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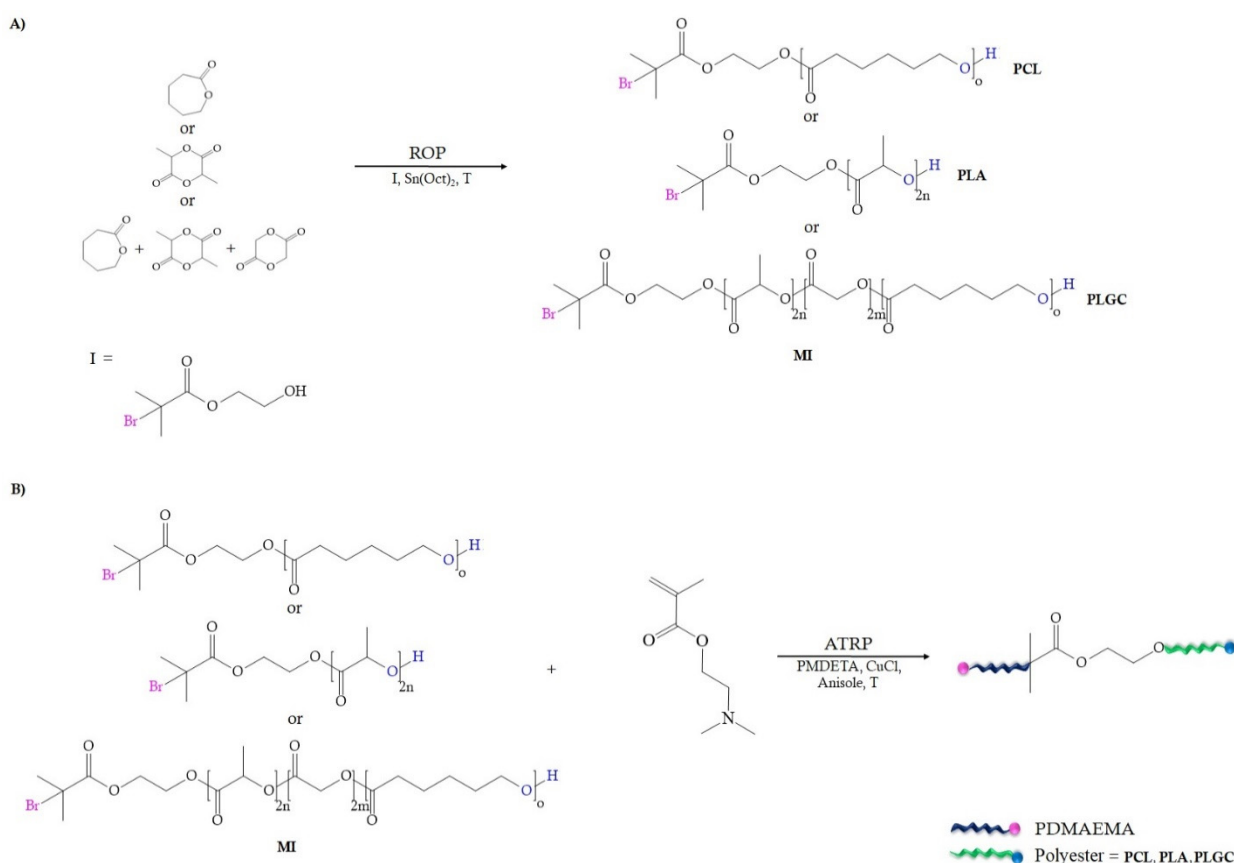
The Influence of Polymer Composition on the Hydrolytic and Enzymatic Degradation of Polyesters and Their Block Copolymers with PDMAEMA

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1. Synthesis of Aliphatic Polyesters and polyester-*b*-PDMAEMA Copolymers



Scheme S1. Schematic representation for the synthesis of linear (A) and amphiphilic block (B) polymers.

1.1. Synthesis of Polyester Macroinitiator (MI1)

Macroinitiators of polyester type were synthesized via coordination-insertion ring-opening polymerization.

