Electronic Supplementary Information

Poly(lactide-*co*-ε-caprolactone) Copolymers by Bis-Thioetherphenolate Group 4 Metal Complexes: Synthesis, Characterization and Morphology

Francesco Della Monica,[a] Ermanno Luciano,[a] Antonio Buonerba,[a] Alfonso Grassi,[a] Stefano Milione[a,] and Carmine Capacchione[a]*

[a] Dipartimento di Chimica e Biologia and NANOMATES, Research Centre for NANOMAterials and nanoTEchnology at Salerno University, Università degli Studi di Salerno, via Giovanni Paolo II, 132-84084 Fisciano (SA), Italy.

* E-mail: smilione@unisa.it

Table of Contents

1. NMR Characterization.

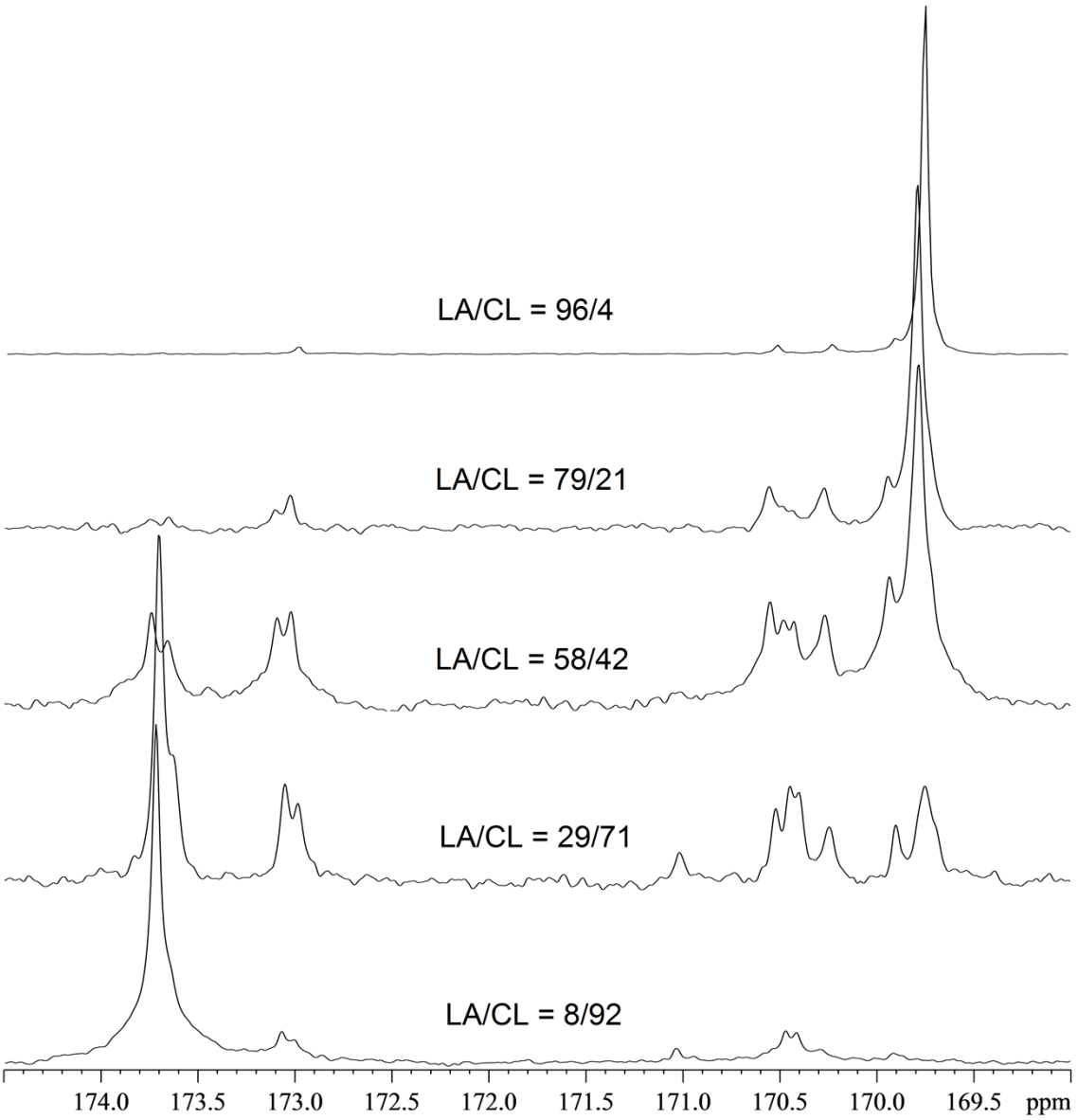

Figure S1. Carbonyl range of ^{13}C NMR spectra ($CDCl_3$, 25 °C) of copolymers obtained by **1**.

