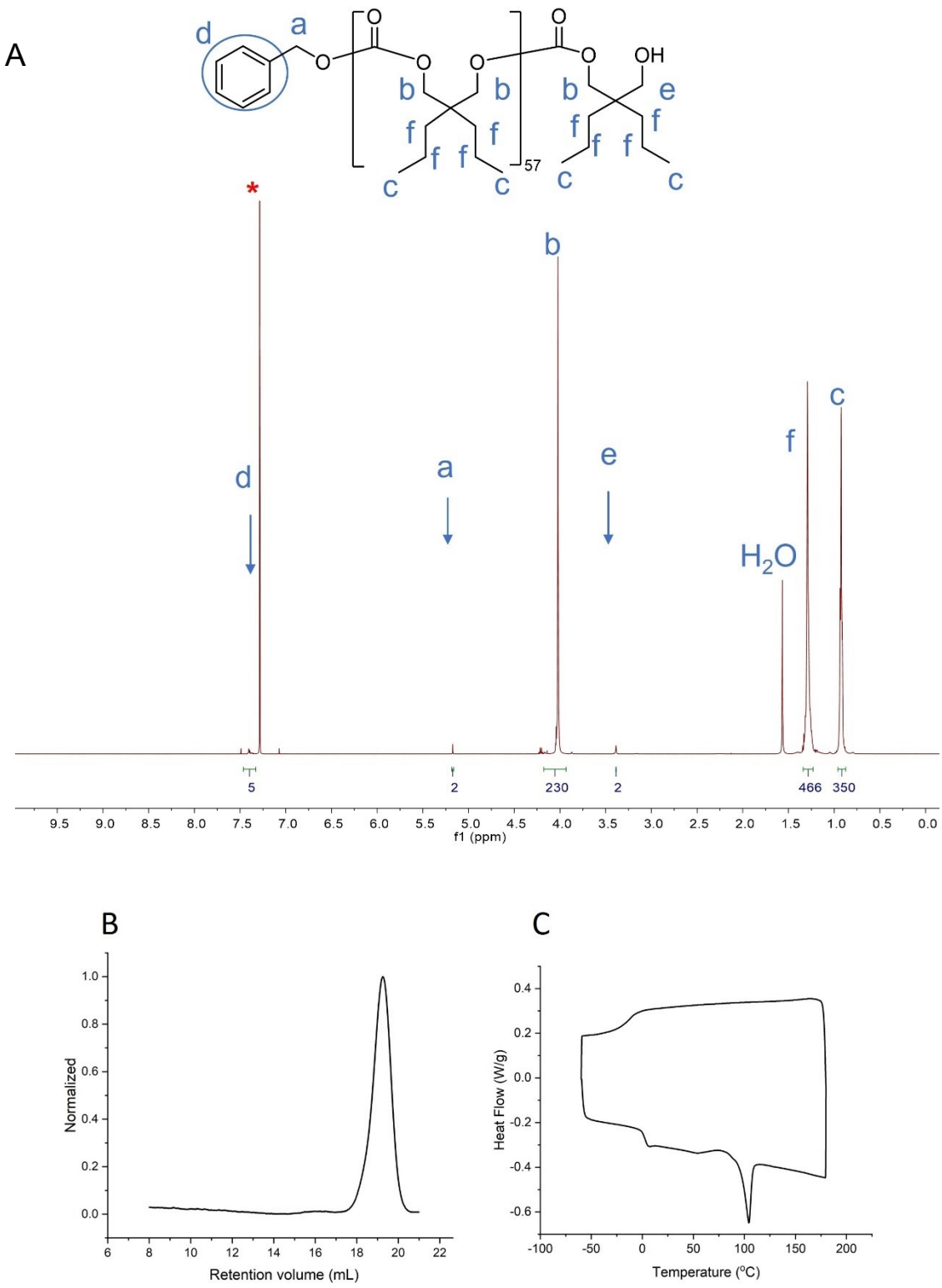
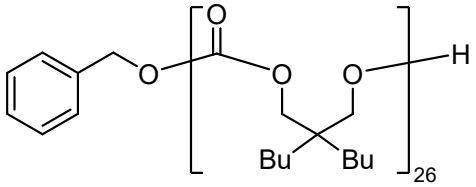


Figure S10: (A) ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of $PDPC_{58}$. Deuterated solvent residual signal denoted by *. (B) GPC chromatogram of $PDPC_{58}$ using Bu_4NBr/THF (1 wt %) as the eluent. (C) DSC thermogram of $PDPC_{58}$ homopolymer. The scan was recorded at a heating and cooling rate of 10 ºC/min.

Synthesis of $PDBC_{26}$



In the nitrogen-filled glovebox, benzyl alcohol (2.7 mg, 1 equiv) and DEC (214 mg, 80 equiv) were added to an oven-dried 2 mL vial equipped with a magnetic bar and dissolved in 200 µL of anhydrous DCM. Diphenyl phosphate (DPP) (16.3 mg, 2 equiv) was added in one portion and the reaction mixture was stirred for 24 h at room temperature. The polymerization was quenched with 20 µL of Et_3N. The reaction mixture was precipitated three times into 45 mL of ice-cold MeOH and collected by centrifugation After drying in vacuo overnight, PDBC was obtained as a colorless oil (65 mg, 30%).

GPC: M_n = 5,210 gmol^{-1}, $Đ_M$ = 1.14, M_n (NMR) = 5,680 gmol^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.43 – 7.33 (m, 5H, H_d), 5.17 (s, 2H, H_a), 4.01 (s, 103H, H_b), 3.38 (d, 2H, H_e), 1.34 – 1.19 (m, 317H, H_f), 0.92 (t, 158H, H_c).
The DP_n value of the PDBC block was determined by comparing the relative integration of the methylene moiety of the benzyl end-group (at 5.17 ppm, H_a) with the integration of the methylene protons adjacent to the carbonate carbons (H_b and H_e) in the PDBC segment.

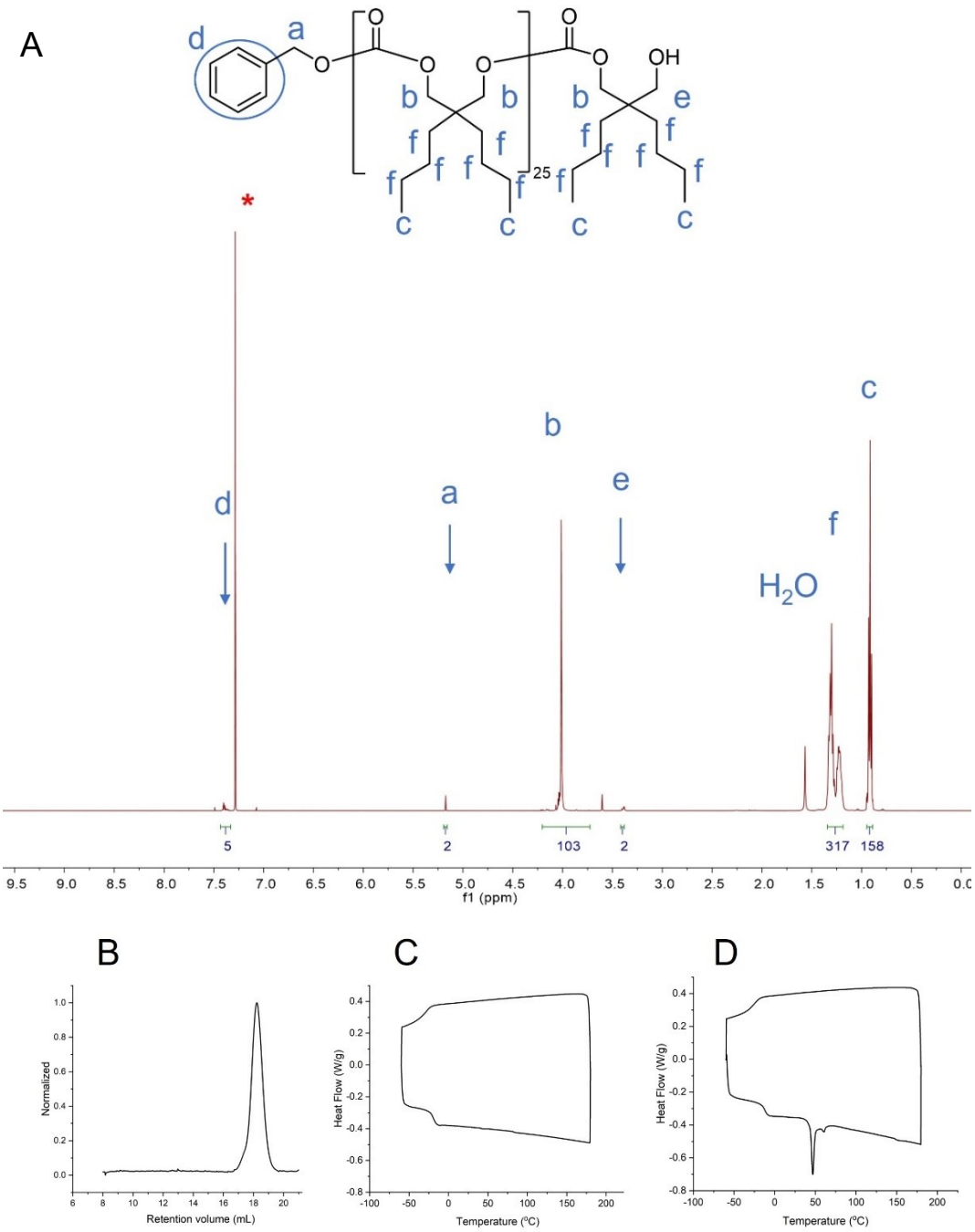
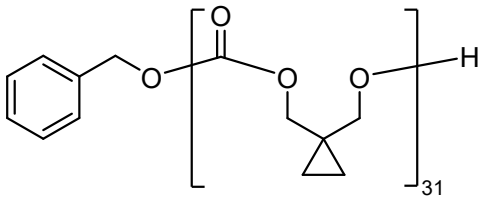


Figure S11: (A) ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of $PDBC_{26}$. Deuterated solvent residual signal denoted by *. (B) GPC chromatogram of $PDBC_{26}$ using Bu_4NBr/THF (1 wt %) as the eluent. (C) DSC thermogram of $PDBC_{26}$ freshly prepared homopolymer. (D) DSC thermogram of $PDBC_{26}$ homopolymer was conducted after storing at room temperature for 3 months. The scan was recorded at a heating and cooling rate of 10 ºC/min.

Synthesis of $PCPC_{31}$



In the nitrogen-filled glovebox, benzyl alcohol (2.7 mg, 1 equiv), CPC (128 mg, 40 equiv) and TU (18.5 mg, 0.05 equiv) were added to an oven-dried 2 mL vial equipped with a magnetic bar and dissolved in 300 µL of anhydrous DCM. A solution of DBU in DCM (38 µL, 100 mg/mL, 0.025 equiv) was added via pipette and the reaction mixture was stirred for 24 h at room temperature. The polymerization was quenched with an excess of benzoic acid (15 mg). The reaction mixture was precipitated three times into 45 mL of ice-cold MeOH and collected by centrifugation. After drying in vacuo overnight, the PCPC was obtained as a white solid (105 mg, 81%).

GPC: M_n = 2,600 gmol^{-1}, $Đ_M$ = 1.10, M_n (NMR) = 4,100 gmol^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.37 (m, 5H, H_d), 5.16 (s, 2H, H_a), 4.08 (s, 122H, H_b), 3.50 (d, 2H, H_e), 0.70 (m, 124H, H_c).

The DP_n value of the PCPC block was determined by comparing the relative integration of the methylene moiety of the benzyl end-group (at 5.16 ppm, H_a) with the integration of the methylene protons adjacent to the carbonate carbons (H_b and H_e) in the PCPC segment.

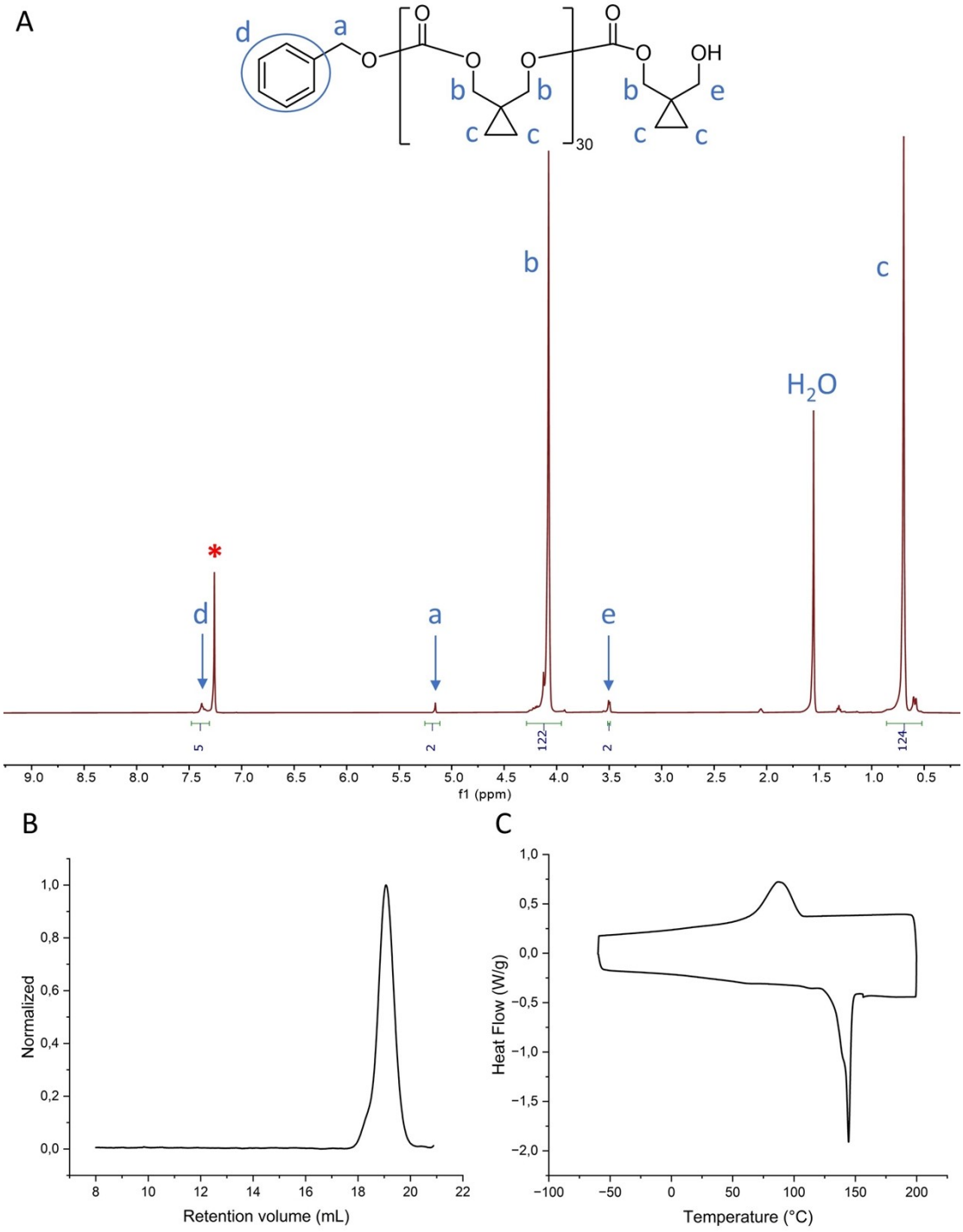
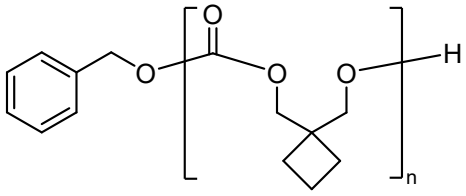


Figure S12: (A) ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of $PCPC_{31.}$ Deuterated solvent residual signal denoted by *. (B) GPC chromatogram of $PCPC_{31}$ using Bu_4NBr/THF (1 wt %) as the eluent. (C) DSC thermogram of $PCPC_{31}$ freshly prepared homopolymer. (D) DSC thermogram of $PDBC_{31}$ homopolymer. The scan was recorded at a heating and cooling rate of 10 ºC/min.

