Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Ambient temperature induced Diels-Alder crosslinked networks based on controlled methacrylate copolymers for enhanced thermoreversibility and self-healability

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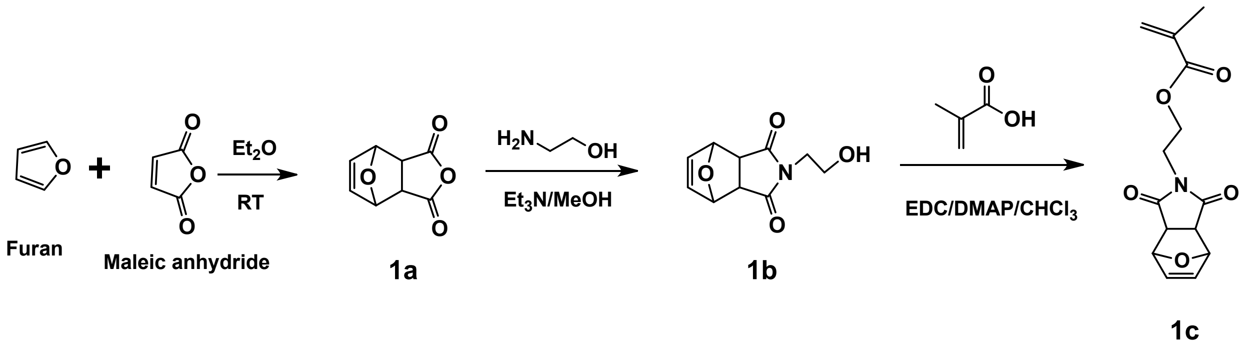
Synthesis of MIMA



(1a) 3a,4,7,7a-tetrahydro-4,7-epoxyisobenzofuran-1,3-dione. Furan (15 mL, 0.2 mol) was added to an organic solution of maleic anhydride (5 g, 0.05 mol) dissolved in diethyl ether (25 mL). The resulting mixture was magnetically stirred at room temperature. After 48 hrs, white solids were isolated by vacuum filtration, washed with diethyl ether (200 mL) twice, and then dried in vacuum oven at room temperature. Yield = 95%. Rf = 0.63 in hexane/ethyl acetate (1/1 v/v).

(1b) 2-(2-hydroxyethyl)-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindole-1,3(2H)-dione. In a three neck round bottom flask equipped with a stirrer and a reflux condenser, **1a** (25 g, 0.15 mol) dissolved in MeOH (380mL) was purged with N2 gas for 10 min in an ice bath. After the dropwise addition of Et_3N (31.5 mL, 0.23 mol) and ethanolamine (13.6mL, 0.23 mol), the resulting mixture was stirred over 20 hrs at 70^{o}C. Then, an additional amount of ethanolamine (1.5 mL, 0.025 mol, 10%) was added to the reaction mixture and then the mixture was stirred for another 2 hrs. The mixture was cooled down to room temperature, subjected to rotary evaporation to reduce its volume to a half, and then stored at -4 °C over night. The formed semi-crystalline solids were collected by filtration and washed with isopropanol before drying in vacuum oven overnight. Yield = 70%.

(1c) 2-(1, 3-dioxo-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindol-2(3H)-yl)ethyl methacrylate. 1b (5 g, 0.024 mol), methacrylic acid (2.4 mL, 0.029 mol), *N*-(3-dimethylaminopropyl)-*N′*-ethylcarbodiimide hydrogen chloride (EDC, 6.6 g, 0.034 mol), and 4-(dimethylamino)pyridine (DMAP, 2.1 g, 0.017 mol) were dissolved in anhydrous 120 mL of $CHCl_3$ and stirred at 35 °C for 24 hrs. The reaction mixture is transferred to a separatory funnel and then additional $CHCl_3$ (200mL) was added. The combined organic layers were washed with water (3 X 100 mL), dried over (Mg_2SO_4) and concentrated. The resulting crude mixture was purified by column chromatography using a mixture of $CHCl_3$ and Ethyl acetate (5:1 v/v). Yield = 75%, R_f = 0.3 with $CHCl_3$/ethyl acetate at 5/1 v/v

Figure S1. ^{1}H-NMR and ^{13}C-NMR spectra of PP-Br in CDCl$_3$.

