

Electronic Supplementary Information

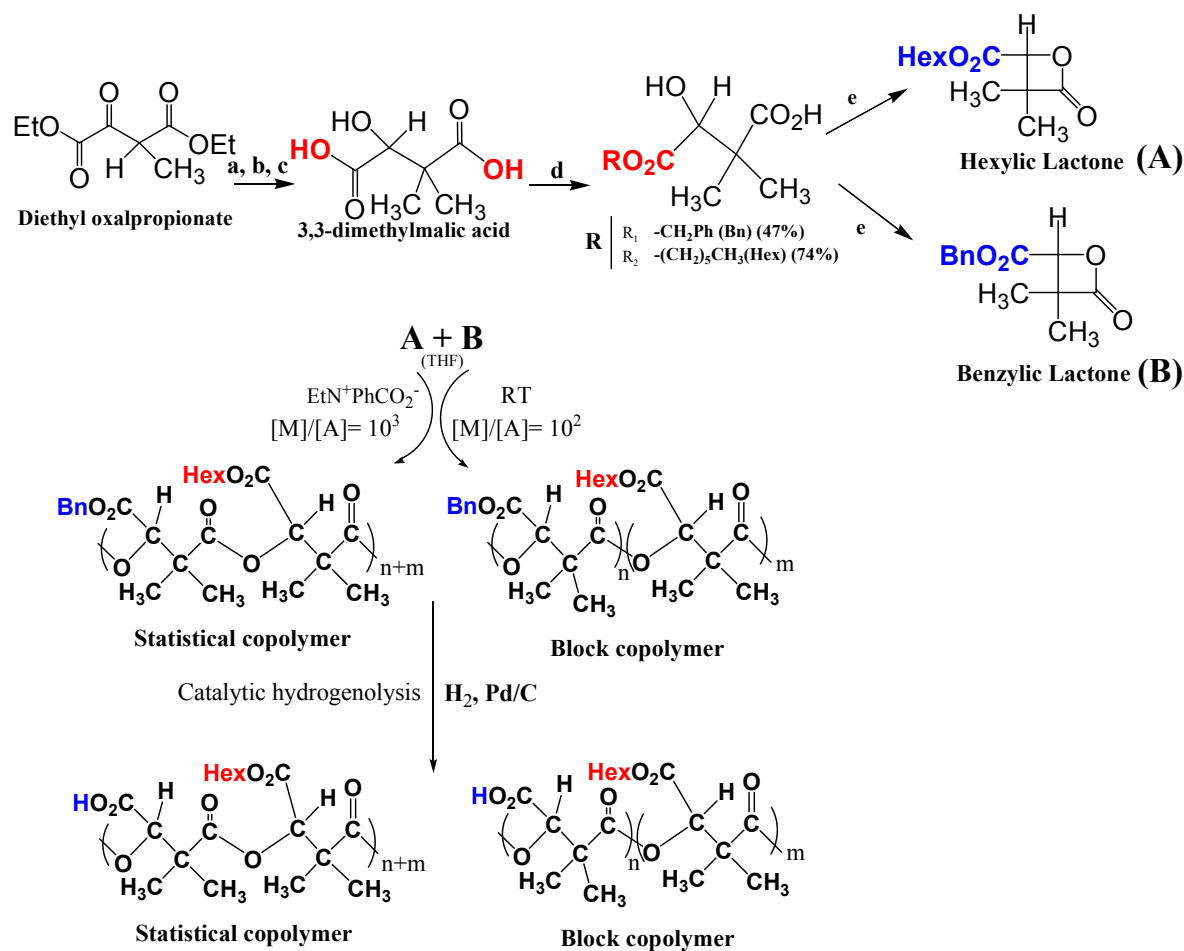
Synthesis of the monomers

Commercial diethyl oxalpropionate (49.2 g, 243 mmol, 1 eq) is alkylated at room temperature in anhydrous toluene (1.5 L) by a methyl group brought by methyl iodide (45 mL, 1.45 mol, 3 eq) under normal conditions in the presence of potassium t-butoxide (31g, 267 mmol, 1.1 eq) and 18-crown-6 ether (5.1 g, 19.4 mmol, 0.08 eq) which plays the complexing agent of potassium cations (**Scheme S1**).

