Electronic Supplementary Material (ESI) for Polymer Chemistry

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

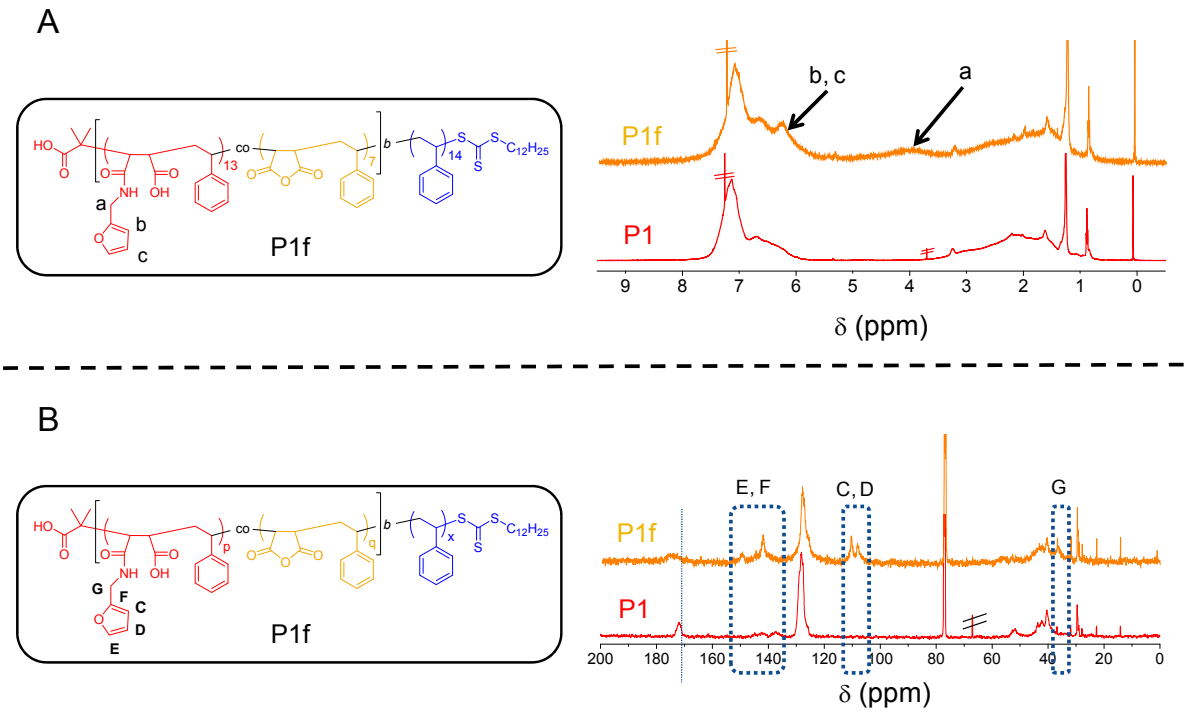


Fig. S1 (A) ^{1}H and (B) ^{13}C NMR spectra of **P1** (red) after functionalization with furfurylamine to give **P1f** (yellow)

