Annexes

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Annex A. Experimental Section

A.1. Synthesis and characterization of MAC monomer

Synthesis and characterization of 2,2,5-Trimethyl-1,3-dioxane-5-carboxylic acid (1). bis-MPA (15.00 g, 111.8 mmol), 2,2-dimethoxypropane (17.47 g, 167.7 mmol) and *p*-toluenesulfonic acid (1.10 g, 5.6 mmol) were solved in acetone (75 mL) and stirred for 2 h at room temperature. The reaction crude was neutralized by NH_3/EtOH (1:1) (2 mL). Acetone was evaporated to dryness and the product solved in DCM (250 mL), washed with water (2x20 mL). The organic layer was dried with magnesium sulphate, filtered and the solvent removed by evaporation obtaining a white solid. Yield = 83 %. **^{1}H-NMR** (400 MHz, CDCl3) δ (ppm) 4.17 (d, 2H, J = 12.4 Hz), 3.70 (d, 2H, J = 12.4 Hz), 1.46 (s, 3H), 1.43 (s, 3H), 1.20 (s, 3H). **^{13}C-NMR** (100 MHz, CDCl3) δ (ppm) 180.09, 98.33, 65.86, 41.72, 25.20, 21.93, 18.40. **FTIR** (KBr) υ (cm^{-1}): 3600-3000 (O-H), 3000-2900 (Csp^3-H), 1725 (C=O).

Synthesis and characterization of allyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate (2). 2,2,5-Trimethyl-1,3-dioxane-5-carboxylic acid (8.80 g, 50.5 mmol) was solved in anhydrous dichloromethane (40 mL) under argon atmosphere. Allyl alcohol (2.64 g, 45.4 mmol) and 4-(dimethylamino)pyridinium *p*-toluenesulfonate (DPTS, 5.6 g, 20.1 mmol) were added while cooling with an ice bath. Solution of *N, N'*-dicyclohexylcarbodiimide (DCC, 12.64 g, 61.3 mmol) was dropwise added. After 15 min, the ice bath was removed and the reaction stirred at room temperature for 72 h. The white precipitate was filtered off and the solvent removed under vacuum. The crude product was purified by column chromatography on silica gel using hexane/ethyl acetate (9/1) as eluent. Dicyclohexylurea (DCU), which appears as by-product, was precipitated in cold diethyl ether and filtered off. The resulting product was dried under vacuum, isolating a yellow oil. Yield = 85 %.

^{1}H-NMR (300 MHz, CDCl3) δ (ppm) 5.97-5.84 (m, 1H), 5.36 (dq, 1H, J= 17.4 Hz, J = 1.5 Hz), 5.22 (dq, 1H, J = 10.5 Hz, J = 1.5 Hz), 4.64 (dt, 2H, J = 5.4 Hz, J = 1.4 Hz), 4.20 (d, 2H, J = 12.0 Hz), 3.64 (d, 2H, J = 11.7 Hz), 1.42 (s, 3H), 1.38 (s, 3H), 1.20 (s, 3H). **^{13}C RMN** (100 MHz, $CDCl_3$) δ (ppm) 173.86, 131.95, 118.03, 98.06, 65.99, 65.28, 41.84, 24.33, 22.91, 18.68.

Synthesis and characterization of allyl 3-hydroxy-2-(hydroxymethyl)-2-methyl-propionate (3). DOWEX® 50-W2 acid resin (2 g) was added to a solution of (2) in methanol (90 mL). The mixture was stirred for 24 h at room temperature. The resin was filtered off and the solvent removed under vacuum obtaining a yellow oil. Yield = 92 %.

^{1}H NMR (400 MHz, CDCl3) δ (ppm): 5.97-5.87 (m, 1H), 5.32 (dq, 1H, J = 17.2 Hz, J = 1.6 Hz), 5.26 (dq, 1H, J = 10.4 Hz, J = 1.4 Hz), 4.67 (dt, 2H, J = 5.6 Hz, J = 1.6 Hz), 3.92 (dd, 2H, J = 10.8 Hz, J = 6.8 Hz), 3.72 (dd, 2H, J = 11.2 Hz, J = 6.4 Hz), 2.90 (t, 2H, J = 6.8 Hz), 1.08 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 175.56, 131.73, 118.40, 68.13, 65.50, 49.19, 17.12. **FTIR** (KBr) υ (cm^{-1}): 3700-3100 (O-H), 3100-3000 (Csp^2-H), 3000-2900 (Csp^3-H), 1721 (C=O), 1650 (C=C).

Synthesis and characterization of 5-Methyl-5-allyloxycarbonyl-1,3-dioxan-2-one (MAC). A solution of (3) (6.10 g, 35.0 mmol) in anhydrous dichloromethane (30 mL) was previously dried for 12 h over activated 4 Å molecular sieves under Ar atmosphere. This solution was added via cannula to a flask and, then, a solution of 1,1′-carbonyldiimidazole (CDI) (6.24 g, 38.5 mmol) solved in the minimum amount of anhydrous dichloromethane was added dropwise. The reaction was stirred for 24 h at room temperature and the crude reaction evaporated to dryness. The mixture was purified by flash column chromatography on silica gel using dichloromethane/ethyl acetate (9/1) as eluent. The resulting product was dried under vacuum, isolating a white powder. Yield = 52 %.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 5.91 (ddt, 1H, J = 16.4 Hz, J = 10.4 Hz, J = 6.0), 5.36 (dq, 1H, J = 17.2 Hz, J = 1.6 Hz), 5.31 (dq, 1H, J = 10.4 Hz, J = 1.2 Hz), 4.71 (m, 4H), 4.22 (d, 2H, J = 10.8 Hz), 1.36 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 170.72, 147.36, 130.41, 119.49, 72.93, 66.62, 40.19, 17.60. **FTIR** (KBr) υ (cm^{-1}): 3150-3000 (Csp^2-H), 3000-2900 (Csp^3-H), 1743 (C=O), 1650 (C=C).

A.2. Synthesis and characterization of PMAC homopolymer

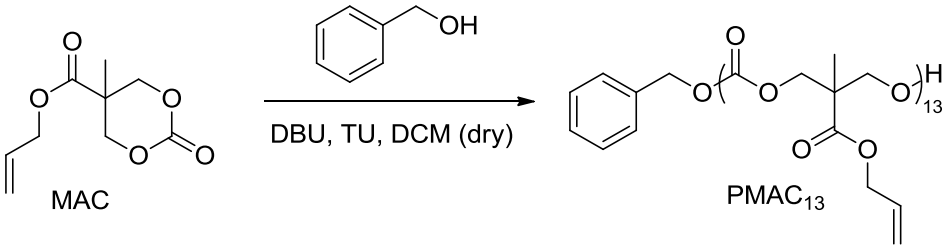


Figure A.1. Synthesis of $PMAC_{13}$ homopolymer.

A solution of benzyl alcohol (62.7 mg, 0.58 mmol), DBU (11.4 mg, 0.075 mmol) and TU (138.7 mg, 0.38 mmol) in dry dichloromethane (7.5 mL) was previously dried for 12 h over activated 4 Å molecular sieves under Ar atmosphere. This solution was added to a Schlenk flask charged with MAC (1.5 g, 7.49 mmol) under Ar atmosphere. After three vacuum-Ar cycles, the reaction was stirred at 35ºC for 8 h. Then, benzoic acid (45 mg, 0.37 mmol) was added and the resulting reaction mixture precipitated in cold hexane. Flash column chromatography on silica gel was performed using hexane/ethyl acetate as eluent, starting with a 8/2 mixture and increasing ethyl acetate content until 3/7. Product was finally precipitated in cold hexane, solved in DCM and evaporated to dryness obtaining a colorless oil. Yield = 66 %.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 7.41-7.33 (m, 5H), 5.95-5.82 (m, 13H), 5.34-.15 (m, 28 H), 5.15 (s, 2 H), 4.64-4.60 (d, 26H, 4.8 Hz), 4.45-4.26 (m, 50 H), 3.77-3.67 (m, 3 H), 2.41 (t, 1H, J = 6.6 Hz), 1.27 (m, 34 H), 1.24 (m, 4 H). **FTIR** (KBr) υ (cm^{-1}): 3600-3350 (O-H), 3150-3000 (Csp^2-H), 3000-2850 (Csp^3-H), 1757 (C=O), 1650 (C=C), 1248 (C-O).

A.3. Functionalization of PMAC by thiol-ene reaction (*Series I*)

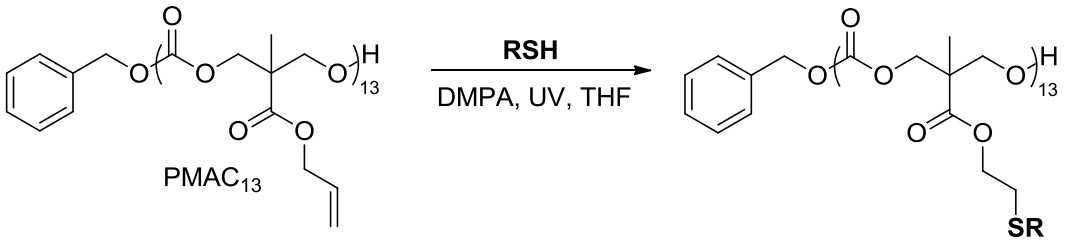


Figure A.2. Functionalization of PMAC by UV light-initiated thiol-ene reaction.

A Schlenk flask charged with $PMAC_{13}$ is flushed with Ar and solved in anhydrous THF ($[PMAC_{13}]_0$ = 0.1 M). After three cycles of Ar/vacuum, the thiol (thiol:ene relation of 2:1) and DMPA ($[PMAC_{13}]$:[DMPA] relation of 1:0.05) were added and other three

cycles of Ar/vacuum were carried out. The reaction was stirred at room temperature under illumination for 4 h using a Hg lamp Philips PL-S 9W with maximum emission at 365 nm, and the crude precipitated in cold diethyl ether. The product was isolated by decantation, solved in dichloromethane and the solvent evaporated to dryness. This process was repeated as times as necessary in order to fully eliminate thiol excess. In the case of PMAC-STEG, the crude was centrifuged after precipitation in order to properly separate the product. Reaction conditions for obtaining the three different functionalized polymers are summarized in Table A.1.

Table A.1. Reaction conditions for functionalization of $PMAC_{13}$ by thiol-ene reaction.

Polymer	$PMAC_{13}$	DSH	TEGSH	DMPA	THF	Yield
PMAC-SD	100.0 mg (0.48 mmol)	103.7 mg (0.96 mmol)	-	6.2 mg (0.024 mmol)	3 mL	67 %
PMAC-STEG	30.0 mg (0.14 mmol)	-	60.5 mg (0.28 mmol)	1.9 mg (0.007 mmol)	1.5 mL	50 %
PMAC-$(SD)_3$-*st*-$(STEG)_{10}$	33.7 mg (0.16 mmol)	8.7 mg (0.08 mmol)	50.9 mg (0.24 mmol)	2.1 mg (0.008 mmol)	1.6 mL	56 %

Characterization of PMAC-SD. **^{1}H-NMR** (400 MHz, $(CD_3)_2CO$) δ (ppm): 7.44-7.36 (m, 5H), 5.19 (s, 2H), 4.34-4.19 (m, 78H), 3.91 (s, 13H), 3.76-3.69 (m, 26H), 3.59-3.55 (m, 26H), 2.74-2.60 (m, 52H), 1.97-1.93 (m, 26H), 1.29 (s, 36H), 1.20 (s, 3H). **FTIR** (KBr) υ (cm^{-1}): 3655-3090 (O-H), 3000-2850 (Csp^3-H), 1753 (C=O), 1250 (C-O).

Characterization of PMAC-STEG. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.37-7.32 (m, 5H), 5.14 (s, 2H), 4.39-4.17 (m, 78 H), 3.71-3.58 (m, 182 H), 3.19 (s, 1H), 2.84 (s, 13H), 2.70 (t, 26H, J = 6.8 Hz), 2.59 (t, 26 H, J = 6.8 Hz), 1.96-1.87 (m, 26H), 1.25 (s, 36H), 1.19 (s, 3H). **FTIR** (KBr) υ (cm^{-1}): 3650-3100 (O-H), 3000-2850 (Csp^3-H), 1754 (C=O), 1248 (C-O).

Characterization of PMAC-$(SD)_3$-*st*-$(STEG)_{10}$. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.38-7.33 (m, 5H), 5.15 (s, 2H), 4.40-4.23 (m, 78H), 3.72 (s, 3H), 3.66-3.60 (m, 152H), 2.73-2.58 (m, 52H), 1.92 (t, 26H), 1.86 (s, 10H), 1.26 (s, 36H), 1.20 (s, 3H). **FTIR** (KBr) υ (cm^{-1}): 3680-3100 (O-H), 3000-2850 (Csp^3-H), 1754 (C=O), 1249 (C-O).

A.4. Synthesis and characterization of PMAC-*b*-MPC.

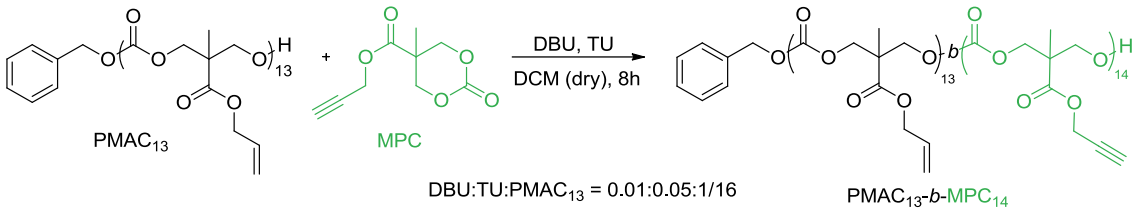


Figure A.3. Copolymerization of PMAC and MPC by organocatalytic ROP.

A solution of DBU (1.8 mg, 0.012 mmol) and TU (21.9 mg, 0.059 mmol) in dry dichloromethane (0.7 mL) was dried for 12 h over activated 4 Å molecular sieves under Ar atmosphere. $PMAC_{13}$ (200 mg, 0.074 mmol) was solved in anhydrous DCM (0.5 mL) and three cycles of Ar/vacuum were carried out. MPC (234.2 mg, 1.18 mmol) and the catalyst solution were sequentially added under Ar atmosphere and three cycles of Ar/vacuum were carried out after each addition. The reaction was stirred at 35ºC for 8 h, after which benzoic acid (7.2 mg, 0.059 mmol) was added to stop the polymerization. The crude reaction was precipitated in cold hexane and purified by preparative SEC using Biobeds SX-1 with THF as eluent and the subsequent precipitation in cold hexane/diethyl ether (1/1) mixture. The polymer was isolated by decantation and evaporation of the solvent, obtaining a colourless oil. Yield = 76 %.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.37 (m, 5H), 5.93-5.84 (m, 13H), 5.33-5.23 (m, 26H), 5.15 (s, 2H), 4.73 (d, 28H, J = 2.4 Hz), 4.63 (d, 23 H, J = 5.6 Hz), 4.44-4.28 (m, 103H), 3.74 (m, 4H), 2.53 (d, 15H, J = 2 Hz), 1.29-1.24 (m, 81H). **FTIR** (KBr) υ (cm^{-1}): 3680-3100 (O-H), 3290 (Csp-H), 3100-3000 (Csp^2-H), 3000-2800 (Csp^3-H), 2131 (C≡C) 1755 (C=O), 1650 (C=C), 1249 (C-O).

A.5. Synthesis and characterization of amphiphilic and thermoresponsive block copolycarbonates (*Series II*)

Synthesis and characterization of 1-Azidohexadecane (N_3-C16).

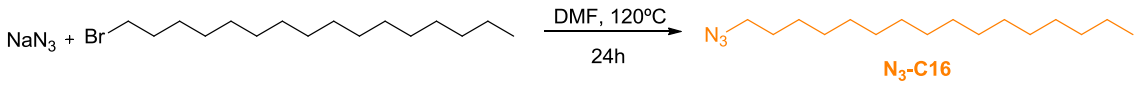


Figure A.4. Synthesis of N_3-C16.

Sodium azide (2.55 g, 38.9 mmol) was solved in DMF (6 mL). A solution of 1-bromohexadecane (3.96 g, 13.0 mmol) in DMF (12 mL) was added to the flask and the reaction was stirred at 120 ºC for 24 h. DMF was partially removed by vacuum distillation and the crude solved in diethyl ether (50 mL), filtered, washed with water (3x100 mL) and dried over anhydrous magnesium sulphate. The solvent was evaporated to dryness giving the product as a yellow oil. Yield = 50 %.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 3.25 (t, 2H, J = 6.8 Hz), 1.60 (p, 2H, J = 6.8 Hz), 1.32 (m, 26H), 0.88 (t, 3H, J = 6.8 Hz). **^{13}C-NMR** (100 MHz, CDCl3) δ (ppm): 51.65, 32.08, 29.84-29.81, 29.70, 29.64, 29.51, 29.31, 29.00, 26.87, 22.84, 14.25. **FTIR** (KBr) υ (cm^{-1}): 3000-2800 (Csp^3-H), 2097 (-N=N=N), 1468 (C-N).

Synthesis and characterization of P(MAC)$_{13}$-*b*-(MPC-C16)$_{14}$. Schlenk flask was charged with $PMAC_{13}$-MPC_{14} (100 mg, 0.255 mmol of propargyl group) and flushed with Ar. A solution of N_3-C16 (136.7 mg, 0.510 mmol) in THF (0.5 mL) was added to the schlenk flask and three cycles of Ar/vacuum were carried out. Solution of $CuSO_4$ (19.1 mg, 0.077 mmol) in water (0.5 mL) was added to another schlenk flask charged with TBTA (40.6 mg, 0.077 mmol), L-ascorbate (30.3 mg, 0.15 mmol) and anhydrous THF (3 mL) under Ar atmosphere. Then, the catalyst solution was added *via* cannula to the reaction schlenk flask and the reaction was stirred at 35ºC for 4 days. The crude reaction was evaporated to dryness, solved in dichloromethane (7 mL), washed with distilled water (1x5mL and 3x3mL) and dried over anhydrous magnesium sulphate. The extraction procedure was repeated two times. Purification was carried out by preparative SEC using Biobeds SX-1 with THF as eluent and precipitation in cold hexane. After decantation, the product was isolated as a yellow oil. Isolated yield = 40 %.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.65 (m, 14H), 7.38-7.35 (m, 5H), 5.91-5.83 (m, 13H), 5.33-5.22 (m, 54H), 5.15 (s, 2H), 4.62 (d, 23H, J = 5.6 Hz), 4.36-4.23 (m, 133H), 1.90 (t, 28H, J = 7.2 Hz), 1.31-1.22 (m, 445H), 0.87 (t, 42H, J = 6.8 Hz).

Synthesis and characterization of P(MAC-STEG)$_{13}$-*b*-(MPC-C16)$_{14}$. A Schlenk flask charged with PMAC$_{13}$-*b*-(MPC-C16)$_{14}$ (75 mg, 0.106 mmol of C=C) was flushed with Ar and solved in anhydrous THF (3.5 mL). After three cycles of Ar/vacuum, the TEGSH (44.5 mg, 0.212 mmol) and DMPA(1.4 mg, 0.005 mmol) were added and other three cycles of Ar/vacuum were carried out. The reaction was stirred at room temperature under 365 nm illumination for 10 h. Since the reaction had not been completed, TEGSH (22.3 mg, 0.106 mmol) and DMPA (1.4 mg, 0.005 mmol) were added and the reaction was stirred at room temperature for another 10 h. The crude reaction was evaporated to dryness and purification was carried out by preparative SEC using Biobeds SX-1 with THF as eluent and precipitation in cold hexane. Isolated yield = 40 %.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.65 (m, 14H), 7.37-7.33 (m, 5H), 5.25-5.20 (m, 28H), 5.15 (s, 2H), 4.62 (d, 23H, J = 5.6 Hz), 4.36-4.21 (m, 157H), 3.66-3.60 (m, 152H), 2.71 (t, 22H), 2.60 (t, 21 H), 1.94-1.90 (m, 50H), 1.31-1.18 (m, 446H), 0.87 (t, 42H, J = 6.8 Hz). **FTIR** (KBr) υ (cm^{-1}): 3660-3200 (O-H), 3143 (Csp^2–H Ar), 3000-2850 (Csp^3 -H), 1753 (C=O), 1256 (C-O).

A.6. Synthesis and characterization of amphiphilic and pH-responsive block copolycarbonates by orthogonal click reactions (*Series III*)

Synthesis and characterization of 2-(Diethylamino)ethyl 5-azidopentanoate (N_3-Am).

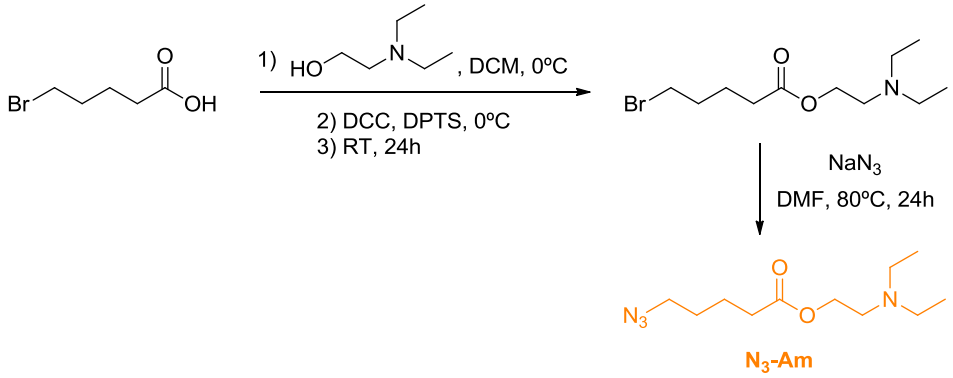


Figure A.5. Synthesis of N_3-Am.

Synthesis of 2-(diethylamino)ethyl 5-bromopentanoate. 5-bromovaleric acid (10.00 g, 53.6 mmol) was solved in anhydrous dichloromethane (28 mL) under argon atmosphere. 2-(diethylamino)ethanol (5.71 g, 48.7 mmol) and DPTS (6.44 g, 21.9 mmol) were added while cooling with an ice bath. Solution of DCC (13.40 g, 64.3 mmol) was dropwise added. After 15 min, the ice bath was removed and the reaction allowed to stir at room temperature for 24 h. The white precipitate was filtered off and the solvent removed under vacuum. The crude product was solved in DMC (25 mL) and washed with HCl 1M (3 x 10 mL). Solution of Na_2CO_3 was added dropwise to the aqueous phase until pH = 9-10. Then, the product was extracted with DCM (3 x 20 mL) and dried over anhydrous magnesium sulphate. The solvent was evaporated giving the amine as a yellow oil. Yield = 79 %.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 4.14 (t, 2H, J = 6.4 Hz), 3.41 (t, 2H, J = 6.8 Hz), 2.68 (t, 2H, J = 6.4 Hz), 2.56 (q, 4H, J = 7.2 Hz), 2.35 (t, 2H, J = 7.2 Hz), 1.90 (m, 2H), 1.77 (m, 2H), 1.02 (t, 6H, J = 7.2 Hz).

Synthesis of 2-(diethylamino)ethyl 5-azidopentanoate (N_3-Am). 2-(diethylamino)ethyl 5-bromopentanoate (1.80 g, 6.4 mmol) was solved in DMF (15 mL). Sodium azide (1.25 g, 19.3 mmol) was added and the reaction was stirred at 80 ºC for 24 h. DMF was distilled off and precipitate eliminated by filtration washing with dichloromethane. After the solvent being evaporated, the product was solved in diethyl ether (20 mL) and washed with water (3 x 20 mL). The organic phase was dried over magnesium sulphate, filtered and the solvent was evaporated to give a yellow oil. Yield = 59 %.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 4.14 (t, 2H, J = 6.3 Hz), 3.28 (t, 2H, J = 6.6 Hz), 2.68 (t, 2H, J = 6.3 Hz), 2.56 (q, 4H, J = 7.2 Hz), 2.35 (t, 2H, J = 7.2 Hz), 1.68 (m, 4H), 1.02 (t, 6H, J = 7.2 Hz). **^{13}C-NMR** (100 MHz, CDCl3) δ (ppm): 173.26, 62.89, 51.22, 51.17, 47.80, 33.74, 28.38, 22.19, 12.00. **FTIR** (KBr) υ (cm^{-1}): 3000-2850 (Csp^3-H), 2099 (-N=N=N), 1736 (C=O), 1458 (C-N).

