

Supporting Information

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1) Materials and physical measurements.

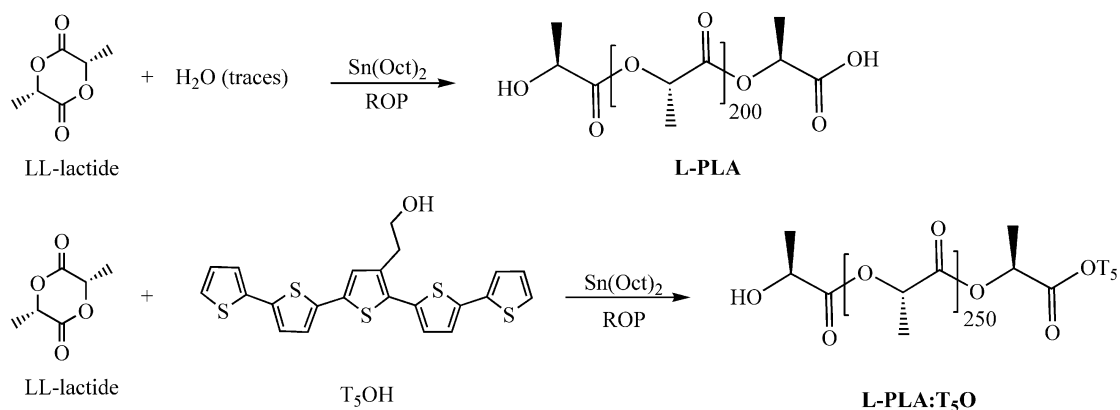
LL-Lactide, (i.e. (3S)-cis-3,6-Dimethyl-1,4-dioxane-dione; Sn(Oct)₂ (Sn(II)-bis-2-ethyl-hexanoate) were purchased from Aldrich with a purity of 98 and 95%, respectively, while T₅OH was synthesized as reported in the literature.[S. Alesi, G. Brancolini, I. Viola, M. L. Capobianco, A. Venturini, N. Camaioni, G. Gigli, M. Melucci, G. Barbarella *Chem. Eur. J* **2009**, *15*, 1876] Importantly, LL-lactide was sublimed before utilization and stored under a N₂-atmosphere. Hexane was purchased from *Romil-SA*, with isomer-n purity of > 95% and all-isomers purity of > 99.5%; CHCl₃ was purchased from VWR (*Anal. Normapur* grade) with a purity of 99.2%, stabilized with ethanol; HPLC-grade CHCl₃ was purchased from Sigma-Aldrich (*Chromasolv*) with a purity of 99.8%, stabilized with amylene. Aforementioned solvents were used without further purification, while CD₂Cl₂ used for NMR experiments was dried over molecular sieves. ¹H and ¹³C{¹H} NMR spectra were obtained with a Bruker Avance DRX-400 spectrometer acquiring spectra at 400.13 and 100.62 MHz, respectively. Chemical shifts are reported in ppm (δ) with reference to TMS as an internal standard. Gel-Permeation Chromatographic (GPC) analyses were obtained by means of a SEC-GPC system equipped with a *Waters 'Binary HPLC 1525'* pump; manual injector with 6-way valve and a 200 μL loop; three in-series *Shodex KF-802.5; KF-803 and KF-804* columns (length: 300 mm each; inner diameter: 8.0 mm; 24500 theoretical plates; exclusion limit for PS: up to 400000 g/mol); RI detector (*Waters, mod. 2414*) and UV-vis detector (*Waters, mod. 2489*). HPLC-grade CHCl₃ (*Chromasolv*, 99.8% purity, stabilized with amylene) was used as eluent at a constant flux of 1 mL/min; columns were kept at 30 °C by a thermostat. The GPC system was calibrated using PS standards and the accuracy was monitored injecting commercial PLA samples of known M_n and M_w. To a sample solution (c.a. 1mg/mL dissolved in HPLC-grade CHCl₃) were supplied with few drops of anhydrous toluene as internal standard and filtered through 0.45 μm PTFE cartridges.

Irradiation tests were performed on polymer solution-cast films using a CO.FO.ME.GRA *Solar Box* (model 3000e), equipped with a Xenon-arc lamp and an outdoor-type UV filter with cut-off < 290 nm to simulate external sunlight exposure. Irradiance was kept at 550 W/m² and black standard temperature (BST) was set at 38 °C. After the treatment in the *Solar Box*, the samples were dissolved in HPLC-grade CHCl₃ and subjected to GPC analysis.

