

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-butanediol (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

$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ 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 °C. 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 °C to 600 °C at a rate of 10 °C 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 °C to 100 °C and then the glass transition temperature were calculated from a second heating run. All runs were performed at a rate of 10 °C 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 $^{\circ}\text{C}$ range and at a heating rate of 3 $^{\circ}\text{C min}^{-1}$. The tensile assays were performed in triplicates on rectangular specimens ($20 \times 5 \times 0.5 \text{ mm}^3$) measuring the strain while applying a ramp of 0.5 N min^{-1} at 25 $^{\circ}\text{C}$. 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 $^{\circ}\text{C}$. 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%). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.35 (d, $J = 2.0 \text{ Hz}$,

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 $\text{HO}-(\text{CH}_2)_m\text{-OH}$ ($m = 2, 3, 4, 10$) 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 °C for 3 h. After that, the polycondensation reaction was left to proceed at 240 °C 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. ^1H -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. ^1H -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. $^1\text{H-NMR}$ (400 MHz, CDCl_3): 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. $^1\text{H-NMR}$ (400 MHz, CDCl_3): 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 (CHCl_3), 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 $37 \text{ }^\circ\text{C}$ 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

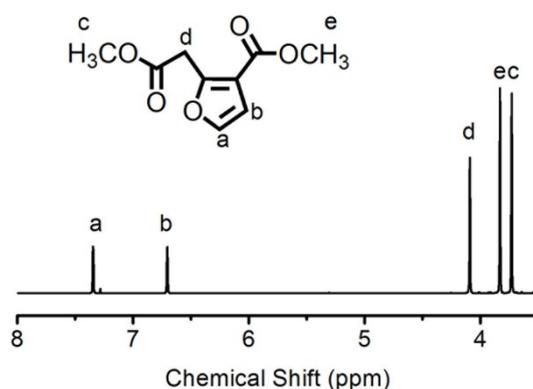


Figure S1. ¹H-NMR spectrum of MCFA

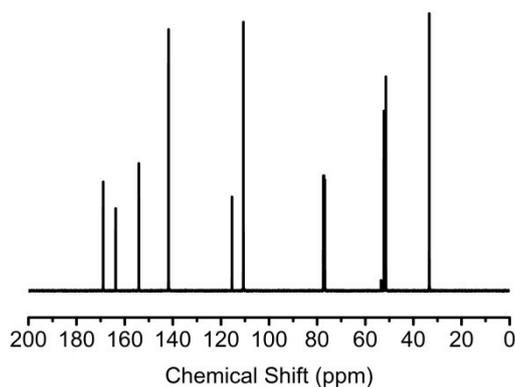


Figure S2. ¹³C-NMR spectrum of MCFA

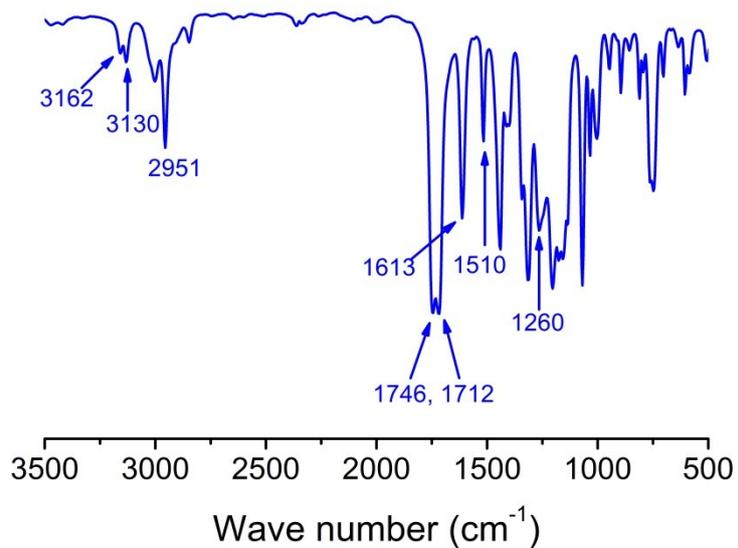


Figure S3. FTIR spectrum of MCFA

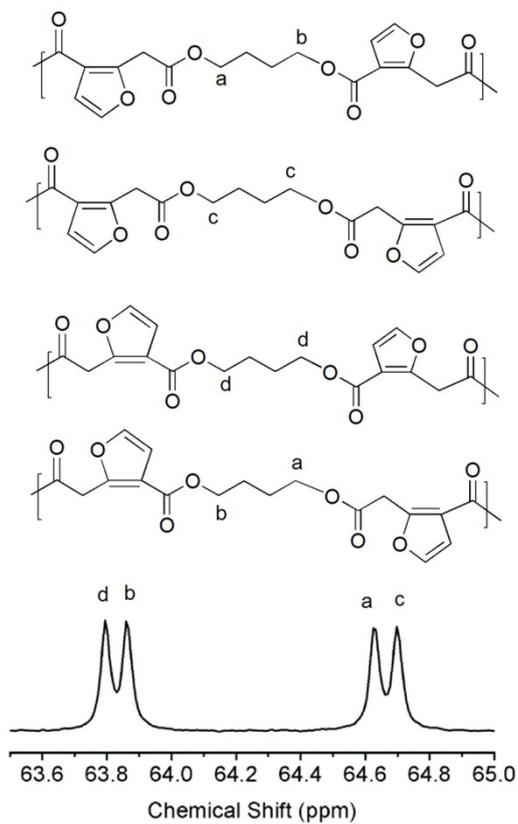


Figure S4. O-CH₂ signals of PE-4 with indication of the dyads responsible for the four peaks

