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Photoinduced Deformation of Hollow Nanospheres Formed by the Self-Assembly of Amphiphilic Random Copolymers and Small Azo-Molecules

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The preparation and characterization of *free*-PMMA$_{42}$-*stat*-P4VP$_{58}$ and *raft*-PMMA$_{45}$-*stat*-P4VP$_{55}$

The copolymer *free*-PMMA$_{42}$-*stat*-P4VP$_{58}$ was obtained via free radical reactionas the following: 4-Vinylpyridine (10.0 mL, 94.1 mmol), MMA (6.2 mL, 76.0 mmol), AIBN (1.0 g, 6.1 mmol) and (35ml) DMF were mixed together and placed in a three neck flask and heated to reflux. The reaction was heated for 18 h at 80℃. After that, the polymer was precipitated by pouring the whole reaction mixture into large amount of cold deionized water. The number-average molecular weight of the copolymer was 53,600 with the polydispersity index of 1.8 as measured by gel permeation chromatography (GPC). The characterization of the polymer has been described in the Supporting Information.The *raft*-PMMA$_{45}$-*stat*-P4VP$_{55}$ was obtained via RAFT copolymerization as the following. A dry schlenk flask was charged with CDB macro-RAFT agent, 4-vinylpyridine(10.0 mL, 94.1 mmol), MMA(6.2 mL, 76.0 mmol), AIBN (0.021 g, 0.13 mmol) ,CDB(0.15g, 0.26mmol), dimethylformamide (15ml). After three freeze-pump-thaw cycles, the reaction mixture was immersed in a thermo stated oil bath at 70℃. After the polymerization was carried out for 40h, the reaction mixture was cooled to -40℃. The polymer was precipitated by pouring the polymer solution into excess water while stirring. The precipitate was collected by filtration, and then dried in a vacuum oven at 60℃ overnight. *raft*-PMMA$_{31}$-*stat*-P4VP$_{69}$ and *raft*-PMMA$_{57}$*stat*-P4VP$_{43}$ are obtained with the same way

^{1}H-NMR spectra were recorded by a Bruker AV II-400 NMR spectrometer at room temperature. Fig. S1 shows the ^{1}H-NMR spectrum and chemical shifts of P4VP-*stat*-MMA respectively. The ^{1}H-NMR spectrum exhibits three distinct groups of peaks. As shown in Fig. S1, the distinct peaks at 8.23ppm and 6.59ppm originate from the pyridine group of 4-vinylpyridine. The peak between

0.3 ppm and 1.1 ppm related to methyl protons of MMA. The blunt peak between 1.1 ppm and 2.7 ppm related to the main chain (-CH-CH_2-) protons of P4VP-*stat*-MMA. The peak between 3.1 ppm and 3.7 ppm related to methoxycarbonyl (-$COOCH_3$) protons. The molar ratio of 4VP: MMA estimated from ^{1}H-NMR spectrum as shown in table.s1

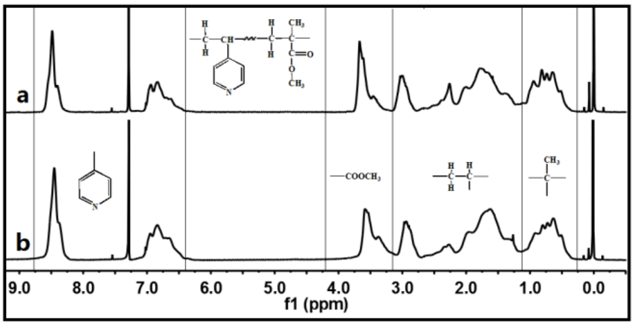

Fig. S1 ^{1}H NMR spectra of: a) *raft*-P4VP-*stat*-MMA, b) *free*-P4VP-*stat*-MMA.

The molecular weight and molecular weight distribution were determined on a Waters 150C gel permeation chromatography (GPC) equipped with three ultrastyragel columns (500, 103, 104 Å) in series and RI 2414 detector at 30℃, and DMF was used as eluent at a flow rate of 1.0 mL min^{-1}. The number-average molecular weight and polydispersity index as show in table.s1

Table.S1. Molecular weight (Mn) and chemical compositions of the copolymers prepared. PDI is the polydispersity index.

