Water Recycling/Removal Using Temperature-Sensitive Hydrogels

Final Report Prepared by

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Preface

Water recycling/removal is a key element in pulp and paper manufacturing. Examples include the concentration of in-process water streams, white-water cleaning, and oxygen-delignification-filtrate and black-liquor spills concentration. Current methods of water removal such as evaporation are energy and cost intensive; here in addition to high capital and maintenance costs, a large amount of energy is needed to provide the heat of vaporization for each kg of water removed. Hence, alternate energy efficient methods are needed.

This project was carried out to develop understanding toward a new water separation method based on temperature sensitive hydrogels. Hydrogels are three-dimensional network polymers that swell on contact with water but do not dissolve. The extent of swelling is determined by the chemical nature of the polymer chains and the crosslinking density. During the swelling and shrinking process, hydrogels preserve their overall shape. It is possible to select a hydrogel which can swell or shrink in response to the environment conditions such as pH, temperature and ionic strength. Detailed background on hydrogels and its various applications can be found in a Hydrogel chapter written by the author in *Kirk-Othmer Encyclopedia of Chemical Technology*, published in 2002 by John Wiley & Sons, New York, (<http://www.mrw.interscience.wiley.com/kirk/articles/hydr Gupta.a01/frame.html>).

The separation is based on the small molecular pore size of the hydrogels. Small molecules such as water can get into the pore and be removed by the hydrogel swelling, whereas large molecules such as lignin and carbohydrates remain outside the hydrogel. The swelling can be reversed by a small shift in the temperature; this behavior is utilized to regenerate the hydrogel and recover water. Various aspects of the hydrogel design are studied. This work has resulted in enhancing our understanding toward the design of an energy efficient water separation process. In addition, the work has resulted into synthesis of a new type of hydrogel called Bulk Hydrogel with Microstructure, which can find applications in many areas of science and technology.

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1.

Summary

The overall objective of this project was to study the proposed Water Recycling/Removal Using Temperature-Sensitive Hydrogels. The main element of this technology is the design of a suitable hydrogel that can perform needed water separation for pulp and paper industry. The specific topics studied are to answer following questions:

- (a) Can water be removed using hydrogel from large molecules such as lignin?
- (b) Can the rate of separation be made faster?
- (c) What are the molecular interactions with hydrogel surface?
- (d) Can a hydrogel be designed for a high ionic strength and high temperature?

Summary of the specific results is given below:

Separation of Lignin from Aqueous Mixtures by Ionic and Nonionic Temperature-Sensitive Hydrogels

Three ionic and nonionic temperature-sensitive hydrogels, poly(N-isopropylacrylamide) (PNIPAAm), poly(N-isopropylacrylamide-co-acrylic acid) (NIPAAm-AA), and poly(N-isopropylacrylamide-co hydroxypropyl methacrylate) (NIPAAm-HPMA), are synthesized and used to concentrate the lignin solutions of interest in the pulp and paper industry. The interactions between hydrogels and solutes play an important role in the separation. Because of the absorption of lignins in the hydrogels, the separation efficiency of the PNIPAAm hydrogel is low. By introducing the hydrophilic monomers AA and HPMA into the NIPAAm hydrogel, the separation efficiencies are increased because of the ionic repulsion between lignin and the incorporated hydrophilic groups. In addition, the separation efficiencies are affected by the extent of cross-linking and the solute concentration. The time dependence of the separation efficiency suggests that the separation is diffusion-controlled.

Publication: Cai, Wensheng; Anderson, Eric C.; Gupta, Ram B. Separation of lignin from aqueous mixtures by ionic and nonionic temperature-sensitive hydrogels. *Ind. Eng. Chem. Res.* (2001), 40(10), 2283-2288

Fast-Responding Bulk Hydrogels with Microstructure

A new method has been used to produce fast-responding bulk hydrogel with microstructure (BHM), having a high swelling ratio. These BHMs were synthesized by first forming poly(N-isopropylacrylamide-co-acrylic acid) (NIPAAm-AA) microgel particles and then crosslinking the particles with NIPAAm monomer. The polymer obtained has desired microstructure, but is bulk (monolithic), hence it can be used in a variety of applications. The NIPAAm-AA microgel particles were characterized by transmission electron microscopy, and the formed BHMs are characterized by scanning electron microscopy. When compared to the conventional bulk hydrogels, the BHMs have a very high swelling ratio and a much faster swelling rate, attributed to the collaboration of the ionized microgel particles and bulk hydrogels. An increase in the microgel particles embedded in the BHM hydrogel provides faster hydrogel

swelling. The amounts of ionic acrylic acid (AA) groups in the hydrogel affect the swelling behavior of the hydrogels.

Publication: Cai, Wensheng; Gupta, Ram B. Fast-responding bulk hydrogels with microstructure. *J. Appl. Polym. Sci.* (2002), 83(1), 169-178.

Poly(N-ethylacrylamide) Hydrogels for Lignin Separation

Poly(N-ethylacrylamide) hydrogel (PEAM) and N-ethylacrylamide bulk hydrogel with micro-structure (EAM-BHM) are prepared. The lower critical solution temperature (LCST) of PEAM is determined to be 73 °C by DSC, and the microstructures of the hydrogels are characterized by SEM. When the microgel particles are incorporated into the matrix of EAM hydrogel, the formed bulk hydrogels have a faster swelling rate and a higher swelling ratio compared to those of the conventional PEAM hydrogels. The swelling diffusion mechanism in PEAM hydrogel changes from Fickian to non-Fickian when the cross-linker content is increased to 8 wt %. Both EAM-BHMs and conventional PEAM can be used to separate lignin at a high temperature ($\neq$ 55 °C, typical in a pulp mill). Due to the microgel particles, the EAM-BHMs have a higher swelling ratio in lignin solution while the large surface area of the microgel also increases the adsorption of lignin on the hydrogel, thus decreasing the separation efficiency. The effects of lignin concentration, separation temperature, and salt on the separation efficiency are also studied.

Publication: Cai, Wensheng; Gupta, Ram B. Poly(N-ethylacrylamide) hydrogels for lignin separation. *Ind. Eng. Chem. Res.* (2001), 40(15), 3406-3412

Thermosensitive and Amphoteric Hydrogel for Salt Solution

A series of N-isopropylacrylamide/[3-(Methacryloylamino)propyl]dimethyl(3-sulfopropyl)ammonium hydroxide] (NIPAAm/MPSA) copolymer hydrogels are prepared with various composition. Swelling of the hydrogels in water, aqueous NaCl, KCl, CaCl₂, MgCl₂ solutions is studied. NIPAAm/MPSA hydrogels have higher swelling in water and salt solutions than poly(N-isopropylacrylamide) (PNIPAAm). Also NIPAAm/MPSA hydrogels are more salt resistant when deswelling in salt solutions. For less than 7 mol% MPSA, the formed hydrogels retain both temperature reversibility and high swelling. Higher content of MPSA (>11 mol.%) leads to better salt resistance but loses thermosensitivity. The swelling of NIPAAm/MPSA hydrogel in 0.05 M NaCl is non-Fickian. In NaCl and KCl aqueous solutions, the zwitterionic hydrogels do not show obvious anti-polyelectrolyte swelling behavior, while in divalent salt CaCl₂ and MgCl₂ solutions, the swelling ability of NIPAAm/MPSA hydrogels is enhanced at low salt concentration, then decreases with further increase in salt concentration. The LCST of NIPAAm/MPSA hydrogels are also affected by concentrated salt solution.

Publication: Cai, Wensheng; Gupta, Ram B. Thermosensitive and Amphoteric Hydrogel for Salt Solution. in press, *J. Appl. Polym. Sci.* (2002).

2.

**Separation of Lignin from Aqueous Mixtures by Ionic and Nonionic
Temperature-Sensitive Hydrogels**

SEPARATIONS

Separation of Lignin from Aqueous Mixtures by Ionic and Nonionic Temperature-Sensitive Hydrogels

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Three ionic and nonionic temperature-sensitive hydrogels, poly(*N*-isopropylacrylamide) (PNIPAAm), poly(*N*-isopropylacrylamide-*co*-acrylic acid) (NIPAAm-AA), and poly(*N*-isopropylacrylamide-*co*-hydroxypropyl methacrylate) (NIPAAm-HPMA), are synthesized and used to concentrate the lignin solutions of interest in the pulp and paper industry. The interactions between hydrogels and solutes play an important role in the separation. Because of the absorption of lignins in the hydrogels, the separation efficiency of the PNIPAAm hydrogel is low. By introducing the hydrophilic monomers AA and HPMA into the NIPAAm hydrogel, the separation efficiencies are increased because of the ionic repulsion between lignin and the incorporated hydrophilic groups. In addition, the separation efficiencies are affected by the extent of cross-linking and the solute concentration. The time dependence of the separation efficiency suggests that the separation is diffusion-controlled.

Introduction

Traditional industrial separation methods include distillation, crystallization, and drying. However, because of the phase change involved in such separations, these processes are energy-consuming. A convenient alternative to traditional separation methods is provided by hydrogels. The hydrogel-based separation requires less energy and is easy to operate. The separation is based on reversible hydrogels that undergo volume transitions in response to small changes in external conditions such as temperature, ionic strength, pH, or pressure.^{1–4}

Temperature-sensitive hydrogels have been studied to concentrate macromolecules by removing water and low-molecular-weight solutes from solution. Most of these applications are based on poly(*N*-isopropylacrylamide) (PNIPAAm) hydrogel. For example, Cussler et al.^{5–8} used PNIPAAm and poly(*N,N*-diethylacrylamide-*co*-sodium acrylate) hydrogels to extract water for the separation of soy proteins, and Sun et al.^{9,10} concentrated aqueous protein solutions using different *N*-alkyl-substituted thermosensitive acrylamide hydrogels. During the separation, the hydrogel absorbs water and excludes the large protein molecules, resulting in the concentration of proteins. It was observed that the separation efficiency increases with increasing solute size and extent of cross-linking.

Recently, Ichijo et al.¹¹ used poly(vinyl methyl ether) hydrogel to recover nonionic surfactants from aqueous solutions. Han et al.¹² and Park et al.¹³ used PNIPAAm hydrogel to concentrate alkaline serine protease and

autographa californica nuclear polyhedrosis, respectively. Park and Igacio^{14,15} used PNIPAAm hydrogel to concentrate cellulases from the fermentation broth of *trichoderma reesei* and studied the effect of hydrogel particle size and geometry on the separation efficiency.

Compared with the traditional separation methods in chemical industry, the advantages of separations using thermosensitive hydrogels are obvious.⁶ The hydrogels can easily be regenerated just by being heated above their lower critical solution temperatures (LCSTs), causing the release of water. Also, hydrogels can separate molecules based on size, i.e., they absorb the small-sized solute and exclude large molecules. However, in practice, the separation is not simply size-selective, as some other factors also influence the separation. The interactions between hydrogels and solutes are important. For example, some solutes are easily absorbed by hydrogels, which decreases the separation efficiency; on the other hand, repulsive interactions between hydrogels and solutes can enhance the separation efficiency.

In the pulp and paper industry, water separation from lignin presents a major cost, particularly in in-process water streams, white-water cleaning, black-liquor spills, and oxygen-delignification filtration. These costs are expected to further increase because of enforcement of the new “cluster rule” legislation, which aims to reduce the load on wastewater treatment plants. Current methods of water removal such as evaporation are energy- and cost-intensive, as a large amount of energy is needed as the heat of evaporation for water removed. A new approach that has lower capital and energy requirements is highly desired.

In this work, we have studied water/lignin separation using NIPAAm-based hydrogels. The swelling behavior and temperature sensitivity of these hydrogels are studied, the results of lignin separation are presented,

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Table 1. Structures and Properties of the Hydrogels

hydrogels	molar feed ratio			hydrogel appearance	LCST (°C)
	NIPAAm CH ₂ CHCONHCH(CH ₃) ₂	AA CH ₂ CHCOOH	HPMA CH ₂ C(CH ₃)COOC ₃ H ₆ OH		
PNIPAAm	100	0	0	opaque	33
NIPAAm-AA	94	6	0	opaque	36
NIPAAm-HPMA	90	0	10	opaque	34

and the chemical selectivity of the hydrogels to lignins is discussed.