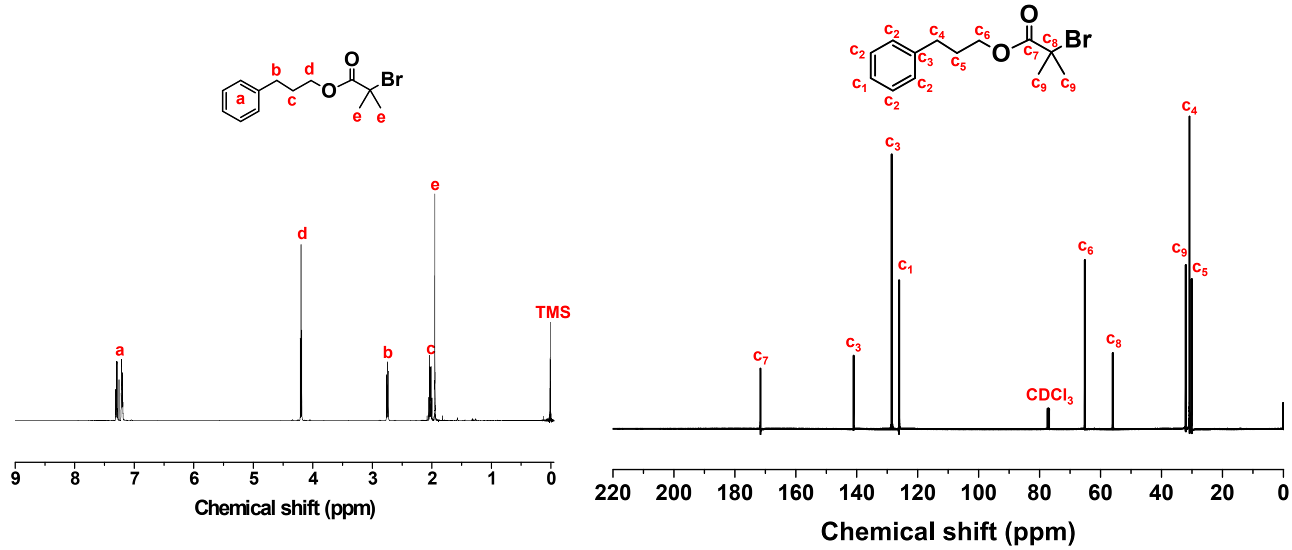


Figure S2. ^{1}H-NMR spectra of CoPMIMA-1 and CoPMA-1 in DMSO-d$_6$.

