Electronic Supplementary Material (ESI) for Polymer Chemistry.

Poly(ethylene-*co*-propylene)/poly(ethylene glycol) elastomeric hydrogels with thermoreversibly cross-linked networks

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Supporting information

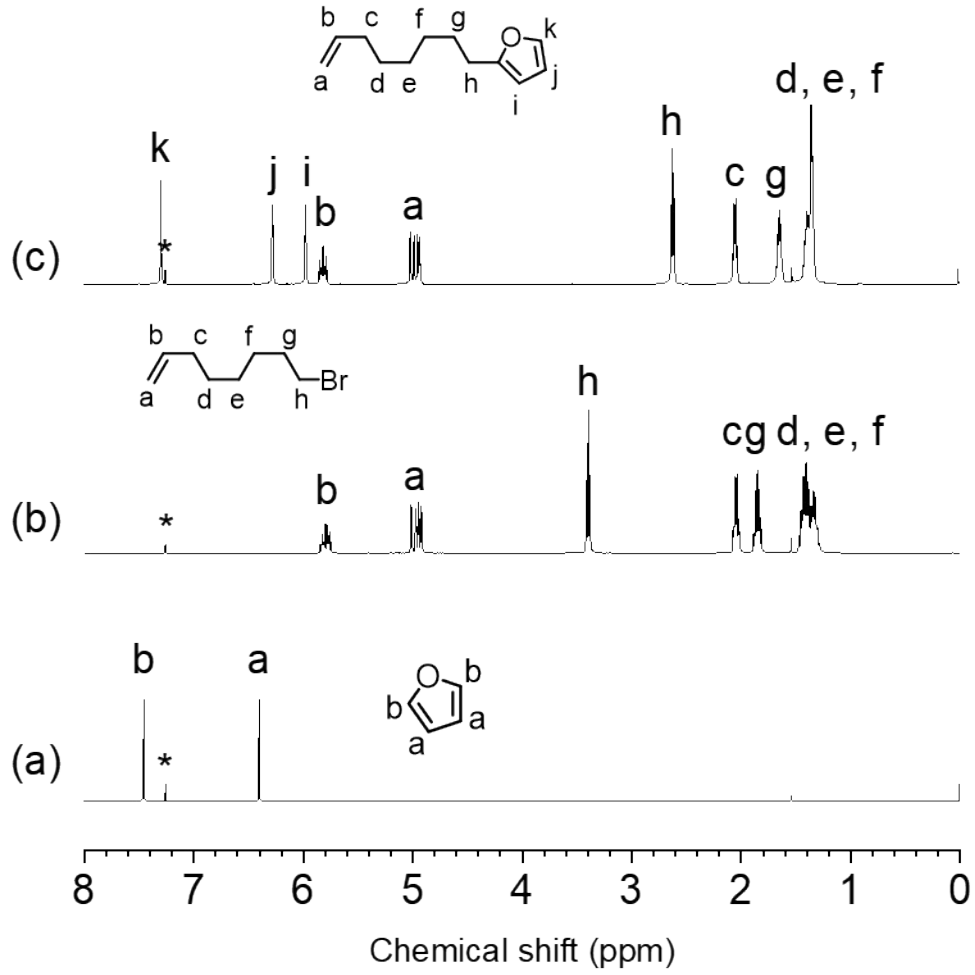
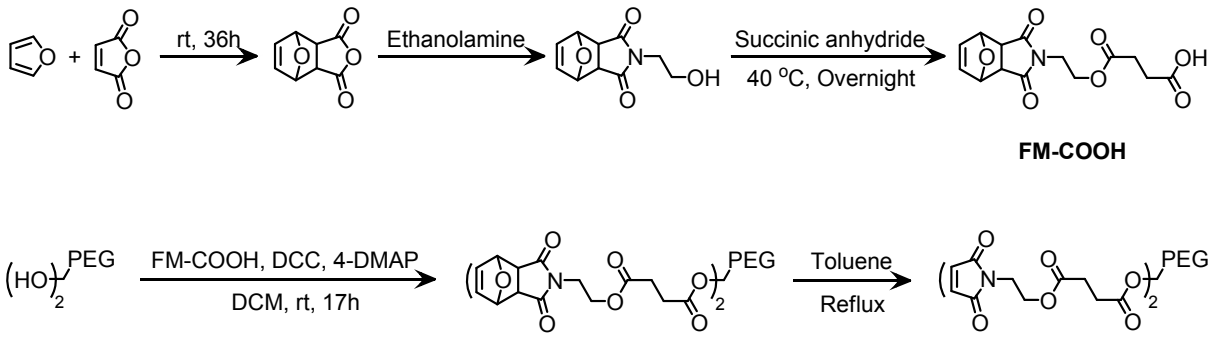