Experimental Section

Materials. NIPAAm, hydroxypropyl methacrylate (HPMA), *N,N'*-methylene-bis(acrylamide) (BIS), ammonium persulfate (APS), and sodium metabisulfite (SBS) (all from Aldrich Chemical Co.) were used as received. The inhibitor from acrylic acid (AA, from Aldrich Chemical Co.) was removed by an inhibitor-remover column. Three kinds of lignins, lignin hydrolytic (from Aldrich Chemical Co.), Indulin AT, and Indulin C (both from Westvaco Chemical Co.), with average molecular weights of 19 300, 2700, and 2700 g/mol, respectively, were used as received.

Synthesis of Hydrogels. Hydrogels were prepared by free-radical aqueous-solution polymerization using BIS as the cross-linking agent. The polymerizations were carried out at room temperature (23 °C) in glass tubes. The monomer feed ratios are shown in Table 1. The monomer concentration was fixed at 10 wt % of the solution. After oxygen was removed by bubbling N₂ for 20 min, the redox initiators APS and SBS were added. The gelation was usually conducted for 1 day; then, the hydrogels were cut into small disks (16 mm diameter and 5 mm thick), washed with ethanol 4–5 times, and dried under vacuum at 50 °C to constant weight. Except as indicated, the amount of the cross-linking agent BIS was kept at 2 wt % of the total monomer. The amounts of the initiators APS and SBS were kept at a 1:1 molar ratio as 0.1 wt % of the total monomers.

Separation of Lignin and Swelling Behavior of the Hydrogels. The separation experiments were conducted in 100-mL wide-mouth bottles. The dry hydrogel disks were put into lignin solutions (0.01 N NaOH for lignin hydrolytic and Indulin AT; aqueous solution for Indulin C). The hydrogel samples were removed from the solvent at regular intervals, the excess surface solvent was blotted with filter paper, and then the samples were weighed and returned to the medium. The raffinate concentration was measured, and the separation efficiency (η) was calculated as

$$\eta = 100 \times \frac{\text{measured concentration change}}{\text{maximum change expected from hydrogel swelling}} \quad (1)$$

Here, the solute concentration changes were measured with an ultraviolet (UV) spectrophotometer (Spectronic Genesys 2). A quartz cell with a path length of 1 cm and a volume of 5 mL was used. Although the entire spectral range of the lignin solution (230–1100 nm) was recorded for each sample, only the absorbance (*A*) at 280 nm was utilized, and the absorbance at 1100 nm was used as baseline. The relationship between the net absorbance (absorbance at 280 nm minus absorbance at 1100 nm) and the solute concentration was confirmed to obey Beer–Lambert law. The maximum change expected

Figure 1. Structure of the repeat unit in lignin hydrolytic.

from hydrogel swelling was achieved in the case of complete solute exclusion by the hydrogel.

The swelling ratio (SR) of the hydrogels is defined as

$$SR = (W_s - W_d)/W_d \quad (2)$$

where *W_s* and *W_d* are the weights of the wet and dry hydrogels, respectively. *W_s* is measured after the surface water has been blotted by filter paper. Except as indicated, the hydrogel swelling experiments were carried out at an ambient temperature of 23 °C.

Infrared Analysis. The lignin samples were pressed into pellets using an evacuable KBr pellet maker kit (P/N 2506-0001, Janoes Tech., Inc.), and the FTIR spectra were obtained using a Perkin-Elmer Spectrum 2000 instrument.

SEM Analysis. The dry hydrogel pieces were examined by scanning electron microscopy (SEM). The samples were first dried under vacuum and gold-coated using a sputter coater (Pelco, model Sc-7) for 60 s and then observed by SEM (Zeiss, model DSM940).

DSC Analysis. DSC (Universal V2.5H TA instrument) was used to determine the transition temperature of the swollen hydrogels. Hydrogel pieces were equilibrated at room temperature in pure water and then sealed into an aluminum pan. An empty sealed aluminum pan was used as the reference. In DSC, the sample was equilibrated at 10 °C for 5 min and then heated to 55 °C at a rate of 2 °C/min. The temperature corresponding to the maximum heat flow was taken as the LCST.

Results and Discussion

Characterization of Lignins. Lignin occupies 20–30% of wood and acts as the glue to hold the fibers together in plants. It is the second most abundant natural polymer on the earth and has a complex molecular formula. In general, lignin molecules have 5–500 substituted phenylpropanoid units.¹⁶ Monomer units in lignin hydrolytic have the chemical structure shown in Figure 1. Indulin AT and Indulin C have similar structures with the formulas $\{(\text{CH}_3)(\text{OH})\text{Ar}(\text{C}_3\text{H}_4\text{O})\}_x$ and $\{(\text{CH}_3)(\text{ONa})\text{Ar}(\text{C}_3\text{H}_4\text{O})\}_x$, respectively. Because Indulin C is a sodium salt, it is soluble in water,

Table 2. Separation of Lignins by Hydrogels at 23 °C after Contacting for 24 Hours

hydrogel	solute	feed conc (ppm)	raffinate conc (ppm)	swelling ratio	separation efficiency η	amount of lignin absorbed (mg/g)
PNIPAAm	lignin hydrolytic	66.9	80.0	16.8	15.3	0.942
	Indulin AT	47.6	49.2	11.0	38.4	0.912
	Indulin C	119.3	151.1	15.4	24.8	2.252
NIPAAm-AA	lignin hydrolytic	54.3	80.3	12.9	71.3	0.406
	Indulin AT	47.8	77.1	19.8	88.3	0.323
	Indulin C	61.4	78.6	29.9	28.8	0.577
NIPAAm-HPMA	lignin hydrolytic	53.2	62.2	7.3	89.0	0.209
	Indulin AT	69.5	81.3	10.6	54.0	0.587
	Indulin C	84.7	90.4	29.8	29.8	1.356

Figure 2. FTIR spectra of the three lignins: Indulin AT, lignin hydrolytic, and Indulin C.

whereas lignin hydrolytic and Indulin AT require an alkaline solution for solubilization.

The FT-IR spectra of the three lignins (Figure 2) show that all three lignins (hydrolytic, Indulin AT, and Indulin C) have typical lignin structures.¹⁶ The peaks at around 3400 cm^{-1} are attributed to the O-H stretch, and the peaks at around 2918 cm^{-1} are attributed to the C-H stretch. Lignin hydrolytic shows a stronger conjugated C=O stretching at 1690 cm^{-1} . The peaks at around 1599, 1508, and 1451 cm^{-1} are from aromatic skeletal vibrations in the lignins; the 1112 and 1026 cm^{-1} peaks are from aromatic C-H in-plane deformation; and the peaks at 828 cm^{-1} are from aromatic C-H out-of-plane bending.

SEM Observation of the Hydrogels. Figure 3 shows the SEM photographs of NIPAAm hydrogels. It can be seen that the three hydrogels have porous structures with pores of micrometer size. The NIPAAm-AA hydrogel has the biggest pore size in the range of

2.5–7.6 μm , and the PNIPAAm hydrogel has the smallest pore size in the range of 0.3–0.7 μm .

Temperature Sensitivity of the Hydrogels. The compositions and LCSTs of the hydrogels synthesized in this work are listed in Table 1. All of the hydrogels synthesized are opaque at room temperature. Based on the DSC results, the LCSTs of the NIPAAm-AA and NIPAAm-HPMA hydrogels are slightly higher than that of the PNIPAAm hydrogel. The phase transition temperature of a hydrogel is determined by a delicate balance between the hydrophilic and hydrophobic groups inside the hydrogels. Because of the presence of the hydrophilic monomers of AA and HPMA, the copolymer hydrogels have higher LCSTs.

All three of the hydrogels are temperature-sensitive (Figure 4), as the swelling decreases sharply when they are heated above their transition temperatures. Figure 5 shows that, because of the strong hydrophilicity of the AA monomer, the NIPAAm-AA hydrogel has a faster swelling rate and a higher swelling ratio in water than the other two hydrogels. After being kept in water for 180 min, the swelling ratio of NIPAAm-AA is 6.9, whereas the swelling ratios of NIPAAm-HPMA and PNIPAAm are only 2.7 and 3.4, respectively.

Lignin Separation Results. The separation of lignins from aqueous solutions was performed with the PNIPAAm, NIPAAm-AA and NIPAAm-HPMA hydrogels for 24 h (Table 2). The lignin concentrations increased because of water removal by hydrogel swelling. The separation efficiency varies with the type of hydrogel and lignin. Although lignin hydrolytic has the highest molecular weight (19 300 g/mol), no molecular-size-selective trend was observed, as the separation efficiencies of the PNIPAAm and NIPAAm-AA hydrogels were not higher for lignin hydrolytic than for Indulin AT or Indulin C. In fact, lignin hydrolytic showed the lowest separation efficiency when used with PNIPAAm. Sun⁹ also observed that separation efficiency did not always increase with molecular size when bovine

Figure 3. SEM photographs of the hydrogels: (a) PNIPAAm, $\times 5000$, pore size = 0.3–0.7 μm . (b) NIPAAm-AA-6, $\times 5000$, pore size = 2.5–7.6 μm . (c) NIPAAm-HPMA, $\times 5000$, pore size = 1.6–3.2 μm .

Figure 4. Temperature sensitivity of the hydrogels after swelling at 23 °C for 24 h.

Figure 5. Swelling rate of the hydrogels in water at 23 °C.

serum albumin (BSA) was separated with PNIPAAm hydrogel through the surface adsorption of BSA on the hydrogel. Hence, for the separation of lignin by NIPAAm-based hydrogels, the interaction between the hydrogel and the solute is important. Because of its nonpolar hydrophobic phenylpropanoid units, lignin can be absorbed on the hydrophobic regions of the NIPAAm matrix. In fact, during our experiments with lignin hydrolytic and Indulin AT, the hydrogels had a weak brown color because of lignin absorption. The absorption decreased the separation efficiencies of the PNIPAAm hydrogel for all three lignins. When the AA and HPMA monomers were incorporated as hydrophilic groups into the hydrogel structures, lignin absorption decreased because of repulsion between the lignin molecules and the hydrogel matrix. As shown in Table 2, lignin hydrolytic absorption on the PNIPAAm hydrogel is 0.942 mg/g of hydrogel, but for the NIPAAm-AA and NIPAAm-HPMA hydrogels, the absorption decreases to 0.406 and 0.209 mg/g, respectively, resulting in a separation efficiency increase from 15% to 71.3% and 89%, respectively. It should be noticed that, although Indulin AT and Indulin C have similar molecular structures and sizes, their separation efficiencies differ greatly; this might be because Indulin C is in salt state, which is more easily absorbed by the hydrogels. From the above experiments, it can be concluded that the chemical selectivity between the hydrogels and the solutes plays a more important role than the solute size. Other factors affecting the separation efficiency include cross-linking, solute concentration, water and lignin diffusion, and hydrogel recycling and are discussed below.

Cross-linking. The effect of the cross-linking agent content in the NIPAAm-AA hydrogel on the separation efficiency is shown in Figure 6. Increasing the amount

Figure 6. Effect of the amount of cross-linking agent on the separation efficiency of lignins by NIPAAm-AA hydrogel after 24 h at 23 °C.

