

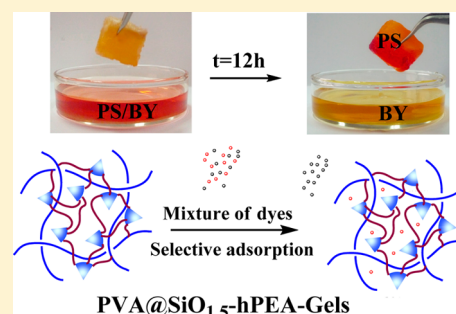
Poly(vinyl alcohol) (PVA)-Enhanced Hybrid Hydrogels of Hyperbranched Poly(ether amine) (hPEA) for Selective Adsorption and Separation of Dyes

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S Supporting Information

ABSTRACT: The unique selective adsorption of hydrophilic dyes gives the hybrid hydrogels of hyperbranched poly(ether amine) ($\text{SiO}_{1.5}$ -hPEA-Gels) potential in the separation. We here introduced poly(vinyl alcohol) (PVA) to enhance the mechanical strength of hybrid hydrogels to extend them into the practical application. A series of PVA-enhanced hybrid hydrogels ($\text{PVA@SiO}_{1.5}$ -hPEA-Gels) were prepared by chemically cross-linking between hydroxyl groups of PVA and trimethoxysilyl groups of hyperbranched poly(ether amine) (TMS-hPEA) in water. The compress stress of $\text{PVA@SiO}_{1.5}$ -hPEA-Gels increased significantly with the increasing content of PVA. Compared to hybrid hydrogel without PVA, the stress of $\text{PVA@SiO}_{1.5}$ -hPEA-1/2-Gel containing 33% PVA increased hundreds of times. The adsorption behavior of the obtained PVA-enhanced hydrogels to ten hydrophilic dyes was investigated in detail. Regardless of their charge states, $\text{PVA@SiO}_{1.5}$ -hPEA-Gels exhibited the quick adsorption to Ponceau S (PS), Rose Bengal (RB), Orange G (OG), and Ponceau SX (PSX) with a high adsorption capacity (Q_{eq}) and very slow adsorption of Bismarck brown Y (BY), Methylene Blue trihydrate (MB), and Rhodamine 6G (R6G) with a low adsorption capacity. The adsorption process was found to follow the pseudo-second-order kinetics, and the introduction of PVA has no obvious effect on the adsorption behavior in this study. The big difference in the adsorption to the different dyes is indicative of the selective adsorption of $\text{PVA@SiO}_{1.5}$ -hPEA-Gels to dyes. A methodology of dynamic separation of dye's mixtures (PS/BY and OG/MB) in water is finally demonstrated by using $\text{PVA@SiO}_{1.5}$ -hPEA-Gels.



INTRODUCTION

Hydrogels are three-dimensional networks of physically or chemically cross-linked hydrophilic polymers in which a large amount of water is interposed.^{1–5} As one special class of soft matter exhibiting particular features and unique properties, hydrogels have been extensively explored for use in various scientific fields.^{2,6–14} Particularly, hydrogels can be used as adsorbents to remove the pollutant from water because of their excellent performance in adsorption of guest molecules such as heavy metal ions,^{15–17} proteins,^{18–20} and water-soluble dyes.^{21–24} Nowadays, removal of dyes from sewage and industrial waste has caused significant concern in the whole world. Despite various adsorbents used to remove dyes from aqueous solutions,^{25–28} hydrogels of 3D cross-linked polymer networks are recognized as effective, efficient adsorbents for the removal of dyes from the polluted water due to their available designs at a molecular level and easy chemically modified with various functional groups.²⁹ Some hydrogels were found to exhibit the selective adsorption to dyes, which provides possibility in separation of dye's mixture during the removal of dyes from the polluted water.³⁰ Usually, the selective adsorption of guest molecules was mostly based on the electrostatic interaction between hydrogel and dyes. Thomas et al. reported that a clay-cross-linked hydrogel can adsorb dyes

with opposite charge selectively and can be used in the separation of a mixture of dyes with opposite charge based on an ion-exchange mechanism.³⁰

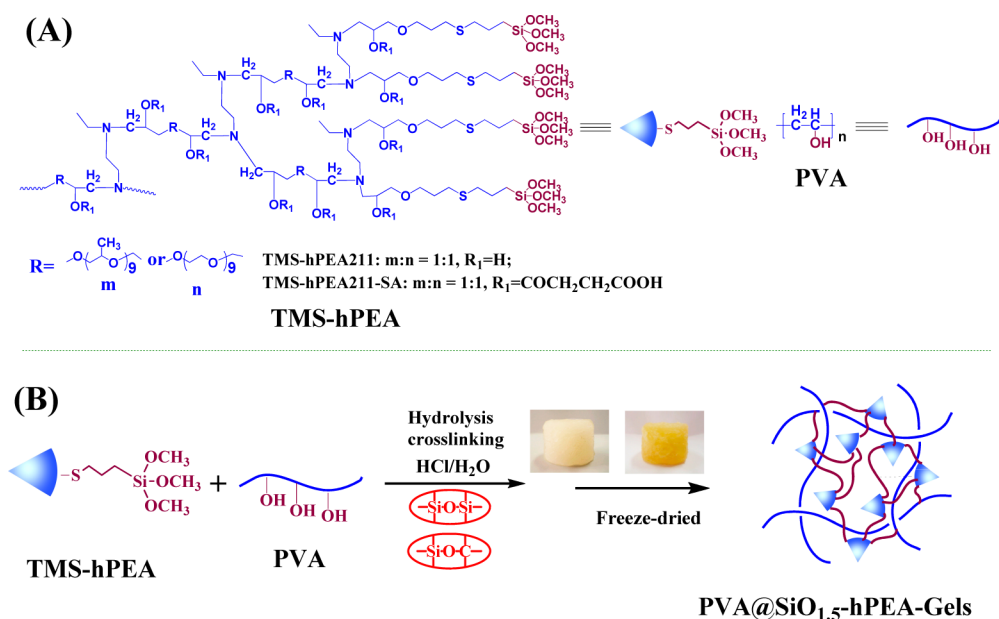
Recently, we reported that the hybrid hydrogel of hyperbranched poly(ether amine)s ($\text{SiO}_{1.5}$ -hPEAs-Gels) exhibited the unique selective adsorption to dyes. $\text{SiO}_{1.5}$ -hPEAs-Gels can be used in dynamic separation of mixture of dyes owing to the unique selective adsorption, which is not based on the electrostatic interaction. This special interaction mechanism between $\text{SiO}_{1.5}$ -hPEAs-Gels and dyes provides an important alternative in separation of dye's mixture.³¹ In our experiments, however, we found that $\text{SiO}_{1.5}$ -hPEAs-Gels were fragile, and their poor mechanical stability might limit their practical application in some fields. To further extend the application field of $\text{SiO}_{1.5}$ -hPEAs-Gels in the controlled separation, in this text we continued to introduce poly(vinyl alcohol) (PVA) into $\text{SiO}_{1.5}$ -hPEAs-Gels to enhance their mechanical strength. The resulting PVA enhanced hybrid hydrogels ($\text{PVA@SiO}_{1.5}$ -hPEA-Gels) were tough and flexible and exhibited good mechanical strength. The compress strain of $\text{PVA@SiO}_{1.5}$ -hPEA-Gels

