

Supporting Information

Hybrid hydrogels of hyperbranched poly(ether amine)s (hPEAs) for selective adsorption of guest molecules separation of dyes

Shujun Deng, Rui Wang, Hongjie Xu, Xuesong Jiang*, Jie Yin

School of Chemistry & Chemical Engineering, State Key Laboratory for Metal Matrix

Composite Materials, Shanghai Jiao Tong University,

Shanghai 200240, People's Republic of China.

Tel.: +86-21-54743268; Fax: +86-21-54747445. E-mail: ponygle@sjtu.edu.cn

Experimental

Materials

Allyl glycidyl ether (AGE, Sigma-Aldrich), succinic anhydride (SA, Sinopharm Chemical), 3-trimethoxysilylpropanethiol (TMS, Sigma-Aldrich) and photoinitiator I-907 (Tronly, Changzhou, China) were used as received. Hyperbranched poly(ether amine)s (hPEAs) with different ratios between poly(propylene oxide) (PPO) and poly(ethylene oxide) (PEO) were synthesized according to the previous report.¹ Different water-soluble dyes Rhodamine 6G (R6G), Rose Bengal Na Salt (RB), Neutral Red (NR), Methylene Blue trihydrate (MB), Methyl Orange (MO), Bismarck brown Y (BY), Ponceau S (PS) and Calcein (Cal) used in this study (Table 1) were purchased from Sinopharm Chemical.

Synthesis of hPEAs-AGE and hPEA-AGE211-SA

hPEAs-AGE with different PPO/PEO ratios were synthesized according to Scheme S1. hPEA (0.06 mol) and Allyl glycidyl ether (0.09 mol) were refluxed in ethanol (120mL) for 24 h with nitrogen protect. The mixture left was washed by n-hexane and the precipitate was dried in vacuum to obtain hPEAs-AGE.

hPEA211-AGE-SA was synthesized via esterification of hydroxyl groups in hPEA-AGE211 with SA (Scheme S1). SA (0.18 mol) and hPEA-AGE211 (0.06 mol

in term of its structure units) were refluxed in chloroform (240 mL) for 12 h with nitrogen protect. The mixture was washed by n-hexane and the precipitate was dried in vacuum to obtain hPEA211-AGE-SA.

Synthesis of TMS-hPEAs and TMS-hPEA211-SA

To the solution of CH₂Cl₂ with trace of photoinitiator I-907, hPEAs-AGE or hPEA211-AGE-SA and TMS (thiol/double bond = 1.3:1) were added. The mixture was irradiated by 365 nm ultraviolet light for 12 h. Then the mixture was poured into n-hexane. After removing the supernatant, the polymer contained trimethoxysilyl moiety was collected and named as TMS-hPEAs or TMS-hPEA211-SA (Scheme S1).

Characterization

Nuclear Magnetic Resonance Spectroscopy (NMR). ¹H nuclear magnetic resonance spectroscopy (¹H NMR) measurements were carried on a Varian Mercury Plus spectrometer, operating at 400 MHz by using CDCl₃ as solvent (TMS internal standard).

Fourier transform infrared spectroscopy (FT-IR) spectra of products were recorded on a Perkin-Elmer Paragon1000 FT-IR spectrometer, operating at a resolution of 4cm⁻¹ and wavenumber range of 4000 to 400 cm⁻¹.

Scanning electron microscopy (SEM) studies were performed on a JSM-7401F electron microscope at 30 kV. The hydrogel samples were lyophilized and coated with gold in vacuo for observation.

UV-vis spectra were recorded on a UV-2550 spectrophotometer (Shimadzu, Japan) at room temperature equipped with circulating water bath.