SEM images were acquired on random-fractured samples (side-views). Samples were coated with a thin gold layer using an Emitech K550x Sputter Coater (exposition time 2 min, at 35 mA). Specimen side-view morphology was analyzed using a Fei Quanta 200 Environmental Scanning Electron Microscopy (ESEM, Fei Corporation, Eindhoven, The Netherlands) operating in high-vacuum mode (10⁻⁴ Torr).

Fluorescence imaging was performed on an inverted Nikon A1 confocal laser scanning microscope equipped with a set of lasers, Argon ion laser, 637 nm red diode laser and a 405 nm pulsed diode laser (Picoquant, Germany). Confocal fluorescence imaging was carried out at 20 °C. The images were collected using a Nikon PLAN APO VC 60× NA 1.40 oil immersion objective using the 488 nm laser line. Pixel dimension for the xy plane corresponds to 0.1 μm. Z-stack was done making 1 μm steps for a section with thickness varying from 10 to 20 μm.

2) NMR characterization of L-PLA and L-PLA:T₅O.



Scheme SI_1. Synthetic route to L-PLA and L-PLA:T₅O.

NMR spectroscopic data for L-PLA: ¹H NMR (400.13 MHz, CD₂Cl₂, 21 °C): δ = 1.48 (d, ³J_{H,H} = 6.9 Hz, CH(CH₃)OH), 1.59 (d, ³J_{H,H} = 6.9 Hz, CH(CH₃)COO), 4.36 (q, ³J_{H,H} = 7.0 Hz, CH(CH₃)OH), 5.19 (q, ³J_{H,H} = 6.9 Hz, CH(CH₃)COO). ¹³C{¹H} NMR (100.62 MHz, CD₂Cl₂, 21 °C): δ = 16.48 (s, CH(CH₃)COO), 20.29 (s, CH(CH₃)OH), 66.65 (s, CH(CH₃)OH), 69.00 (s,

CH(CH₃)COO), 169.52 (s, CH(CH₃)COO), 172.19 (s, CH(CH₃)COOH), 175.02 (s, OOCCH(CH₃)OH).

NMR spectroscopic data for L-PLA:T₅O: ¹H NMR (400.13 MHz, CD₂Cl₂, 21 °C): δ = 1.48 (d, ³J_{H,H} = 7.0 Hz, 3 H, CH(CH₃)OH), 1.52 (d, ³J_{H,H} = 7.0 Hz, CH(CH₃)COO), 3.19 (t, ³J_{H,H} = 6.8 Hz, 2 H, CH₂CH₂O), 4.36 (q, ³J_{H,H} = 7.0 Hz, 1 H, CH(CH₃)OH), 4.45 (t, ³J_{H,H} = 6.8 Hz, 2 H, CH₂CH₂O), 5.19 (q, ³J_{H,H} = 6.8 Hz, CH(CH₃)COO), 7.08-7.31 (m, 11 H, Ar-H). ¹³C{¹H} NMR (100.62 MHz, CD₂Cl₂, 21 °C): δ = 16.47 (s, CH(CH₃)COO), 20.29 (s, CH(CH₃)OH), 28.47 (s, CH₂CH₂O), 64.56 (s, CH₂CH₂O), 66.65 (s, CH(CH₃)OH), 69.00 (s, CH(CH₃)COO), 120.83-137.47 (s, Ar-C), 169.49 (s, CH(CH₃)COO), 174.99 (s, OOCCH(CH₃)OH).