Synthesis of $PCBC_n$



In the nitrogen-filled glovebox, benzyl alcohol (2.7 mg, 1 equiv), CBC (142 mg, 40 equiv) and TU (18.5 mg, 0.05 equiv) were added to an oven-dried 2 mL vial equipped with a magnetic bar and dissolved in 300 µL of anhydrous DCM. A solution of DBU in DCM (38 µL, 100 mg/mL, 0.025 equiv) was added via pipette and the reaction mixture was stirred for 24 h at room temperature. The polymerization was quenched with an excess of benzoic acid (15 mg). The reaction mixture was precipitated three times into 45 mL of ice-cold MeOH and collected by centrifugation. After drying in vacuo overnight, the PCBC was obtained as a white solid (90 mg, 62%).

No ^{1}H-NMR and GPC characterization of $PCPC_n$ could be performed as the homopolymer is insoluble.

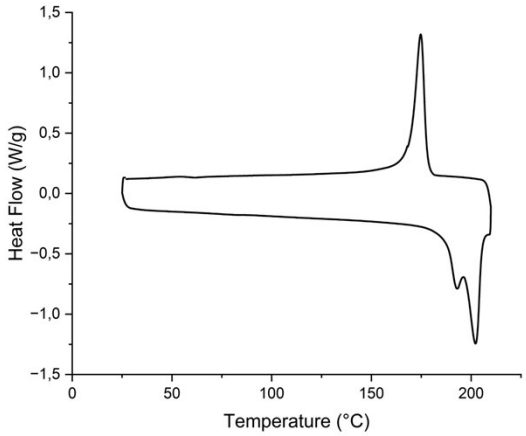
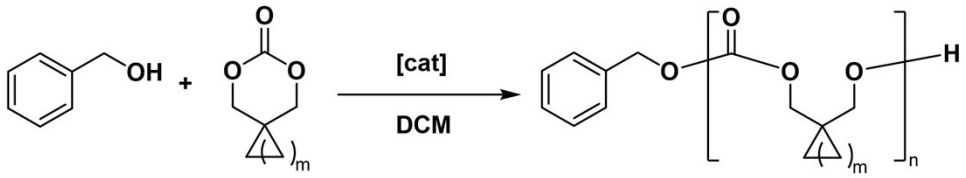


Figure S13: DSC thermogram of $PDBC_{31}$ homopolymer. The scan was recorded at a heating and cooling rate of 10 ºC/min.

Table S1: Synthesis of polycarbonate homopolymers with cyclic side groups via ROP.



m = 1, 2

R	*Polymer*[b]	M_n (g/mol)[c]	$Đ_m$[c]	T_m (°C)[d]	T_c (°C)[d]	T_g (°C)[d]
C_3H_6[a]	$PCPC_{31}$	2 600	1.10	144	87	51
C_4H_8[a]	$PCBC_n$	-[g]	-[g]	182, 200[e]	175	-[f]

[a]TU (N-(3,5-trifluoromethyl)phenyl-N-cyclohexyl- thiourea) was used as the catalyst, DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene) was used as base for the polymerization. [b]Determined by ^{1}H NMR spectroscopy. [c]Determined by GPC versus polystyrene standards. [d]Determined from the DSC thermogram. [e]Two temperatures indicate two distinct peaks in the DSC data, suggesting coexistence of two crystal forms. [f]The absence of the T_g value is due to annealing of the polymer. [g] No ^{1}H-NMR spectroscopy and GPC characterization due to insolubility of the homopolymer.

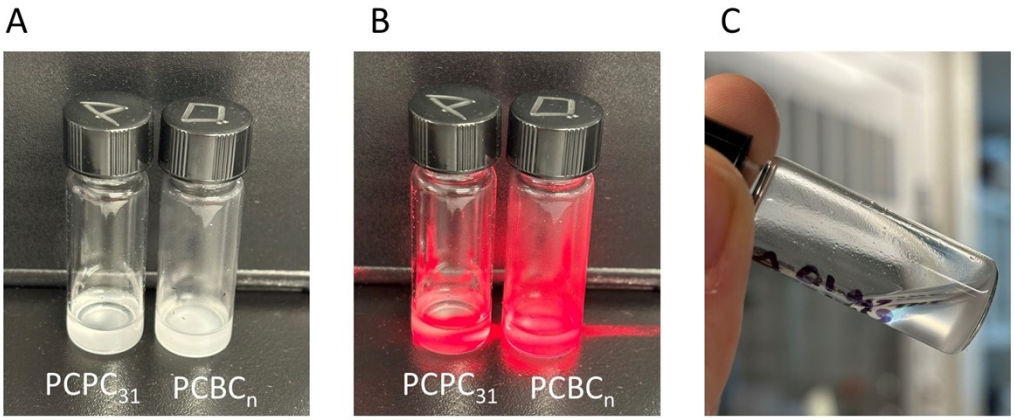
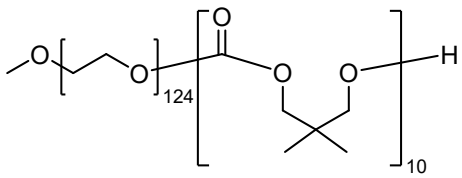


Figure S14: (A) Photo of attempt to solubilize $PCPC_{31}$ and $PCBC_n$ in THF (10 mg/mL). (B) Photo of the tyndall effect of $PCPC_{31}$ and $PCBC_n$ in THF (10 mg/mL) showing poor solubility of the homopolymers. A red laser pointer as used as a light source. (C) Close up of $PCPC_{31}$ in THF (10 mg/mL) after heating to 70 °C, showing that the homopolymer is insoluble.

2.3 Block copolymer syntheses by living ring-opening polymerizations

Synthesis of $PDTC_{10}$-*b*-PEG_{124}



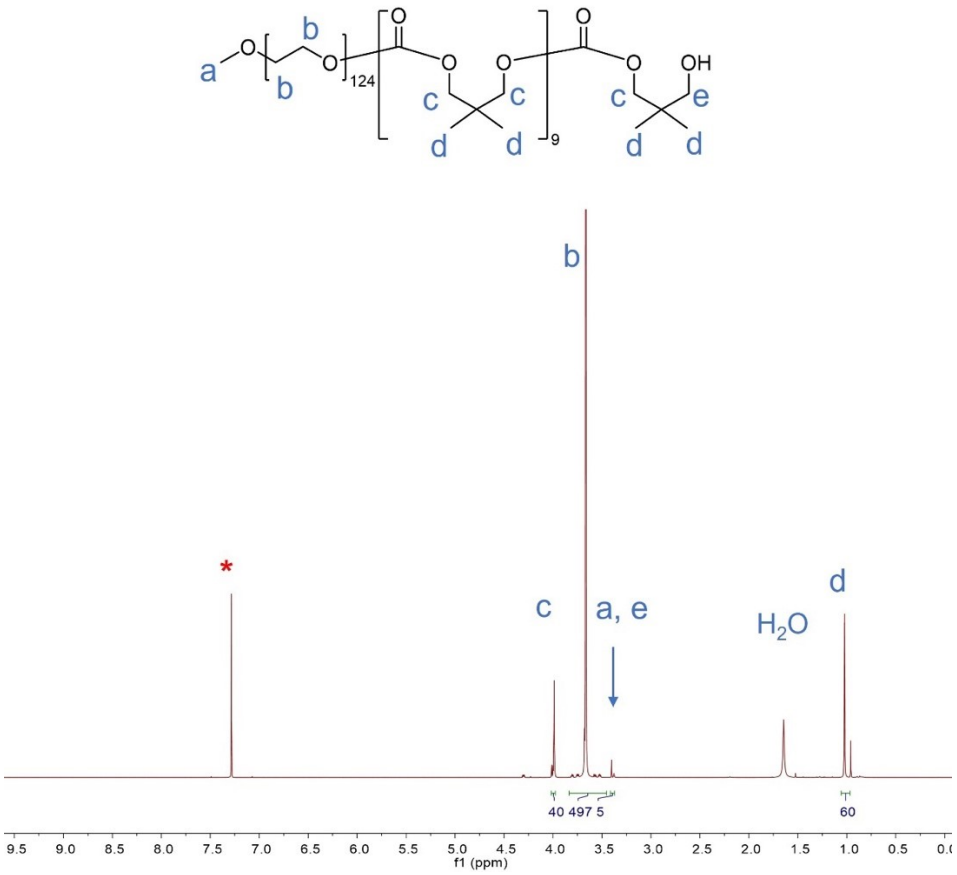
In the nitrogen-filled glovebox, PEG_{135} (50 mg, 1 equiv) and DTC (26 mg, 20 equiv) were added to an oven-dried 2 mL vial equipped with a magnetic bar and dissolved in 300 µL of anhydrous DCM. A solution of DBU in DCM (15 µL, 100 mg/mL, 1 equiv) was added via pipette and the vial was capped. The reaction mixture was stirred for 24 h at room temperature and quenched with an excess of benzoic acid (15 mg). The reaction mixture was precipitated three times into 45 mL of ice-cold MeOH and collected by centrifugation. After drying in vacuo overnight, the block polymer was obtained as a white solid (67 mg, 83%).

GPC: M_n = 7,770 $gmol^{-1}$, $Đ_M$ = 1.05, M_n (NMR) = 6,800 $gmol^{-1}$.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 4.00 (d, 40H, H_c), 3.67 (s, 497H, H_b), 3.40 (m, 5H, H_a and H_e), 1.02 (m, 60H, H_d).

The DP_n value of the PDTC block was determined by comparing the relative integration of the methoxy end-group of PEG (at 3.40 ppm, H_a) with the integration of the methylene protons adjacent to the carbonate carbons (at 3.99 ppm) in the PDTC segment.

A



B

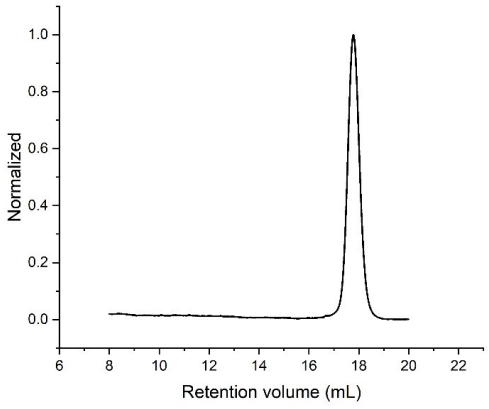
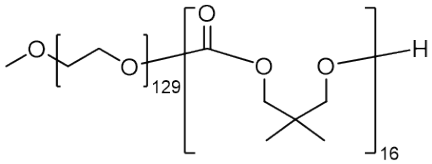


Figure S15: (A) ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of $PDTC_{10}$-*b*-PEG_{124}. Deuterated solvent residual signal denoted by *. (B) GPC chromatogram of $PDTC_{10}$-*b*-PEG_{124} using Bu_4NBr/THF (1% v/v) as the eluent.

Synthesis of $PDTC_{16}$-*b*-PEG_{129}



In the nitrogen-filled glovebox, PEG_{135} (50 mg, 1 equiv) and DTC (39 mg, 30 equiv), were added to an oven-dried 2 mL vial equipped with a magnetic bar and dissolved in 300 µL of anhydrous DCM. A solution of DBU in DCM (15 µL, 100 mg/mL, 1 equiv) was added via pipette and the vial was capped. After stirring the reaction mixture for 24 h at room temperature the polymerization was quenched with an excess of benzoic acid (15 mg). The reaction mixture was precipitated three times into 45 mL of ice-cold MeOH and collected by centrifugation. After drying in vacuo overnight, the block polymer was obtained as a white solid (76 mg, 80%).

GPC: M_n = 9,600 $gmol^{-1}$, $Đ_M$ = 1.07, M_n (NMR) = 7,780 $gmol^{-1}$.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 3.99 (s, 64H, H_c), 3.67 (s, 516H, H_b), 3.40 (m, 5H, H_a and H_e), 1.02 (s, 96H, H_d).

The DP_n value of the PDTC block was determined by comparing the relative integration of the methoxy end-group of PEG (at 3.40 ppm, H_a) with the integration of the methylene protons adjacent to the carbonate carbons (at 3.99 ppm) in the PDTC segment.

