

**Supporting Information for**

**Covalent Stabilization of Inverse Bicontinuous Cubic Structures of Block Copolymer**

**Bilayers by Photodimerization of Indene Pendant Groups of Polystyrene Hydrophobic**

**Blocks**

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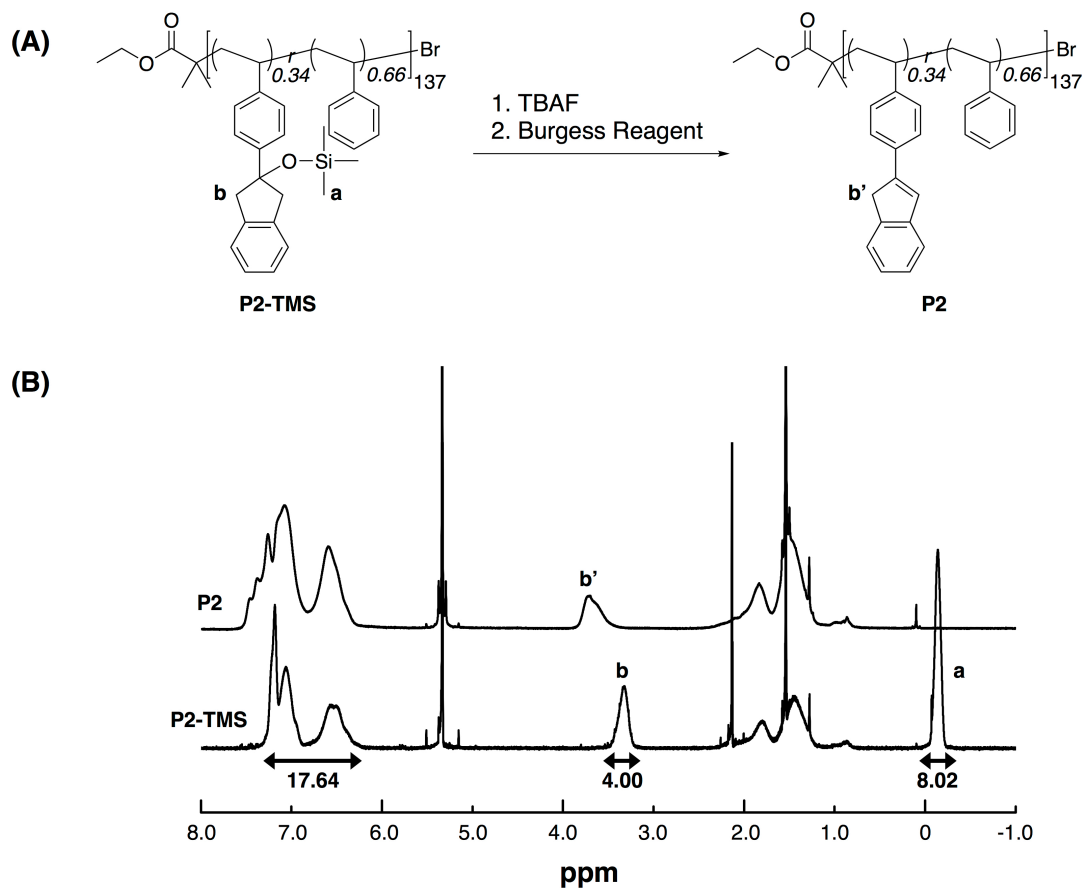
1. A coincidence of the composition ratio of 1-TMS and styrene to the feed ratio

- Feed ratio

[Initiator]: [1-TMS]: [Styrene] = 1: 72 (30%): 168 (70%)

- $DP_n$  ratio

1-TMS: Styrene = 46 (34%): 91 (66%)

