Self-assembly of an azobenzene-containing polymer prepared by multi-component reaction: supramolecular nanospheres with photo-induced deformation properties

Shuai Wang, Ning Zhang, Xiaopeng Ge, Yingbo Wan, Xiaohong Li, Li Yan, Yijun Xia and Bo Song*

Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, The Key Lab of Health Chemistry and Molecular Diagnosis of Suzhou, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, P. R. China. Tel: +86 (512) 65882507; E-mail: songbo@suda.edu.cn

^{1}H NMR result of MCP-azo-OH

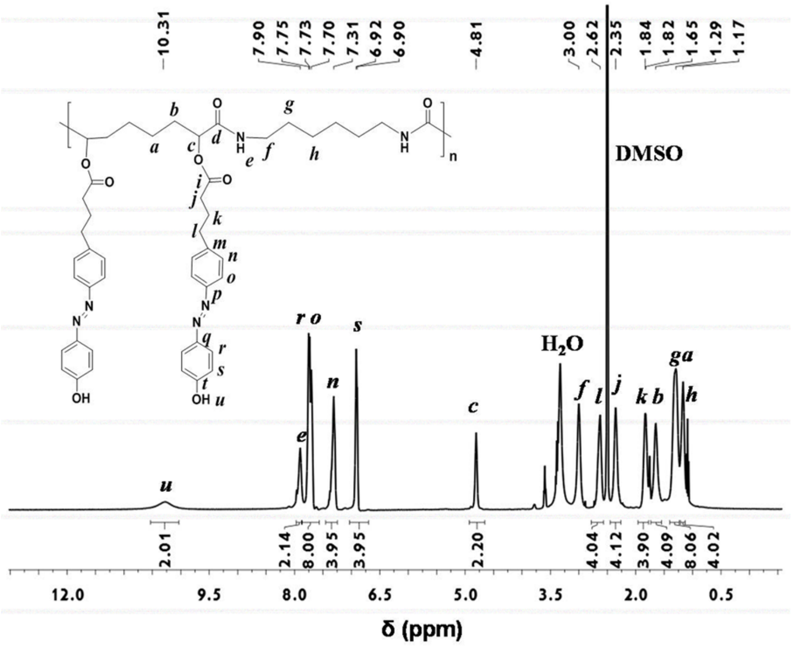

Fig. S1 600MHz ^{1}H NMR spectra of MCP-azo-OH in DMSO-d_6

The determination of aggregation concentration of MCP-azo-OH in THF

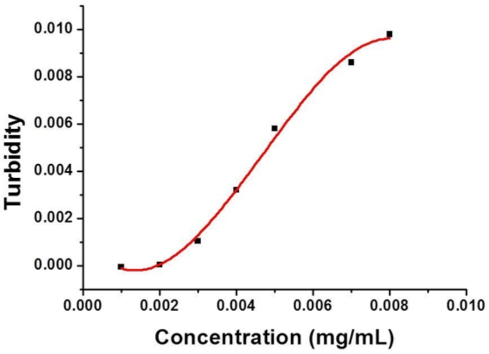

Fig. S2 Plot of the turbidity at 600 nm versus the concentration of the MCP-azo-OH in THF.

As shown in Fig. S2, the aggregation concentration has been determined by measuring the scattering of MCP-azo-OH solution in THF. And a critical value of aggregation is about 0.02 mg/mL, which indicates that THF is a selective solvent for MCP-azo-OH.

DLS result of the MCP-azo-OH in THF (0.5 mg/mL)

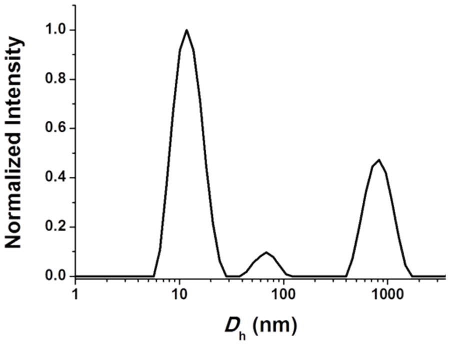

Fig. S3 The hydrodynamic diameter (*D_h*) distribution of the nanospheres in THF with the concentration of 0.5 mg/mL. The polydispersity index (PDI) is 0.490.

2D-NMR results of MCP-azo-OH

All the 2D-NMR spectra were collected at 25 ˚C on an Agilent Direct-Drive II 600MHz spectrometer equipped with four broad-band rf channels and a 5 mm ^{1}H-^{19}F/^{15}N-^{31}P pulse field gradient probe.

