Supplementary Materials

Macromolecular dyes by chromophore-initiated ring opening polymerization of L-lactide

Francesca Cicogna ^{1,*}, Guido Giachi ², Luca Rosi ², Elisa Passaglia ¹, Serena Coiai ¹, Roberto Spiniello ¹, Federico Prescimone ^{3,4} and Marco Frediani ²

- ¹ Consiglio Nazionale delle Ricerche Istituto di Chimica dei Composti OrganoMetallici, Sede Secondaria di Pisa (CNR ICCOM-SS-Pisa), 56124 Pisa, Italy; francesca.cicogna@pi.iccom.cnr.it (F.C.); elisa.passaglia@pi.iccom.cnr.it (E.P.); serena.coiai@pi.iccom.cnr.it (S.C.); roberto.spiniello@pi.iccom.cnr.it (R.S.)
- ² Dipartimento di Chimica "U. Schiff" Università degli Studi di Firenze, 50019 Sesto Fiorentino, Italy.; guidogiachi@gmail.com (G.G.); luca.rosi@unifi.it (L.R.); marco.frediani@unifi.it (M.F.)
- ³ Dipartimento di Chimica e Chimica Industriale Università di Pisa, 56126 Pisa, Italy; federico.prescimone@bo.ismn.cnr.it
- ⁴ Consiglio Nazionale delle Ricerche Istituto per lo Studio dei Materiali Nanostrutturati Sede Secondaria di Bologna, (CNR ISMN-SS-Bologna CNR), 40129 Bologna, Italy
- * Correspondence: francesca.cicogna@pi.iccom.cnr.it; Tel.: +39-050-31523393

| | chromophore in whos in comparison with theoretical value in the feed | | | | | | |
|--|--|--------------------------|-------|------------------------------|--------------------------|--|--|
| | Sample | λ _{max} (nm) | Amax | Chromophore in MDs (wt.%) | | | |
| | * | | | Calculated ¹ | Theoretical ² | | |
| | MDCA5 | 344 | 0.300 | | | | |
| | | 330 | 0.284 | 47 | 7.4 | | |
| | | 294 | 1.248 | 4./ | | | |
| | | 264 | 1.375 | | | | |
| | MDFM5 | 301 | 0.185 | | | | |
| | | 291 | 0.171 | 4.7 | 6.8 | | |
| | | 268 | 0.613 | | | | |
| | MDDR5 | 483 | 1.03 | 10.6 | 12.1 | | |

Table S1. UV-Vis absorption maxima of MDCA5, MDFM5 and MDDR5 in CHCl₃ and calculated amount of chromophore in MDs in comparison with theoretical value in the feed

¹ These values are calculated on the basis of absorbance determined by collecting UV spectra on MDs chloroform solution (see the experimental part for concentration) and the molar extinction coefficients reported in Table S5. ² These values are calculated transforming the percent by mol used in the polymerization reaction (i.e. 5 mol% of the chromophore with respect to L-lactide for these samples), in percent by weight considering also the molecular weight of chromophores.



Figure S1. ¹H-NMR of a crude polymerization product, enlargement on the C<u>H</u> quartet signals of L-lactide centered at 5.04 ppm and of MD main chain centered at 5.16 ppm, monitored to assess lactide conversion.



| Table S2. | Main | FT-IR | band | of L-la | actide | and | PLA |
|-----------|------|-------|------|---------|--------|-----|-----|
|-----------|------|-------|------|---------|--------|-----|-----|

| Vibration | L-lactide | PLA |
|------------------------|-----------------------|------------------------|
| Stretching C=O | 1770 (cyclic lactone) | 1755 (aliphatic ester) |
| Stretching C-O-C asym. | 1273 (cyclic lactone) | 1183 (aliphatic chain) |
| Stretching C-O-C sym. | 1095 (cyclic lactone) | 1089 (aliphatic chain) |
| COO ring breathing | 934 (cyclic lactone) | |



Figure S3. 1H-NMR spectrum of MDFM5 (CDCl3)



Figure S4. ¹H-NMR spectrum of MDFM5 (CDCl₃).