Prior to the synthesis, the Schlenk reactor was subjected to silanization. For this purpose, 6% chlorotrimethylsilane solution in toluene was prepared in a Schlenk reactor, and left for 24 hours. After 24 hours, the solution was poured out of the reactor, which was then immersed into a hot oil bath (120 °C) and heated under vacuum for 2 hours. After cooling the reactor to room temperature, CL (27 mmol, 3 mL) and HEBIB (0.27 mmol, 39 µL) were introduced under argon. Then the mixture was subjected to the three freeze-

pump-thaw cycles. Next, the appropriate amount of ROP catalyst was introduced into the reactor (150 μ L, 6% solution of $\text{Sn}(\text{Oct})_2$ in toluene). The polymerization process was allowed to continue for 0.5 hour at 130 $^{\circ}\text{C}$. The reaction mixture was diluted with dichloromethane, and then the polymer was precipitated in methanol. The crude product was redissolved in dichloromethane and re-precipitated in methanol. The resulting product was transferred to a previously weighed vial and dried to constant weight. Yield: 86%, $M_{n,\text{theo}} = 12800$ g/mol, $M_{n,\text{SEC}} = 21100$ g/mol, $\bar{D} = 1.38$).

1.2. Synthesis of polyester-*b*-PDMAEMA (Example for I) via ATRP

Macroinitiator (PCL, 50.33 mg; 0.05 mmol/1 initiating site), DMAEMA (0.8 mL; 5 mmol), PMDETA (10 μ L; 0.05 mmol), and anisole (0.6 mL; 75 vol% of monomer) were placed in a Schlenk flask and then degassed by three freeze-pump-thaw cycles. After that CuCl (4.7 mg; 0.05 mmol), was added, and the reaction flask was immersed in an oil bath at 45 $^{\circ}\text{C}$. The reaction was stopped after 2 hours by exposing the reaction mixture to air. After dilution of reaction mixture with CH_2Cl_2 , the $\text{CuCl}/\text{PMDETA}$ complex was removed by passing through basic alumina column. The organic solvent was evaporated and the final product was precipitated in *n*-heptan and dried to constant mass. Yield: 58%, $M_{n,\text{theo}} = 19100$ g/mol, $M_{n,\text{SEC}} = 33000$ g/mol, $\bar{D} = 1.24$).

2. Characterization of Polyesters and polyester-*b*-PDMAEMA Copolymers before Degradation

2.1. Gas Chromatography (GC)

Conversion of DMAEMA was determined by gas chromatography. The chromatograph (6850 Network GC System, Agilent Technologies) was equipped with a flame ionization detector. Injector and detector temperatures were kept constant at 250 $^{\circ}\text{C}$ (conditions: anisole was used as an internal standard, initial column temperature 40 $^{\circ}\text{C}$; column final temperature 200 $^{\circ}\text{C}$). The conversion was calculated by detecting the decrease of the monomer peak area relative to the internal standard peak area. The degree of polymerization (DP) and subsequent $M_{n,\text{GC}}$ was calculated based on the initial molar ratio of monomer to initiator and conversions obtained from GC. The number average molecular weights of copolymers were calculated by a summary of the weight of PDMAEMA block and polyester macroinitiator, which chains lengths were calculated on the basis of end groups on ^1H NMR spectrum. *Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR)*

ATR-FTIR analysis was carried out with a NICOLET 670 spectrophotometer at room temperature by attenuated total reflection (ATR) method. Spectra were recorded at 16 scans per spectrum and 4 cm^{-1} resolution in the range of 4000–400 cm^{-1} .