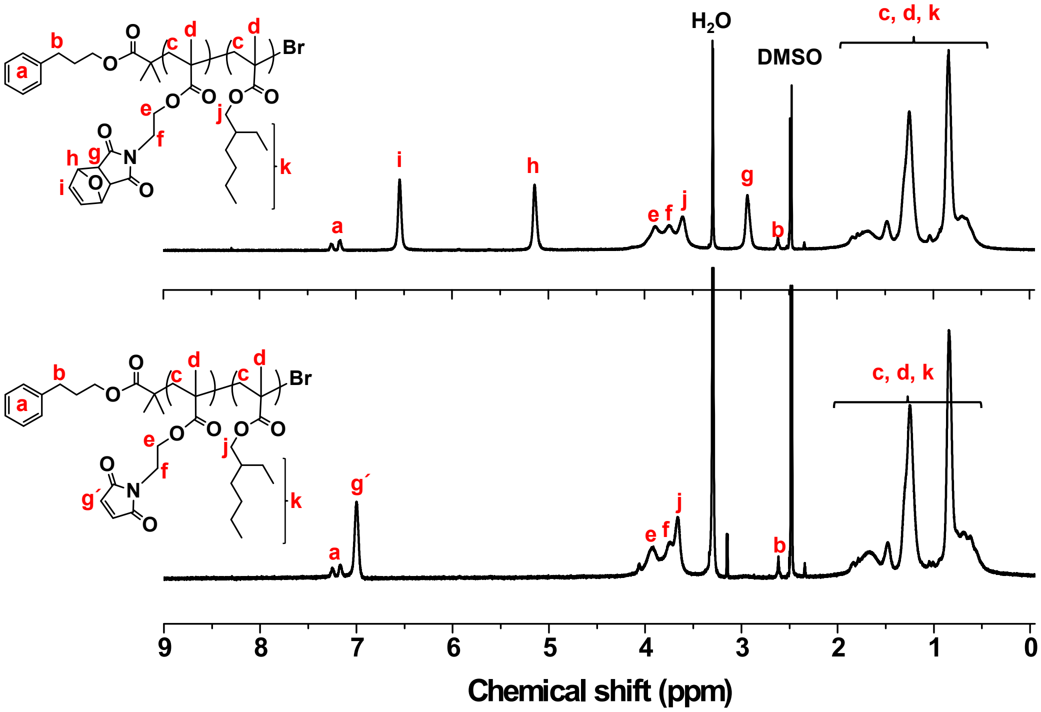


Figure S3. ^{1}H-NMR spectra of CoPMIMA-2 and CoPMA-2 in DMSO-d_6.

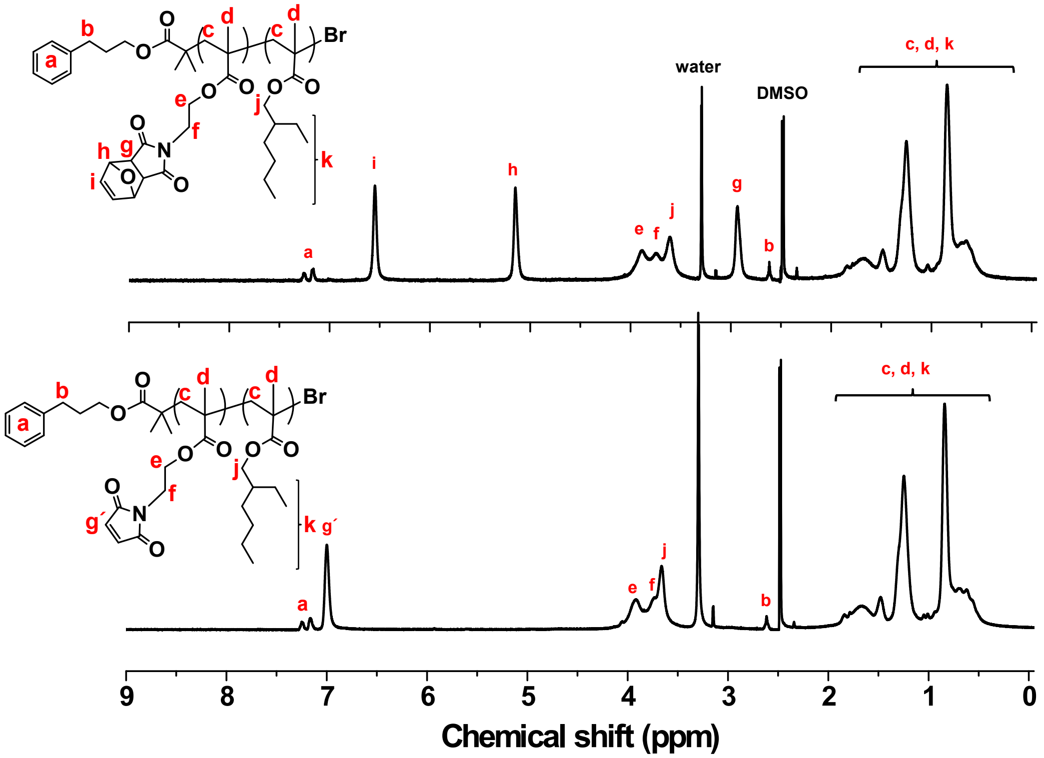


Figure S4. ^{1}H-NMR spectra of CoPMIMA-3 and CoPMA-3 in DMSO-d_6.