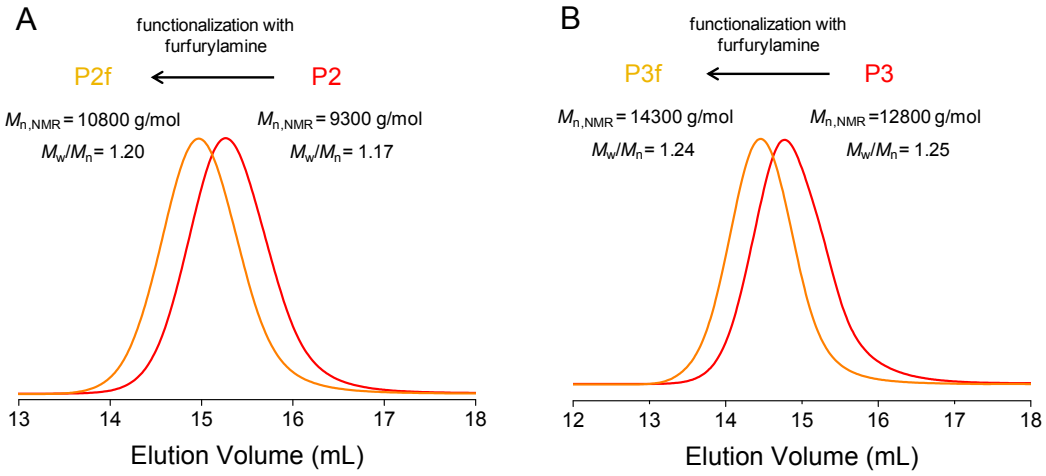


Fig. S2 (A) SEC refractive index traces of P(S-*alt*-MAn)$_{20}$-*b*-PS$_{47}$ before (**P2**) (red line) and after (**P2f**) (yellow line) functionalization with furfurylamine (B) SEC refractive index traces of P(S-*alt*-MAn)$_{20}$-*b*-PS$_{81}$ before (**P3**) (red line) and after (**P3f**) (yellow line) functionalization with furfurylamine

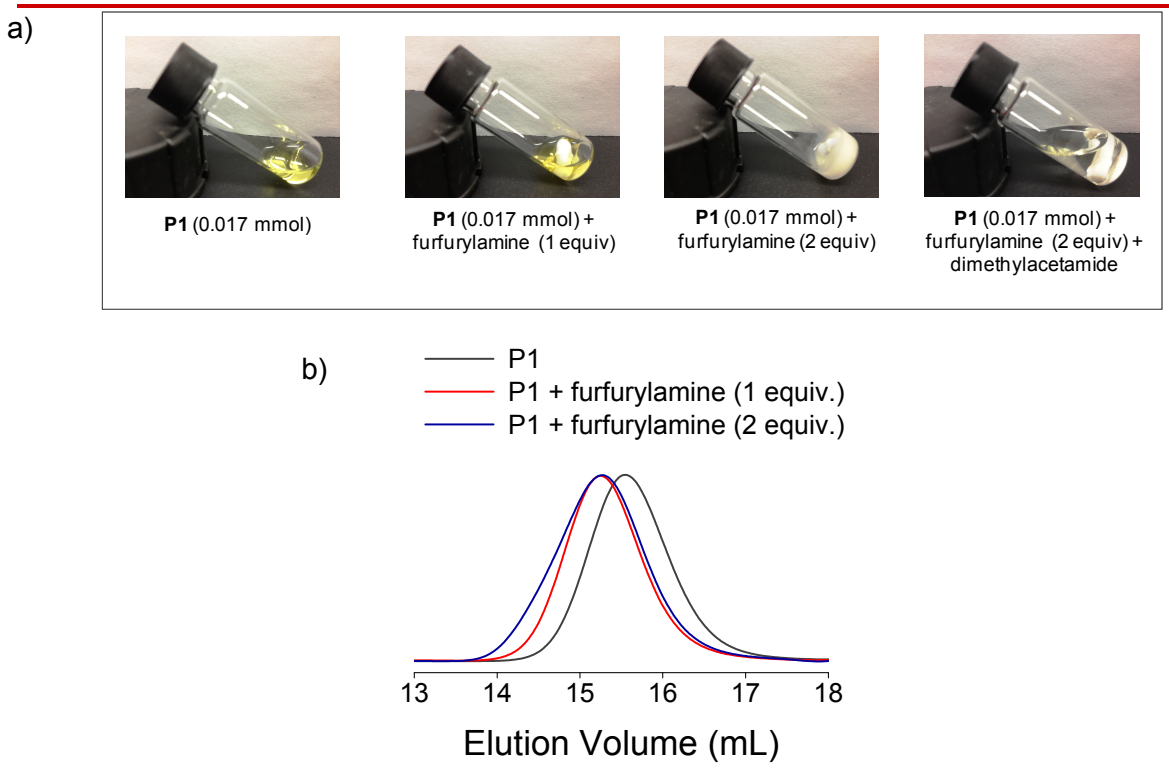
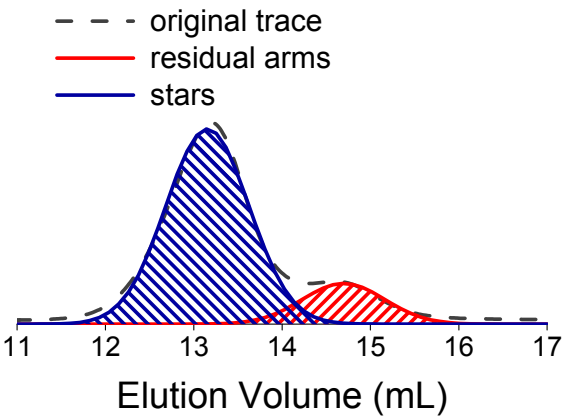