Figure S1 ^{1}H-HMR spectra of (a) furan, (b) 8-Br-1-octane, and (c) 8-furyl-1-octane



Scheme S1 Synthesis route of bis-maleimide-capped poly(ethylene glycol) ($(MI)_2PEG$)

Synthesis of FM-COOH:
4-(2-(((3-acetyl-7-oxabicyclo[2,2,1]-hept-5-en-2-yl)carbonyl)amino)ethoxy)-4-oxobutanoic acid)

The synthesis of 4-(2-Hydroxy-ethyl)-10-oxa-4-aza-tricyclo[5.2.1.02,6]dec-8-ene-3,5-dione was performed according to literature [1]. 4-(2-Hydroxy-ethyl)-10-oxa-4-aza-tricyclo[5.2.1.02,6]dec-8-ene-3,5-dione (10g, 47.80mmol) was dissolved in 300 ml 1,4-dioxane in a round bottom flask equipped with magnetic stirrer. Subsequently, trimethylamine(25.30 g，250 mmol)，DMAP(11.68 g, 95.6 mmol) and succinic anhydride(19.14 g, 191.2 mmol) were added and the reaction mixture was stirred at 40 °C overnight. The solution was washed with 1M HCl, extracted with DCM, and dried over Na_2SO_4, the solvent was removed under reduced and the residue was recrystallized from ethanol to give a white crystal.^{1}H-NMR (400 MHz, CDCl3, Figure 1c): δ = 6.51 (2H, s, CH=CH, bridge protons), 5.26 (2H, s, -CHO, bridge-head protons), 4.26 (2H, t, $NCH_2CH_2OC=O$), 3.75 (2H, t, $NCH_2CH_2OC=O$), 2.88 (2H, s, CH=CH, bridge protons), 2.67–2.54 (4H, m, $C=OCH_2CH_2C=OOH$).

