[*Electronic Supplementary Information (ESI)*]

Hollow microspheres of amphiphilic azo homopolymers: self-assembly and photoinduced deformation behavior

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1. Materials

Analytical pure tetrahydrofuran (THF) from commercial source was refluxed with cuprous chloride and distilled for dehydration prior to use. Deionized water (resistivity>18 MΩ·cm) was obtained from a Milli-Q water purification system. Other reagents and solvents were used as received without further purification. BP-AZ-CA was synthesized through the azo-coupling reaction between an epoxy-based precursor polymer (BP-AN) and diazonium salt of 4-aminobenzoic acid. The preparation and characterization details of BP-AZ-CA is given as follows, which can be seen in detail in our previous paper.[1]

Preparation of BP-AN. Equimolar quantities of the diglycidyl ether of bisphenol A (7.6 g, 0.02 mol) and aniline (1.86 g, 0.02 mol) were homogeneously mixed under gradual heating and polymerized at 110 °C for 48 h. The product (9.4 g) was dissolved in $CHCl_3/CH_3OH$ mixed solvent (4:1, 50 mL) and precipitated in 500 mL of acetone. The polymer was collected by filtration and dried under vacuum for at least 24 h. The typical IR absorption bands of the epoxide groups at 915 and 3058 cm^{-1} nearly disappeared. The T_g of the polymer was determined to be 91 °C. ^{1}H NMR (DMSO): δ 7.08 (CH, 6H, d), 6.82 (CH, 4H, d), 6.74 (CH, 2H,d), 6.55

(CH, 1H, m), 5.27 (OH, 1H, d), 5.08 (OH, 1H, d), 4.06 (CH, 2H, m), 3.89 (CH$_2$, 4H, s), 3.75–3.34 (CH$_2$, 4H, m), 1.56 (CH$_3$, 6H, s).

Preparation of BP-AZ-CA. The diazonium salt of 4-aminobenzoic acid was prepared by adding an aqueous solution of sodium nitrite (0.04 g, 0.578 mmol in 0.1 mL of water) dropwise into a solution of 4-aminobenzoic acid (0.0686 g, 0.5 mmol) in a homogeneous mixture of 0.05 mL of sulfuric acid and 1 mL of glacial acetic acid. The mixture was stirred at 5 °C for 5 min before the excess nitrous acid was decomposed by addition of 0.05 g of sulfamic acid in a suitable amount of water. The diazonium salt solution was added dropwise into a solution of BP-AN (0.1892 g, 0.4 mmol) in 30 mL of *N, N'*-dimethylformamide (DMF) at 0 °C. After the solution was stirred at 0 °C for 12 h, the mixture was poured into water under agitation while adding a few drops of hydrochloric acid. The precipitate was collected by filtration and washed with plenty of water until neutral stage was achieved. The polymer was further purified by extraction with chloroform several times and dried under vacuum for at least 24 h. The number-average molecular weight of the polymer was 41000 with the polydispersity index of 2.2 obtained by GPC. The degree of functionalization (DF) of the azo polymer was about 100% estimated by ^{1}H NMR. IR (KBr, cm^{-1}): 3446, 2965, 2937, 2877, 1742, 1596, 1566, 1510, 1472, 1436, 1396, 1362, 1322, 1285, 1234, 1192, 1167, 1143, 1096, 1048, 998, 968, 928, 875, 826, 722, 653, 634, 573, 554, 403. ^{1}H NMR: δ 8.06 (CH, 2H, d), 7.81 (CH, 2H, d), 7.75 (CH, 2H, ov), 7.07 (CH, 4H, br), 6.92 (CH, 4H, ov), 6.85 (CH, 4H, d), 5.49 (OH, 2H, br), 4.12 (CH, 2H, br), 3.92 (CH$_2$, 4H, br), 3.80-3.49 (CH$_2$, 4H, br), 1.55 (CH$_3$, 6H, s).

2. Experiment and Characterization

2-1. Laser light scattering (LLS)

Laser light scattering experiments were performed on a commercial LS instrument

(ALV/DLS/SLS-5022F) equipped with a multi-τ digital time correlator (ALV/LSE-5003) and a solid-state laser (Uniphase, output power = 22 mW at λ = 632.8 nm). The dispersions used in LLS experiments were clarified by a 0.80 μm Millipore filter. All the measurements were carried out at 25±0.1 $^{\circ}$C.