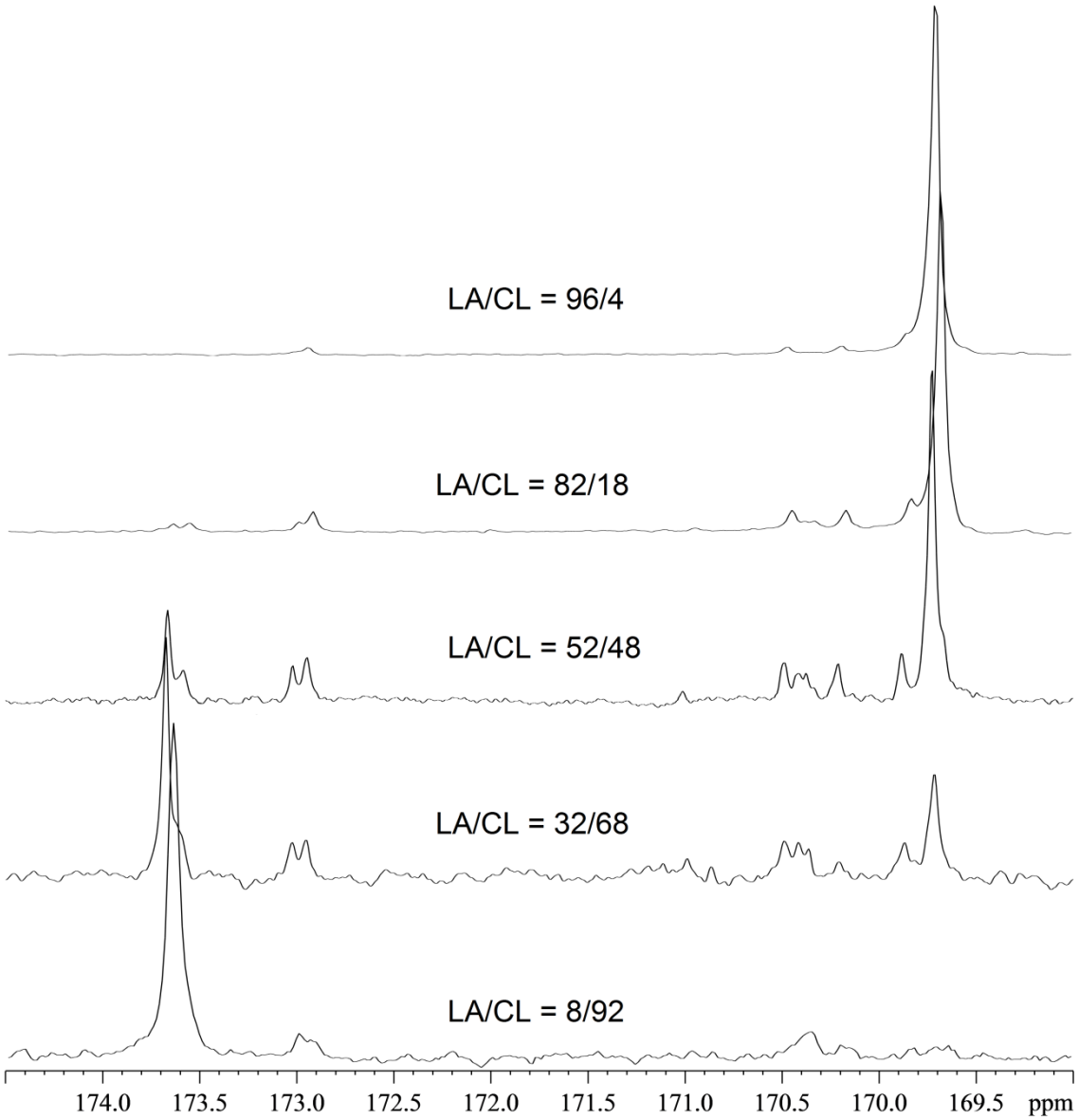

Figure S2. Carbonyl range of ^{13}C NMR spectra ($CDCl_3$, 25 °C) of copolymers obtained by **2**.