Synthesis and characterization of P(MAC)$_{13}$-*b*-(MPC-Am)$_{14}$. Schlenk flask was charged with $PMAC_{13}$-MPC_{14} (90 mg, 0.23 mmol of propargyl group) and flushed with Ar. A solution of N_3-Am (111.0 mg, 0.46 mmol) in DMF (0.8 mL) was added to the schlenk flask and three cycles of Ar/vacuum were carried out. L-ascorbate (9.1 mg, 0.046 mmol) was added to a schlenk flask charged with a solution of $CuSO_4$ (11.5 mg,

0.046 mmol) in DMF (1 mL) and 3 cycles of Ar/vacuum were carried out. When the catalyst mixture turned to green, it was added *via* cannula to the reaction schlenk flask and the reaction was stirred at 35ºC for 4 days. The crude reaction was evaporated to dryness and solved in dichloromethane (30 mL). In order to remove copper, the crude was washed with potassium cyanide (KCN) solution 15 % (w/w) (40 mL), distilled water (40 mL) and brine (40 mL); and the organic phase dried over anhydrous magnesium sulphate, filtered and evaporanted to dryness. The resultant product was precipitated in cold hexane twice. Product was isolated as a yellow oil. Yield = 45 %. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.65 (m, 14H), 7.38-7.35 (m, 5H), 5.91-5.83 (m, 13H), 5.33-5.22 (m, 54H), 5.15 (s, 2H), 4.62 (d, 23H, J = 5.6 Hz), 4.36-4.23 (m, 133H), 1.90 (t, 28H, J = 7.2 Hz), 1.31-1.22 (m, 445H), 0.87 (t, 42H, J = 6.8 Hz).

Synthesis and characterization of P(MAC-STEG)$_{13}$-*b*-(MPC-Am)$_{14}$. A Schlenk flask charged with PMAC$_{13}$-*b*-(MPC-Am)$_{14}$ (65 mg, 0.095 mmol of C=C) was flushed with Ar and solved in anhydrous THF (1.5 mL). After three cycles of Ar/vacuum, the TEGSH (38.7 mg, 0.19 mmol) and DMPA(1.2 mg, 0.005 mmol) were added and other three cycles of Ar/vacuum were carried out. The reaction was stirred at room temperature under 365 nm illumination for 10 h. Since the reaction had not been completed, TEGSH (19.4 mg, 0.0.95 mmol) and DMPA (1.2 mg, 0.005 mmol) were added and the reaction was stirred at room temperature for another 10 h. The crude reaction was precipitated in cold diethyl ether and isolated by decantation.

A.7. Synthesis and characterization of amphiphilic and light-responsive block copolycarbonates by orthogonal click reactions (*Series IV*)

Synthesis of PMAC$_{15}$. TU (148.1 mg, 0.4 mmol) was added to a schlenk flask and dried under vacuum for 1 h. DBU (12.2 mg, 0.08 mmol), benzyl alcohol (50.8 mg, 0.47 mmol) and dry DCM (16 ml) were then added under Ar atmosphere. MAC monomer (1.6 g, 8 mmol) was finally added and the reaction stirred at 35 ºC for 1 h and 15 min. Then, benzoic acid (50 mg, 0.4 mmol) was added and the resulting reaction mixture precipitated in cold hexane. Flash column chromatography on silica gel was performed using hexane/ethyl acetate as eluent, starting with a 8/2 mixture and increasing ethyl acetate content until 3/7. Product was finally precipitated in cold hexane, solved in DCM and evaporated to dryness obtaining a colorless oil. Yield = 55 %.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.38-7.33 (m, 5H), 5.95-5.82 (m, 15H), 5.33-5.22 (m, 30 H), 5.15 (s, 2H), 4.65-4.59 (m, 30H), 4.44-4.26 (m, 58 H), 3.76-3.67 (m, 2 H), 2.46 (t, 1H, J = 6.6 Hz), 1.27 (m, 41 H), 1.24 (m, 3H). **FTIR** (KBr) υ (cm^{-1}): 3600-3350 (O-H), 3150-3000 (Csp^2-H), 3000-2850 (Csp^3-H), 1757 (C=O), 1650 (C=C), 1248 (C-O).

Synthesis and characterization of of $PMAC_{15}$-*b*-MPC_{15}. TU (50.6 mg, 0.137 mmol) was added to a schlenk flask and dried under vacuum for 1 h. DBU (4.2 mg, 0.03 mmol) and dry DCM (2.5 ml) were then added under Ar atmosphere. After 3 Ar-vacuum cycles, catalytic solution was added to a schlenk flask changed with $PMAC_{15}$ homopolymer (500.0 mg, 0.161 mmol) and MPC monomer (542.0 mg, 2.73 mmol) solvend in dry DCM (3 mL).The reaction was stirred at 35 ºC for 1 h. Then, benzoic acid (17 mg, 0.14 mmol) was added and the resulting reaction mixture precipitated in cold hexane. Purification was performed by three consecutive precipitations in cold methanol, isolating the product as a colorless oil. Yield = 70 %.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.37 (m, 5H), 5.93-5.84 (m, 15H), 5.33-5.23 (m, 30H), 5.15 (s, 2H), 4.73 (d, 31H, J = 2.4 Hz), 4.63 (m, 30 H), 4.44-4.28 (m, 124H), 3.74 (m, 3H), 2.53 (d, 15H, J = 2 Hz), 2.43 (t, 1H, J=6.5 Hz) 1.29-1.24 (m, 91H). **FTIR** (KBr) υ (cm^{-1}): 3680-3100 (O-H), 3290 (Csp-H), 3100-3000 (Csp^2-H), 3000-2850 (Csp^3-H), 2131 (C≡C) 1755 (C=O), 1650 (C=C), 1249 (C-O).

Synthesis of N_3-AZO

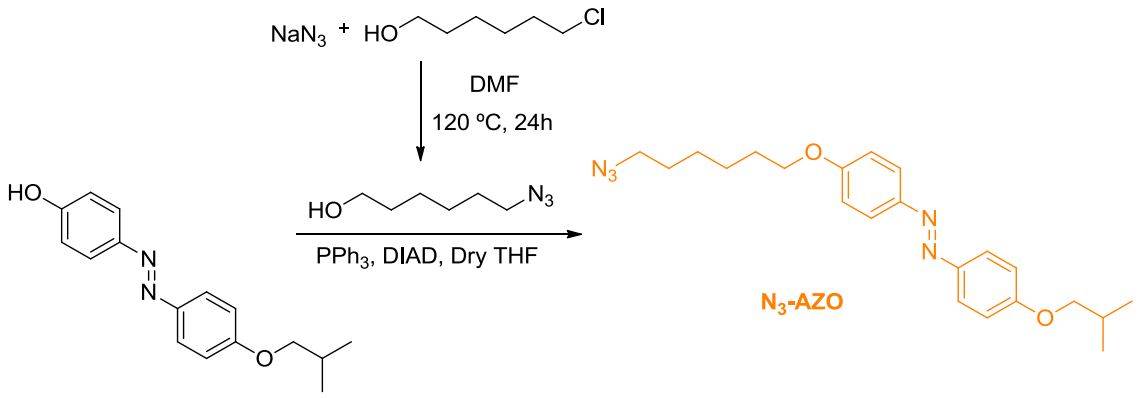


Figure A.6. Synthesis of N_3-AZO.

Synthesis and characterization of 6-azidohexan-1-ol. Sodium azide (8.86 g, 134.9 mmol) was added to a solution of 6-chlorohexanol (6.14 g, 45.0 mmol) in DMF (27

mL). The reaction was stirred at 120 ºC for 24 h. DMF was distilled off and the resultant mixture was solved in diethyl ether (50 mL) and washed with water (3x100 mL). The organic layer was dried of magnesium sulphate, filtered and evaporated to obtain the product as a yellow oil. Yield = 50%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ (ppm): 3.50 (q, 2H, J = 6.0 Hz), 3.27 (t, 2H, J = 6.9 Hz), 1.61 (m, 4H), 1.41 (m, 4H), 1.26 (t, 1H, J = 5 Hz). **^{13}C-NMR** (100 MHz, CDCl3) δ (ppm): 62.86, 51.50, 32.66, 28.92, 26.64, 25.44. **FTIR** (KBr) υ (cm^{-1}): 3641-3100 (O-H), 3000-2850 (Csp^3-H), 2096 (-N=N=N).

Synthesis and characterization N_3-AZO. 6-azidohezanol (3.62 g, 25.3 mmol), 4-Isobutyloxy-4'-hydroxyazobenzene (6.84 g, 25.3 mmol) and diisopropyl azodicarboxylate (DIAD) (5.12 g, 25.3 mmol) were solved in dry THF (90 mL) under Ar atmosphere and cooled down in an ice bath. Then, triphenylphospine (PPh3) (1.45 g, 5.54 mmol) solved in anhydrous THF (10 mL) was added dropwise. The mixture was stirred for 24 h at room temperature. Solvent was evaporated to dryness and the crude recrystallized in ethanol and filtered, obtaining an orange solid. Yield = 70 %. **^{1}H-NMR** (300 MHz, CDCl3, δ, ppm): 7.87-7.84 (m, 4H), 7.00 - 6.97 (m, 4H), 4.04 (t, 2H, J = 6.0 Hz), 3.80 (d, 2H, J = 6.6 Hz), 3.30 (t, 2H, J = 6.6 Hz), 2.17 - 2.08 (m, 1H), 1.88 - 1.79 (m, 2H), 1.70 - 1.64 (m, 2H), 1.57 - 1.45 (m, 2H), 1.28-1.26 (m, 2H), 1.05 (d, 6H, J = 6.9 Hz). **^{13}C-NMR** (100 MHz, CDCl3) δ (ppm): 161.46, 161.17, 124.44, 114.83, 114.79, 74.83, 68.17, 51.53, 29.24, 28.95, 28.43, 26.66, 25.82, 19.38. **FTIR** (KBr) υ (cm^{-1}): 3100-3000 (Csp^2-H), 3000-2850 (Csp^3-H), 2101 (-N=N=N), 1600-1580 (C_{Ar}-C_{Ar}), 1471 (N=N), 1238 (C-O).

Synthesis and characterization of $P(MAC)_{15}$-*b*-$(MPC\text{-}AZO)_{15}$. Schlenk flask was charged with $PMAC_{15}$-MPC_{15} (300 mg, 0.74 mmol of propargyl group) and flushed with Ar. A solution of N_3-AZO (585.6 mg, 1.48 mmol) was added to the schlenk flask and solved in DMF (2.5 mL) before three cycles of Ar/vacuum were carried out. L-ascorbate (44 mg, 0.22 mmol) was added under Ar atmosphere to a schlenk flask charged with a solution of $CuSO_4$ (55.4 mg, 0.22 mmol) and PMDETA (38.5 mg, 0.22 mmol) in DMF (2.5 mL), and 3 cycles of Ar/vacuum were carried out. When the catalyst mixture turned to dark green, the catalyst mixture was added *via* cannula to the reaction schlenk flask and it was stirred at 35ºC for 4 days. The crude reaction was evaporated to dryness and solved in dichloromethane (40 mL). In order to remove copper, the crude was washed with distilled water (6x30 mL) and brine (30 mL); and

the organic phase dried over anhydrous magnesium sulphate, filtered and evaporanted to dryness. Purification was carried out by preparative SEC using Biobeds SX-1 with THF as eluent and precipitation in cold ethanol. After decantation, the product was isolated as an orange solid. Isolated yield = 30 %.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.85-7.83 (m, 58H), 7.62-7.55 (m, 15H), 7.37 (m, 5H), 7.00-6.93 (m, 58H), 5.91-5.83 (m, 15H), 5.33-5.23 (m, 56H), 5.15 (s, 2H), 4.63 (d, 29H, J = 5.6 Hz), 4.33-4.26 (m, 140H), 3.98 (m, 30H), 3.77 (m, 30H), 2.10 (s, 15H), 1.92 (s, 30H), 1.77 (s, 30H), 1.50 (m, 30H), 1.39 (m, 30H), 1.27-1.17 (m, 85H), 1.03 (d, 90H, J=6 Hz). **FTIR** (KBr) υ (cm^{-1}): 3655-3260 (O-H), 3100-3000 (Csp^2-H), 3000-2850 (Csp^3-H), 1756 (C=O), 1601-1581 (C=C).

Synthesis and characterization of P(MAC-STEG)$_{15}$-*b*-(MPC-AZO)$_{15}$. PMAC-*b*-(MPC-Azo) (40 mg, 0.05 mmol of C=C group), TEGSH (31.5 mg, 0.15 mmol) and AIBN (3.3 mg, 0.02 mmol) are added to a schlenk flask under Ar atmosphere and solved in dry and deoxygenated dioxane. After 3 Ar-vacuum cycles, schleck was introduced into a silicon batch at 90 ºC, and the reaction was stirred for 3 days. The resulting mixture was precipitated in cold diethyl ether, centrifuged and the product isolated by decantation (this procedure was performed twice). After removing solvent by evaporation, product was isolated as an orange solid. Yield = 50 %.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.85-7.83 (m, 56H), 7.62-7.55 (m, 15H), 7.37 (m, 5H), 7.00-6.93 (m, 56H), 5.33-5.23 (s, 28H), 5.15 (s, 2H), 4.33-4.26 (m, 170H), 3.97 (m, 30H), 3.77-3.60 (m, 207H), 2.8 (s, 10H), 2.71 (t, 23H, J=6.4 Hz), 2.60 (t, 22H, J=7.4 Hz), 2.09 (m, 15H), 1.92 (m, 52H), 1.77 (m, 30H), 1.50 (m, 30H), 1.38 (m, 30H), 1.25-1.17 (m, 90H), 1.03 (d, 88H, J=6 Hz).

Annex B- ^{1}H-NMR, ^{13}C-NMR and FTIR spectra

B.1. Synthesis and characterization of MAC monomer

2,2,5-Trimethyl-1,3-dioxane-5-carboxylic acid (1)

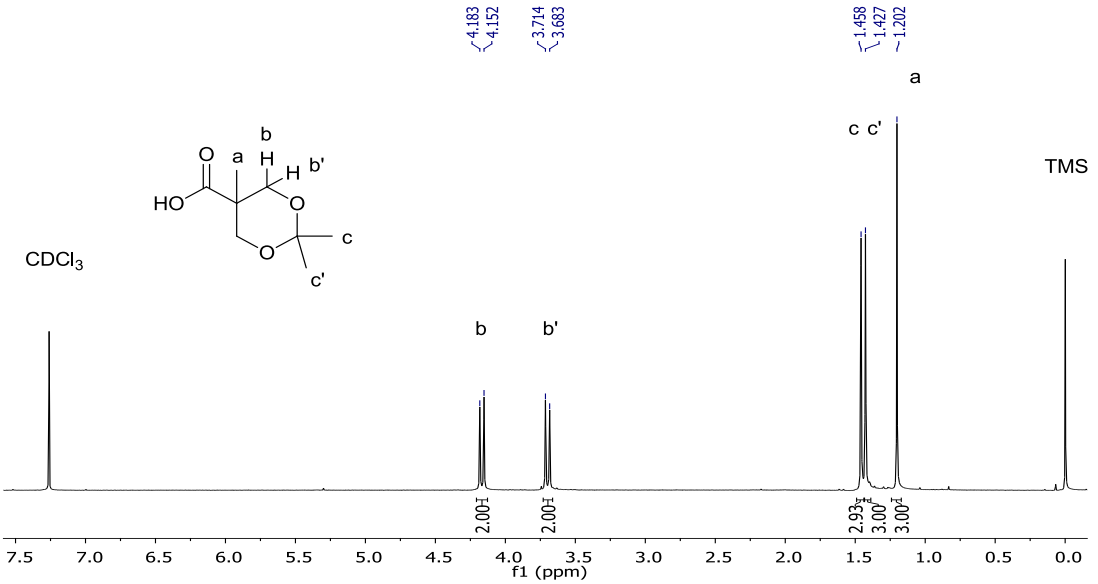


Figure B.1. *^{1}H NMR, (400MHz, CDCl3, δ (ppm))*

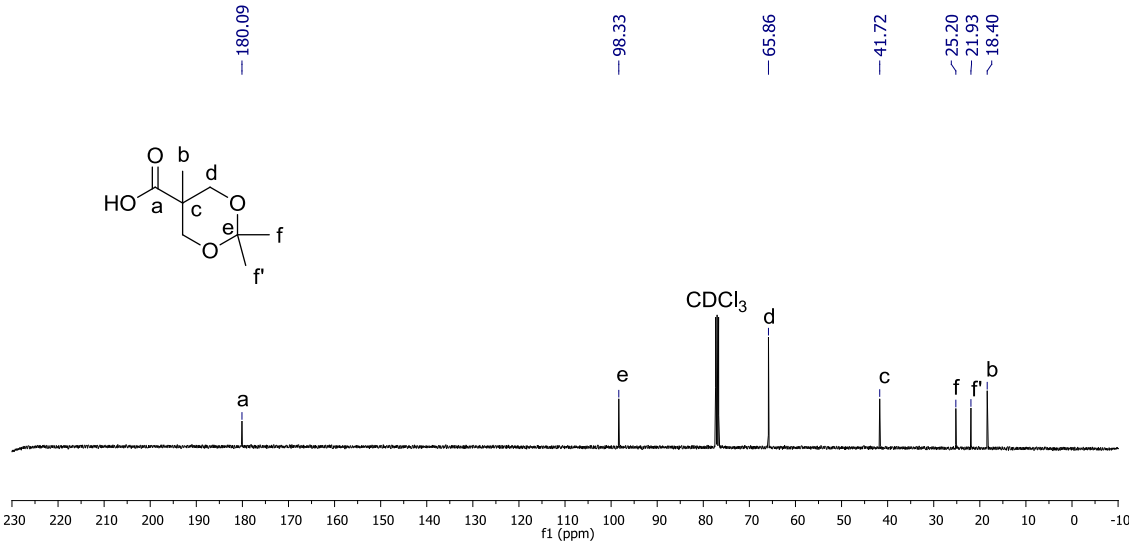


Figure B.2. *^{13}C NMR, (100MHz, $CDCl_3$, δ (ppm))*

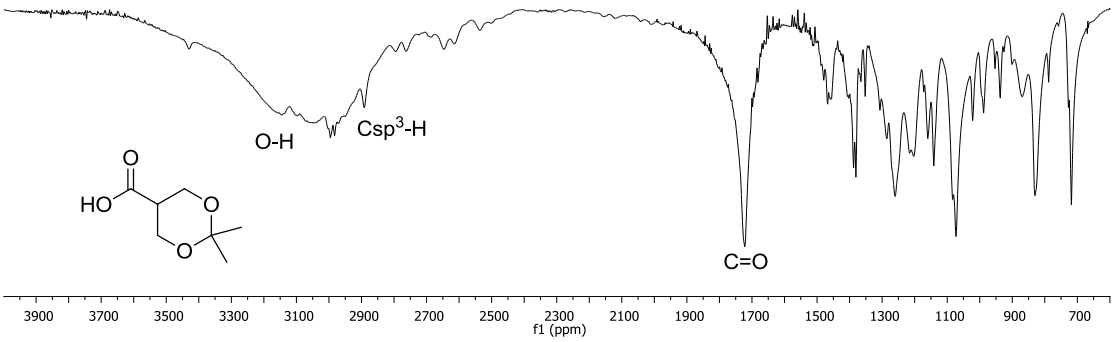


Figure B.3. *FTIR (KBr)*

2,2,5-trimethyl-1,3-dioxane-5-carboxylate (2)

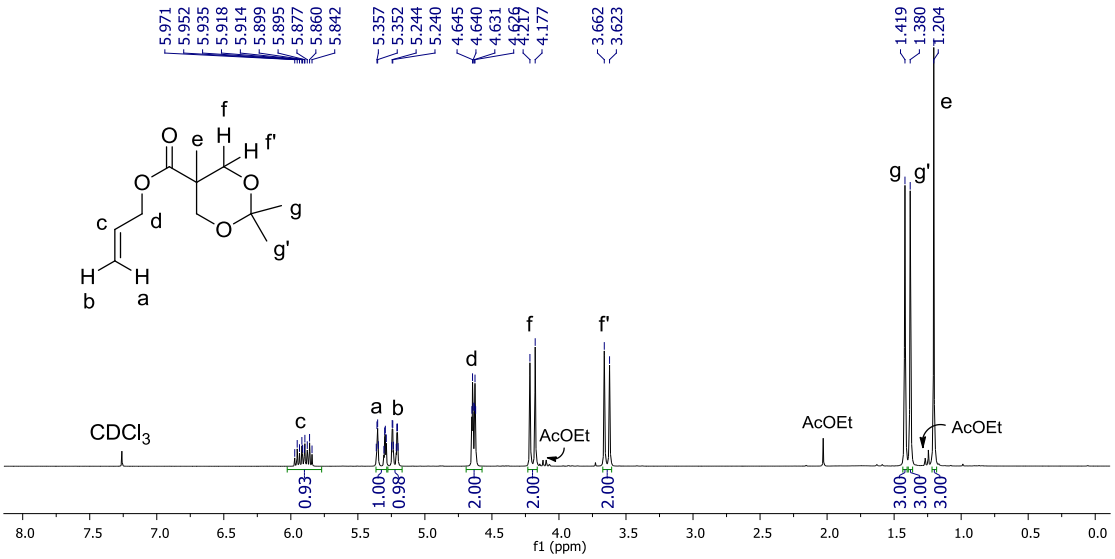


Figure B.4. *^{1}H NMR, (300MHz, CDCl3, δ (ppm))*

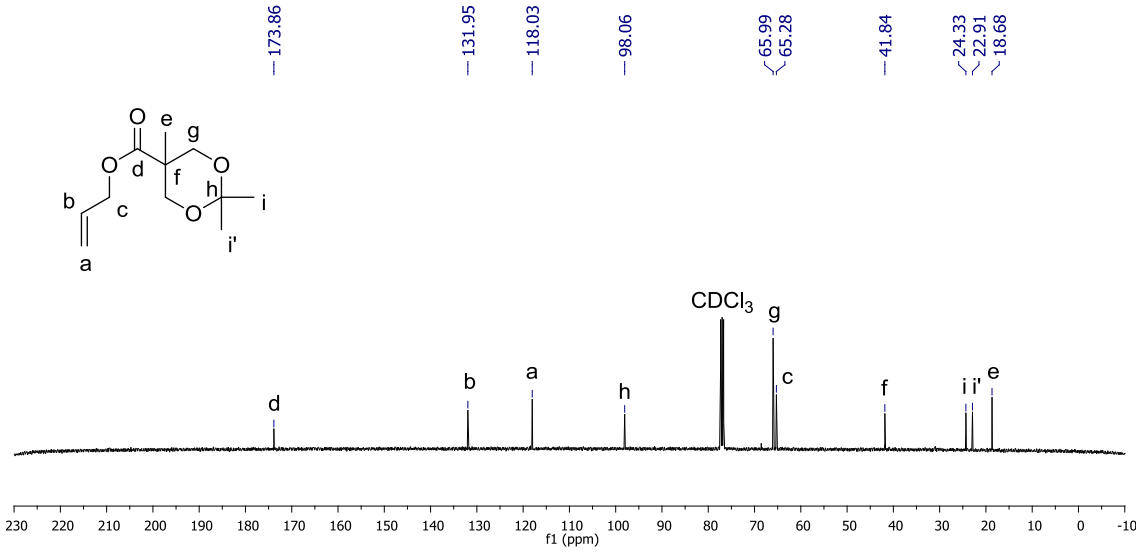


Figura B.5. *^{13}C NMR, (100MHz, $CDCl_3$, δ (ppm))*

Allyl 3-hydroxy-2-(hydroxymethyl)-2-methyl-propionate (3)

