

- Supporting Information -

Synthesis of Poly(L-Lactide) and Gradient Copolymers from a L-Lactide/Trimethylene Carbonate Eutectic Melt.

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Experimental section

Materials. 1,3-Dioxan-2-one, TMC (Pugh&Co) and L-lactide (L-LA, GALACTIC, Belgium) were recrystallized twice from dried toluene and stored in a glove box under dry nitrogen atmosphere before use. Benzyl alcohol, BnOH (Aldrich, 98%) and CH₂Cl₂ were dried over CaH₂ for 48 hours at r.t., distilled under reduced pressure and stored in a glove box under dry nitrogen atmosphere before use. Toluene was dried using a MBraun Solvent Purification System (model MB-SPS 800) equipped with alumina drying columns. Diazabicyclodecene (1,8-diazabicyclo-[5.4.0]undec-7-ene, DBU, Fluka) was dried over BaO, distilled and stored in a glove box.

Characterizations. ¹H NMR spectra were recorded in CDCl₃ at a concentration of 30 mg/0.6mL on a Bruker AMX500 (500 MHz) or AMX300 (300 MHz), with shift reported in part-per-million downfield from tetramethylsilane used as internal reference. Size exclusion chromatography (SEC) was performed in THF (with 2% triethylamine added) at 35 °C using a Polymer Laboratories liquid chromatograph equipped with a PL-DG802 degasser, an isocratic HPLC pump LC 1120 (flow rate = 1 mL/min), a Marathon autosampler (loop volume = 200 μL, solution conc. = 1 mg/mL), a PL-DRI refractive index detector and three columns: a PL gel 10 μm guard column and two PL gel Mixed-B 10 μm columns (linear columns for separation of MW_{PS} ranging from 500 to 10⁶ daltons). Poly(styrene) standards were used for calibration. Differential scanning calorimetry (DSC) measurements were carried out with a DSC Q200 apparatus from T.A. Instruments under nitrogen flow (heating rate: 1°C/min when applied on L-LA/TMC mixtures and 5°C/min for P(L-LA)-*b*-P(TMC)).

Theoretical methodology. The interaction energies have been estimated as the energy difference between the total energy of the complex and the energy of the isolated compounds. The energy of the isolated compounds has been calculated at the DFT level using the wB97XD functional including dispersion corrections¹ and a 6-31g(d,p) basis set. Since the potential energy surface of the complexes exhibits many minima, our procedure to find the global minimum relies on four different steps: (i) complexes containing two molecules (L-LA/L-LA, L-LA/TMC, or TMC/TMC) are built and optimized at the Molecular Mechanics level using the Dreiding force field² with COMPASS charges³ (for each complex, four different initial relative orientations of the molecules have been chosen); (ii) from the optimized structures, molecular dynamics simulations (NVT, 100K, 100ps, frames saved every 1ps) were performed in order to explore the whole potential energy surface; (iii) all

frames generated during the molecular dynamics runs exhibiting a different energy after being optimized at the molecular mechanics level have then been subjected to a geometry optimization at the DFT level using the wB97XD functional and a 6-31g(d,p) basis set; (iv) finally, the energy of the complex is obtained after running a single point DFT calculations on the most stable complex of step (iii), using the same functional and basis set and the counterpoise method⁴ to remove the basis set superposition error.

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General procedure for the preparation of poly(L-Lactide)-b-poly(TMC) copolymer. In a glove box, 0.2g of L-LA (1.4 mmol) are mixed with 0.2g of TMC (1.96 mmol) in a dried glass vial. After 10-15 minutes of intensive shaking at r.t., the responsive liquid eutectic melt appears (density of eutectic: 1.059). A mixture of benzyl alcohol (1.5 μ L; 1.37×10^{-5} mol) and DBU (2 mg; 1.38×10^{-5} mol) is then added on the eutectic solution. The medium is immediately homogenized by mixing for about 10 seconds. After 20 seconds (30 sec in total), the as-obtained PLLA starts to nucleate and crystallizes out of the eutectic. Before total crystallization (ideally just after the nucleation), 0.6 g of CH_2Cl_2 is added to solubilize the entire medium. The solution is then kept under agitation for 16 hours before its precipitation in a ten-fold excess of heptane (10 ml). Yield : 81.25%. Conversions in both L-LA and TMC are 99 and 63%, respectively, as determined by ^1H NMR. $M_n\text{GPC} = 22,000$ g/mol, $\text{Đ}_M = 1.64$. Before DSC analysis, the copolymer is solubilised in CH_2Cl_2 and precipitated “drop-by-drop” in excess of heptane. This treatment is realized twice.