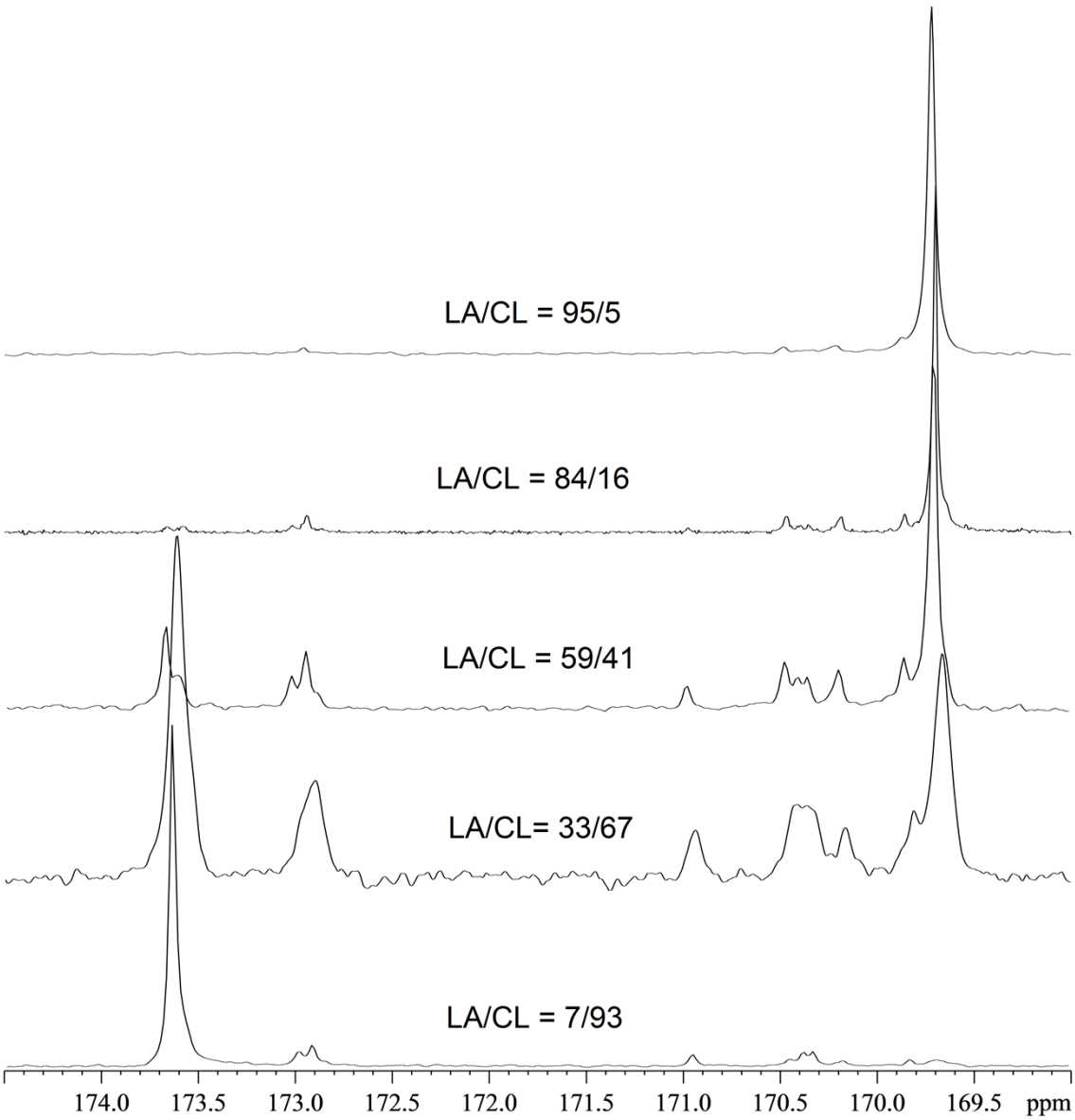

Figure S3. Carbonyl range of ^{13}C NMR spectra ($CDCl_3$, 25 °C) of copolymers obtained by **3**.

2. Evaluation of average block lengths.

The average block lengths of L-lactide (L_{LA}) and ε-caprolactone (L_{CL}) units in the copolymers were calculated using the following equations (P.Vanhoorne, P.Dubois, R. Jeromeand P.Teyssie, *Macromolecules*, 2012, **25**, 37-44):

$$L_{CL} = \left(\frac{I_{CCC} + I_{LLCC}}{I_{CCLL} + I_{LLCLL}}\right) + 1$$

$$L_{LA} = \frac{\left(I_{LLLLLL} + \left(\frac{I_{LLLLC+CLLLL}}{2}\right)\right)}{\left(\left(\frac{I_{LLLLC+CLLLL}}{2}\right) + I_{CLC}\right) + 1} * \frac{1}{2}$$

in which *I* indicates the integral of the signals attributed to triad sequence in the carbonyl range of ^{13}C NMR spectrum, the subscript C stands for the caproyl unit and the subscript L stands for the lactidyl unit.
The figure S4 shows the calculated values respect to the theoretical values in the case of an ideal random copolymerization with $r_{LA} = r_{CL} = 1$ ($L_{m1} = r_{m2} + r_{m1}$ $[m_1]/[m_2]$).