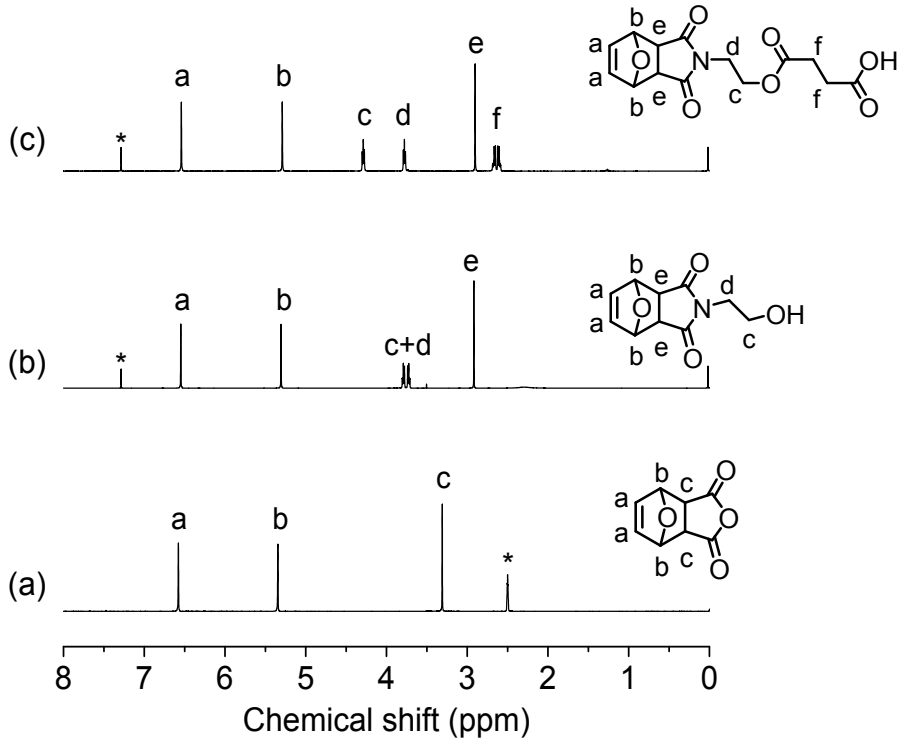


Figure S2 ^{1}H-NMR spectra of (a) Maleic anhydride, (b) 4-(2-Hydroxy-ethyl)-10-oxa-4-aza-tricyclo[5.2.1.02,6]dec-8-ene-3,5-dione, and (c) FM-COOH

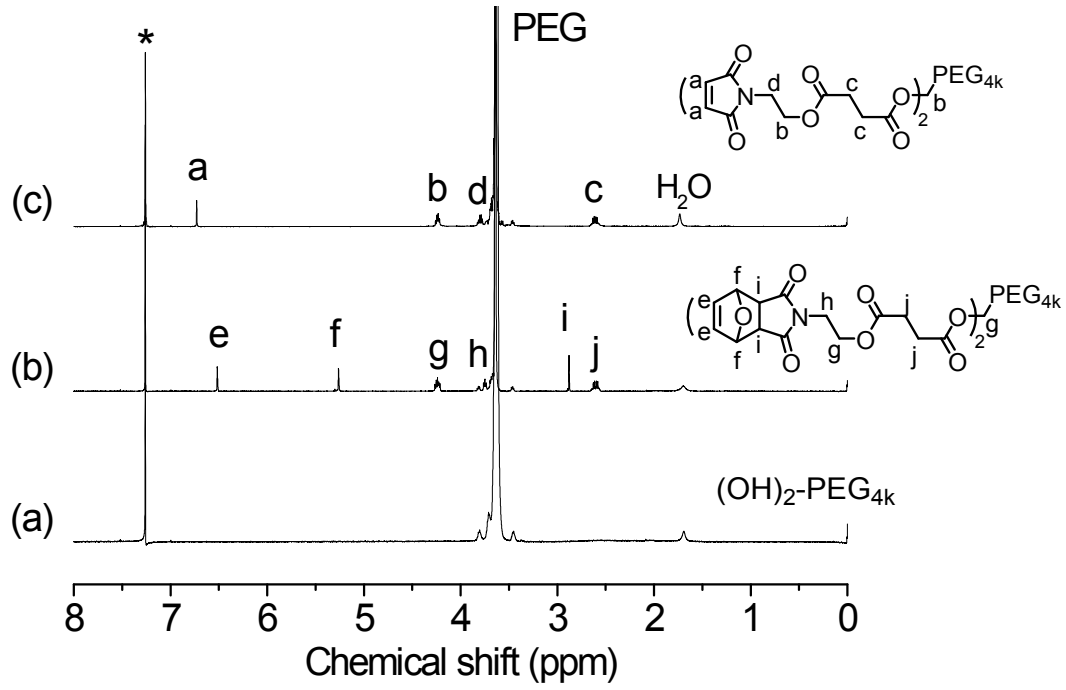


Figure S3 ^{1}H-NMR spectra of (a) $(OH)_2$-PEG_{4k}, (b) furan protected $(MI)_2$-PEG_{4k} and (c) $(MI)_2$-PEG_{4k}