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Scheme 1. (A) Structures of TMS-hPEAs and Poly(vinyl alcohol); (B) the Whole Process To Prepare Hybrid Hydrogels (PVA@SiO_{1.5}-hPEA-Gels)^a



^aInset is the picture of the hydrogel before and after freeze-dried.

increased hundreds of times more than that of SiO_{1.5}-hPEA-Gels. The systematic investigation of host–guest interaction between PVA@SiO_{1.5}-hPEA-Gels and hydrophilic dyes indicates that PVA@SiO_{1.5}-hPEA-Gels can also adsorb dyes selectively. On the basis of the selective adsorption, finally, we provided an approach to separate the mixture of dyes. It should be noted that PVA@SiO_{1.5}-hPEA-Gels can keep the original shape after separation and recycle due to their excellent mechanical strength.

EXPERIMENTAL SECTION

Materials. Trimethylsilane containing hyperbranched poly(ether amine)s (TMS-hPEA211 and TMS-hPEA211-SA) for fabrication of hybrid hydrogels were synthesized according to our previous reports.³¹ Poly(vinyl alcohol) (PVA AH-26, DP = 2600, alcoholysis degree of 99%) and water-soluble dyes Rose Bengal Na Salt (RB), Calcein (Cal), Fluorescein (FR), Orange G (OG), Ponceau SX (PSX), Bismarck brown Y (BY), Ponceau S (PS), Neutral Red (NR), Rhodamine 6G (R6G), and Methylene Blue trihydrate (MB) used in this study were supplied by Sinopharm Chemical.

Preparation of PVA@SiO_{1.5}-hPEA-Gels and PVA Hydrogel. The TMS-hPEA211 or TMS-hPEA211-SA was dispersed into PVA aqueous solution with the designed feed to form semitransparent solution. The total solid content of TMS-hPEA and PVA keeps 0.2 g/mL. The solution was then added several drops of hydrochloric acid for catalysis of hydrolysis of trimethoxysilyl groups. After hydrolyzing for 2 days and further freeze-dried overnight, the cross-linked hybrid hydrogels named as PVA@SiO_{1.5}-hPEA-Gels were obtained. For comparison, the pure PVA hydrogel was prepared by repeatedly freeze–thawing a aqueous solution containing 11% w/w poly(vinyl alcohol) (PVA).³² It should be noted that this physical PVA hydrogel prepared by freeze–thawing cannot be dissolved in water due to the strong interaction between PVA chains.^{33,34}

Characterization. Scanning electron microscopy (SEM) was performed on a Sirion-200 electron microscope (FEI Company) at 5 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.

Compressive Stress–Strain Measurements. The compressive measurements of the hydrogels were conducted at 25 °C by using an Instron model 4465 testing machine (Instron Corp.) at a crosshead speed of 5 mm/min. The hydrogel samples were cut into cylinders (15 mm in diameter and 15–20 mm in thickness).

Swelling of PVA@SiO_{1.5}-hPEA-Gels. The swelling ratio (SR) of PVA@SiO_{1.5}-hPEA-Gels was measured in distilled water at 25 °C. The freeze-dried gels were weighed (W_d) first. At an interval time the swollen samples were taken out to be weighed (W_t) after removing excess water with moistened filter paper. SR was calculated as $\text{SR} = (W_t - W_d)/W_d \times 100$. The equilibrium swelling ratio (ESR) was calculated as $\text{ESR} = (W_e - W_d)/W_d \times 100$, where W_e is the swollen weight of the gel at equilibrium.

Adsorption of Water-Soluble Dyes. For adsorption experiments ten hydrophilic dyes were chosen for experiments. 10 mg of dried gel was added into 6 mL of dye's aqueous solution at pH 7.2, and the initial concentration of all dyes is 200 μM. The gels were allowed to adsorb dyes at 25 °C until reaching equilibrium. The equilibrium adsorption capacity (Q_{eq}) of dyes onto PVA@SiO_{1.5}-hPEA-Gels was defined as follows³⁵

$$Q_{\text{eq}} = \frac{C_0 - C_{\text{eq}}}{M} V \quad (1)$$

where Q_{eq} (mmol/g) is the amount adsorbed per gram of hybrid hydrogel at equilibrium, C_0 is the initial concentration of dyes in the solution (mmol/L), C_{eq} is the concentration of dyes at equilibrium (mmol/L), V is the volume of the solution (L), and M is the mass of the hybrid hydrogel used (g). Three factors including the initial concentration of dyes (C_0), the volume of the solution of dyes (V), and the mass of the hydrogel (M) affect the value of Q_{eq} . The latter two factors can be concluded as one factor (K) and K (g/L) can be calculated as M/V . K can be named as the concentration of hydrogel in the solution of dyes. Under certain range of the initial concentration of dyes and the concentration of hydrogel in the solution, Q_{eq} increased with the increasing of C_0 and $1/K$. Q_{eq} will remain the same if the values of C_0 and $1/K$ are large enough. In experiments the initial concentration of dyes (C_0) and $1/K$ in the solution were large enough to ensure the accuracy of Q_{eq} values. The adsorption behavior was traced by UV–vis spectra, and dye concentration was calculated by the absorbance at the maximum absorption.

Table 1. Composition, Equilibrium Swelling Ratio, and Mechanical Properties of Hybrid Hydrogels

sample	composition PVA/TMS-hPEA (wt)	swelling ESR (%)	stress at 25% strain ^a σ (kPa)	compress test stress at 60% strain ^b σ (kPa)	appearance after test
SiO _{1.5} -hPEA211-Gel	0:1	502	0.02 ^c	14 ^c	fracture
PVA@SiO _{1.5} -hPEA-1/4-Gel	1:4	284	8.1	3.73×10^3	recover
PVA@SiO _{1.5} -hPEA-1/3-Gel	1:3	168	13	4.52×10^3	recover
PVA@SiO _{1.5} -hPEA-1/2-Gel	1:2	139	92	1.05×10^4	recover
PVA@SiO _{1.5} -hPEA-SA-1/2-Gel	1:2	336	2.9	1.44×10^3	recover

^aMechanical properties of hybrid hydrogels were measured before freeze-dried. ^bMechanical properties of hybrid hydrogels were measured after freeze-dried. ^cStress values were obtained when SiO_{1.5}-hPEA211-Gel is broken because the steady stress of SiO_{1.5}-hPEA211-Gel cannot be obtained due to fracture before the fixed strain.