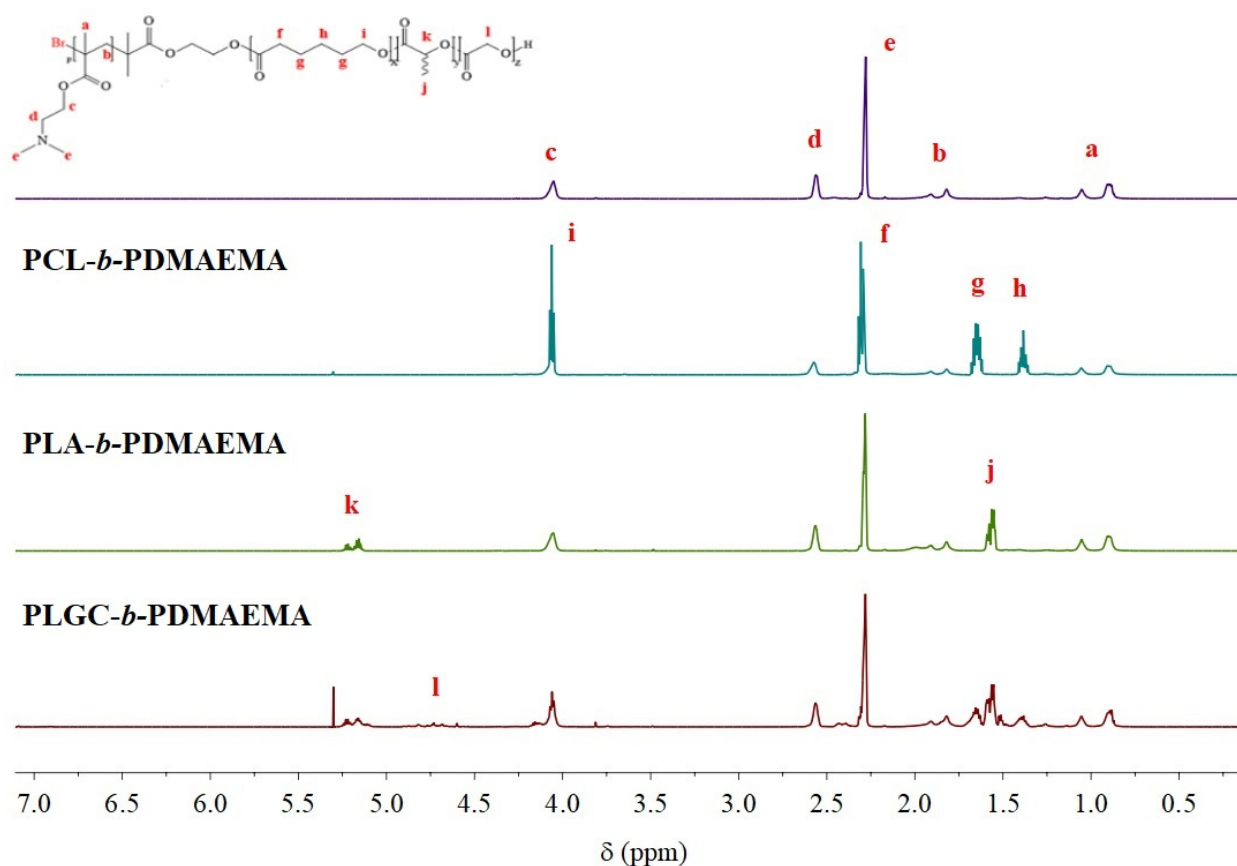


Figure S1. ^1H NMR (600 MHz, CDCl_3) spectra of obtained copolymers before degradation.

^1H NMR (600 MHz, CDCl_3 , δ) for PDMAEMA: 4.10–4.00 (2H, s, $-\text{O}-\text{CH}_2-$); 2.61–2.53 (2H, s, $-\text{CH}_2-\text{N}(\text{CH}_3)_2$); 2.35–2.25 (6H, s, $-\text{N}(\text{CH}_3)_2$); 2.10–1.75 (2H, m, $-\text{CH}_2-$); 1.15–0.80 (3H, m, $-\text{CH}_3$)

^1H NMR (600 MHz, CDCl_3 , δ) for PCL-*b*-PDMAEMA: 4.10–4.00 (2H, t, $-\text{O}-\text{CH}_2-$); 3.79–3.76 (2H, $-\text{CH}_2-\text{OH}$); 2.61–2.53 (2H, s, $-\text{CH}_2-\text{N}(\text{CH}_3)_2$); 2.35–2.25 (2H, m, $-\text{C}(\text{O})-\text{CH}_2-$); 1.68–1.60 (4H, m, $-\text{C}(\text{O})-\text{CH}_2-\text{CH}_2-\text{CH}_2-$); 1.41–1.34 (2H, m, $-\text{C}(\text{O})-\text{CH}_2-\text{CH}_2-\text{CH}_2-$); 1.15–0.80 (3H, m, $-\text{CH}_3$).

^1H NMR (600 MHz, CDCl_3 , δ) for PLA-*b*-PDMAEMA: 5.28–5.10 (1H, m, $-\text{CH}(\text{CH}_3)-\text{O}-$); 4.44–4.22 (1H, q, $-\text{CH}(\text{CH}_3)-\text{OH}$); 4.10–4.00 (2H, t, $-\text{O}-\text{CH}_2-$); 2.61–2.53 (2H, s, $-\text{CH}_2-\text{N}(\text{CH}_3)_2$); 2.35–2.25 (6H, s, $-\text{N}(\text{CH}_3)_2$); 2.10–1.75 (2H, m, $-\text{CH}_2-$); 1.60–1.51 (3H, m, $-\text{CH}_3$); 1.15–0.80 (3H, m, $-\text{CH}_3$).

