Supporting Information

Thermally resistant thermadapt shape memory crosslinked polymers based on silyl ether dynamic covalent linkages for self-folding and self-deployable smart 3D structures

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Table S1 Gel fraction of EPSis in DMF at 150 °C for 24 h

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gel fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPSi-0.3</td>
<td>97.7±0.08</td>
</tr>
<tr>
<td>EPSi-0.5</td>
<td>98.4±0.09</td>
</tr>
<tr>
<td>EPSi-0.7</td>
<td>99.2±0.10</td>
</tr>
<tr>
<td>EPSi-0.9</td>
<td>99.4±0.06</td>
</tr>
</tbody>
</table>

Fig. S1 Structures of model compounds used in the study.

Fig. S2 $^1$H NMR spectrum of model compound 1.
Fig. S3 $^1$H NMR spectrum of model compound 2.

Fig. S4 $^1$H NMR spectrum of model compound 5.
Fig. S5 $^1$H NMR spectrum of model compound 6.

Fig. S6 $^1$H NMR spectra of model compounds mixture (a) and after holding at 160 °C for 1 h (b).
Fig. S7 Mass spectra of model compounds mixture of 5 and 6.

Fig. S8 Mass spectra of model compounds mixture of 5 and 6 after holding at 160 °C for 1 h.
Fig. S9 Multiple reconfiguration of EPSi-0.3 (a), EPSi-0.5 (b), EPSi-0.7 (c) and EPSi-0.9 (d).
Table S2 Integrated performances of thermadapt shape memory polymers (TASMPs) in literatures and this work.

<table>
<thead>
<tr>
<th>TASMP (sample name)</th>
<th>Dynamic bonds</th>
<th>$T_g$/$T_m$ (°C)</th>
<th>$T_{di}$ (°C)</th>
<th>Tensile properties</th>
<th>$R_f$ (%)</th>
<th>$R_s$ (%)</th>
<th>$R_{ret}$ (%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPSi-0.5</td>
<td>Hydroxyl silyl ether bonds</td>
<td>129.3</td>
<td>314</td>
<td>82.4 ± 1.3</td>
<td>8.0 ± 0.3</td>
<td>1864 ± 52</td>
<td>95.6</td>
<td>99.2</td>
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<tr>
<td>E51/SA/1%graphene (EP-1wt%)</td>
<td>Transesterification</td>
<td>48.3</td>
<td>348</td>
<td>22.9 ± 1.7</td>
<td>44</td>
<td>1232 ± 23.5</td>
<td>98</td>
<td>99</td>
</tr>
<tr>
<td>E51/SA (EP)</td>
<td>Transesterification</td>
<td>42.9</td>
<td>345</td>
<td>12.0 ± 0.8</td>
<td>~6</td>
<td>565.9 ± 10.1</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>EP/MHHPA/PGE (epoxy 3)</td>
<td>Transesterification</td>
<td>75</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>98</td>
<td>99</td>
</tr>
<tr>
<td>Eu-EP/SA (1:0.5) (R=1:0.5)</td>
<td>Transesterification</td>
<td>53</td>
<td>310</td>
<td>25</td>
<td>8.5</td>
<td>1400</td>
<td>91.8</td>
<td>~100</td>
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<tr>
<td>Poly(caprolactone) networks</td>
<td>Transesterification</td>
<td>~55</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>&gt;98</td>
<td>&gt;98</td>
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<tr>
<td>Polyanhydride networks (PAH/PCL PU)</td>
<td>Transesterification</td>
<td>~30</td>
<td>--</td>
<td>4-5</td>
<td>150-200</td>
<td>--</td>
<td>86-87</td>
<td>78-93</td>
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<tr>
<td>Epoxidized natural rubber/carbon nanodot (ENR/CD-35)</td>
<td>Transesterification</td>
<td>~40</td>
<td>--</td>
<td>17.9</td>
<td>452</td>
<td>1.5</td>
<td>&gt;98</td>
<td>&gt;98</td>
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<tr>
<td>Thermoset polyurethane</td>
<td>Transcarbamoylation</td>
<td>~41</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>98</td>
<td>99</td>
</tr>
<tr>
<td>System</td>
<td>Reaction</td>
<td>Tg/°C</td>
<td>ρ/g·cm⁻³</td>
<td>E⁻/kJ·mol⁻¹</td>
<td>E⁺/kJ·mol⁻¹</td>
<td>η/µPa·s</td>
<td>Tg/°C</td>
<td>ρ/g·cm⁻³</td>
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<tr>
<td>Thermoset polyurethane (PU-4) Transcarbamoylation</td>
<td>~80</td>
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<td>99.7</td>
<td>97.9</td>
<td>~98</td>
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<td>Thermoset polyurethane (PUU3) Transcarbamoylation</td>
<td>~40</td>
<td>--</td>
<td>~1.1</td>
<td>~520</td>
<td>--</td>
<td>95</td>
<td>95</td>
<td>~98</td>
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<td>Thermoset polyurethane (P1) Transcarbamoylation</td>
<td>~50</td>
<td>--</td>
<td>8.16±0.57</td>
<td>13.04±2.9</td>
<td>~98</td>
<td>&gt;94</td>
<td>&gt;94</td>
<td>&gt;98</td>
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<td>BGPP/FA/BM (DA0.2) Diels-Alder</td>
<td>35</td>
<td>--</td>
<td>--</td>
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<td>--</td>
<td>88.8</td>
<td>87.5</td>
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<td>-73, 75</td>
<td>--</td>
<td>15.3-18.5</td>
<td>600~890</td>
<td>Photo</td>
<td>Photo</td>
<td>--</td>
<td>[S12]</td>
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<tr>
<td>MDS-EPO Disulfide</td>
<td>41.4</td>
<td>268.8</td>
<td>10.9±2.2</td>
<td>0.60±0.17</td>
<td>1990±130</td>
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<td>100</td>
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<tr>
<td>Polysulfide networks (poly(S-PTMP)-51) Disulfide</td>
<td>36.4</td>
<td>252.9</td>
<td>~5</td>
<td>~15</td>
<td>--</td>
<td>Photo</td>
<td>Photo</td>
<td>--</td>
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<tr>
<td>Thermoset polyurethane (PU10) Diselenide</td>
<td>57</td>
<td>17</td>
<td>100</td>
<td>--</td>
<td>91</td>
<td>97</td>
<td>~90</td>
<td>[S15]</td>
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<td>PCL networks (PCL-6Indole) Reversible TAD Chemistry</td>
<td>50</td>
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<td>99</td>
<td>96-99</td>
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<td>Metallosupramolecular networks (CP2-Ni) Metal–ligand interactions</td>
<td>~50</td>
<td>--</td>
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<td>99</td>
<td>95</td>
<td>~98</td>
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</table>

a: Data not given in the reference.
References