Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

pH-Responsive Cagelike Porous Polymer Microspheres Prepared via Consecutive RAFT Polymerization Induced by γ-Ray Radiation

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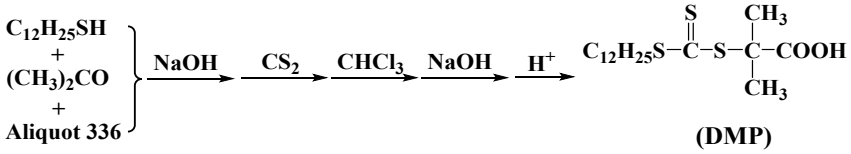
I. Synthesis of 2-dodecylsulfanylthiocarbonylsulfanyl-2-methylpropinoic acid (DMP) as the chain transfer agent for RAFT polymerization.

The DMP was synthesized according to the previous report,[1] as illustrated in Scheme 1. Briefly, 8.076 g of 1-dodecanethiol, 19.24 g of acetone, and 0.649 g of Aliquot 336 (phase transfer catalyst) were mixed in a three-neck flask in an ice-water bath under a nitrogen atmosphere. 6.708 g of sodium hydroxide solution (50%) was added into the above solution within 20 min under a mechanical stirring at 250 rpm. Fifteen minutes later, 3.042 g of carbon disulfide dissolved in 4.036 g of acetone was added within 20 min. After 10 minutes, 7.125 g of chloroform was added in one portion. Subsequently, another 32 g of sodium hydroxide solution (50 %) was added dropwise within 30 min. The reaction system was stirred overnight. Then, 60 mL of water and 10 mL of concentrated HCl (37%) were added in order. Nitrogen was purged into the flask to evaporate off acetone with the help of vigorous stirring. The remaining solid was collected with a Buchner funnel, and then dispersed in 100 mL of 2-propanol. After being filtered the undissolved solid off, the 2-propanol solution was concentrated into a dark yellow oleosus liquid, and dried in a vacuum oven at 30 °C for 24 h. The resultant dark brown crude product was recrystallized in hexane twice to get 8.247 g of yellow crystalline solid.