Separation of Dyes Mixture. The separation experiments were conducted in mixture of PS-BY and OG-MB at pH 7.2. The concentration of hydrogel in solution was fixed at 2 g/L, and the initial concentration ratios $[PS]_0/[BY]_0$ and $[OG]_0/[MB]_0$ were 0.9 and 0.7, respectively. The dye concentration in the solution and the removal of dyes were traced and determined by UV-vis spectra at 25 °C.

RESULTS AND DISCUSSION

Preparation and Characterization of PVA@SiO_{1.5}-hPEA-Gels Hybrid Hydrogels. The whole strategy for fabrication of PVA@SiO_{1.5}-hPEA-Gels is illustrated in Scheme 1. Through the well-known hydrolysis between trimethoxysilane groups of hPEA and hydroxyl groups of PVA, water-soluble PVA can be easily bonded chemically to the network of SiO_{1.5}-hPEA-Gels to improve their mechanical strength (Figure S1).^{36–39} The other important reason to choose PVA as reinforcement is that PVA is expected to have no effect on the unique selective adsorption to dyes (Figure S2). This is indeed true and will be discussed later. Two types of hyperbranched poly(ether amine)s (TMS-hPEA and TMS-hPEA-SA) were used for fabrication of hybrid hydrogels. The introduction of carboxyl groups (SA) will be helpful for understanding the effect of charge state of the obtained hybrid hydrogels. In the synthesis of the hybrid hydrogels, TMS-hPEA or TMS-hPEA-SA was directly dispersed into PVA aqueous solution to form the semitransparent solution. Through the hydrolysis and condensation of TMS in the presence of hydrochloric acid, the semitransparent solution became cross-linked to form the hybrid hydrogels (PVA@SiO_{1.5}-hPEA-Gels; see inset of Scheme 1). Through this approach, four hybrid hydrogels with different formulation were prepared and are listed in Table 1.

After further freeze-drying to remove water, the internal morphology of the dried hybrid hydrogels was examined by SEM (Figure S3). No obvious porous microstructures can be found in PVA@SiO_{1.5}-hPEA-Gels and PVA@SiO_{1.5}-hPEA-SA-Gels, which is in contrast to the highly porous sponge-like SiO_{1.5}-hPEA-Gels.³¹ This might be ascribed to the porous filled with PVA polymer chains. The swelling kinetics of the dried hybrid hydrogels were carried out in water at 25 °C. After immersed in water for 120 min, the swelling behavior of all PVA-enhanced hybrid hydrogels reached equilibrium (Figure 1), and their equilibrium swelling ratios (ESR) are summarized in Table 1. The swelling speed of PVA-enhanced hybrid hydrogels decreased with the increasing PVA content from PVA@SiO_{1.5}-hPEA-1/4-Gel to PVA@SiO_{1.5}-hPEA-1/2-Gel, and the value of ESR also decreased obviously with the increasing content of PVA. This can be explained by that PVA

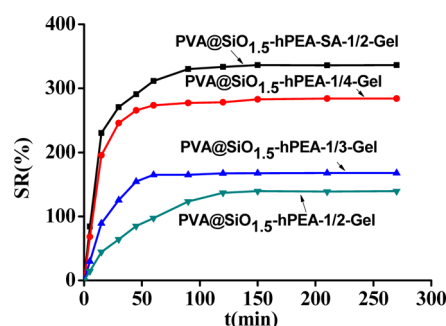


Figure 1. Swelling kinetics of PVA@SiO_{1.5}-hPEA-Gels in aqueous solution at 25 °C (pH = 7.2).

is not as hydrophilic as hPEA. The more content of PVA will lead to the less water adsorption. In addition, due to the introduction of SA groups which makes the obtained hybrid hydrogel zwitterionic, PVA@SiO_{1.5}-hPEA-SA-1/2-Gel exhibited the highest water adsorption among these four PVA-enhanced hydrogels. Meanwhile, there is no weight loss before and after swelling in distilled water, indicating that PVA should be chemically bonded to the hydrogel network.

Because the hybrid hydrogel of SiO_{1.5}-hPEA-Gel is fragile, we expected to introduce PVA to enhance the mechanical strength for the practical application. As shown in Figure 2A,B, the low stress and deformation lead to the breaking of SiO_{1.5}-hPEA-Gel without PVA. On the contrast, PVA-enhanced hybrid hydrogels (PVA@SiO_{1.5}-hPEA-1/2-Gel before and after freeze-dried) do not break under the high press (Figure 2C,E). They recover to their original shape quickly after the release of load (Figure 2D,F). The mechanical strength of four PVA-enhanced hybrid hydrogels before and after freeze-dried was investigated by compression test as well as SiO_{1.5}-hPEA-Gel, as shown in Figure 2G,H. SiO_{1.5}-hPEA211-Gel before and after freeze-dried broke at the stresses of 0.2 and 14 kPa, respectively. It should be mentioned here that four PVA-enhanced hybrid hydrogels did not break in the compression test, and fracture stress values could not be obtained. PVA@SiO_{1.5}-hPEA-1/2-Gel before and after freeze-dried did not break even at the stresses of 92 and 10 530 kPa, respectively. The stresses sustained by PVA@SiO_{1.5}-hPEA-1/2-Gel in two forms (before and after freeze-dried) were at least 460 and 750 times more than that of SiO_{1.5}-hPEA211-Gel, respectively. The stress sustained by PVA-enhanced hybrid hydrogels increases from PVA@SiO_{1.5}-hPEA-1/4-Gel to PVA@SiO_{1.5}-hPEA-1/2-Gel. This might be ascribed to the increasing cross-linking density, which resulted from the increasing content of PVA. During the process of the freeze-