PMMA$_m$-*stat*-P4VP$_n$	Mn (g mol^{-1})	VP(%)	MMA:VP	PDI
free-PMMA$_{42}$-*stat*-P4VP$_{58}$	53600	58%	42:58	1.80
raft-PMMA$_{31}$-*stat*-P4VP$_{69}$	49500	69%	31:69	1.22
raft-PMMA$_{45}$-*stat*-P4VP$_{55}$	51000	55%	45:55	1.20
raft-PMMA$_{57}$*stat*-P4VP$_{43}$	48900	43%	57:43	1.19

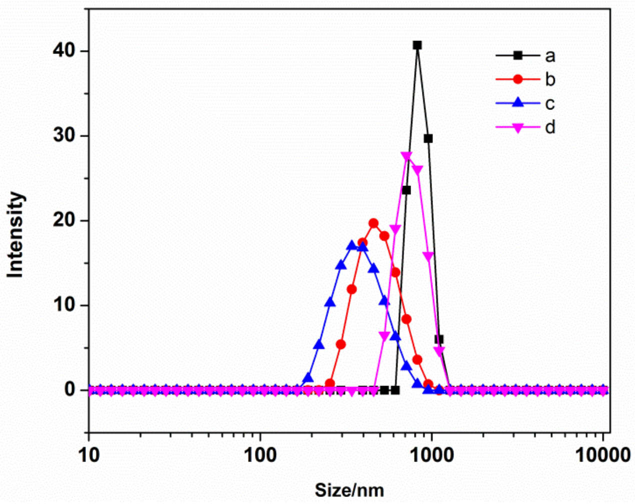

Fig.S2 Size distribution profile of polymer nanospheres formed by the self-assembly of (a) *raft*-PMMA$_{45}$-*stat*-P4VP$_{55}$-AZO$_1$ (b) *raft*-PMMA$_{45}$-*stat*-P4VP$_{55}$-AZO$_{0.4}$ (c) *raft*-PMMA$_{57}$-*stat*-P4VP$_{43}$-AZO$_{0.7}$ (d) *raft*-PMMA$_{31}$-*stat*-P4VP$_{69}$-AZO$_{0.7}$

The confirm that hydrogen bonds are formed between P4VP-*stat*-MMA and Azo

The existence of the hydrogen bond in the azo-complex aggregates was confirmed by FT-IR. Fig. S3 shows the IR spectra of *raft*-P4VP-*stat*-MMA, azo, and aggregate of azo-complex. The absorption peaks at 1597, 1556, and 1450 cm-1 in Fig. S3a can be assigned to the ring vibration of 4VP and 1728 can be assigned to carbonyl stretching o MMA of copolymer. The broad absorption band around 3450 cm-1 and the absorption appearing at1890 and 680 cm^{-1} in Fig. S3b indicate that the phenolic hydroxyl group is not in a free but in an associated state in pure Azo. As shown in Fig. S3c, a O-H stretching vibration appeared at 1900 cm^{-1} and out-of-plane vibration at 690 cm^{-1} indicates that the phenolic hydroxyl groups is in a less associated state than that in pure Azo. Moreover, a O-H stretching vibration appeared at 2550 cm^{-1} shows that the phenolic hydroxyl groups forms stronger hydrogen bonds than those in pure Azo. Therefore, the above results confirm that hydrogen bonds are formed between P4VP-*stat*-MMA and Azo.

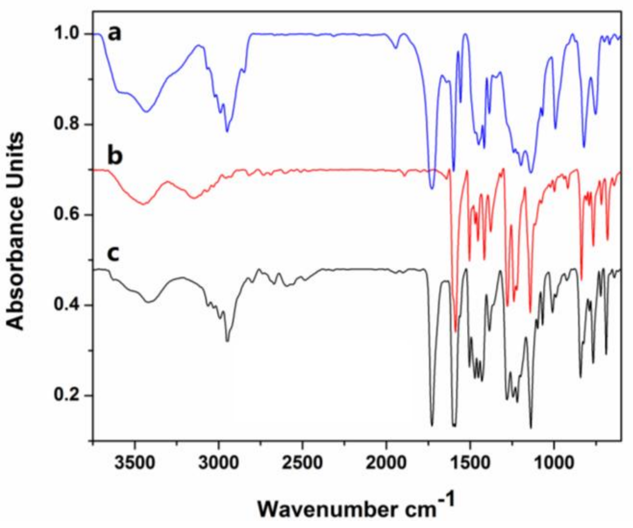

Fig. S3 IR spectrum of: a) P4VP-*stat*-MMA, b) AZO, c) azocomplex.