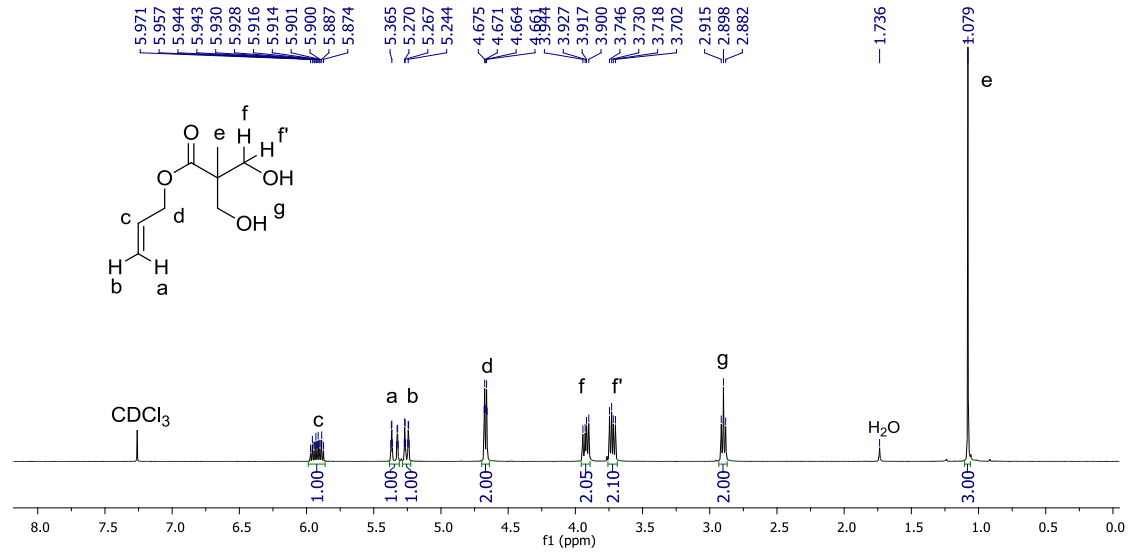


Figure B.6. *^{1}H NMR, (400MHz, CDCl3, δ (ppm))*

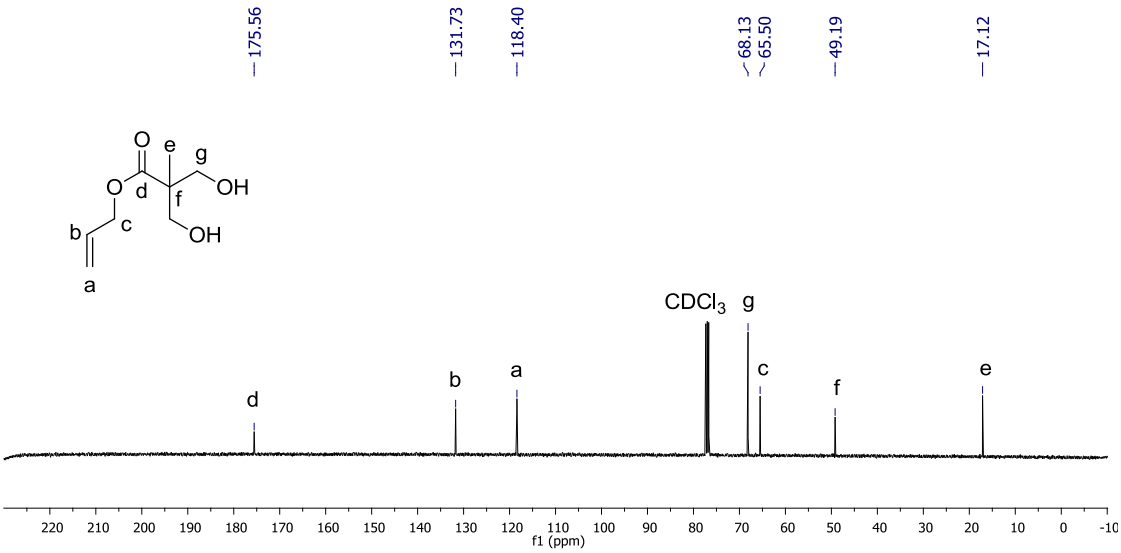


Figura B.7. *^{13}C NMR, (100MHz, $CDCl_3$, δ (ppm))*

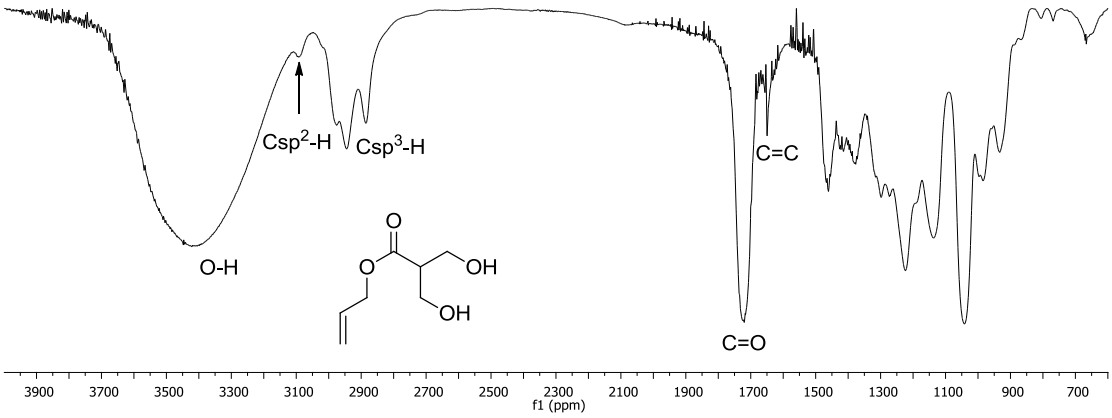


Figure B.8. FTIR (KBr)

5-Methyl-5-allyloxycarbonyl-1,3-dioxan-2-one (MAC)

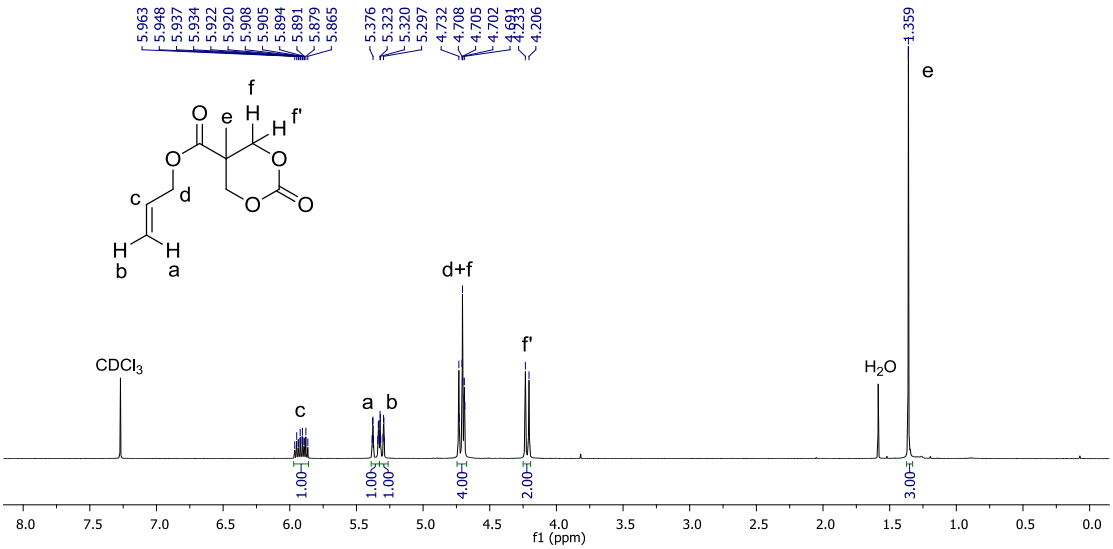


Figure B.9. *^{1}H NMR, (400MHz, $CDCl_3$, δ (ppm))*

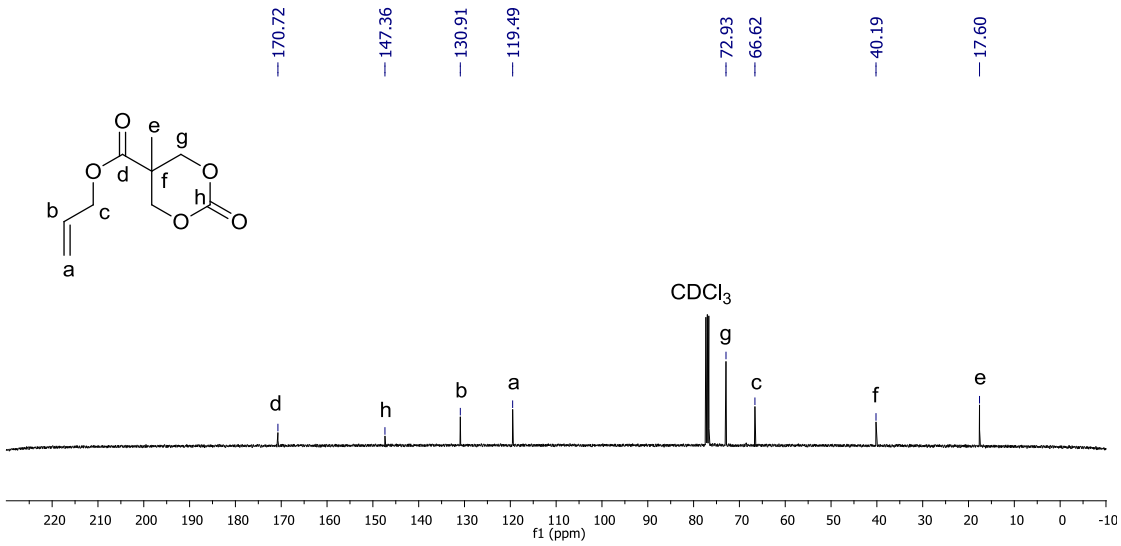


Figura B.10. *^{13}C NMR, (100MHz, $CDCl_3$, δ (ppm))*

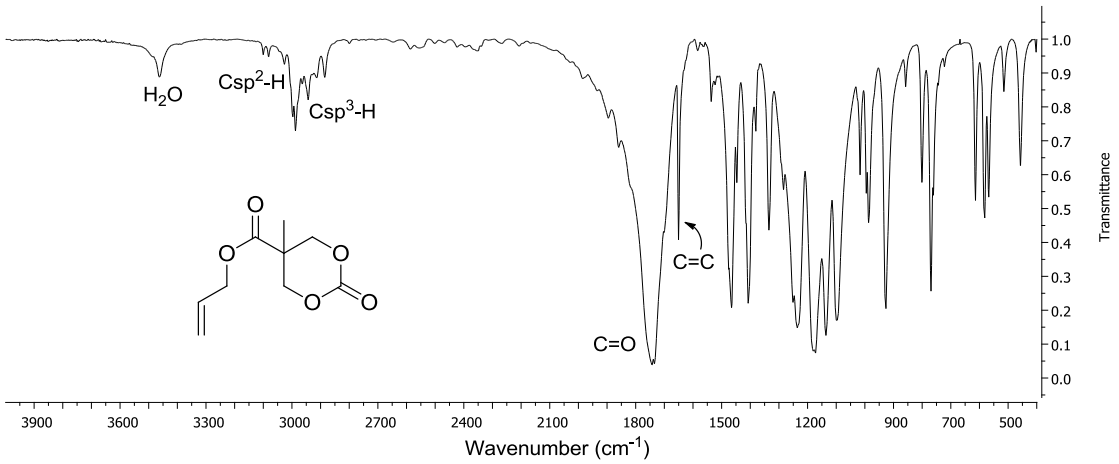


Figure B.11. *FTIR (KBr)*

B.2. Synthesis and characterization of PMAC homopolymer

$PMAC_{13}$

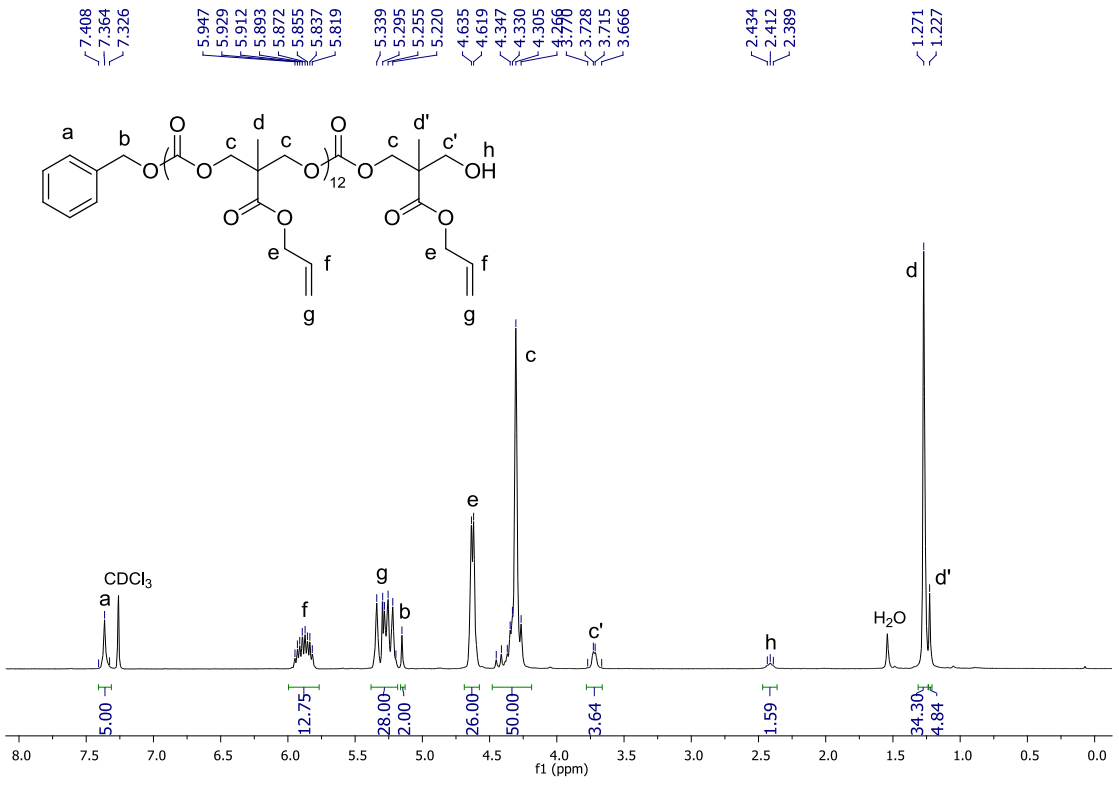


Figure B.12. *^{1}H NMR, (400MHz, CDCl3, δ (ppm))*

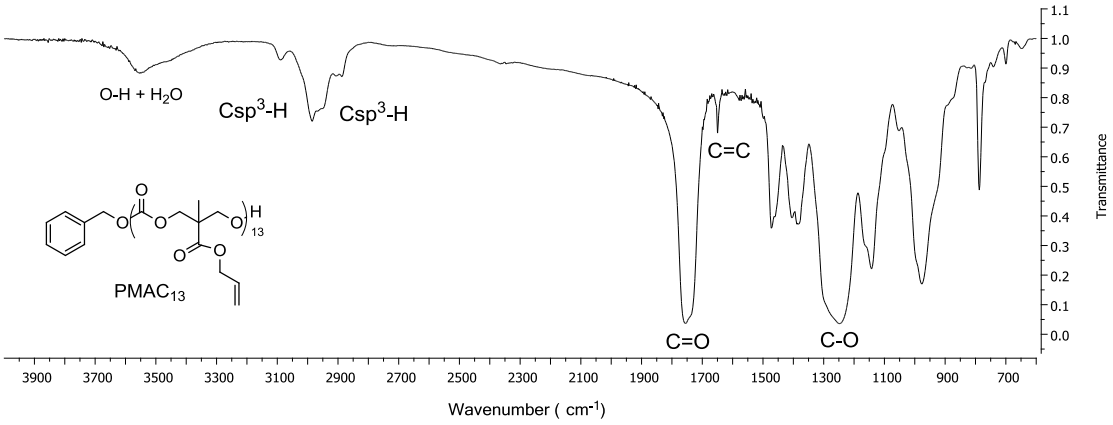


Figure B.13. *FTIR (KBr)*

B.3. Functionalization of PMAC by thiol-ene reaction (*Series I*)

PMAC-SD

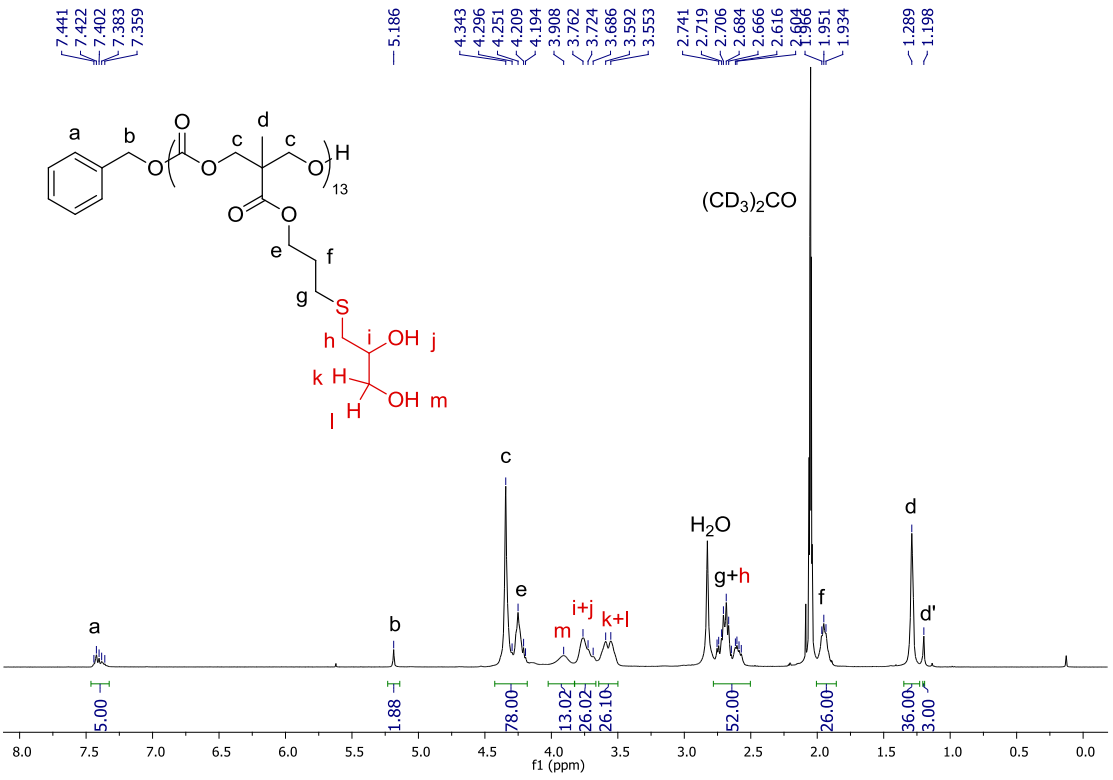


Figure B.14. *^{1}H NMR, (400MHz, $(CD_3)_2CO$, δ (ppm))*

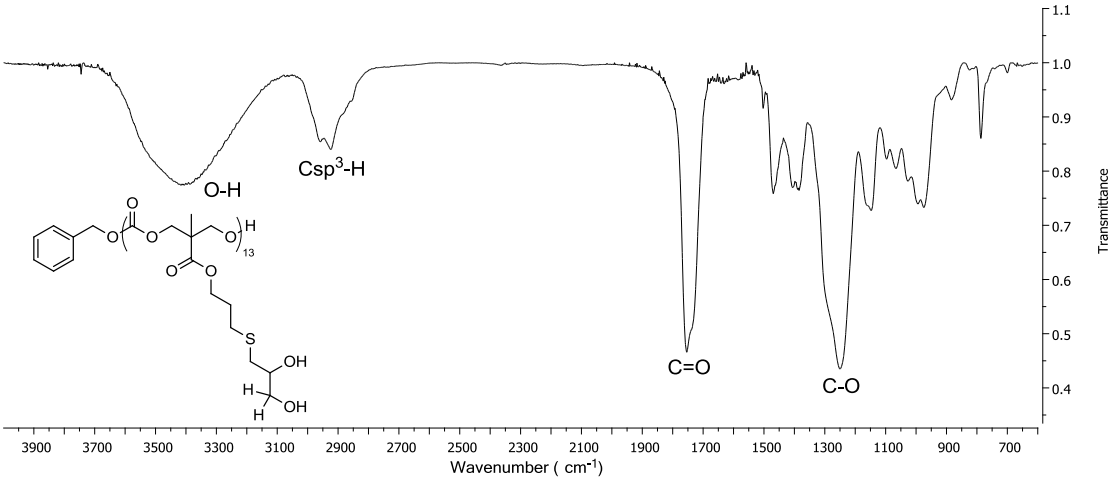


Figure B.15. *FTIR (KBr)*

PMAC-STEG

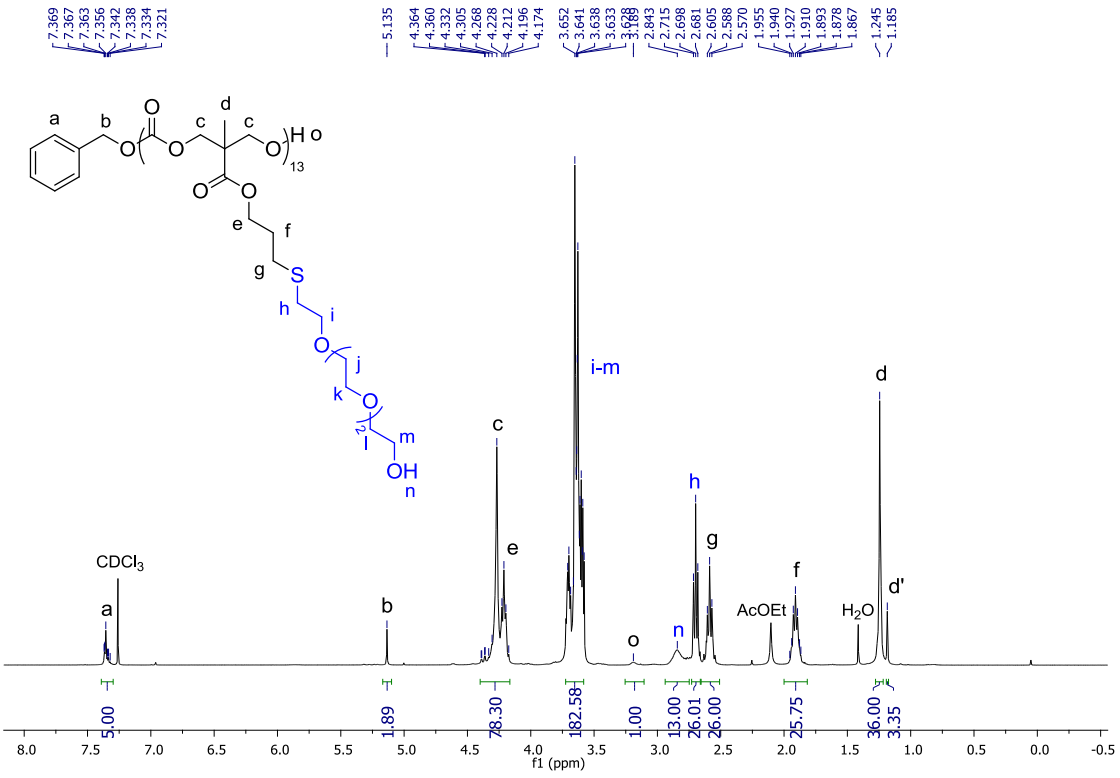


Figure B.16. *^{1}H NMR, (400MHz, $CDCl_3$, δ (ppm))*

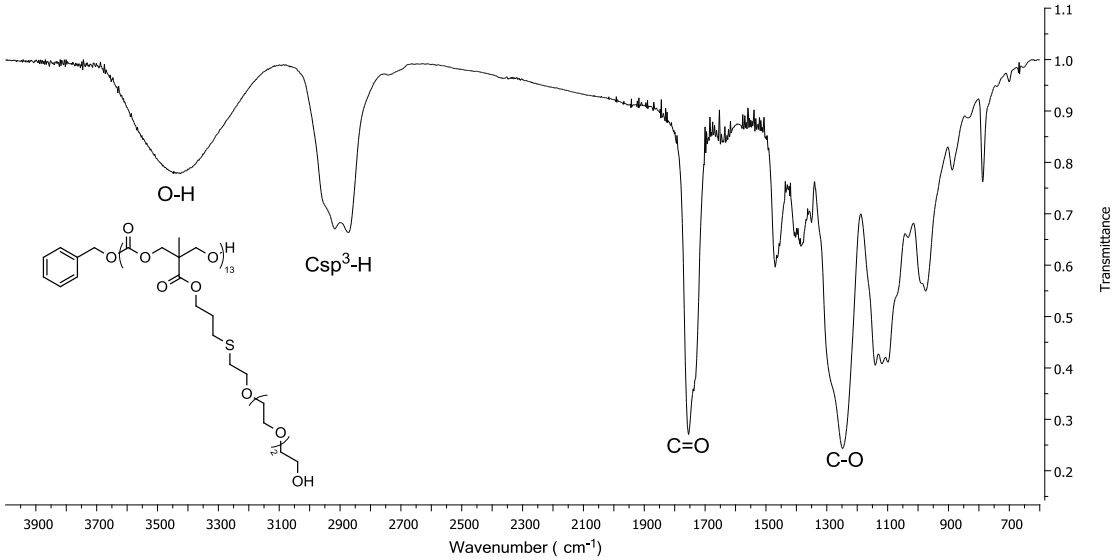


***Figure B.17**. FTIR (KBr)*

PMAC-(STEG)-*st*-(SD)