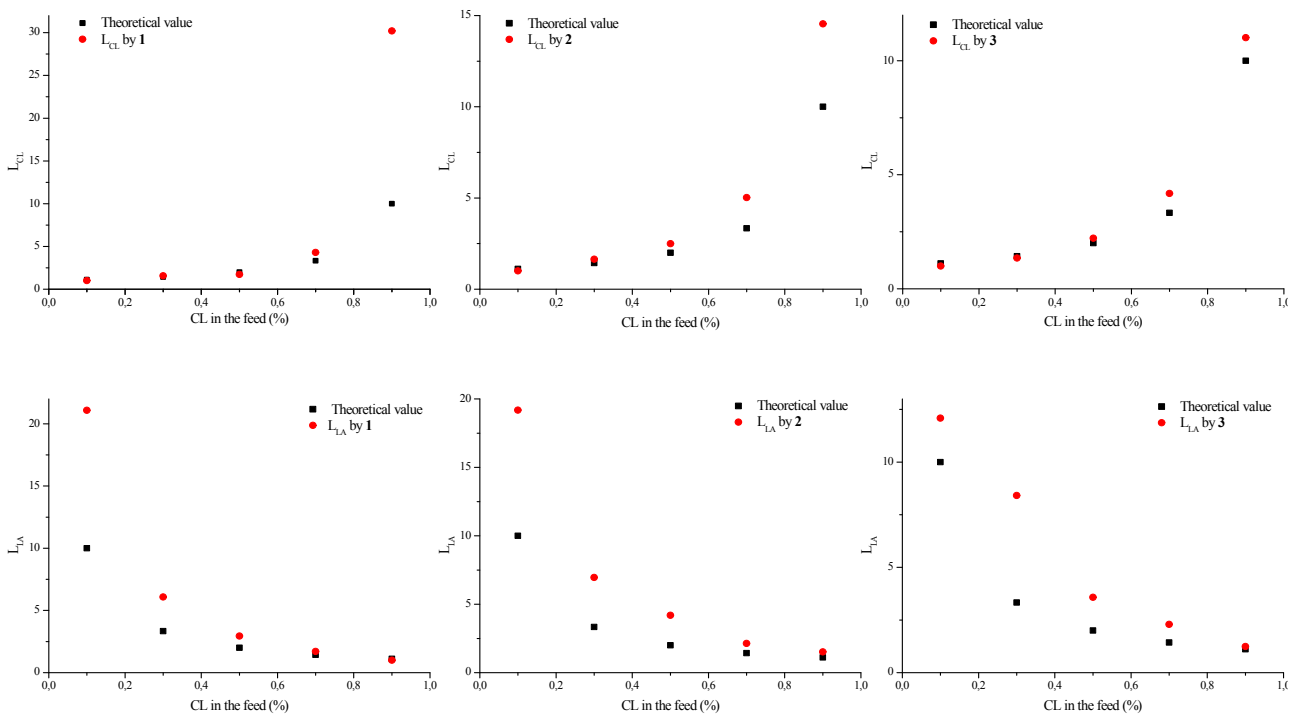

Figure S4. Average block lengths of caprolactone (up) and lactide (down) in the copolymers obtained by **1** (left), **2** (middle) and **3** (right).

3. Thermal Analysis.

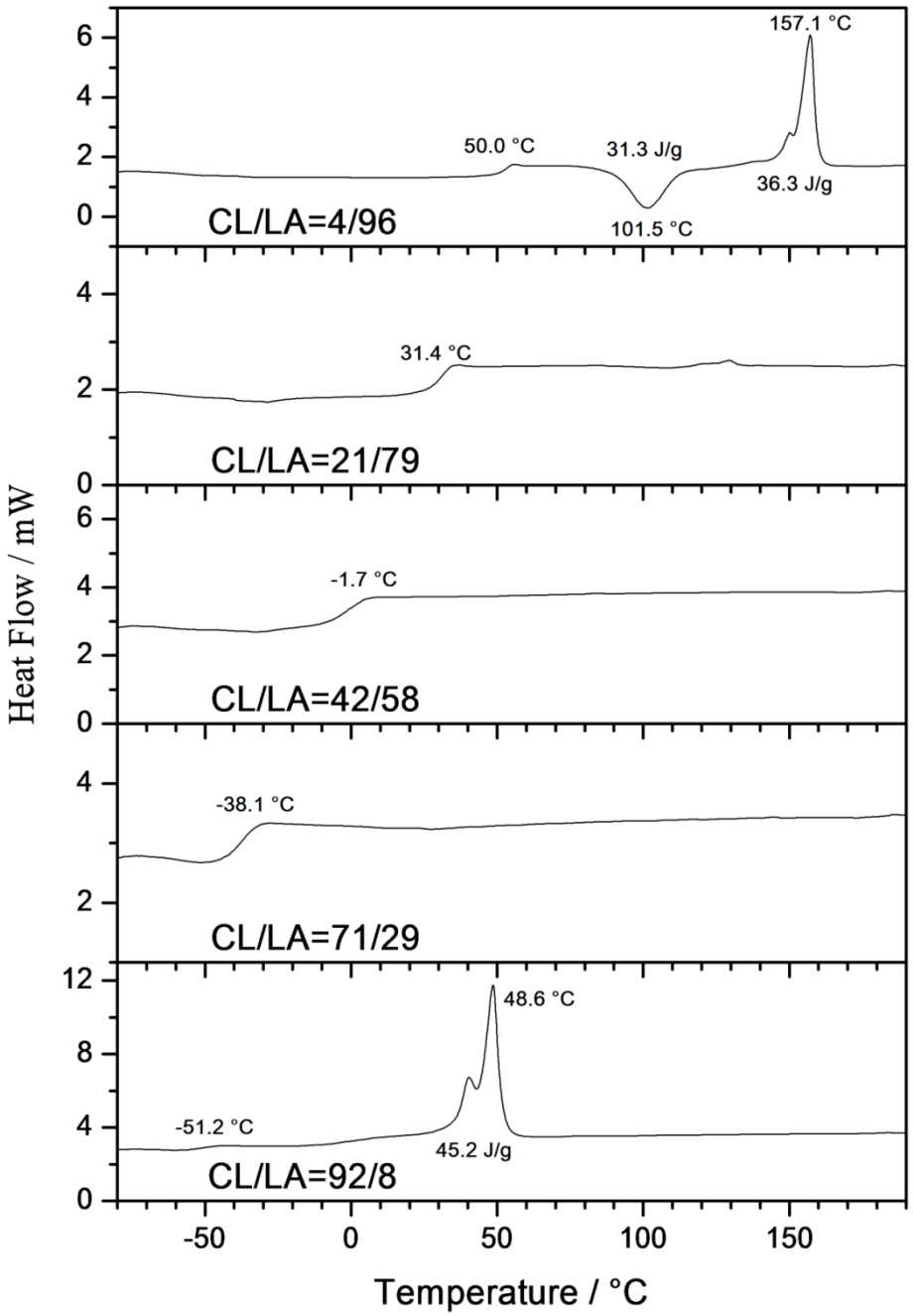

Figure S5. DSC thermograms of the CL/LA copolymers obtained with complex **1** (profiles from second heating cycles with a heating rate of 10°C min^{-1}).