Fig. S3 (a) Photographs of the solutions of **P1** in THF with different amounts of furfurylamine after 22 h at 50 °C (The physically crosslinked gel obtained in the presence of 2 equiv. of furfurylamine is possibly a result of complexation between the pendant acid groups on the polymer backbone and 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)].

a)



b)

$$\% \text{ Arms} = \frac{\text{Area}_{\text{Arms}}}{\text{Area}_{\text{Arms}} + \text{Area}_{\text{Stars}}} \times 100$$

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	$M_{n,\,arm}$[a] (g/mol)	$M_{w,\,star}$[b] (kg/mole)	Aggregation number (N_{agg})[c] (arms/star)	D_h[d] (nm)
P1f[e]	7100	40300	5676	138
P2f[f]	10,800	1500	139	29
P3f[f]	14300	460	32	21
P3f[g]	14300	2120	148	38

[a]Calculated by ^{1}H NMR, [b]Determined by static light scattering, [c]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). [d]Determined by dynamic light scattering, [e][polymer] = 30 mg/mL and furan:maleimide = 1:2.6, [f][polymer] = 50 mg/mL and furan:maleimide ≈ 1:2, [g]Core-crosslinked micelles in toluene at [polymer] = 30 mg/mL and furan:maleimide ≈ 1:2