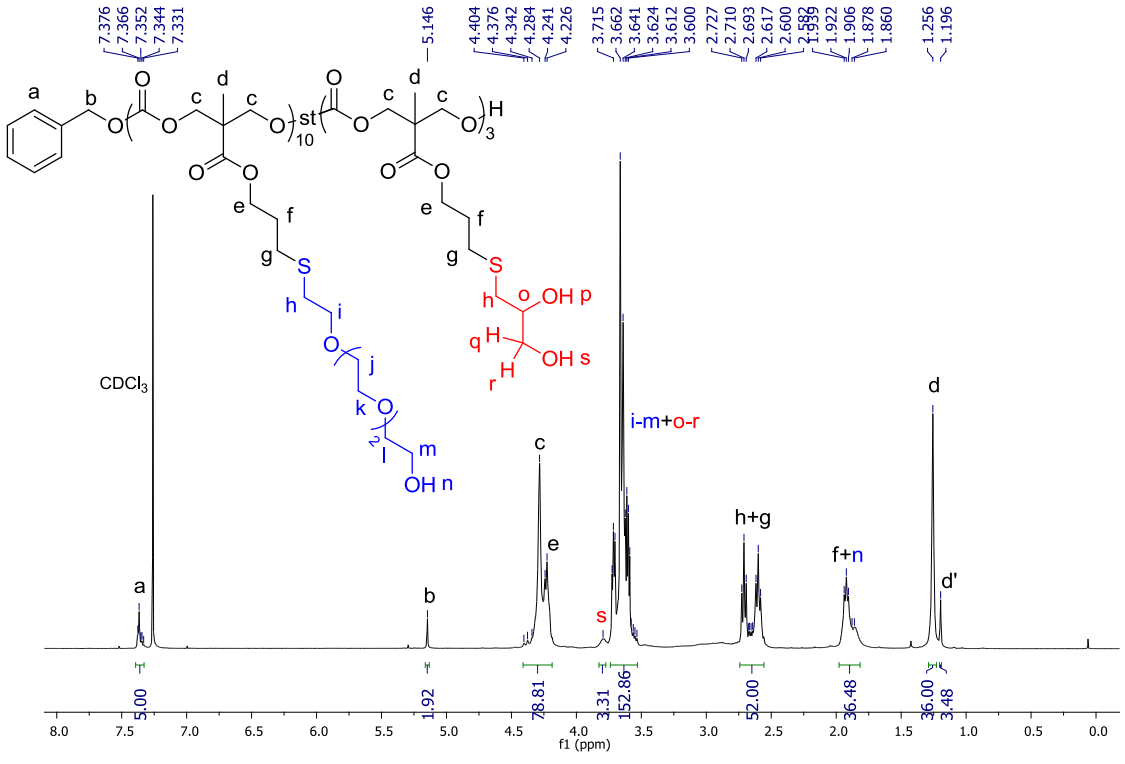


***Figure B.18.** ^{1}H NMR, (400MHz, $CDCl_3$, δ (ppm))*

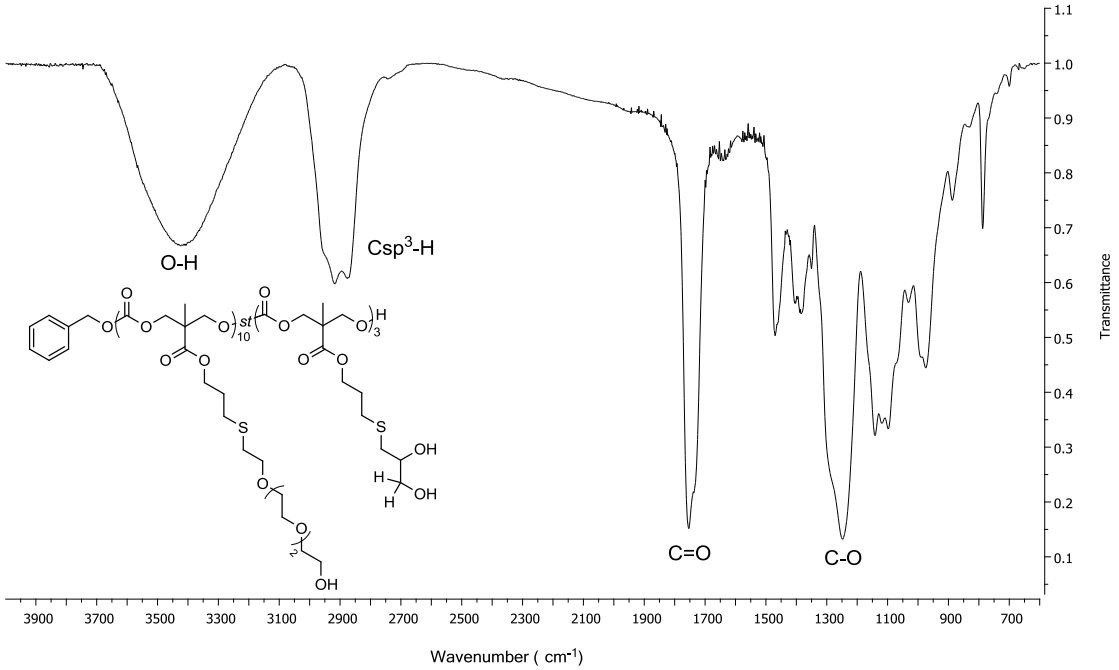


Figure B.19. *FTIR (KBr)*

B.4. Synthesis and characterization of PMAC-*b*-MPC.

$PMAC_{13}$-*b*-MPC_{14}

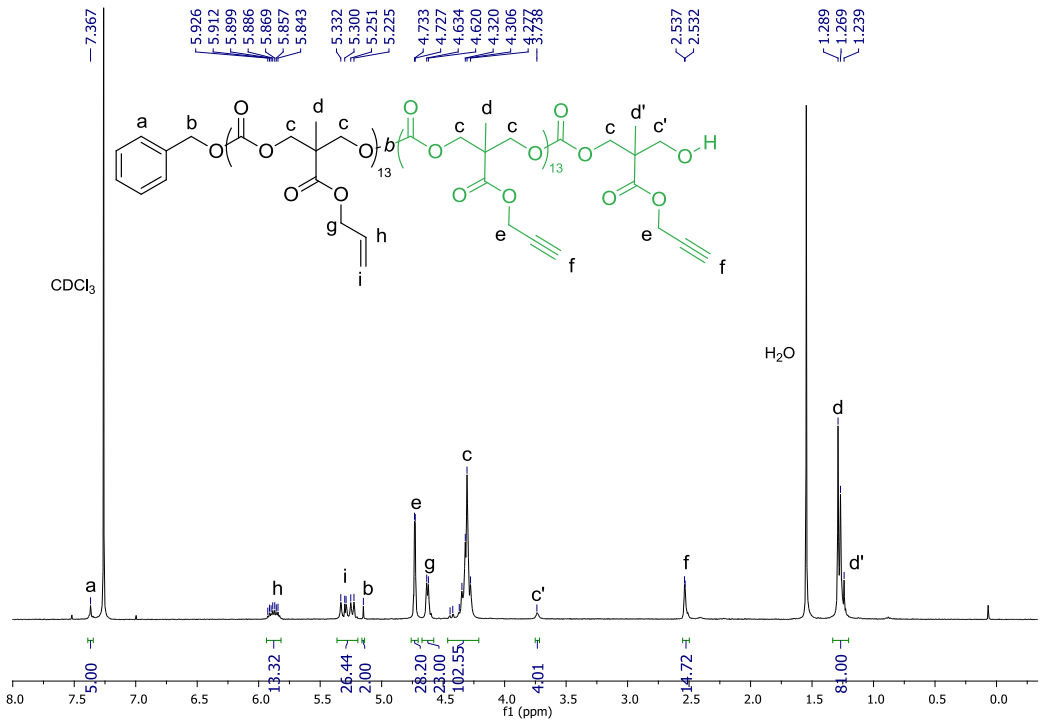


Figure B.20. *^{1}H NMR, (400MHz, $CDCl_3$, δ (ppm))*

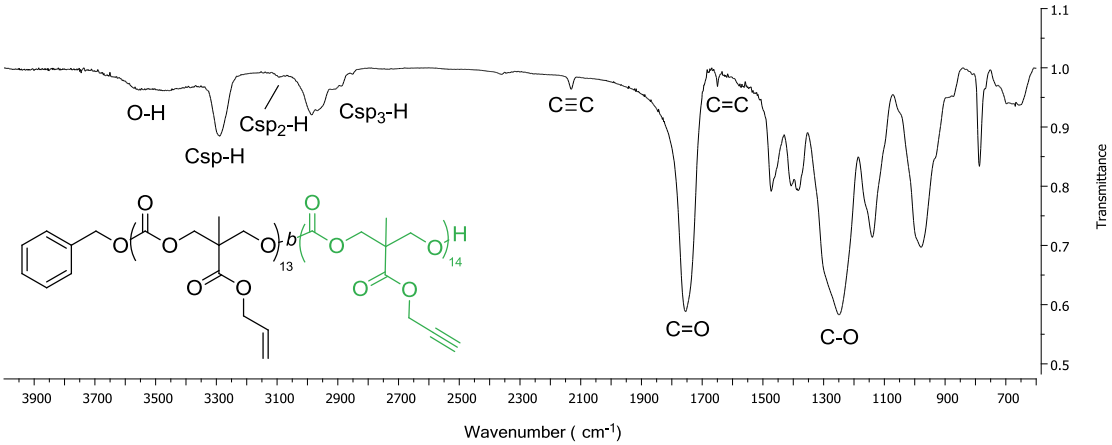


Figure B.21. *FTIR (KBr)*

B.5. Synthesis and characterization of amphiphilic and thermoresponsive block copolycarbonates (*Series II*)

1-Azidohexadecane (N_3-C16)

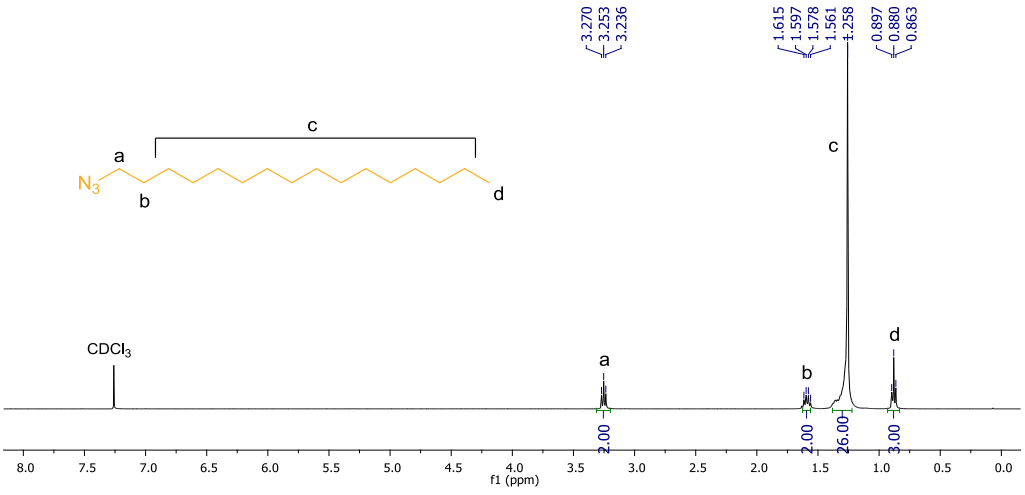


Figure B.22 *^{1}H NMR, (400MHz, $CDCl_3$, δ (ppm))*

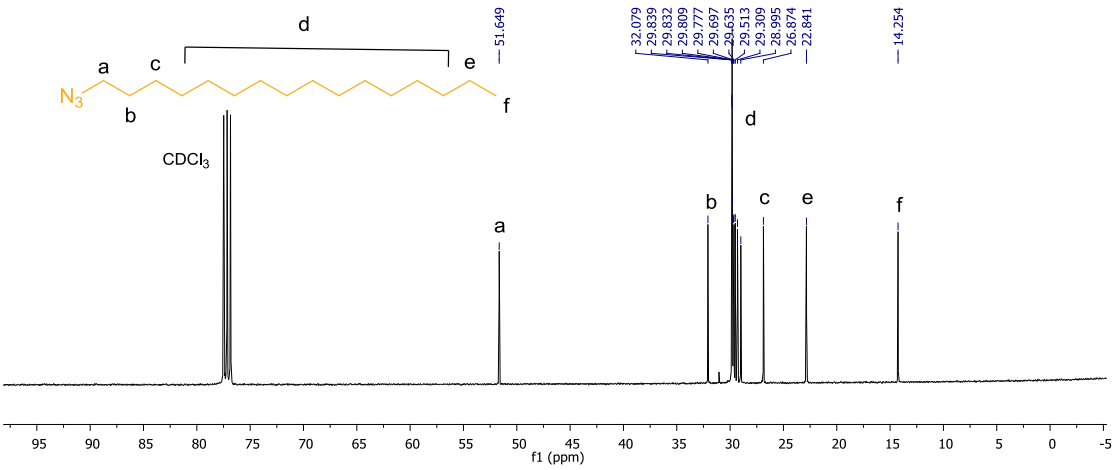


Figura B.23. *^{13}C NMR, (100MHz, $CDCl_3$, δ (ppm))*

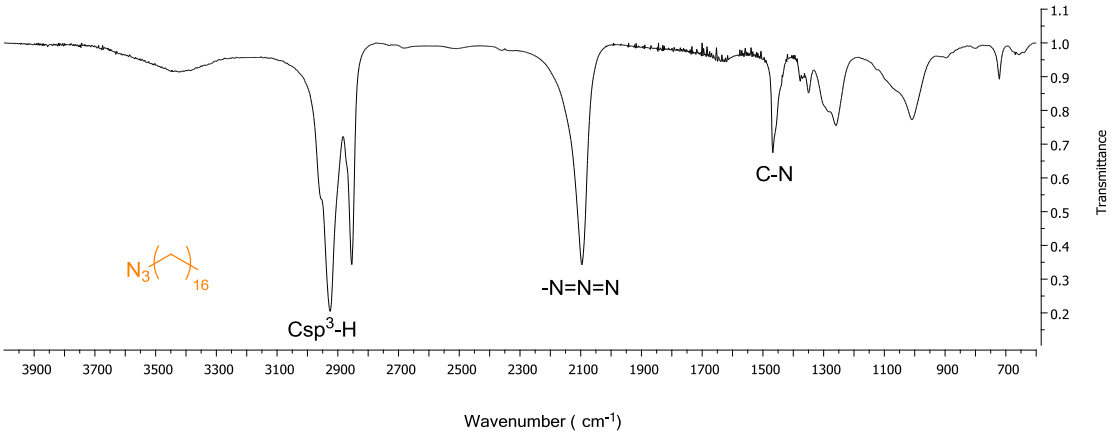


Figure B.24. *FTIR (KBr)*

P(MAC)$_{13}$-*b*-(MPC-C16)$_{14}$

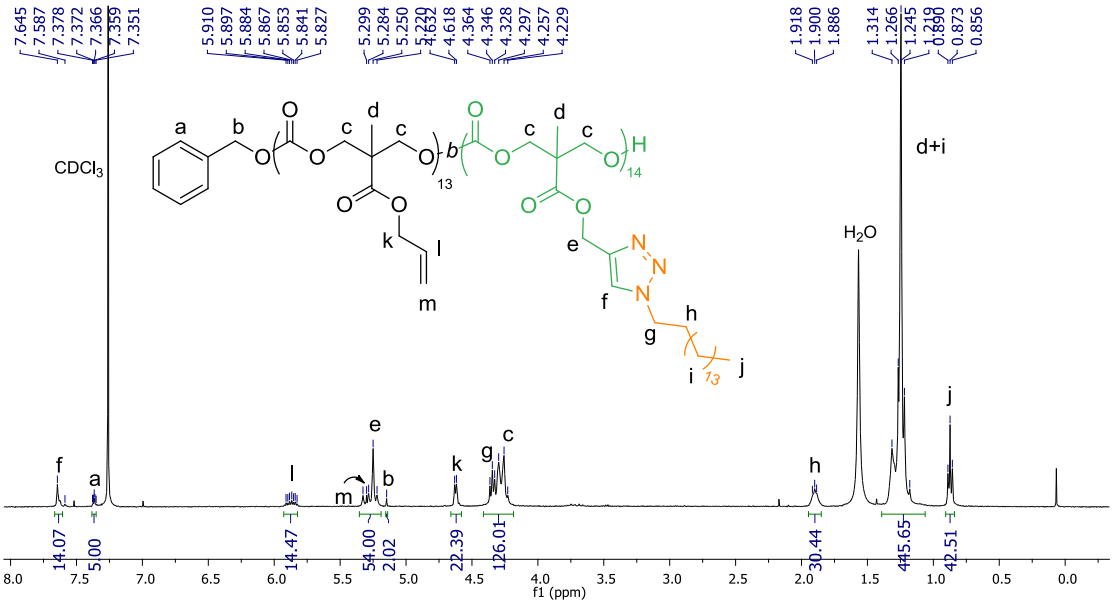


Figure B.25. *^{1}H NMR, (400MHz, $CDCl_3$, δ (ppm))*

P(MAC-STEG)$_{13}$-*b*-(MPC-C16)$_{14}$

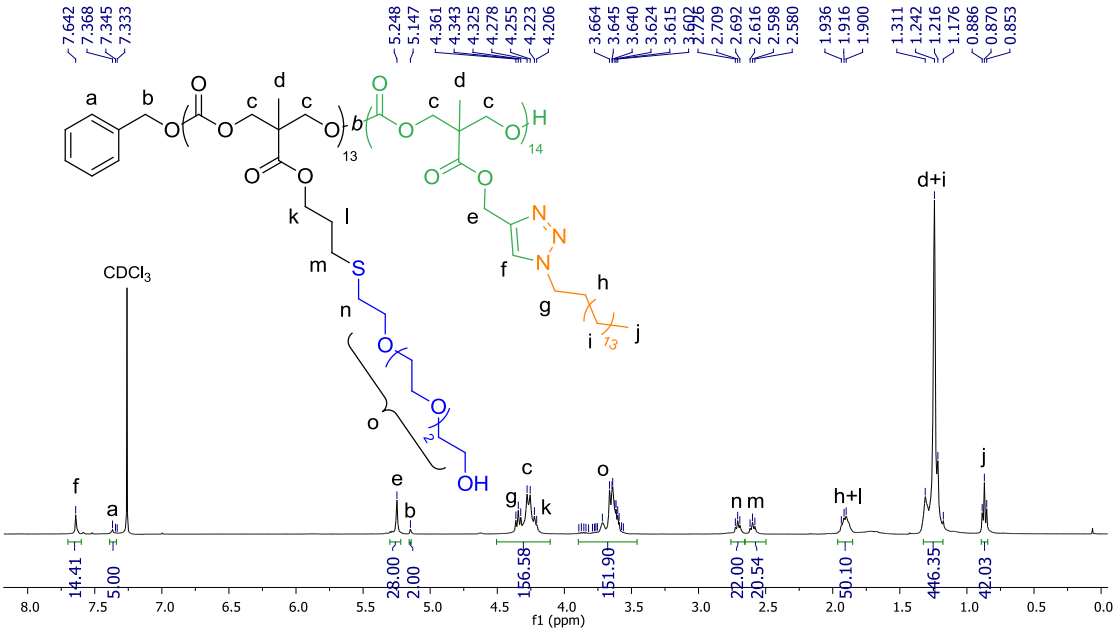


Figure B.26. *^{1}H NMR, (400MHz, $CDCl_3$, δ (ppm))*

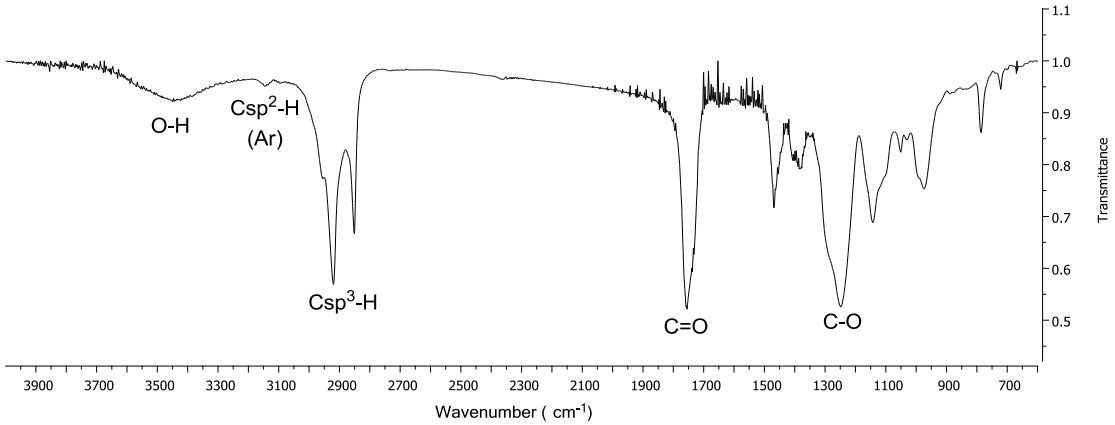


Figure B.27. *FTIR (KBr)*

B.6. Synthesis and characterization of amphiphilic and pH-responsive block copolycarbonates by orthogonal click reactions (*Series III*)

2-(diethylamino)ethyl 5-bromopentanoate

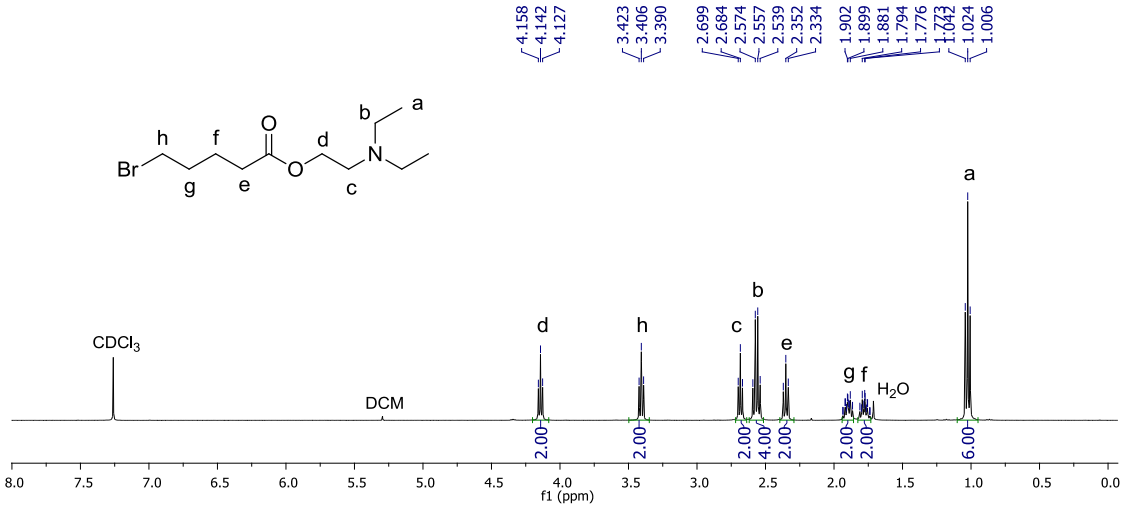


Figure B.28. *^{1}H NMR, (400MHz, $CDCl_3$, δ (ppm))*

2-(diethylamino)ethyl 5-azidopentanoate (N_3-Am)