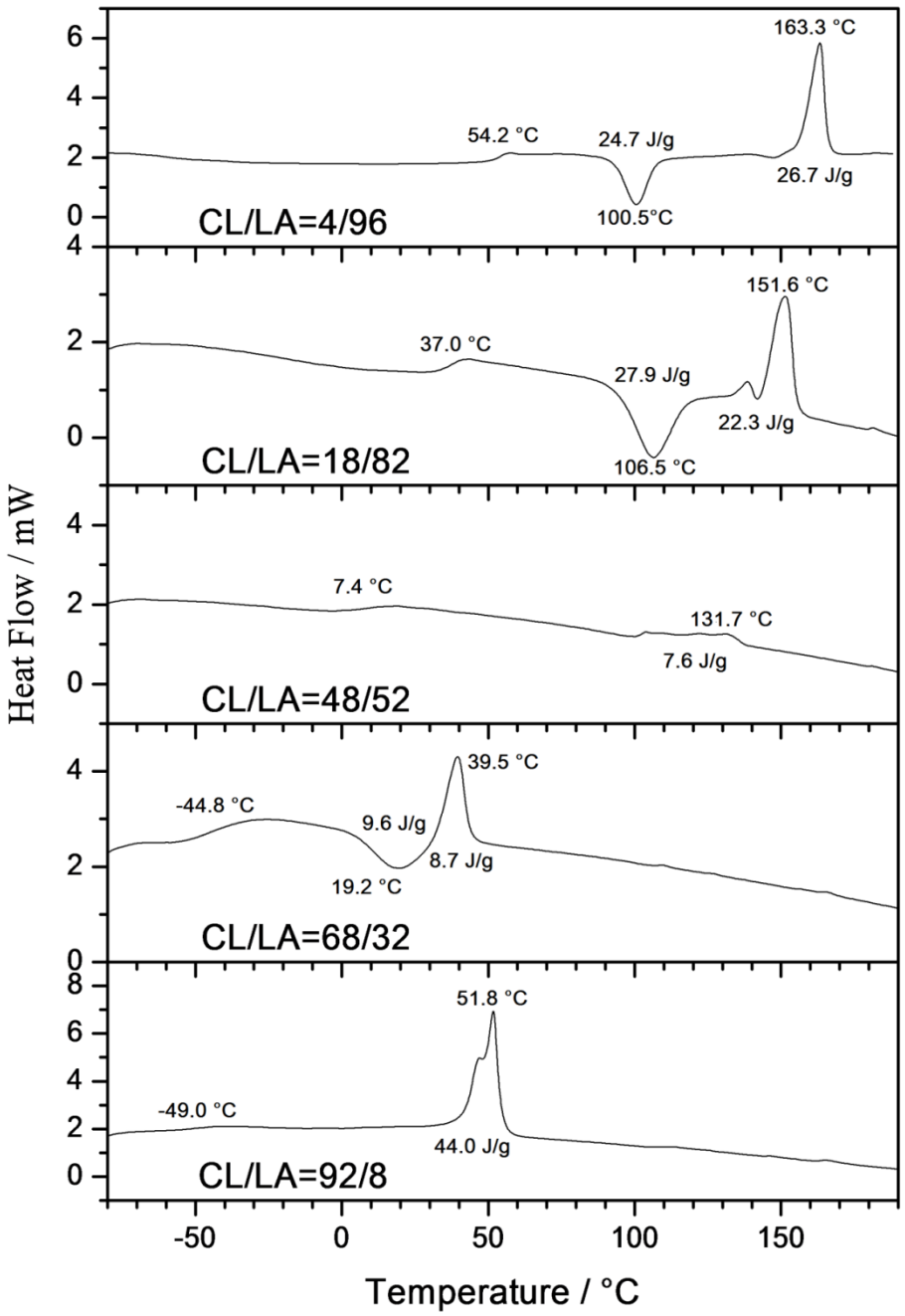

Figure S6. DSC thermogram of the copolymers CL/LA obtained with complex **2** (profiles from second heating cycles with a heating rate of 10°C min^{-1}).