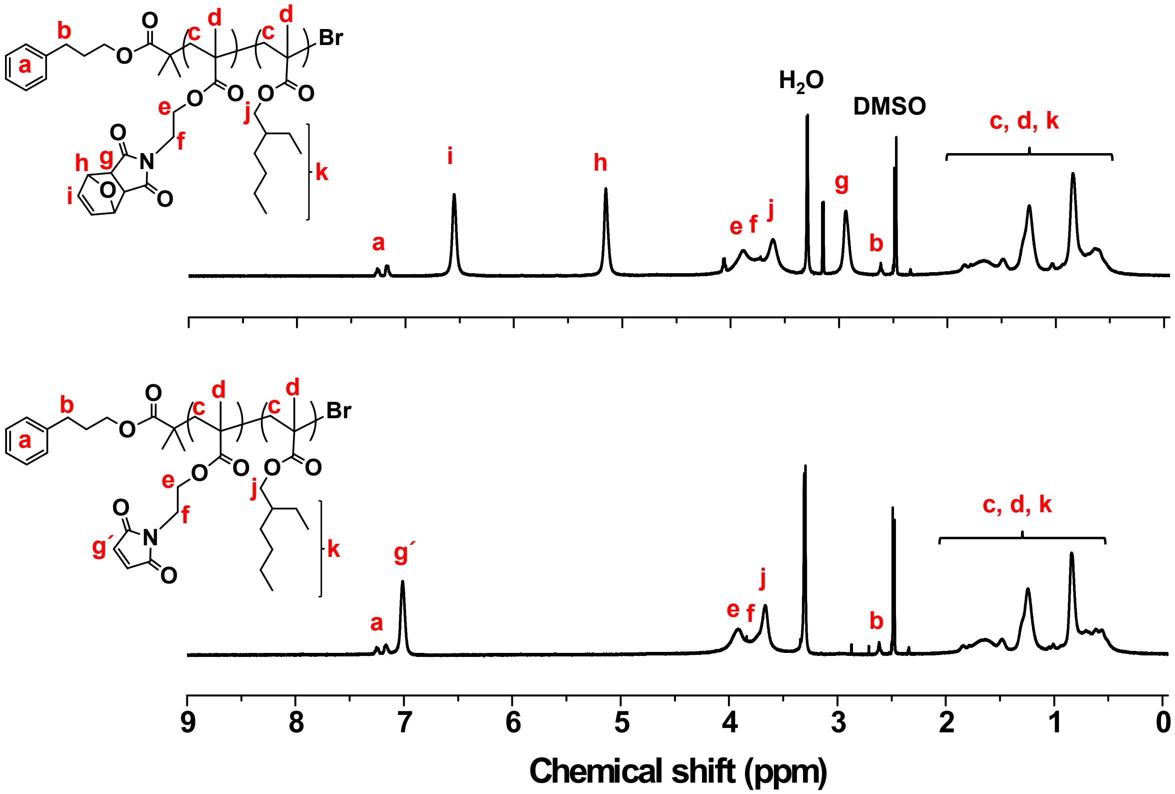


Figure S5. GPC traces for a series of CoPMIMA.