3) Absorption and emission spectra of T₅OH in CH₂Cl₂ solution

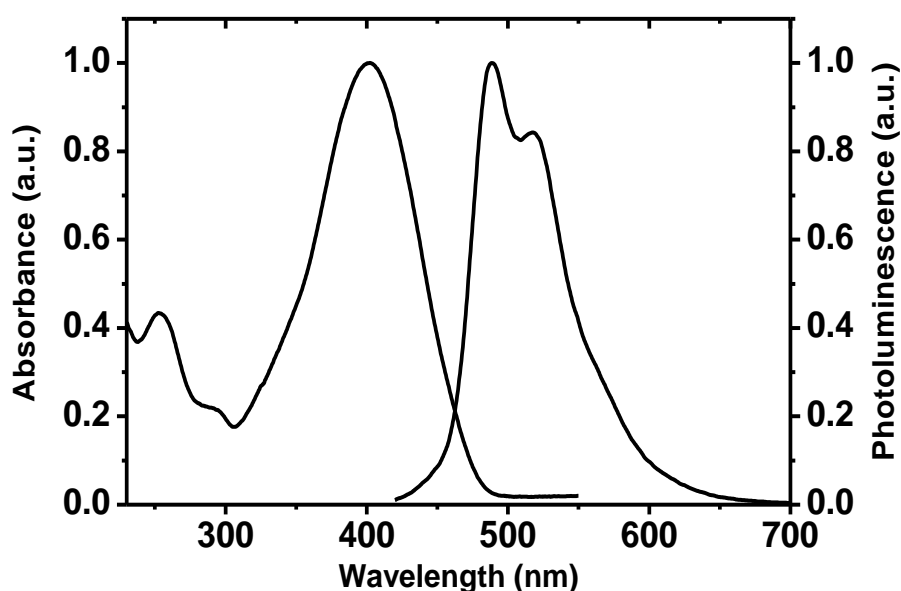


Fig. SI_1. Normalized absorption and emission spectra of T₅OH in CH₂Cl₂ solution (~10⁻⁵ M).