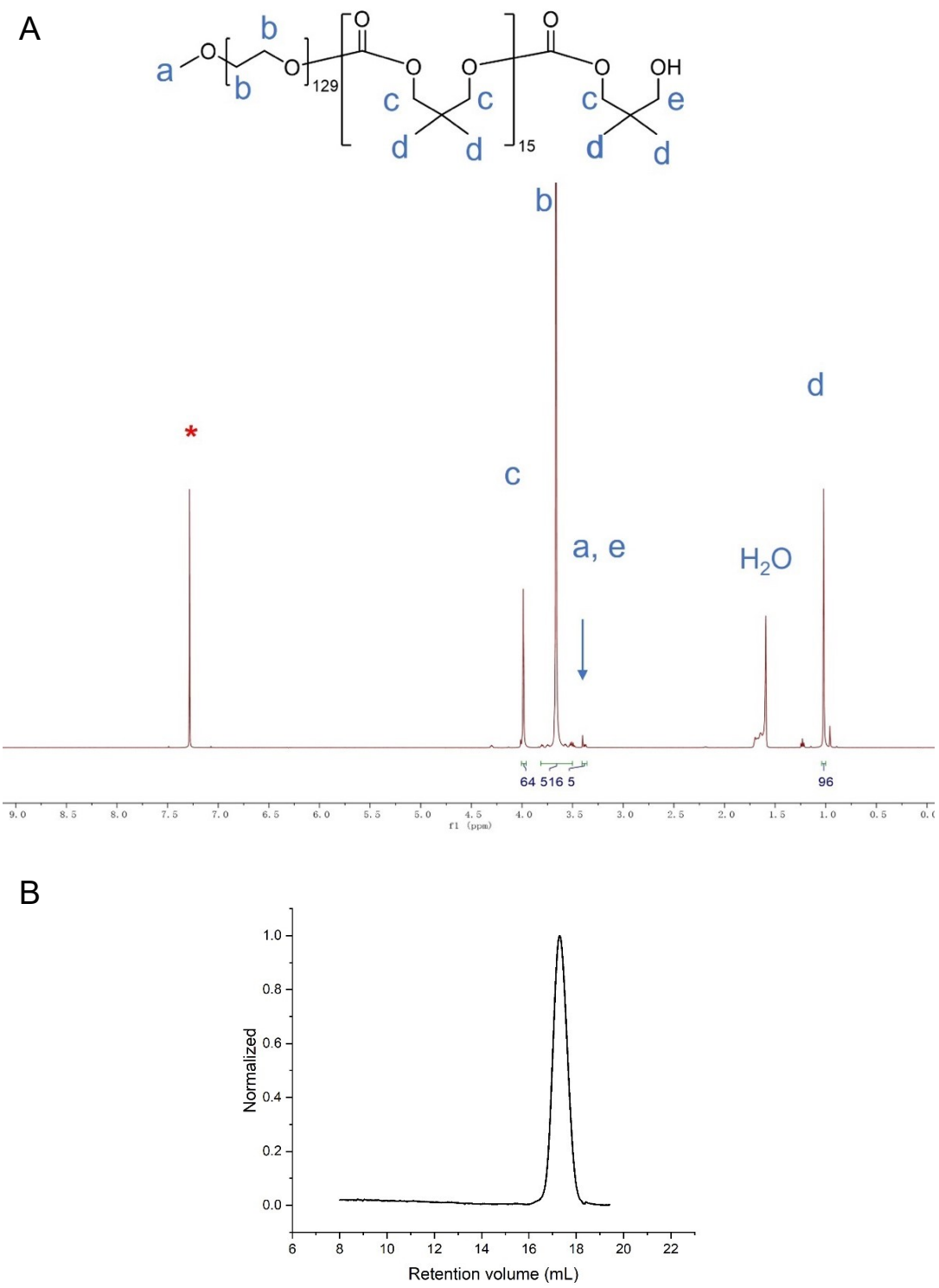
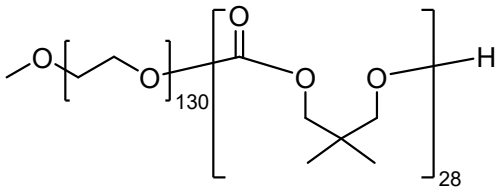


Figure S16: (A) ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of $PDTC_{16}$-*b*-PEG_{129}. Deuterated solvent residual signal denoted by *. (B) GPC chromatogram of $PDTC_{16}$-*b*-PEG_{129} using Bu_4NBr/THF (1% v/v) as the eluent.

Synthesis of $PDTC_{28}$-*b*-PEG_{130}



In the nitrogen-filled glovebox, PEG_{135} (50 mg, 1 equiv) and DTC (39 mg, 40 equiv), were added to an oven-dried 2 mL vial equipped with a magnetic bar and dissolved in 300 µL of anhydrous DCM. A solution of DBU in DCM (15 µL, 100 mg/mL, 1 equiv) was added via pipette and the vial was capped. The reaction mixture was stirred for 24 h at room temperature and then quenched with an excess of benzoic acid (15 mg). The reaction mixture was precipitated three times into 45 mL of ice-cold MeOH and collected by centrifugation. After drying in vacuo overnight, the block polymer was obtained as a white solid (77 mg, 94%).

GPC: M_n = 11,750 gmol^{-1}, $Đ_M$ = 1.07 M_n (NMR) = 9,400 gmol^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 3.99 (s, 112H, H_c), 3.67 (s, 518H, H_b), 3.40 (m, 5H, H_a and H_e), 1.02 (s, 168H, H_d).

The DP_n value of the PDTC block was determined by comparing the relative integration of the methoxy end-group of PEG (at 3.40 ppm, H_a) with the integration of the methylene protons adjacent to the carbonate carbons (at 3.99 ppm) in the PDTC segment.

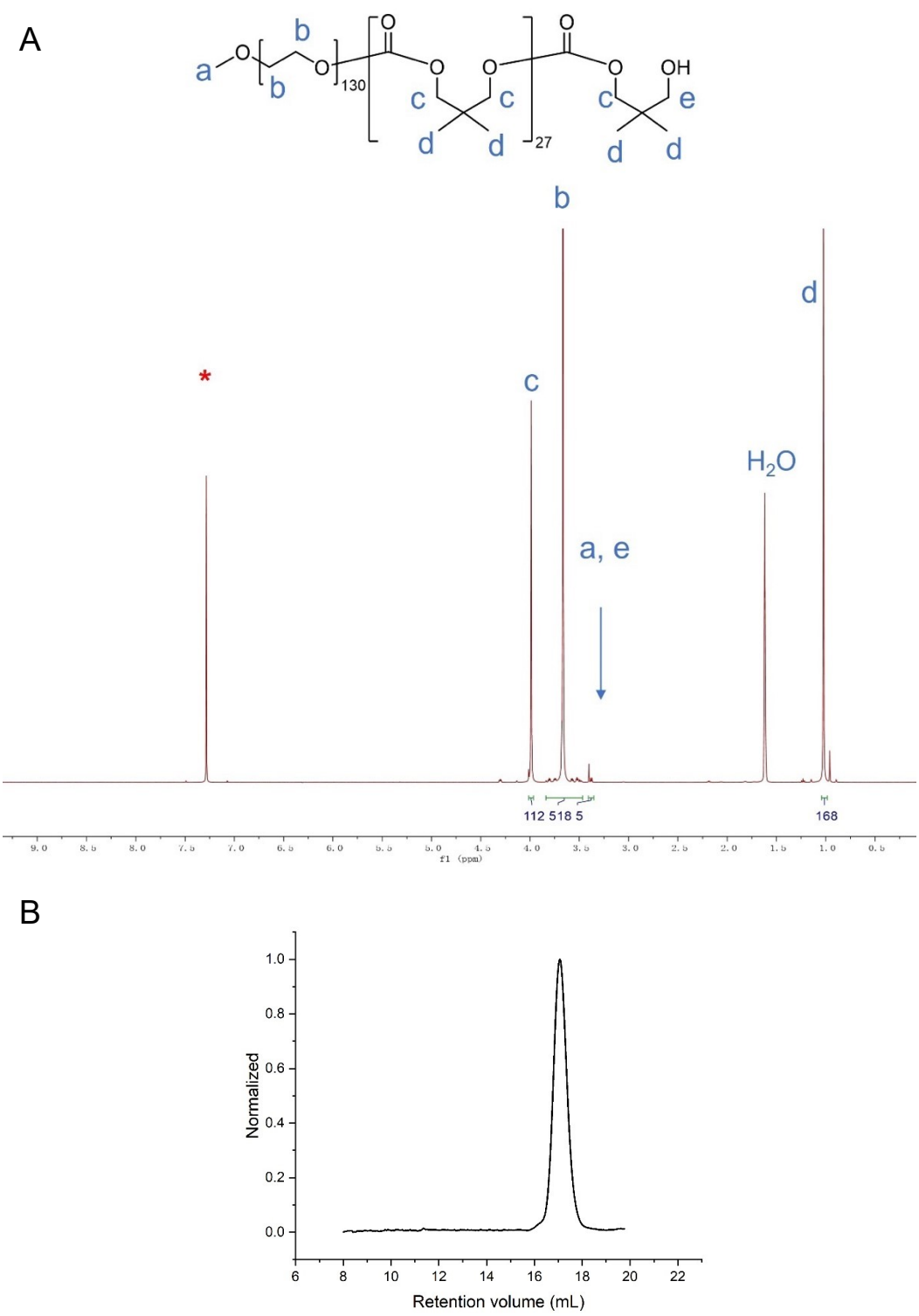
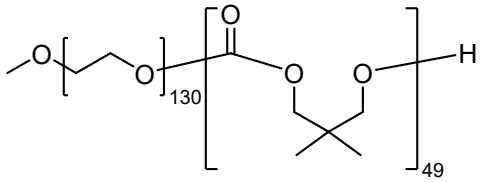


Figure S17: (A) ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of $PDTC_{28}$-*b*-PEG_{130}. Deuterated solvent residual signal denoted by *. (B) GPC chromatogram of $PDTC_{28}$-*b*-PEG_{130} using Bu_4NBr/THF (1% v/v) as the eluent.

Synthesis of $PDTC_{49}$-*b*-PEG_{130}



In the nitrogen-filled glovebox, PEG_{135} (50 mg, 1 equiv) and DTC (104 mg, 80 equiv) were added to an oven-dried 2 mL vial equipped with a magnetic bar and dissolved in 300 µL of anhydrous DCM. A solution of DBU in DCM (15 µL, 100 mg/mL, 1 equiv) was added via pipette and the vial was capped. The reaction mixture was stirred for 24 h at room temperature and then quenched with an excess of benzoic acid (15 mg). The reaction mixture was precipitated three times into 45 mL of ice-cold MeOH and collected by centrifugation. After drying in vacuo overnight, the block polymer was obtained as a white solid (94 mg, 58%).

GPC: M_n = 13,700 gmol^{-1}, $Đ_M$ = 1.06, M_n (NMR) = 12,140 gmol^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 3.99 (s, 196H, H_c), 3.67 (s, 520H, H_b), 3.40 (m, 5H, H_a and H_e), 1.02 (s, 294H, H_d).

The DP_n value of the PDTC block was determined by comparing the relative integration of the methoxy end-group of PEG (at 3.40 ppm, H_a) with the integration of the methylene protons adjacent to the carbonate carbons (at 3.99 ppm) in the PDTC segment.

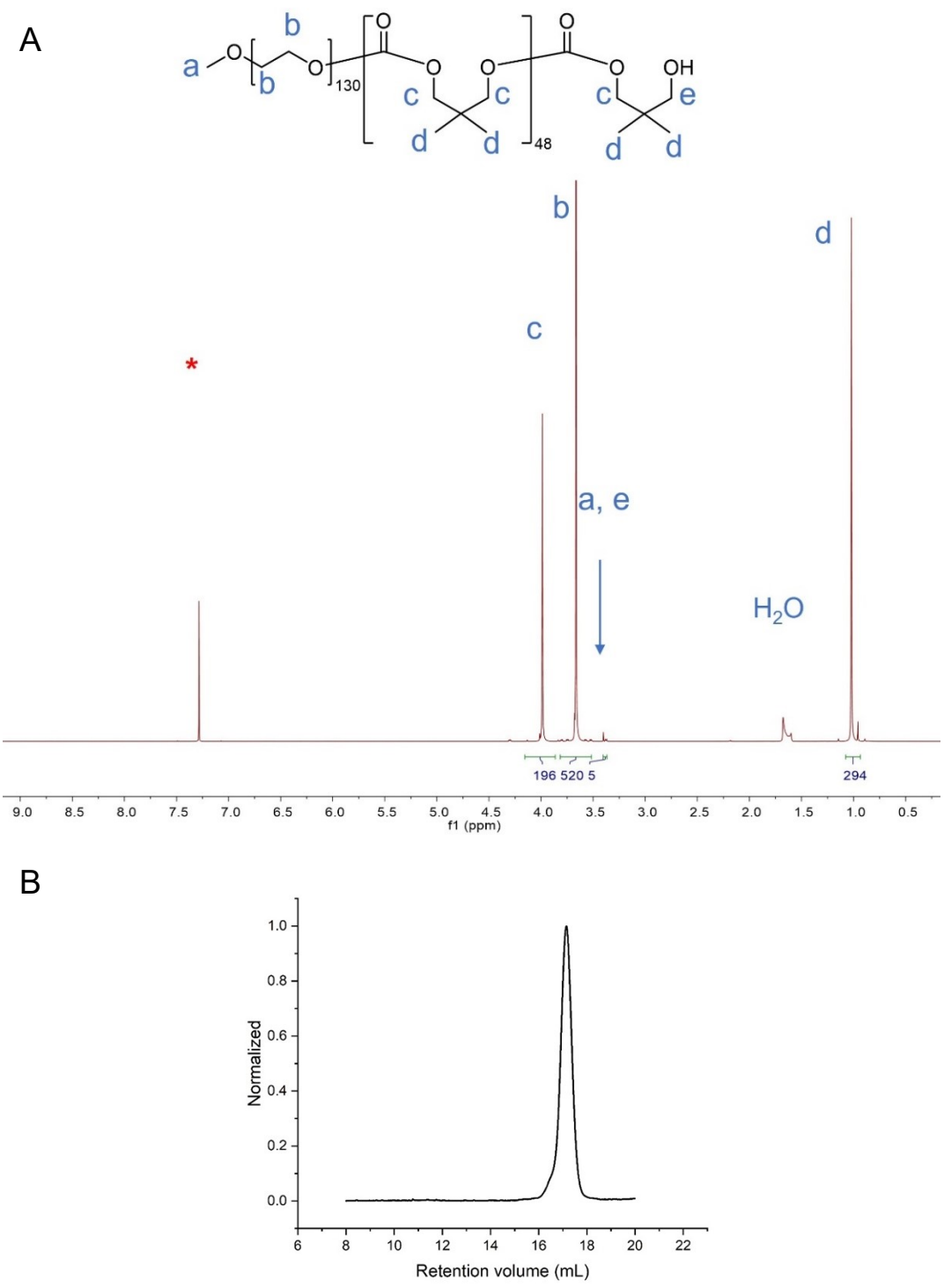
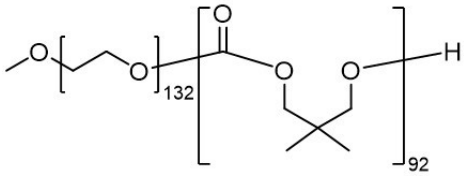


Figure S18: (A) ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of $PDTC_{49}$-*b*-PEG_{130}. Deuterated solvent residual signal denoted by *. (B) GPC chromatogram of $PDTC_{49}$-*b*-PEG_{130} using Bu_4NBr/THF (1% v/v) as the eluent.