Figure 7. Effect of the Indulin AT concentration on the separation efficiency of NIPAAm-AA hydrogel after 24 h at 23 °C.

of BIS causes the hydrogel to be more cross-linked, thereby decreasing the pore size. With an increase in the BIS content, the separation efficiencies first increase, reaching a maximum at about 6 wt % cross-linking, and then decrease. Cussler et al.⁵ reported that the separation efficiency of PNIPAAm to vitamin B and poly(ethylene glycol) increased with higher degrees of cross-linking. However, in their experiments, the amount of the cross-linking agent was less than 6 wt %, and no separations at higher cross-linking contents were reported. The results in Figure 6 suggest that, as the higher cross-linking (BIS% > 6 wt %) provided smaller pores to exclude more lignin, the swelling ability of the hydrogel was also reduced greatly. Less water was absorbed, and the absorption of lignin was not reduced, causing a decrease in the final separation efficiency.

Solute Concentration. The influence of solute concentration on the separation efficiency and swelling ratio of the NIPAAm-AA hydrogel is shown in Figure 7. The swelling ratio decreases with increasing concentration of Indulin AT, which could be attributed to the differences in the chemical potential of water between water and Indulin AT solutions, as explained by Champ et al.¹⁷ for other systems. Figure 8 shows that, with increasing Indulin AT concentration, the amount of solute absorbed by the NIPAAm-AA hydrogel increases, causing a decrease in the separation efficiency shown in Figure 7.

Water and Lignin Diffusion. Figure 9 shows the effect of time on the lignin hydrolytic separation efficiency for the PNIPAAm and NIPAAm-AA hydrogels. The separation efficiencies reach a maximum within the first few hours and then decrease for longer separation times. The NIPAAm hydrogel shows a maximum separation

Figure 8. Absorption of Indulin AT by NIPAAm-AA hydrogel after 24 h at 23 °C.

Figure 9. Lignin hydrolytic separation efficiency versus time at 23 °C.

efficiency after 3 h, and the NIPAAm-AA hydrogel shows a maximum separation efficiency after 5 h. Extending the separation time does not increase the separation efficiency. This suggests that the separation process is mainly diffusion-controlled. When the hydrogel begins to swell, it takes up water and some lignin hydrolytic. The separation efficiency of lignin hydrolytic is governed by the difference in the rates of diffusion of water and lignin hydrolytic into the hydrogel network. Because of the difference in their affinities and molecular sizes, water initially diffuses faster than lignin. A high amount of water is absorbed during the first few hours, resulting in a large separation efficiency. With more water entering the hydrogel network, the osmotic pressure inside the hydrogel network decreases, resulting in a drop in the water flux and the separation efficiency at later times.

Hydrogel Recycling. Figures 10 and 11 show the water removal results for hydrogels undergoing multiple cycles. All three hydrogels have good water uptake capacities (5.8–7.4 g of water/g of hydrogel) in Indulin AT solution for the first cycle. For the later cycles, the water removal ability remains the same, confirming that the hydrogels exhibit good temperature reversibility. Interestingly, the separation efficiencies for the second and third cycles are higher than those for the first cycle. For the first cycle of water removal, the separation efficiencies for the PNIPAAm, NIPAAm-AA, and NIPAAm-HPAM hydrogels to Indulin AT are 34.5%, 40.9%, and 49.7%, respectively; after the third water removal cycle, the separation efficiencies increase to

Figure 10. Water uptake by the hydrogels from Indulin AT solution for multiple cycles.

Figure 11. Lignin (Indulin AT) separation efficiency for multiple cycles.

74.7%, 85.2%, and 95.8%, respectively. The increase in the separation efficiency is attributed to the saturation of the lignin absorption sites in the hydrogels after the first cycle. During the second and third cycles, no further absorption of lignin occurs, resulting in the increased separation efficiency.

Conclusions

Chemical selectivity plays an important role in the separation of lignins by temperature-sensitive NIPAAm hydrogels. The separation efficiency increases upon incorporation of AA and HPMA monomers into the hydrogel networks, because of the molecular repulsion between the hydrogels and the lignin molecules. The separation efficiency varies with the separation time, suggesting that the separation process is diffusion-controlled. The water removal experiments for multiple cycles show that the hydrogels exhibit good temperature reversibility and water removal ability for the concentration of lignin solutions.

Acknowledgment

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Fast-Responding Bulk Hydrogels with Microstructure

Fast-Responding Bulk Hydrogels with Microstructure

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ABSTRACT: A new method was used for the production of fast-responding bulk hydrogels with microstructure (BHMs) with a high swelling ratio. These BHMs were synthesized first by the formation of poly(*N*-isopropylacrylamide-co-acrylic acid) (NIPAAm-AA) microgel particles and then by the crosslinking of the particles with *N*-isopropylacrylamide monomer. The polymer obtained had the desired microstructure but was bulk (monolithic), so it could be used in a variety of applications. The NIPAAm-AA microgel particles were characterized with transmission electron microscopy, and the formed BHMs were characterized with scanning electron microscopy. Compared with conventional bulk hydrogels, the BHMs had very high swelling ratios and much faster swelling rates attributable to the collaboration of the ionized microgel particles and bulk hydrogels. An increase in the microgel particles embedded in the BHMs provided faster hydrogel swelling. The number of ionic acrylic acid groups in the hydrogels affected their swelling behavior. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 169–178, 2002

Key words: hydrogel; microstructure; separation

INTRODUCTION

In the past 20 years, a considerable amount of research has been focused on polymer hydrogels that can undergo volume transitions in response to external physical or chemical stimuli such as pH,^{1,2} pressure,^{3,4} ionic strength,^{5,6} electric field,⁶ and temperature.^{7,8} These materials have been studied extensively because of their applications in various technologies, including controlled drug release,^{9,10} electrophoresis,¹¹ and bioseparation.^{12,13} Among stimuli-sensitive hydrogels, poly(*N*-isopropylacrylamide) (PNIPAAm) is the most widely studied thermosensitive hydrogel; it undergoes a reversible volume phase transition at 32°C [lower critical solution temperature (LCST)].

For molecular separation applications, bulk hydrogels are needed in which swelling and shrinking are two important factors. Tanaka and Fillmore¹⁴ reported that the hydrogel swelling rate is inversely proportional to the square of a linear dimension of the hydrogel. In general, bulk hydrogels take a long time to reach equilibrium swelling, from several hours to days, which is the main drawback for their practical usage. Therefore, attempts are being made to increase the swelling speed, and various synthesis methods have been suggested to prepare bulk hydrogels with fast responses and high swelling ratios.

Wu et al.¹⁵ synthesized hydrogels with macroporous structures to increase the pore volume and surface area of bulk hydrogels for fast swelling/deswelling of PNIPAAm. They synthesized the hydrogels at temperatures above the LCST of the polymer by heating the reactor near the end of the polymerization. In addition, they added to the monomer solution another LCST monomer, hydroxypropyl cellulose, which worked as a pore-

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forming agent, precipitating above its LCST (42°C). These hydrogels have larger pore volumes, larger average pore sizes, and faster macromolecular permeation rates in comparison with PNIPAAm synthesized by conventional methods. The macroporous PNIPAAm hydrogels have higher swelling ratios at temperatures below the LCST and exhibit faster deswelling and reswelling rates.

Comb-type grafted chains have been introduced to PNIPAAm backbones and crosslinked for rapid deswelling.¹⁶ This comb-type grafted hydrogel has the same composition as conventional PNIPAAm but has a different architecture. The molecular mobility of the graft-type hydrogel is improved because of the freely mobile grafted chains. Higher equilibrium swellings at lower temperatures are observed for graft-type hydrogels than for normal hydrogels; longer graft chains result in higher equilibrium swelling because of the freely mobile grafted chains. These modified hydrogels can swell or deswell within 20 min. However, the swelling ratios are not improved in comparison with those of the PNIPAAm hydrogel.

Park and Park¹⁷ and Chen et al.¹⁸ synthesized hydrogels with super pores and open channels by introducing a gas into the monomer solutions during the polymerization. The formed hydrogel foams have gas cells, most of which are connected to form open channels. The size and number of the gas cell can be controlled by the monomer concentration, solution viscosity, crosslinking extent, surfactant, and type and amount of gas introduced into the polymerizing solution. The pore sizes in the superporous dried hydrogels are in the range of hundreds of micrometers. These hydrogel foams can fully swell within hours and can absorb more water than 100 times their own weight. However, the large pore size of the hydrogel restricts its application in some circumstances such as bioseparation processes, for which large pore sizes are not favorable because of the reduction in the separation efficiency.

Freeze drying and subsequent hydration in water are another way of accelerating the deswelling of PNIPAAm hydrogels. Using scanning electron microscopy (SEM), Kato and Takahashi¹⁹ showed that the freeze-drying treatment made the hydrogel more porous, producing a weaker shrinking force, which made expansion easier compared with that of the conventional hydrogel.

Zhang and Zhou²⁰ synthesized PNIPAAm with water/acetone (1/1 v/v) as a mixed solvent during

the hydrogel crosslinking reaction to obtain a faster deswelling rate. They proposed that during the polymerization process, the produced polymer chains were quite soluble and widely expanded in the mixed solvent. This may lead to the large swelling ratio of the hydrogel synthesized with mixed solvents. The swelling behaviors of the new hydrogel were not reported.

Hydrogels that have micrometer-level dimensions have also been synthesized, first by Standinger and Husemann,²¹ and they were later named microgels by Baker.²² Because microgel particle dimensions change upon shear, the microgels provide rheological control for automotive surface coatings. Microgels also show promise in pharmaceutical applications. The study of temperature- and pH-sensitive microgel particles has been an area of growing interest for a number of different applications.^{23–26} The microgel particles have diameters ranging from 50 nm to 5 μ m.²⁷ The bulk hydrogels need a long time to achieve full swelling, whereas a microgel particle can achieve a steady swelling state in less than a second when the temperature is changed because of its small size and large surface area. The rapid swelling/deswelling kinetics is one of the beneficial features of microgels in comparison with bulk hydrogels. More recently, researches have been able to combine the properties of two or more bulk hydrogels by forming interpenetrating polymer networks (IPNs), especially combining the pH and temperature sensitivities.^{28,29} Inside IPN hydrogels, each network may retain its own properties, whereas the proportions of the networks are varied independently. The combined properties of the IPNs can be controlled by the ratios of their component monomers.

Temperature-sensitive hydrogels have been used to extract water and low molecular weight solutes from solutions to concentrate the macromolecules.^{30–32} Most of these applications are limited PNIPAAm hydrogels, which can be pH- or temperature-sensitive and so can be regenerated with changes in the hydrogel pH or temperature for the release of absorbed water. In a comparison with traditional separation methods, such as distillation, in the chemical industry, the advantages of using thermosensitive hydrogels to extract solvents are obvious: these hydrogels can be easily regenerated by the temperature being raised above the LCST of the hydrogels, making the hydrogels release the absorbed water.

In the pulp and paper industry, the removal of water presents a major cost in manufacturing,

particularly water from in-process water streams, which mainly contain lignin and water (e.g., from white water cleaning, black-liquor spills, and oxygen-delignification filtration). The costs will increase greatly because of the enforcement of the new cluster rule legislation, which aims to reduce the load on waste treatment plants. Current methods of water removal such as evaporation are energy- and cost-intensive because of the large amount of energy needed for the evaporation for water. Hence, new approaches with lower energy and lower capital investment are needed.

In this article, we discuss the preparation of fast-responding bulk hydrogels with microstructure (BHMs). The swelling behavior of the new hydrogels is compared with that of conventional bulk hydrogels. The effects of the microgel particle loadings and the acrylic acid (AA) contents in the final BHMs on the swelling behavior are also studied. Finally, these BHMs are used to concentrate lignin (lignin hydrolytic and Indulin AT), blue dextran, and bovine serum albumin. Separation results are presented.

EXPERIMENTAL

Materials

N-Isopropylacrylamide (NIPAAm), *N,N'*-methylenebis(acrylamide) (BIS), ammonium persulfate (APS), and sodium metabisulfite (SBS) were all obtained from Aldrich Chemical Co. (Milwaukee, WI). Before AA (Aldrich Chemical) was used, the inhibitor was removed with inhibitor-remover packing (Aldrich Chemical). Buffer solutions with pH values of 3–10 were acquired from Fisher Scientific Co. (Houston, TX). Lignin hydrolytic [weight-average molecular weight (M_w) = 19,300 g/mol; Westvaco Chemical Co., Charleston Hgts., SC], Indulin AT (M_w = 2700 g/mol; Westvaco Chemical), blue dextran (M_w = 2,000,000 mol/g; Aldrich Chemical), and bovine serum albumin (M_w = 66,430 g/mol; Aldrich Chemical) were used as received.