4) Scanning Electron Microscopy

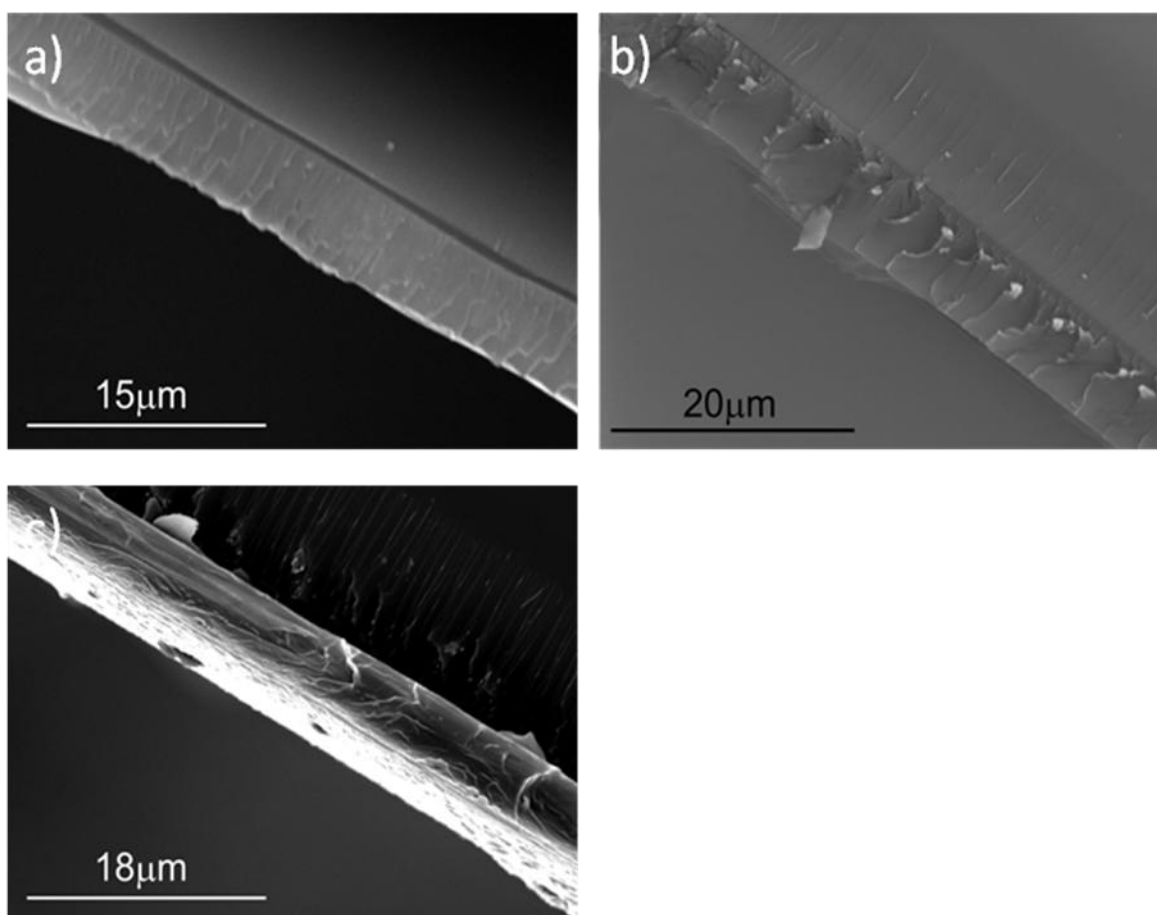


Fig. SI_2. SEM micrographs of random-fractured Au-coated film (side-views) on a quartz support: a) L-PLA: T₅O, b) L-PLA@T₅OH, and c) PMMA@T₅OH.

SEM micrographs of the three random-fractured films (side-view) revealed different morphologies for the L-PLA- and PMMA-based systems. While dye-doped L-PLA samples present regularly stacked L-PLA lamellae along with the fractured area, the PMMA sample presents as amorphous. Moreover, no appreciable morphological difference between the two L-PLA-based samples is observed.

5) Laser Scanning Confocal Microscopy

Fluorescence imaging was performed on an inverted Nikon A1 laser scanning confocal microscope equipped with a set of lasers, Argon ion laser, 637 nm red diode laser and a 405 nm pulsed diode laser (Picoquant, Germany). Confocal fluorescence imaging was carried out on the samples at 20 °C. The images were collected using a Nikon PLAN APO VC 60× NA 1.40 oil immersion objective and the 488 nm laser line. Pixel dimension for the xy plane corresponds to 0.1 μm.

We performed 3D imaging and the thickness of the optical section correspond to 10, 16 and 20 μm respectively for L-PLA:T₅O, LPLA@T₅OH and L-PMMA@T₅OH. Homogeneity is confirmed also along the z-direction. Figure SI_3 shows one xy slice of 1 μm thickness of the optical section. Below and at the right we can observe, respectively, the xz and yz cross section corresponding in position to the orange lines shown in the xy plane.