Synthesis of $PDTC_{92}$-*b*-PEG_{132}

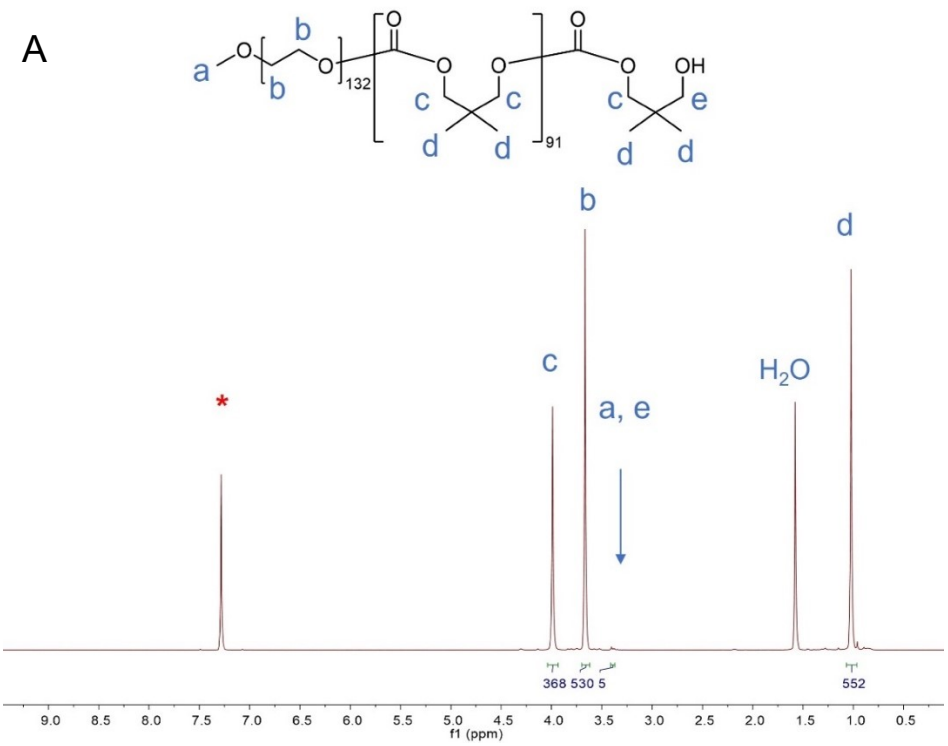


In the nitrogen-filled glovebox, PEG_{135} (85 mg, 1 equiv) and DTC (330 mg, 150 equiv) were added to an oven-dried 2 mL vial equipped with a magnetic bar and dissolved in 480 µL of anhydrous DCM. A solution of DBU in DCM (20 µL, 100 mg/mL, 0.8 equiv) was added via pipette and the vial was capped. The reaction mixture was stirred for 24 h at room temperature and then quenched with an excess of benzoic acid (15 mg). The reaction mixture was precipitated three times into 45 mL of ice-cold MeOH and collected by centrifugation. After drying in vacuo overnight, the block polymer was obtained as a white solid (270 mg, 63%).

GPC: M_n = 20,310 gmol^{-1}, $Đ_M$ = 1.06, M_n (NMR) = 17,820 gmol^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 3.99 (s, 368H, H_c), 3.67 (s, 530H, H_b), 3.40 (m, 5H, H_a and H_e), 1.02 (s, 550H, H_d).

The DP_n value of the PDTC block was determined by comparing the relative integration of the methoxy end-group of PEG (at 3.40 ppm, H_a) with the integration of the methylene protons adjacent to the carbonate carbons (at 3.99 ppm) in the PDTC segment.



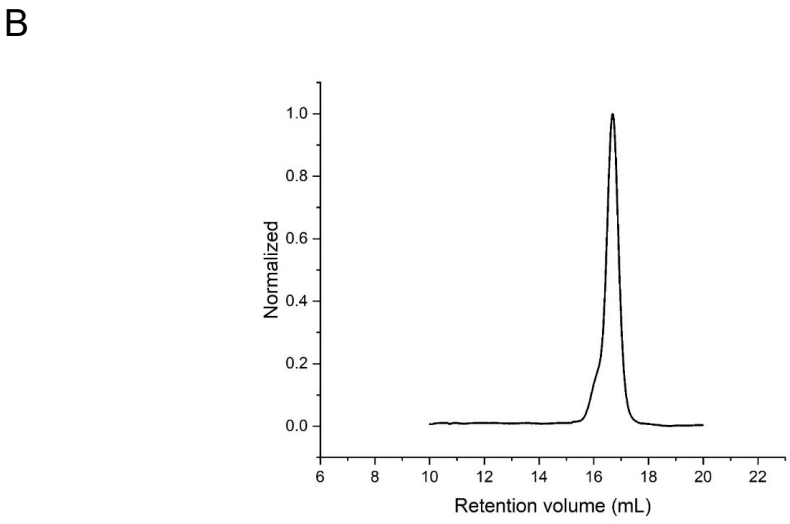
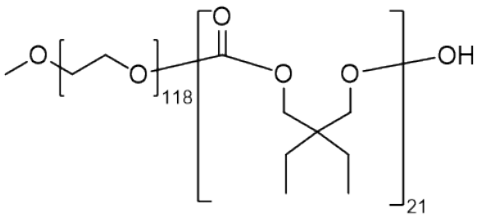


Figure S19: (A) ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of $PDTC_{92}$-*b*-PEG_{132}. Deuterated solvent residual signal denoted by *. (B) GPC chromatogram of $PDTC_{92}$-*b*-PEG_{132} using Bu_4NBr/THF (1% v/v) as the eluent.

Synthesis of $PDEC_{21}$-*b*-PEG_{118}



In the nitrogen-filled glovebox, PEG_{135} (50 mg, 1 equiv), ETC (48 mg, 30 equiv) and TU (4 mg, 1.2 equiv) were added to an oven-dried 2 mL vial equipped with a magnetic bar and dissolved in 150 µL of anhydrous DCM. A solution of DBU in DCM (18 µL, 100 mg/mL, 1.2 equiv) was added via pipette and the vial was capped. The reaction mixture was stirred for 24 h at room temperature and then quenched with an excess of benzoic acid (15 mg). The reaction mixture was precipitated three times into 45 mL of ice-cold Et_2O and collected by centrifugation. After drying in vacuo overnight, the block polymer was obtained as a white solid (81 mg, 76%).

GPC: M_n = 12,100 gmol^{-1}, $Đ_M$ = 1.05, M_n (NMR) = 8,550 gmol^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 4.00 (s, 82H, H_c), 3.64 (s, 460H, H_b), 3.38 (m, 5H, H_a and H_f), 1.36 (s, 84H, H_d), 0.84 (s, 127H, H_d).

The DP_n value of the PDEC block was determined by comparing the relative integration of the methoxy end-group of PEG (at 3.40 ppm, H_a) with the integration of the methylene protons adjacent to the carbonate carbons (at 4.00 ppm) in the PDEC segment.

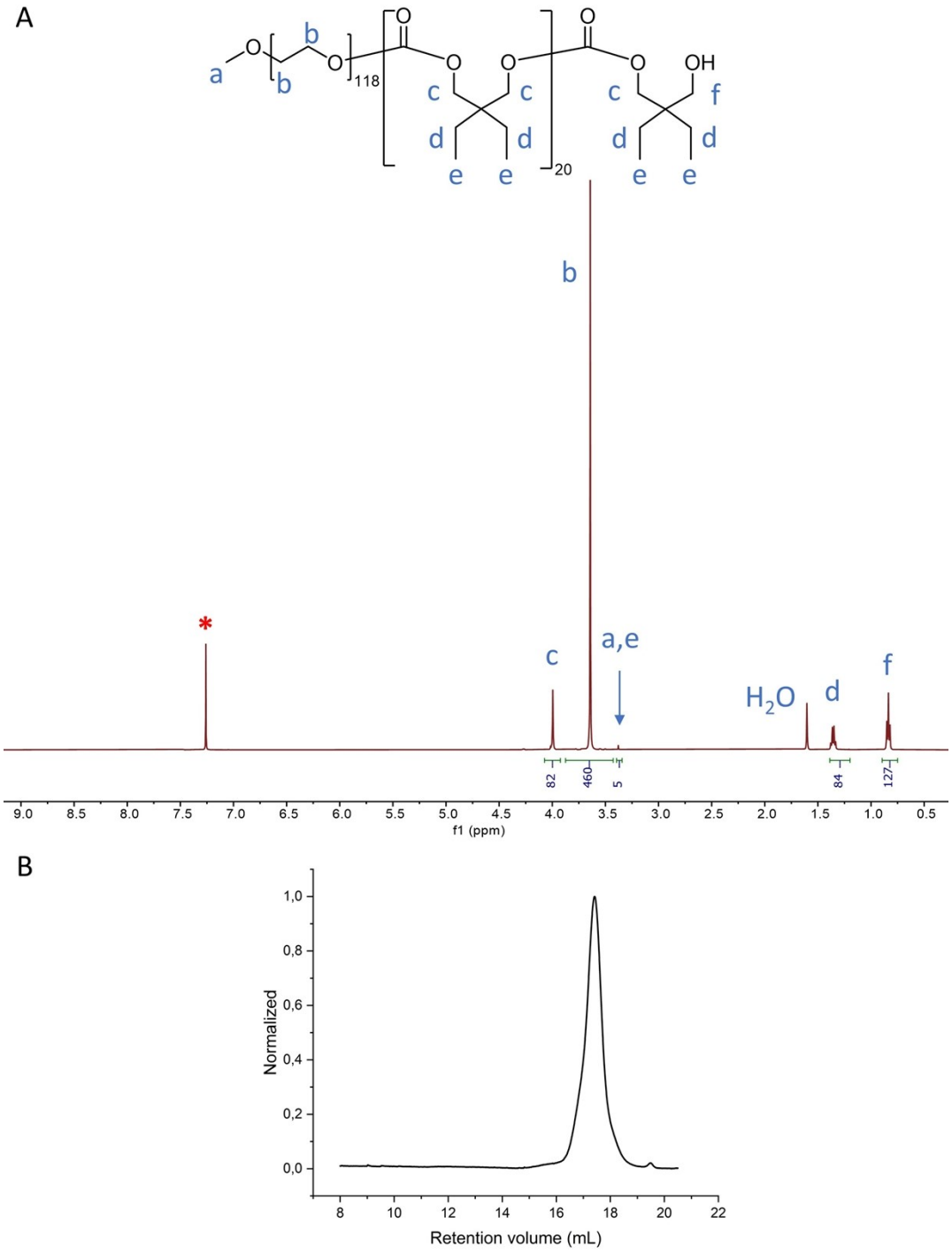
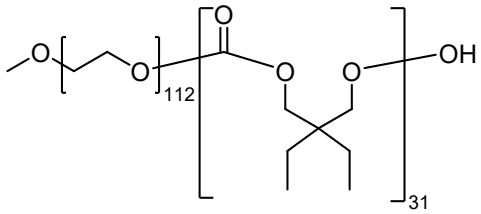


Figure S20: (A) ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of $PDEC_{21}$-*b*-PEG_{118}. Deuterated solvent residual signal denoted by *. (B) GPC chromatogram of $PDEC_{21}$-*b*-PEG_{118} using Bu_4NBr/THF (1% v/v) as the eluent.

Synthesis of $PDEC_{31}$-*b*-PEG_{112}



In the nitrogen-filled glovebox, PEG_{135} (50 mg, 1 equiv), ETC (79 mg, 50 equiv) and TU (4 mg, 1 equiv) were added to an oven-dried 2 mL vial equipped with a magnetic bar and dissolved in 150 µL of anhydrous DCM. A solution of DBU in DCM (18 µL, 100 mg/mL, 1.2 equiv) was added via pipette and the vial was capped. The reaction mixture was stirred for 24 h at room temperature and then quenched with an excess of benzoic acid (15 mg). The reaction mixture was precipitated three times into 45 mL of ice-cold Et_2O and collected by centrifugation. After drying in vacuo overnight, the block polymer was obtained as a white solid (99 mg, 72%).

GPC: M_n = 13,700 $gmol^{-1}$, $Đ_M$ = 1.05, M_n (NMR) = 9,900 $gmol^{-1}$.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 4.00 (s, 120H, H_c), 3.64 (s, 448H, H_b), 3.37 (m, 5H, H_a and H_f), 1.36 (s, 122H, H_d), 0.84 (s, 183H, H_d).

The DP_n value of the PDEC block was determined by comparing the relative integration of the methoxy end-group of PEG (at 3.37 ppm, H_a) with the integration of the methylene protons adjacent to the carbonate carbons (at 4.00 ppm) in the PDEC segment.