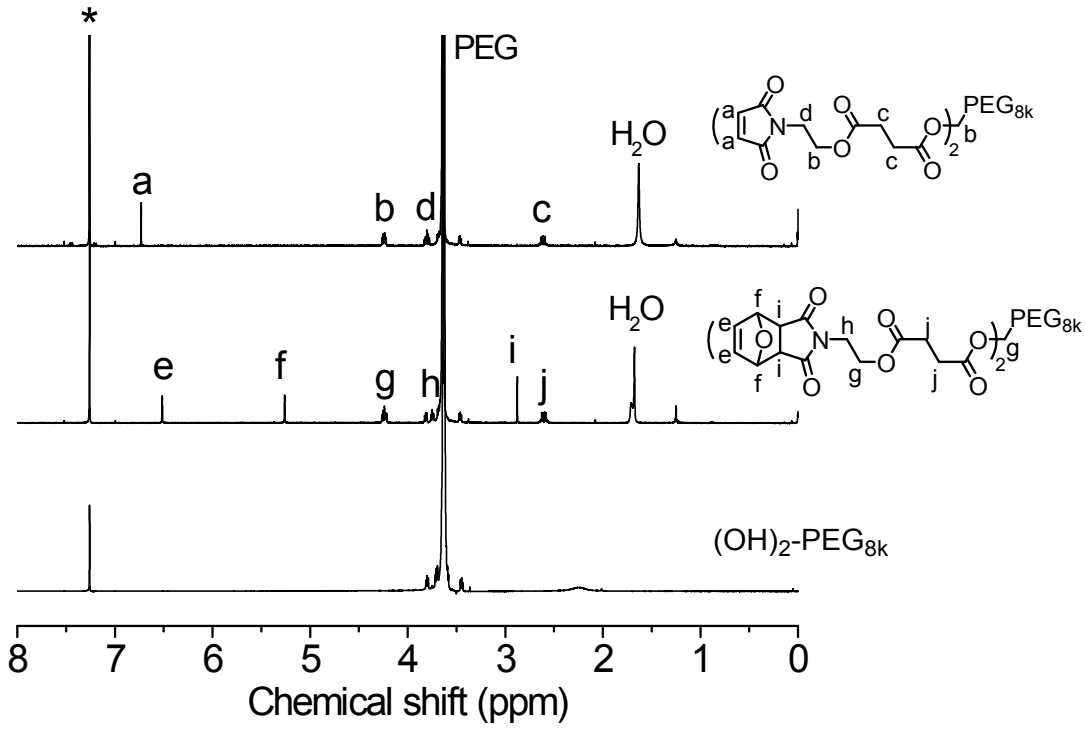


Figure S4 ^{1}H-NMR spectra of (a) $(OH)_2$-PEG_{8k}, (b) furan protected $(MI)_2$-PEG_{8k} and (c) $(MI)_2$-PEG_{8k}

