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)$_2$PEG)

**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[5.2.1.0$^{2,6}$]dec-8-ene-3,5-dione was performed according to literature 1. 4-(2-Hydroxy-ethyl)-10-oxa-4-aza-tricyclo[5.2.1.0$^{2,6}$]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$_2$SO$_4$, the solvent was removed under reduced and the residue was recrystallized from ethanol to give a white crystal. $^1$H-NMR (400 MHz, CDCl$_3$, Figure 1c): $\delta = 6.51$ (2H, s, CH=CH, bridge protons), 5.26 (2H, s, -CHO, bridge-head protons), 4.26 (2H, t, NCH$_2$CH$_2$OC=O), 3.75 (2H, t, NCH$_2$CH$_2$OC=O), 2.88 (2H, s, CH=CH, bridge protons), 2.67–2.54 (4H, m, C=OCH$_2$CH$_2$C=OOH).
Figure S2 $^1$H-NMR spectra of (a) Maleic anhydride, (b) 4-(2-Hydroxy-ethyl)-10-oxa-4-aza-tricyclo[5.2.1.0$_{2,6}$]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 1 in 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 1 in 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$_{C_{12}}$ and elastomer hydrogel samples in Table 2
Table S1  Tensile test results for elastomer hydrogels in dry and hydrogel forms

<table>
<thead>
<tr>
<th>Samples</th>
<th>Strain at break, $\varepsilon_b$ (%)</th>
<th>Stress at break, $\sigma_b$ (Mpa)</th>
<th>Young’s modulus, $E$ (Mpa)</th>
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<tbody>
<tr>
<td>2k02</td>
<td>178.4±20.9</td>
<td>0.76±0.02</td>
<td>0.84±0.07</td>
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<tr>
<td>4k02</td>
<td>240.2±24.3</td>
<td>1.12±0.14</td>
<td>0.94±0.06</td>
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<tr>
<td>8k01</td>
<td>384.3±45.8</td>
<td>4.23±0.38</td>
<td>20.20±1.60</td>
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<tr>
<td>8k02</td>
<td>295.1±24.9</td>
<td>4.82±0.07</td>
<td>23.27±0.40</td>
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<tr>
<td>8k05</td>
<td>121.8±21.0</td>
<td>6.09±0.47</td>
<td>26.04±3.25</td>
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<tr>
<td>2k02(H)</td>
<td>212.7±13.8</td>
<td>0.78±0.02</td>
<td>0.65±0.03</td>
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<td>4k02(H)</td>
<td>355.1±26.7</td>
<td>1.12±0.11</td>
<td>0.67±0.06</td>
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<td>8k01(H)</td>
<td>436.4±3.3</td>
<td>0.90±0.12</td>
<td>0.58±0.05</td>
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<tr>
<td>8k02(H)</td>
<td>370.8±19.9</td>
<td>1.10±0.07</td>
<td>0.89±0.16</td>
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<td>EPR$_{C12}$</td>
<td>375.2±5.2</td>
<td>0.90±0.01</td>
<td>0.42±0.03</td>
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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

<table>
<thead>
<tr>
<th>Polymer dose (mL$^{-1}$)</th>
<th>2 mg</th>
<th>4 mg</th>
<th>10 mg</th>
<th>20 mg</th>
<th>40 mg</th>
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<tr>
<td>Cell viability (%)</td>
<td>94.3±3.6</td>
<td>93.3±3.1</td>
<td>88.5±2.5</td>
<td>84.8±2.5</td>
<td>77.5±4.2</td>
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</tbody>
</table>

References