

Supporting information for:

New sustainable polymers and oligomers for cultural heritage conservation

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Materials and methods

Sebacic acid (> 98.0%), adipic acid (> 99.0%) and succinic acid (> 99.0%) were purchased from TCI chemicals. 1,6-Hexanediol (99.0%), 1,4-butanediol (99.0%), poly(hexamethylene diisocyanate) (PHDI; 1,300-2,200 cP) and tetrahydrofuran (inhibitor free, anhydrous, \geq 99.9%) were purchased from Sigma Aldrich. Castor oil (pharma grade, 89.2%wt of ricinoleic acid) was purchased from Gioma Varo Srl (Milan, Italy). Paraffin and Paraloid B72 were purchased from CTS (Vicenza, Italy) and used as received. All chemicals were used without any further purification.

Synthetic procedures

Synthesis of oligoesters O1 to O5

The preparation of oligoesters **O1** to **O5** was performed via the polycondensation in bulk of selected dicarboxylic acid and diol. The oligoesters prepared in this study were obtained from a two-step polycondensation reaction of one carboxylic acid and one diol. Equimolar quantities of 85 mmol for both dicarboxylic acid and diol were transferred in a round bottom flask connected to a dean-stark trap. The mixture was heated at 180 °C and was kept at this temperature for 4 hours resulting in the distillation of water produced from the oligomerization. Subsequently, the water was separated and the mixture was connected to a membrane pump (15 mbar) and let stirring at 180 °C for 4 additional hours. The resulting oligoester was cooled to room temperature and aliquots were collected for SEC and NMR analysis. In an exemplary reaction, **O1** was obtained from the polycondensation of 17.2 g (85 mmol) of sebacic acid and 10.1 g (85 mmol) of hexanediol. Each compound was transferred in a 100 mL round bottom flask, and the oligomerization was performed as described above. The resulting material appeared as a white hard wax.

Oligo(hexylene sebateate) (**O1**): Yield: 23.1 g (95%). ^1H NMR (400 MHz, CDCl_3): δ/ppm = 1.29–1.35 (m, 8 H, $-\text{OC}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$), 1.42 (m, 4 H, Hexanediol- $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$), 1.67 (m, 8 H, $-\text{CH}_2\text{CH}_2\text{OC}(\text{O})\text{CH}_2\text{CH}_2-$), 2.32 (m, 4 H, $-\text{CH}_2\text{C}(\text{O})\text{O}-$), 3.68 (t, 0.32 H, $-\text{CH}_2\text{O}-$), 4.04 (t, 3.68 H, $-\text{CH}_2\text{O}-$).

Oligo(hexylene adipate) (**O2**): Yield: 16.9 g (87%). ¹H NMR (400 MHz, CDCl₃): δ/ppm = 1.41 (m, 4 H, -CH₂CH₂CH₂O-), 1.70 (m, 8 H, CH₂CH₂OC(O)CH₂CH₂-), 2.36 (m, 4 H, -CH₂C(O)O-), 3.69 (t, 0.19 H, -CH₂O-), 4.10 (t, 3.81 H, -CH₂-O-).

Oligo(hexylene succinate) (**O3**): Yield: 16.4 g (96%). ¹H NMR (400 MHz, CDCl₃): δ/ppm = 1.41 (m, 4 H, -CH₂CH₂CH₂O-), 1.68 (m, 4 H, CH₂CH₂O-), 2.66 (m, 4 H, -CH₂C(O)O-), 3.68 (t, 0.14 H, -CH₂O-), 4.13 (t, 3.86 H, -CH₂O-).

Oligo(butylene sebacate) (**O4**): Yield: 20.4 g (93%). ¹H NMR (400 MHz, CDCl₃): δ/ppm = 1.34 (m, 8 H, -OC(O)CH₂CH₂CH₂CH₂-), 1.65 (m, 4 H, -OC(O)CH₂CH₂-), 1.74 (m, 4 H, -CH₂CH₂OC(O)-), 2.33 (m, 4 H, -CH₂C(O)O-), 3.73 (t, 0.25 H, -CH₂O-), 4.13 (t, 3.75 H, -CH₂O-).

Oligo(butylene adipate) (**O5**): Yield: 15.9 g (93%). ¹H NMR (400 MHz, CDCl₃): δ/ppm = 1.61–1.83 (m, 8 H, CH₂CH₂-OC(O)-CH₂CH₂-), 2.37 (m, 4 H, -CH₂C(O)O-), 3.72 (t, 0.31 H, -CH₂O-), 4.13 (t, 3.69 H, -CH₂O-).

Synthesis of castor oil-polyurethanes

The preparation of oligoesters-enriched castor oil polyurethanes was adjusted from a literature protocol. 21.6 g of castor oil (72 m% in respect to the total mass) and 3.0 g (10 m%) of the selected oligoester (**O1** to **O5**) were transferred in a 40 mL glass flask equipped with a magnetic stirrer. The mixture was heated to 80 °C and was stirred for 10 minutes until complete dissolution of the oligoesters. Subsequently, 5.4 g of poly(hexamethylene diisocyanate) (PHDI; 18 m%) were added to the reaction and stirred at 80 °C for 10 minutes. The resulting mixture was casted in a polyethylene bag and was transferred in a custom-made mold consisting of two glass slides (14 x 11 cm), spaced with a 2 mm separator, and kept in position with clamps. At last, the mold was transferred in a pre-heated oven at 80 °C for 16 hours. The cured gels were removed from the oven and used for characterization. The final materials are called **G1** to **G5**, according to the nomenclature given to the oligoesters (**O1** to **O5**).