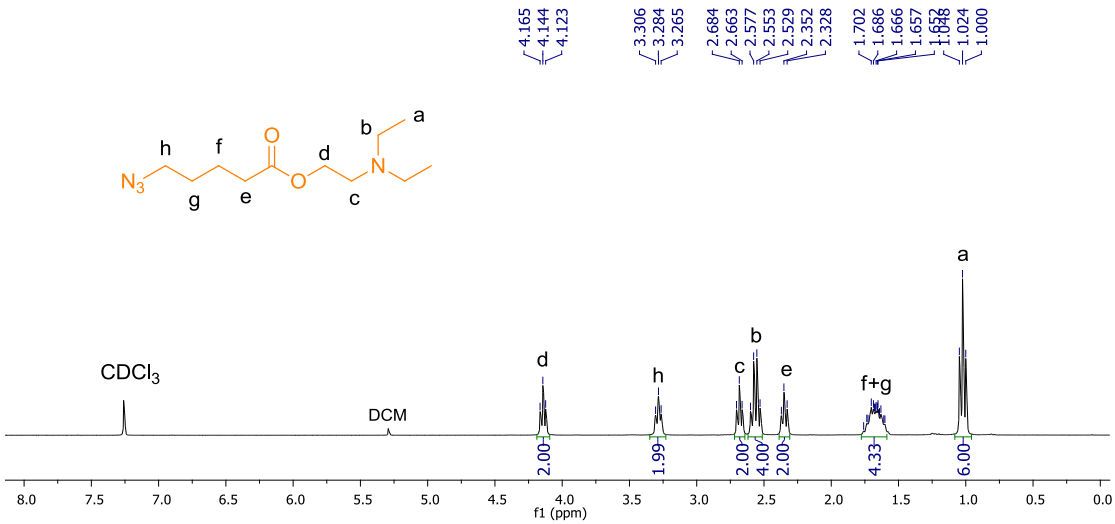


Figure B.29. *^{1}H NMR, (300MHz, $CDCl_3$, δ (ppm))*

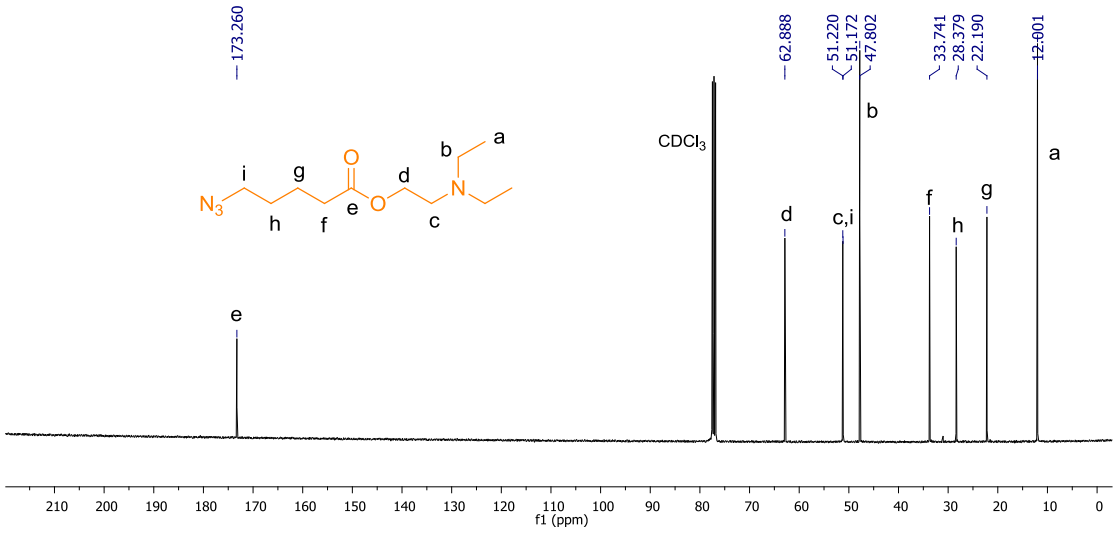


Figura B.30. *^{13}C NMR, (100MHz, $CDCl_3$, δ (ppm))*

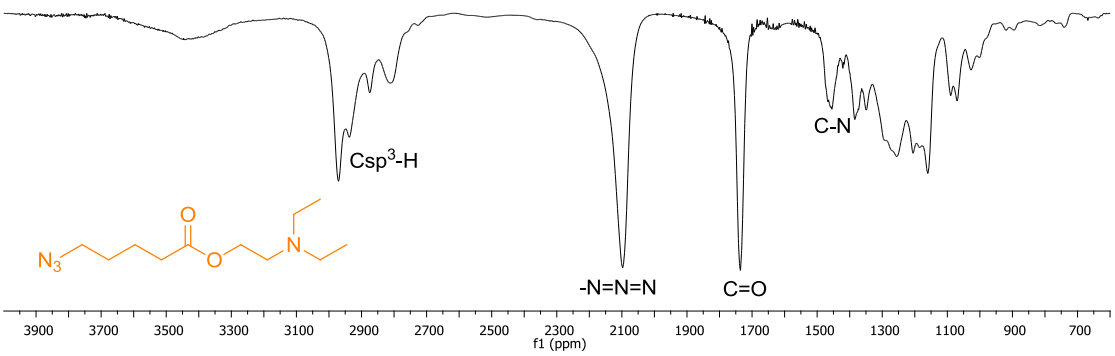


Figure B.31. *FTIR (KBr)*

$PMAC_{13}$-*b*-$(MPC\text{-}Am)_{14}$

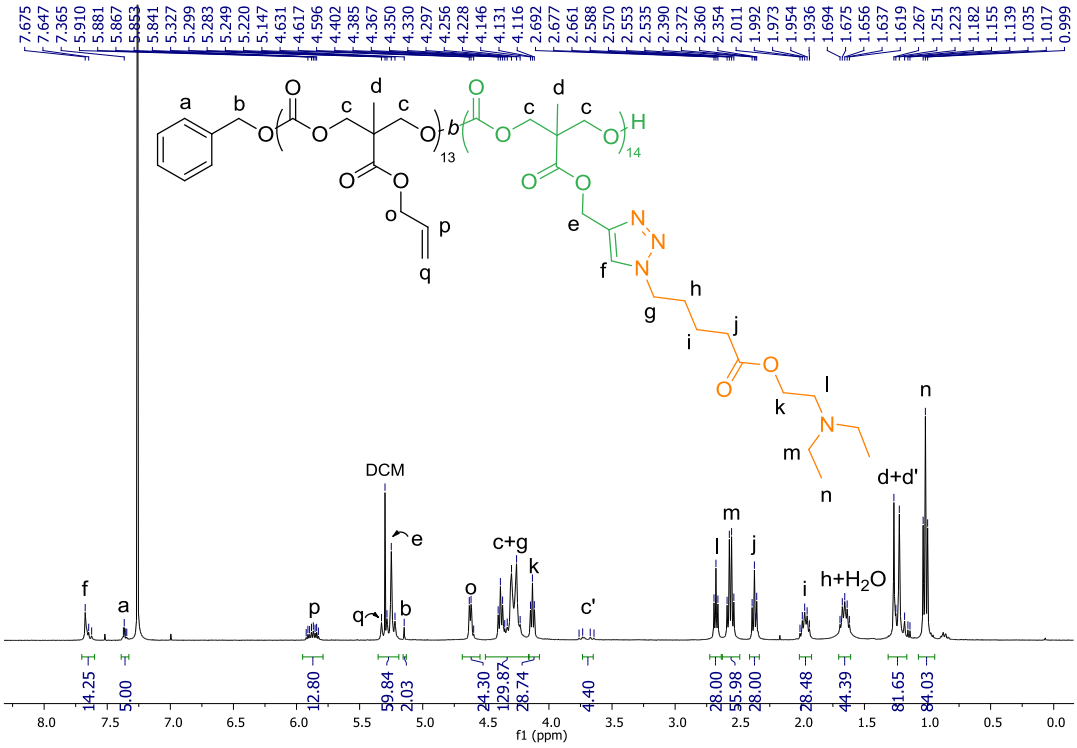


Figure B.32. *^1H NMR, (400MHz, $CDCl_3$, δ (ppm))*

$P(MAC\text{-}STEG)_{13}$-*b*-$(MPC\text{-}Am)_{14}$

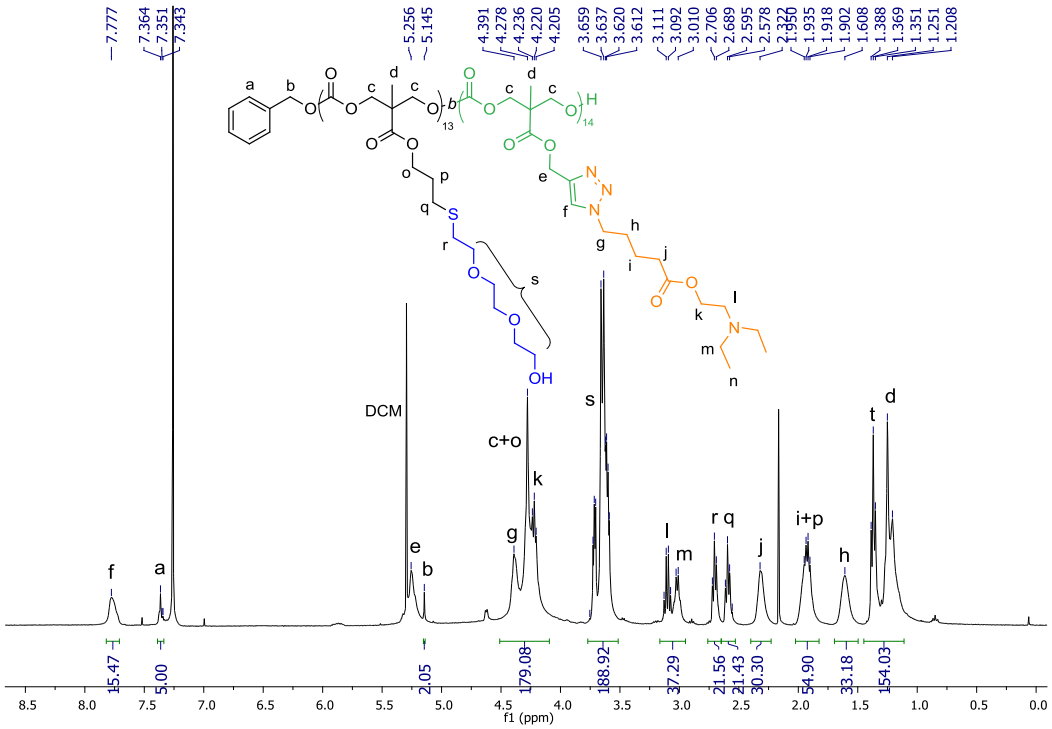


Figure B.33. *^{1}H NMR, (400MHz, $CDCl_3$, δ (ppm))*

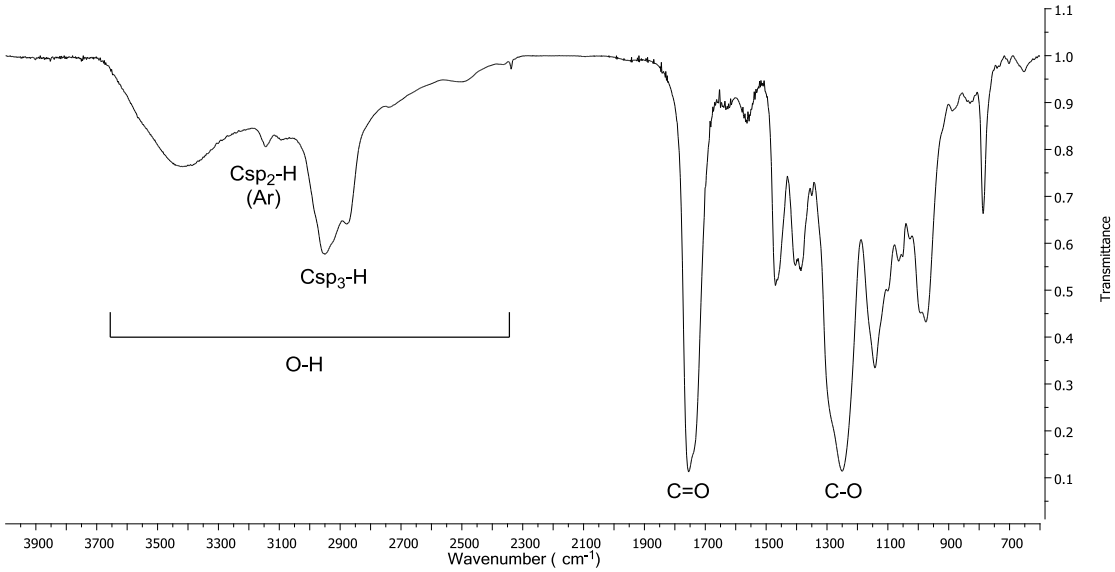


Figure B.34. *FTIR (KBr).*

B.7. Synthesis and characterization of amphiphilic and light-responsive block copolycarbonates by orthogonal click reactions (*Series IV*)