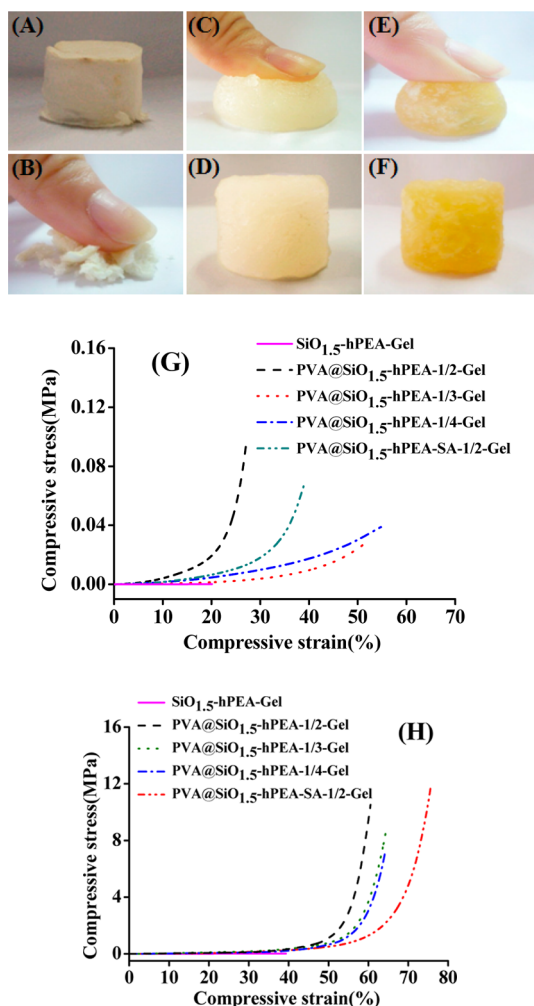


Figure 2. Pictures of (A) and (B) SiO_{1.5}-hPEA211-Gel were readily broken by compressing. (C) PVA@SiO_{1.5}-hPEA-1/2-Gel before freeze-dried was highly compressed and (D) after 10 min compression. (E) PVA@SiO_{1.5}-hPEA-1/2-Gel after freeze-dried was highly compressed and (F) after 10 min compression. Compressive stress-strain curves of gels (G) before and (H) after freeze-dried.

thawing, the rich PVA phase of crystallites can be formed, resulting in the physical cross-linked network.^{32–34} Therefore, hybrid hydrogel of PVA@SiO_{1.5}-hPEA might have the characteristics of the double network, leading to the enhancement of mechanical strength.^{40–42} For convenient comparison, the stresses at the same strain 25% (before freeze-dried) and 60% (after freeze-dried) are listed in Table 1. Both types of stress for PVA@SiO_{1.5}-hPEA-Gels increase with the increasing PVA content. Compared to PVA@SiO_{1.5}-hPEA-1/2-Gel, the stress of PVA@SiO_{1.5}-hPEA-SA-1/2-Gel is lower, which might be due to the existence of SA groups. Generally, the graft of the flexible ester groups to the polymer backbone leads to the low modulus. The mechanical strength of the hybrid hydrogel is dramatically improved hundreds of times by the introduction of PVA. The obtained PVA-enhanced hybrid hydrogels exhibit the excellent mechanical strength, which make them keep their shapes in the following experiments of adsorption and separation of dyes.

Selective Adsorption of Hydrophilic Dyes. We studied the adsorption behavior of the obtained four PVA-enhanced hybrid hydrogels to ten hydrophilic dyes in water. Their

structure is illustrated in Figure 3, and they can be divided into three types: fluorescein dyes including RB, Cal, and FR, azo dyes including OG, PSX, PS, and BY, and other dyes including NR, R6G, and MB. The adsorption experiments were conducted in an aqueous solution of dyes. The initial concentrations of dyes and the hybrid hydrogels in solutions were fixed at 100 μ M and 2 g/L, respectively. After addition of PVA@SiO_{1.5}-hPEA-1/2-Gel for 12 h, the color of RB, OG, PS, and PSX solutions turned obviously light, while BY, R6G, and MB solutions kept almost unchanged (Figure S4). Taking RB and MB as example, it can be seen with the naked eye that most of RB was adsorbed by PVA@SiO_{1.5}-hPEA-1/2-Gel (Figure 4A), but MB still stayed in solution (Figure 4B). UV-vis spectra of dye solution before and after addition of PVA@SiO_{1.5}-hPEA-1/2-Gel for 12 h were recorded for the adsorption of dyes (Figure 4A,B). More than 90% RB was absorbed by the hybrid hydrogel, while less than 5% MB was absorbed. As an important parameter for adsorbents in practical applications, the saturated adsorption capacities (Q_{eq}) were calculated by tracing the UV-vis spectra of solution of dyes. As shown in Figure 4C, the four hybrid hydrogels exhibited the high Q_{eq} to RB, Cal, FR, OG, PSX, and PS regardless of charge states of both hydrogel and dye while possessed the low Q_{eq} to BY, NR, R6G, and MB. We also found that Q_{eq} of adsorbing RB and PS by SiO_{1.5}-hPEA-Gels was close to Q_{eq} of adsorbing the same dyes by PVA@SiO_{1.5}-hPEA-Gels, suggesting that the introduction of PVA has no obvious effect on the adsorption behavior in this study. Here it further indicated that the electrostatic interaction between the host hydrogels and the guest dyes is not the predominant factor to Q_{eq} because the negatively charged PVA@SiO_{1.5}-hPEA-SA-1/2-Gel did not show more adsorption of cationic dye such as BY, R6G, and MB than the positively charged PVA@SiO_{1.5}-hPEA-1/2-Gel. The large difference in Q_{eq} suggests that PVA-enhanced hybrid hydrogels exhibited the selective interaction to the hydrophilic dyes. The introduction of PVA has no effect on the unique selective adsorption to dyes because both of the color of PS and MB dye solution stayed unchanged after adding the pure PVA hydrogel for 12 h (Figure S2).

To further understand the interaction between the hybrid hydrogels and dyes, adsorption kinetics of ten dyes by four obtained hybrid hydrogels were investigated in aqueous solution (Figure 5 and Figure S5). For the dyes with high Q_{eq} such as RB, Cal, FR, OG, PSX, and PS, the adsorption capacity increased rapidly initially and then continued to increase with the contact time at a relatively slow rate. In contrast, the adsorption rate and capacity of BY, NR, R6G, and MB by the four hybrid hydrogels are much lower regardless of their charge states, indicating that the electrostatic interaction between dyes and the hybrid hydrogels has no obvious effect on the adsorption kinetics. This was further supported by the adsorption experiments of PS onto PVA@SiO_{1.5}-hPEA-1/2-Gel conducted in the solution under different pH 4, 7.2, and 8 (Figure S6). No significant influence of pH on dye adsorption for PS can be observed even in the wide pH range from 4 to 8.