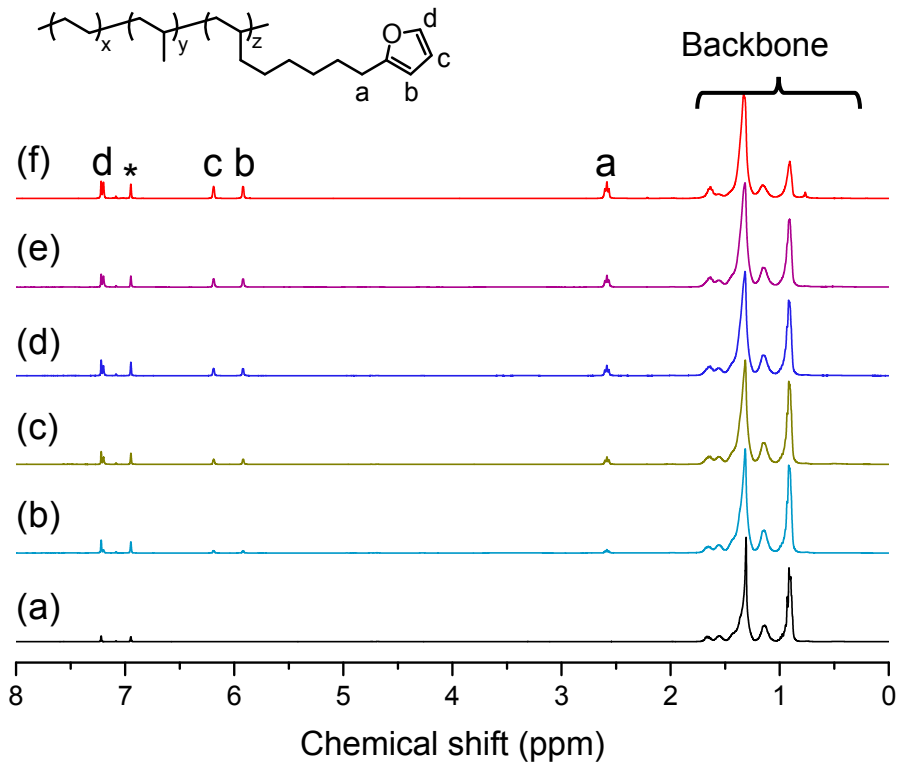


Figure S5 ^{1}H-NMR spectra of (a) E/P copolymer (run 1) and E/P/FO terpolymers containing (b) 1.4 mol%, (c) 3.3 mol%, (d) 4.6 mol%, (e) 5.5 mol%, (f) 10.7 mol% (solvent: 1,2-dichlorobenzene-d_4, 120 °C)

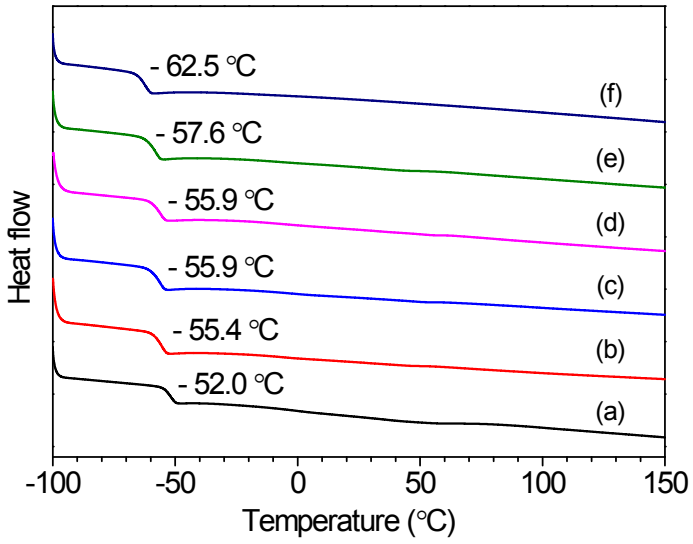


Figure S6 DSC curves of the (a) E/P copolymer (run 1in Table 1), E/P/FO terpolymers containing (b) 1.4 mol%, (c) 3.3 mol%, (d) 4.6 mol%, (e) 5.5 mol%, (f) 10.7 mol% of FO units (runs 2–6 in Table 1) with the feeding ratio of E/P = 1 in gas