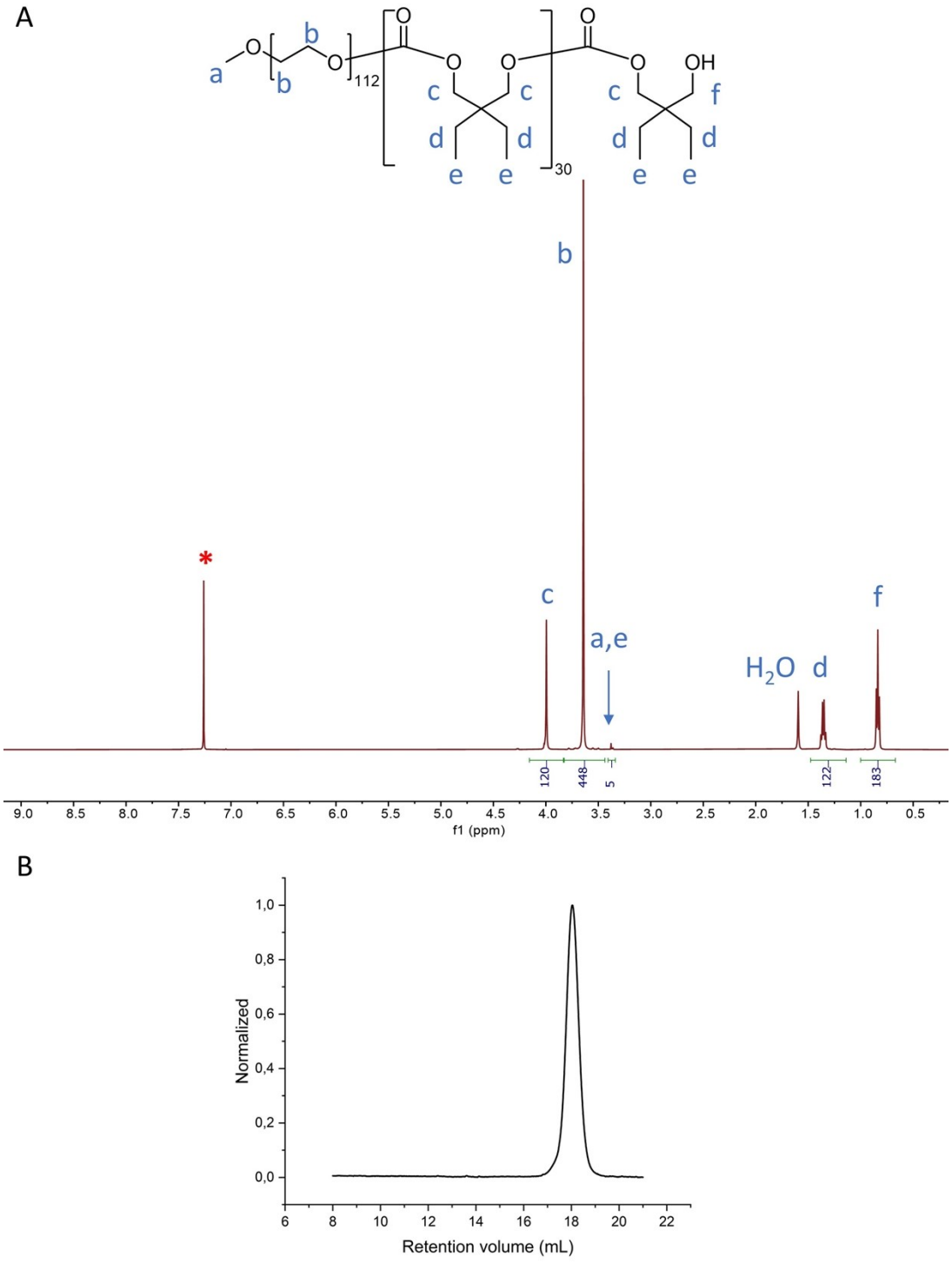
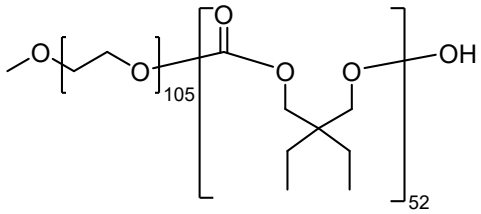


Figure S21: (A) ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of $PDEC_{31}$-*b*-PEG_{112}. Deuterated solvent residual signal denoted by *. (B) GPC chromatogram of $PDEC_{31}$-*b*-PEG_{112} using Bu_4NBr/THF (1% v/v) as the eluent.

Synthesis of $PDEC_{52}$-*b*-PEG_{105}



In the nitrogen-filled glovebox, PEG_{135} (50 mg, 1 equiv), ETC (126 mg, 80 equiv) and TU (4 mg, 1 equiv) were added to an oven-dried 2 mL vial equipped with a magnetic bar and dissolved in 150 µL of anhydrous DCM. A solution of DBU in DCM (18 µL, 100 mg/mL, 1.2 equiv) was added via pipette and the vial was capped. The reaction mixture was stirred for 24 h at room temperature and then quenched with an excess of benzoic acid (15 mg). The reaction mixture was precipitated three times into 45 mL of ice-cold Et_2O and collected by centrifugation. After drying in vacuo overnight, the block polymer was obtained as a white solid (140 mg, 75%).

GPC: M_n = 16,800 gmol^{-1}, $Đ_M$ = 1.07, M_n (NMR) = 12,900 gmol^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 3.99 (s, 204H, H_c), 3.64 (s, 421H, H_b), 3.37 (m, 5H, H_a and H_f), 1.36 (s, 206H, H_d), 0.84 (s, 309H, H_d).

The DP_n value of the PDEC block was determined by comparing the relative integration of the methoxy end-group of PEG (at 3.37 ppm, H_a) with the integration of the methylene protons adjacent to the carbonate carbons (at 3.99 ppm) in the PDEC segment.

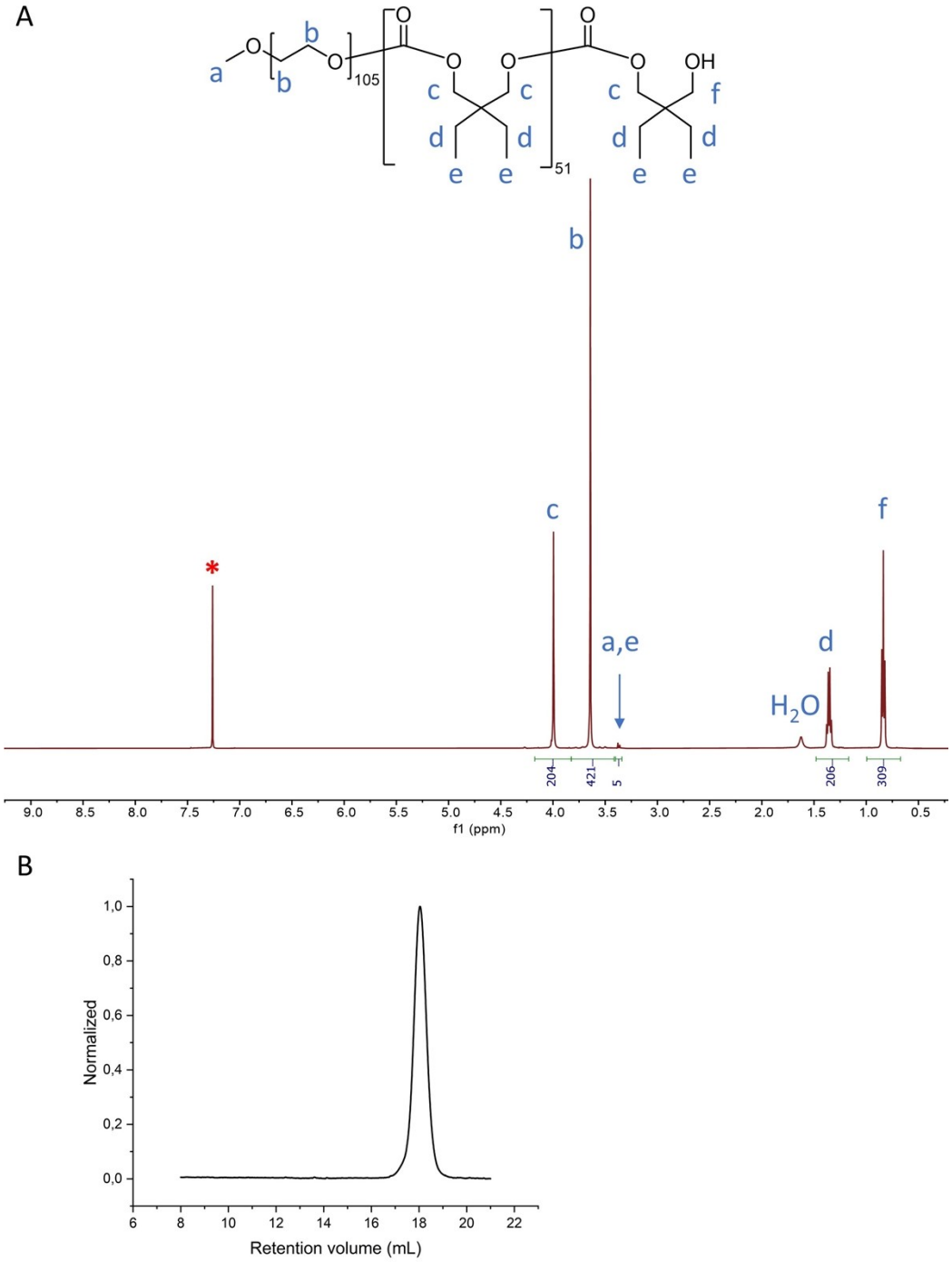
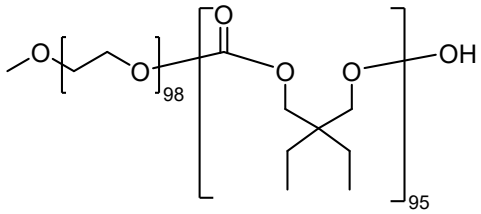


Figure S22: (A) ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of $PDEC_{52}$-*b*-PEG_{105}. Deuterated solvent residual signal denoted by *. (B) GPC chromatogram of $PDEC_{52}$-*b*-PEG_{105} using Bu_4NBr/THF (1% v/v) as the eluent.

Synthesis of $PDEC_{95}$-*b*-PEG_{98}



In the nitrogen-filled glovebox, PEG_{135} (50 mg, 1 equiv), ETC (237 mg, 150 equiv) and TU (6 mg, 1.5 equiv) were added to an oven-dried 2 mL vial equipped with a magnetic bar and dissolved in 200 µL of anhydrous DCM. A solution of DBU in DCM (23 µL, 100 mg/mL, 1.5 equiv) was added via pipette and the vial was capped. The reaction mixture was stirred for 24 h at room temperature and then quenched with an excess of benzoic acid (15 mg). The reaction mixture was precipitated three times into 45 mL of ice-cold Et_2O and collected by centrifugation. After drying in vacuo overnight, the block polymer was obtained as a white solid (227 mg, 76%).

GPC: M_n = 22,200 gmol^{-1}, $Đ_M$ = 1.09, M_n (NMR) = 19,400 gmol^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 4.00 (s, 369H, H_c), 3.64 (s, 392H, H_b), 3.37 (m, 5H, H_a and H_f), 1.36 (s, 380H, H_d), 0.84 (s, 568H, H_d).

The DP_n value of the PDEC block was determined by comparing the relative integration of the methoxy end-group of PEG (at 3.37 ppm, H_a) with the integration of the methylene protons adjacent to the carbonate carbons (at 4.00ppm) in the PDEC segment.

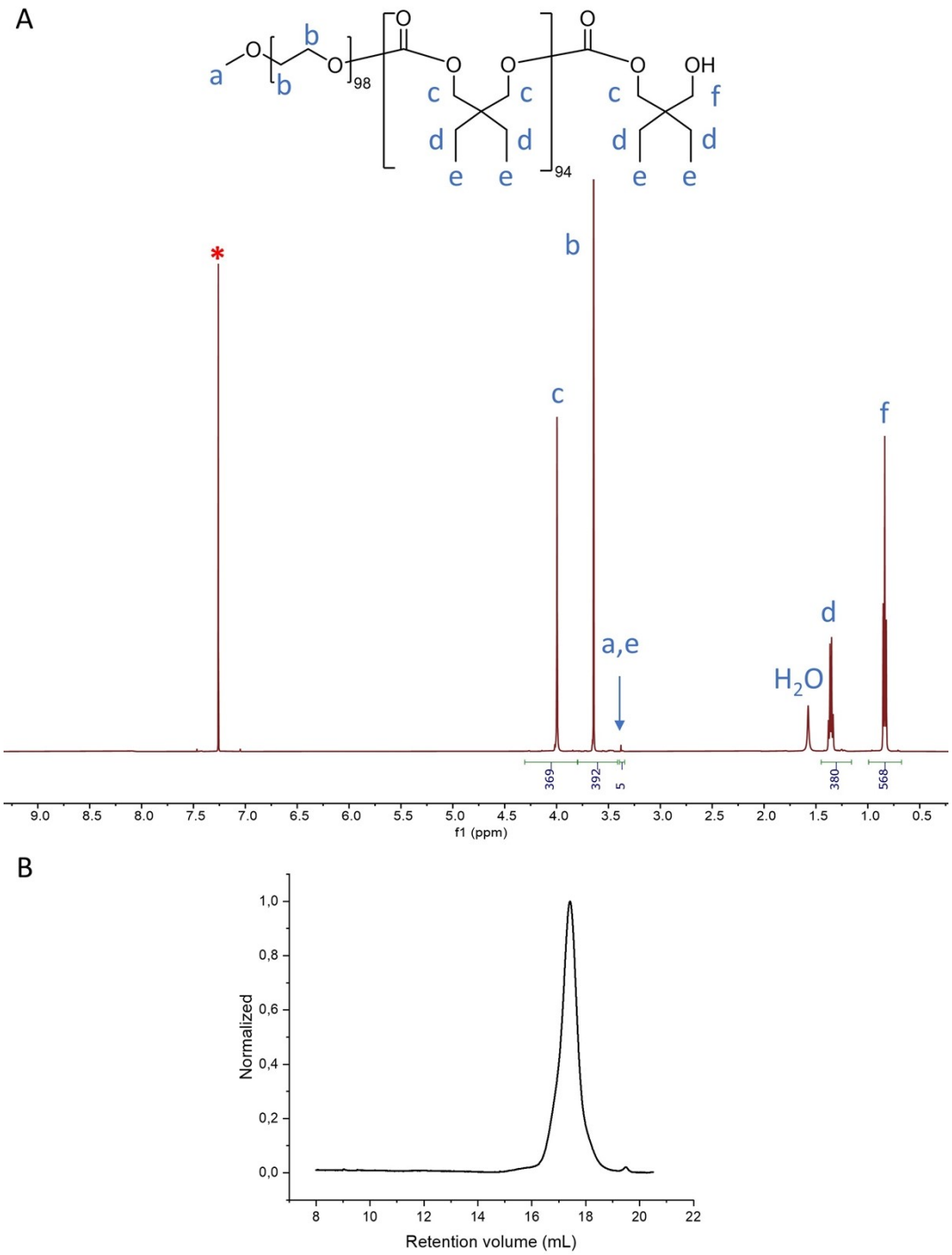
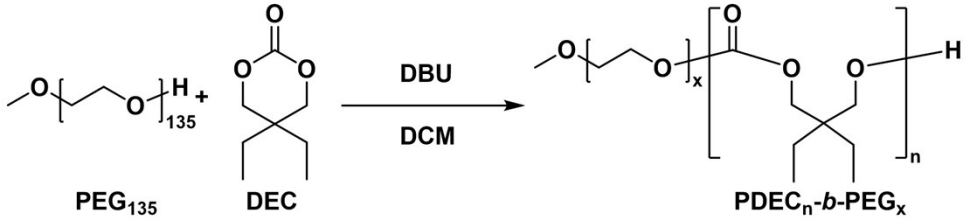


Figure S23: (A) ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of $PDEC_{95}$-*b*-PEG_{98}. Deuterated solvent residual signal denoted by *. (B) GPC chromatogram of $PDEC_{95}$-*b*-PEG_{98} using Bu_4NBr/THF (1% v/v) as the eluent.