Pseudo-second-order equation was used to analyze the adsorption kinetics to investigate the adsorption mechanism of dyes onto the hybrid hydrogels:³⁵

$$\frac{dQ_t}{dt} = k(Q_{eq} - Q_t)^2 \quad (2)$$

Integrating this equation by applying the initial conditions $Q_t = 0$ at $T = 0$ and $Q_t = Q_t$ at $T = t$, eq 2 becomes

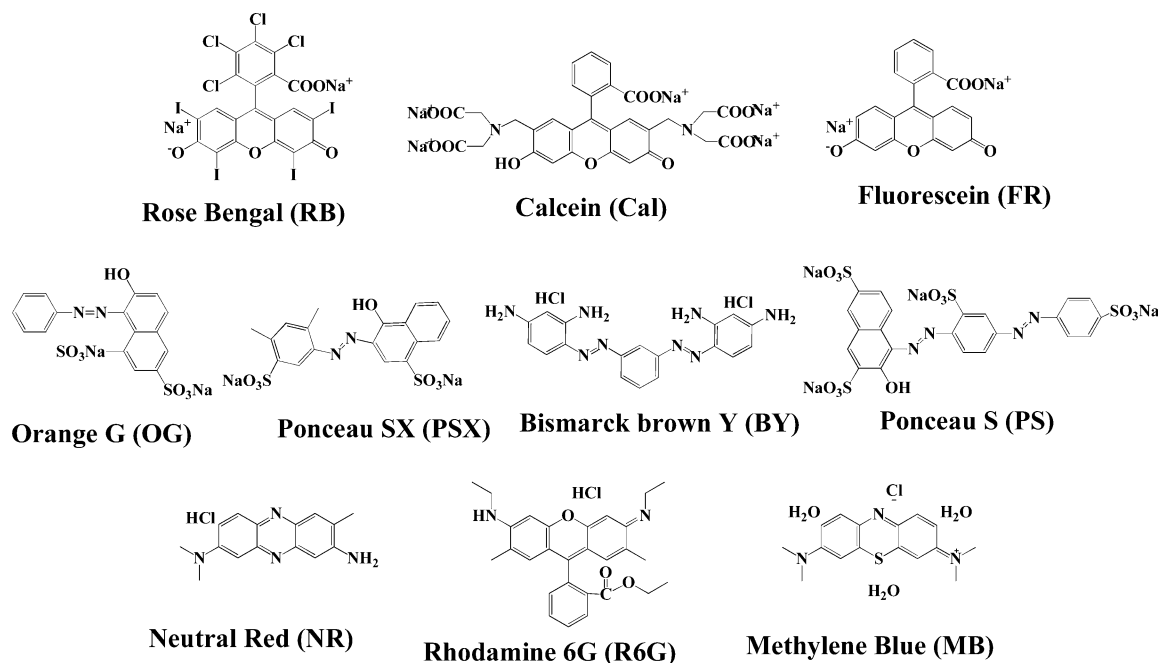


Figure 3. Chemical structure and abbreviation of ten hydrophilic dyes.

$$\frac{t}{Q_t} = \frac{1}{kQ_{eq}^2} + \frac{t}{Q_{eq}} \quad (3)$$

where k is the pseudo-second-order adsorption rate constant. On the basis of the eq 3, we studied the adsorption kinetics of ten dyes. We here provided the pseudo-second-order equation of only six dyes (OG, PS, PSX, RB, CAL, and FR) with strong adsorption for the clear comparison. The plots in Figure 6 and Figure S7 demonstrate that pseudo-second-order equations fitted well to the whole range of the contact time, and the correlation coefficient (R^2) is very high. The values of k and Q_{eq} calculated from the slope and intercept of plots are summarized in Table 2 and Table S1. The value of $Q_{e,exp}$ is closed to that of $Q_{e,cal}$, further indicating that the pseudo-second-order model applied to the adsorption of dyes onto gels. According to the data of k and Q_{eq} summarized in Table 2 and Table S2, we found that electrostatic interaction and PVA have no obvious effect on the adsorption kinetics of the hybrid hydrogels to the hydrophilic dyes. For dyes with extremely low adsorption capacity such as BY, R6G, MB, and NR, k value will be very large because the intercepts of plots are close to zero and become uncertain. The extremely large values of k of dyes such as BY, R6G, MB, and NR do not make sense and are not summarized in Table 2 and Table S2. Through only comparing with the values of k and Q_{eq} of dyes with high adsorption capacity such as RB, PS, PSX, OG, Cal, and FR, we came to the conclusion that the strength of interaction between hydrogels and dyes can be reflected by k and Q_{eq} : large Q_{eq} and k mean a strong affinity. For example, Q_{eq} of PVA@SiO_{1.5}-hPEA-1/2-Gel to OG (1.01×10^{-2} mmol/g) is about 100 times higher than that of PVA@SiO_{1.5}-hPEA-1/2-Gel to MB (1.06×10^{-4} mmol/g), and k of PVA@SiO_{1.5}-hPEA-1/2-Gel to RB (2.25×10^1) is around 14 times more than that of PVA@SiO_{1.5}-hPEA-1/2-Gel to FR (1.61×10^{-1}). The big difference in k and Q_{eq} between different dyes suggested that PVA-enhanced hybrid hydrogels also possess the unique selective adsorption to dyes.

The isotherm study for dyes onto PVA@SiO_{1.5}-hPEA-1/2-Gel was conducted to understand how hybrid hydrogels and

the hydrophilic dyes interact with each other and estimate the characteristics of the adsorption system. OG and MB were chosen for isotherms study because of the big difference in k and Q_{eq} of OG and MB, indicating that the hybrid hydrogels exhibited completely different affinities to OG and MB. The equilibrium adsorption data were analyzed by using the Langmuir and Freundlich isotherm models (Figure S8 and Table S2). We found that the Langmuir model is suitable for describing the adsorption equilibrium of OG by the hybrid hydrogels and that the adsorption of MB follows the Freundlich model. Therefore, the chemisorption dominates in the adsorption of OG with strong affinity onto the hybrid hydrogels from isotherms studies. In summary, PVA-enhanced hybrid hydrogels exhibited the selective adsorption to dyes, and the introduction of PVA and charge state has no obvious effect on interaction between hydrogels and dyes.