Synthesis of the Microgel Particles

The microgel particles were synthesized by the surfactant free emulsion polymerization method.³³ Monomers NIPAAm and AA in the appropriate molar ratios were added into a 500-mL flask with a reflux condenser and a magnetic stirrer. The crosslinker (BIS) contents were kept at 2

wt % of the total monomer, and the total monomer concentrations were kept at 1 wt % of the solution. After the solution was purged with N₂ for half an hour, the initiator APS was added. The reaction temperature was maintained at 65°C. The reactions were allowed to proceed for 6–8 h, and the mixture was kept overnight at room temperature for completion of the reactions. Finally, the microgel solutions were concentrated under vacuum at room temperature to be used for further polymerization.

Characterization of the Microgel Particles

We used transmission electron microscopy (TEM) to observe the microgel particles. We prepared the TEM samples by placing a dilute drop of aqueous microgel particles onto the sample grid and allowing them to dry in air; the samples were observed under TEM (Zeiss EM 10CR; Carl Zeiss, Heidelberg, Germany).

Formation of the BHM

The NIPAAm monomer, microgel solution, and crosslinker BIS were mixed in a 50-mL, round-bottom bottle. The feed ratios of microgel particles to monomer were varied with changes in the concentration of the microgel solutions. The solution was shaken for 20 min for complete dissolution of the monomers and then purged with N₂ for 20 min for removal of the oxygen. Then, the redox initiators APS and SBS were added to the reaction mixture and polymerized at room temperature for 24 h. The formed bulk hydrogels were cut into disk form and put into ethanol to wash out the unreacted monomer, and the ethanol was changed every few hours during the washing process. Then, the hydrogels were vacuum-dried at 50–60°C for 1 day. The dried hydrogels were stored in a desiccator for further experiments. Conventional poly(*N*-isopropylacrylamide-*co*-acrylic acid) (NIPAAm-AA) bulk hydrogels were synthesized with a similar procedure, but without microgel. The NIPAAm-AA bulk hydrogel with *n* mol % AA in the feed ratio has been labeled NIPAAm-AA-*n*.

Characterization of the BHMs and Bulk Hydrogels

The surface structures of dry hydrogel pieces were examined via SEM. The hydrogel samples were first dried in a vacuum and coated with gold with a sputter coater (Pelco model Sc-7; Ted Pella, Inc., Redding, CA) for 60 s and then observed via SEM (Zeiss model DSM940; Carl Zeiss).

Differential Scanning Calorimetry (DSC) Analysis

DSC (Universal V2.5H TA Instrument; New Castle, DE) was used for the determination of the transition temperatures of the swelled hydrogels. Hydrogel pieces were first equilibrated at room temperature in pure water and then sealed into an aluminum pan. An empty aluminum sealed pan was used as a reference. In DSC, the sample was equilibrated at 10°C for 5 min and then heated to 55°C at rate of 2°C/min. The temperature corresponding to the maximum heat flow was taken as the LCST.

Measurement of the Swelling Capacity of the Hydrogels

The swelling ratios of the conventional bulk hydrogel and BHMs were measured as follows: a dried piece of hydrogel was placed in deionized water (pH ~ 6.8) at a desired temperature for 1 day, the hydrogel swelled up to equilibrium, the hydrogel was taken out, surface water was removed with filter paper, and the weight of the wet hydrogel was recorded. The swelling ratio (SR) is defined as

$$SR = (W_s - W_d)/W_d \quad (1)$$

where W_s is the weight of the wet hydrogel and W_d is the weight of the dry hydrogel.

Measurement of the Swelling and Deswelling Speeds of Hydrogels

The swelling and deswelling kinetics of bulk hydrogels and BHMs were measured gravimetrically at fixed temperatures. The extent of swelling was measured at different time intervals. The water uptake and water retention were calculated as indications of the response speed of the hydrogels:

$$W_U = 100 \cdot (W_t - W_d)/(W_e - W_d) \quad (2)$$

$$W_R = 100 \cdot (W_t - W_d)/(W_e - W_d) \quad (3)$$

where W_U is the water uptake percentage during swelling, W_R is the water retention percentage during deswelling, W_t is the weight of the gel at a particular time, W_d is the weight of the initial dry hydrogel, and W_e is the weight of the hydrogel at maximum swelling.

Figure 1 Transmission electron micrograph of NIPAAm-AA microgel particles (original magnification, 5000 $\times$).

Molecular Separation Experiments

In the separation experiments, various known amounts of dry hydrogel pieces were added to solutions to be concentrated at different temperatures (lignin hydrolytic and Indulin AT were dissolved in 0.01N NaOH, and blue dextran and bovine serum albumin were dissolved in water). The changes in the solution concentration before and after hydrogel contact were measured with an ultraviolet spectrophotometer (Spectronic Genesis 2; Spectronic Instruments, Rochester, NY). The separation efficiency (η) was defined as

$$\eta = 100 \times \frac{\text{(measured concentration change)}}{\text{maximum change expected from hydrogel swelling}}$$

The maximum concentration change is based on the assumption that no macromolecule penetrates the hydrogel.

RESULTS AND DISCUSSION

Characterization of NIPAAm-AA Microgel Particles and NIPAAm-(NIPAAm-AA)_{micro} BHM

Figure 1 is a TEM photograph of NIPAAm-AA microgel particles; here the particles are 500–700 nm. NIPAAm-AA microgels are ionic particles because of the carboxylic charge on AA. In these microgel particles, the AA groups tend to lie on the surface of the particles, and NIPAAm groups lie toward the inside; this prevents aggregation

Figure 2 Schematic illustration of the formation of a BHM based on microgel particles.

between microgel particles and makes the microgel particles more stable in the aqueous solutions. In this conformation, the carboxyl groups on the microgel particle surface can also be further crosslinked under suitable conditions, forming interpenetrating network structures. Bouillot and

Vincent³⁴ prepared poly(acrylic acid)/poly(acrylamide) (PAA/PAM) interpenetrating network particles. The second polymer, PAA, was synthesized in the presence of the first polymer, PAM microgel particles. Within the IPN microgel particles, there were cooperative interactions between the PAA and PAM chains, exhibiting sharp swelling transitions for the PAA/PAM particles. A higher swelling ratio was also observed above the upper critical solution temperature in comparison with the ratio for the poly(acrylic acid-*co*-acrylamide) copolymer microgel particles. On the basis of this ideal, we propose that when the monomer NIPAAm is mixed with the NIPAAm-AA microgel solution and crosslinker, the ionic microgel particles can be crosslinked with one another and into the bulk matrix, forming a BHM (Fig. 2).

Figure 3 shows SEM photographs of prepared

(a) NIPAAm-(NIPAAm-AA)_{micro}-9.2

(b) NIPAAm-(NIPAAm-AA)_{micro}-20

(c) NIPAAm-(NIPAAm-AA)_{micro}-42.7

(d) NIPAAm-(NIPAAm-AA)_{micro}-54.2

Figure 3 SEM photographs of NIPAAm-(NIPAAm-AA)_{micro} with different amounts of the microgel [(a-c) original magnification, 2000 $\times$; (d) original magnification, 5000 $\times$].

Figure 4 Effect of temperature on the swelling ratios of PNIPAAm and NIPAAm-AA-6 bulk hydrogels and NIPAAm-(NIPAAm-AA)₂₅ (40 wt% microgel).

NIPAAm-(NIPAAm-AA)_{micro} BHMs with different NIPAAm-AA microgel contents. With an increasing feed ratio of the NIPAAm-AA microgel, more microgel particles are embedded into the matrix. When the feed ratio of the microgel is 9.2 wt %, few particles can be seen inside the matrix of the BHM; when the microgel amount in the feed ratio increases to 54.2 wt %, which is a majority of the volume in the BHM, a porous sponge structure is observed. The formed porous sponge structure indicates that the BHM has a more compatible network structure. Because this porous sponge structure is mainly composed of the microgel particles, which have fast a swelling rate when the temperature is changed, the BHM should display a fast response to external temperature changes.

Swelling Behavior of the BHMs and Bulk Hydrogels

The temperature dependence of the equilibrium swelling ratios of PNIPAAm and NIPAAm-AA-6 bulk hydrogels and NIPAAm-(NIPAAm-AA)_{micro} BHM (40 wt % microgel particles) is illustrated in Figure 4. Both BHMs and bulk hydrogels are temperature-sensitive. From 5 to 25°C, these hydrogels have higher swelling ratios, suggesting that the hydrogen-bonding interactions between polymer chains and water are dominant at low temperatures. When the temperature is raised above the transition temperature, the hydrophobic interactions between the polymer chains become dominant and break the delicate balance between hydrogen-bonding and hydrophobic interactions, causing the hydrogel to collapse, decreasing the swelling ratio dramatically. Com-

pared with the bulk hydrogels, the BHM shows much higher equilibrium swelling at room temperature. At 25°C, the BHM swelling ratio reaches 78, whereas both PNIPAAm and NIPAAm-AA-6 have swelling ratios below 20.

Figure 5 shows the swelling rate of the BHM and the PNIPAAm and NIPAAm-AA-6 hydrogels. The BHM swells much faster at room temperature. Within 5 h, it can swell to 80% of the maximum value, and within 10 h, the BHM swells to 90% of the maximum value; however, the PNIPAAm and NIPAAm-AA-6 bulk hydrogels only have 40% and 60% of their maximum water uptake, respectively, after 10 h of contact. The fast swelling rate of the BHM may be due to the collaborative interaction of both the microgel particles and the hydrogen-bonding interactions between the PNIPAAm matrix and water. When water enters the BHM network, the microstructures swell first, causing the whole interconnected matrix to swell afterward. This collaboration of the swelling of the ionized particles and bulk matrix enhances the swelling rate of the whole BHM matrix.

The deswelling behavior of hydrogels at 50°C is shown in Figure 6. Because 50°C is higher than the volume-transition temperature of the hydrogels, the three hydrogels release water sharply in the beginning and slowly later on. Because of the hydrophilicity of AA groups, NIPAAm-AA and BHM deswell slower than the PNIPAAm hydrogel. The BHM gives off 50% of its total water within 100 min.

pH Sensitivity

Figure 7 shows that both NIPAAm-(NIPAAm-AA)_{micro} BHMs and NIPAAm-AA bulk hydrogel are pH-sensitive, whereas PNIPAAm is not. BHMs

Figure 5 Comparison of the swelling kinetics of PNIPAAm and NIPAAm-AA-6 bulk hydrogels and NIPAAm-(NIPAAm-AA)₂₅ (40% microgel) at 23°C.

Figure 6 Deswelling speeds of PNIPAAm and NIPAAm-AA-6 bulk hydrogels and NIPAAm-(NIPAAm-AA)₂₅ (40% microgel) at 50°C.

reach maximum swelling at pH 8, after which the swelling decreases with an increase in the pH. The NIPAAm-AA bulk hydrogel does not show such a maximum within the experimental pH range. This difference in the pH sensitivity of the two hydrogels can be attributed to the different architectures of the acid groups in the hydrogels. In the BHM, all the acid groups lie on the surface of the microgel particles, and the NIPAAm molecular chains are linked through the active carboxyl groups, leading to the formation of the bulk hydrogel through microgel bridging. With an increase in the pH, more AA groups are ionized, and the electrostatic repulsion between the ionized groups results in a more expanded network. However, in high-pH solutions, the dissociated cations from the alkaline salt also increase, decreasing the ionic repulsion by shielding the ionic acid groups, and so the swelling decreases at a higher pH value. In BHMs, because all AA groups are in the microgel particles, they are easily

Figure 7 Swelling behavior as a function of pH at 23°C for PNIPAAm and NIPAAm-AA-6 bulk hydrogels and BHMs with different amounts of the microgel.