DSC Results of L-LA/TMC mixtures :

TMC(mg)	L-LA(mg)	LA/(LA+TMC)	melting point 1 (°C)	melting point 2 (°C)	Enthalpy Eutectic (J/g)	Enthalpy comonomer (J/g)
1	0	0	46	46		
9,1	3,4	0,209268646	19,42	30,88	36,6	7,6
7,4	9,7	0,481459854	21,74	50,1	56,12	2,39
3,7	10,6	0,669888476	21,16	93,41	28,72	30,99
1	1	0,414634146	21,2	21,2		
0	1	1	98,3	98,3		120

Figures :

FIGURE S1 : DSC analyses of pure L-LA and of two L-LA/TMC mixtures

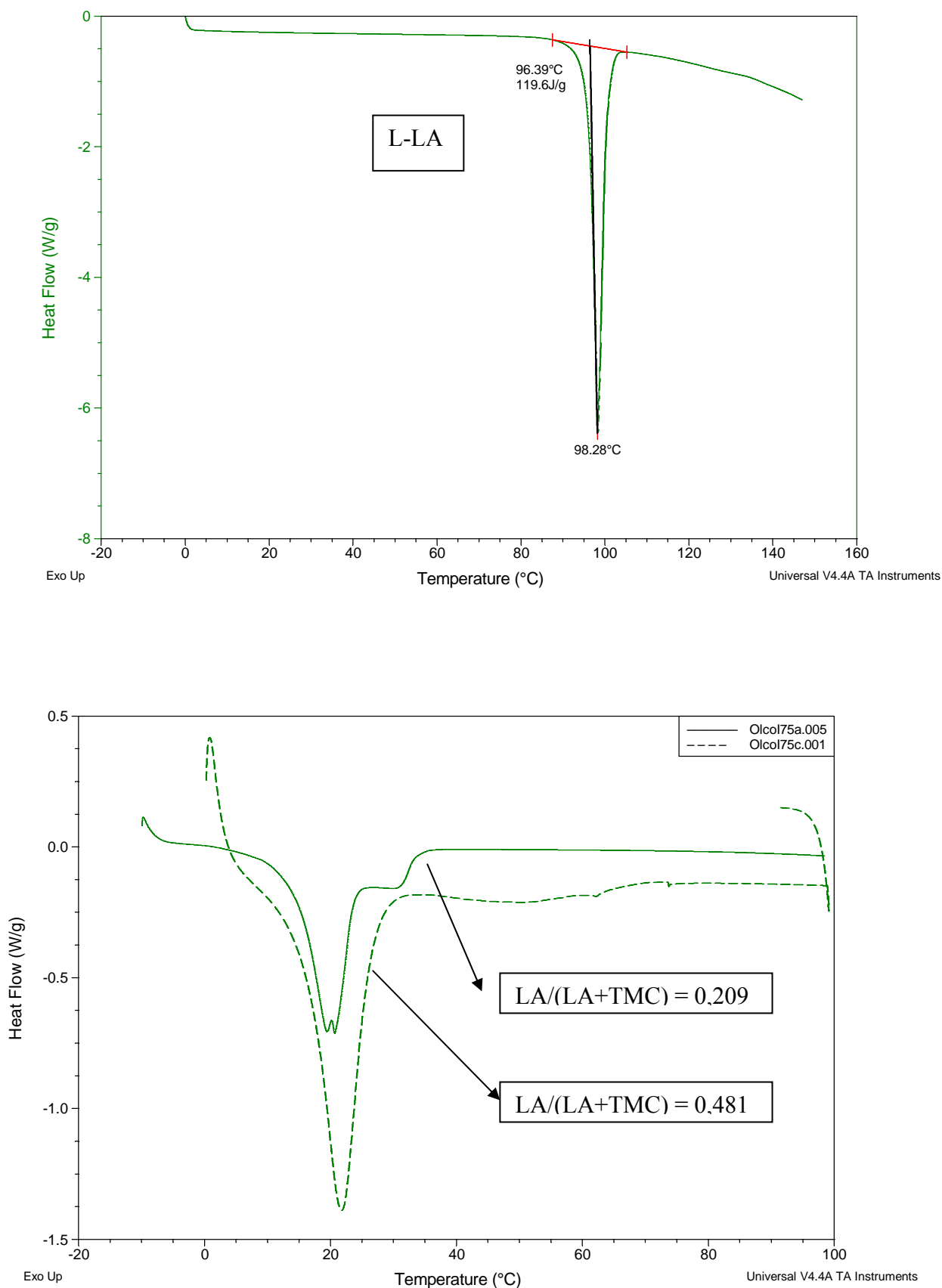


FIGURE S2 : ^1H NMR analyses of pure L-LA (in red), pure TMC (in green) and their corresponding eutectic (in blue)