Cleaning procedures

Cleaning trials were conducted on frosted glass slides (5 x 5 cm²). Over the frosted surface, about 800 mg of a solution of Paraloid B72 (10% m/m in methyl ethyl ketone) and of paraffin wax (10% m/m in p-xylene) was deposited using a glass pipette. Glass slides were let dry for 3 days under the hood, at room temperature. After the deposition of the coatings, the frosted glass became transparent. Cleaning tests were performed using **G1**, swollen in p-xylene for 1 h, and **G5**, swollen in acetone for 1 h. After swelling, gels were removed from the solvent, shaped using scissors and gently dried using blotting paper. The gel was then placed over the coating and covered with a plastic film to avoid evaporation. A small weight (about 10 grams) was placed over the gel to grant proper contact. After 10 minutes, the gel was removed from the glass slide. No mechanical action was performed over the treated surface. A second application, using another piece of swollen gel, was performed on the same spot. The cleaned spot of the glass turned from transparent to opaque, because of the removal of the coating that makes the frosted glass surface smooth.

Instruments

¹H NMR and DOSY NMR were measured at 25 °C on a Bruker AVIII400 UltraShield Plus spectrometer. The residual ¹H peak of the deuterated solvent was used for chemical shift referencing. All NMR data interpretation was performed with TopSpin software (v.3.6.4). DOSY NMR analysis were performed as described from Bruker. Briefly, two preparatory experiments (ledbpgp2s1d) were performed with gradient strength 2 and 95%. Refinement experiments were performed (P30 between 1100 and 2400 μs) in order to achieve 5 % residual signal of the measurement performed with 95 % signal attenuation in comparison with the measurement performed with 2 % signal attenuation. Afterwards, DOSY NMR measurement were started (pulse program: ledbpgp2s). Diffusion data were obtained according to T1/T2 relaxation times with variable gradient fitting method.

SEC measurements were performed utilizing a system composed of a Shodex ERC-3215α degasser connected with a Waters 1525 binary HPLC pump, a Waters 1500 series heater set at 25 °C, a Wyatt miniDAWN TREOS detector, a

Wyatt Viscostar–II detector and a Wyatt OPTILAB T–rEX detector, two Shodex columns (GPC KF–802.5 and GPC KF–803) employing THF as eluent with a flow rate of 1.0 mL min⁻¹. A set of polystyrene standards (PS, 400 g mol⁻¹ < M_p < 50 kg mol⁻¹) samples were purchased from shodex and used for calibration. All data evaluation was performed according to standard procedures employing ASTRA software and ORIGIN for curve fitting.

The clogP was calculated employing the software DataWarrior (OSIRIS; v. 5.5.0). For the calculation of the parameters from the **Ox** series, dimeric structures were considered.

Solvents employed for DOSY NMR analysis and properties at 25 °C

Solvent	logP	Viscosity [25 °C] [mPas]
Acetone-d ₆	-0.24	0.295
Tetrahydrofurane-d ₈	0.46	0.480
CD ₂ Cl ₂	1.25	0.410
CDCl ₃	1.63	0.563
Benzene-d ₆	2.13	0.608
Toluene-d ₈	2.73	0.560

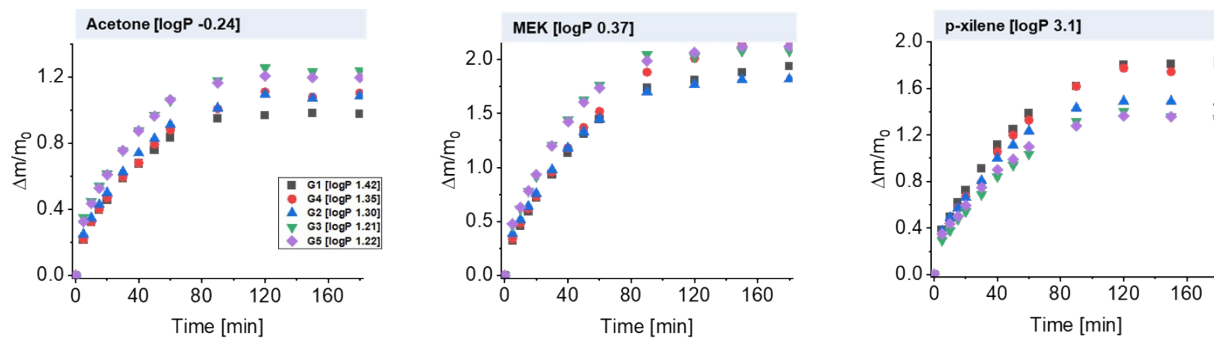


Figure S1: Swelling experiments of the newly synthesized castor oil polyurethanes containing 10 m% of oligoesters **O1** to **O5**. **Left:** Relative uptake ($\Delta m/m_0$) of the gelled systems in acetone over time. **Middle:** Relative uptake ($\Delta m/m_0$) of the gelled systems in methylethylketone (MEK) over time. **Right:** Relative uptake ($\Delta m/m_0$) of the gelled systems in methylethylketone (MEK) over time. Errors are included in the markers.