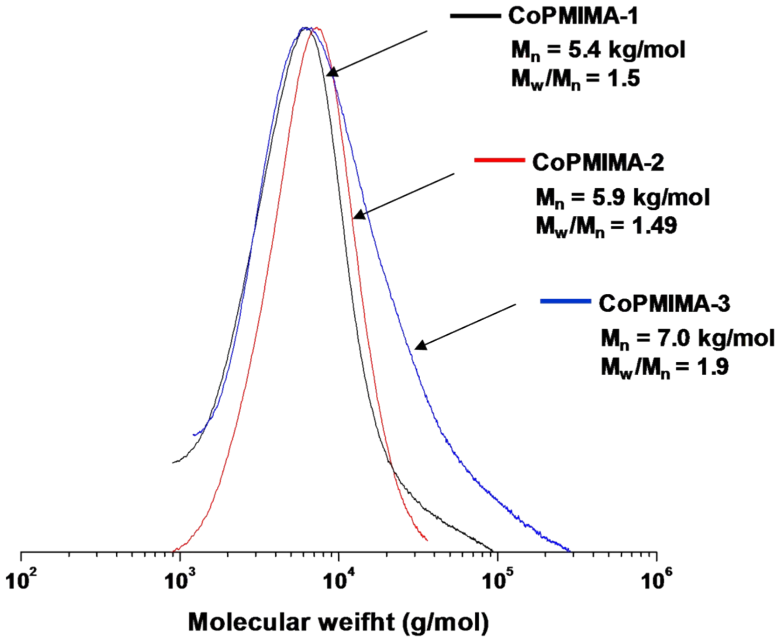


Figure S6. DSC (a) and TGA (b) traces of CoPMIMA copolymers with different mole ratios of MIMA/EHMA units.

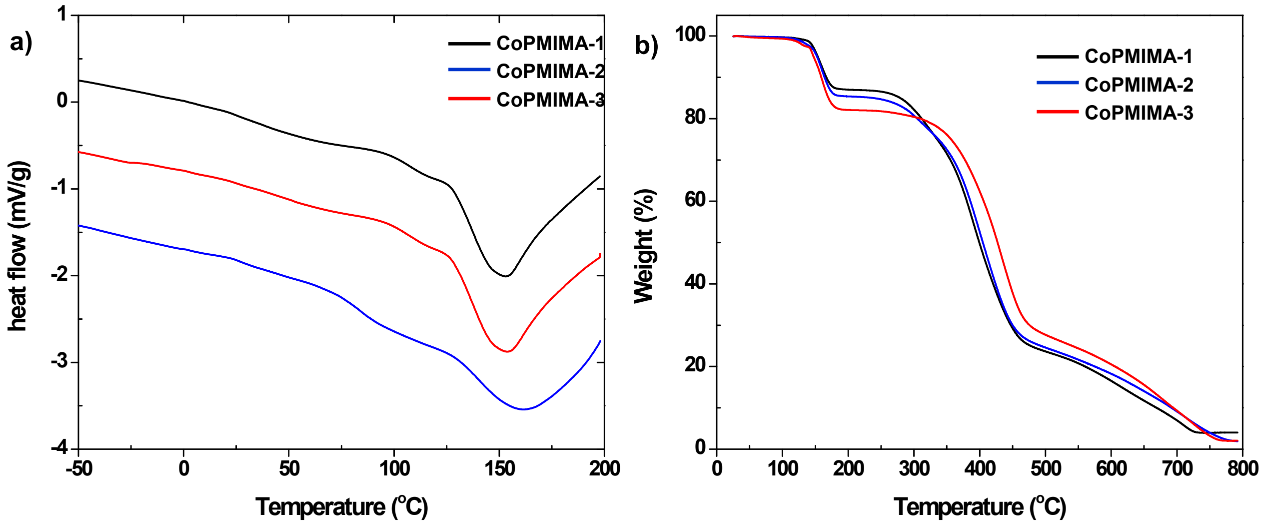


Figure S7. ^{13}C-NMR spectra of TFu in $CDCl_3$.