The dynamic light scattering (DLS) was used to determine the hydrodynamic radius (R_h) and polydispersity of colloidal spheres formed in aqueous media. The scattering angle used for the DLS measurement was 90°. For a system of polydispersed particles in suspension, the first-order electric field correlation function $g^{(1)}(t)$ is related to the linewidth distribution function $G(\Gamma)$ by

$$g^{(1)}(t) = \int_0^\infty G(\Gamma)e^{-\Gamma t}d\Gamma \tag{1}$$

where t denotes the delay time. Two methods (the cumulant analysis and the CONTIN analysis) are used for data processing. The cumulant analysis (Eq. 2) was used to describe logarithm of the first-order electric field correlation function ($g^{(1)}(t)$) as a series expansion of time (t), where the first cumulant ($<\Gamma>$, the decay rate of the process) yields the z-averaged diffusion coefficient and the second cumulant (μ_2) is related to the second moment of the distribution of relaxation times.[2]

$$\ln [g^{(1)}(t)] = -<\Gamma>t + (\mu_2/2)t^2 - (\mu_3/6)t^3 + ... \tag{2}$$

$$\mu_2 = \int_0^\infty G(\Gamma)(\Gamma - <\Gamma>)^2 d\Gamma \tag{3}$$

where G(Γ) is a linewidth distribution function and Γ is given by

$$\Gamma = Dq^2 \tag{4}$$

where D is the translation diffusion coefficient, and q [$=(4\pi n/\lambda_0) \sin (\theta/2)$] is the scattering vector, θ is the scattering angle, n is the refractive index of the solvent, and λ_0 is the wavelength of the incident light. The average hydrodynamic radius ($<R_h>$) was obtained from the particle diffusion coefficient based on the Stokes-Einstein equation.[3]

$$<R_\text{h}> = \frac{k_\text{B}T}{6\pi\eta D} \tag{5}$$

where k_B is the Boltzmann constant, T is the absolute temperature, and η is the viscosity of the

solvent. The cumulant methods can result in $<\Gamma>$ and μ_2 directly, which is most reliable for a

variance $\mu_2/<\Gamma>^2 \leq 0.3$. The hydrodynamic radius distribution $f(R_\text{h})$ was obtained by the

CONTIN program in the correlator.[4] The Laplace inversion (CONTIN analysis) of the

measured electric field correlation function $g^{(1)}(t)$ can result in a linewidth distribution function

$G(\Gamma)$. For a diffusive relaxation, Γ is related to the translational diffusion coefficient by $\Gamma = Dq^2$.

Therefore, $G(\Gamma)$ can be converted to a hydrodynamic radius distribution $f(R_\text{h})$ according to the

Stokes-Einstein equation.

The static light scattering (SLS) was employed to determine the weight-average molar

mass of the colloidal spheres ($M_\text{w,sphere}$), the radius of gyration (R_g), and the second virial

coefficient (A_2).[2] The particles scatter light according to the following relation:

$$\frac{KC}{R(q)} = \frac{1}{M_\text{w}}(1+\frac{1}{3}q^2 <R_\text{g}^2>)+2A_2C \tag{6}$$

where K $[=4\pi^2 n^2 (\text{d}n/\text{d}C)^2/(\lambda_0^4 N_\text{A})]$ is the contrast factor, q $[=(4\pi n/\lambda_0)\sin(\theta/2)]$ is the scattering

vector, C is the concentration, θ is the scattering angle, $R(q)$ is the Rayleigh ratio at the angle of

measurement, n is the refractive index of the solvent, $\text{d}n/\text{d}C$ is the specific refractive index

increment, λ_0 is the wavelength of the incident light, N_A is the Avogadro number, and A_2 is the

second virial coefficient. The parameters could be estimated through the Zimm plot analysis.

The extrapolations regarding to C and θ yield $M_\text{w,sphere}$ from the intercept on the ordinate as well

as A_2 and $<R_\text{g}^2>$ from the slope of the corresponding curves. In this study, the colloidal

dispersion was so dilute that the extrapolation of C to zero was not necessary.

2-2. Transmission electron microscopy (TEM)

TEM images were obtained by using a JEOL-JEM-1200EX electron microscope with an accelerating voltage of 120 kV. The TEM samples were prepared by casting diluted sphere dispersions onto the copper grids coated with a thin polymer film and then dried in a 30 $^{\circ}$C vacuum oven for 12 h. No staining treatment was performed for the measurement.