Separation of the Mixture of Dyes. Motivated by the excellent mechanical strength and unique selective adsorption of the obtained hybrid hydrogels, PVA@SiO_{1.5}-hPEA-Gels can be extended into the practical application in separation. Because PVA@SiO_{1.5}-hPEA-Gels exhibit different adsorption capacities to different dyes, dyes with high Q_{eq} and k can be adsorbed, while dyes with low Q_{eq} and k are expected to stay in solution. By using PVA@SiO_{1.5}-hPEA-1/2-Gel, first we separated mixtures of PS-BY. The initially concentration ratio of PS and BY ($[PS]_0/[BY]_0$) in solution was 0.9. PVA@SiO_{1.5}-hPEA-1/2-Gel was immersed into the mixture solution of PS and BY. The color of solution turned from red to brown with the contact time. After 12 h, the color of the solution became brown of BY, while the hybrid hydrogel immersed in solution turned red of PS, suggesting that PVA@SiO_{1.5}-hPEA-1/2-Gel adsorbed PS selectively from the mixed solution of PS and BY (Figure 7A). UV-vis spectra were used to trace the whole separation process to check the change of dye's concentration in solution. As shown in Figure 7B,C, the concentration of BY kept unchanged with the increasing contact time, while the concentration of PS in solution decreased obviously from the initial 11 μ M to almost zero. In other words, the purity of BY in

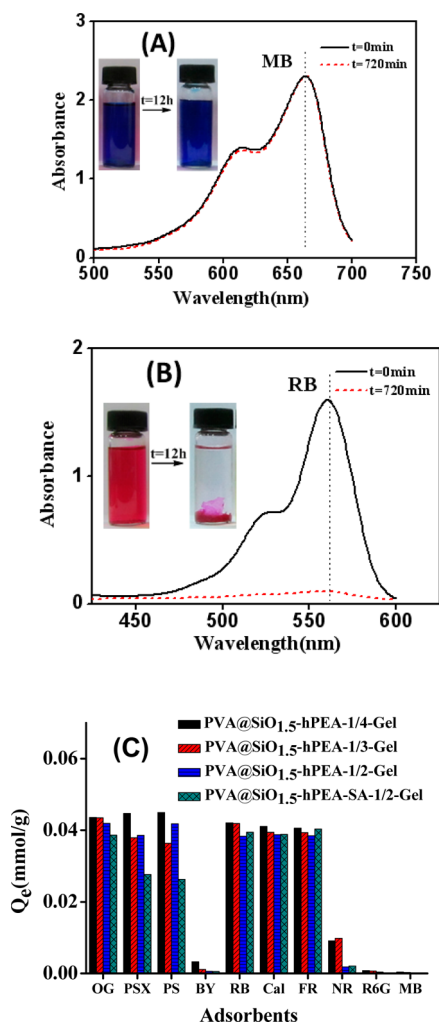


Figure 4. UV-vis spectra of RB (A) and MB (B) before and after adsorption by PVA@SiO_{1.5}-hPEA-1/2-Gel for 12 h. Inset pictures are photos of solution of RB and MB before and after adsorption by PVA@SiO_{1.5}-hPEA-1/2-Gel for 12 h. (C) Saturated adsorption capacities of PVA@SiO_{1.5}-hPEA-1/4-Gel, PVA@SiO_{1.5}-hPEA-1/3-Gel, PVA@SiO_{1.5}-hPEA-1/2-Gel, and PVA@SiO_{1.5}-hPEA-SA-1/2-Gel after freeze-dried at 25 °C. Initial dye concentration is 200 μM, and hydrogel concentration keeps at 1.67 mg/mL.

the solution increased from the initial 53% to 100% after separation. It is notable that both of PS and BY are azo dyes. Therefore, the mixture of the same type of dyes can be separated in the presence of the PVA-enhanced hybrid hydrogels.

The same method was also used to separate the mixture of OG and MB. The initial concentration ratio of OG and MB in solution ($[OG]_0/[MB]_0$) is 0.7. After addition of PVA@SiO_{1.5}-hPEA-1/2-Gel for 12 h, the color of solution became purple-blue of MB and the PVA@SiO_{1.5}-hPEA-1/2-Gel immersed in solution turned orange of OG, indicating that OG was adsorbed by PVA@SiO_{1.5}-hPEA-1/2-Gel selectively from the mixed solution (Figure S9A). The concentration of MB with lower Q_{eq} stayed unchanged in solution, while the concentration of OG decreased obviously with the increasing contact time (Figure S9B,C). After separation for 12 h, the concentration ratio of OG and MB in solution ($[OG]_{eq}/[MB]_{eq}$) decreased to 0, suggesting complete separation of OG from the aqueous solution of OG and MB. Finally, regeneration

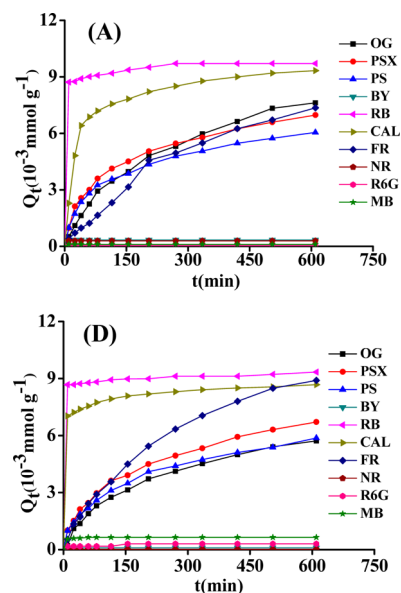


Figure 5. Adsorption capacity Q_t versus time curves for the adsorption of RB, Cal, FR, OG, PSX, PS, BY, NR, R6G, and MB onto (A) PVA@SiO_{1.5}-hPEA-1/2-Gel and (B) PVA@SiO_{1.5}-hPEA-SA-1/2-Gel at 25 °C.

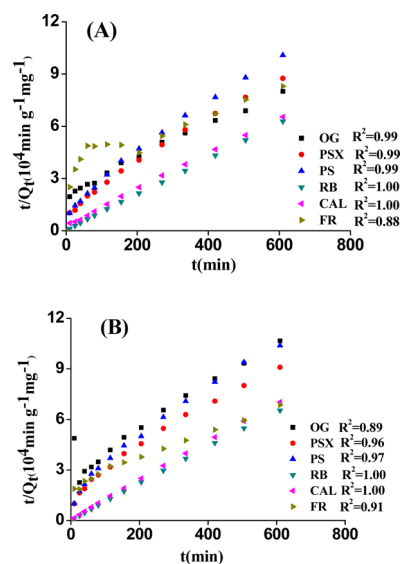


Figure 6. Pseudo-second-order adsorption kinetics of OG, PSX, PS, RB, Cal, and FR onto (A) PVA@SiO_{1.5}-hPEA-1/2-Gel and (B) PVA@SiO_{1.5}-hPEA-SA-1/2-Gel at 25 °C.

of the hybrid hydrogels was demonstrated, which is important in practical application. After immersed in water and dialyzed for 72 h, the dyes could be removed from the hybrid hydrogels and the pure hybrid hydrogels were obtained, which is convenient for their regeneration (Figure 8). It should be noted that the PVA-enhanced hybrid hydrogels can keep their shapes in the whole separation and regeneration experiments due to their good mechanical performance.