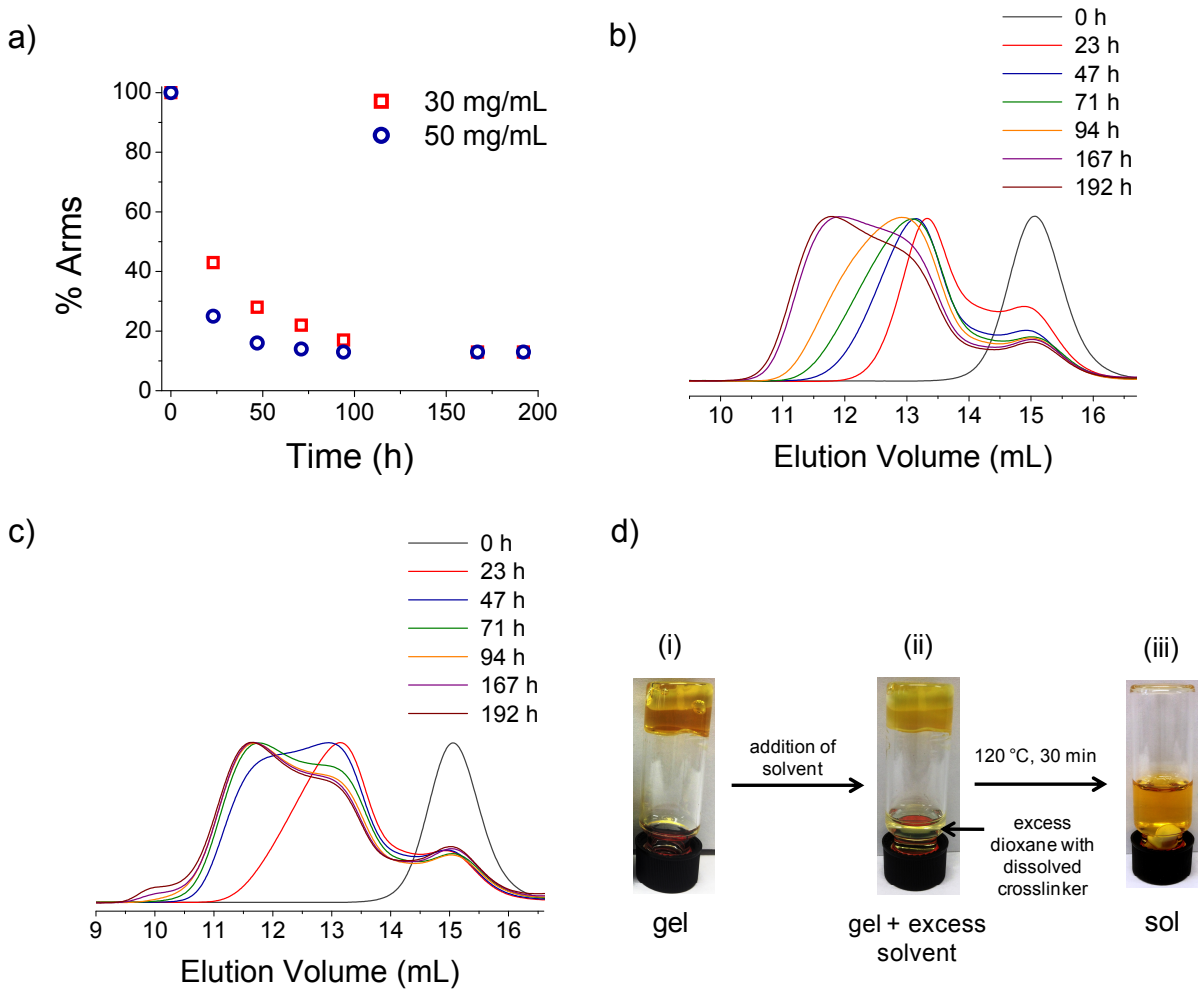


Fig. S5 Results for core-crosslinked star formation via Diels-Alder reactions between **P1f** and 4,4′-bismaleimido diphenylmethane {[**P1f**] = 30, 50, and 100 mg/mL in 1,4-dioxane (furan:maleimide= 1:2.6 equiv., temperature = 50°C)} (a) kinetics of the star formation reaction at [**P1f**] = 30 mg/mL and 50 mg/mL (b) SEC refractive index traces showing the progress of star formation at [**P1f**] = 30 mg/mL (c) SEC refractive index traces showing the progress of star formation at [**P1f**] = 50 mg/mL (d) crosslinked gel obtained at [**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)