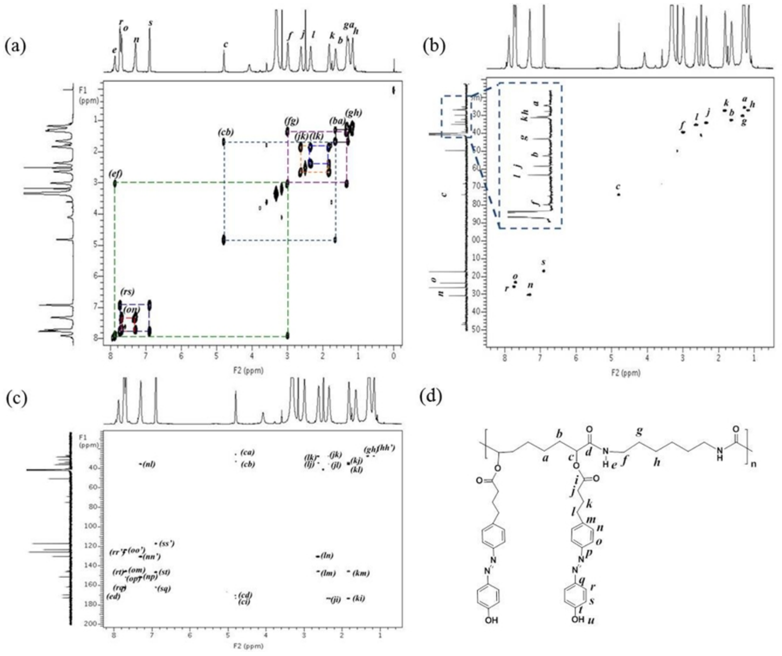

Fig. S4 2D-NMR spectra (a) gCOSY, (b) gHSQC, (c) gHMBC and (d) the corresponding molecular structure of MCP-azo-OH in DMSO-d_6

^{1}H-^{1}H gCOSY 2D-NMR. The ^{1}H-^{1}H gCOSY (gradient Correlation Spectroscopy) experiment was performed with the standard Agilent sequence. This was done with a 9.6 kHz spectral width, 0.15 s acquisition time, 1 s relaxation delay, and 8.4 µs 90° pulse width; a total of 8 transients were averaged for each 2 × 256 increments using the states method of phase sensitive detection in f1. Processing was done with shifted sine bell weighting functions in both dimensions and zero-filling to a 4096 × 4096 data matrix prior to Fourier transformation.

^{1}H{^{13}C} gHSQC 2D-NMR. The standard ^{1}H{^{13}C} gHSQC (gradient Heteronuclear Single Quantum Coherence spectroscopy) sequence was applied (while ^{1}H and ^{13}C are the observed and indirectly detected nuclei, respectively). Experiments were performed based on 90° pulse widths of 8.4 and 8.6 µs for ^{1}H and ^{13}C, respectively. The ^{1}H dimension had a spectral width of 9.6 kHz and the ^{13}C dimension had a spectral width of 25.6 kHz, acquisition time of 0.15 s, and 1 s relaxation delay; a total of 8 transients were averaged for each 2 × 256 increments using the States method[1] of phase sensitive detection in f1. The data were zero-filled to 4096 × 2048 and weighted with sine bell and shifted sine bell functions prior to Fourier transformation.

^{1}H{^{13}C} gHMBC 2D-NMR. The standard ^{1}H{^{13}C} gHMBC (gradient Heteronuclear Multiple Bond Correlation spectroscopy) sequence was applied (while ^{1}H and ^{13}C are the observed and indirectly detected nuclei, respectively). Experiments were performed based on 90° pulse widths of 8.4 and 8.6 μs for ^{1}H and ^{13}C, respectively. The ^{1}H dimension had a spectral width of 7.8 kHz and the ^{13}C dimension had a spectral width of 36.2 kHz, acquisition time of 0.15 s, and 1 s relaxation delay; a total of 8 transients were averaged for each 2 × 256 increments using the States method of phase sensitive detection in f1. The data were zero-filled to 4096 × 4096 and weighted with sine bell and shifted sine bell functions prior to Fourier transformation.

The size of the nanospheres remains as it forms when further increase the stirring rate after preparation in water

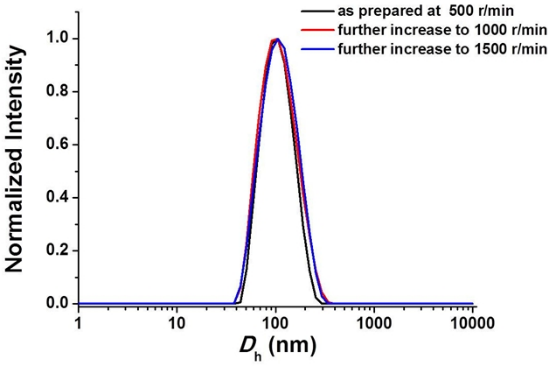

Fig. S5 D_h distributions of the nanospheres as prepared at 500 r/min, and further increase to 1000 r/min and 1500 r/min.