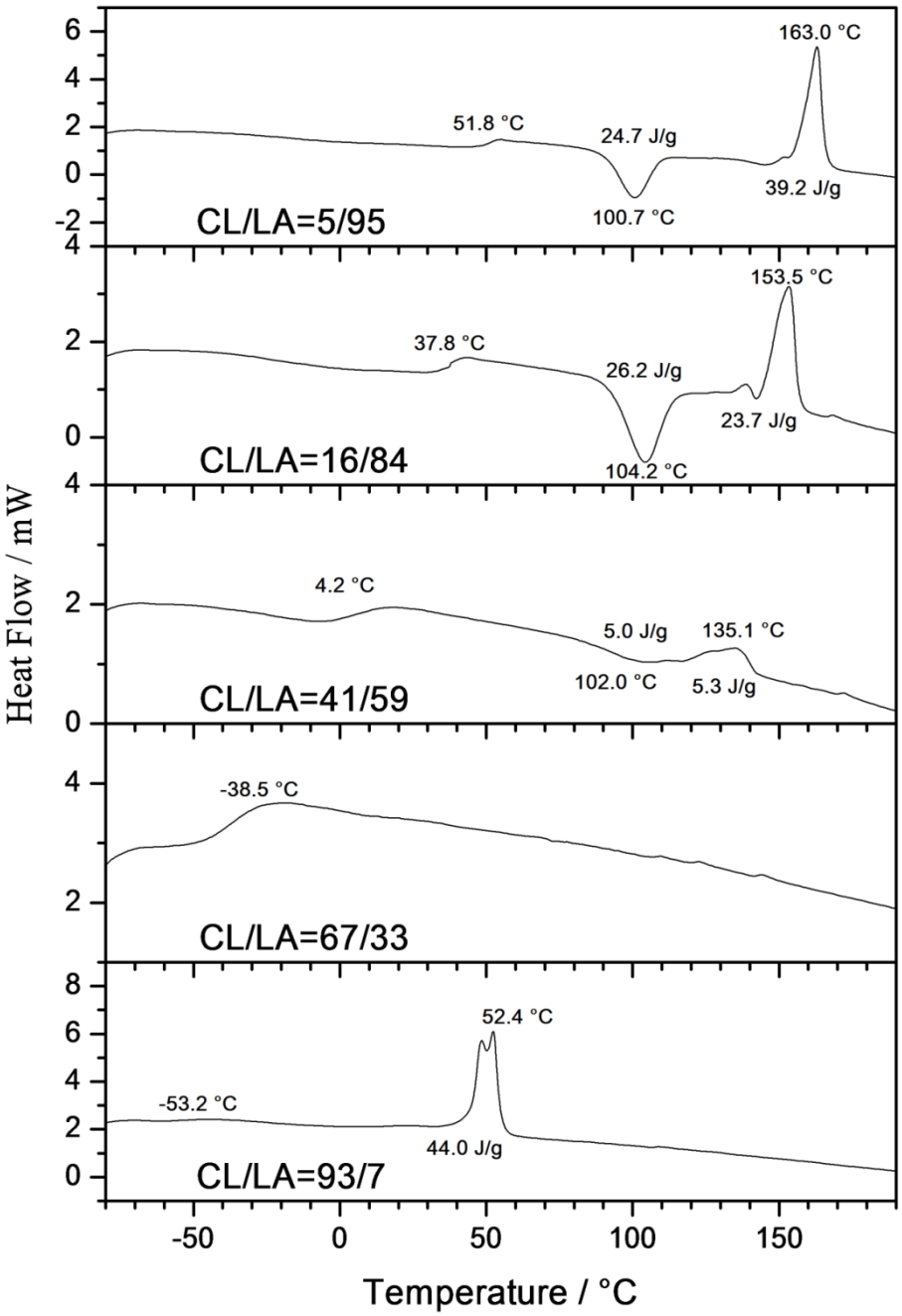

Figure S7. DSC thermogram of the copolymers CL/LA obtained with complex **3** (traces of the second heating cycle with a heating rate of 10°C min^{-1}).

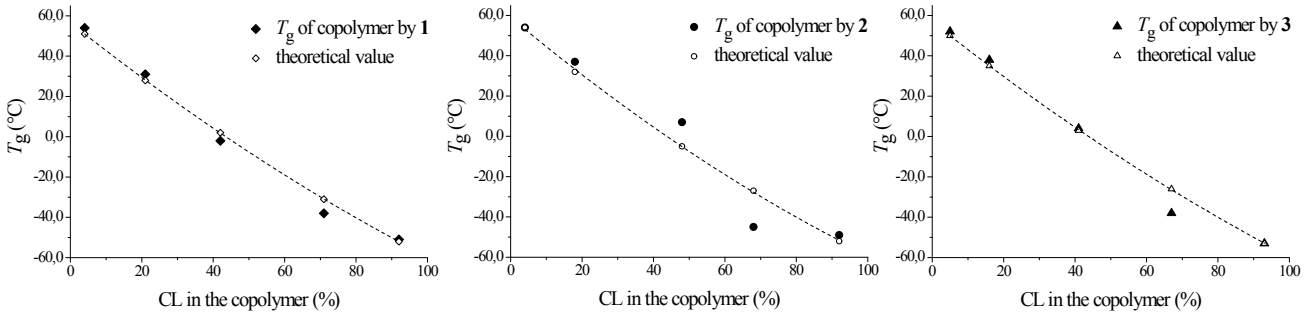

Figure S8. Plots of the dependence of T_g of CL/LA copolymers on the molar % caprolactone in copolymers.