Scheme S1 Synthesis process of DMP

II. The UV-vis absorption spectra of the aqueous solutions containing different RhB-loaded cagelike porous microspheres.

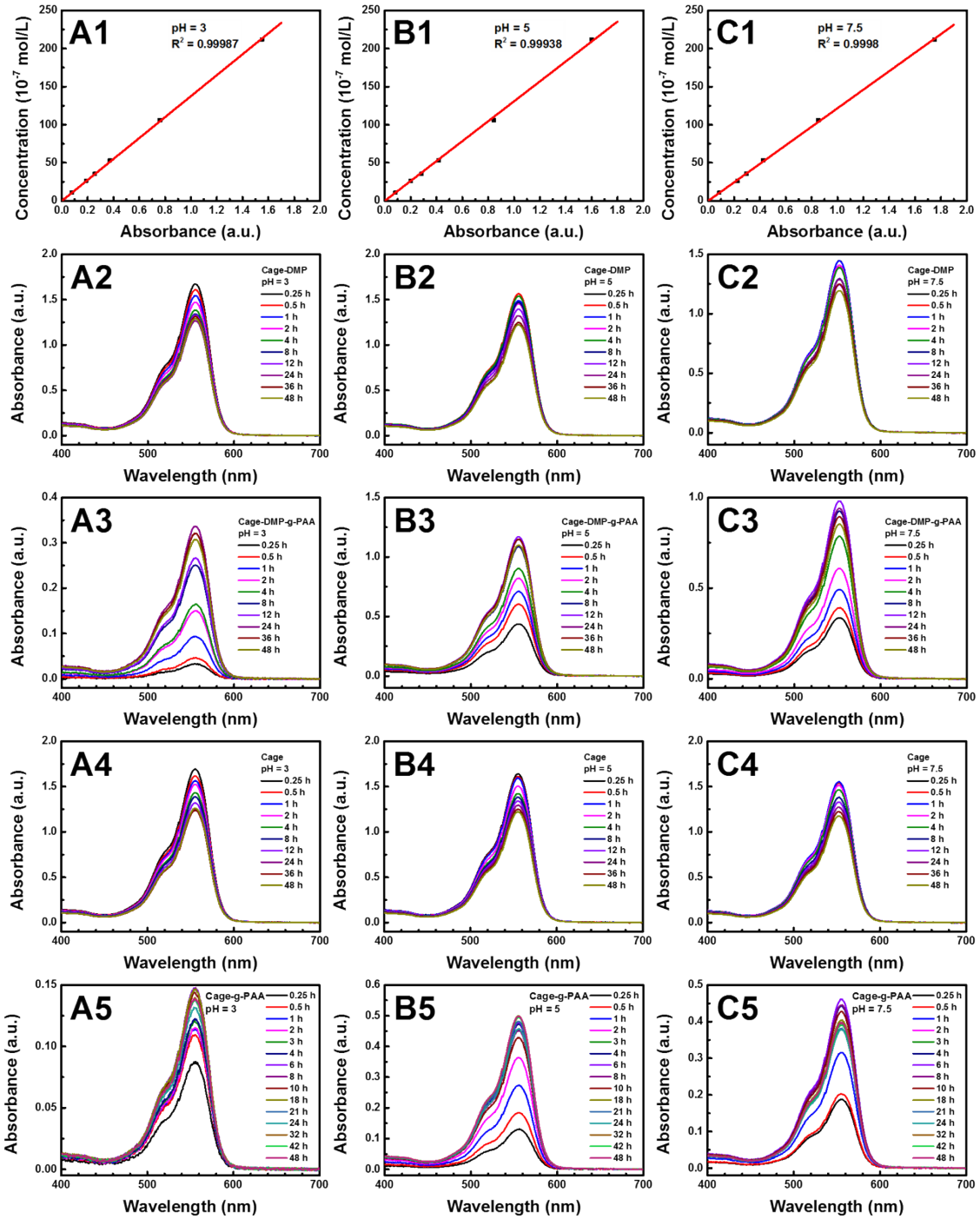


Fig. S1: The standard work curves of the aqueous solution of RhB at different pH (A1, B1, C1) and the UV-vis spectra of the PBS solution containing different RhB-loaded cagelike

porous microspheres. The absorbance of RhB solution at 556 nm (pH = 3), 555 nm (pH = 5), and 553 nm (pH = 7.5) was used to obtain the working curves for the solutions with the corresponding pH.

III. XPS spectra of different SPS microspheres.

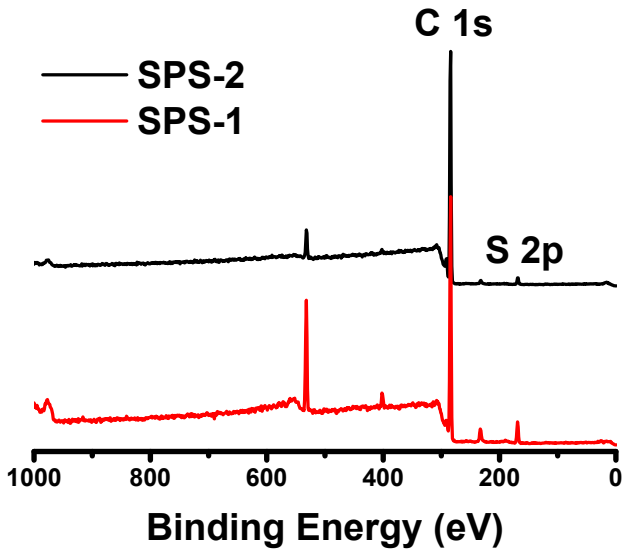


Fig. S2 XPS spectra of SPS-1 and SPS-2 microspheres.

The atomic ratio of C and S of different SPS microspheres can be calculated from Fig.S2. The atomic ratio of C and S of SPS-1 are 86.23% and 2.52% respectively. The atomic ratio of C and S of SPS-2 are 93.43% and 1.27% respectively.

