Electronic Supplementary Information for

Dynamic-Covalent Nanostructures Prepared by Diels-Alder Reactions of Styrene-Maleic Anhydride-Derived Copolymers Obtained by Cascade Block Copolymerization

Abhijeet P. Bapat, a Jacob G. Ray, b Daniel A. Savin, b Emily A. Hoff, b Derek L. Patton, b Brent S. Sumerlin* a, c

a Department of Chemistry, Southern Methodist University, 3215 Daniel Avenue, Dallas, TX 75275-0314 USA. Fax: (214) 768-4089; Tel: (214) 768-8802; E-mail:bsumerlin@mail.smu.edu

b School of Polymers and High Performance Materials, The University of Southern Mississippi, Hattiesburg, Mississippi 39406, USA.

c Center for Drug Discovery, Design, & Delivery, Southern Methodist University, Dallas, TX, 75275, USA
**Fig. S1** (A) $^1$H and (B) $^{13}$C NMR spectra of P1 (red) after functionalization with furfurylamine to give P1f (yellow)
**Fig. S2** (A) SEC refractive index traces of P(S-alt-MAn)$_{20}$-b-PS$_{47}$ before (P2) (red line) and after (P2f) (yellow line) functionalization with furfurylamine (B) SEC refractive index traces of P(S-alt-MAn)$_{20}$-b-PS$_{81}$ before (P3) (red line) and after (P3f) (yellow line) functionalization with furfurylamine.
**Fig. S3** (a) Photographs of the solutions of P1 in THF with different amounts of furfurylamine after 22 h at 50 °C (The physically crosslinked gel obtained in the presence of 2 equiv. of furfurylamine is possibly a result of complexation between the pendant acid groups on the polymer backbone and the excess furfurylamine, leading to reduced solubility in 1,4-dioxane. Addition of dimethyl acetamide to the gel resulted in a clear solution), (d) SEC refractive index traces of P1 before (grey line), and after functionalization with furfurylamine [(1 equiv., red line) and (2 equiv., blue line)].
Fig. S4 a) Example of Gaussian multi-peak fitting analysis of the SEC trace of stars containing residual arms. b) Equation for calculation of % Arms based on the Gaussian multi-peak fitting analysis of the SEC traces.
Table S1 Typical results for synthesis of core-crosslinked stars and micelles by Diels-Alder reaction between 4,4’-bismaleimido diphenylmethane and the furan functional block copolymers P1f, P2f and P3f

| Polymer | $M_{n, arm}$<sup>a</sup> (g/mol) | $M_{w, star}$<sup>b</sup> (kg/mole) | Aggregation number ($N_{agg}$)<sup>c</sup> (arms/star) | $D_h$
<sup>d</sup> (nm) |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>P1f&lt;sup&gt;e&lt;/sup&gt;</td>
<td>7100</td>
<td>40300</td>
<td>5676</td>
<td>138</td>
</tr>
<tr>
<td>P2f&lt;sup&gt;f&lt;/sup&gt;</td>
<td>10,800</td>
<td>1500</td>
<td>139</td>
<td>29</td>
</tr>
<tr>
<td>P3f&lt;sup&gt;f&lt;/sup&gt;</td>
<td>14300</td>
<td>460</td>
<td>32</td>
<td>21</td>
</tr>
<tr>
<td>P3f&lt;sup&gt;g&lt;/sup&gt;</td>
<td>14300</td>
<td>2120</td>
<td>148</td>
<td>38</td>
</tr>
</tbody>
</table>

<sup>a</sup> Calculated by $^1$H NMR,  
<sup>b</sup> Determined by static light scattering,  
<sup>c</sup> Approximate aggregation number calculated by dividing $M_{w,star}$ by $M_{n,arm}$ (it should be noted that these values are approximate because the molecular weight of the arms were $M_n$ values determined by NMR and the molecular weight of the stars are $M_w$ values determined by light scattering).  
<sup>d</sup> Determined by dynamic light scattering,  
<sup>e</sup> [polymer] = 30 mg/mL and furan: maleimide = 1:2.6,  
<sup>f</sup> [polymer] = 50 mg/mL and furan: maleimide ≈ 1:2,  
<sup>g</sup> Core-crosslinked micelles in toluene at [polymer] = 30 mg/mL and furan: maleimide ≈ 1:2
**Fig. S5** Results for core-crosslinked star formation via Diels-Alder reactions between \( \text{P1f} \) and 4,4’-bismaleimido diphenylmethane \{[\text{P1f}] = 30, 50, and 100 mg/mL in 1,4-dioxane (furan:maleimide= 1:2.6 equiv., temperature = 50°C)\} (a) kinetics of the star formation reaction at [\text{P1f}] = 30 mg/mL and 50 mg/mL (b) SEC refractive index traces showing the progress of star formation at \([\text{P1f}] = 30\) mg/mL (c) SEC refractive index traces showing the progress of star formation at \([\text{P1f}] = 50\) mg/mL (d) crosslinked gel obtained at \([\text{P1f}] = 100\) mg/mL (i), unchanged gel after addition of solvent and mixing for 15 days at room temperature (ii), and clear solution obtained after decrosslinking of the gel via the retro Diels-Alder reaction (iii)
**Fig. S6** Results for core-crosslinked star formation via Diels-Alder reaction between P2f and 4,4'-bismaleimido diphenylmethane ([P2f] = 30, 50, and 100 mg/mL in 1,4-dioxane (furan:maleimide = 1:2 equiv., temperature = 50°C)) (a) kinetics of the star formation reaction at [P2f] = 30 mg/mL and 50 mg/mL (b) SEC refractive index traces showing the progress of star formation at [P2f] = 30 mg/mL (c) SEC refractive index traces showing the progress of star formation at [P2f] = 50 mg/mL (d) crosslinked gel obtained at [P2f] = 100 mg/mL (i), unchanged gel after addition of solvent and mixing for 15 days at room temperature (ii), and clear solution obtained after decrosslinking of the gel via the retro Diels-Alder reaction (iii)
Fig. S7 AFM height and phase images of the stars obtained via the Diels-Alder reaction of 4,4′-bismaleimido diphenylmethane and (a) P2f and (b) P1f (stars were formed at [P2f] = 50 mg/mL and [P1f] = 30 mg/mL in 1,4-dioxane).
**Fig. S8** Solution size distributions of stars obtained at $[\text{P3f}]=30$ (green), 50 (red), and 100 mg/mL (blue) compared to the unimers (grey) after ~195 h of Diels-Alder reaction in presence of 4,4’-bismaleimido diphenylmethane crosslinker (furan:maleimide = 1:2.1 equiv.)