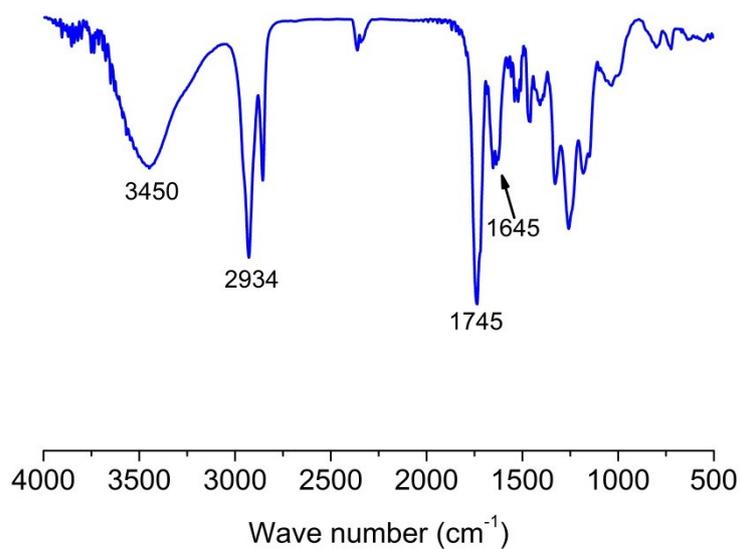


Figure S5. FTIR spectrum of X-PE-10

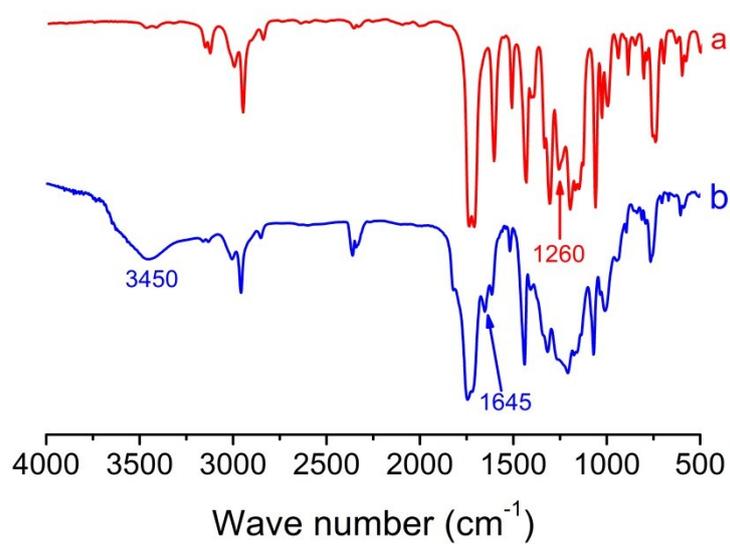


Figure S6. FTIR spectra of MCFA before (a) and after (b) exposure to sun

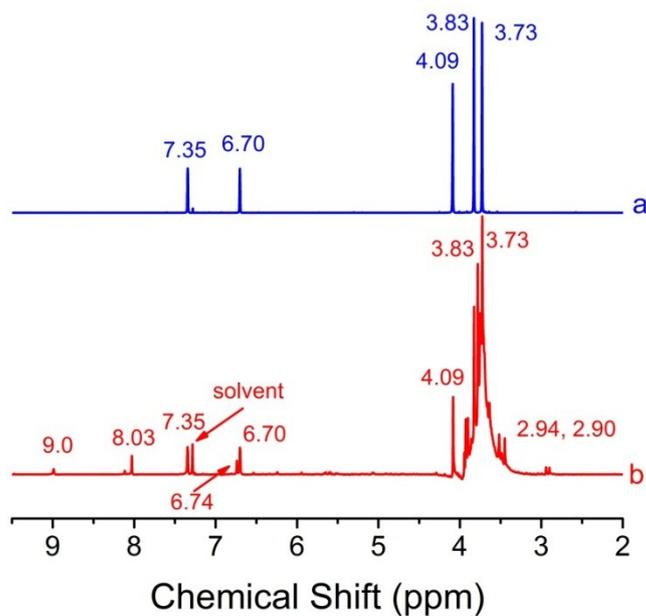


Figure S7. $^1\text{H-NMR}$ spectra of MCFA before (a) and after (b) exposure to sun