Table S2: Synthesis of PDEC-*b*-PEG BCPs via organometallic ROP



Block Polymer	PDEC DP_n[a]	M_n (g/mol)[b]	$Đ_m$[b]	PDEC:PEG block ratio[a]
$PDEC_{21}$-*b*-PEG_{118}	21	12 100	1.05	1:6
$PDEC_{31}$-*b*-PEG_{112}	31	13 700	1.05	1:4
$PDEC_{52}$-*b*-PEG_{105}	52	16 800	1.07	1:2
$PDEC_{95}$-*b*-PEG_{98}	95	22 200	1.09	1:1

[a]Determined by ^{1}H NMR spectroscopy. [b]Determined by GPC versus polystyrene standards.

3. Self-Assembly Procedures

Compositions of all solvents for self-assembly are given as v:v. All of TEM images were obtained after the nanoplatelets were negatively stained with uranyl acetate (3 wt % in MeOH).

Self-Assembly Procedure of PDEC-*b*-PEG Block Polymer in 15:85 THF: MeOH

20 µL of THF and 10 µL of a 10 mg/mL solution $PDEC_{21}$-*b*-PEG_{118} in THF were added to 170 µL of MeOH in a vial. The resulting solution (0.5 mg/mL in 15:85 THF: MeOH) was manually shaken for ~10 s and annealed for 2 h at 70 °C. Then, the solution was cooled to 23 °C over 2 h, and aged for 24h. The resulting solution was analyzed by TEM. A similar procedure was conducted with other block polymers, including $PDEC_{31}$-*b*-$PEG_{112,}$ $PDEC_{52}$-*b*-PEG_{105} and $PDEC_{95}$-*b*-$PEG_{98.}$

Self-Assembly Procedure of PDTC-*b*-PEG Block Polymer in 15:85 THF: MeOH

100 µL of THF and 50 µL of a 10 mg/mL solution $PDTC_{10}$-*b*-PEG_{124} in THF were added to 8500 µL of MeOH in a vial. The resulting solution (0.5 mg/mL in 15:85 THF: MeOH) was manually shaken for ~10 s and annealed for 2 h at 70 °C. Then, the solution was cooled to 23 °C over 2 h, and aged for 24 h. The resulting solution was analyzed

by TEM. A similar procedure was conducted with other block polymers, including $PDTC_{16}$-*b*-PEG_{129}, $PDTC_{28}$-*b*-PEG_{130}, $PDTC_{49}$-*b*-PEG_{130}, $PDTC_{92}$-*b*-PEG_{132}.

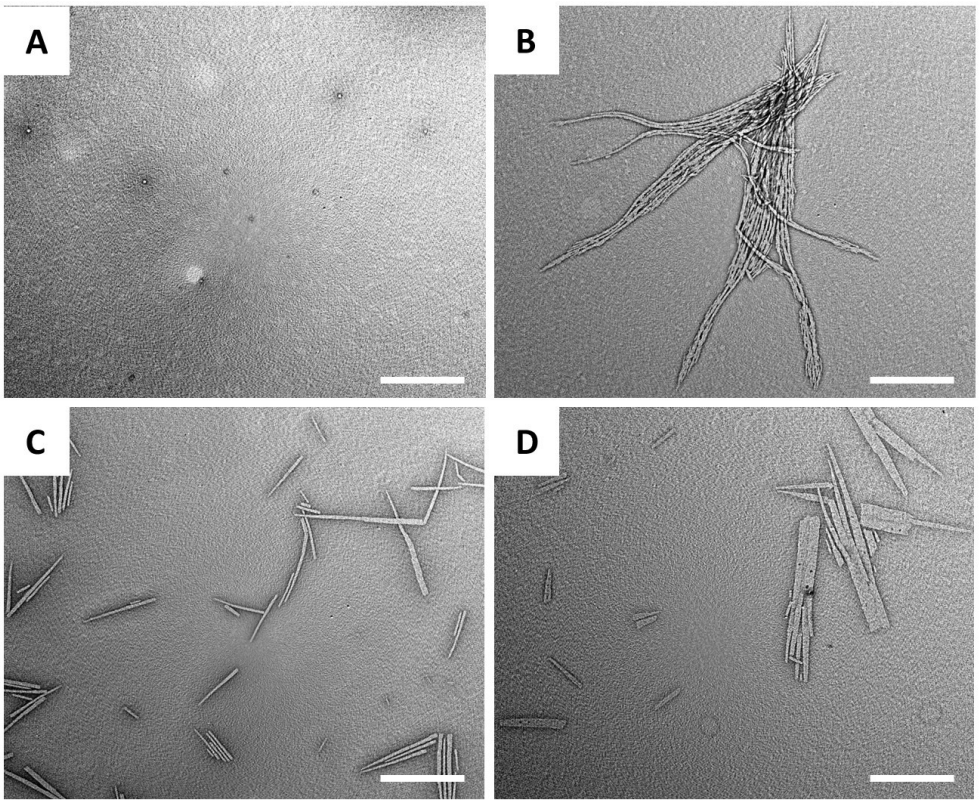


Figure S24: TEM images of micelles prepared via homogeneous nucleation in MeOH:THF (v:v) 85:15 at 0.5 mg/mL by heating polymer samples to 70 °C for 2 h before cooling to 23 °C over a period of 2 h and aging over 24 h. (A) $PDEC_{21}$-*b*-PEG_{118} (B) $PDEC_{31}$-*b*-PEG_{112}. (C) $PDEC_{52}$-*b*-PEG_{105}. (D) $PDEC_{95}$-*b*-PEG_{98}. Scale bars = 1000 nm. TEM images were stained with uranyl acetate (3 wt % in MeOH)

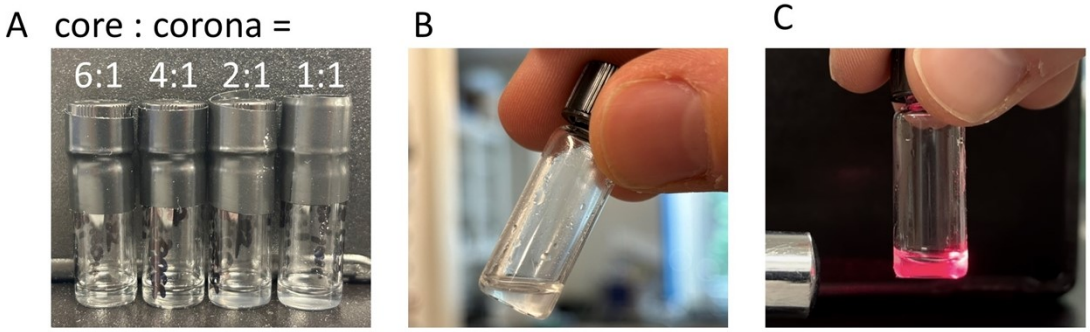


Figure S25: (A) Photos of the homogeneous nucleation experiments in MeOH:THF (v:v) 85:15 at 0.5 mg/mL by heating polymer samples to 70 °C for 2 h before cooling to 23 °C over a period of 2 h and aging over 24 h. (B) Visible precipitation of $PDEC_{95}$-*b*-PEG_{98} (core:corona = 1:1). (C) Tyndall effect of 0.5 mg/mL $PDEC_{95}$-*b*-PEG_{98} in MeOH:THF (v:v) 85:15 by using a red laser pointer as a light source, highlighting the poor colloidal stability of the nanostructures.

Self-assembly procedure of PDTC-*b*-PEG block polymer in 5:95 THF: MeOH

50 μL of a 10 mg/mL solution $PDTC_{92}$-*b*-PEG_{132} in THF were added to the 950 μL of MeOH in a vial. The resulting solution (0.5 mg/mL in 5:95 THF: MeOH) was manually shaken for ~10 s and annealed for 2 h at 70 °C. Then, the solution was cooled to 23 °C over 2 h and aged for 24 h. The resulting solution was analyzed by TEM.

Preparation of $PDTC_{92}$-*b*-PEG_{132} seed micelles by sonication

The polydisperse 2D platelet micelles derived from $PDTC_{92}$-*b*-PEG_{132} were fragmented by ultrasonication at 0 °C for 3 h using an ultrasonication processor. The resulting seed micelles were imaged by TEM.

Preparation of $PDTC_{92}$-*b*-PEG_{132} low disperse platelets with controlled area by seeded growth (living CDSA)

For seeded growth micelles with $m_{unimer}/m_{seed} \leq 50$: aliquots of $PDTC_{92}$-*b*-PEG_{132} unimer (10 mg/mL in THF), equivalent to corresponding m_{unimer}/m_{seed}, were added to diluted seed platelet solutions in 5:95 THF: MeOH (400 μL) at 40 ℃. The solution was shaken for about 10 s and aged for 24 h at 23 ºC.

For seeded growth micelles with m_{unimer}/m_{seed} ratios of 100, 200: aliquots of $PDTC_{92}$-*b*-PEG_{132} unimer (10 mg/mL in THF), equivalent to corresponding m_{unimer}/m_{seed}, were added to diluted seed nanofiber solution in 5:95 THF: MeOH (400 μL) at 40 ℃. The unimer was added in intervals of 50 m_{unimer}/m_{seed} every 24 h.

The statistical analysis of contour areas measurements for $PDTC_{92}$-*b*-PEG_{132} nanoplatelets is shown in **Figure 3**.

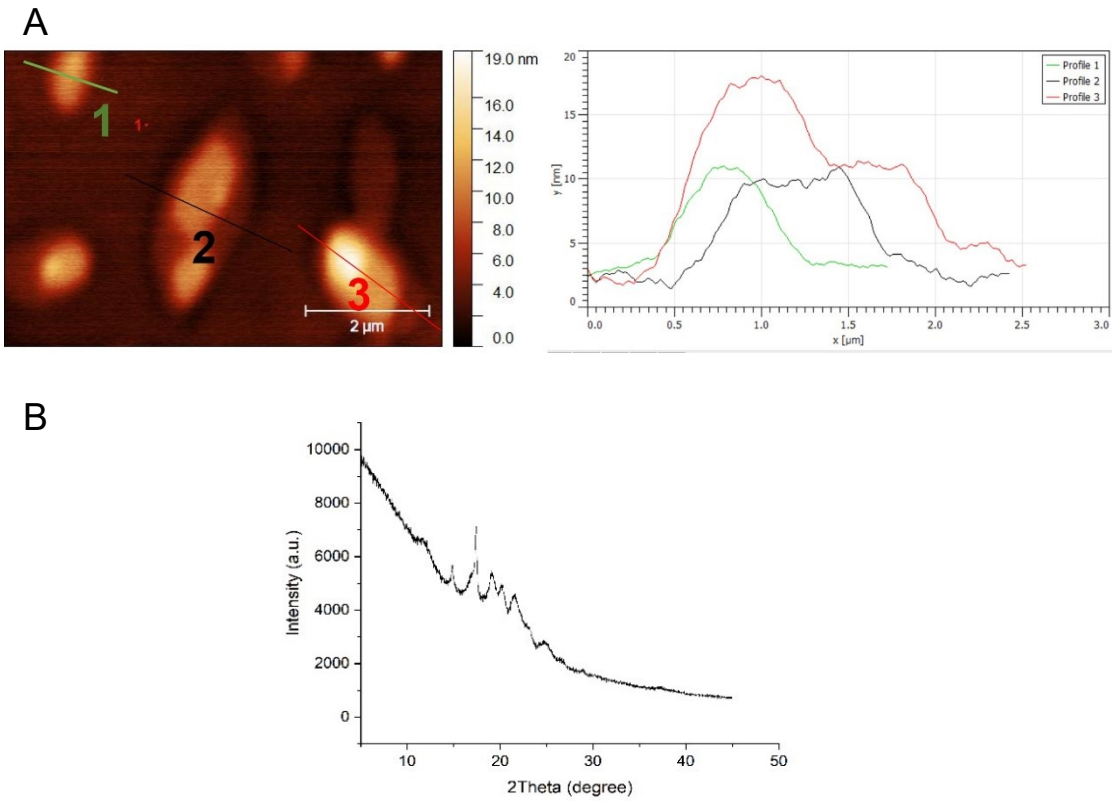


Figure S26: (A) Atomic force microscopy (AFM) images of 2D platelets prepared from MeOH:THF = 95:5 at 0.5 mg/mL by heating polymer samples to 70 °C before cooling to 23 °C over a period of 2 h and aging for 24 h. The profile showed a height of about 8 nm. (B) The X-ray diffraction (XRD) measurement was performed on thin films cast from nanoplatelet solutions.