The test of Uv-vis

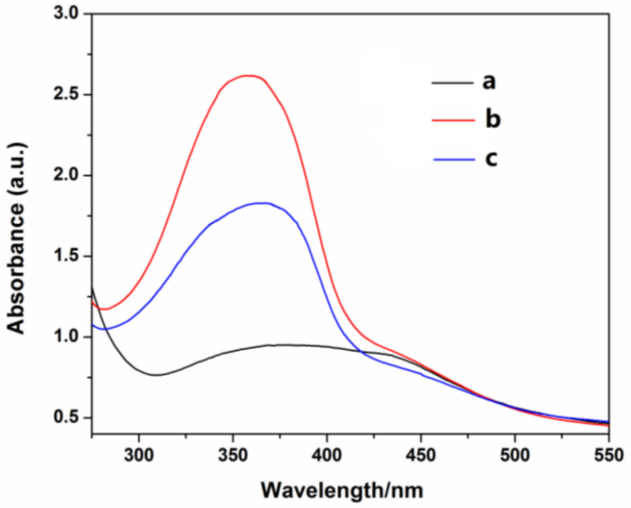

Fig. S4 UV-vis spectra of: a) pure AZO, b) azocomplex aggregates before irradiation, c) azocomplex aggregates after irradiation.

UV-Vis spectra were recorded by Unico UV-2800A spectrophotometer from 275 nm to 600 nm at 25℃. AZO was tested by coating the ethanol solution of AZO on the quartz plate after evaporation of ethanol. Azocomplex aggregate that was tested before irradiation was also tested by coating the dispersion liquid of aggregates on the quartz plate. After that it was irradiated by a linearly polarized Ar$^+$ laser beam (405 nm, 100mW cm^{-2}) and was tested for UV-Vis.

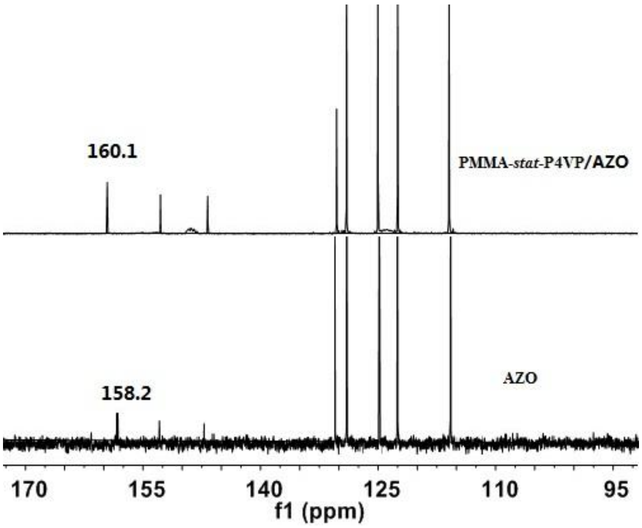

Fig. S5 ^{13} C NMR results of azo and the mixture of PMMA-*stat*- P4VP/AZO in CDCl3

The formation of the hydrogen bonds is supported by ^{13}C NMR spectroscopy measurements. For example, the signal of the phenolic hydroxyl carbon of AZO solution in chloroform shifts from 158.2 to 160.1 ppm upon addition of PMMA-stat-P4VP solution (1:1,w/w), which reflects that the self-association of the phenolic hydroxyl is disrupted and an intermolecular hydrogen bond forms between the carboxyl hydroxyl group and the pyridyl group. In addition, in the spectrum of the blend solution, the peak at 158.2 ppm totally disappears, which denotes that azo have completely attached to the PMMA-stat-P4VP chains.