Results and Supporting Figures

The whole process for synthesis of TMS-hPEAs is illustrated in Figure S1. Firstly, a series of hPEAs-AGE with different hydrophobicity were synthesized via nucleophilic substitution/ring-opening reaction of epoxy and amine, which were named as hPEA101-AGE, hPEA211-AGE, and hPEA321-AGE, respectively. The carboxyl groups were then introduced into the backbone of hPEA211-AGE through esterification of hydroxyl groups and named as hPEA211-AGE-SA. Trimethoxysilane

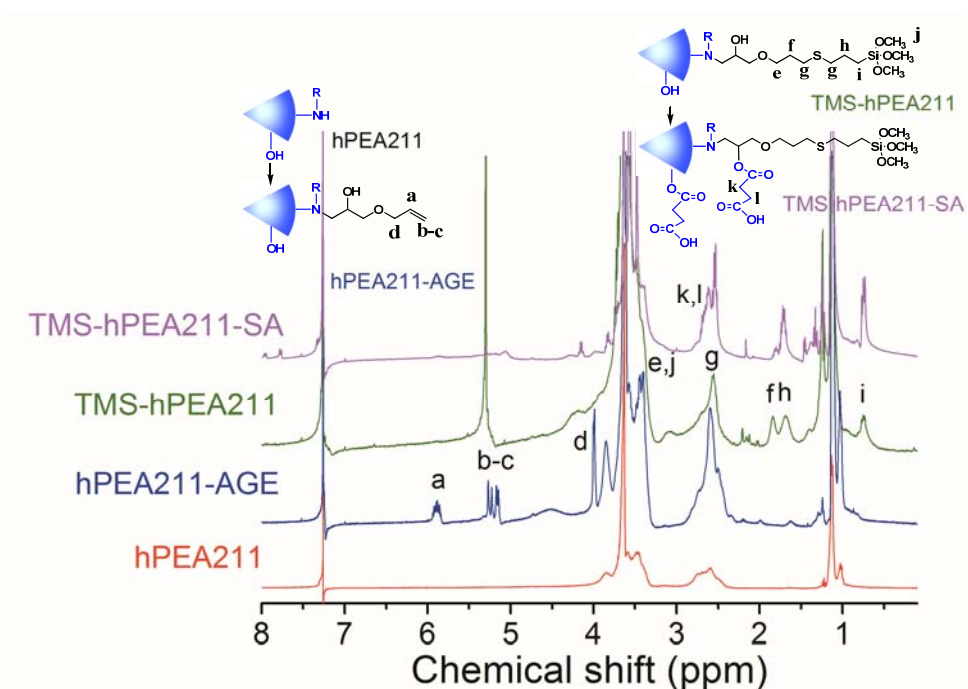


Figure S2. ^1H NMR spectra of hPEA211, hPEA211-AGE, TMS-hPEA211 and TMS-hPEA211-SA in CDCl_3 .

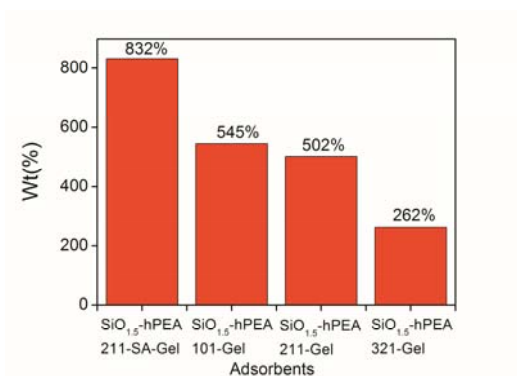


Figure S3. Swelling ratio of SiO_{1.5}-hPEA211-SA-Gel, SiO_{1.5}-hPEA101-Gel, SiO_{1.5}-hPEA211-Gel and SiO_{1.5}-hPEA321-Gel after immersed in water for 72 h at 25 °C.