Figure S5. Chromatograms collected during SEC analysis of the samples (a) MDFM1-MDFM10 and (b) MDDR1-MDDR7



Scheme S1. 1) Propagation reaction: active chain attacks the ester bond of lactone, the opposite reaction is the depolymerization; 2) intermolecular transfer reaction: active chain attacks an ester bond internal to another polymer chain, this chain can be active (metal alkoxide terminated) or dormant (alcohol terminated).

| | ting | | Second | heating | eating | | | |
|-----------|------------------|-------------------|---------------|--|--------------------|-----------|-------------------|--|
| Sample | T_{m} | $\Delta H_{ m m}$ | Crystallinity | T_{cc} | $\Delta H_{ m cc}$ | Tm | $\Delta H_{ m m}$ | |
| - | (°C) | (J/g) | (%)2 | (°C) | (J/g) | (°C) | (J/g) | |
| | 1(0 5 | EE 7 | (0.0 | 113.0 | -41.7 | 160.5 | 19.3 | |
| MDCAI | MDCAI 168.5 | 55.7 | 60.0 | | | 150.0 | 7.0 | |
| | 156 7 | 66.0 | 71 0 | 102.0 | 40.0 | 149.0 | 30.8 | |
| MDCA5 | 156.7 | 00.0 | /1.0 | | -40.0 | 136.0 | 10.1 | |
| | 148.0 | 28 7 | 11.6 | 112.0 | 16.0 | 145.0 | 15.8 | |
| MDCAS | 143.3 | 30.7 | 41.0 | 112.0 | -10.9 | 133.0 | - | |
| MDC 47 | 139 5 | 183 | 52.0 | 108.0 | -85 | 136.0 | 8.6 | |
| MDCA | 159.5 | 40.0 | 52.0 | 100.0 | -0.5 | 128.0 | - | |
| MDCA10 | 128.5 | 31.0 | 33.3 | 105.0 | -12 | 129.0 | 0.5 | |
| MDCMI0 | 119.2 | 51.0 | 00.0 | Second heating T_{cc} ΔH_{cc} T_m (°C) (J/g) (°C) 113.0 -41.7 160.5 113.0 -41.7 150.0 103.0 -40.0 136.0 112.0 -16.9 133.0 108.0 -8.5 136.0 105.0 -1.2 129.0 98 -39.1 155.0 98 -39.1 147.0 101 -35.1 133.0 106 -25.6 129.0 98 -39.1 147.0 101 -35.1 133.0 102 -25.6 129.0 102 -25.0 134.0 102 -33.0 137.0 103 -30.1 134.0 105 -30.1 134.0 105 -30.1 134.0 126.0 - - | 127.0 | 0.0 | | |
| MDFM1 | 157.6 | 7.6 52.5 | 56.5 | 98 | -39.1 | 155.0 | 44 4 | |
| | 107.0 | | | | | 147.0 | 11.1 | |
| MDFM3 | 147.5 | 58.3 | 62.7 | 101 | -35.1 | 146.0 | 39.4 | |
| 111011110 | 145.0 | 00.0 | 02.7 | 101 | 00.1 | 133.0 | | |
| MDFM5 | 138.5 | 55.4 | 59.6 | 106 | -25.6 | 141.0 | 26.8 | |
| | | | | | | 129.0 | 20.0 | |
| MDFM7 | 139.5 | 48.5 | 52.1 | 102 | -25.0 | 5.0 134.0 | 26.3 | |
| | 132.0 | | | | | 123.0 | | |
| MDFM10 | 107.8 | 38.2 | 41.1 | - | _ | - | - | |
| | 116.1 | | | | | | | |
| MDDR1 | 154.4 | 76.5 | 82.2 | 98 | -25.2 | 151.0 | 53.8 | |
| | 148.9 | | | | | | | |
| MDDR3 | 139.3 | 58.7 | 63.1 | 102 | -33.0 | 137.0 | 37.9 | |
| | | | | | | 128.0 | | |
| MDDR5 | MDDR5 132.5 77.0 | 35 132.5 77.0 | 82.8 | 105 | -30.1 | 134.0 | 30.9 | |
| MODDE | | | | | 126.0 | | | |
| MDDR7 | 89.4 | 24.3 | - | - | - | - | - | |
| MDDR10 | n.d | n.d | n.d | n.d | n.d | n.d | n.d | |

