

## Supporting Information

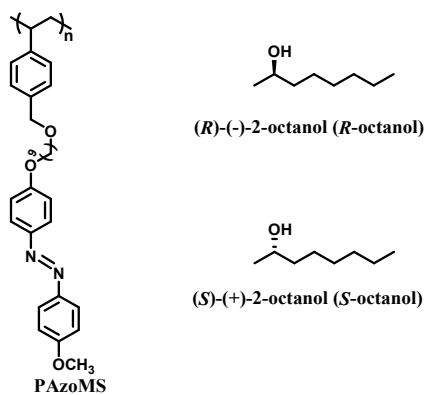
# Construction of Photoresponsive Polymer Particles with Supramolecular Helicity from Achiral Monomer by Helix-Sense-Selective Polymerization

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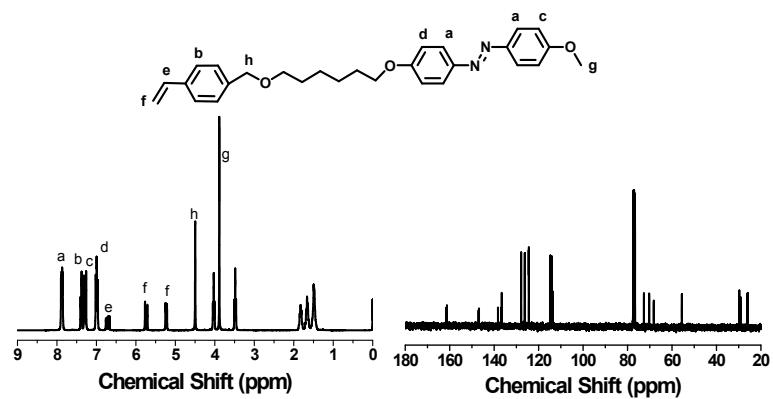
Zhu

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**Scheme S1.** Chemical structures of PAzoMS, (*R*)-(-)-2-octanol and (*S*)-(+)-2-octanol.



**Fig. S1.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of AzoMS measured in CDCl<sub>3</sub>.

**Table S1.** Effects of Solvent Mixture and Polymerization Time on Formation of Microspheres.

S-Octanol as Chiral Additive.<sup>a</sup>

Entry	S-Octanol/EtOH <sup>b</sup>	Time (h)	Yield <sup>c</sup> (%)	M <sub>n</sub> <sup>d</sup> (g/mol)	Particle diam <sup>e</sup> (nm)	g <sub>CD</sub> <sup>f</sup>
P-1S	0.05/2.95	24	79.3	24300	1530	0.00065
P-2S	0.10/2.90	24	76.8	23600	1390	0.00093
P-3S	0.30/2.70	24	72.3	23900	1150	0.00118
P-4S	0.50/2.50	24	75.1	32000	980	0.00066
P-5S	0.30/2.70	6	75.7	19600	590	0.00041
P-6S	0.30/2.70	12	71.8	21200	720	0.00045
P-7S	0.30/2.70	18	71.9	22900	980	0.00073
P-8S	0.30/2.70	30	72.5	25200	1160	0.00061
P-9S	0.30/2.70	36	78.2	28900	1200	0.00031

<sup>a</sup> Polymerization conditions: AzoMS, 20 mg/mL; AIBN, 0.23 mg/mL; PVP, 1 mg/mL; Temperature, 70 °C.

