ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Self-curing furan-based elastic thermosets derived from citric acid

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1. Detailed Experimental Procedure

1.1. Materials
Citric acid (98%), pyridine (98%), chloroacetaldehyde (40% aqueous solution),
ethylene glycol (99%), 1,3-propanediol (99.5%), 1,4-butandiol (99%) and 1,10-
decanediol (99.5%) were purchased from Sigma-Aldrich. Tetrabutyl titanate (TBT)
(98%), methanol (99%) and chloroform (99%) were purchased from Tianjin Chemical
Reagent Co. (Tianjin, China) and used without further purification.

1.2. General methods

$^1$H-NMR and $^{13}$C-NMR spectra were recorded in CDCl$_3$ at room temperature on a
Bruker AVANCE III NMR spectrometer operating at 400 and 100.6 MHz,
respectively. Tetramethylsilane was used as the internal reference. Infrared spectra
were recorded by a Bruker-Tensor 27 spectrometer using the attenuated total
reflection (ATR) mode. The number average molecular weight ($M_n$) and weight
average molecular weight ($M_w$) and the molecular weight distribution (PDI) were
determined by gel permeation chromatography (GPC, Waters 2414 system Milford,
MA) at 35 ºC. THF was used as the eluent at a flow rate of 1.0 mL min$^{-1}$. Thermodynamic stability was analyzed by thermo gravimetric analyses using Seiko
Exstar 6000 TGA quartz rod microbalance. Polymer sample were heated from 40 ºC
to 600 ºC at a rate of 10 ºC min$^{-1}$. The temperature of 5% weight loss and the
temperature of the maximum weight loss rate was obtained by calculated. Differential
scanning calorimetry thermograms was measured using a differential scanning
calorimeter (Netzsch PC-200). About 5 mg samples were first heated from -50 ºC to
100 ºC and then the glass transition temperature were calculated from a second
heating run. All runs were performed at a rate of 10 ºC min$^{-1}$. Dynamic mechanical
analysis (DMA) were performed using a TA DMA 2928 in the controlled force-
tension film mode with a preload force of 0.1 N, an amplitude of 10 μm, and at a
fixed frequency of 1 Hz in the -60 to 75 ºC range and at a heating rate of 3 ºC min\(^{-1}\). The tensile assays were performed in triplicates on rectangular specimens (20 × 5 × 0.5 mm\(^3\)) measuring the strain while applying a ramp of 0.5 N min\(^{-1}\) at 25 ºC. A preload force of 0.05 N and a soak time of 3 min were used. All films for dynamic mechanical analysis (DMA) and tensile tests were prepared with a thickness of 200 μm by casting from a chloroform solution at a concentration of 100 g L\(^{-1}\).

1.3. Synthesis of dimethyl 1,3-acetonedicarboxylate

Dimethyl 1,3-acetonedicarboxylate was synthesized by decarboxylation of citric acid with concentrated sulfuric acid, followed by esterification with methanol according to a reported literature.\(^1\)

1.4. Synthesis of methyl 3-(methoxycarbonyl)furan-2-acetate (MCFA)

MCFA was synthesized from dimethyl acetonedicarboxylate using literature procedures with some modifications.\(^2\) Briefly, a solution of chloroacetaldehyde (26.5 mL, 40%) in water was added dropwise to a solution of dimethyl 1,3-acetonedicarboxylate (25.0 g, 143.5 mmol) in pyridine (50 mL) with stirring. Stirring was continued for 48 h at 50 ºC. Then the reaction mixture was poured into ice water and extracted with ethyl acetate (200 mL). The organic layer was washed successively with 2 M HCl, 5% NaHCO\(_3\), 10% NaOH and brine, and then dried over MgSO\(_4\). The solvent was evaporated and the product was purified by fractionation to give MCFA as a colorless liquid (22.8 g, 80%). \(^1\)H-NMR (400 MHz, CDCl\(_3\)): δ 7.35 (d, \(J = 2.0\) Hz,
1H), 6.71 (d, J = 2.0 Hz, 1H), 4.09 (s, 2H), 3.83 (s,3H), 3.73 (s,3H). $^{13}$C-NMR (400 MHz, CDCl$_3$): δ 169.9, 163.1, 154.1, 141.3, 115.2, 110.5, 52.1, 51.6, 33.5. IR (cm$^{-1}$): 3162, 3130, 2951, 1746, 1712, 1613, 1510, 1260, 947, 894, 745.