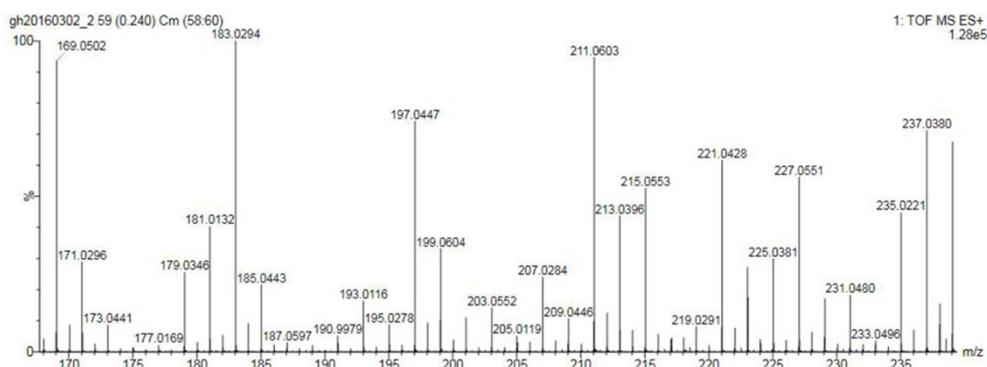


Figure S8. HRMS spectrum of MCFA after exposure to sun

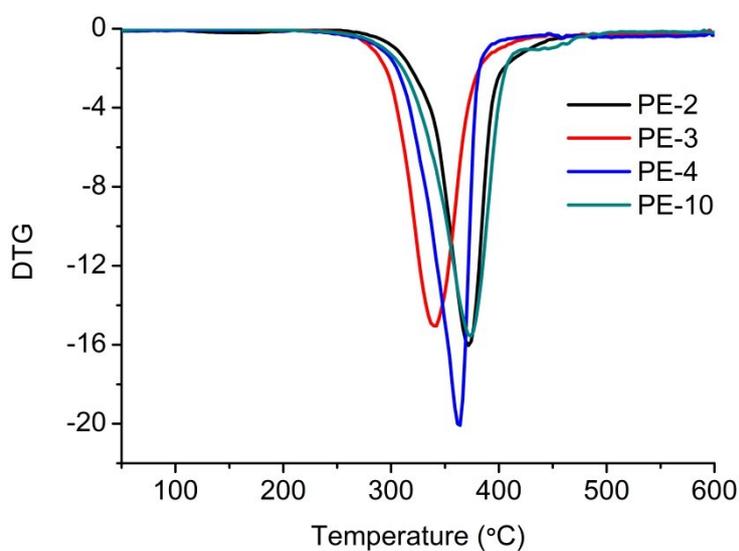


Figure S9. DTG derivative curves of PE-ms at a heating rate of 10 °C min^{-1}

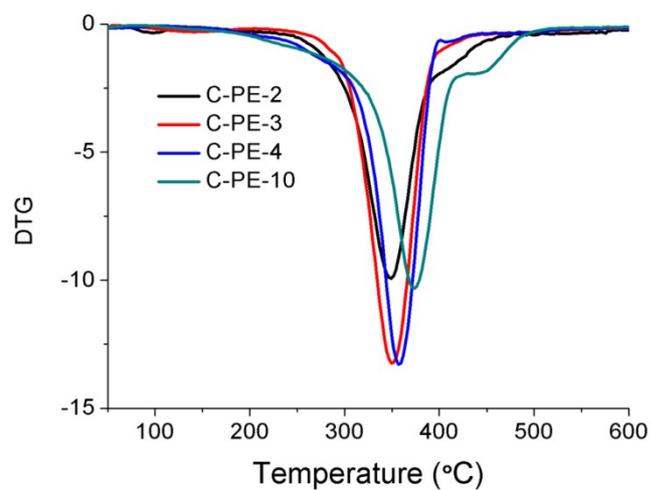


Figure S10. DTG derivative curves of C-PE-ms at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$

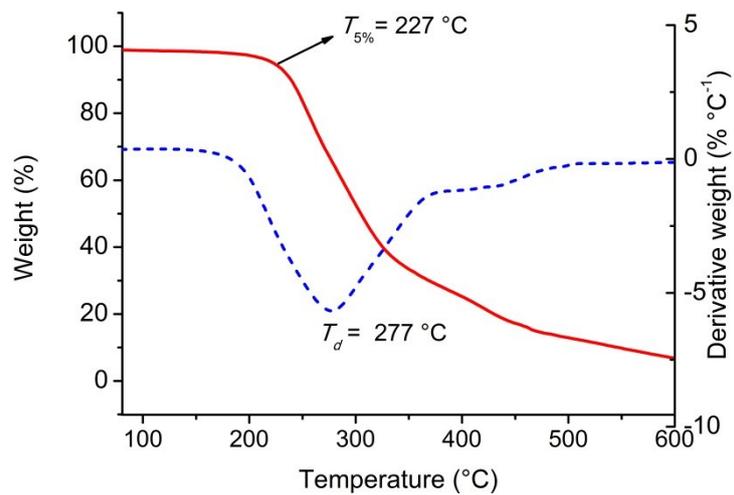