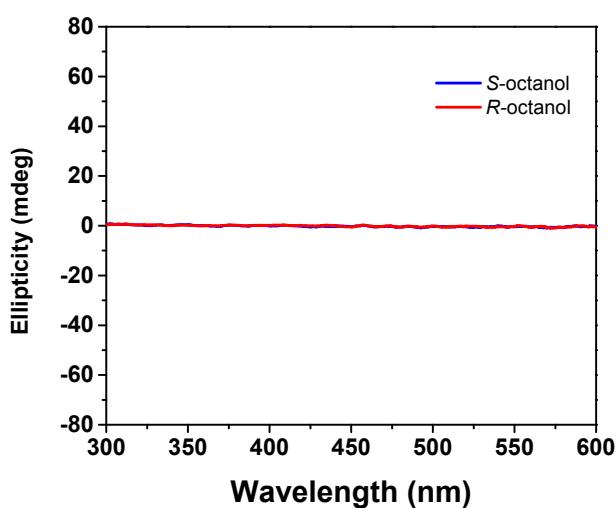
<sup>b</sup> Volume ratio of octanol and EtOH; Total solvent volume: 3 mL.

<sup>c</sup> Determined gravimetrically.

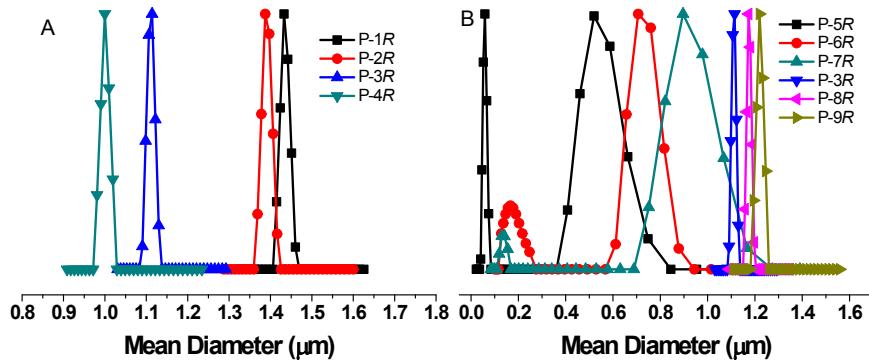
<sup>d</sup> Determined by GPC according to PS standards in THF.

<sup>e</sup> Mean diameters of particles in EtOH measured by DLS.

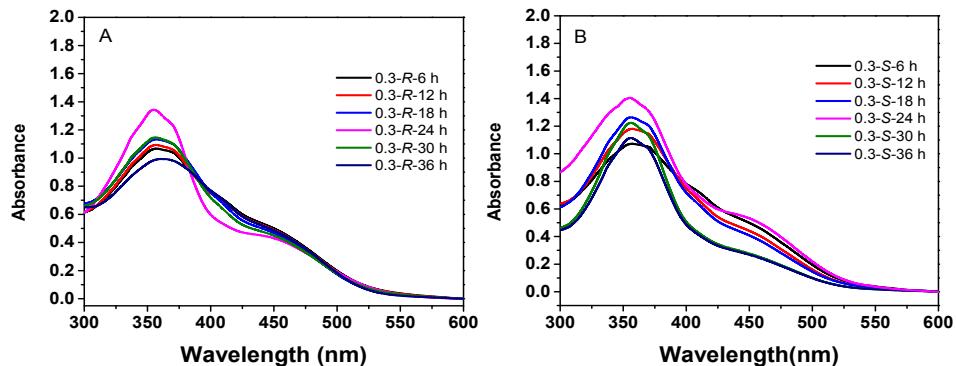
<sup>f</sup> g<sub>CD</sub> values at 360 nm.



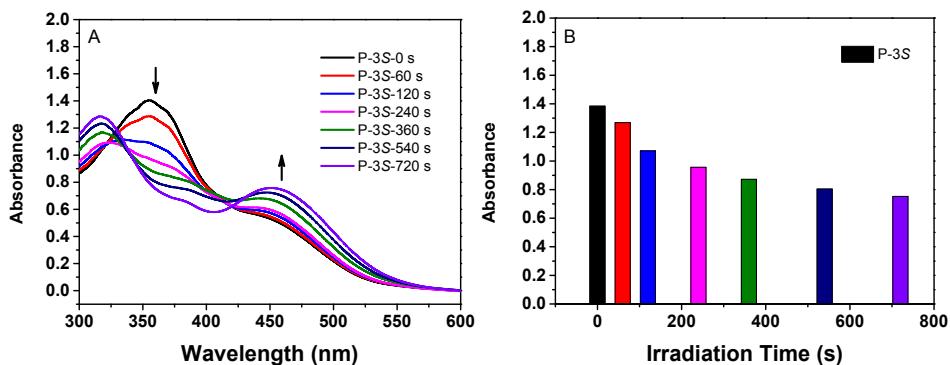
**Fig. S2.** CD spectra of chiral octanol in ethanol solution.