1.5. Polymer synthesis

Thermoplastic polyesters (PE-ms) were synthesized from MCFA in combination with corresponding linear diol by polycondensation. MCFA and the aliphatic diol HO-(CH$_2$)$_m$-OH (m = 2, 3, 4, 10) were introduced into a three-necked round-bottom flask equipped with a mechanical stirrer, a nitrogen inlet, and a vacuum outlet, a molar excess of 100, 50, 50 and 10% was used for ethylene glycol, 1,3-propanediol, 1,4-butanediol, and 1,10-decanediol, respectively. The apparatus was replaced by nitrogen three times at room temperature, heated under stirring until homogenization of the mixture, and then tetrabutyl titanate (TBT, 0.6% molar with respect to MCFA) was added. Transesterification reaction were carried out under a low nitrogen flow at 170 ºC for 3 h. After that, the polycondensation reaction was left to proceed at 240 ºC for 5 h under dynamic vacuum (0.03-0.06 mbar). Finally, the resulting polymers were cooled to room temperature and dissolved in chloroform, and precipitated with methanol to remove unreacted monomers and formed oligomers, collected by filtration, and dried under vacuum to obtain the PE-ms as viscous liquid.

$PE-2$. $^1$H-NMR (400 MHz, CDCl$_3$): δ 7.34 (m, 1H), 6.70 (m, 1H), 4.5 (t, 2H), 4.4 (t, 2H), 4.3 (t, 2H), 4.1 (s, 2H). FT-IR, ν (cm$^{-1}$): 2925, 2854, 1741 (C=O), 1719 (C=O), 1615, 1512, 1022, 953, 890,746.

$PE-3$. $^1$H-NMR (400 MHz, CDCl$_3$): δ 7.35 (m, 1H), 6.70 (m, 1H), 4.37 (t, 2H), 4.28
(m, 2H), 4.18 (t, 2H), 4.1 (s, 2H). IR, ν (cm⁻¹): 2922, 2841, 1742 (C=O), 1713 (C=O), 1610, 1517, 1022, 953, 889,746.

**PE-4.** ¹H-NMR (400 MHz, CDCl₃): δ 7.35 (m, 1H), 6.70 (m, 1H), 4.2 (m, 4H), 4.1 (s, 2H), 1.8 (t, 4H). IR, ν (cm⁻¹): 2922, 2847, 1742 (C=O), 1713 (C=O), 1610, 1512, 1068, 1022, 958, 889,746.

**PE-10.** ¹H-NMR (400 MHz, CDCl₃): δ 7.35 (m, 1H), 6.70 (m, 1H), 4.2 (t, 4H), 4.1 (t, 2H), 4.09 (s, 2H), 1.6 (m, 2H), 1.7 (m, 2H), 1.30 (m, 12H). IR, ν (cm⁻¹): 2922, 2847, 1742 (C=O), 1713 (C=O), 1610, 1512, 1068, 1022, 987, 889,746.

### 1.6. Self-curing of PE-ms in sunlight

The general procedure to prepare the cured polyester films in sunlight was as follows: a freshly prepared polymer solution at a concentration of 100 g L⁻¹ was casted into a round Teflon plate to make a film. The plate was placed under a flow of air at room temperature for 24 h to evaporate the solvent (CHCl₃), which was subsequently cured under the irradiation of sunlight at room temperature for a week. After the solvent was completely removed, a slightly yellow transparent thermoset film was obtained.

### 1.7. Hydrolytic and Enzymatic Degradation Procedures

Both the hydrolytic and enzymatic degradation for C-PE-ms were investigated using weight-loss method. The above cured films of C-PE-ms were cut into 10 mm diameter, 20 to 30 mg weight disks. For hydrolytic degradation, three parallel samples were immersed in vials containing 10 mL citric acid buffer (pH 2.0), and the vials were placed in a 37 °C shaking bath. After incubation for the scheduled 42 days, the samples were rinsed thoroughly with distilled water and dried in a vacuum oven at 40
°C until constant weight and weighted. The enzymatic degradation was carried out at
37 °C in vials containing 10 mL of the enzymatic medium, consisting of a pH 7.4
buffered sodium phosphate solution containing lipase from porcine pancreas (10 mg).
The buffered enzyme solution was replaced every 72 h to maintain the enzyme
activity. After incubation for the scheduled 42 days, the disks were washed
thoroughly with distilled water, dried to constant weight in vacuum and weighted.

2. Characterization

![Figure S1. ¹H-NMR spectrum of MCFA](image)

![Figure S2. ¹³C-NMR spectrum of MCFA](image)
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Reference