4. AFM Characterization.

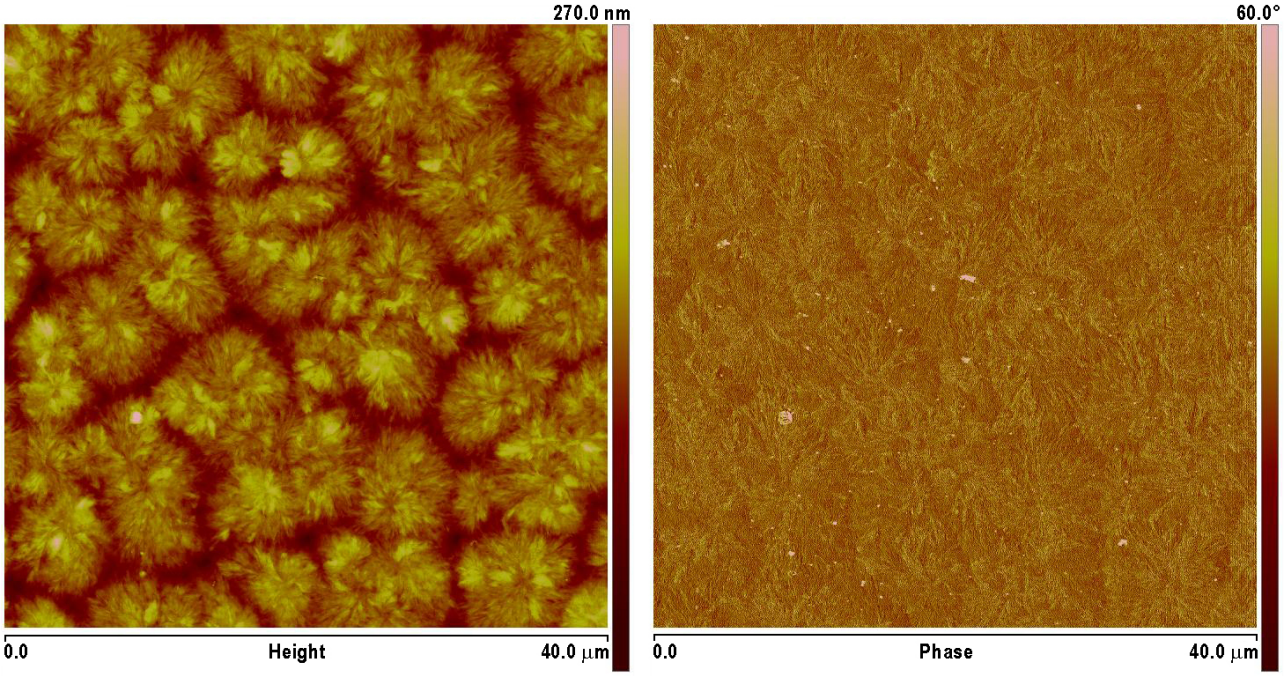

Figure S9. Height and phase contrast TM-AFM micrographs of CL/LA copolymer of run **6** of Table 1 thermal treated at 50 °C for 15 min.

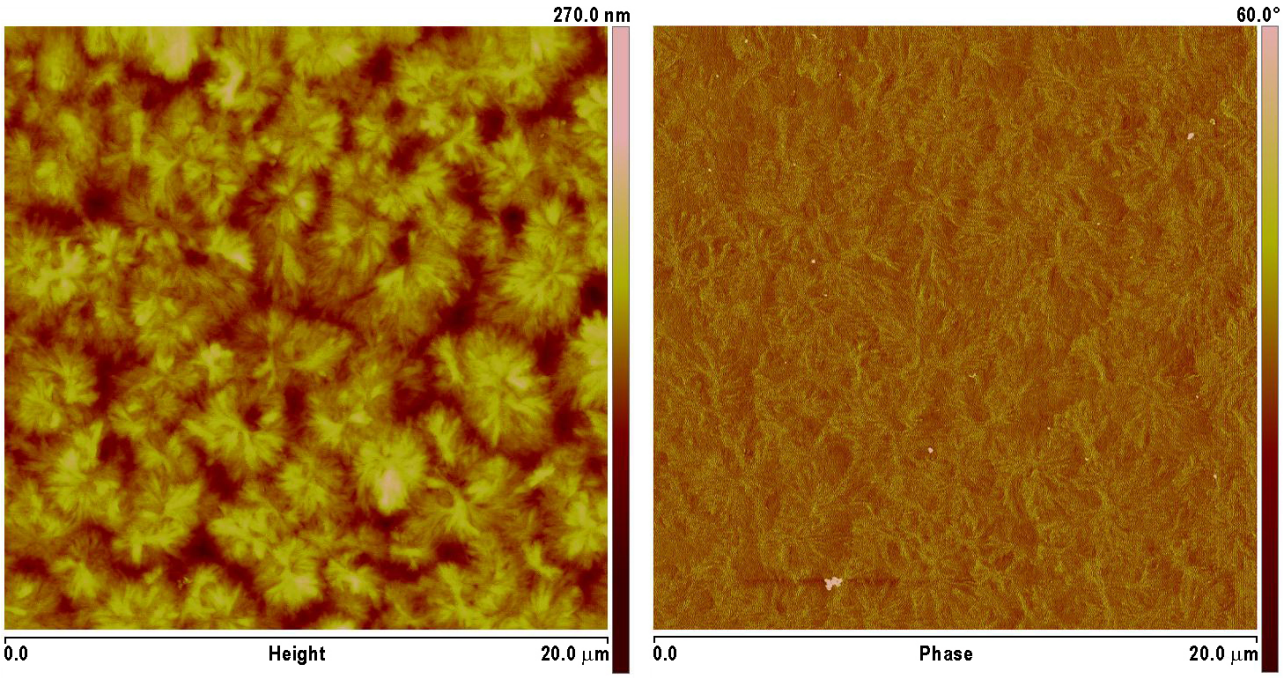

Figure S10. Height and phase contrast TM-AFM micrographs of CL/LA copolymer of run **11** of Table 1 annealed at 50 °C for 15 min.