Figure 8 Swelling ratios of BHM and NIPAAm-AA bulk hydrogels with the same amount of AA.

shielded by the dissociated cations, causing a drop in the swelling at pHs higher than 8.

Effect of the AA Amount on the Swelling Behavior

Figure 8 confirms that the AA group architecture in the hydrogel plays an important role in the

(a)

(b)

Figure 9 Effect of the amount of the microgel on the swelling behavior of the BHMs: (a) microgel NIPAAm-AA-15 and (b) microgel NIPAAm-AA-25.

Figure 10 DSC diagrams of NIPAAm-AA-6 hydrogel and BHM (16.4 wt % microgel).

swelling behavior of hydrogels. In Figure 8, the swelling rates of the NIPAAm-(NIPAAm-AA)_{micro} BHM and NIPAAm-AA-3 bulk hydrogel are compared; both are 3 wt % AA. Despite the small number of AA groups in the BHM, these groups greatly influence the swelling rate in comparison with the bulk hydrogel. The swelling rate of BHM is much faster than that of the NIPAAm-AA bulk hydrogel, which suggests that incorporating microgel particles accounts for the fast response of the BHM.

Effect of the Amount of the Microgel on the Swelling Behavior

The amount of the microgel particles in the BHM is very important for the swelling behavior (Fig. 9). A larger amount of the microgel in the hydrogel results in faster BHM swelling. When microgel contents are less than 20 wt %, the swelling ratio increases slowly, but when the microgel content is more than 30 wt %, there is a big increase in the swelling. This confirms that the swelling speed is mainly determined by the amount of the microgel in the BHM.

Thermal Analysis of the BHM and Bulk Hydrogel

The transition of the hydrogel in response to temperature changes can be observed with thermal analysis. Figure 10 shows DSC diagrams of the fully hydrated hydrogel of NIPAAm-AA-6 and

the BHM containing 16.4 wt % microgel. The temperature corresponding to the maximum of the heat flow is defined as the LCST of the swollen hydrogel. With the incorporation of AA groups, the transition temperature of NIPAAm-AA-6 increases to 35.9°C, higher than the temperature for PNIPAAm (LCST = 33.8°C; not shown in Fig. 10). On the contrary, the transition temperature of the BHM is decreased to 31.4°C. This difference can be attributed to the different architectures of AA groups in the hydrogels. The transition enthalpy calculated from the peak areas are 12.57 and 12.80 J/g for NIPAAm-AA-6 and BHM, respectively. These values are different than the enthalpy of the PNIPAAm hydrogel transition, 14 J/g at a heating rate of 0.5°C/min.³⁵

Separation of Macromolecules with BHMs

The concentration and recovery of solutes from dilute aqueous solutions are needed in the pharmaceutical, chemical, and environmental industries. Traditional separation methods, such as distillation and chromatography, are expensive. Hydrogel-based separation is promising because of the low energy costs. The separation is based on the absorption of water and low molecular weight solutes by the hydrogel, leaving behind a concentrated solution of larger molecules. The hydrogel is regenerated by being heated to its LCST, which usually is only slightly different from the current temperature.

Table I Separation of Lignin Hydrolytic with NIPAAm-(NIPAAm-AA)_{micro} BHM Hydrogels After Contact for 24 h at 23°C

AA in the BHM (wt %)	Microgel in the BHM (wt %)	SR	η
0.85	16.4	26.2	12.6
1.67	16.6	25.6	13.7
2.55	13.0	34.4	51.0
3.61	16.3	40.8	47.2
6.14	28.1	72.2	33.6

Tables I and II show the separation results for lignin hydrolytic and Indulin AT with NIPAAm-(NIPAAm-AA)_{micro} BHMs. Good separation efficiencies are achieved for both lignins. Both the AA and microgel contents affect the separation efficiency and swelling ratio. The swelling ratio increases with higher microgel contents in the BHM. For a given amount of the microgel, a larger amount of AA results in a higher swelling ratio and separation efficiency.

The NIPAAm-(NIPAAm-AA)_{micro} BHM has a maximum separation efficiency for lignin hydrolytic and Indulin AT when the microgel content is 13 wt %. A higher content of the microgel in the BHM increases the swelling rate and ratio, but the separation efficiency decreases. For example, when the microgel content is 28.1 wt %, although the swelling ratios of the BHM in the lignin hydrolytic and Indulin AT are as high as 72.2 and 77.9, the separation efficiencies are only 33.6 and 40%, respectively.

Tables III and IV show the separation results for blue dextran and bovine serum albumin with the NIPAAm-(NIPAAm-AA)_{micro} BHMs. Because both blue dextran and bovine serum albumin have larger molecular sizes than lignin molecules ($M_w = 2,000,000$ for blue dextran; $M_w = 66,430$

Table II Separation of Indulin AT with NIPAAm-(NIPAAm-AA)_{micro} BHM Hydrogels After Contact for 24 h at 23°C

AA in the BHM (wt %)	Microgel in the BHM (wt %)	SR	η
0.85	16.4	22.6	42.4
1.67	16.6	35.0	51.8
2.55	13.0	34.6	75.1
3.61	16.3	38.7	64.6
6.14	28.1	77.9	40.0

Table III Separation of Blue Dextran with NIPAAm-(NIPAAm-AA)_{micro} BHM Hydrogels After Contact for 24 h at 23°C

AA in the BHM (wt %)	Microgel in the BHM (wt %)	SR	η
0.85	16.4	18.3	65.2
1.67	13	15.8	72.7
3.61	16.3	37.7	95.2

for bovine serum albumin) and the molecular attraction between the hydrogels and solutes is lower, the separation efficiencies are high. Also, a higher microgel content in the BHMs results in higher swelling. The separation efficiencies for blue dextran and bovine serum albumin are as high as 95.2 and 88.7%, respectively.

CONCLUSION

A method for synthesizing BHMs has been developed. Compared with conventional hydrogels, the BHMs have a faster response along with a high swelling ratio and thermosensitivity. The faster response is due to the collaborative interactions between the ionized microgel particles and the bulk matrix. On contact with a solution, the microgel particles swell first, causing the overall bulk matrix to swell quickly. Because of their high absorption capacity and temperature sensitivity, the BHMs can be used to efficiently concentrate or separate macromolecules. Separations are demonstrated with NIPAAm-(NIPAAm-AA)_{micro} BHMs to concentrate lignin hydrolytic, Indulin AT, blue dextran, and bovine serum albumin in aqueous solutions.

Table IV Separation of Bovine Serum Albumin with NIPAAm-(NIPAAm-AA)_{micro} BHM Hydrogels After Contact for 24 h at 23°C

AA in the BHM (wt %)	Microgel in the BHM (wt %)	SR	η
0.85	16.4	35.5	88.7
1.67	13.0	71.3	73.6
3.61	16.3	72.7	54.7

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4.

Poly(N-ethylacrylamide) Hydrogels for Lignin Separation

Poly(*N*-ethylacrylamide) Hydrogels for Lignin Separation

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Poly(*N*-ethylacrylamide) hydrogel (PEAM) and *N*-ethylacrylamide bulk hydrogel with microstructure (EAM-BHM) are prepared. The lower critical solution temperature (LCST) of PEAM is determined to be 73 °C by DSC, and the microstructures of the hydrogels are characterized by SEM. When the microgel particles are incorporated into the matrix of EAM hydrogel, the formed bulk hydrogels have a faster swelling rate and a higher swelling ratio compared to those of the conventional PEAM hydrogels. The swelling diffusion mechanism in PEAM hydrogel changes from Fickian to non-Fickian when the cross-linker content is increased to 8 wt %. Both EAM-BHMs and conventional PEAM can be used to separate lignin at a high temperature (~55 °C, typical in a pulp mill). Due to the microgel particles, the EAM-BHMs have a higher swelling ratio in lignin solution while the large surface area of the microgel also increases the adsorption of lignin on the hydrogel, thus decreasing the separation efficiency. The effects of lignin concentration, separation temperature, and salt on the separation efficiency are also studied.

Introduction

Hydrogels are cross-linked polymer networks that swell but do not dissolve in water. In the past 20 years, considerable research attention has been focused on poly(*N*-isopropylacrylamide) (PNIPAAm), a temperature sensitive hydrogel, which can undergo a jumpwise volume transition above the lower critical solution temperature (LCST) at 33 °C.^{1–3} The thermosensitivity of hydrogels makes them attractive in applications including controlled drug release,^{4,5} electrophoresis,⁶ and bioseparation.^{7,8} Especially hydrogels have been proposed for use in the concentration or separation of solutes for a wide range of biological and synthetic materials produced in dilute solutions. Examples include recoveries of soy proteins,⁹ cellulase enzymes from fermentation broths,¹⁰ dextran and Bovine serum albumin,^{8,11} textile dyes,¹² and nonion surfactant¹³ from aqueous media. Compared to the traditional separation methods in the chemical industry, the advantages of the separation using thermosensitive hydrogels are obvious. The separation is based on uptake of water and low molecular weight solutes by the hydrogel, leaving behind the concentrated solution of large molecules. The hydrogels can be easily regenerated for further use by a mild heating above the LCST to expel the water.

In addition to PNIPAAm, some other *N*-substituted acrylamide hydrogels have also been reported to undergo volume phase transition in water: poly(*N,N*-diethylacrylamide) hydrogels were demonstrated to have a LCST of 32 °C,¹⁴ poly(*N,N*-propylacrylamide) hydrogel has a LCST of 25 °C,¹⁵ and poly(*N*-cyclopropylacrylamide) hydrogel has a LCST of 48 °C.¹⁶ The hydrophobic interaction plays an important role in determining the LCST and swelling behavior of the *N*-alkylacrylamide hydrogels.¹⁷ An increase in the alkyl chains produces a dramatic decrease in the transition temperature. In addition, the ratio of hydrophobic to hydrophilic units within the side chains is important

in determining if the hydrogel will exhibit thermoswelling or thermoshrinking behavior. Among the *N*-alkylacrylamide hydrogels, poly(*N*-ethylacrylamide) (PEAM) has the highest transition temperature, although varying LCST values have been reported. Taylor et al.¹⁸ reported in their early work that the cloud point of PEAM aqueous solution is 74 °C, while Liu and Zhu recently indicated that the LCST of PEAM solution is 82 °C.¹⁹ Ito et al. reported that PEAM hydrogel has a transition temperature of 72 °C,²⁰ but Seker and Ellis¹⁷ demonstrated that the transition temperature of PEAM hydrogel is 80 °C. On the other hand, PEAM microgel was reported to have a LCST of around 80 °C.²¹ Further experiments are needed to get the accurate transition temperature of PEAM hydrogels.

Microgel are cross-linked particles with diameters ranging from 50 nm to 5 μ m.²² The bulk hydrogels need a long time to reach full swelling, whereas a microgel particle can reach a steady swelling state in <1 s when temperature is changed, because of the small size and large surface area. The rapid swelling/deswelling rate is the major beneficial feature of microgels in comparison with bulk hydrogels.

In the pulp and paper industry, water separation from lignin presents a major cost, particularly in in-process water streams, white water cleaning, black-liquor spills, and oxygen-delignification filtration. These costs will further increase due to the enforcement of the new "cluster rule" legislation, which aims to reduce the load on wastewater treatment plants. Current methods of water removal such as evaporation are energy and cost intensive; a large amount of energy is needed to reach the heat of evaporation for the water to be removed. The temperature of lignin solutions in the pulp and paper industry is usually between 50 and 60 °C, which is higher than the LCST of PNIPAAm hydrogels. Hence, for separation of lignin by hydrogel, a hydrogel with a higher LCST is needed. In this study, PEAM hydrogel and PEAM bulk hydrogel with microstructure (BHM) were prepared and their swelling behaviors were compared. The separation results of lignin by the synthesized hydrogels were also presented, and the factors affecting the separation result were discussed.