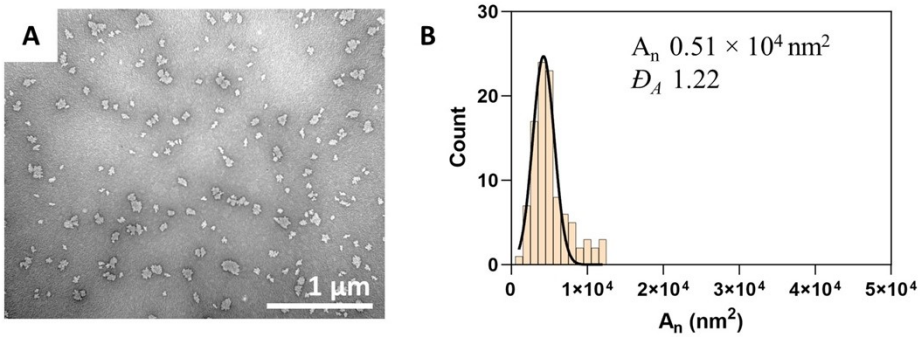


Figure S27: (A) TEM image of 2D seeds with an area of 0.51×10^4 nm^2 ($Đ_A$ = 1.22) and a concentration of 0.5 mg/ml in MeOH: THF = 95: 5 prepared by sonication of disperse platelets from $PDTC_{92}$-*b*-PEG_{132} for 3 h at 0 °C and (B) the contour area histogram for the corresponding platelets.

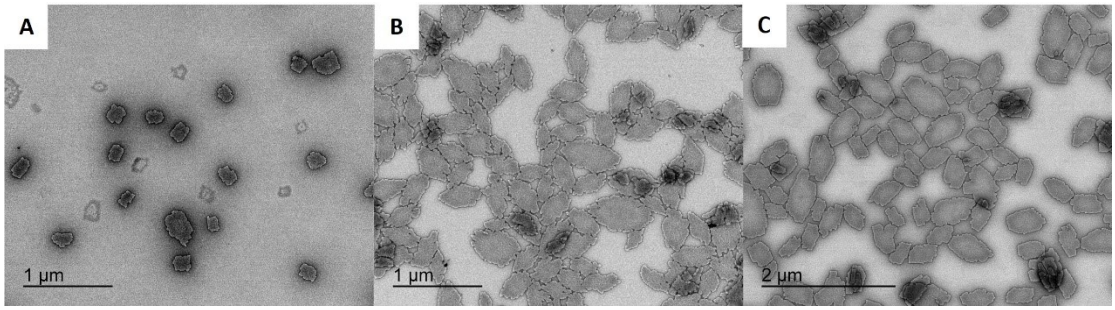
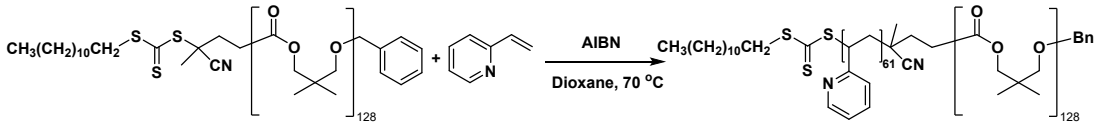


Figure S28: TEM images of 2D platelet micelles of $PDTC_{92}$-*b*-PEG_{132} prepared by a seeded growth approach with unimer-to-seed mass ratios of 20 at different temperatures. $PDTC_{92}$-*b*-PEG_{132} unimer (10 mg/mL) in THF was added to the seed micelles in MeOH (0.025 mg/mL, 0.4 mL) at different temperatures of (A) 23 °C, (B) 30 °C, (C) 40 °C. The samples were stained with uranyl acetate (3 wt % in MeOH).

Synthesis of $PDTC_{128}$-*b*-$P2VP_{61}$



$PDTC_{128}$-CTA (50 mg, 1 equiv), 2-vinylpyridine (189 mg, 400 equiv), and AIBN (0.3 mg, 0.2 equiv) were dissolved in dioxane (2 mL) in a Schlenk tube. The reaction mixture was stirred for 20 min at 23 °C followed by three freeze-pump-thaw cycles. The reaction mixture was placed in a preheated heating oil bath at 70 °C and stirred for 6.5 h. Then, the reaction was quenched by submersion in liquid nitrogen. The product was precipitated three times in ice-cold hexane. The product was dried overnight in vacuo to yield $PDTC_{128}$-*b*-$P2VP_{61}$ as a light-yellow solid (70 mg, 15%).

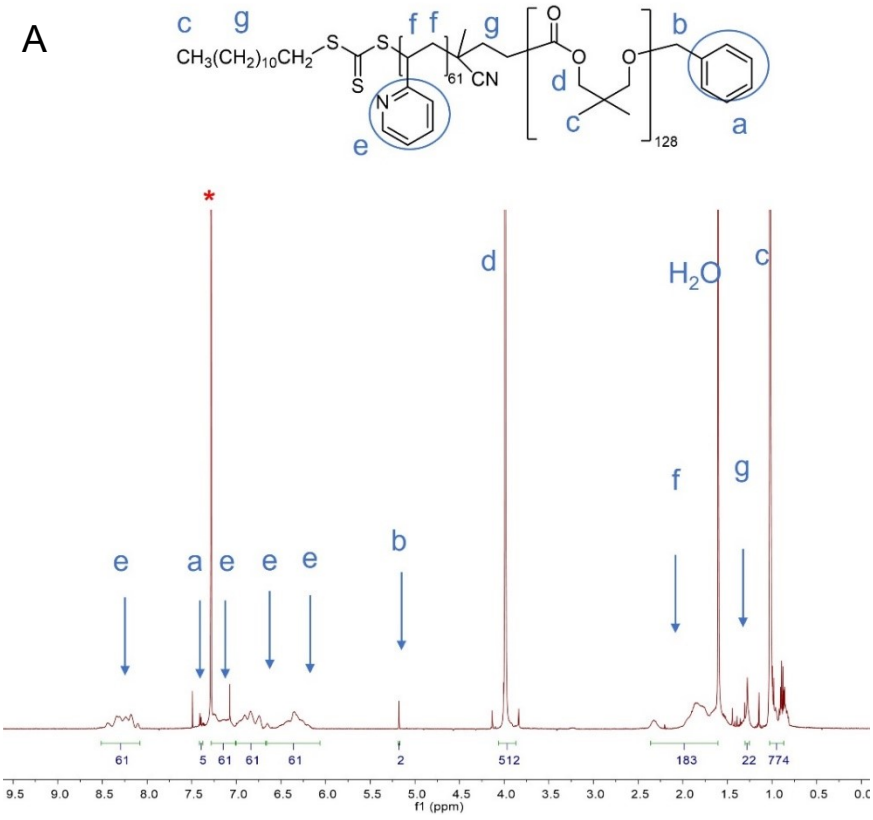
(CTA = 4-Cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid)

GPC: M_n = 29 080 gmol^{-1}, $Đ_M$ = 1.10, M_n (NMR) = 26 390 gmol^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.52 – 8.08 (m, 61H, H_e), 7.42 – 7.37 (m, 5H, H_a), 7.16 (m, J = 88.8 Hz, 61H, H_e), 6.83 (m, J = 40.2 Hz, 61H, H_e), 6.50 (m, 61H, H_e), 5.18 (s, 2H, H_b), 3.99 (s, 512H, H_d), 2.09 (d, 183H, H_f), 1.28 (s, 22H, H_g), 1.02 (s, 774H, H_c).

The DP_n of the PDTC block was determined by comparing the relative integrations of the methylene proton adjacent to the carbonate carbons (H_d) in the PDTC segment with the integration of the methylene group of benzyl end-group (at 5.17 ppm, H_a). The DP_n of the P2VP block was determined by comparing the integrations of the pyridyl protons

(H_e) in the P2VP segment with the integration of the methylene group of benzyl end-group (at 5.17 ppm, H_a).



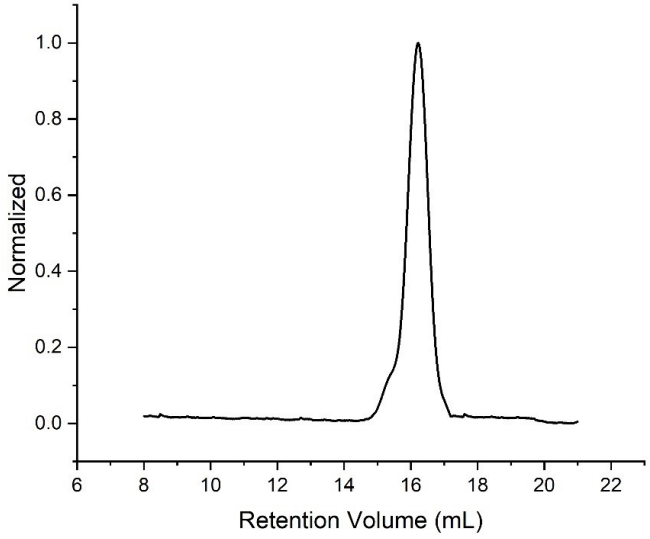


Figure S29: (A) ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of $PDTC_{128}$-*b*-$P2VP_{61}$. Deuterated solvent residual signal denoted by *. (B) GPC chromatogram of $PDTC_{128}$-*b*-$P2VP_{61}$ using Bu_4NBr/THF (1% v/v) was used as the eluent.

$PDTC_{92}$-*b*-PEG_{132} -*m*- $PDTC_{128}$-*b*-$P2VP_{61}$ Coblock Comicelles

To 400 μL of preformed $PDTC_{92}$-*b*-PEG_{132} platelet solution (A_n = 10.09×10^4 nm^2, $Đ_A$ = 1.07, 0.067 mg/mL, MeOH: THF 95:5 v:v), 25 μL of a of $PDTC_{128}$-*b*-$P2VP_{61}$ unimer solution (10 mg/mL in THF) were added at 40 ℃. The solution was manually shaken for ~10 s and aged for 24 h at 23 °C. The resulting 2D platelets were analyzed by TEM after staining as shown in **Figure S30B.**

$PDTC_{92}$-*b*-PEG_{132} -*m*- $PDTC_{128}$-*b*-$P2VP_{61}$ -*m*- $PDTC_{92}$-*b*-PEG_{132}-Dy Triblock Comicelles

To 400 μL of a prepared $PDTC_{92}$-*b*-PEG_{132} -*m*- $PDTC_{128}$-*b*-$P2VP_{61}$ coblock comicelles solution (A_n = 45.58×10^4 nm^2, $Đ_A$ = 1.07, 0.15 mg/mL, MeOH:THF 95:5 v:v) was added 1.56 μL of a $PDTC_{92}$-*b*-PEG_{132}-Dy unimer solution (10 mg/mL in THF) at 40 °C. The solution was manually shaken for ~10 s and aged for 24 h at 23 °C. The resulting 2D platelets were analyzed by TEM after staining as shown in **Figure 30C.**

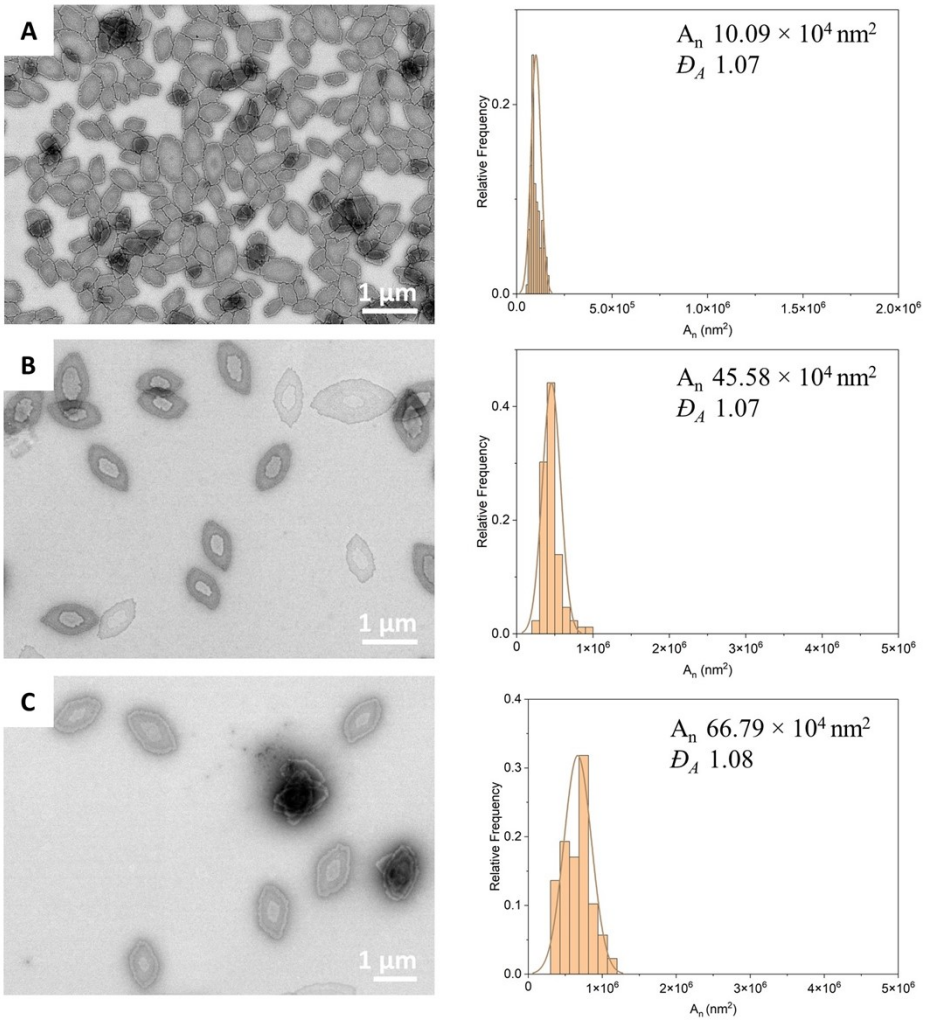
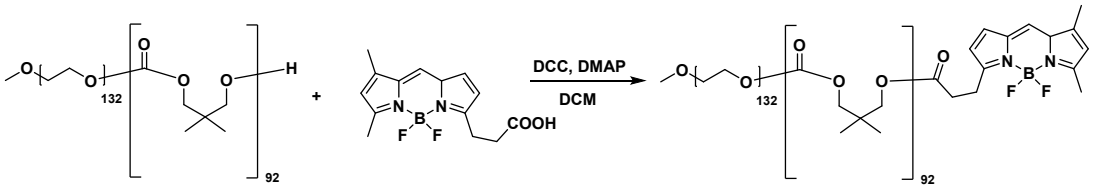


Figure S30: (A) TEM image of $PDTC_{92}$-*b*-PEG_{132} 2D platelets with an area of 10.09×10^4 nm^2 ($Đ_A$ = 1.07) in MeOH : THF = 95:5 and the contour area histogram for the corresponding platelets. (B) TEM image of PEG-*b*-P2VP block comicelles with an area of 45.58×10^4 nm^2 ($Đ_A$ = 1.07) in MeOH : THF = 95:5 prepared from preformed $PDTC_{92}$-*b*-PEG_{132} platelets ($A_n = 10.09\times10^4$ nm^2, $Đ_A$ = 1.07) and $PDTC_{128}$-*b*-$P2VP_{61}$ unimer and the contour area histogram for the corresponding platelets. (C) TEM image of PEG-*b*-P2VP-*b*-PEG-Dy triblock comicelles with an area of 66.79×10^4 nm^2 ($Đ_A$ = 1.08) in MeOH : THF = 95:5 prepared from PEG-*b*-P2VP block comicelles and $PDTC_{92}$-*b*-PEG_{132}-Dy unimer and the contour area histogram for the corresponding platelets.