$PMAC_{15}$

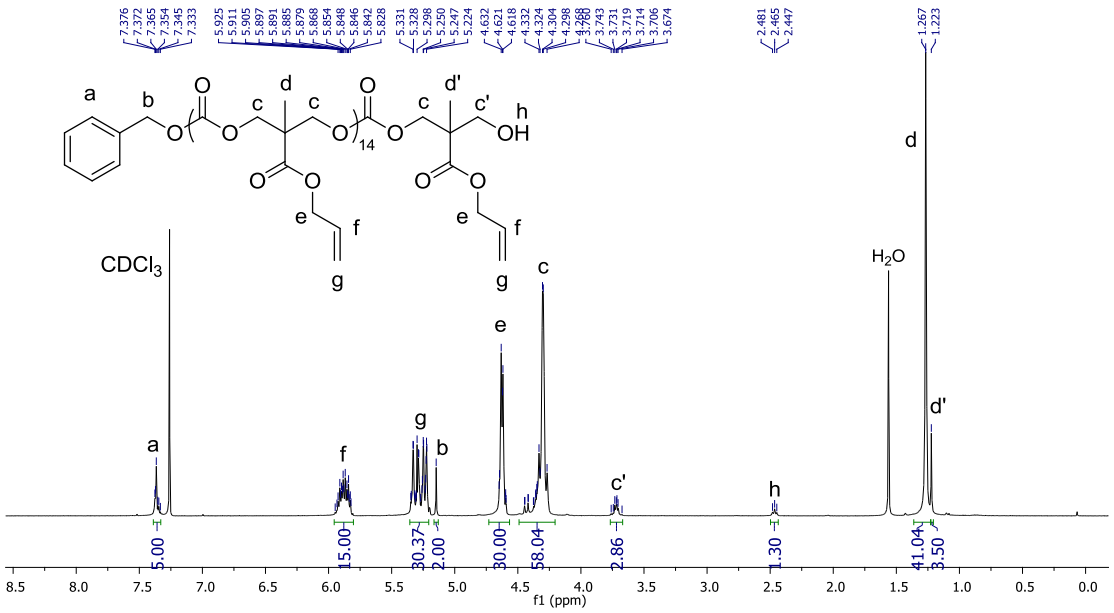


Figure B.35. *^{1}H NMR, (400MHz, $CDCl_3$, δ (ppm))*

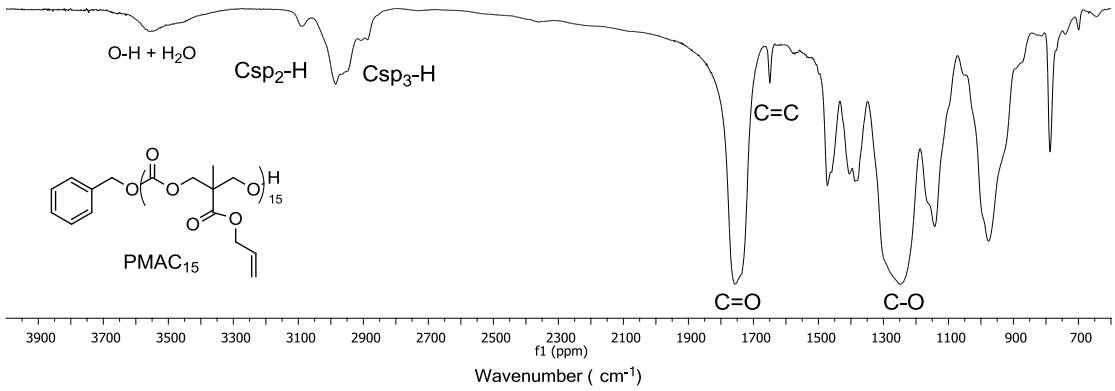


Figure B.36. *FTIR (KBr).*

PMAC$_{15}$-*b*-PMPC$_{15}$

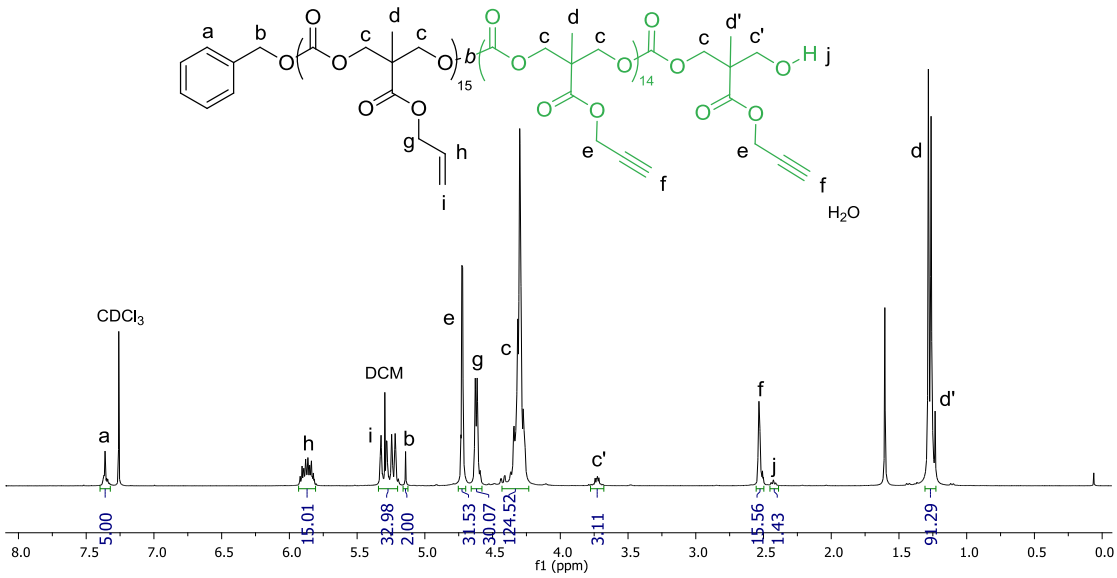


Figure B.37. *^{1}H NMR, (400MHz, $CDCl_3$, δ (ppm))*

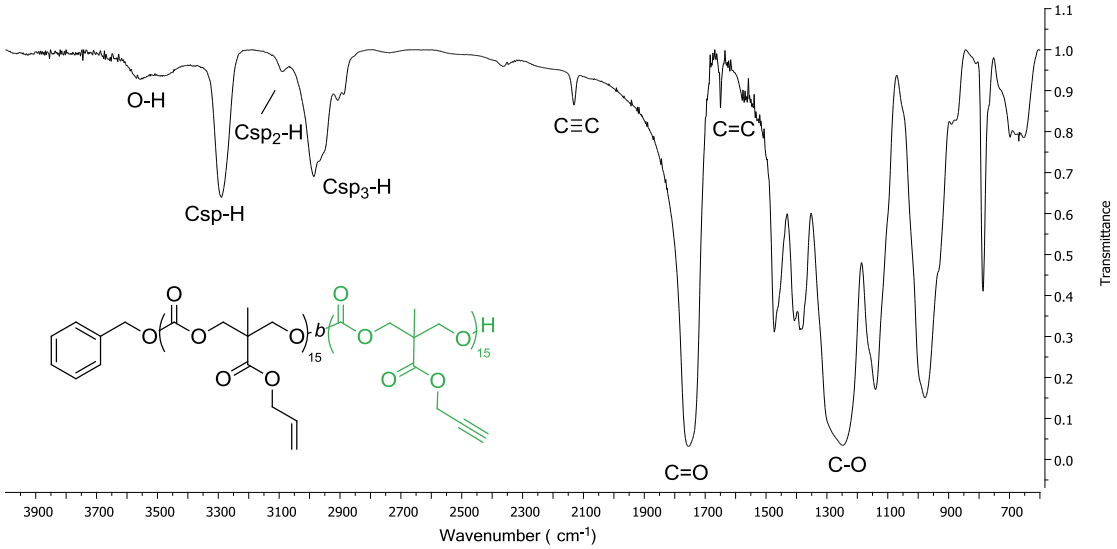


Figure B.38. *FTIR (KBr)*

6-azidohexan-1-ol

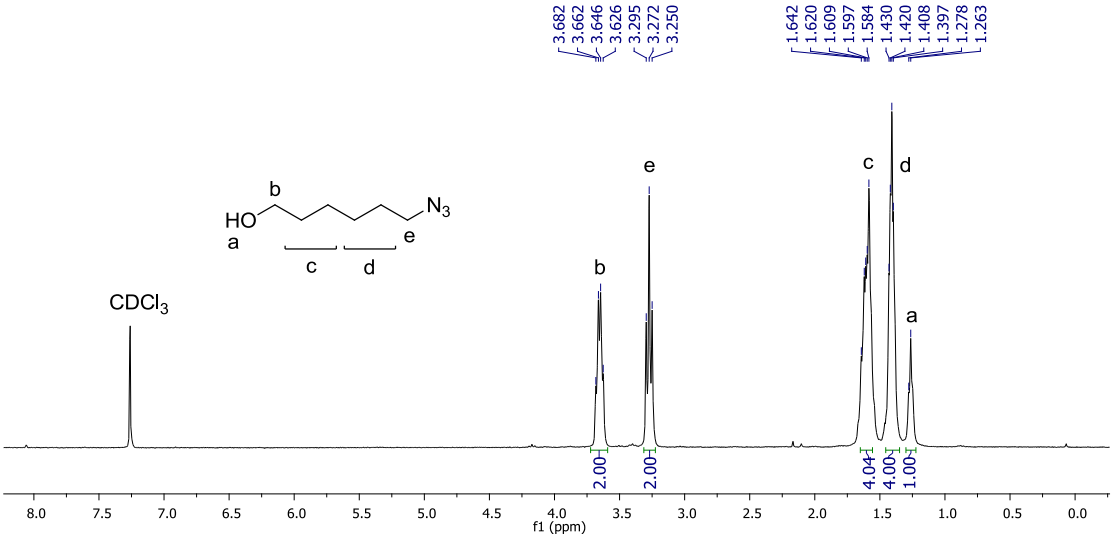


Figure B.39. *^{1}H NMR, (300MHz, $CDCl_3$, δ (ppm))*

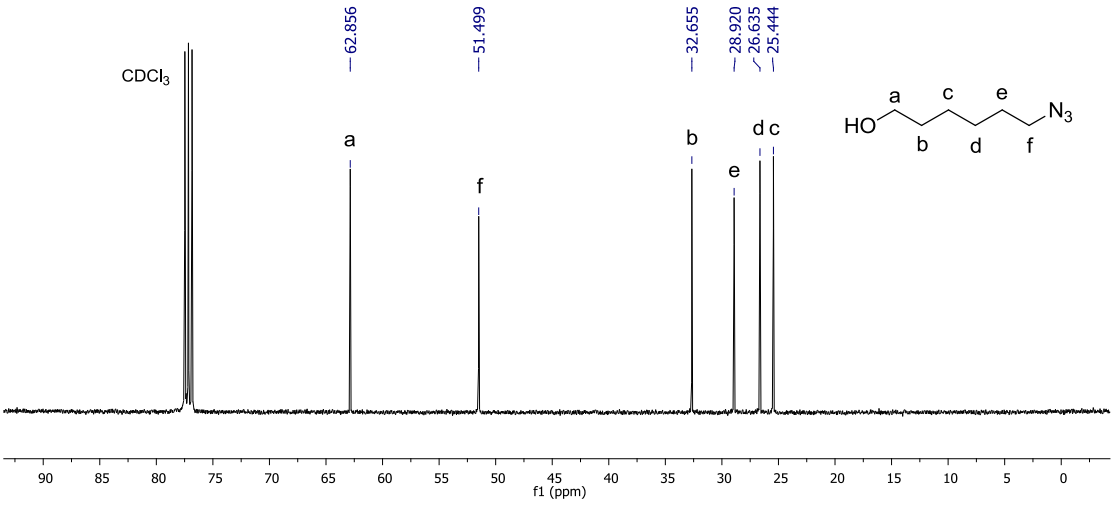


Figure B.40. *^{13}C NMR, (100MHz, $CDCl_3$, δ (ppm))*

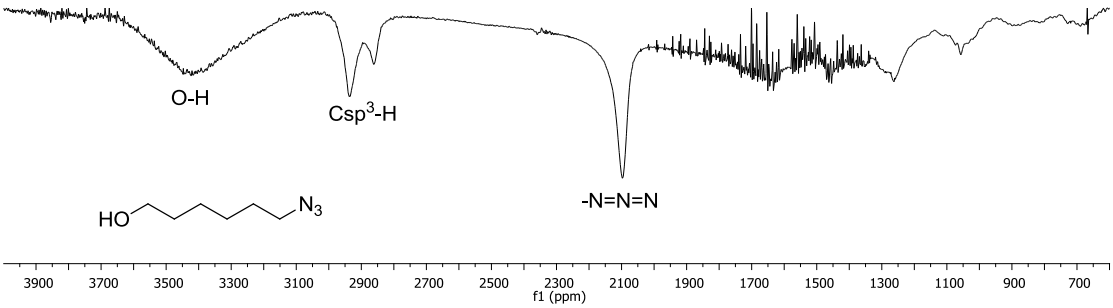


Figure B.41. *FTIR (KBr)*

N_3-Azo

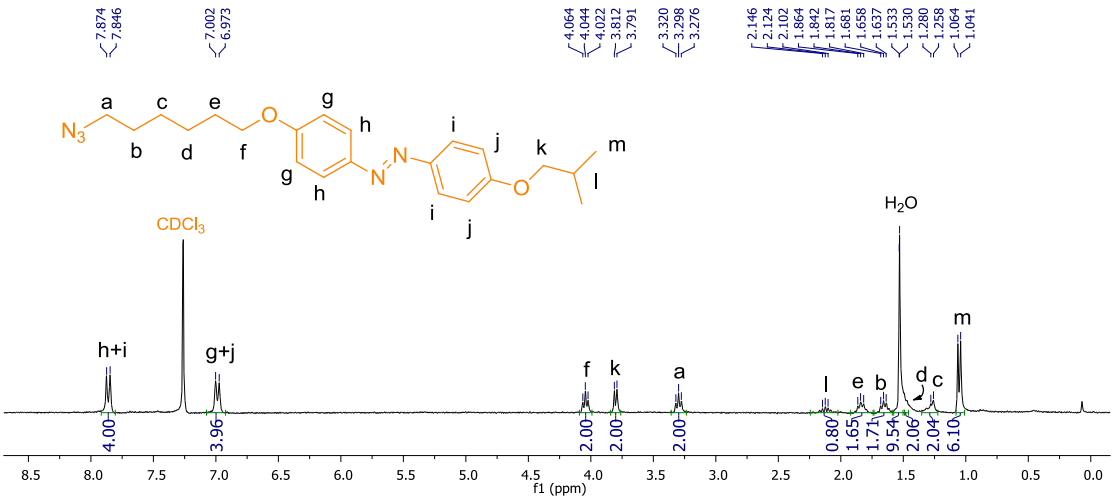


Figure B.42. *^1H NMR, (300MHz, $CDCl_3$, δ (ppm))*

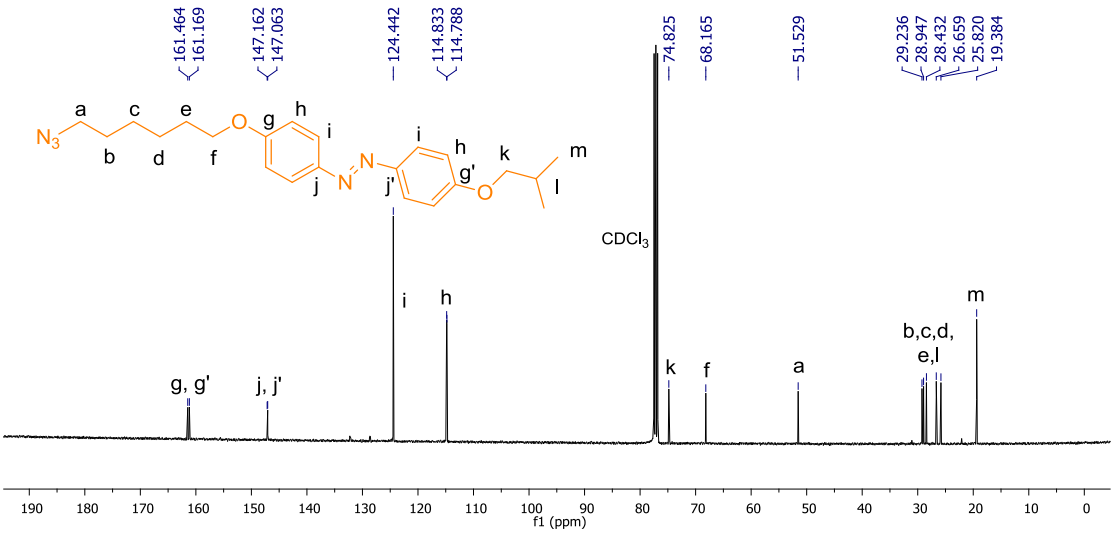


Figure B.43. *^{13}C NMR, (100MHz, $CDCl_3$, δ (ppm))*

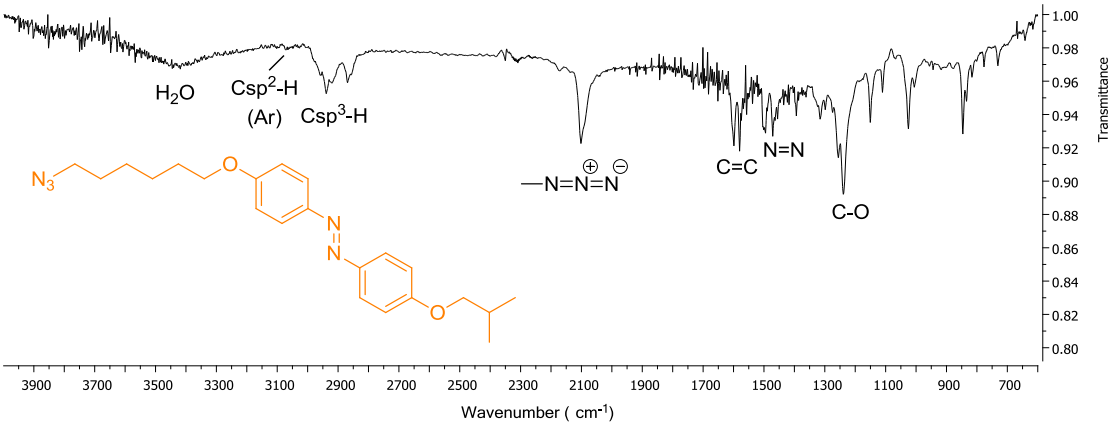


Figure B.44. *FTIR (KBr)*

$PMAC_{15}$-*b*-$(MPC\text{-}Azo)_{15}$

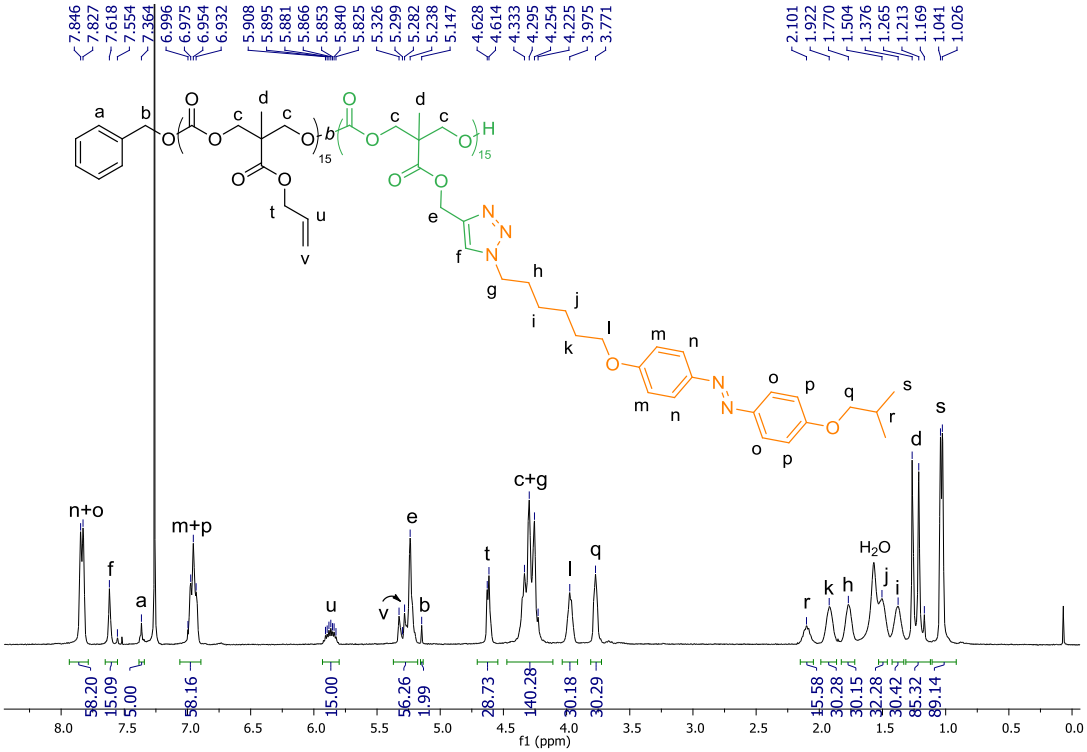


Figure B.45. *^{1}H NMR, (400MHz, $CDCl_3$, δ (ppm))*

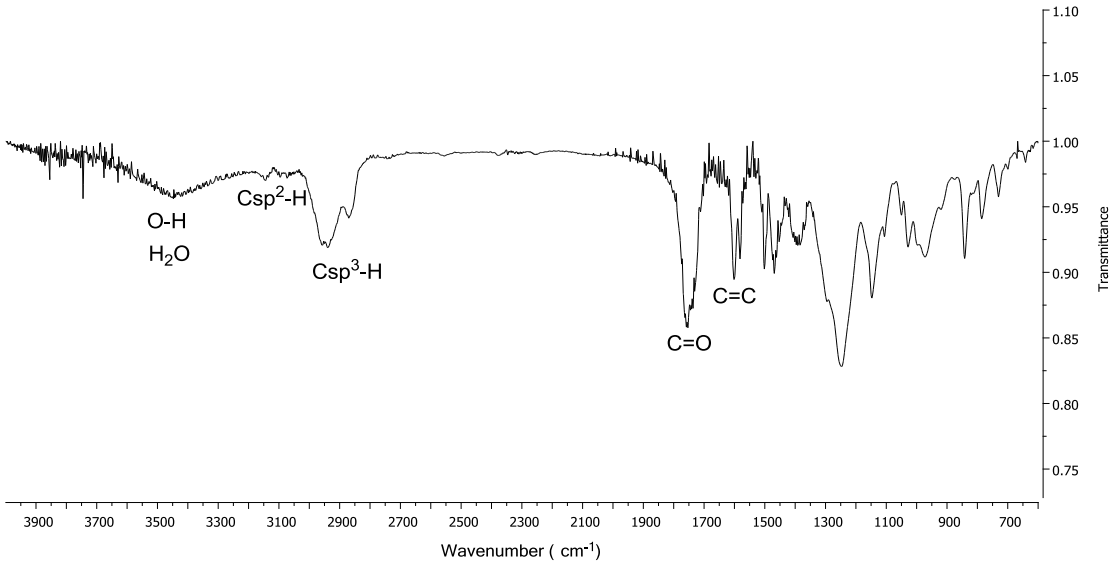


Figure B.46. *FTIR (KBr)*

P(MAC-STEG)-*b*-(MPC-Azo)

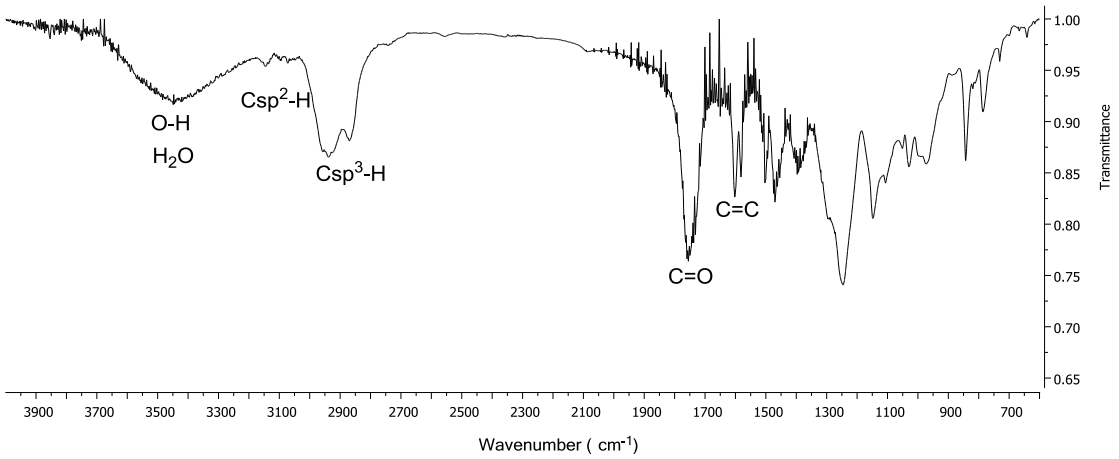


Figure B.47. *FTIR (KBr)*

Annex C- MS analysis

$PMAC_{13}$

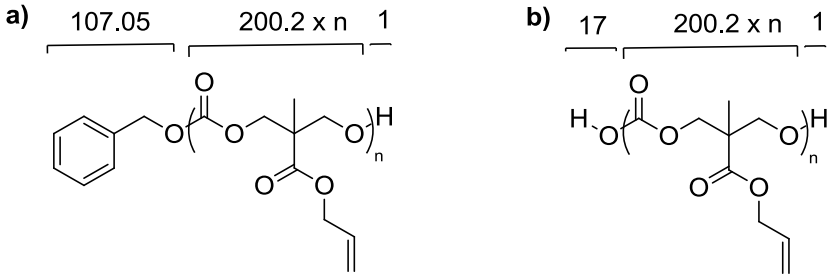


Figure C.1. PMAC schematized structure (a) and proposed structure for low molecular weight distribution (b).

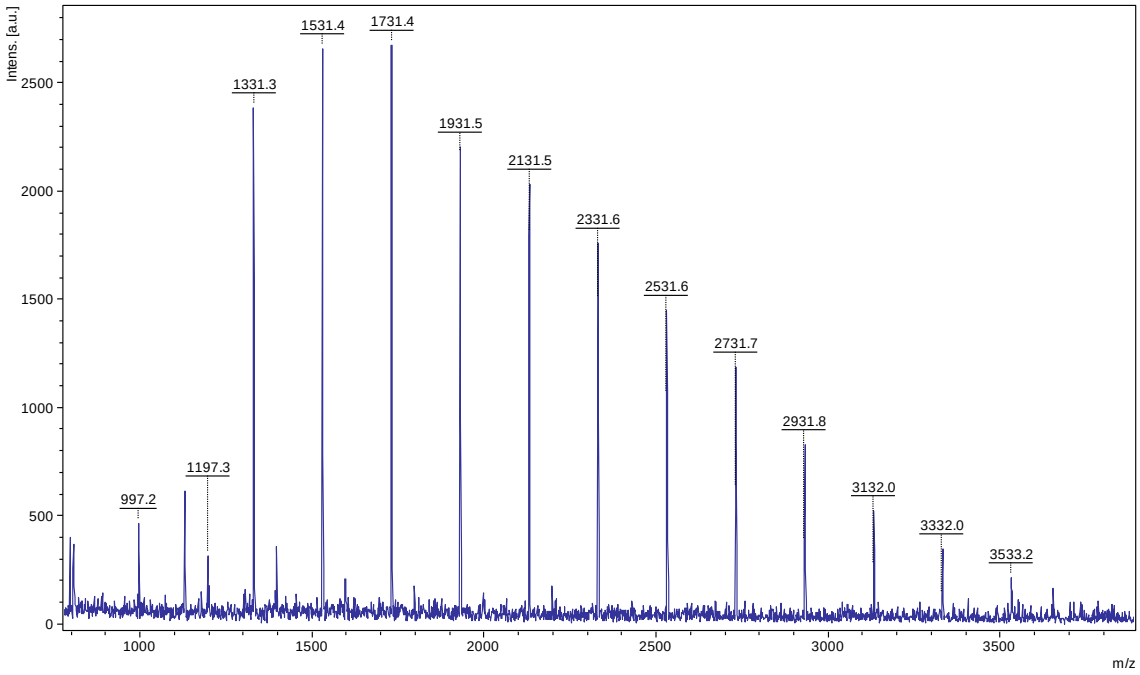
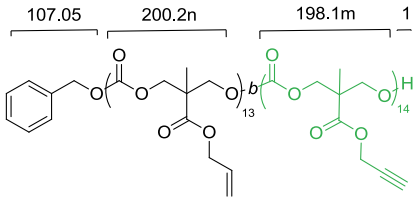


Figure C.2. MALDI-ToF MS of $PMAC_{13}$ (Autoflex, matrix: DCTB).

$PMAC_{13}$-*b*-MPC_{14}



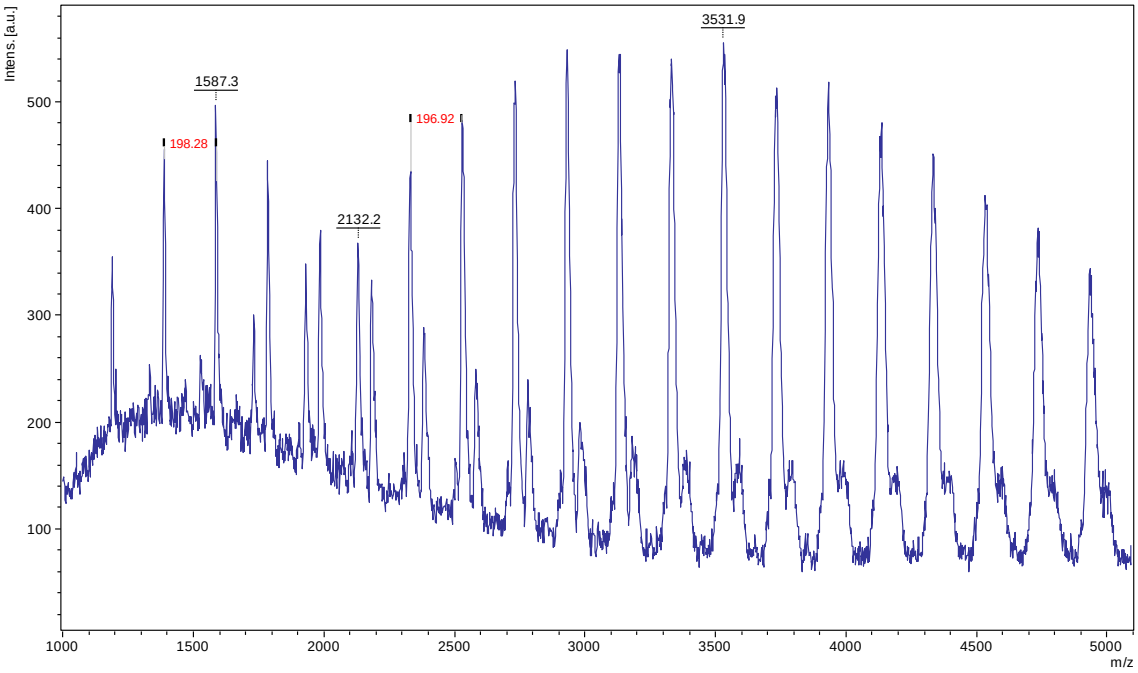
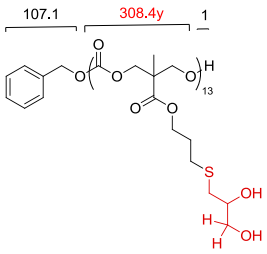


Figure C.3. MALDI-ToF MS of $PMAC_{13}$-*b*-MPC_{14} (Microflex, matrix: DCTB).

PMAC-SD



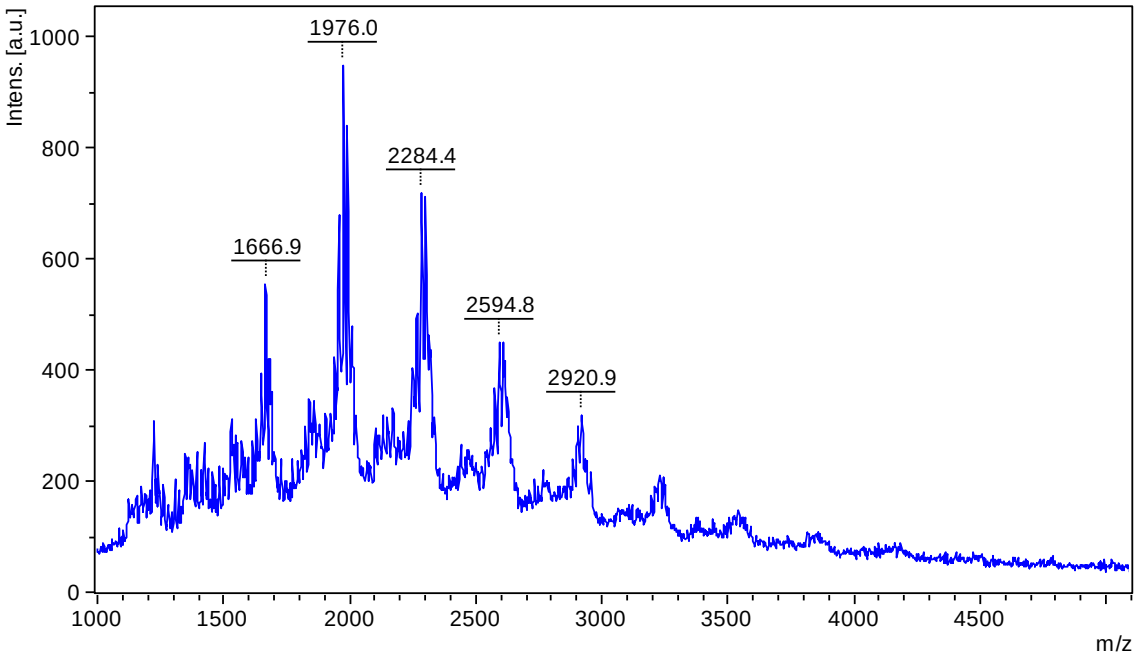


Figure C.4. MALDI-ToF MS of PMAC-SD (Microflex, matrix: DCTB).

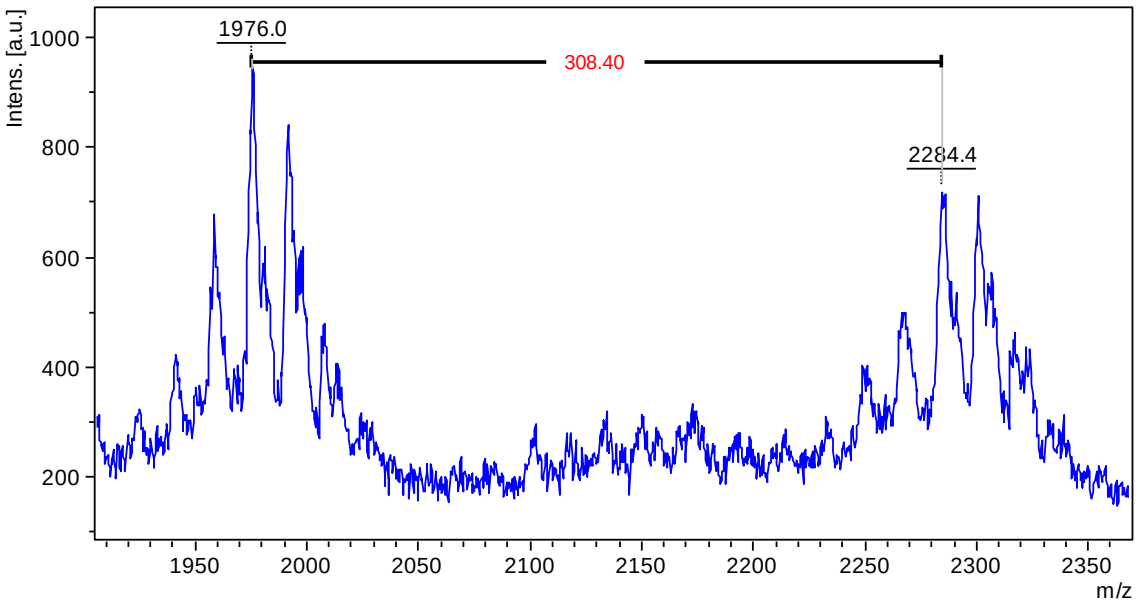


Figure C.5. MALDI-ToF MS of PMAC-SD 1900-2350 m/z region (Microflex, matrix: ditranol).

PMAC-STEG

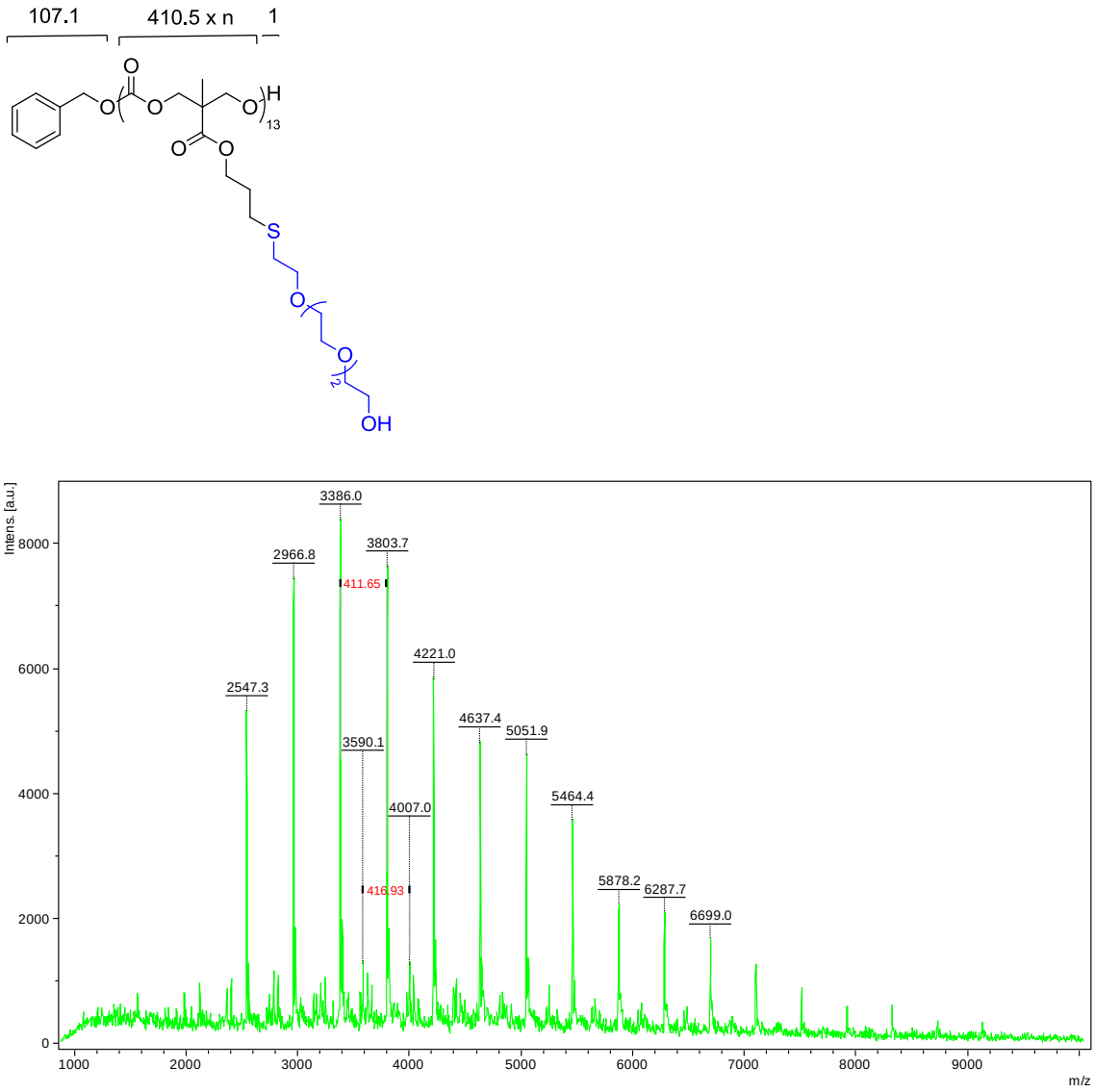


Figure C.6. MALDI-ToF MS of PMAC-STEG (Autoflex, matrix: DCTB).