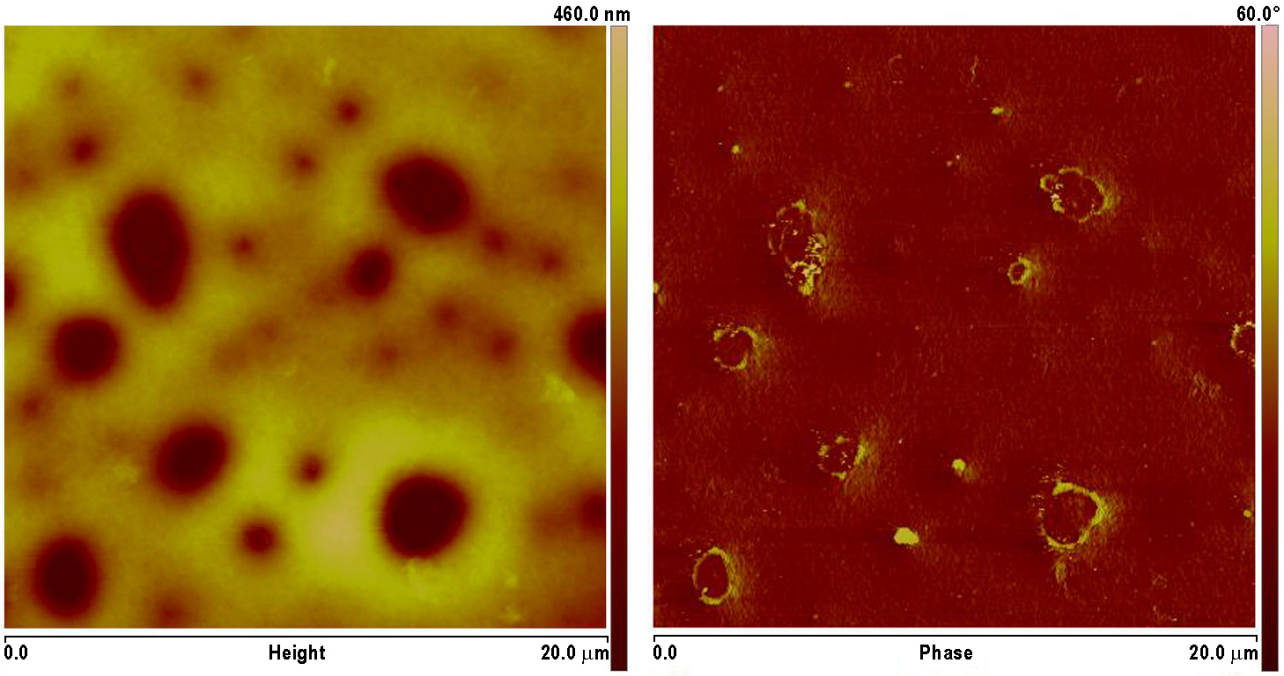

Figure S11. Height and phase contrast TM-AFM micrographs of CL/LA copolymer of run **8** of Table 1.

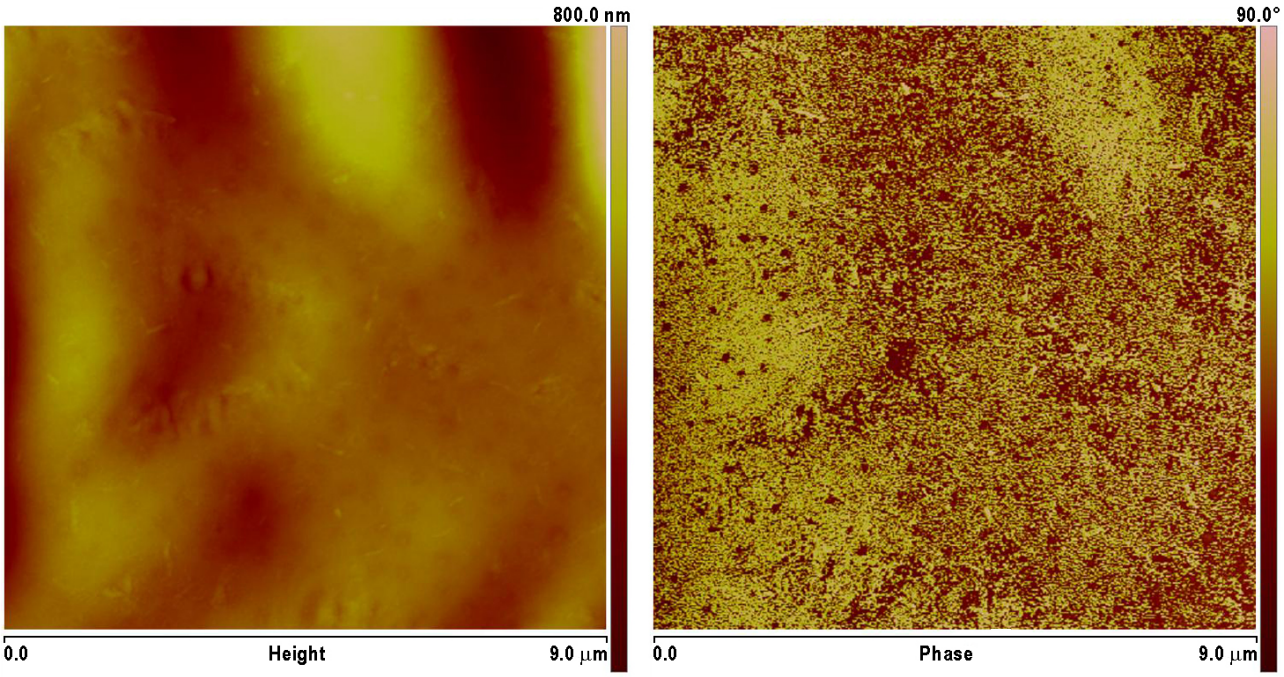

Figure S12. Height and phase contrast TM-AFM micrographs of CL/LA copolymer of run **5** of Table 1 annealed at 100 °C for 15 min.