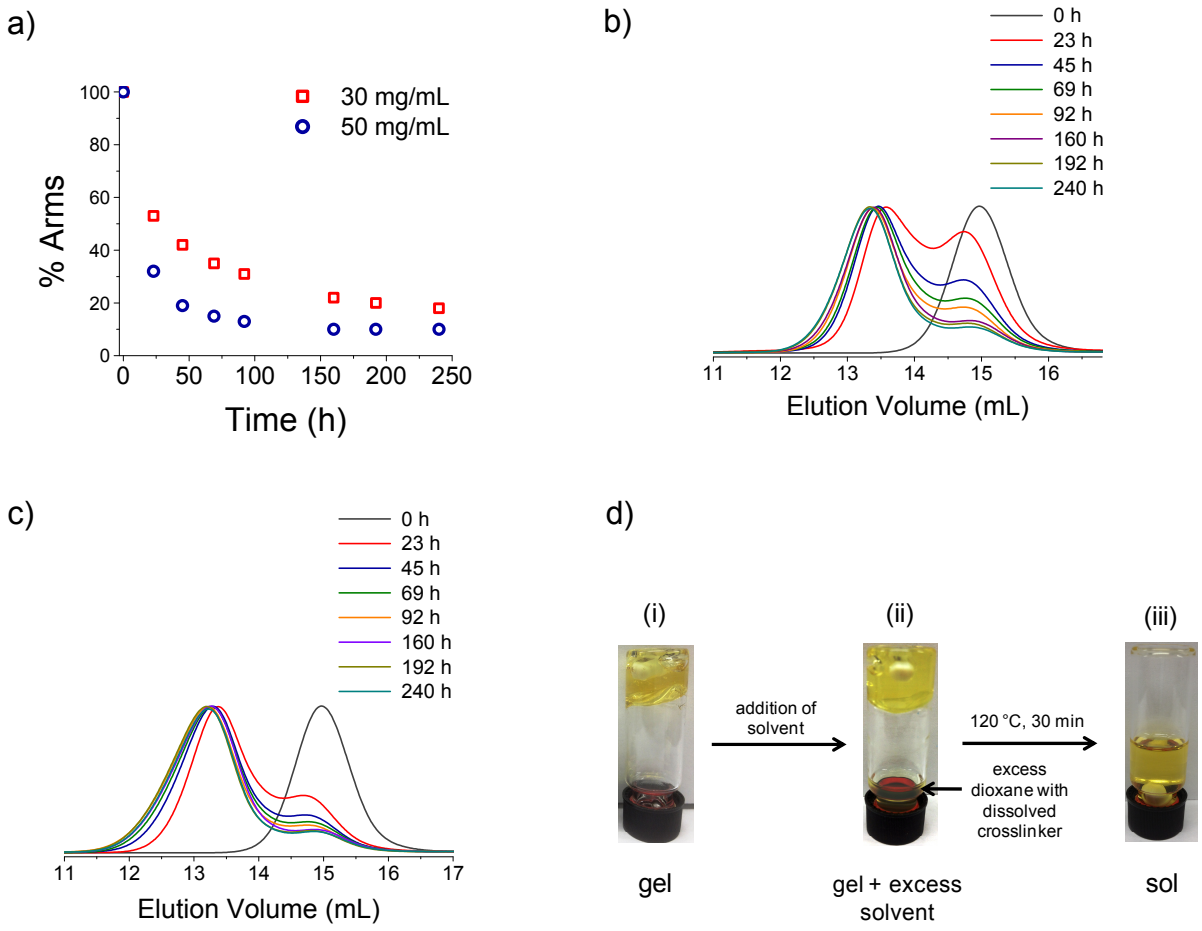


Fig. S6 Results for core-crosslinked star formation via Diels-Alder reaction between **P2f** and 4,4′-bismaleimido diphenylmethane {[**P2f**] = 30, 50, and 100 mg/mL in 1,4-dioxane (furan:maleimide = 1:2 equiv., temperature = 50°C)} (a) kinetics of the star formation reaction at [**P2f**] = 30 mg/mL 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)