P(MAC-STEG)-*st*-(MAC-SD)

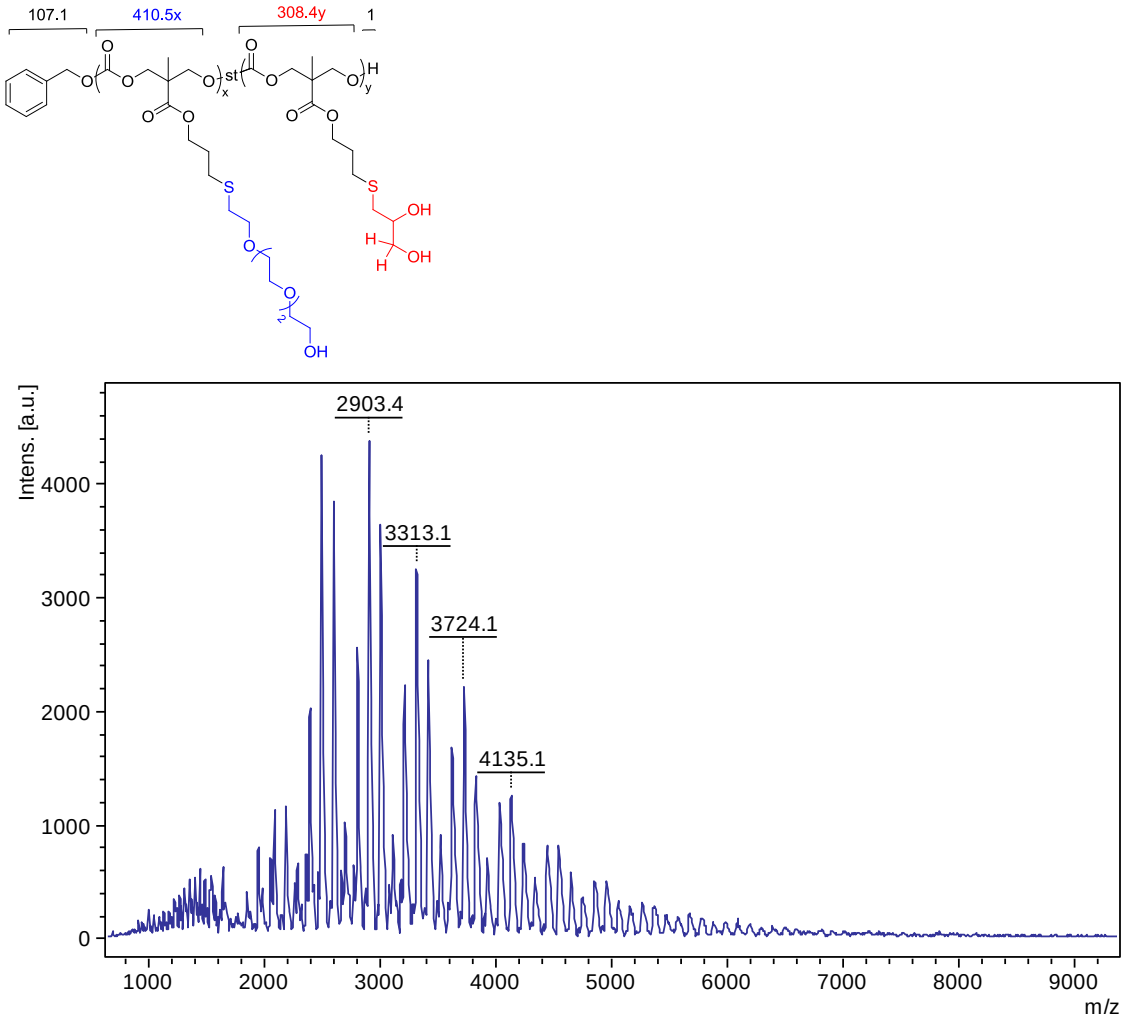


Figure C.7. MALDI-ToF MS of PMAC-STEG-*st*-SD (Microflex, matrix: DCTB).

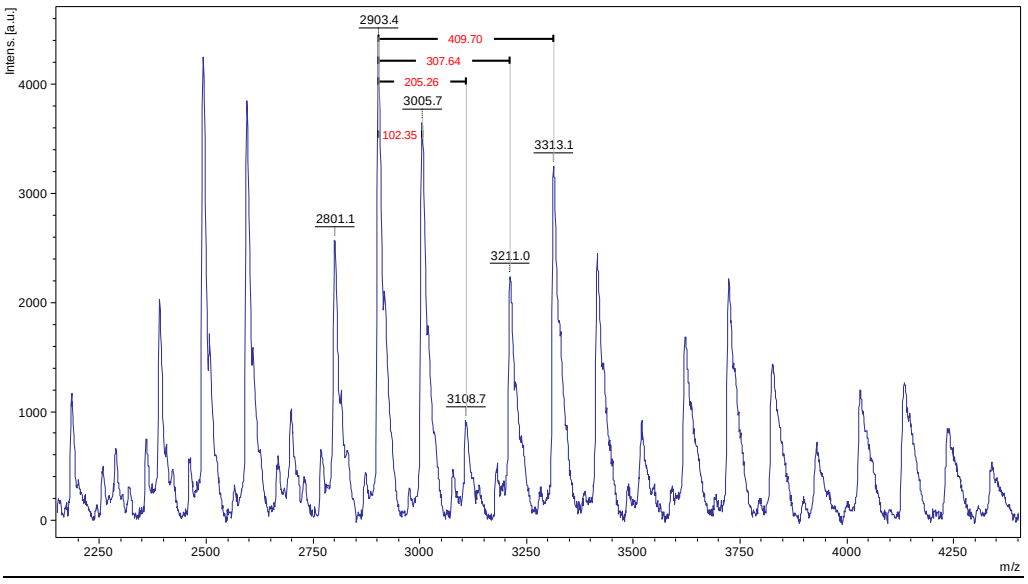


Figure C.8. MALDI-ToF MS of PMAC-STEG-*st*-SD 2250-4250 m/z region (Microflex, matrix: DCTB).

P(MAC-STEG)$_{13}$-*b*-(MPC-C16)$_{14}$

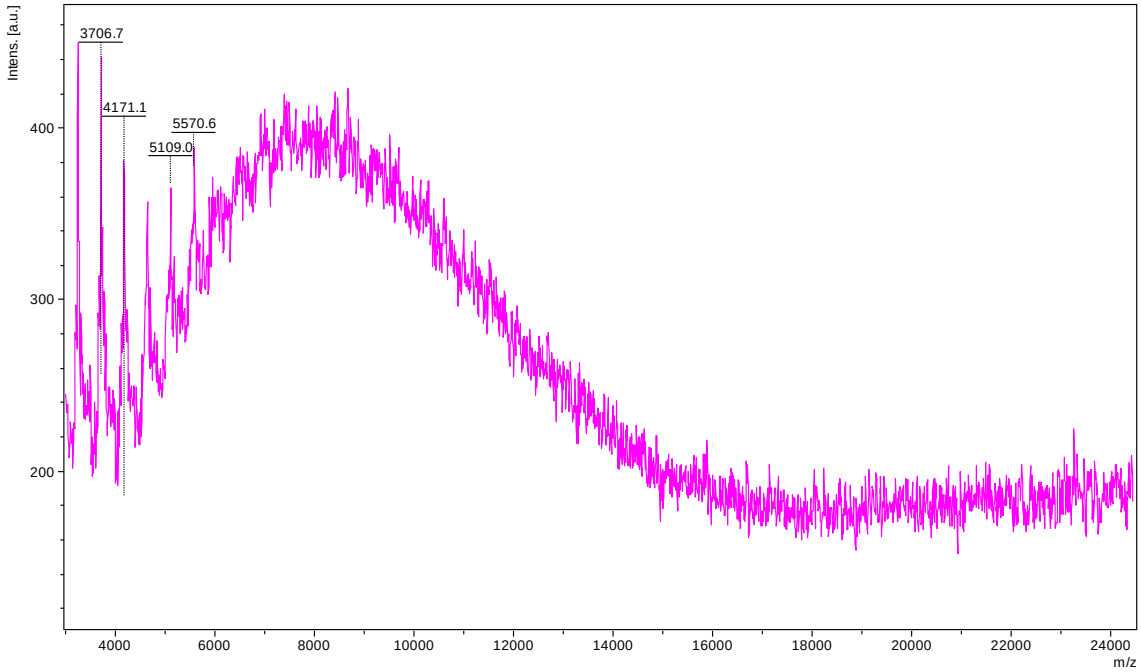


Figure C.9. MALDI-ToF MS of P(MAC-STEG)-*b*-(MPC-C16) (Microflex, matrix: DCTB).

$PMAC_{15}$

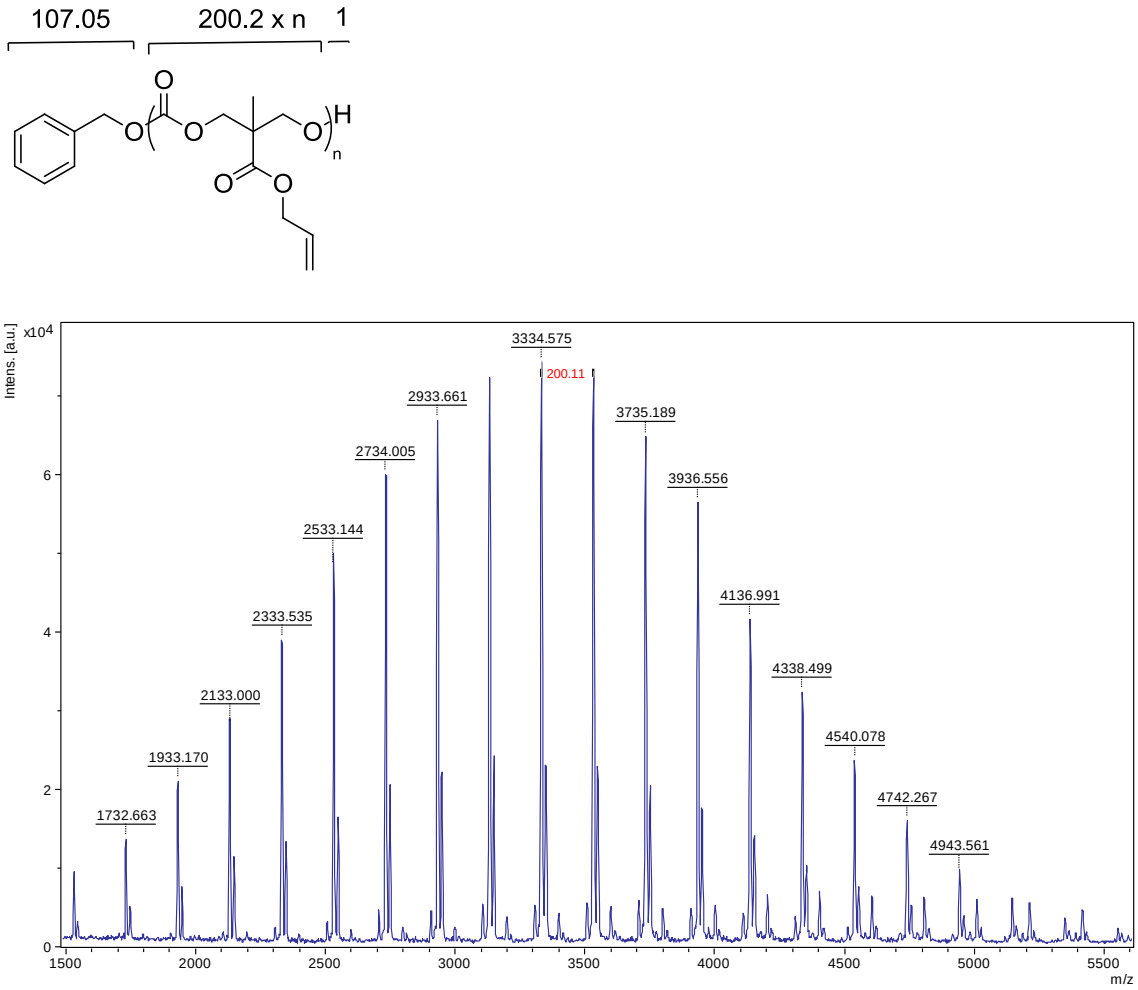


Figure C.10. MALDI-ToF MS of $PMAC_{15}$ (Autoflex, matrix: DCTB).

$PMAC_{15}$-*b*-MPC_{15}

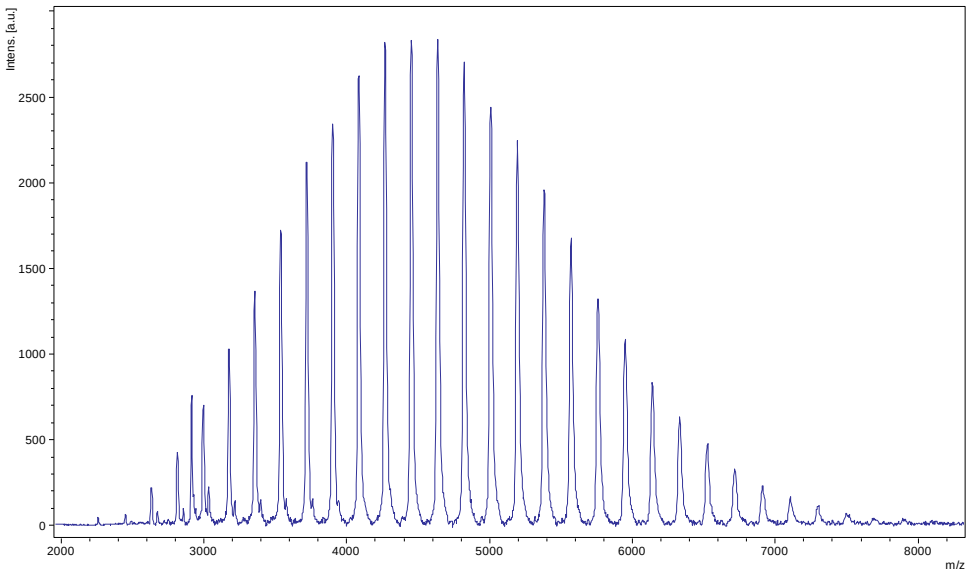


Figure C.11. MALDI-ToF MS of $PMAC_{15}$-*b*-MPC (Microflex, matrix: DCTB).

Annex D- Size Exclusion Chromatography (SEC)

Table D.1. Data from SEC analysis.

Sample	M_n	Polydispersity (*Đ*)
$PMAC_{13}$	3192	1.12
PMAC-SD	3659	1.11
PMAC-STEG	5840	1.11
PMAC-STEG-*st*-SD	4996	1.12
$PMAC_{13}$-*b*-MPC_{14}	6720	1.15
P(MAC-STEG)-*b*-(MPC-C16)	13440	1.18
$PMAC_{15}$	3861	1.08
$PMAC_{15}$-*b*-MPC_{15}	7517	1.07
PMAC-*b*-(MPC-Azo)	11170	1.07
P(MAC-STEG)-*b*-(MPC-Azo)	13102	1.10

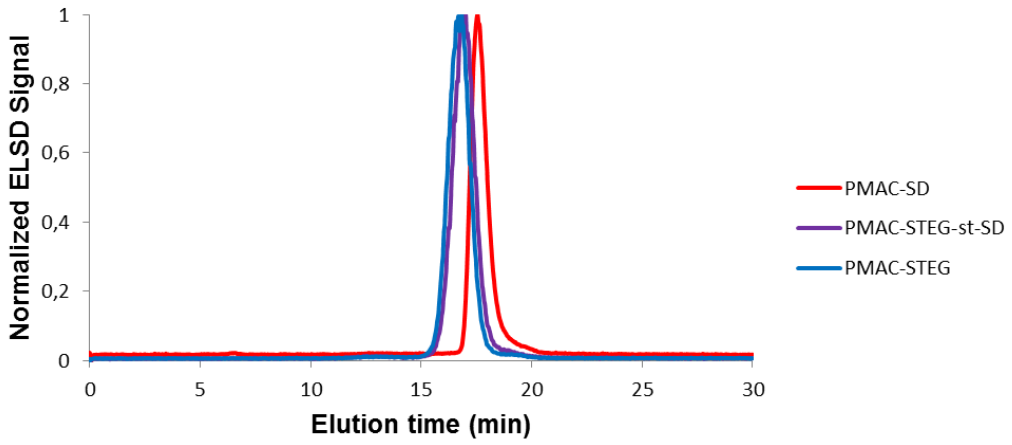


Figure D.1. SEC analysis of functionalized homopolymers: PMAC-SD, PMAC-STEG-*st*-SD and PMAC-STEG.

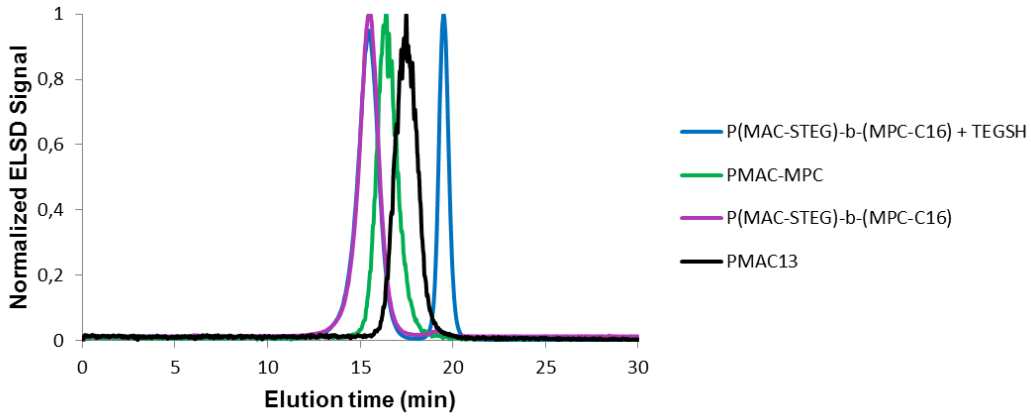


Figure D.2. SEC analysis of $PMAC_{13}$, $PMAC_{13}$-*b*-MPC_{14}, P(MAC-STEG)-*b*-(MPC-C16) and the later plus an aliquot of TEGSH, which seems to coincide with the second peak shown in P(MAC-STEG)-*b*-(MPC-C16) curve.

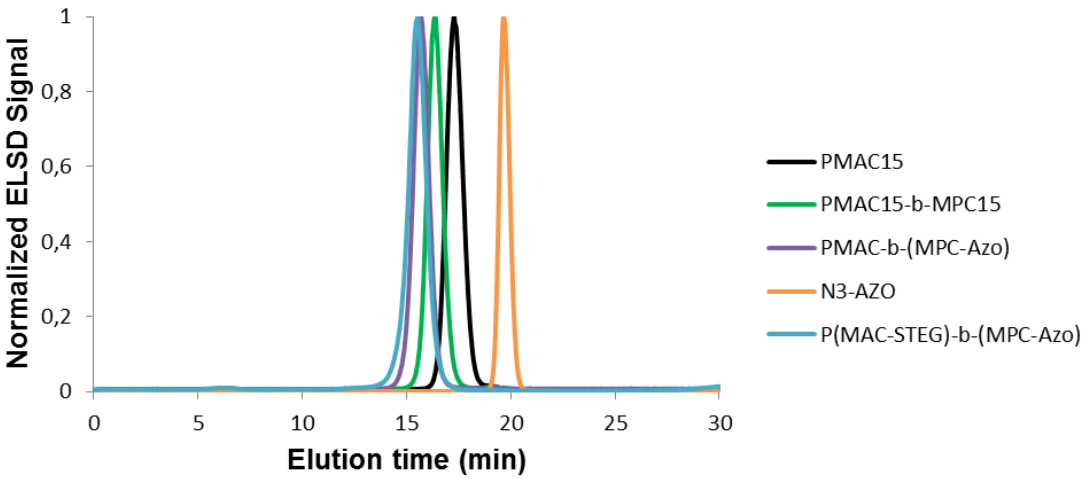


Figure D.3. SEC analysis of $PMAC_{15}$, $PMAC_{15}$-*b*-MPC_{15}, N_3-AZO, P(MAC)-*b*-(MPC-Azo) and P(MAC-STEG)-*b*-(MPC-Azo) that proves the orthogonal functionalization of both blocks.

Annex E- Temperature-controlled UV-vis spectroscopy

E.1. Scan rate dependence

- PMAC-STEG

Table E.1. T_{cp} scan rate dependence for PMAC-STEG.

	Cloud point temperature (ºC)	
Scan rate	**Heating**	**Cooling**
0.5 ºC/min	25	23.5
1 ºC/min	24	21

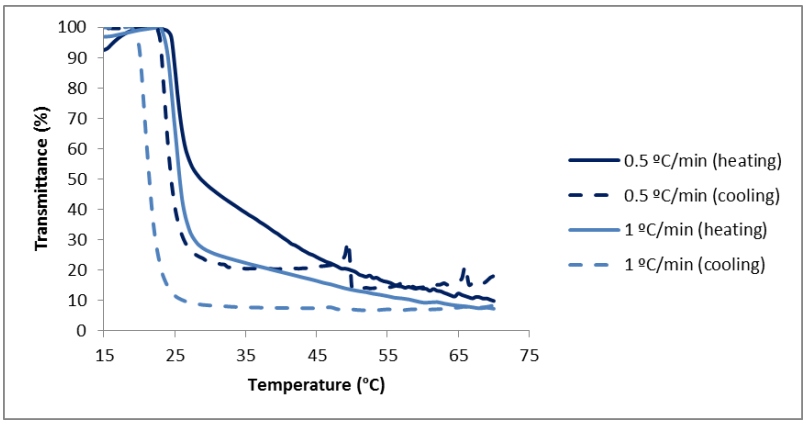


Figure E.1. T_{cp} scan rate dependence for PMAC-STEG.

- PMAC-STEG-*st*-SD

Table E.2. T_{cp} scan rate dependence for PMAC-STEG-*st*-SD.

	Cloud point temperature (ºC)	
Scan rate	**Heating**	**Cooling**
0.5 ºC/min	16.5	15
1 ºC/min	17	14

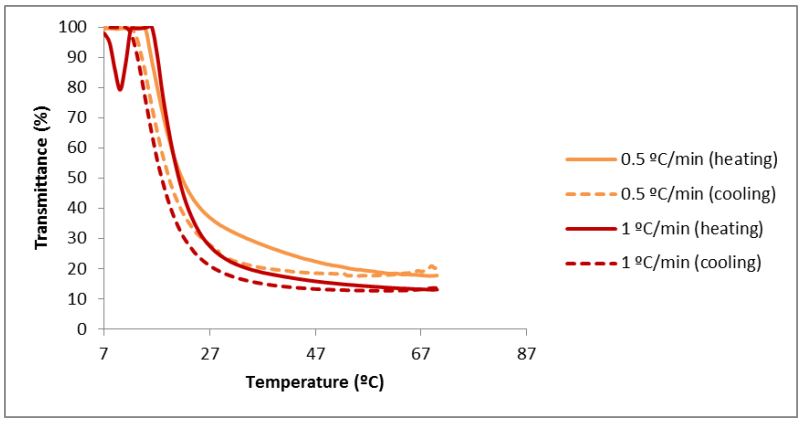


Figure E.2. T_{cp} scan rate dependence for PMAC-STEG-*st*-SD.