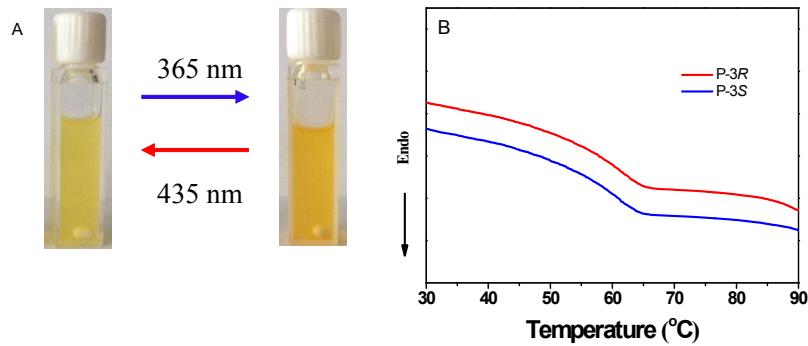
**Fig. S3.** DLS curves of Azo-OAPPs with (A) different *R*-octanol/EtOH volume fractions and (B) different polymerization time. The Azo-OAPPs are taken from Table 1.



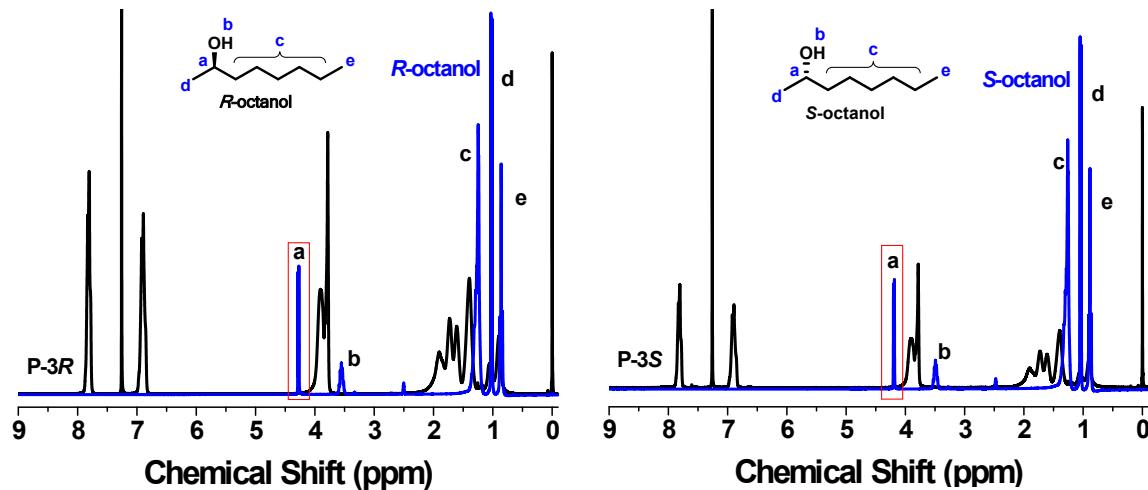
**Fig. S4.** UV-vis spectra of Azo-OAPPs with different polymerization time in ethanol dispersion.