CONCLUSION

We prepared a series of hybrid hydrogels (PVA@SiO_{1.5}-hPEA-Gels) by chemically cross-linking between poly(vinyl alcohol) (PVA) and trimethoxysilyl groups of hyperbranched poly(ether amine) (TMS-hPEA) in water and demonstrated that PVA can

Table 2. Kinetics Parameters Describing the Adsorption of Dyes onto PVA@SiO_{1.5}-hPEA-Gels

	PVA@SiO _{1.5} -hPEA-1/2-Gel				PVA@SiO _{1.5} -hPEA-SA-1/2-Gel			
	$Q_{e,exp}$ (mmol/g)	k^a (g/mmol min)	$Q_{e,cal}$ (mmol/g)	R^2	$Q_{e,exp}$ (mmol/g)	k^a (g/mmol min)	$Q_{e,cal}$ (mmol/g)	R^2
OG	1.01×10^{-2}	4.68×10^{-1}	1.01×10^{-2}	0.991	6.85×10^{-3}	8.25×10^{-1}	7.09×10^{-3}	0.885
PSX	7.82×10^{-3}	1.44×10^0	7.68×10^{-3}	0.992	8.20×10^{-3}	1.42×10^0	7.30×10^{-3}	0.963
PS	7.53×10^{-3}	1.76×10^0	6.63×10^{-3}	0.991	6.80×10^{-3}	1.77×10^0	6.28×10^{-3}	0.966
BY	3.35×10^{-4}		3.35×10^{-4}	1.000	8.89×10^{-5}		8.89×10^{-5}	1.000
RB	9.72×10^{-3}	2.25×10^1	9.79×10^{-3}	1.000	9.35×10^{-3}	3.13×10^1	9.29×10^{-3}	1.000
CAL	9.97×10^{-3}	3.45×10^0	9.68×10^{-3}	0.999	8.77×10^{-3}	1.51×10^1	8.68×10^{-3}	1.000
FR	9.36×10^{-3}	1.61×10^{-1}	1.31×10^{-2}	0.880	1.02×10^{-2}	4.60×10^{-1}	1.13×10^{-2}	0.907
NR	2.95×10^{-4}		2.95×10^{-4}	1.000	1.63×10^{-5}		1.63×10^{-5}	1.000
R6G	3.49×10^{-5}		3.49×10^{-5}	1.000	3.03×10^{-4}		3.22×10^{-4}	0.983
MB	1.06×10^{-4}		1.06×10^{-4}	1.000	6.47×10^{-4}		6.49×10^{-4}	1.000

^aFor dyes with extremely low adsorption capacity such as BY, R6G, MB, and NR, because the intercepts of plots are infinitely close to zero, k values will be infinitely close to large values and make no sense, and k values for these dyes cannot be provided.

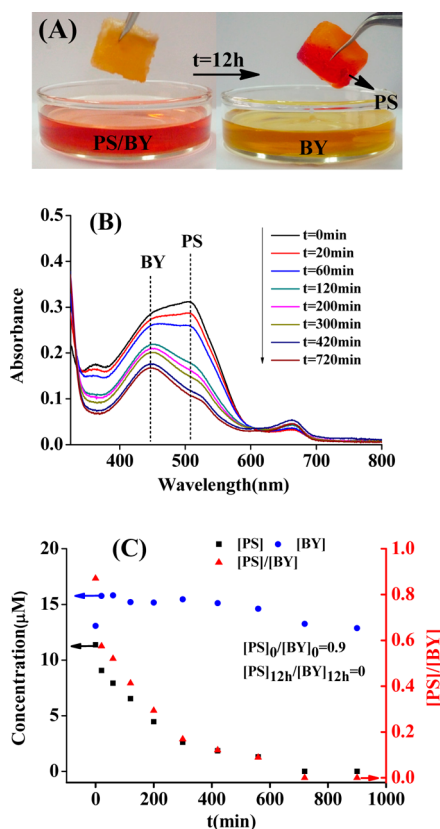


Figure 7. One-pot separation of mixed dyes PS-BY in aqueous solution. Photograph of PS-BY (A) and before and after separation for 12 h by using PVA@SiO_{1.5}-hPEA-1/2-Gel at 25 °C. UV-vis spectra of PS-BY (B) during separation experiment. (C) Dye concentration of [PS] and [BY] and dye concentration ratio of the mixed dyes in solution ([PS]/[BY]). Comparison of [PS] (■) and [BY] (●) with [PS]/[BY] (▲). Concentration of PVA@SiO_{1.5}-hPEA-1/2-Gel in solution was fixed at 2 g/L.

enhance the mechanical performance of the obtained hybrid hydrogels significantly. The stress of PVA@SiO_{1.5}-hPEA-Gels increased hundreds of times with the increasing content of PVA. The detailed investigation of adsorption behavior of PVA@SiO_{1.5}-hPEA-Gels to ten hydrophilic dyes indicates that the adsorption process follows the pseudo-second-order kinetics. Regardless of their charge states, PVA@SiO_{1.5}-hPEA-Gels exhibited the quick adsorption to PS, RB, OG, and PSX with a high Q_{eq} and slow adsorption of BY, MB, and R6G with

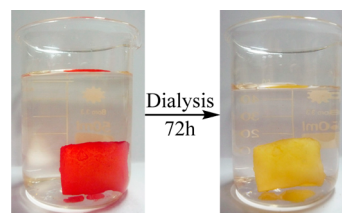


Figure 8. Regeneration of PVA@SiO_{1.5}-hPEA-1/2-Gel adsorbing PS through dialysis in water for 72 h.

a low Q_{eq} . The introduction of PVA has no obvious effect on the adsorption behavior in this study. The big difference in the adsorption to the different dyes suggests the selective adsorption of PVA@SiO_{1.5}-hPEA-Gels to dyes. Because of the great reinforcement in the mechanical strength and the selective adsorption to dyes, PVA@SiO_{1.5}-hPEA-Gels was used to separate mixture of dyes, which might lead to the practical application of PVA@SiO_{1.5}-hPEA-Gels in the separation.

■ ASSOCIATED CONTENT

Supporting Information

Tables S1 and S2, Figures S1–S9. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Tsitsilianis, C. *Soft Matter* **2010**, 6 (11), 2372–2388.
- (2) Wang, Q.; Hou, R.; Cheng, Y.; Fu, J. *Soft Matter* **2012**, 8 (22), 6048–6056.