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Experimental Section

Materials. All materials except acrylic acid (AA) are used as received. The EAM is obtained from Monomer-Polymer and Dajac Laboratories Inc. (Feasterville, PA). Lignin (Indulin AT, $M_w = 2700$ g/mol) is obtained from Westvaco Chemical Co. All other materials are obtained from Aldrich. Inhibitors are removed from AA by an inhibitor-removing column before use.

Preparation of the Hydrogels. The hydrogels are prepared in aqueous solutions via free radical polymerization of monomers in the presence of the cross-linker N,N' -methylenebis(acrylamide) (BIS) and redox initiators ammonium persulfate (APS) and sodium metabisulfite (SBS). EAM-AA microgel particles are prepared by a surfactant-free aqueous polymerization method.²¹ EAM and AA in the appropriate molar ratios are added into a 500 mL flask with a reflux condenser and a magnetic stirrer. The cross-linker (BIS) contents are kept at 2 wt % of the total monomer amount, and total monomer concentrations are kept at 1 wt % of the solution. After the solution is purged by N_2 for 0.5 h, the initiator APS (0.5 wt %) is added. The reactions are carried out at 80 °C for 6–8 h, and the mixture is kept overnight at room temperature. Finally, the microgel solutions are concentrated under vacuum at room temperature for further polymerization. To prepare BHM, EAM, EAM-AA microgel solution, and cross-linker BIS (2 wt %) are mixed in a 50 mL round-bottom bottle. The solution is shaken for 20 min to make sure all monomers are completely dissolved. The solution is then purged with N_2 for 20 min to remove the dissolved oxygen. The redox initiators APS and SBS (0.1 wt %) are added into the reaction mixture and polymerized at room temperature for 24 h. The formed bulk hydrogels are cut into disk form and put in ethanol to extract out the unreacted monomer. The ethanol is changed every few hours. Then the hydrogels are dried at 50–60 °C under vacuum for 1 day. The dried hydrogels are stored in a desiccator for further experiments. The formed bulk hydrogels with n wt % of microgel content are termed as EAM-BHM- n . Conventional PEAM bulk hydrogels are prepared by a similar procedure, without microgel content. Except when mentioned, the BHM polymerization temperature is fixed at room temperature (23 °C).

Characterization of Microgel Particles. Transmission electron microscopy (TEM) was used to observe the microgel particles. The TEM sample was prepared by placing a dilute drop of aqueous microgel particles onto the sample grid and allowing it to dry in air; the samples were observed via TEM (Zeiss EM 10CR).

Structure of Hydrogels by Scanning Electron Microscopy (SEM). The structures of dry hydrogel pieces are examined by scanning electron microscopy (SEM). The hydrogel samples are first dried in a vacuum and coated with gold using a sputter coater (Pelco, model Sc-7) for 60 s and then observed by SEM (Zeiss, model DSM940).

DSC Analysis. DSC (Universal V2.5H TA Instrument) is used to determine the transition temperature of the swollen hydrogels. Hydrogel pieces were first equilibrated at room temperature in pure water and then sealed in an aluminum pan. An empty aluminum sealed pan is used as a reference. In DSC, the sample is equilibrated at 10 °C for 5 min and then heated to 55 °C at a rate of 2 °C/min. The temperature corresponding to the maximum heat flow is taken as the LCST.

Measurement of Swelling Ratio. The dried hydrogel (mass = W_d) is immersed in an excess amount of deionized water at the desired temperature until swelling equilibrium is attained. The mass of wet sample (W_w) is measured after removing the surface water with blotting paper. The swelling ratio (SR) is then calculated on the basis of the masses of wet hydrogel and dry hydrogel:

$$SR = (W_w - W_d)/W_d \quad (1)$$

The water uptake and water retention are calculated as indications of the response speed of the hydrogels, as

$$W_U = 100 \times (W_t - W_d)/(W_e - W_d) \quad (2)$$

$$W_R = 100 \times (W_t - W_d)/(W_e - W_d) \quad (3)$$

where W_U is the percent water uptake during swelling, W_R is the percent water retention during deswelling, W_t is the weight of the gel at a particular time, W_d is the weight of the initial dry hydrogel, and W_e is the weight of the hydrogel at maximum swelling.

Dynamic Swelling. The dried hydrogel is immersed in excess water at 55 °C, and swelling is measured by weighing the samples with time. The diffusion coefficient is calculated from

$$\frac{M_t}{M_\infty} = \left(\frac{4}{\sqrt{\pi}} \right) \left(\frac{D t}{L^2} \right)^{1/2} \quad \text{for} \quad \frac{M_t}{M_\infty} \leq 0.6 \quad (4)$$

where t is time, L is the initial thickness of the dried sample, M_t is the amount of water absorbed at time t , M_∞ is the amount of water absorbed at equilibrium, and D is the diffusion coefficient.

Measurement of Thermoreversibility. The dried hydrogel samples were immersed in deionized water at room temperature until swelling equilibrium. Then each swollen sample was removed to fresh deionized water at 85 °C, and the collapsed hydrogel was weighed at various time intervals. After that, the hydrogel was removed to deionized water at 55 °C for swelling and the swollen hydrogel was weighed at various time intervals. This cooling–heating process was repeated for three cycles.

Lignin Separation. A known amount of dried hydrogel is added into lignin solutions (dissolved in 0.01 N NaOH) to be concentrated at the desired temperature. The change in the lignin concentration is measured using an ultraviolet visible spectrophotometer (Spectronic Genesis 2), and the separation efficiency (η) is calculated as

$$\eta = 100 \times \frac{\text{(measured concentration change)}}{\text{(change expected from hydrogel swelling)}}$$

The maximum concentration change is based on assuming that no lignin penetrates the hydrogel.

Results and Discussion

TEM Picture of EAM-AA Microgel Particles. Figure 1 is a TEM photograph of EAM-AA microgel particles containing 15 wt % AA. EAM-AA microgels are ionic particles due to carboxylic charge on AA. In these microgel particles, the AA groups tend to lie on

Figure 1. TEM of EAM-AA microgel particles, $\times 5000$.

Figure 2. Schematic of the synthesis of bulk hydrogel with microstructure (BHM) using microgel particles.

the surface of the particles and EAM groups toward the inside, which prevents the aggregation between microgel particles and making the microgel particles stable in the aqueous solutions. This conformation renders the possibility of forming further interpenetrating network structures under suitable conditions. Figure 2 is a schematic illustration of forming bulk hydrogel based on microgel particles. When the monomer EAM is mixed with an EAM-AA microgel solution and cross-linker, the ionic microgel particles are cross-linked with EAM monomer, forming the bulk matrix with the microstructure.

SEM Micrographs of EAM Hydrogels. Varying the polymerization temperature can control the structure of the temperature-sensitive hydrogels. Wu et al.²³ found that PNIPAAm hydrogels synthesized above the LCST have a macroporous structure and a fast swelling behavior. Figure 3 shows the SEM photographs of PEAM and EAM-BHM hydrogels. Similar to PNIPAAm hydrogel prepared at different temperatures, the PEAM synthesized at 85 °C shows more macroporous structure than PEAM synthesized at 23 °C. In addition, PEAM hydrogel is transparent when synthesized at 23 °C but is opaque when synthesized at 85 °C. At 85 °C, the polymerization is carried out in a two-phase system: the solid phase consists of dispersed PEAM hydrogel; the other phase includes the liquid solution of monomer, cross-linker, and water. The precipitation enhances the nonuniform cross-linking in the hydrogel, resulting in a more macroporous structure compared to that of the hydrogels synthesized below LCST. Figure 3 also shows,

with increasing of EAM-AA microparticle contents, more microgels are embedded in the hydrogel matrix.

Swelling Behavior of Poly(N-ethylacrylamide) Hydrogel. In our previous work, we have reported that, with the incorporation of NIPAAm-AA ionic microgel particles into the NIPAAm bulk matrix, the formed BHMs have a faster response and higher swelling ratio compared with those of conventional hydrogels.²⁴ Similar results are obtained for the EAM hydrogel system shown here. Figure 4 shows the swelling behavior of PEAM and EAM-BHM. In 4.5 h, EAM-BHM-20 reaches 46.2% of the maximum swelling, while conventional PEAM only reaches 28.3% of the maximum swelling at ambient temperature. Also EAM-BHM shows a much higher equilibrium swelling ratio than the conventional PEAM hydrogel. The fast swelling of BHM is mainly due to the cooperative interaction of both microgel particles and the hydrogen bonding interactions between the EAM matrix and water. When the BHM swells in water, the microstructure swells first, and because the microgel particles are embedded in the matrix, the whole interconnected matrix swells afterward; this collaboration of swelling of the ionized particles and bulk matrix enhances the swelling rate of the whole BHM matrix. Figure 5 shows that, at 85 °C, both PEAM and EAM-BHM deswell fast, within the first 60 min, PEAM releases the 85% water absorbed, and EAM-BHM-20 releases 65% of the water absorbed.

Figure 6 compares the temperature sensitivities of PEAM and EAM-BHM hydrogels. The hydrogels show continuous volume collapse when temperature is increased. With the ionic groups inside, EAM-BHM hydrogels have a higher transition temperature than that of PEAM hydrogels.²⁵ With an increase in the extent of cross-linking, the transition temperatures of PEAM hydrogels increase, because when temperature is above the LCST, the hydrophobic interactions between N-ethyl groups in EAM hydrogel become dominant, making the state of water in the hydrogel change from bound water to free water, causing the swelling ratio to decrease. Figure 6 also shows that an increase in the microgel contents increases the swelling of EAM-BHM hydrogels. Because PEAM hydrogels have a continuous volume collapse when temperature is increased above the LCST, the volume transition is not as sharp as that in PNIPAAm hydrogel; hence, the transition temperature could not be determined accurately from swelling ratio versus temperature data. This may be a reason for the different LCST values reported for the PEAM hydrogel in the literature.

Analysis of DSC Thermogram. The transition of the hydrogel in response to the temperature change can be observed accurately by thermal analysis. When temperature is above the LCST of the hydrogel, phase transition occurs inside the water-swollen hydrogel, which is indicated by a peak in the heat flow. Figure 7 shows the DSC diagram of the fully hydrated PEAM hydrogel. A major endothermic peak appears at 73 °C, which could be attributed to the LCST of the hydrated PEAM hydrogel.

pH Dependence of EAM-BHM Hydrogel. Because EAM-BHM hydrogels have acidic AA groups, the solution pH will affect the swelling ratio of hydrogels. Figure 8 shows the swelling of EAM-BHM as a function of pH at 55 °C. The hydrogel pieces were put into pH buffer solutions with swelling for 10 h before the swelling ratios were measured. Figure 8 shows that the swelling

(a) PEAM-1, x5,000

(b) PEAM-2, x 3,000

(c) EAM-BHM-20, x3,000

(d) EAM-BHM-47, x3,000

Figure 3. SEM microphotographs: (a) PEAM synthesized at 23 °C; (b) PEAM synthesized at 85 °C; (c) EAM-BHM-20; (d) EAM-BHM-47 hydrogel.

Figure 4. Swelling behavior of EAM hydrogels at 55 °C.

ratio reaches maximum at neutral pH and gradually decreases with increasing acidity or basicity. In the BHM, all AA groups tend to be on the surface of the microgel particles, and EAM molecular chains are linked through the active carboxyl groups, leading to the formation of bulk hydrogel through microgel bridging. With an increase in the pH, more AA groups are

Figure 5. Deswelling behavior of EAM hydrogels at 85 °C.

ionized, and the electrostatic repulsion between the ionized groups results in a more expanded network. But at high pH, the concentration of the dissociated cations from the alkaline salt increases, which causes a decrease in the ionic repulsion due to shielding of the ionic acid groups. Hence, the swelling decreases at higher pH.

Figure 6. Temperature sensitivity of EAM hydrogels.