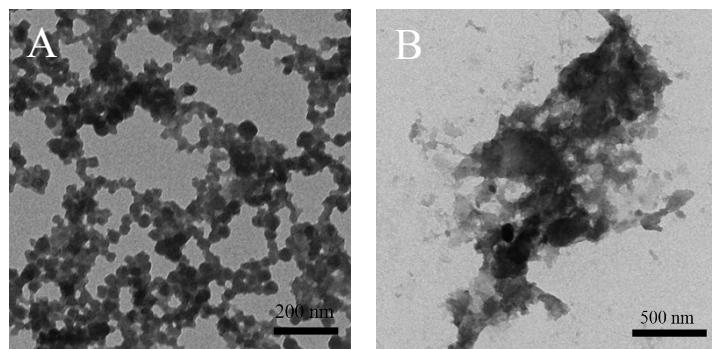
**Fig. S5.** (A) UV-vis spectra of P-3S Azo-OAPPs upon 365 nm light irradiation with different time intervals in ethanol dispersion. (B) UV-vis values of (A) at 360 nm.



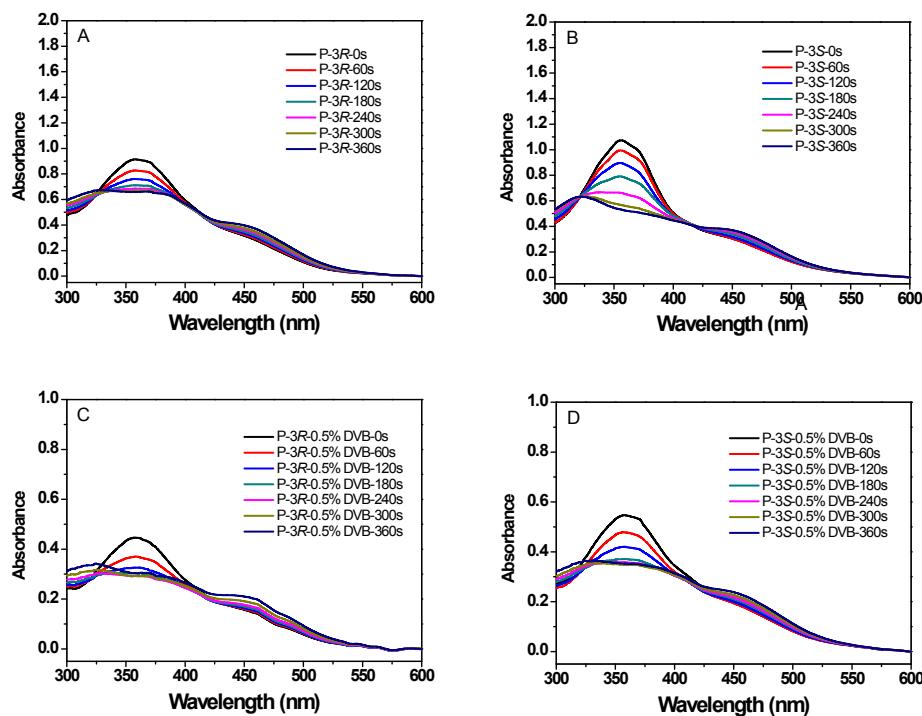
**Fig. S6.** (A) The color change of P-3R Azo-OAPPs dispersion in the process of photoisomerization. (B)  $T_g$  analysis of P-3R/3S Azo-OAPPs. P-3R/3S are taken from Table 1 and Table S1.



**Fig. S7.**  $^1\text{H}$  NMR spectra of P-3R/3S and R-/S-octanol.



**Fig. S8.** TEM images of cross-linked Azo-OAPPs. (A) P-3R with 0.5 wt % DVB (B) P-3R with 1.0 wt % DVB.



**Fig. S9.** UV-vis spectra of (A) P-3R (B) P-3S (C) P-3R-0.5% DVB (D) P-3S-0.5% DVB Azo-OAPPs upon 365 nm light irradiation in ethanol dispersion.