2-3. Laser irradiation

Fig. S1 illustrates the schematic diagram of experimental setup for the laser light irradiation. A linearly polarized beam from an Ar^{+} laser at 488 nm was used as the light source. The spatially filtered laser beam was expanded and collimated. The intensity of the laser beam was about 80 mW cm^{-2}. The linearly polarized laser beam was incident perpendicularly to the TEM grid surfaces containing the colloids. The light irradiation experiment was carried out at room temperature under an ambient condition.
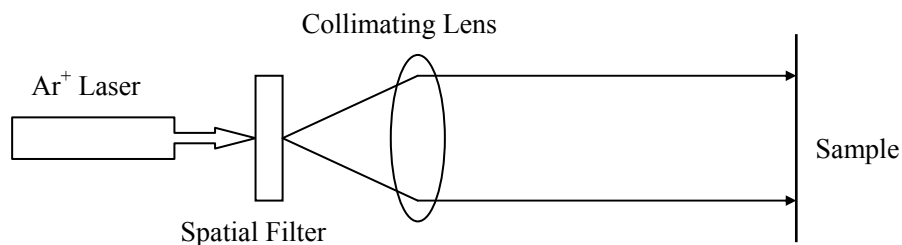

Fig. S1 Illustration of experimental setup for the laser light irradiation.

3. Additional Characterization Data

The relationship between the average hydrodynamic diameter ($<R_h>$) of the hollow microspheres and the initial polymer concentrations in THF was studied by DLS. The similar relationship for colloidal spheres with solid interiors was also obtained for comparison. The $<R_h>$, the polydispersity index (PDI=$\mu_2/<\Gamma>^2$), and (M_w/M_n)$_{particle}$ are given in Table S1.

Table S1. DLS experimental results of hollow spheres and spheres with solid interiors

Samples	C_p (mg/mL)[a]	$<R_h>$ (nm)	PDI ($\mu_2/<\Gamma>^2$)[b]	$(M_w/M_n)_{particle}$[c]
Solid spheres	0.3	117	0.033	1.13
	0.8	190	0.043	1.17
	1.0	216	0.038	1.15
	1.5	289	0.072	1.29
Hollow spheres	0.3	131	0.039	1.16
	0.8	223	0.040	1.16
	1.0	265	0.037	1.15
	1.2	307	0.055	1.22
	1.5	377	0.062	1.25

[a] C_p: the initial polymer concentration in THF.

[b] The polydispersity index.

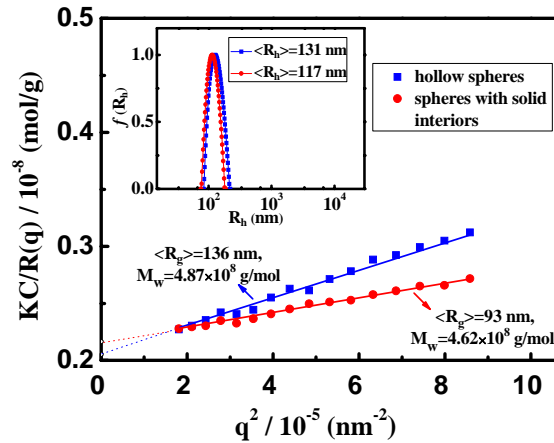[c] $(M_w/M_n)_{particle} \approx 1+4(\mu_2/<\Gamma>^2)$.[4]

Fig. S2 Typical Zimm plot of the BP-AZ-CA hollow microspheres and colloidal spheres with solid interiors in the water dispersion for the SLS analyses. The initial polymer concentration in THF was 0.3 mg/mL. The SLS experiments were performed at scattering angles between 18.5° and 41°, at 1.5° intervals. The concentration of the BP-AZ-CA colloidal dispersion was 5.00×10^{-6} g/mL. The inset shows the hydrodynamic radius distribution $f(R_h)$ of hollow spheres (the blue curve) and spheres with solid interiors (the red curve).
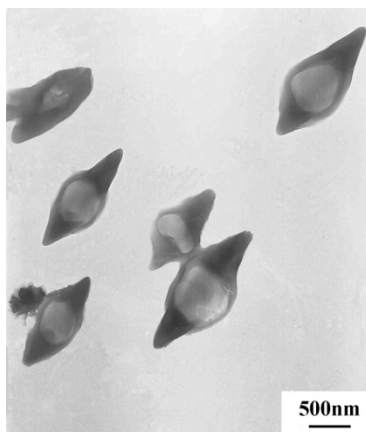
Fig. S3. Typical TEM micrographs of hollow microspheres composed of BP-AZ-CA with average diameter of 531 nm after being irradiated with a linearly polarized Ar^+ laser beam (488 nm, 80 mW cm^{-2}) for 40 min.

References

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