Figure S11. TGA traces (solid line) and derivative curves (dashed line) of X-PE-10 at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$

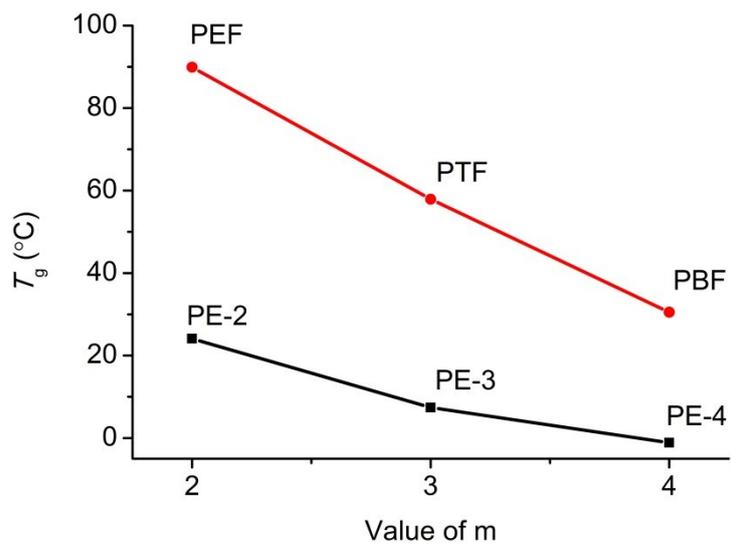


Figure S12. Comparison of T_g s between FDCA-based polyesters and MCFA-based polyesters

Reference

- 1 J. Poldy, R. Peakall, R. A. Barrow, *Eur. J. Org. Chem.* 2012, **2012**, 5818-5827.
- 2 M. Ergun, C. Dengiz, M. S. Özer, E. Şahin, M. Balci, *Tetrahedron*, 2014, **70**, 5993-5998.