E.2. Concentration dependence

- PMAC-STEG

Table E.3. Tcp concentration dependence for PMAC-STEG

	Cloud point temperature (ºC)	
Concentration	**Heating**	**Cooling**
1 mg/mL	24	21
0.5 mg/mL	27	23
0.1 mg/mL	37	36

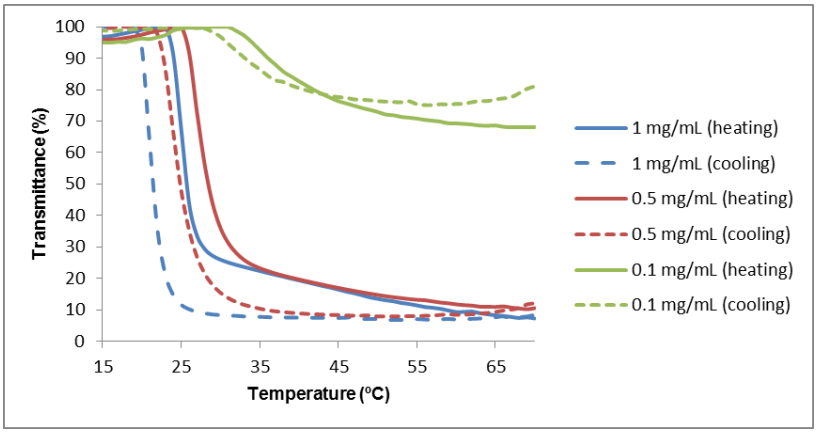


Figure E.3. T_{cp} concentration dependence for PMAC-STEG.

- PMAC-STEG-*st*-SD

Table E.4. Tcp concentration dependence for PMAC-STEG-*st*-SD

	Cloud point temperature (ºC)	
Concentration	**Heating**	**Cooling**
1 mg/mL	16.5	14
0.5 mg/mL	16	17
0.1 mg/mL	24	20

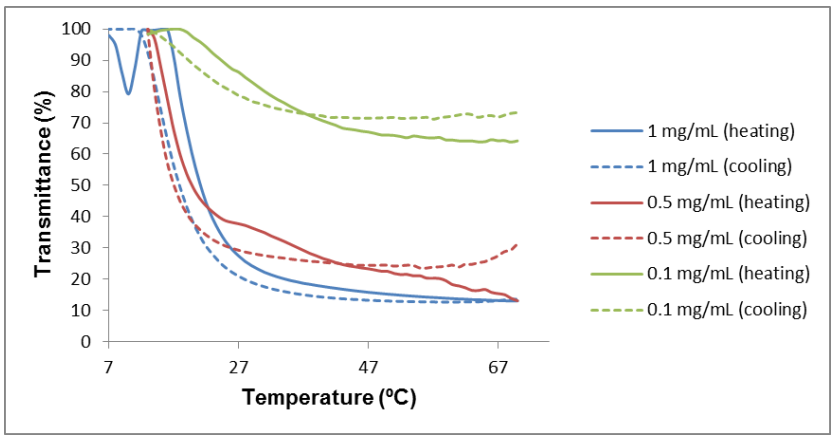


Figure E.4. T_{cp} concentration dependence for PMAC-STEG-*st*-SD.

Annex F- TEM Images

F.1. PMAC-STEG (0 ºC)

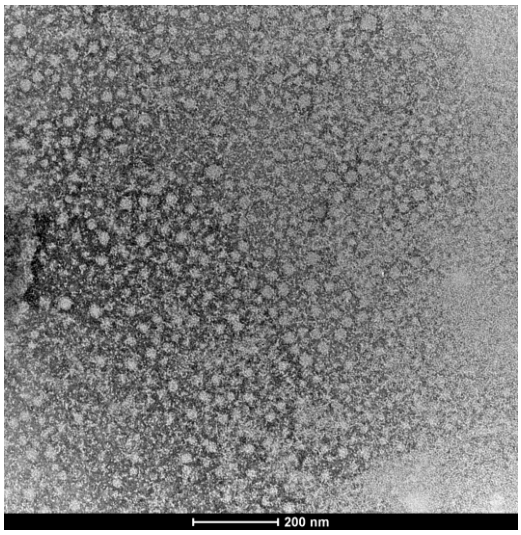


Figure F.1. TEM image of PMAC-STEG aggregates at 0 ºC.

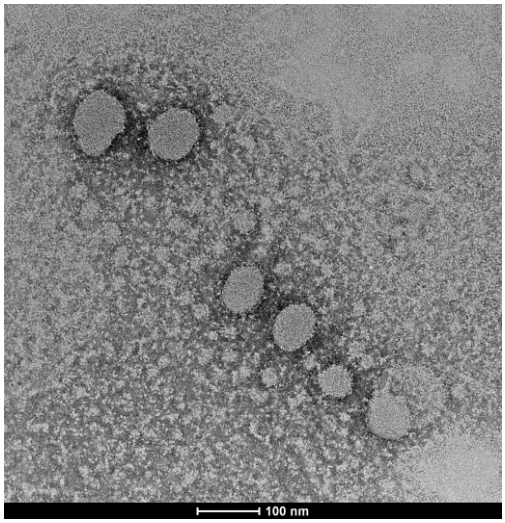


Figure F.2. TEM image of PMAC-STEG aggregates at 0 ºC.

F.2. PMAC-STEG (50 ºC)

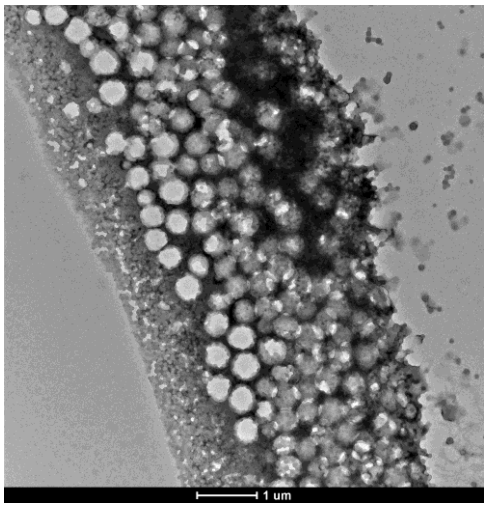


Figure F.3. TEM image of PMAC-STEG at 50 ºC.

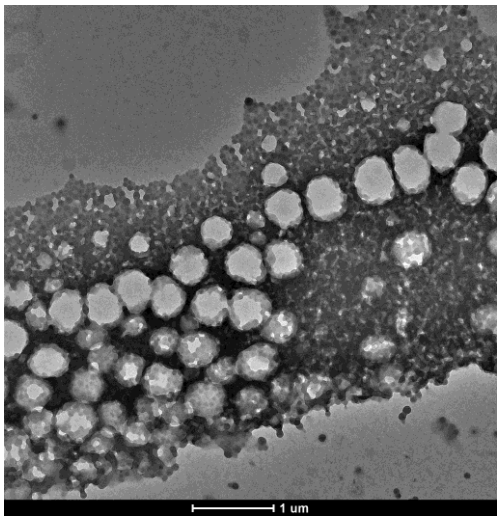


Figure F.4. TEM image of PMAC-STEG at 50 ºC.

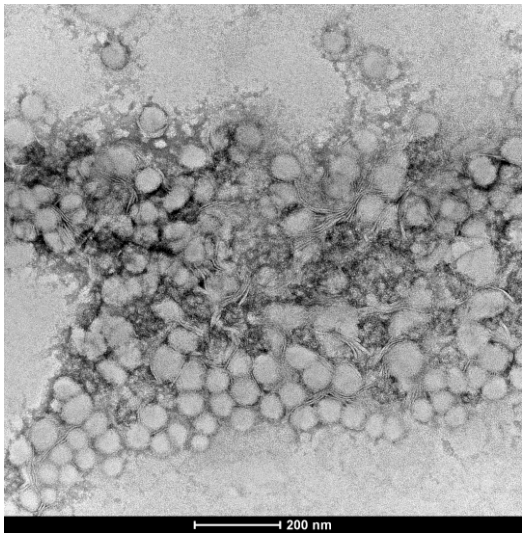


Figure F.5. TEM image of PMAC-STEG at 50 ºC.

F.3. PMAC-STEG-*st*-SD (0 ºC)

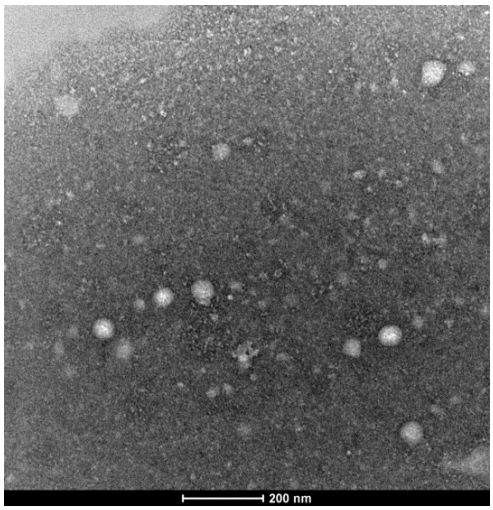


Figure F.6. TEM image of PMAC-STEG-*st*-SD at 0 ºC.

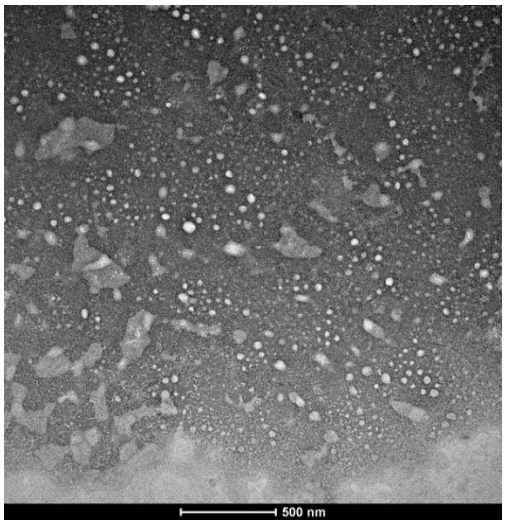


Figure F.7. TEM image of PMAC-STEG-*st*-SD at 0 ºC.

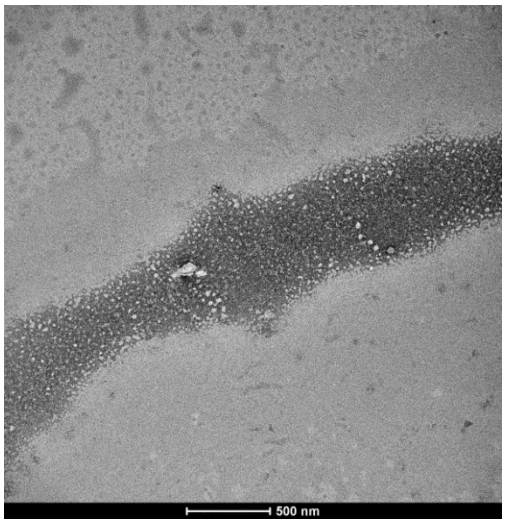


Figure F.8. TEM image of PMAC-STEG-*st*-SD at 0 ºC.

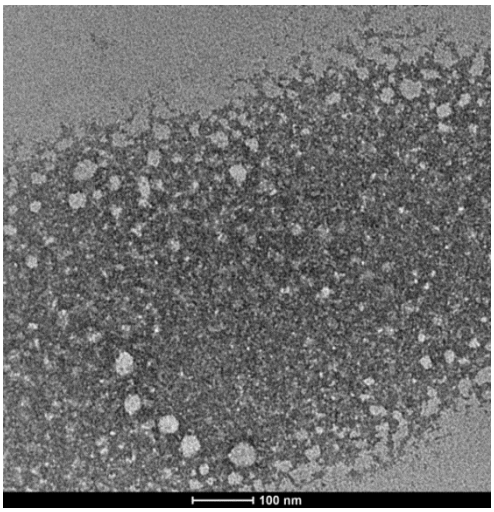


Figure F.9. TEM image of PMAC-STEG-*st*-SD at 0 ºC.

F.4. PMAC-STEG-*b*-SD (50 ºC)

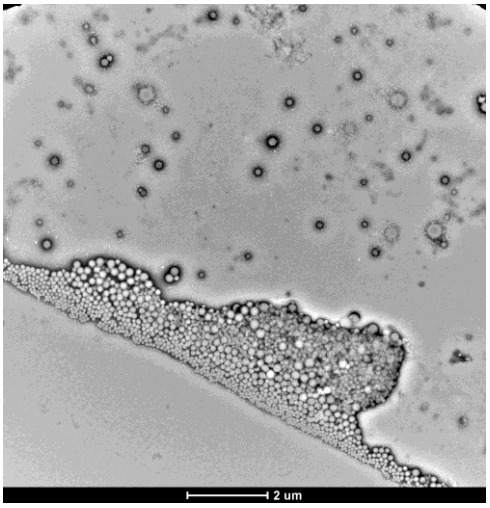


Figure F.10. TEM image of PMAC-STEG-*st*-SD at 50 ºC.

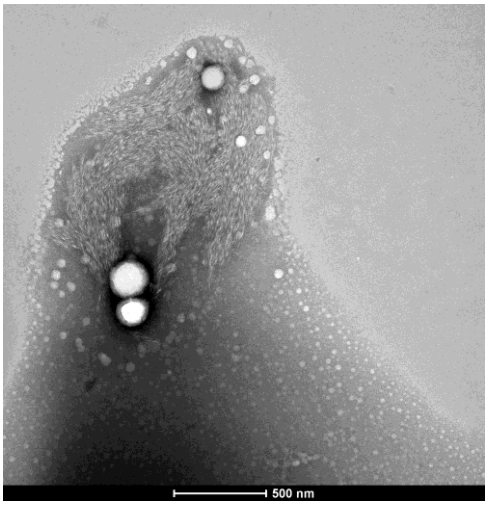


Figure F.11. TEM image of PMAC-STEG-*st*-SD at 50 ºC.

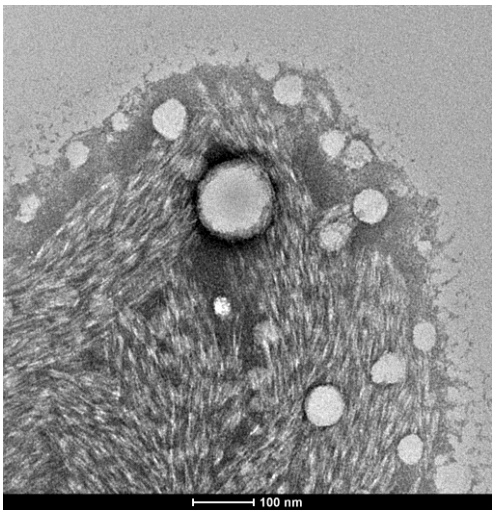


Figure F.12. TEM image of PMAC-STEG-*st*-SD at 50 ºC.

F.5. P(MAC-STEG)-*b*-(MPC-C16) (room temperature)

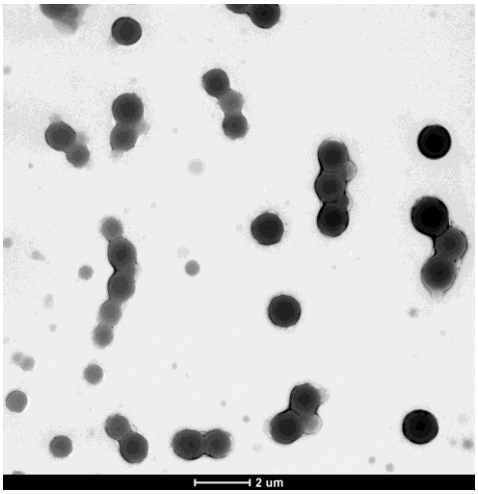


Figure F.13. TEM image of P(MAC-STEG)-*b*-(MPC-C16) before dialysis where a major contribution of > 1µm aggregates is observed.

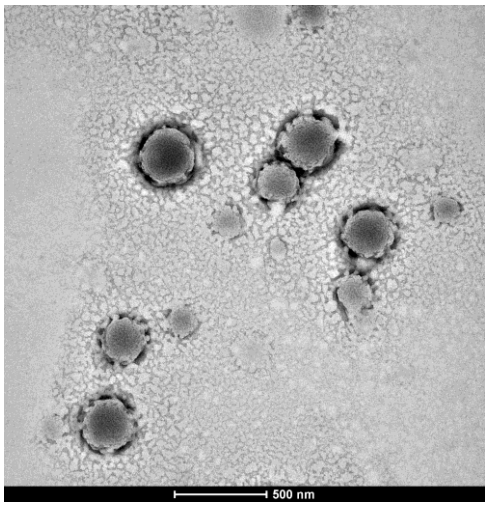


Figure F.14. TEM image of P(MAC-STEG)-*b*-(MPC-C16) before dialysis where 300 to 150 nm aggregates are observed.

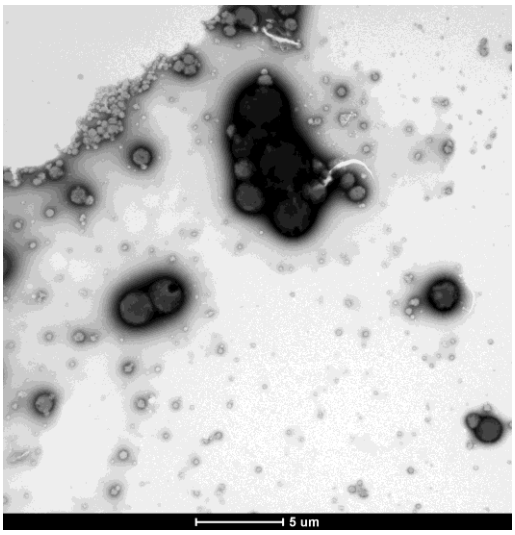


Figure F.15. TEM image of P(MAC-STEG)-*b*-(MPC-C16) after dialysis where macroscopic aggregates are clearly observed.

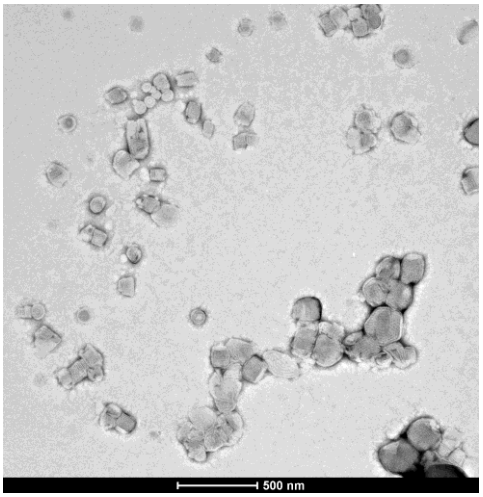


Figure F.16. TEM image of P(MAC-STEG)-*b*-(MPC-C16) after dialysis where aggregates of diverse morphology are shown.

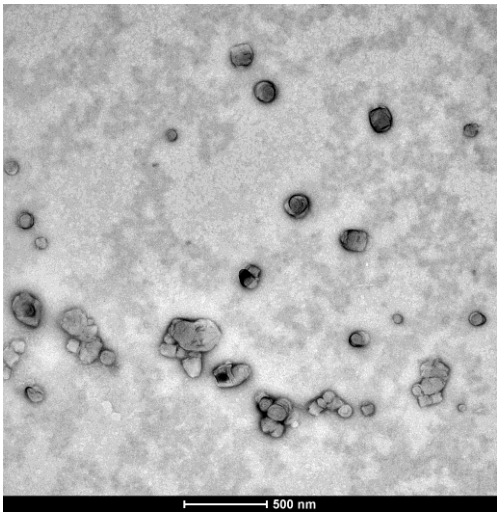


Figure F.17 TEM image of P(MAC-STEG)-*b*-(MPC-C16) after filtration where aggregates of diverse morphology are shown.

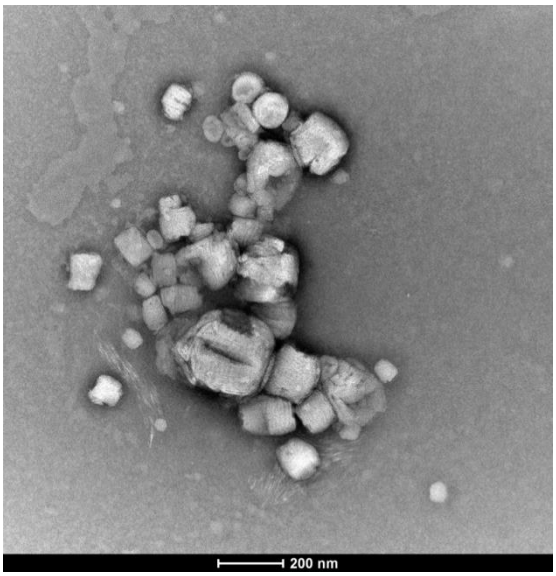


Figure F.18. TEM image of P(MAC-STEG)-*b*-(MPC-C16) after filtration where aggregates of diverse morphology are shown.

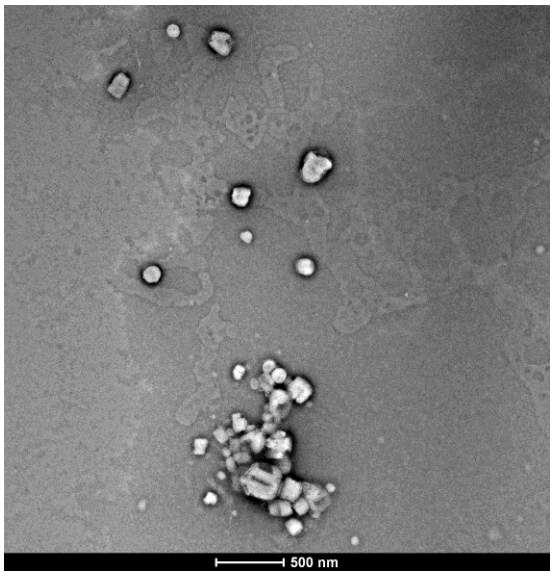


Figure F.19. TEM image of P(MAC-STEG)-*b*-(MPC-C16) after filtration where aggregates of diverse morphology are shown.

Annex G- Instruments and techniques

Nuclear Magnetic Resonance (^{1}H-NMR and ^{13}C-NMR). ^{13}C-NMR spectra were recorded using a Bruker AV-400 (100 MHz) equipment, whereas ^{1}H-NMR spectra were recorded in both Bruker AV-400 (400 MHz) equipment and Bruker AVANCE III (300 MHz). Both $CDCl_3$ and Acetone-D_6 have been used as solvent.

Infrared Spectroscopy (FTIR). FTIR spectroscopy was performed with a Bruker Vertex 70. Samples were prepared in KBr pellets (2% wt).

MS analysis. MS analysis was carried out using Bruker Microflex and Autoflex equipments for MALDI-TOF experiments and both DCM and THF were used as solvents.

Gel Permeation Chromatography (GPC). GPC was carried out using a Waters Alliance 2695 HPLC with an evaporative light scattering detector (ELS) Waters 2424 and Styragel® columns (7.8 x 300 mm) HR2 and HR4, using THF as eluent (flow 1mL/min). Calibration was made with poly(methyl methacrylate) standards. Samples were prepared by dissolving 2 mg of product in 2 mL of THF (HPLC) and filtering throigh a 1 micron PTFE filter.

Ultraviolet-visible spectroscopy (UV-vis). For monitoring co-solvent method through turbidimetry, an ATI Unicam UV4-200 spectrophotometer and quartz cuvettes with a path length of 1 cm were employed. Besides, for UV irradiation experiments, an Agilent Cary UV-Vis-NIR spectrophotometer was employed. Irradiation was performed using a Hg lamp Philips PL-S 9W with maximum emission at 365 nm for one minute and, then, measuring absorbance in the UV-region.

Temperature-controlled UV-cis spectroscopy. For determining T_{cp} by turbidimetry method, Agilent Cary 6000i UV-Vis-NIR spectrophotometer and quartz cuvettes with a path length of 1 cm were employed.

Dynamic Light Scattering (DLS). DLS measurements were carried out in a Malvern Instrument Nano ZS using a He-Ne laser with a 633 nm wavelength, with quartz cuvettes. Samples were diluted in Milli-Q water to reach a concentration of 100 μg/mL. For measurements at different temperatures, it was stabilized for 15 min at each temperature before the measurement.

Transmission Electron Microscopy (TEM). TEM studies were performed at "Servicio de Microscopía Electrónica de Materiales" from "Laboratorio de Microscopías Avanzadas" of the University of Zaragoza. A transmission electron microscope FEI Tecnai T20 (LaB_6) was employed operating at 200 kV. Sample preparation was carried out by depositing sample solution (10 μL) on a copper grid with carbon film and, after 30 s, removing sample excess by capillarity. The sample was then dyed using uranyl acetate (10 μL) and, again, excess of dye was removed by capillarity after 30 s. Uranyl acetate was manipulated at "Centro de Investigación Biomédica de Aragón (CIBA)" for preventing radioactive residues.