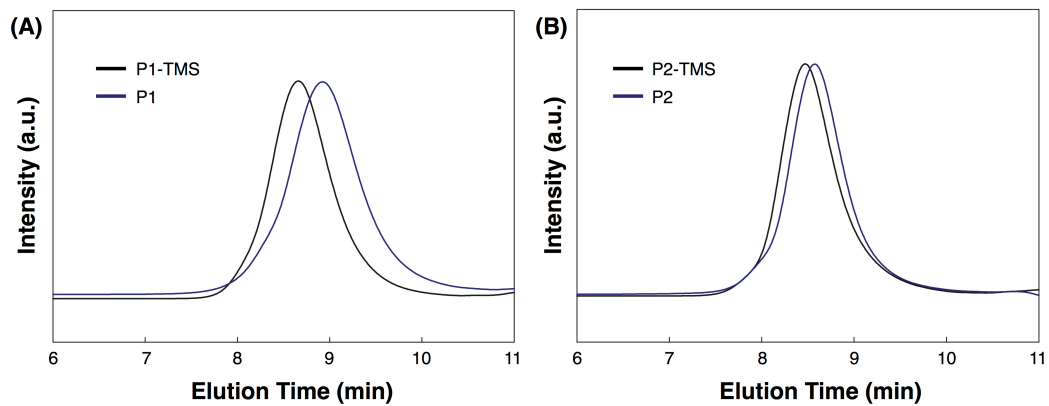


**Figure S1.** (A) A scheme for post-modification of **P2-TMS** to **P2**. (B)  $^1\text{H}$  NMR spectra of **P2-TMS** and **P2**. The  $DP_n$  ratio was calculated based on the **P2-TMS** spectrum.

## 2. GPC analysis of P1-TMS, P2-TMS, P1 and P2

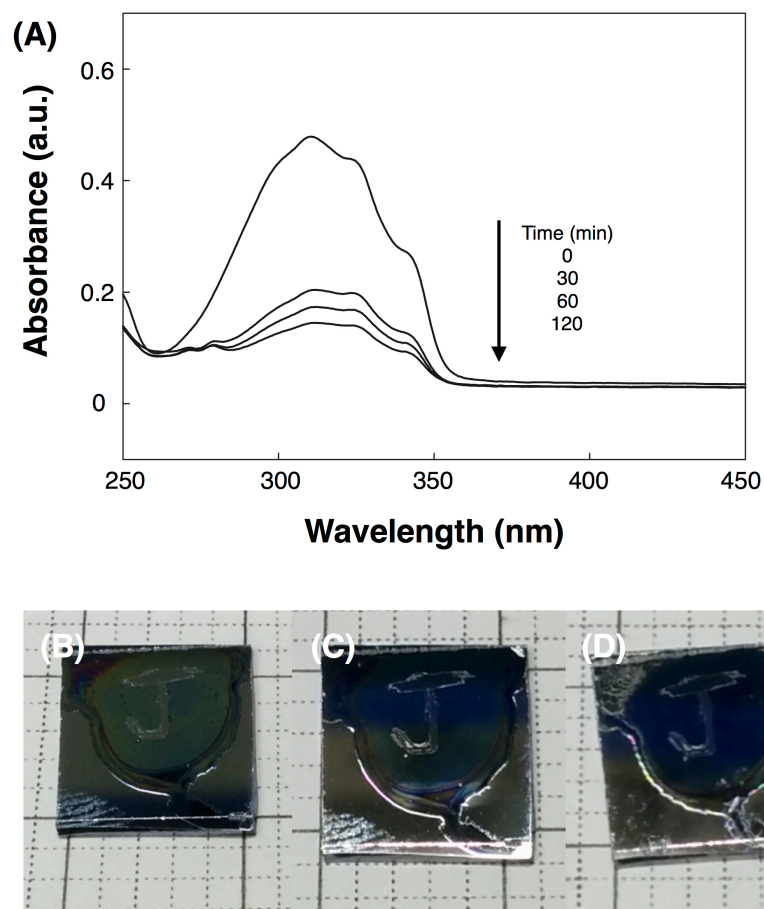
**Table S1.** Molecular weight ( $M_n$ ) and polydispersity index ( $\mathcal{D}$ ) of **P1-TMS**, **P2-TMS**, **P1** and **P2**

Sample	$M_n$ (kg mol <sup>-1</sup> )	$\mathcal{D}$
<b>P1-TMS</b>	17.9	1.34
<b>P1</b>	12.1	1.50
<b>P2-TMS</b>	23.8	1.36
<b>P2</b>	21.6	1.38