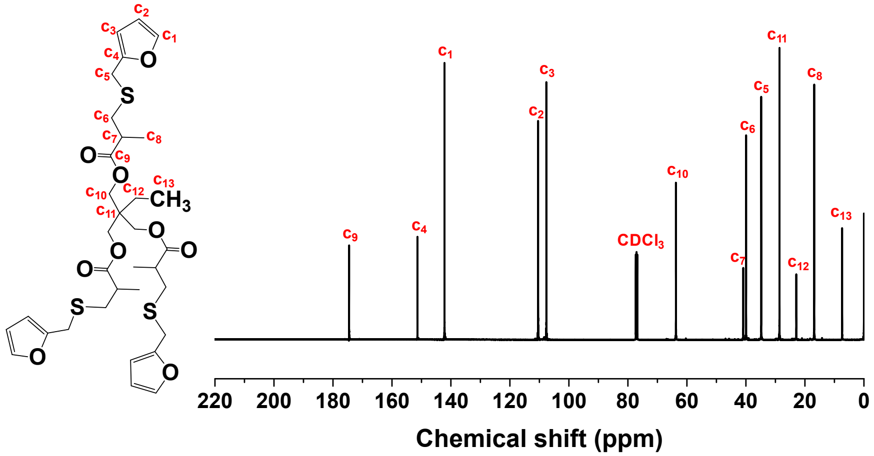


Figure S8. DSC diagrams (a, b) and TGA traces (c, d) of cross-linked films cast at 60 °C (a, c) and 25 °C (b, d) from reactive blends of CoPMA-2 and TFu at mole equivalent ratios of maleimide/furan group = 1/1 (F1M1), 2/1 (F2M1), and 3/1 (F3M1).

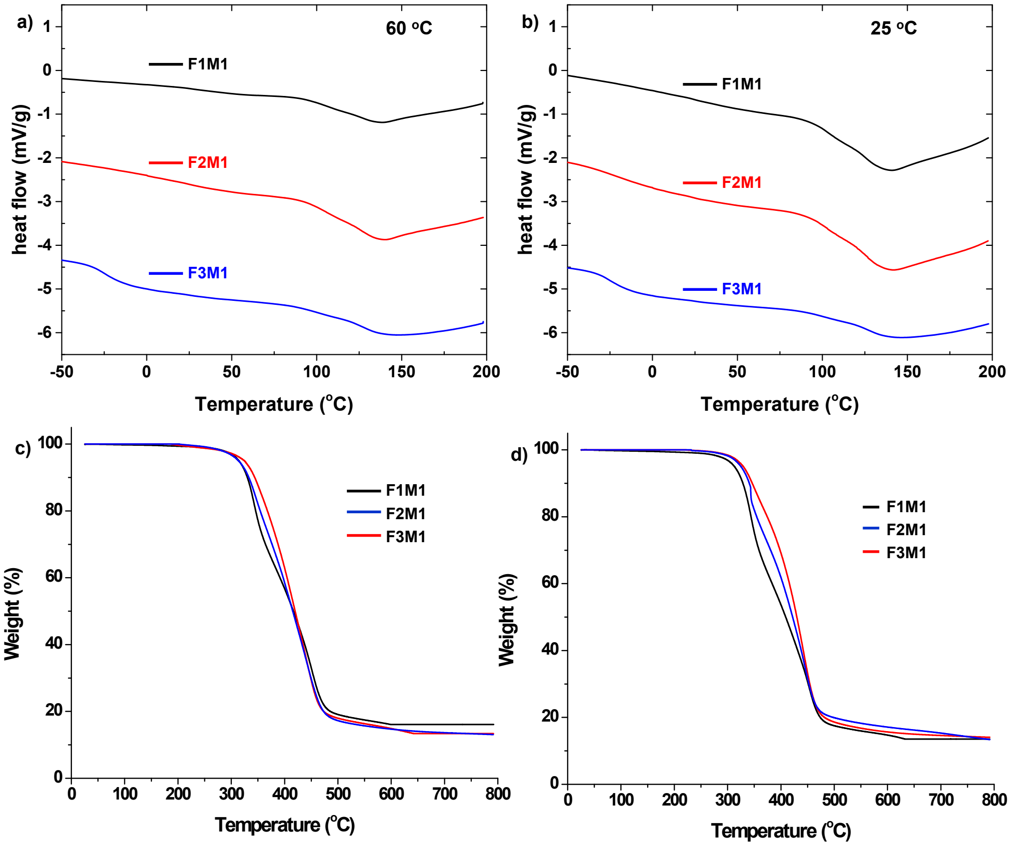


Figure S9. Microscope images of DA-crosslinked F3M1 films cast from a reactive blend of CoPMA-2 and TFu at 3/1 mole equivalent ratio of maleimide/furan group before and after being annealed at 85 °C over days.