DLS results for MCP-azo-OH nanospheres in THF and water

Table S1. Preparation conditions and DLS results for MCP-azo-OH nanoparticles in THF

C (mg/ml)	D_h (nm)	PDI
0.10	265	0.212
0.05	187	0.141
0.01	138	0.316

The samples were prepared by stirring the solution of MCP-azo-OH with different concentrations at room temperature for at least 72 h.

Table S2. Preparation Conditions and DLS Results for MCP-azo-OH Nanoparticles in water

stirring rate (r/min)	D_h (nm)	PDI
0	164	0.113
500	116	0.105
1000	88	0.115
1500	75	0.147

The initial concentration of MCP-azo-OH in THF is 0.5 mg/ml. The samples were prepared by dropping the THF suspension into water at different stirring rates.

The irradiation induced deformation of the nanospheres is irreversible

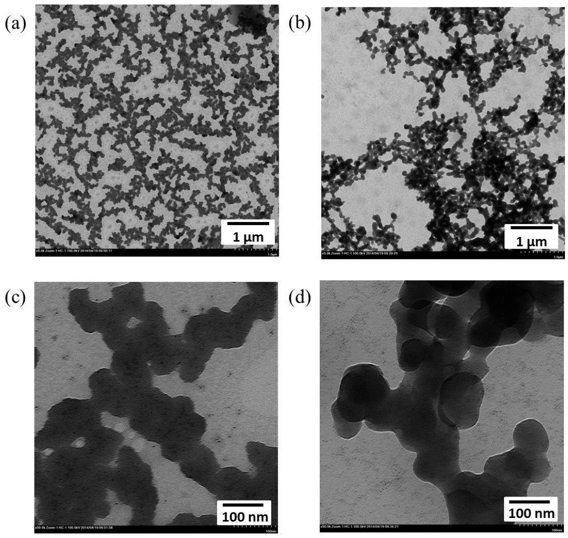

Fig. S6 TEM images of the nanospheres after being irradiated with UV light (365 nm, 40 mW·cm^{-2}, 25 min) (a) & (c), and subsequently irradiated with visible light (450 nm, 40 mW·cm^{-2}, 35 min) (b) & (d). The spheres were prepared by dropping the THF suspension (0.5 mg/mL) into water at the stirring rate of 1000 r/min, and then casted onto the copper net.

Heating to 40 °C has no effect to the morphology of the nanospheres

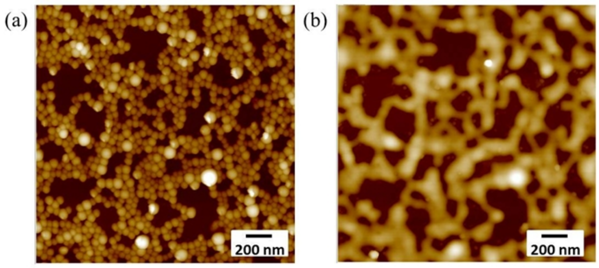

Fig. S7 AFM images of the nanospheres processed by heating (a) and irradiation (b) on the same piece of substrate. The spheres were prepared by dropping the THF suspension (0.5 mg/mL) into water at the stirring rate of 1500 r/min, and casted onto silicon substrate. The substrate was heated to 40 ˚C and kept for 1 h. The irradiation was carried out with 365 nm UV light with power of 20 mW·cm^{-2} for 10 min.

The hydrogen bonds still exist after irradiation

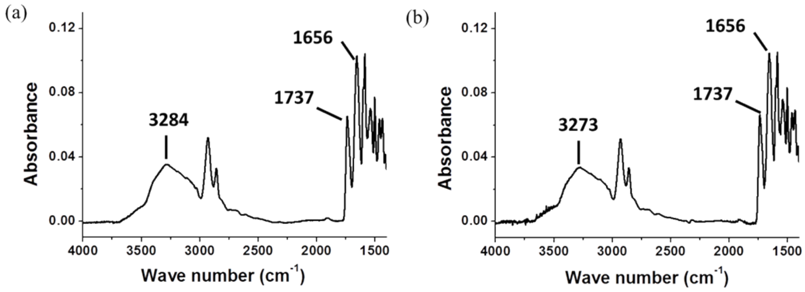

Fig. S8 FTIR spectra of the nanospheres processed before (a) and after irradiation (b). The spheres were prepared by dropping the THF suspension into water, and casted onto CaF_2 substrate. The irradiation was carried out with 365 nm UV light with power of 20 mW·cm^{-2} for 30 min.

Reference:

1. D. J. States, R. A. Haberkorn, D. J. Ruben, *J. Magn. Reson.*, 1982, **48**, 286.