Temperature Reversibility of PEAM Hydrogels. Figure 9 shows the temperature reversibility of a series of PEAM hydrogels between 55 and 85 °C. The hydrogels swell and deswell when transferred between lower and higher temperatures, demonstrating that the volume phase transition is reversible. It could be seen that reswelling is slower than deswelling. The swelling ratios of reswelling are lower than the equilibrium swelling ratio of the hydrogel, which might be due to the fact that reswelling of the hydrogel has not reached equilibrium swelling during the experiment time range. In the first reswelling cycle, the PEAM hydrogels containing 3, 5, and 8 wt % BIS can reswell to 70%, 60%, and 70% of their initial equilibrium swellings, respectively.

Swelling Kinetics and Separation of Lignin by EAM Hydrogels. Molecular separation by a temperature sensitive hydrogel is based on the idea that the hydrogel absorbs water and other small molecules but excludes large molecules. Indulin AT is a lignin with the formula $\{(\text{CH}_3)(\text{OH})\text{Ar}(\text{C}_6\text{H}_4\text{O})\}_x$, soluble in alkaline water. To study the swelling kinetics of hydrogels in lignin solutions, initial swelling data can be fitted to the exponential heuristic equation for mass transfer.²⁶

$$\frac{M_t}{M_\infty} = K t^n \quad \text{for} \quad \left(\frac{M_t}{M_\infty} \leq 0.6 \right) \quad (5)$$

where K is a characteristic constant of the hydrogel and n is a kinetic exponent of the mode of solute transport. Values of n and K are calculated from the slopes and intercepts of the plot of $\log(M_t/M_\infty)$ versus $\log(t)$. For disk-shape samples, n is 0.5 if the swelling is by Fickian diffusion, n is between 0.5 and 1.0 for non-Fickian diffusion, n is 1.0 for case II diffusion, and n is >1 for super-case-II diffusion.²⁶ On the other hand, according to eq 5, hydrogels should initially absorb solutes in proportion to the square root of time if the swelling is by Fickian mode. Figure 10 shows the swelling ratios of PEAM and EAM-BHM hydrogels versus square root of time in lignin solutions at 55 °C. EAM-BHM hydrogels have obviously higher swelling ratios than PEAM hydrogels. Table 1 shows K , n , and D values for the EAM hydrogels obtained using eqs 4 and 5. K values for EAM-BHM hydrogels are much higher than those for PEAM hydrogels, suggesting the high swelling ability of EAM-BHM hydrogels in lignin solutions. Except for PEAM (BIS = 8 wt %) hydrogel, the other hydrogels have n values between 0.48 and 0.54, which indicates the mechanism of swelling is mainly Fickian diffusion and the polymer chain relaxation has little effect on the rate of swelling. For PEAM (BIS = 8 wt %) hydrogel, n is 0.78, which indicates that the diffusion of lignin solution to the hydrogel is non-Fickian, and the polymer chain relaxation plays a major role in the rate of swelling.

Table 2 shows the separation results for lignin by EAM hydrogels after 24 h at 55 °C. PEAM hydrogels have good separation efficiency for lignin; almost all the lignin is separated from water. Although microgel structure increases the swelling ability of BHM hydrogel, the separation efficiency decreases greatly compared to that of PEAM hydrogel. The decrease in separation efficiency is due to the microgel particles embedded in the bulk matrix. Park and Ignacio²⁷ reported that higher separation efficiency was achieved for large hydrogel particles compared to small hydrogel particles in the

Figure 7. DSC thermogram of PEAM hydrogel.

Figure 8. pH dependence of EAM-BHM-47 at 55 °C.

Figure 9. Swelling ratios of PEAM hydrogel as a function of time with cycling of temperature between 85 and 55 °C.

Figure 10. Swelling ratio of EAM hydrogels as a function of square root of time in the lignin solution.

Table 1. Initial Diffusion Coefficient (D), Kinetic Exponent (n), and Characteristic Constant (K) for Lignin-Solution Diffusion in PEAM and EAM-BHM Hydrogels at 55 °C

hydrogel	n	K	$D (\times 10^7 \text{ cm}^2/\text{S})$
PEAM (BIS = 1 wt %)	0.49	0.19	2.76
PEAM (BIS = 3 wt %)	0.48	0.26	3.11
PEAM (BIS = 8 wt %)	0.78	0.26	3.65
EAM-BHM-20	0.47	1.27	2.52
EAM-BHM-47	0.54	2.53	2.82

separation of cellulase. In BHM, microgel particles have a large surface area, which increases the adsorption of lignin at the hydrogel surface and decreases the separation efficiency. So, with an increase in the microgel particle contents, the separation efficiency decreases.

Effect of Lignin Concentration. Figure 11 shows the effect of solute concentration on the separation by EAM-BHM. Because of the large surface area of microgel particles in EAM-BHM, the adsorption of lignin increases with an increase in the lignin concentration;

Table 2. Separation Results for Lignin by EAM Based Hydrogels at 55 °C after 24 h with Initial Lignin Concentrations around 150 ppm

hydrogel	swelling ratio (SR)	separation efficiency (η)
PEAM (BIS = 1 wt %)	9.8	100
PEAM (BIS = 3 wt %)	7.1	99
PEAM (BIS = 5 wt %)	6.6	99
PEAM (BIS = 8 wt %)	5.1	100
EAM-BHM-20	15.2	41
EAM-BHM-47	27.1	34

Figure 11. Effect of lignin concentration on the swelling ratio and the separation efficiency of EAM-BHM-20 at 55 °C after separating for 10 h.

Figure 12. Temperature effect on the separation of lignin by EAM-BHM-40 after 24 h. The initial lignin concentration is about 80 ppm.

hence, the separation efficiency decreases sharply. The separation efficiency is 94% for 28 ppm lignin, but the efficiency decreases to 13% for the 326 ppm concentration. On the other hand, the swelling ratio of the hydrogel does not change much when solution concentration is varied during this concentration range.

Effect of Separation Temperature. Separation temperature strongly impacts both hydrogel swelling and separation efficiency (Figure 12). The swelling ratio of EAM-BHM-40 decreases linearly with an increase in the temperature. The separation efficiency first decreases sharply from 25 to 35 °C and then slowly at higher temperatures. When temperature is increased from 25 to 65 °C, the separation efficiency decreases from 98% to 64%, whereas the swelling ratio decreases from 45 to 34.

Effect of Additives on Swelling and Separation Behavior. A sharp volume phase transition in PNIPAAm hydrogel with added NaCl is reported due to the chloride ions.²⁸ Figure 13 shows the effect of added Na_2CO_3 on the swelling of EAM-BHM-40 and separation of lignin. The salt addition collapses the hydrogel with a continuous volume decrease. When Na_2CO_3 concentration is increased from 0.078 to 0.42 M,

Figure 13. Effect of Na_2CO_3 concentration on the hydrogel swelling and separation of lignin by EAM-BHM-40 at 55 °C after 24 h.

the swelling ratio decreases from 13.8 to 3.2. The separation efficiency for lignin increases with added salt, because the volume collapse of the hydrogel reduces the pore size of the hydrogel; hence, more lignin is excluded from the hydrogel. When Na_2CO_3 concentration is higher than 0.157 M, almost all the lignin is separated.

Conclusion

The transition temperature of PEAM hydrogel is determined to be 73 °C by DSC. After incorporating EAM-AA microgel into the EAM bulk matrix, the formed BHMs have both faster swelling rates and higher swelling ratios as compared to those of the conventional PEAM hydrogels. With increasing extent of cross-linking in PEAM hydrogel, the diffusion mode changes from Fickian to non-Fickian. Because of the presence of acrylic acid groups, EAM-BHM shows pH sensitivity. Both PEAM and EAM-BHM hydrogels can be used to concentrate lignin at a high temperature, 55 °C. Compared to PEAM hydrogel, the EAM-BHM has a higher swelling ratio and a lower separation efficiency, because of the adsorption of lignin on the large surface area of microgel particles. With an increase in the solute concentration or separation temperatures, the separation efficiency decreases. A small amount of Na_2CO_3 salt can sharply collapse the hydrogel volume, decreasing the swelling in lignin solution containing this salt.

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Thermosensitive and Ampholytic Hydrogel for Salt Solutions

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Abstract

A series of N-isopropylacrylamide/[3-(Methacryloylamino)propyl]dimethyl(3-sulfopropyl)ammonium hydroxide] (NIPAAm/MPSA) copolymer hydrogels are prepared with various composition. Swelling of the hydrogels in water, aqueous NaCl, KCl, CaCl₂, MgCl₂ solutions is studied. NIPAAm/MPSA hydrogels have higher swelling in water and salt solutions than poly(N-isopropylacrylamide) (PNIPAAm). Also NIPAAm/MPSA hydrogels are more salt resistant when deswelling in salt solutions. For less than 7 mol% MPSA, the formed hydrogels retain both temperature reversibility and high swelling. Higher content of MPSA (>11 mol.%) leads to better salt resistance but loses thermosensitivity. The swelling of NIPAAm/MPSA hydrogel in 0.05 M NaCl is non-Fickian. In NaCl and KCl aqueous solutions, the zwitterionic hydrogels do not show obvious anti-polyelectrolyte swelling behavior, while in divalent salt CaCl₂ and MgCl₂ solutions, the swelling ability of NIPAAm/MPSA hydrogels is enhanced at low salt concentration, then decreases with further increase in salt concentration. The LCST of NIPAAm/MPSA hydrogels are also affected by concentrated salt solution.

Key words: hydrogels, amphiphiles, thermo properties, iso-propylacrylamide

Introduction

Stimuli-responsive hydrogels have received attention since the last few decades for applications in bioseparation, medicine and pharmaceutical fields. These stimuli include temperature¹⁻³, pH^{4, 5}, pressure⁶ and electric field^{7, 8}. Although many responsive hydrogels have been studied, hydrogels from derivatives or copolymers of acrylamide, especially poly(N-isopropylacrylamide) (PNIPAAm) have been most popular⁹⁻¹¹. On the other hand, a polyelectrolyte hydrogels with charged groups produce an electrostatic repulsion force among the electrolyte groups when swelling in water increasing the expansion of the hydrogel network. But the coulombic forces within polyelectrolyte hydrogels with dissociable polyions are sensitive to the internal pH and the amount of mobile ions in external solution. Adding salt into the swollen polyelectrolyte hydrogel may cause a volume collapse, due to the changes of the water structure induced by ion hydration and shielding the charge repulsion by the salt.

Linear ampholytic polymers are known for antipolyelectrolyte behavior that is characterized by increasing chain expansion in presence of salt solution. This behavior is attributed to the breakage of the intra- or inter-macromolecular attractions between ionic groups due to salt screening¹². There are two methods to prepare the ampholytic hydrogels: (1) copolymerizing a anionic monomer with a cationic monomer¹³, and (2) incorporating a zwitterionic monomer into the hydrogel network^{14, 15}. It has been shown that the hydrogels prepared from the first method show anti-electrolytic properties only in

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a narrow composition range at nearly net-zero charge densities. At non-zero charge density composition, the hydrogels show polyelectrolyte behavior¹². On the other hand, by using zwitterionic monomers it is easier to get the net-zero charge density on the hydrogel network, due to an equal amount of negative and positive charge within zwitterionic monomer chains. Different hydrogels with various zwitterionic components have been studied. NIPPAAm hydrogel copolymerized with zwitterionic monomer N-(3-acrylamidopropyl)-N,N-dimethylammonium propanesulfonate (DMAAPS)¹⁵ shows antipolyelectrolyte swelling only at some NaCl concentrations. NIPPAAm hydrogel copolymerized with zwitterionic comonomer 1-(3-sulfopropyl)-2-vinyl-pyridinium-betaine (SPV) shows a high swelling at low NaCl concentration and decreased swelling at higher concentrations¹⁶.