^1H NMR (600 MHz, CDCl_3 , δ) for PLGC-*b*-PDMAEMA: 5.28–5.10 (1H, m, $-\text{CH}(\text{CH}_3)-\text{O}-$); 4.92–4.56 (2H, m, $-\text{CH}_2-\text{O}-$); 4.44–4.22 (1H, q, $-\text{CH}(\text{CH}_3)-\text{OH}$); 4.10–4.00 (2H, t, $-\text{O}-\text{CH}_2-$); 3.79–3.76 (2H, m, $-\text{CH}_2-\text{OH}$); 2.61–2.53 (2H, s, $-\text{CH}_2-\text{N}(\text{CH}_3)_2$); 2.35–2.25 (6H, s, $-\text{N}(\text{CH}_3)_2$); 2.10–1.75 (2H, m, $-\text{CH}_2-$); 1.68–1.60 (4H, m, $-\text{C}(\text{O})-\text{CH}_2-\text{CH}_2-\text{CH}_2-$); 1.60–1.51 (3H, m, $-\text{CH}_3$); 1.41–1.34 (2H, m, $-\text{C}(\text{O})-\text{CH}_2-\text{CH}_2-\text{CH}_2-$); 1.15–0.80 (3H, m, $-\text{CH}_3$)

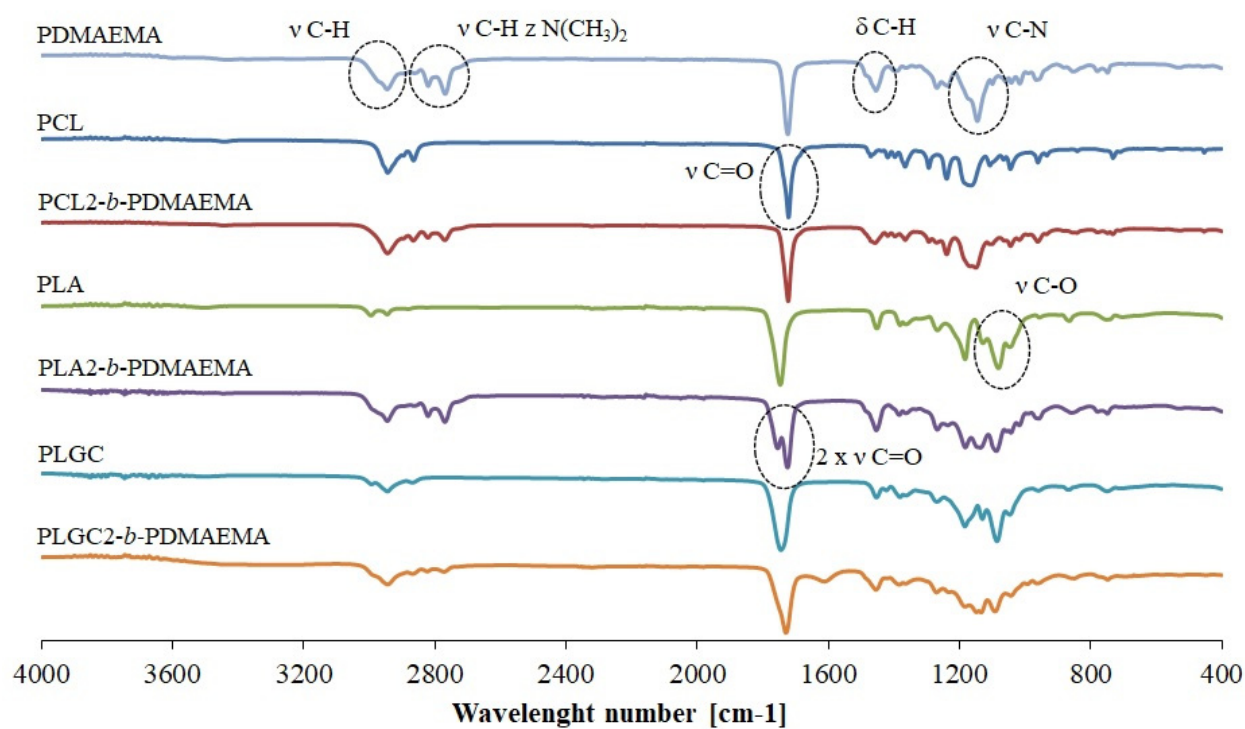


Figure S2. ATR-FTIR spectra of obtained polymers before degradation.