Synthesis of $PDTC_{92}$-*b*-PEG_{132}-Dy (Dy = BODIPY)



$PDTC_{92}$-*b*-PEG_{132} (60 mg, 1 equiv), BODIPY-FL carboxylic acid (2.1 mg, 2 equiv) and DMAP (0.04 mg, 0.1 equiv) were added to an oven-dried 10 mL vial equipped with a magnetic bar and dissolved in 3 mL of DCM. The reaction mixture was stirred for 20 min at 23 °C. Then, DCC (3.4 mg, 2.5 equiv) was added and the reaction mixture was stirred overnight at 23 °C. The reaction mixture was precipitated three times into ice-cold Et_2O and collected by centrifugation. After drying in vacuo PDTC-*b*-PEG_{123}-Dy was obtained as an orange solid (52 mg, 87%). UV-vis measurements were used to confirm the attachment of the BODIPY dye to the block copolymer.[3] The UV-vis spectrum of the dye-labeled block polymer showed strong absorbance at about 500 nm. In contrast, the starting materials $PDTC_{92}$-*b*-PEG_{132} did not show any obvious absorbance at a wavelength from 250 nm to 800 nm, indicating $PDTC_{92}$-b-PEG_{132} was labeled with the dye BODIPY successfully.

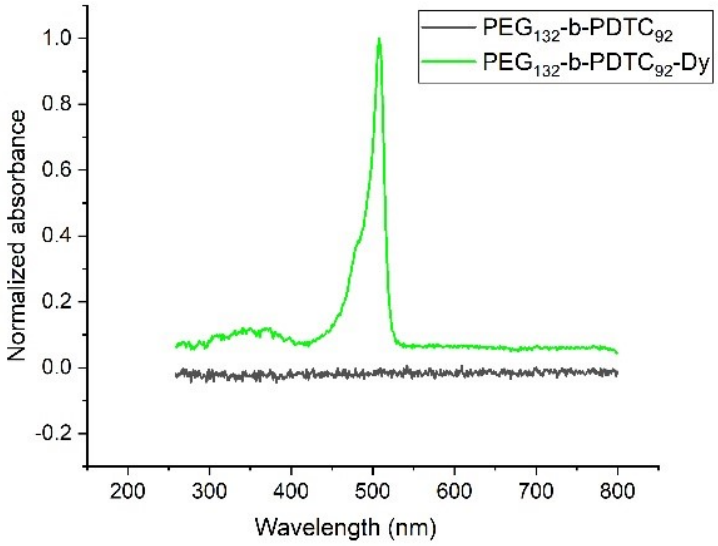


Figure S31: UV-vis spectrum of $PDTC_{92}$-*b*-PEG_{132}-Dy in $CHCl_3$ (green trace) and $PDTC_{92}$-*b*-PEG_{132} in $CHCl_3$ (black trace).

4. Aqueous Stability and Biocompatibility Studies

To a 0.42 mL solution of $PDTC_{92}$-*b*-PEG_{132} seed micelles ($A_n = 0.23\times10^4$ nm^2, $Đ_A = 1.35$, 0.48 mg/mL, MeOH) was added 80 μL of a 10 mg/mL THF solution of $PDTC_{92}$-*b*-PEG_{132} at 40 °C. The solution was manually shaken for ~10 s and aged for 24 h at 23 °C. The resulting 2D platelets (0.5 mL, 2 mg/mL in MeOH:THF 10:1 v:v) were analyzed by TEM as shown in **Figure S32A**.

A nanoplatelet solution (0.5 mL, 2 mg/mL in MeOH: THF 10:1) was dialyzed against water for 72 h (molecular weight cut-off (MWCO = 12,000-14,000 Da Spectra/Por). The water was replaced five times. The resulting platelets were analyzed by TEM as shown in **Figure S32B**. The micelles were stored at room temperature for 1 month and then analyzed by TEM as shown in **Figure S32C**.

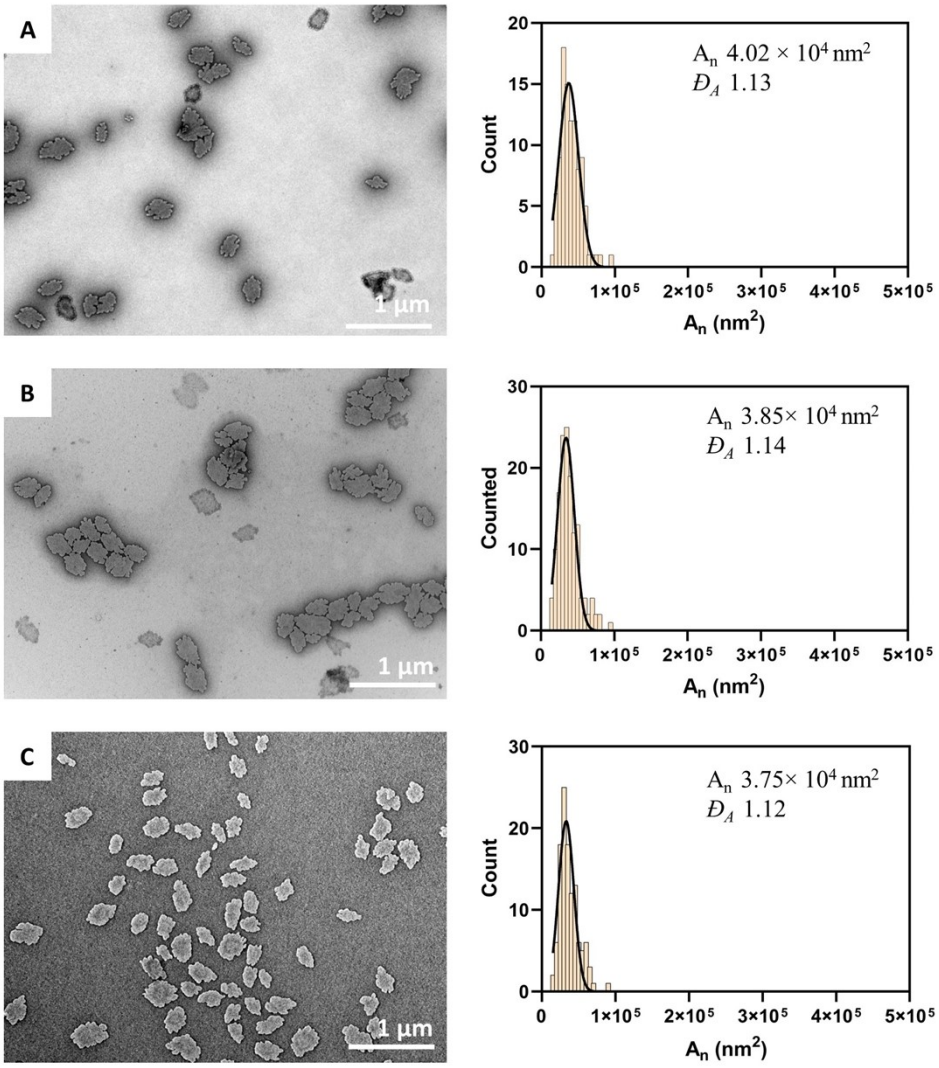


Figure S32: (A) TEM image of 2D platelets with an area of 4.02×10^4 nm^2 ($Đ_A$ = 1.13) at a concentration of 2 mg/ml in MeOH: THF = 95: 5 prepared by living CDSA from $PDTC_{92}$-*b*-PEG_{132} and the contour area histogram for the corresponding platelets. (B) TEM image of 2D platelets with an area of 3.85×10^4 nm^2 ($Đ_A$ = 1.14) after dialysis into water and the contour area histogram for the corresponding platelets. (C) TEM image of 2D platelets with an area of 3.75×10^4 nm^2 ($Đ_A$ = 1.12) in water stored for 1 month at 23 °C and the contour area histogram for the corresponding platelets.

Culture Protocols

U-87 MG (Human glioblastoma cell line) was grown in Dulbecco's Minimal Essential Medium (DMEM) and WI-38 (Caucasian fibroblast-like fetal lung cells) was grown in Minimal Essential Medium (MEM). All growth media were supplemented with 10% fetal bovine serum (FBS). Confluent cultures (80% or less) were detached from the surface using trypsin (Tryp LE Express) and plated at $1x10^4$ cells/well ($1x10^5$ cells/mL) in 96-well plates. Cell culture media and additives were purchased from ThermoFisher Scientific.

Cell Viability Assays

The biocompatibility of $PDTC_{92}$-*b*-PEG_{132} based 2D platelet micelles ($A_n = 3.85\times10^4$ nm^2, $Đ_A = 1.14$) and 2,2-dimethylpropane-1,3-diole on U-87 MG and WI-38 was evaluated after 24 h of incubation and analyzed with the cell viability assay CellTiter-Glo 2.0 (Promega). CellTiter-Glo 2.0 determines the number of viable cells by quantifying ATP, which indicates the presence of metabolically active cells. The resulting luminescence signal is directly proportional to the number of viable cells. U-87 MG and WI-38 were incubated with 0 – 100 µg/mL of 2D platelet micelles ($A_n = 3.85\times10^4$ nm^2, $Đ_A = 1.14$) and 0 - 250 µg/mL of 2,2-dimethylpropane-1,3-diol for 24 h. Polyethyleneimine (PEI) homopolymer (0.5 µM/mL) was used as a positive control. Each experiment was repeated in triplicate and each data point was repeated in triplicate. The cell viability assay was used according to the manufacturer protocol (Promega). For the addition of the assay, 50 µL of the growth media was removed from each well and 50 µL of CellTiter-Glo 2.0 was added (total volume 100 µL). After 30 min of incubation and stabilization of the luminescence signal, the luminescence was measured using a plate reader. The results were expressed as a percentage compared to the control cells without 2D platelet micelles or 2,2-dimethylpropane-1,3-diole present using GraphPad Prism 10 (**Table S2 and S3**).

Table S3: Cell viability of U-87 MG and WI-38 cells after the addition of 2D platelets (BCP = $PDTC_{92}$-*b*-PEG_{132}) at different concentrations ranging from 1-100 µg/mL. PEI was used as a positive control.

2D platelet micelles (µg/ml)		100	75	50	25	10	5	2.5	1	PEI (1 µg/mL)
U-87 MG	Mean (% of control)	94	89	90	97	93	83	84	85	5
	σ (% of control)	14	16	11	12	13	16	7	16	1
WI-38	Mean (% of control)	106	116	108	107	100	105	103	103	10
	σ (% of control)	13	19	19	15	13	20	19	21	3

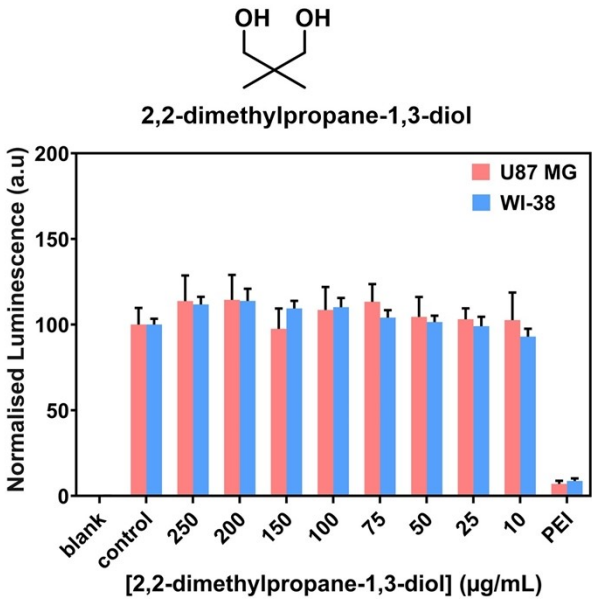


Figure S33: (A) Biocompatibility study of 2,2-dimethylpropane-1,3-diol towards U-87 MG and WI-38 after 24 h exposure with concentrations ranging from 10-250 µg/mL. PEI was used as a positive control (500 µg/mL). Cell viability was analyzed using CellTiter-Glo 2.0.

Table S4: Cell viability of WI-38 and U-87 MG cells after the addition of 2,2-dimethylpropane-1,3-diol at different concentrations ranging from 10-250 µL/mL. PEI was used as a positive control.

2,2-dimethylpropane-1,3-diol (µg/ml)		250	200	150	100	75	50	25	10	PEI (1 µg/mL)
U-87 MG	Mean (% of control)	114	115	98	109	1113	104	103	103	7
	σ (% of control)	24	23	19	21	16	18	10	25	3
WI-38	Mean (% of control)	112	114	110	110	104	102	99	93	9
	σ (% of control)	6	10	6	8	6	5	8	6	2

5. References

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