After methylation, the resulting product was reduced with NaBH₄ (4.13 g, 109 mmol, 0.5 eq) in absolute ethanol. The product has undergone a saponification in the presence of K₂CO₃ (97.8 g, 708 mmol, 6 eq) and water, leading to the formation of the 3,3-dimethylmalic acid.

The latter is treated by trifluoroacetic anhydride (TFAA) (42.62 g, 203.55 mmol, and 3.3 eq) to form the intermediate cyclic anhydride. Benzylic or hexylic alcohol was added after TFAA evaporation to produce whether benzylic or hexylic monoester.

The last step of the synthesis is the lactonization, which consists of a Mitsunobu reaction, by adding the triphenylphosphine (PPh₃) (6.23 g, 23.78 mmol, 1 eq for benzylic lactone) and (15.1 g, 57.6 mmol, 1 eq for hexylic lactone) and diisopropylazodicarboxylate (DIAD) (4.80, 23.7 mmol, 1 eq for benzylic lactone and 11.6 g, 57.6 mmol, 1 eq for hexylic lactone) in anhydrous tetrahydrofuran (THF) (80.75 mL for benzylic lactone, 195 mL for hexylic lactone). Mixture was stirred 1 hour at 0 °C then 3 hours at room temperature⁵¹. Reactions were followed by thin layer chromatography. After complete reactions, THF was evaporated under vacuum and the resulting Ph₃PO was precipitated in cold diethyl ether. The crude lactones were purified by column chromatography on silica gel with ethyl acetate / cyclohexane eluent with the proportion of 2/8 (v/v) for benzylic lactone and 1/9 (v/v) for hexylic lactone, leading to the formation of pure oils of hexylic or benzylic lactones. Formation of the different lactones was confirmed by FTIR technique by following the appearance of a new vibration band at 1835 cm⁻¹ (C=O stretching of the lactonic function) besides the ester band already exists at 1754 cm⁻¹ (**Figure S3**) with a refractive index of 1.567 on a λ= 589.3 nm. Pure lactones formation was confirmed by NMR which gave ¹H NMR (CD₃COCD₃, 400MHz) (δ ppm): 1.18 (s, 3H), 1.51(s, 3H), 4.96(s, 1H), 5.29 (s, 2H), 7.39 (m, 5H), for benzylic lactone and ¹H NMR (CD₃COCD₃, 400MHz) (δ ppm): 0.88(t, 3H), 1.28 (s, 3H), 1.29 (m, 6H), 1.41 (s, 3H), 1.68(m, 2H), 4.23(t,2H), 4.91(s, 1H) for hexylic lactone.



(a) Methylation: Toluene, tBuOK, 18-crown-6-ether, CH_3I , 12h at RT, 90% , (b) Reduction: NaBH_4 , EtOH, 3h, RT, 66%, (c) Basic hydrolysis: K_2CO_3 , H_2O , 3h, 74%, (d) Monoesterification: TFAA, ROH, 3h, (e) Lactonization: DIAD, PPh_3 , THF: $[\text{R}_1 = -\text{CH}_2\text{Ph}$, 61%, $\text{R}_2 = -(\text{CH}_2)_5\text{CH}_3$, 30%].