Table S3. DSC data of MDs¹

¹ Heating and cooling scan was carried out at 20°C/min. ² Crystallinity was evaluated on the first heating scan and considering ΔH_m (PLA100%) = 93.1 J/g [Ref 17 and Ref 18 main text].



Figure S6. DSC curves of first heating (a) and second heating (b) scan of samples MDFM1-MDFM10. Heating and cooling scans were carried out at 20°C/min. The curves were vertically shifted for clarity.



Figure S7. DSC curves of first heating (a) and second heating (b) scan of samples MDDR1-MDDR7. Heating and cooling scans were carried out at 20°C/min. The curves were vertically shifted for clarity.



Figure S8. DSC curves of the second heating scan of samples MDCA5, MDFM5 and MDDR5. Heating and cooling scans were carried out at 10°C/min. The curves are vertically shifted for clarity.

| | | | , 0 | | , | 0 |
|--------|------------|----------------|--------------------|-------------------|-------------------|----------------------------|
| Sampla | $T_{ m g}$ | $T_{\rm cc^b}$ | $\Delta H_{ m cc}$ | $T^{\mathrm{m}b}$ | $\Delta H_{ m m}$ | Crystallinity ^b |
| Sample | (°C) | (°C) | (J/g) | (°C) | (J/g) | (%) |
| MDCA5b | 44.6 | 87.9 | -4.8 | 148.5 | 56.5 | 56 |
| MDFM5b | 47.8 | 98.0 | -28.3 | 137.0 | 49.6 | 23 |
| | | | | 145.3 | | |
| MDDR5b | 22.7 | 85.0 | -28.3 | 105.2 | 36.8 | 9 |
| | | | | 116.4 | | |

Table S4. DSC data of MDs prepared by using 5 mol% of initiator, second heating scan^a

^a Heating and cooling scan was carried out at 10°C/min; ^b Crystallinity was evaluated on the second heating scan and considering Δ Hm (100%) = 93.1 J/g [Ref 17 and Ref 18 main text].

| | С | HCl3 ² | EtOH 95% ² | | |
|--------|-----------------|---|-----------------------|----------------------------|--|
| Sample | λ_{max} | λmax Emax | | Emax | |
| | (nm) | (L mol ⁻¹ cm ⁻¹) | (nm) | (L mol ⁻¹ cm-1) | |
| CA | 344 | 4780 | 343 | 4230 | |
| | 330 | 4426 | 329 | 3877 | |
| | 294 | 19460 | 293 | 17885 | |
| | 264 | 21400 | 261 | 21145 | |
| FM | 301 | 7200 | 300 | 6764 | |
| | 291 | 6000 | 289 | 5086 | |
| | 268 | 19300 | 266 | 17400 | |
| DR | 483 | 30951 | 507 | 32408 | |

Table S5. Absorption maxima and corresponding molar extinction coefficient ¹ of CA, FM and DR in CHCl₃ and in EtOH 95%

¹ Molar extinction coefficients were evaluated by calibration curves by collecting spectra at different concentration of the chromophore. ² Dielectric constants of CHCl₃ = 4.81; Dielectric constant of EtOH = 25.30 [Ref 41 main text].



Figure S9. Chromatograms collected during SEC analysis of PLA/MDCA5, PLA/MDFM5 and PLA/MDDR5.