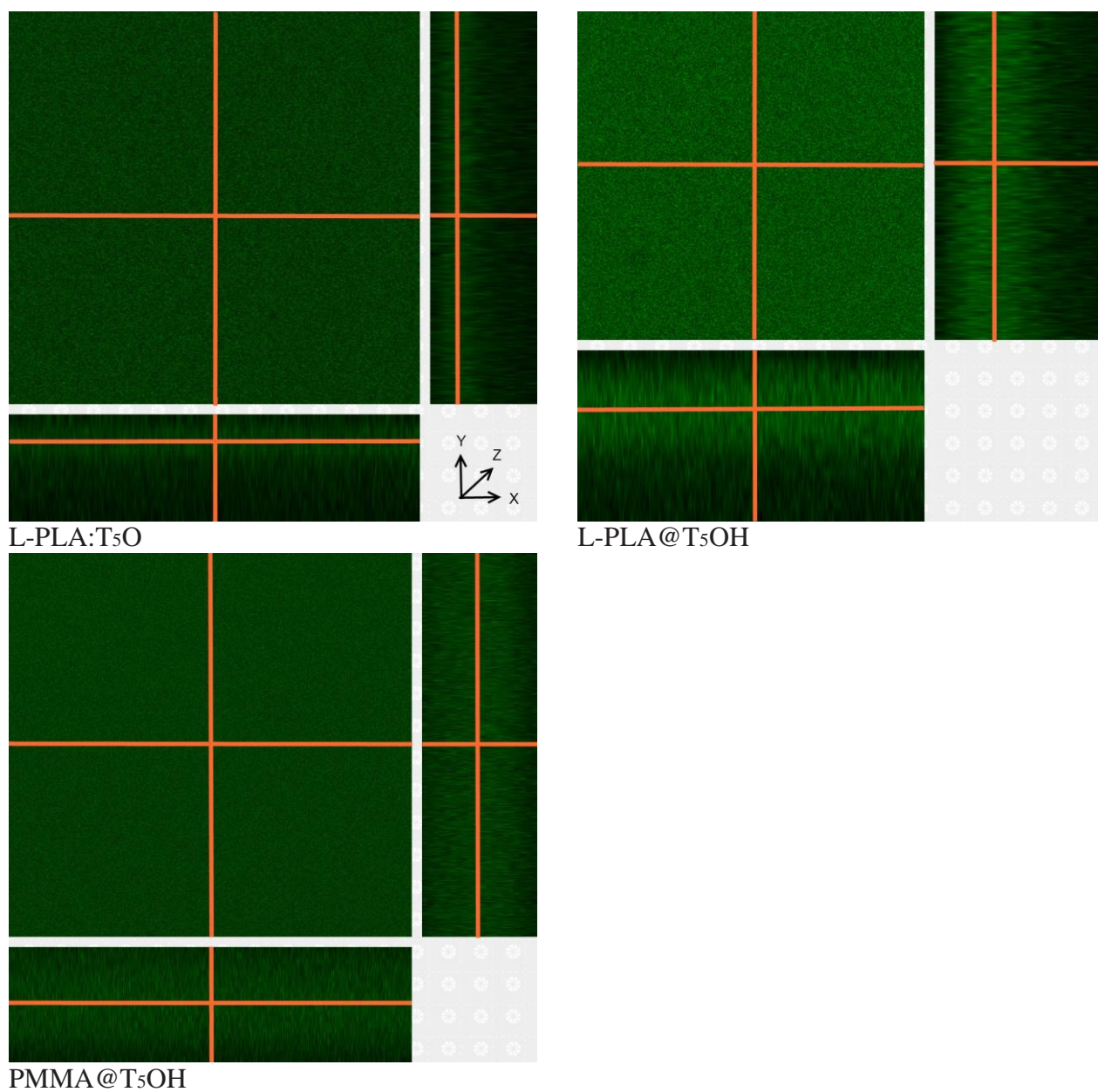


Fig. SI_3

6) Comparative irradiation tests of L-PLA@T₅OH and L-PLA:T₅O.

The blend was prepared by mixing L-PLA with T₅OH in a 1:27 weight ratio in order to mimic the molar ratio between polymer chain and dye in L-PLA:T₅O. A solution of the blend and L-PLA:T₅O (40 mg in 1 mL of HPLC-grade CHCl₃) was deposited onto glass slices (150 μL per spot, equivalent to approx 0.6 mg of dry sample) followed by the evaporation of the solvent at room temperature. The glass slices were then kept in a excicator until their weight was constant.

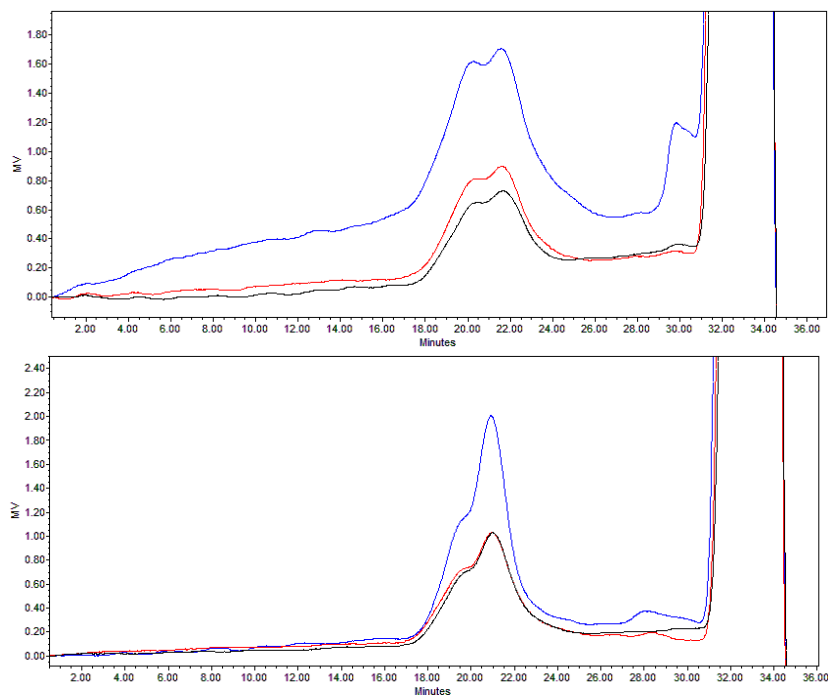


Fig. SI_4. GPC curves of L-PLA@T₅OH (top) and L-PLA:T₅O (bottom). Blue: no exposure; black: 2 days exposure; red: 3 days exposure.