Scheme S1: Synthesis procedure of statistical and block PDMMLA copolymers

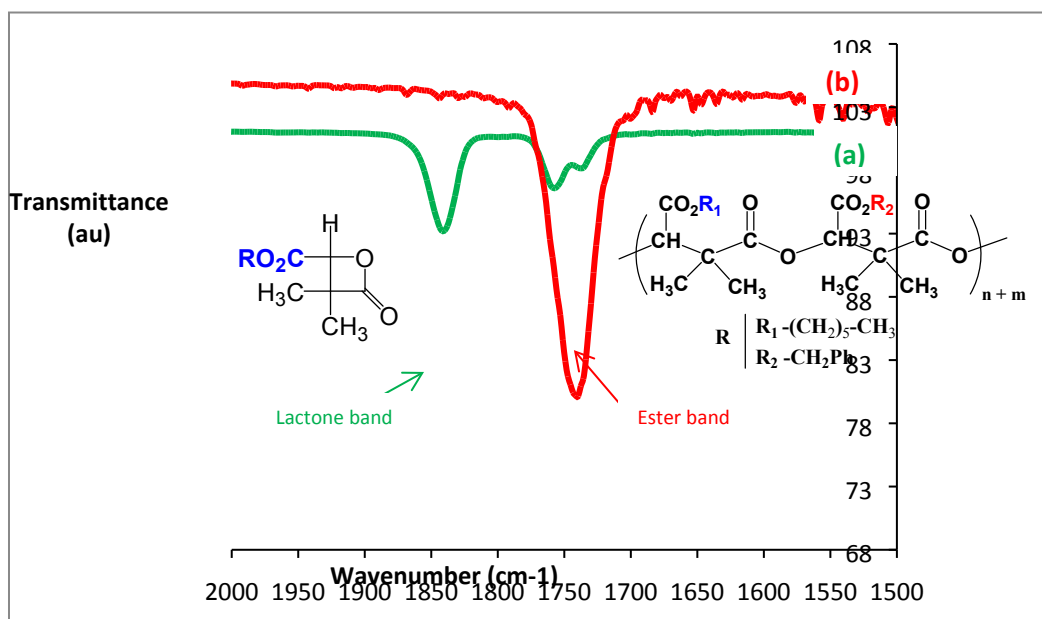


Figure S3: FT-IR spectrum of lactone (a) and statistical copolymer (b)

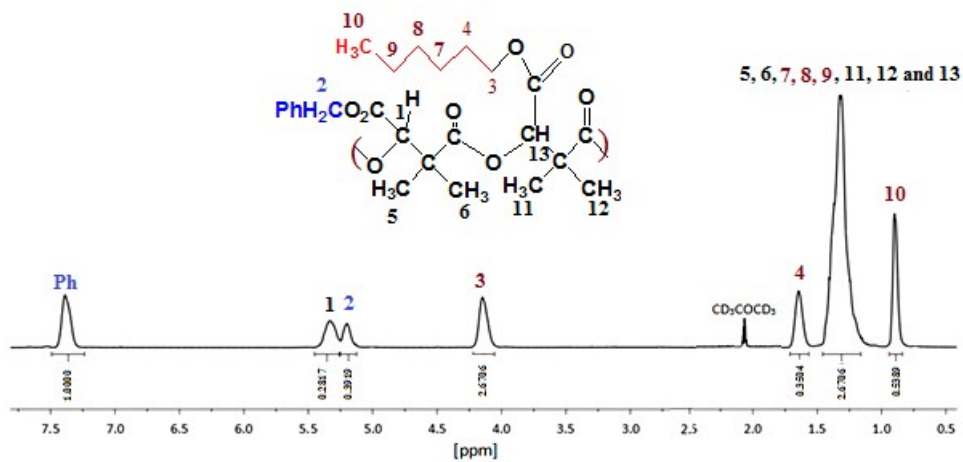


Figure S4: ^1H NMR spectrum of PDMMLAH₃₀-co-Hex₇₀

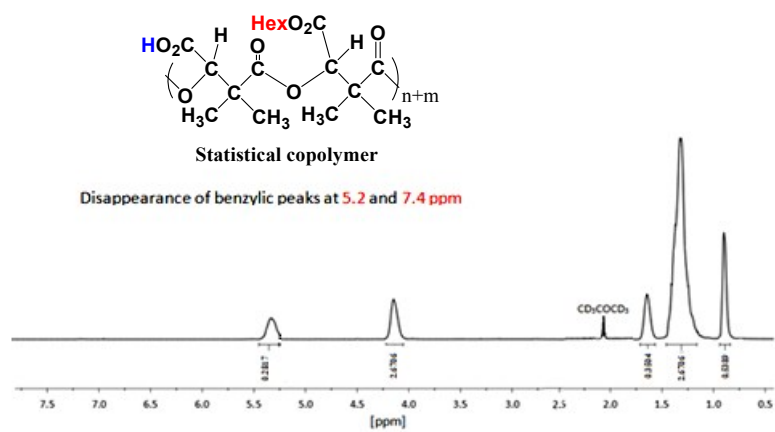


Figure S5: ¹H NMR spectrum profile of deprotected statistical copolymers