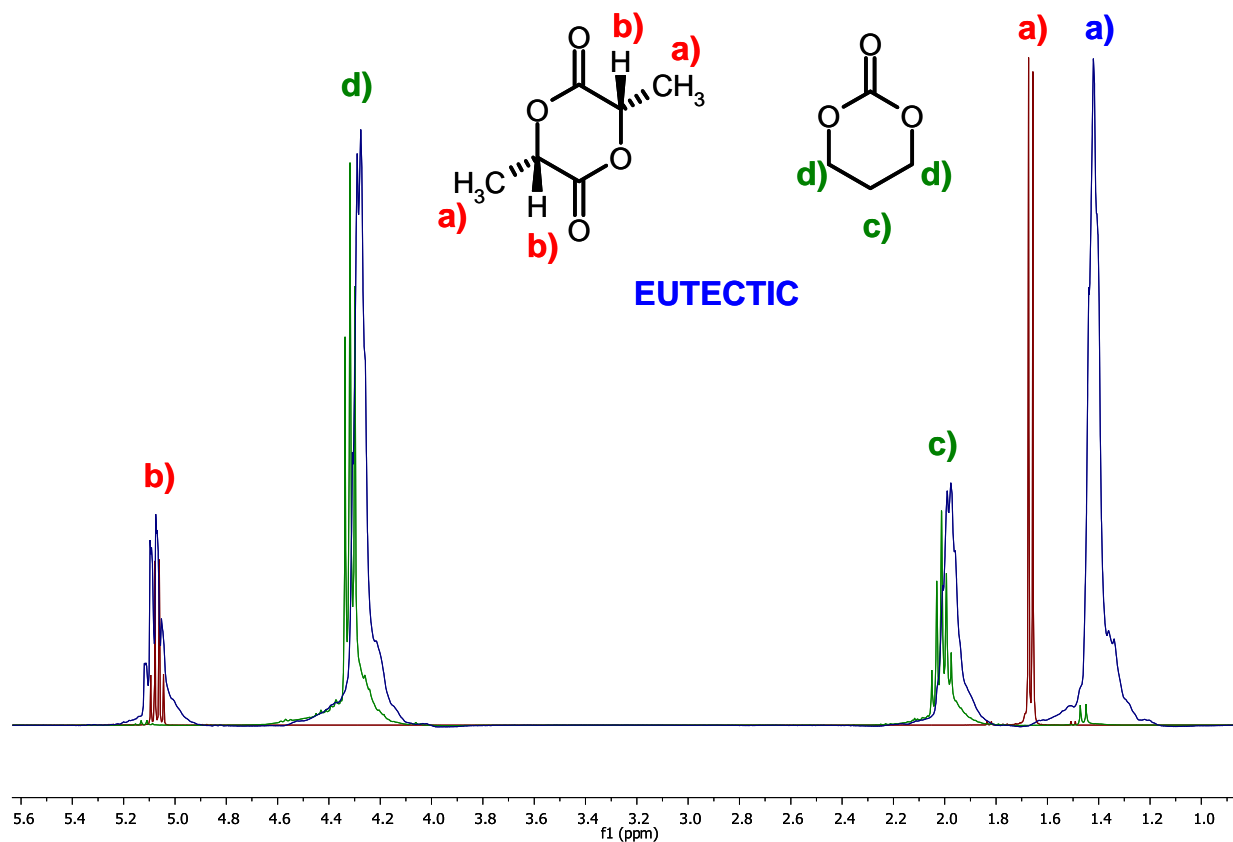


Table S11 :

Table S11: (top) DFT-calculated (wB97XD/6-31g(d,p)) interaction energies (in kcal/mol) for GLA/GLA, TMC/GLA, and TMC/TMC complexes as well as the change in energy (ΔE , in kcal/mol) associated to the eutectic formation ; (bottom) DFT-calculated (wB97XD/6-31g(d,p)) interaction energies (in kcal/mol) for MA/MA, TMC/MA, and TMC/TMC complexes as well as the change in energy (ΔE , in kcal/mol) associated to the eutectic formation.

GLA/GLA	TMC/GLA	TMC/TMC	ΔE
10.90	12.00	12.07	-1.03

MA/MA	TMC/MA	TMC/TMC	ΔE
8.12	9.91	12.07	+0.37