Figure S10. DSC curves (second heating scan): (a) PLA, PLA/MDCA5, PLA/MDFM5 and PLA/MDDR5 and (b) PLA, PLA/CA, PLA/FM and PLA/DR. The curves were vertically shifted for clarity. Heating and cooling scans were carried out at 10°C/min

Table S6. Ratio between the emission intensity of the band at 350 and 360 nm of the spectra of PLA/CA and PLA/MDCA5

| Sample | I350/1360 |
|---|-----------|
| PLA/CA aluminum side | 0.86 |
| PLA/CA Teflon side | 0.88 |
| PLA/CA aluminum side after annealing | 0.72 |
| PLA/CA Teflon side after annealing | 0.72 |
| | |
| PLA/MDCA5 aluminum side | 0.84 |
| PLA/MDCA5 Teflon side | 0.85 |
| PLA/MDCA5 aluminum side after annealing | 0.72 |
| PLA/MDCA5 Teflon side after annealing | 0.72 |

Microwave assisted Synthesis of Macromolecular Dyes (MD) by using FM as co-initiator

This synthesis was carried out by using FM as co-initiator, reagents in bulk (see the conventional synthesis method in the main text for stoichiometry) are weighted directly into dedicated 10 mL vials and capped with the provided septum without oxygen removal. A CEM Explorer monomodal reactor (max. power output = 300 W) equipped with IR optical thermometer and a 48 positions autosampler was employed in Dynamic Field Tuning mode. Irradiation was auto regulated to achieve the following set temperature gradient: r. T. \rightarrow 30 °C; 30 °C, isothermal (hold for 1 minute); 30 °C \rightarrow 60 °C; 60 °C, isothermal (hold for 1 minute); 60 °C \rightarrow 90 °C; 90 °C, isothermal (hold for 1 minute); 120 °C \rightarrow 130 °C; 130 °C, isothermal (hold for 20 minutes); 130 °C \rightarrow r. T. Pressurized air cooling option was disabled in order to enhance homogeneity. Purification was performed as reported for the conventional procedure in the experimental part (main text). Yields ranged from 65% to 85%. The samples are named MDFMmw (where mw is for microwave assisted synthesis) followed by a number corresponding to the percentage of FM with respect to L-lactide. For example, in the case of sample prepared by using 5 mol% of FM with respect to L-lactide and the reaction was microwave assisted the acronym is MDFMmw5.

| | | First heating | | | Second heating | | | |
|------------|-------|---------------|------------------|-------|--------------------|-------|-------------------|--|
| Sample | Tm | ΔH_m | Crystallinity | Tcc | $\Delta H_{ m cc}$ | Tm | $\Delta H_{ m m}$ | |
| | (°C) | (J/g) | (%) ² | (°C) | (J/g) | (°C) | (J/g) | |
| MDEM.mars1 | 161.1 | 00 (| 88.8 | 116.0 | -45.5 | 156.0 | 47 1 | |
| | 156.1 | 02.0 | | | | 147.0 | 4/.1 | |
| | 157.2 | 60.2 | 64.7 | 110.0 | -36.4 | 152.0 | 41.2 | |
| MDFMmw3 | 151.5 | | | | | 140.0 | | |
| | 146.7 | 49.2 | 52.9 | 113.0 | -19.3 | 145.0 | 17.0 | |
| MDFMINW5 | 140.1 | | | | | 137.0 | 17.0 | |
| | 140.5 | 41.0 | 44.9 | 113.0 | -7.9 | 140.0 | 7.2 | |
| MDFMmW/ | 132.6 | 41.8 | | | | 132.0 | 7.3 | |
| | 133.9 | 20.0 | 22.0 | 114.0 | | 10(0 | 1 - | |
| MDFMmw10 | 125.3 | 30.0 | 32.2 | | -1.2 | 136.0 | 1.5 | |

Table S7. DSC data of MDFMmws¹

¹ Heating and cooling scans were carried out at 20°C/min. ² Crystallinity was evaluated on the first heating scan and considering ΔH_m (PLA100%) = 93.1 J/g [Ref 17 and Ref 18 main text].