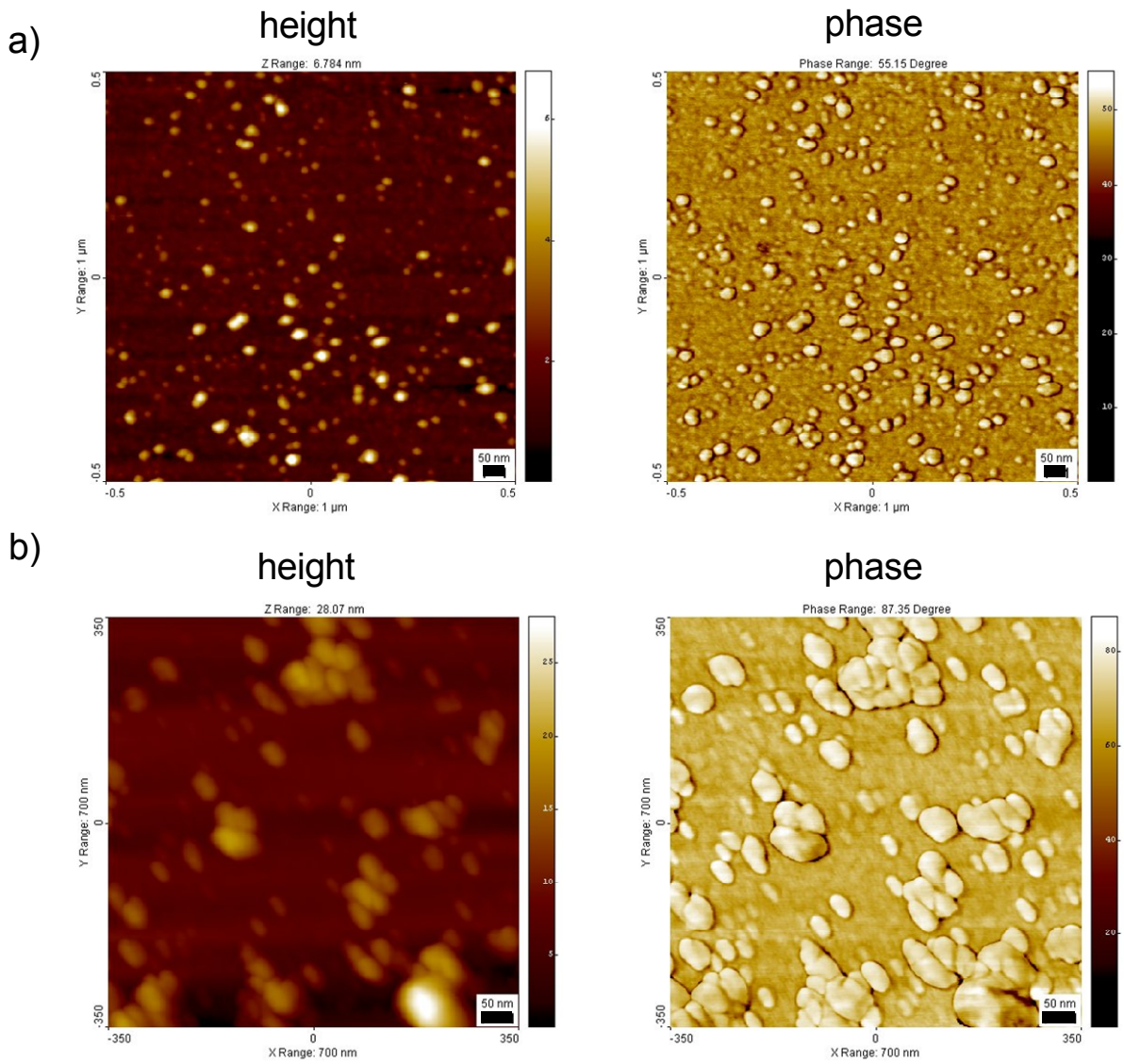


Fig. S7 AFM height and phase images of the stars obtained *via* the Diels-Alder reaction of 4,4´-bismaleimido diphenylmethane and (a) **P2f** and (b) **P1f** (stars were formed at [**P2f**] = 50 mg/mL and [**P1f**] = 30 mg/mL in 1,4-dioxane).

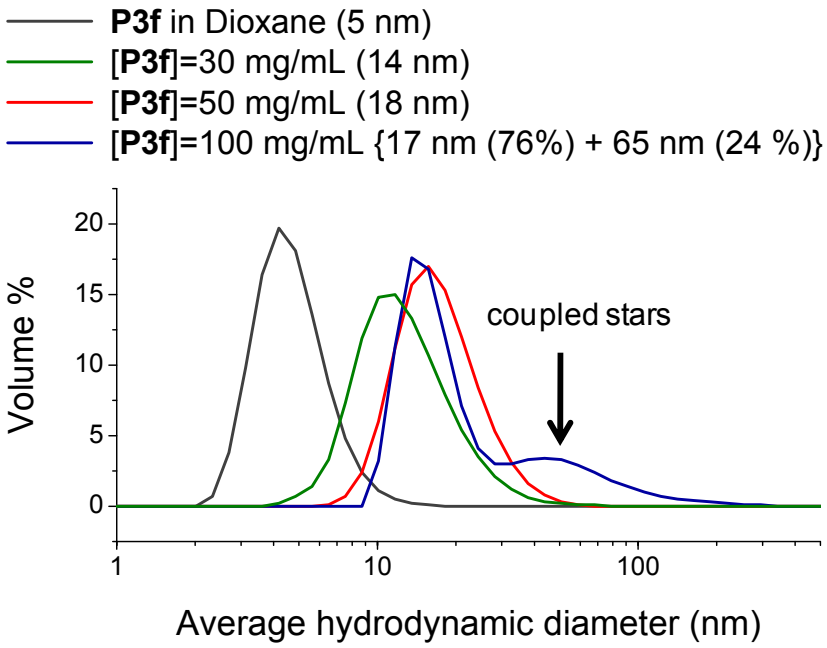


Fig. S8 Solution size distributions of stars obtained at [**P3f**] = 30 (green), 50 (red), and 100 mg/mL (blue) compared to the unimers (grey) after ~195 h of Diels-Alder reaction in presence of 4,4´-bismaleimido diphenylmethane crosslinker (furan:maleimide = 1:2.1 equiv.)