IV. ^{1}H NMR spectra of Cage-DMP-2, Cage-2 and DMP

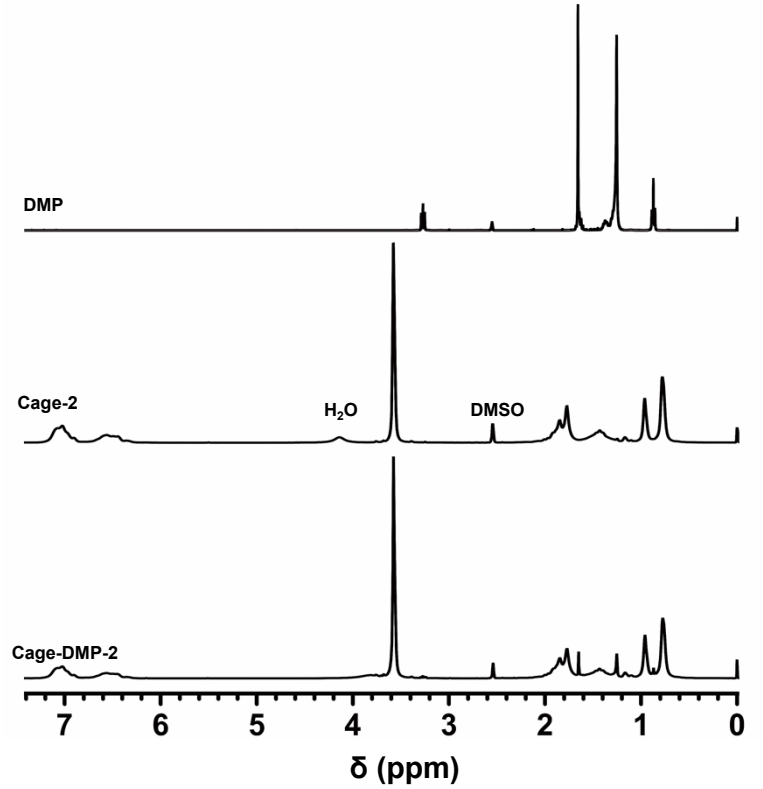


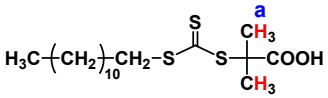
Fig. S3 ^{1}H NMR spectra of Cage-DMP-2, Cage-2 and DMP.

The theoretical simulation of ^{1}H chemical shift can be based on the empirical Equation S1.[2]

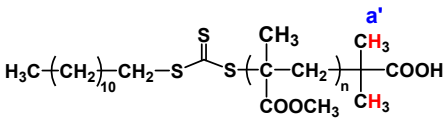
$$\delta_{CH_3CR_1R_2R_3} = 0.86 + \sum_i Z_{\beta_i} \quad \text{(S1)}$$

Where Z_β is the increments for substituents in β position.

Thus, the simulated ^{1}H chemical shifts of –CH_3 groups in DMP combined with polymer chains are calculated as:



$$\delta_a = 0.86 + 0.05 + 0.23 + 0.37 = 1.51$$



$$\delta_{a'} = 0.86 + 0.05 + 0.23 + 0.05 = 1.19$$

V. RAFT polymerization of AA in THF initiated by AIBN

The synthesis of PAA_{50}-DMP was carried out according to the method reported by He et al.[3] AA (1.80 g), DMP (182 mg), THF (4.0 mL), and AIBN (8.2 mg) were mixed under magnetic stirring. After three freeze-evacuate-thaw cycles, the system was vacuum sealed, and heated to 75 °C under magnetic stirring, and then cooled to room temperature after 2 h. The product, labeled as PAA_{50}-DMP, was precipitated in 20-fold excessive diethyl ether, collected by filtration, and finally vacuum dried at room temperature overnight.

References:

1. Lai, J. T.; Filla, D.; Shea, R. *Macromolecules* **2002**, *35*, 6754.

2. Ern, P.; Philippe, B.; Martin, B. In *Structure Determination of Organic Compounds Tables of Spectral Data*, 4th ed.; Springer-Verlag: Berlin and Heidelberg, Germany, 2009; p 160.

3. He, W. D.; Sun, X. L.; Wan, W. M.; Pan, C. Y. *Macromolecules* **2011**, *44*, 3358.