The purpose of the present investigation is to prepare hydrogel with both temperature reversibility and high water swelling in aqueous salt solution. Hydrogels based on NIPAAm and zwitterionic comonomer [3-(Methacryloylamino)propyl]dimethyl(3-sulfopropyl)ammonium hydroxide] (MPSA) are prepared, the swelling behavior in various salt solutions is studied and antipolyelectrolyte behaviors is discussed.

Experimental Section

Materials

Monomer NIPAAm, N,N-methylene-bis(acrylamide) (BIS), ammonium persulfate (APS) and sodium metabisulfite (SBS) (all from Aldrich Chemical Co.) were used as received. Zwitterionic monomer MPSA (from Aldrich Chemical Co.) was purified by recrystallization with acetone before use. All other materials are from Aldrich Chemical Co. and used as received.

Preparation of the Hydrogels

Hydrogels were prepared by free-radical aqueous-solution polymerization using BIS as a crosslinking agent. Various amount of NIPAAm and MPSA were mixed in water at a total concentration of 10 wt.% in a 50 ml round bottom bottle. After removing oxygen by bubbling N₂ for 20 minutes, the redox initiators APS and SBS were added. The polymerization was carried at 50-60 °C for 24 hours then the hydrogels were cut into small disks (16 mm diameter, and 2 mm thick). The hydrogel disks were immersed in excess of deionized water at room temperature for a few days to remove of the residual unreacted monomers. The hydrogels were then dried under vacuum below 50 °C. The amount of crosslinking agent BIS was kept as 2 wt.% of the total monomer. The amount of initiators APS and SBS were kept at equal molar ratio and as 0.1 wt.% of the total monomers.

Measurement of the Swelling Capacity of Hydrogels

The swelling ratios of the hydrogels were measured over a range of temperature (10 to 65 °C) in deionized water (pH~ 6.8) and aqueous solutions of NaCl, KCl, CaCl₂, and MgCl₂. After swelling reach equilibrium, the hydrogels were taken out and surface water was removed off by filter paper, then the weights of wet hydrogels were recorded. The swelling ratio (SR) is defined as:

$$SR = (W_s - W_d) / W_d \quad (1)$$

where, W_s and W_d are the weights of wet and dry hydrogels, respectively.

Swelling and Deswelling Rates

The dried hydrogel disk is immersed in excess water or salt solution at room temperature, and swelling is measured by weighting the samples with time. The diffusion coefficient is calculated from equation (2)¹⁷:

$$\frac{M_t}{M_\infty} = \left(\frac{4}{\sqrt{\rho}} \right) \left(\frac{D \times t}{L^2} \right)^{1/2}, \quad \text{for } \frac{M_t}{M_\infty} \leq 0.6 \quad (2)$$

where, t is time, L is the initial thickness of the dried sample, M_t is the water absorbed at time t , and the M_∞ is the water absorbed at equilibrium, and D is the diffusion coefficient.

The deswelling of deionized-water-swollen hydrogel was measured by putting it into 1 M NaCl solution at room temperature. The weight of the hydrogel was recorded at different time intervals, the water retention is calculated by:

$$W_R = 100 \cdot SR(t)/SR(E) \quad (3)$$

where, $SR(t)$ and $SR(E)$ are the swelling ratio at time t and at equilibrium state, respectively.

Results and Discussion

Temperature Sensitivity of NIPAAm/MPSA Hydrogels

For polymerization of NIPAAm/MPSA hydrogels in aqueous solution, the feed ratio of the copolymer hydrogels and the hydrogel properties at room temperature are listed in Table 1. Hydrogel loses temperature sensitivity with increase in the concentration of MPSA monomer. When MPSA in the feed ratio is 11 mol%, the copolymer hydrogels do not have obvious cloud point even when temperature was raised to 75 °C. Incorporation of zwitterionic monomer MPSA increases the hydrophilicity of the PNIPAAm hydrogel which in turn increases the swelling ratios of the hydrogels at room temperature.

Figure 1 shows the temperature dependence of swelling ratio in pure water for NIPAAm/ MPSA hydrogels. It is shown that around transition temperature, N-M-2 and N-M-3 hydrogels have sharp transitions in swelling because of the shift in hydrophilic-hydrophobic balance caused by raising temperature; while the swelling ratio of N-M-4 and N-M-5 hydrogels decrease linearly with increasing of temperature, indicating that the high content of MPSA results in the loss of temperature sensitivity. Hence, to maintain the temperature sensitivity of the NIPAAm/MPSA, the feed ratio of zwitterionic monomer in the polymerization should not be greater than 11 mol.%.

Swelling Kinetics of NIPAAm/ MPSA Hydrogels

Figure 2 shows the swelling kinetics of NIPAAm/ MPSA hydrogels in 0.05 M NaCl aqueous solution. The swelling equilibrium is reached in 24 hours at 25 °C. The initial swelling data are fitted to the exponential heuristic equation¹⁷:

$$\frac{M_t}{M_\infty} = Kt^n \quad \text{for } \left(\frac{M_t}{M_\infty} \leq 0.6 \right) \quad (4)$$

where K is a characteristic constant of the hydrogel and n is a kinetic exponent of the mode of solute transport. Values of n and K are calculated from the slopes and intercepts of the plot of $\log(M_t/M_\infty)$ versus $\log(t)$. For disk-shape samples, n is 0.5 if the swelling is

by Fickian diffusion, n is between 0.5 and 1.0 for non-Fickian diffusion, n is 1.0 for case II diffusion, and n is greater than 1 for super-case-II diffusion¹⁸. Table 2 shows K , n , and D values for the NIPAAm/MPSA hydrogels obtained using Equations 2 and 4. The results indicate that for all case $n > 0.5$, suggesting that the swelling transport of these hydrogel in NaCl solution is non-Fickian transport.

Salt Effect on the Swelling Behavior

Monovalent Salt

The swelling of NIPAAm/MPSA hydrogels with different concentration of NaCl is illustrated in Figure 3. With increase in NaCl concentration, the hydrogel swelling decreases, while in very dilute salt solution (10^{-4} to 0.05 M), the swelling ratio almost remains constant. This result is similar to the observation by Lee and Yeh¹⁵ for poly(N-isopropylacrylamide-co-N,N'-dimethyl(acrylamidopropyl)ammonium propane sulfonate (NIPAAm/DMAAPS) hydrogel. In the aqueous solution of a linear zwitterionic polymer, the anionic and cationic groups of the zwitterionic monomer can form complex through interchain or intergroup associations, which is broken in presence of salt, thus giving rise to chain expansion in salt solution, displaying anti-polyelectrolyte behavior. In Figure 3, no obvious anti-polyelectrolyte swelling behavior for NIPAAm/MPSA hydrogels was observed. This could be attributed to that the added NaCl may not break the interchain association so easily in crosslinking structure as in linear structure. The net charge of the NIPAAm-MPSA hydrogel is zero, the decrease of swelling ratio is just caused by the reduction of chemical potential of water with addition of salt, so the swelling ratios do not decrease sharply at low NaCl concentration. While in ionic hydrogel system like poly(N-isopropylacrylamide-co-acrylic acid) (NIPAAm/AA)¹⁶, the swelling ratio of the hydrogel has been observed to decrease sharply when KCl salt concentration is above 0.001 M, which is due to the shielding of the anionic charge by salt. Figure 3 also shows that hydrogels with higher content of MPSA have higher swelling ratios. Incorporation of MPSA increases the hydrophilicity of the hydrogel due to the amide and sulphate groups of MPSA. Similar results were observed in KCl solution, which are not illustrated here.

NIPAAm/MPSA hydrogel also lose the temperature sensitivity with increasing in NaCl concentration (Figure 4). Hydrogel N-M-1 exhibits lower critical solution temperature in up to 0.1 M NaCl, but in 1 M NaCl, the swelling of N-M-1 decreases linearly with increasing of temperature. At the higher concentration of NaCl reduced chemical potential of water makes the hydrogel volume collapse even at low temperatures.

The deswelling behaviors of PNIPAAm and NIPAAm/ MPSA are shown in Figure 5. After putting the swollen hydrogel in 1 M NaCl solution, all hydrogels show volume collapse. NIPAAm/MPSA hydrogels have higher water retention ability than PNIPAAm in concentrated salt solution. After 5.3 hours, PNIPAAm keeps 29% of water absorbed, while N-M-1, N-M-3, N-M-5 can keep 49%, 45%, and 50% water, respectively. This indicates that although NIPAAm/ MPSA hydrogels do not show anti-polyelectrolyte behavior in NaCl solution, these are more salt resistant than PNIPAAm.

Divalent Salt

Anti-polyelectrolyte behaviors for NIPAAm/MPSA hydrogels were observed in divalent salt, MgCl_2 and CaCl_2 (Figures 6 and 7). Initially, the swelling increases with salt concentration in dilute solution, but decreases at higher salt concentrations. In CaCl_2 solution, hydrogel swelling increases with salt concentration in range of dilute solution, reaching maximum at 0.01 M CaCl_2 , then decreases with further increase in the salt concentration. The similar behavior is observed in MgCl_2 solution, except the maximum swelling ratio occurs at 0.05 M MgCl_2 which should be attributed to the different hydrated ionic radii of Ca^{2+} and Mg^{2+} . The swelling also increases with the increase in zwitterionic monomer composition. There are two competing interactions in the salt solution of zwitterionic hydrogels: (a) salt decreases the chemical potential of water, making solvent poorer than aqueous solution, this will decrease the swelling; and (b) small amount of salt can break the strong association between zwitterionic monomers by shielding the positive and negative charges, causing the network expansion and increasing the swelling ratio. Figures 6 and 7 suggest that divalent cation salts more easily break the complexation between zwitterionic groups, thus making the crosslinking polymer chain expansive. These two contrary interactions determine if the hydrogel could show obvious anti-polyelectrolyte behavior in salt solution or not. If the interaction between salt and zwitterionic groups is stronger, the hydrogels tend to show anti-polyelectrolyte behavior. This anti-polyelectrolyte behavior is suppressed at higher salt concentrations because of the large amount of unbounded ions screen the expansion between ionic groups.

Deswelling of NIPAAm/ MPSA hydrogels at concentrated CaCl_2 solution (0.5 M) is shown in Figure 8. Anti-polyelectrolyte behavior is suppressed and hydrogel volume collapses. It could be seen that zwitterionic hydrogels still have higher water content when deswelling in concentrated divalent salt solution than PNIPAAm which does not have zwitterionic groups.

Conclusions:

1. When MPSA in NIPAAm/ MPSA hydrogels exceed 11 mol.%, the hydrogel loses the thermoreversibility. The swelling of NIPAAm/ MPSA hydrogel increases with increase in MPSA content.

2. In monovalent salt (NaCl and KCl) solutions, NIPAAm/ MPSA hydrogel does not show obvious anti-polyelectrolyte behavior, while in CaCl_2 and MgCl_2 solutions, it shows anti-polyelectrolyte swelling behavior in dilute salt solution, but at higher salt concentration, the swelling ratio decreases.
3. After incorporation of zwitterionic monomer MPSA, the formed hydrogels have higher swelling ratio in salt solution and a higher water content while deswelling in concentrated salt solution.

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Table 1. Properties of NIPAAm/ MPSA hydrogels

Sample No.	Feed Composition (mol%)		Cloud Point (°C)	Swelling Ratio at 25 °C
	NIPAAm	MPSA		
N-M-0	100	0	28-32	11.5
N-M-1	97.5	2.5	28-32	13.8
N-M-2	94.4	5.6	30-35	16.2
N-M-3	93	7	33-40	17.2
N-M-4	89	11	>75	19.1
N-M-5	85	15	>75	24.9

Table 2. Initial Diffusion Coefficient (D), Kinetic Exponent (n), and Characteristic Constant (K) for NIPAAm/MPSA Hydrogels in 0.05 M NaCl

Hydrogels	K	n	$D (\times 10^7 \text{ cm}^2/\text{s})$
N-M-1	0.128	0.7175	3.48
N-M-2	0.123	0.7532	2.16
N-M-3	0.113	0.7756	2.4