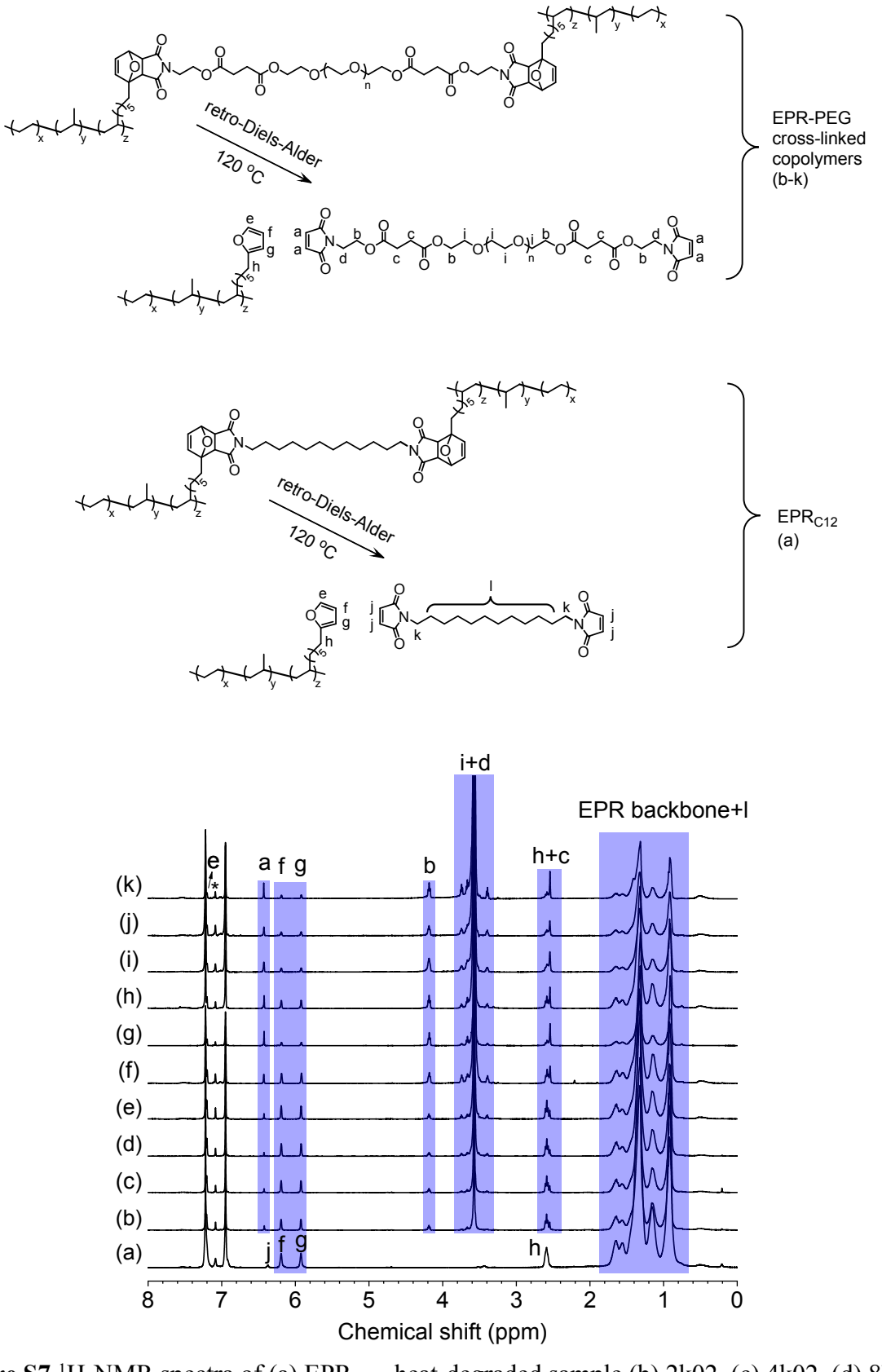


Figure S7 ^{1}H-NMR spectra of (a) EPR$_{C12}$, heat-degraded sample (b) 2k02, (c) 4k02, (d) 8k01, (e) 8k02, (f) 8k05, (g) 2k20, (h) 4k10, (i) 4k20, (j) 8k10 and (k) 8k20 in Table 2 at 120 °C for 5 min (solvent: 1,2-dichlorobenzene-d_4,120 °C)