- (3) Park, T. G.; Hoffman, A. S. *Macromolecules* **1993**, *26* (19), 5045–5048.
- (4) Cai, T.; Yang, W. J.; Zhang, Z.; Zhu, X.; Neoh, K. G.; Kang, E. T. *Soft Matter* **2012**, *8* (20), 5612–5620.
- (5) Ahn, S. K.; Kasi, R. M.; Kim, S. C.; Sharma, N.; Zhou, Y. *Soft Matter* **2008**, *4* (6), 1151–1157.
- (6) Pochan, D. J.; Schneider, J. P.; Kretsinger, J.; Ozbas, B.; Rajagopal, K.; Haines, L. J. *Am. Chem. Soc.* **2003**, *125* (39), 11802–11803.
- (7) Torres-Lugo, M.; Peppas, N. A. *Macromolecules* **1999**, *32* (20), 6646–6651.
- (8) Schneider, J. P.; Pochan, D. J.; Ozbas, B.; Rajagopal, K.; Pakstis, L.; Kretsinger, J. J. *Am. Chem. Soc.* **2002**, *124* (50), 15030–15037.
- (9) Kim, J.; Nayak, S.; Lyon, L. A. *J. Am. Chem. Soc.* **2005**, *127* (26), 9588–9592.
- (10) Gong, J. P. *Soft Matter* **2010**, *6* (12), 2583–2590.
- (11) Lee, J. W.; Kim, S. Y.; Kim, S. S.; Lee, Y. M.; Lee, K. H.; Kim, S. *J. J. Appl. Polym. Sci.* **1999**, *73* (1), 113–120.
- (12) Jeong, B.; Kim, S. W.; Bae, Y. H. *Adv. Drug Delivery Rev.* **2002**, *54* (1), 37–51.
- (13) Martens, P. J.; Bryant, S. J.; Anseth, K. S. *Biomacromolecules* **2003**, *4* (2), 283–292.
- (14) Peppas, N. A.; Hilt, J. Z.; Khademhosseini, A.; Langer, R. *Adv. Mater.* **2006**, *18* (11), 1345–1360.
- (15) Karadag, E.; Uzüm, O. B.; Kundakci, S.; Saraydin, D. *J. Appl. Polym. Sci.* **2007**, *104* (1), 200–204.
- (16) Oren, S.; Çaykara, T.; Kantoglu, Ö.; Güven, O. *J. Appl. Polym. Sci.* **2000**, *78* (12), 2219–2226.
- (17) Kaşgöz, H.; Özgümüş, S.; Orbay, M. *Polymer* **2003**, *44* (6), 1785–1793.
- (18) Horbett, T. A.; Hoffman, A. S. *Appl. Chem. Protein Interfaces* **1975**, *145* (11), 230–254.
- (19) Kawaguchi, H.; Fujimoto, K.; Mizuhara, Y. *Colloid Polym. Sci.* **1992**, *270* (1), 53–57.
- (20) Barbucci, R.; Magnani, A.; Leone, G. *Polymer* **2002**, *43* (12), 3541–3548.
- (21) Solpan, D.; Sen, M.; Kölge, Z.; Guven, O. *Radiat. Phys. Chem.* **2008**, *77* (4), 428–433.
- (22) Akkaya, M. C.; Emik, S.; Guclu, G.; Iyim, T. B.; Ozgumus, S. *J. Appl. Polym. Sci.* **2009**, *114* (2), 1150–1159.
- (23) Saraydin, D.; Karadag, E.; Guven, O. *J. Appl. Polym. Sci.* **2001**, *79* (10), 1809–1815.
- (24) Ray, S.; Das, A. K.; Banerjee, A. *Chem. Mater.* **2007**, *19* (7), 1633–1639.
- (25) Arami, M.; Limaee, N. Y.; Mahmoodi, N. M.; Tabrizi, N. S. *J. Colloid Interface Sci.* **2005**, *288* (2), 371–376.
- (26) Wong, Y. C.; Szeto, Y. S.; Cheung, W. H.; McKay, G. *Langmuir* **2003**, *19* (19), 7888–7894.
- (27) Ho, K. Y.; McKay, G.; Yeung, K. L. *Langmuir* **2003**, *19* (7), 3019–3024.
- (28) Choy, K. K. H.; Porter, J. F.; McKay, G. *J. Chem. Eng. Data* **2000**, *45* (4), 575–584.
- (29) Adhikari, B.; Palui, G.; Banerjee, A. *Soft Matter* **2009**, *5* (18), 3452–3460.
- (30) Thomas, P. C.; Cipriano, B. H.; Raghavan, S. R. *Soft Matter* **2011**, *7* (18), 8192–8197.
- (31) Deng, S.; Wang, R.; Xu, H. J.; Jiang, X. S.; Yin, J. *J. Mater. Chem.* **2012**, *22* (19), 10055–10061.
- (32) Ricciardi, R.; Auriemma, F.; De Rosa, C.; Lauprêtre, F. *Macromolecules* **2004**, *37* (5), 1921–1927.
- (33) Ricciardi, R.; Mangiapia, G.; Lo Celso, F.; Paduano, L.; Triolo, R.; Auriemma, F.; De Rosa, C.; Lauprêtre, F. *Chem. Mater.* **2005**, *17*, 1183–1189.
- (34) Valentín, J. L.; Lopez, D.; Hernandez, R.; Mijangos, C.; Saalwachter, K. *Macromolecules* **2009**, *42*, 263–272.
- (35) Zhou, L.; Gao, C.; Xu, W. *ACS Appl. Mater. Interfaces* **2010**, *2* (5), 1483–1491.
- (36) Tripathi, B. P.; Shahi, V. K. *ACS Appl. Mater. Interfaces* **2009**, *1* (5), 1002–1012.
- (37) Peng, F.; Lu, L.; Sun, H.; Wang, Y.; Liu, J.; Jiang, Z. *Chem. Mater.* **2005**, *17* (26), 6790–6796.
- (38) Zhang, Q. G.; Liu, Q. L.; Chen, Y.; Chen, J. H. *Ind. Eng. Chem. Res.* **2007**, *46* (3), 913–920.
- (39) Zhang, Q. G.; Liu, Q. L.; Zhu, A. M.; Xiong, Y.; Zhang, X. H. *J. Phys. Chem. B* **2008**, *112* (51), 16559–16565.
- (40) Bryant, S. J.; Davis-Arehart, K. A.; Luo, N.; Shoemaker, R. K.; Arthur, J. A.; Anseth, K. S. *Macromolecules* **2004**, *37*, 6726–6733.
- (41) Suekama, T. C.; Hu, J.; Kurokawa, T.; Gong, J. P.; Gehrke, S. H. *ACS Macro Lett.* **2013**, *2*, 137–140.
- (42) Liang, S. M.; Hu, J.; Wu, Z. L.; Kurokawa, T.; Gong, J. P. *Macromolecules* **2012**, *45*, 4758–4763.