**Figure S2.** GPC spectra of (A) **P1-TMS**, **P1** and (B) **P2-TMS**, **P2**.

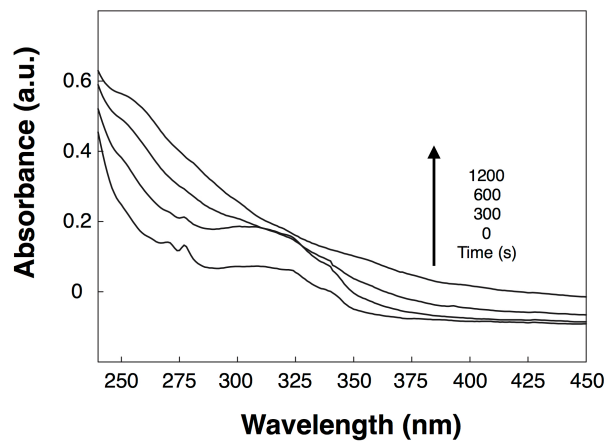
### 3. Cross-linking of film of P1



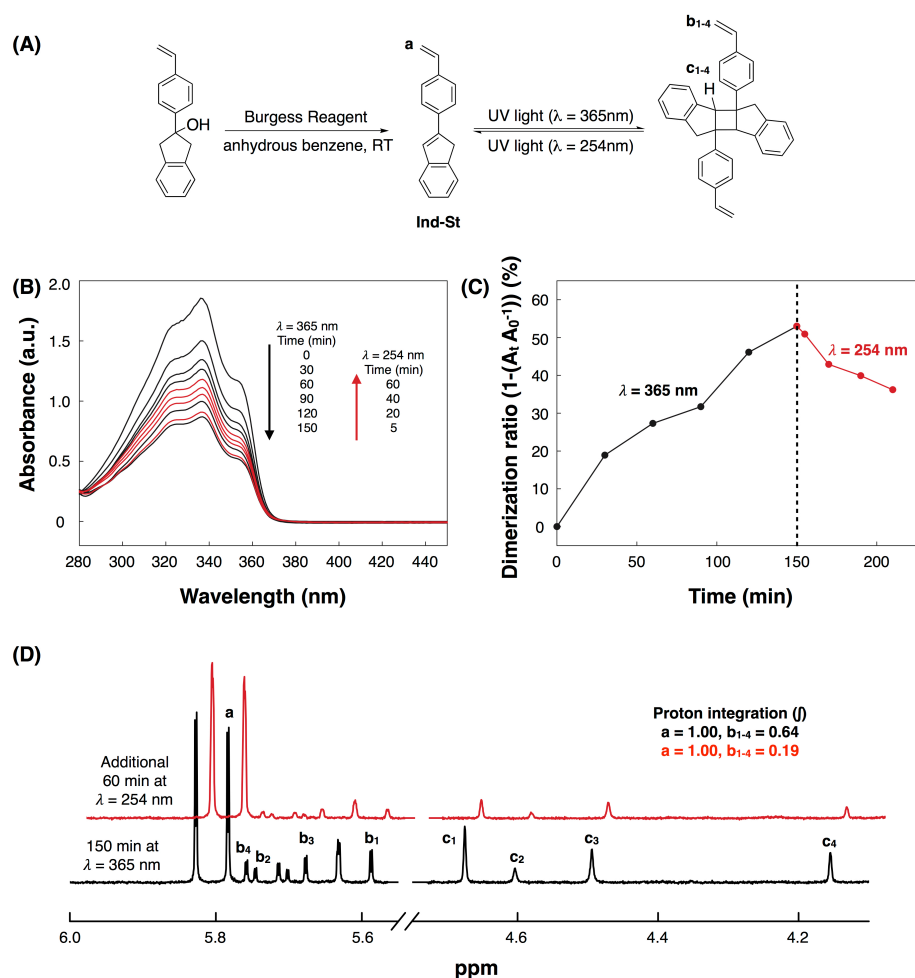
**Figure S3.** (A) UV-Vis spectra of polymer film of **P1** spin-coated onto square quartz plate (2 cm x 2 cm) at irradiation of UV light ( $\lambda > 300$  nm, 200 W) for different exposure time. (B-D) Photographs of polymer film of **P1** spin-coated onto silicon wafer (1 cm x 1 cm) with scratch. (B) Polymer film of **P1** before and (C) after 2 h of UV light irradiation. (D) Cross-linked polymer film of **P1** after soaking in THF for 1 h.



4. Short-wavelength UV light ( $\lambda = 254$  nm) exposure to cross-linked **P1** solution & demonstration of [2 + 2]-cycloaddition and retro-cyclization of indenylstyrene model compound



**Figure S4.** UV-Vis spectra of cross-linked **P1** in  $\text{CH}_2\text{Cl}_2$  at short-wavelength UV light ( $\lambda = 254$  nm, 6 W) irradiation for different exposure times.