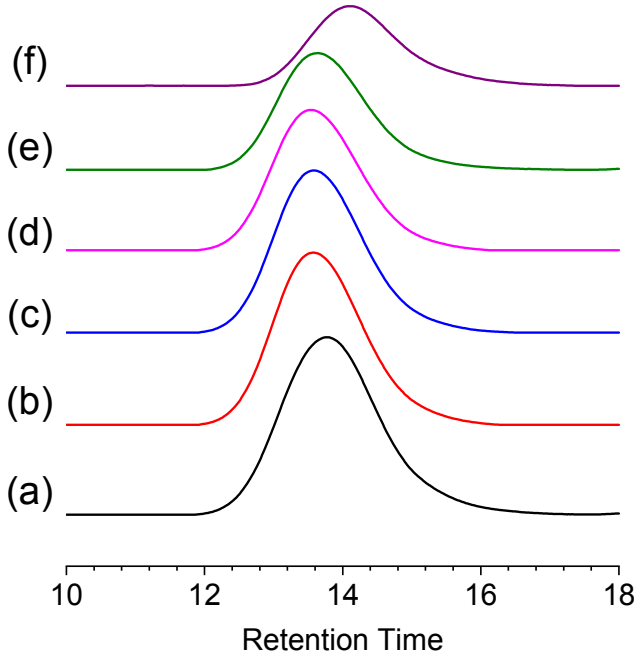


Figure S8 GPC curves of the (a) E/P copolymer (run 1in Table 1), E/P/FO terpolymers containing (b) 1.4 mol%, (c) 3.3 mol%, (d) 4.6 mol%, (e) 5.5 mol%, (f) 10.7 mol% of FO units (runs 2–6 in Table 1) with the feeding ratio of E/P = 1 in gas

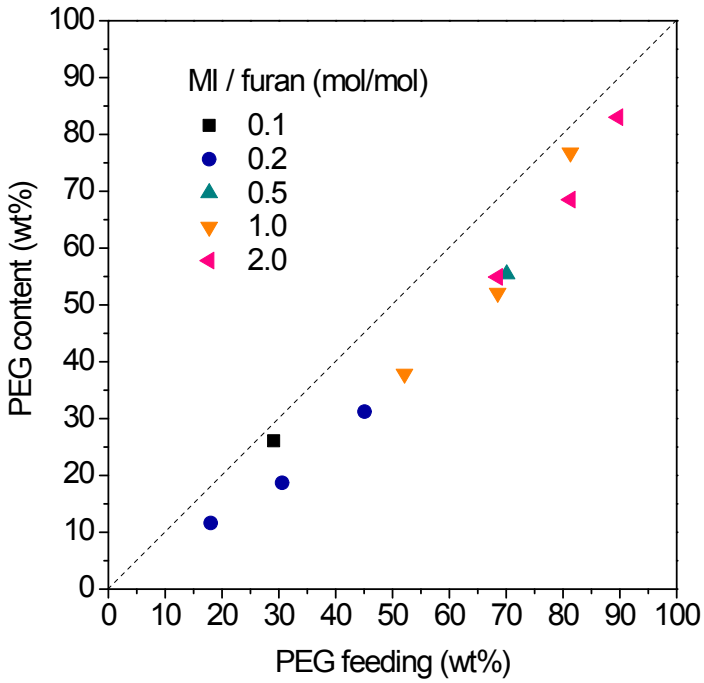


Figure S9 The relationship of the PEG feeding and incorporation in the DA reaction