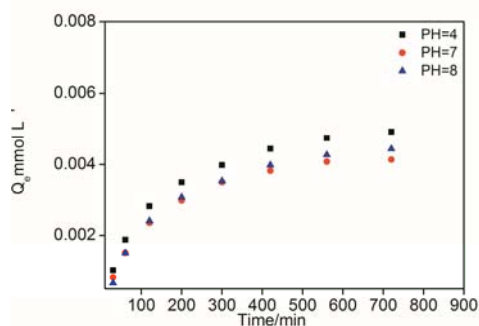


Figure S4. Effect of pH on the adsorption of PS by SiO_{1.5}-hPEA211-Gel

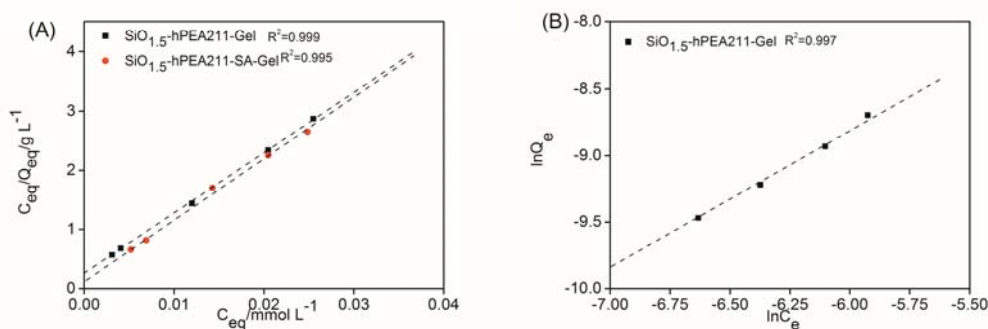


Figure S5. (A) Linearized Langmuir isotherms of PS on SiO_{1.5}-hPEA211-Gel and SiO_{1.5}-hPEA211-SA-Gel. (B) Linearized Freundlich isotherms of MB on SiO_{1.5}-hPEA211-Gel at 25 °C. 10 mg hybrid hydrogels were added into 6 ml dye's aqueous solution.

The equilibrium adsorption data was analyzed by using the Langmuir and Freundlich isotherm models. The form of the Langmuir isotherm is expressed as follows²

$$\frac{C_{eq}}{Q_{eq}} = \frac{C_{eq}}{Q_{max}} + \frac{1}{K_L Q_{max}} \quad (1)$$

where C_{eq} (mmol/L) is the equilibrium concentration of the dyes in the solution, Q_{eq} (mmol/g) is the amount of dyes adsorbed at the equilibrium, Q_{max} (mmol/g) is the maximum capacity of the hybrid hydrogel, K_L (L/mmol) is the Langmuir adsorption constant. Unlike the Langmuir model, the Freundlich model is used to describe the adsorption of an adsorbate on a heterogeneous surface of an adsorbent³. The linearized form of the Freundlich isotherm can be given as follows³

$$\ln Q_{eq} = \ln K_F + b_F \ln C_{eq} \quad (2)$$

Where C_{eq} (mmol/L) is the equilibrium concentration of the dyes in the solution, Q_{eq} (mmol/g) is the amount of dyes adsorbed at the equilibrium, K_F is the Freundlich constant, and b_F is a constant for depicting the adsorption intensity.

Figure S6(A) shows the linear Langmuir isotherms for PS onto $SiO_{1.5}$ -hPEA211-Gel and $SiO_{1.5}$ -hPEA211-SA-Gel, and the corresponding correlation coefficients for adsorption of PS onto $SiO_{1.5}$ -hPEA211-Gel and $SiO_{1.5}$ -hPEA211-SA-Gel are 0.999 and 0.995, respectively. The high correlation coefficients indicated that the Langmuir model is suitable for describing the adsorption equilibrium of PS by the hybrid hydrogels. As shown in the linear Freundlich isotherms for MB onto $SiO_{1.5}$ -hPEA211-Gel (Figure S6B), the corresponding correlation coefficient is 0.997. The high correlation coefficient confirmed that the adsorption of MB obeyed the Freundlich model. Due to the very low adsorption, the adsorption isotherm for MB onto $SiO_{1.5}$ -hPEA211-SA-Gel could not be obtained.

References:

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2. Langmuir, I. *J. Am. Chem. Soc.* 1916, 38, 2221-2295
3. Freundlich, H. M. F. *Phys. Chem.* 1906, 57, 385