**Figure S5.** (A) Schematic procedures for preparation of a model compound 4-indenylstyrene (**Ind-St**) and its [2 + 2]-cycloaddition at long-wavelength UV light ( $\lambda = 365\text{nm}$ ) and retro-cyclization of indene dimers at short-wavelength UV light ( $\lambda = 254\text{ nm}$ ). (B) UV-Vis spectra of **Ind-St** in benzene ( $1\text{ mg mL}^{-1}$ ) with irradiation of long-wavelength UV light (black) and short-wavelength UV light (red), sequentially, for different exposure times. (C) Plot of the UV exposure time against the dimerization ratio ( $1 - (A_t/A_0)^{-1}$ ), where  $A_0$  and  $A_t$  are the absorbance values at  $337\text{ nm}$  at time 0 and  $t$ , respectively. The dimerization ratio at  $t = 150\text{ min}$  was  $53.0\%$  and  $t = 210\text{ min}$  was  $36.2\%$ . (D)  $^1\text{H}$  NMR spectra of **Ind-St** solution after irradiation of long-wavelength UV light (black) and short-wavelength UV light (red), sequentially. “b<sub>1-4</sub>” and “c<sub>1-4</sub>” are caused by 4 different isomers of indene dimers.<sup>1</sup> The dimerization ratio calculated by the proton integration ( $(\int b)/(\int a + \int b)^{-1}$ ) was  $39.0\%$  at  $t = 150\text{ min}$  and was  $16.0\%$  at  $t = 210\text{ min}$ .

## 5. A coincidence of the composition ratio of indenylstyrene in the hydrophobic block and stability of the self-assembled structures

**Table S2.** Characterization of additional polymers containing indene species

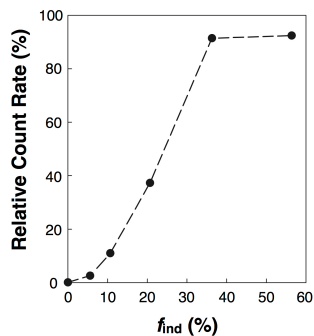
Sample	Initiator	$DP_n$ (St) <sup>a</sup>	$DP_n$ (Ind-St) <sup>a</sup>	$f_{\text{Ind}}$ (%) <sup>a</sup>	$f_{\text{PEG}}$ (%) <sup>b</sup>	$M_n$ (kg mol <sup>-1</sup> ) <sup>1</sup> H NMR <sup>a</sup>	$M_n$ (kg mol <sup>-1</sup> ) GPC <sup>c</sup>	$\bar{D}$ GPC
<b>P1S</b>	(PEG550) <sub>3</sub>	169	10	5.6	8.1	22.0	25.0 <sup>e</sup>	1.12
<b>P2S</b>	(PEG550) <sub>3</sub>	175	21	10.7	7.2	24.6	21.7 <sup>e</sup>	1.09
<b>P3S</b>	(PEG550) <sub>3</sub>	126	33	20.7	7.7	23.0	20.5	1.08

<sup>a</sup>Degree of polymerization ( $DP_n$ ), indenylstyrene ratio of hydrophobic block ( $f_{\text{Ind}}$ ) and  $M_n$  were calculated from <sup>1</sup>H NMR integration of deprotected polymers (**P-OH**). <sup>b</sup>The molecular weight ratio of the PEG domain ( $f_{\text{PEG}}$ ) to that of the hydrophobic block (1650 g mol<sup>-1</sup> for (PEG550)<sub>3</sub> initiator). <sup>c</sup>GPC data were measured from deprotected polymers (**P-OH**).

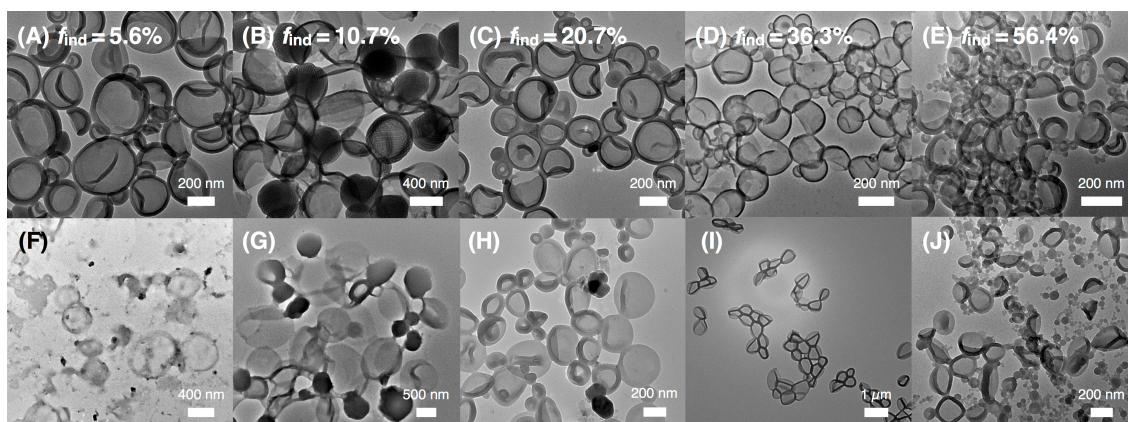
**Table S3.** DLS count rates of cross-linked polymer vesicles with various indenylstyrene ratio