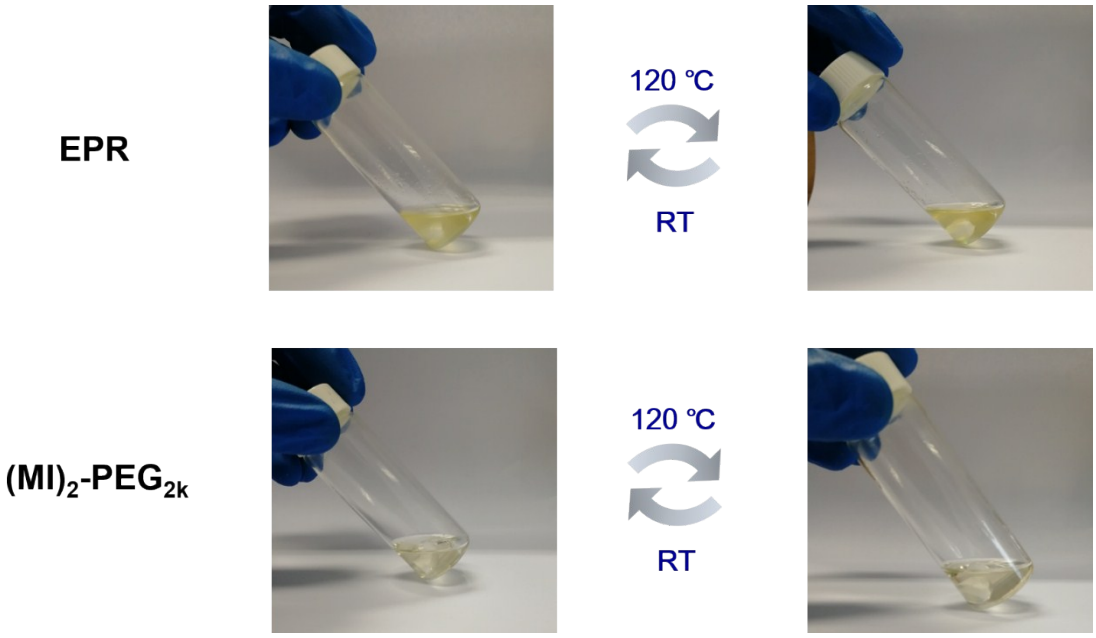


Figure S10 Images of EPR and $(MI)_2$-PEG_{2k} solutions at room temperature and 120 °C (5 wt% of polymer in 1,2-dichlorobenzene)

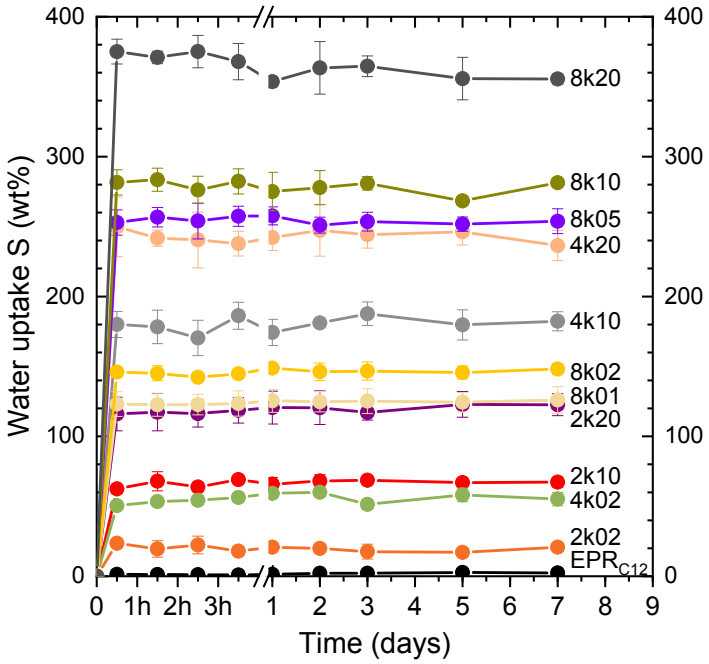


Figure S11 Swelling ratio as a function of time for EPR_{C12} and elastomer hydrogel samples in Table 2

Table S1 Tensile test results for elastomer hydrogels in dry and hydrogel forms

Samples	Strain at break, ε_b (%)	Stress at break, σ_b (Mpa)	Young's modulus, E (Mpa)
2k02	178.4±20.9	0.76±0.02	0.84±0.07
4k02	240.2±24.3	1.12±0.14	0.94±0.06
8k01	384.3±45.8	4.23±0.38	20.20±1.60
8k02	295.1±24.9	4.82±0.07	23.27±0.40
8k05	121.8±21.0	6.09±0.47	26.04±3.25
2k02(H)	212.7±13.8	0.78±0.02	0.65±0.03
4k02(H)	355.1±26.7	1.12±0.11	0.67±0.06
8k01(H)	436.4±3.3	0.90±0.12	0.58±0.05
8k02(H)	370.8±19.9	1.10±0.07	0.89±0.16
EPR_{C12}	375.2±5.2	0.90±0.01	0.42±0.03

Table S2 Effect of copolymer weight on the cytotoxicity of EPR-PEG copolymer 8k02 measured by MTT assay after 48 h incubation with MC3T3-L1 cells

Polymer dose (mL^{-1})	2 mg	4 mg	10 mg	20 mg	40 mg
Cell viability (%)	94.3±3.6	93.3±3.1	88.5±2.5	84.8±2.5	77.5±4.2

References

1. Duan, H.; Wang, Y.; Wang, L.; Min, Y.; Zhang, X.; Du, B. An Investigation of the Selective Chain Scission at Centered Diels–Alder Mechanophore under Ultrasonication. *Macromolecules* 2017, 50, 1353-1361.