Sample	$f_{\text{Ind}}$ (%)	Count rate ( $\times 10^3$ Kcps) <sup>a</sup>		Relative count rate THF/Water (%)
		diluted in water	diluted in THF	
<b>P1S</b>	5.6	106.6	2.8	2.6
<b>P2S</b>	10.7	134.2	14.7	11.0
<b>P3S</b>	20.7	80.2	29.9	37.3
<b>P6</b>	36.3	49.0	44.8	91.4
<b>P5</b>	56.4	50.0	46.2	92.4

<sup>a</sup>Same amount of cross-linked vesicles were diluted in water and THF respectively.

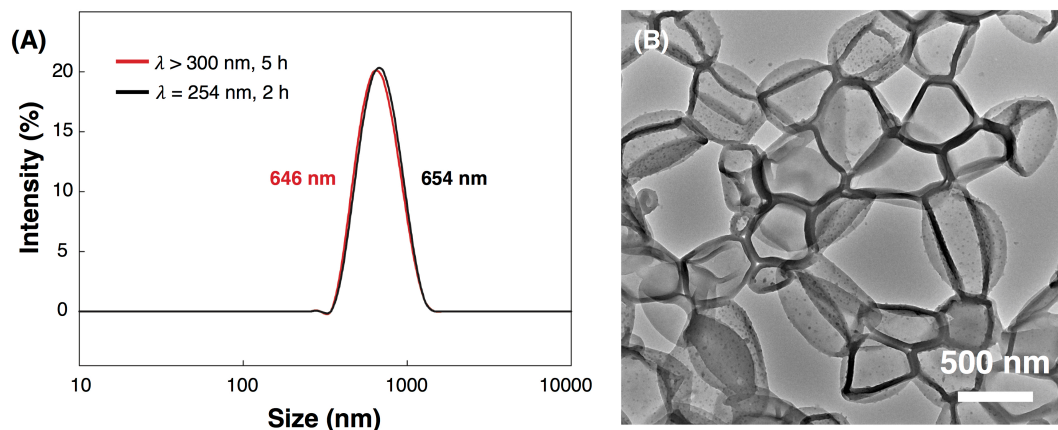


**Figure S6.** Plot of  $f_{ind}$  vs. relative count rate. Critical content of indenylstyrene in the hydrophobic block for decent cross-linking was around 30%.



**Figure S7.** (A-E) TEM images of non-cross-linked vesicles of (A) **P1S** ( $f_{ind} = 5.6\%$ ), (B) **P2S** ( $f_{ind} = 10.7\%$ ), (C) **P3S** ( $f_{ind} = 20.7\%$ ), (D) **P6** ( $f_{ind} = 35.3\%$ ) and (E) **P5** ( $f_{ind} = 56.4\%$ ). (F-J) TEM images of cross-linked vesicles of (F) **P1S**, (G) **P2S**, (H) **P3S**, (I) **P6** and (J) **P5** after changing the dispersion solvent to THF.

## 6. Short-wavelength UV light ( $\lambda = 254$ nm) exposure to cross-linked vesicles of P4



**Figure S8.** (A) Dynamic light scattering size plots of the self-assembled structures of **P4** exposed to long-wavelength UV light ( $\lambda > 300$  nm, 5 h) in a tetrahydrofuran (THF) solution (red) and sequentially exposed to short-wavelength UV light ( $\lambda = 254$  nm, 2 h) in a THF solution (black). (B) TEM image of vesicles of **P4** exposed to short-wavelength UV light after changing the dispersion solvent to THF.

## Reference

- (1) Wolff, T.; Schmidt, F.; Volz, P. Regioselectivity and Stereoselectivity in the Photodimerization of Rigid and Semirigid Stilbenes. *J. Org. Chem.* **1992**, *57*, 4255-4262.