

Water-Sorption and Metal-Uptake Behavior of pH-Responsive Poly (*N*-acryloyl-*N'*-methylpiperazine) Gels

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ABSTRACT: Hydrogels based on *N*-acryloyl-*N'*-methylpiperazine (AcrNMP) swelled extensively in solutions of low pH due to the protonation of the tertiary amine. The water transport in the gels under an acidic condition was non-Fickian and nearly Fickian in neutral pH with the collective diffusion coefficients determined as 2.08×10^{-7} and $5.00 \times 10^{-7} \text{ cm}^{-2} \text{ s}^{-1}$, respectively. These gels demonstrated good metal-uptake behavior with various divalent metal ions, in particular, copper and nickel, with the uptake capacity increased with increasing pH. The swelling ratio of the gel in the presence of metal ions decreased with increasing metal ion uptake. The results suggest that high metal ion uptake can lead to physical crosslinking arising from the interchain metal complex formation. The metal-loaded gels could be stripped easily with 1M H_2SO_4 without any loss in their uptake capacity. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 268–273, 2001

Key words: hydrogel; *N*-acryloyl-*N'*-methylpiperazine; swelling kinetics, metal uptake; noncompetitive

INTRODUCTION

Hydrogels are three-dimensionally crosslinked hydrophilic polymer networks capable of swelling and retaining a large volume of water in the swollen state. Depending on the type of monomers incorporated into the gels, they can also be made to respond to a variety of external stimuli such as pH,¹ temperature,² salts,³ and the electric field,⁴ leading to what are known as “stimuli-responsive” polymers. These polymers have found some promising applications such as in the controlled delivery of medicinal drugs,⁵ artificial muscles,⁶ sensor systems,⁷ and bioseparations.⁸

A pH-sensitive gel is formed from crosslinking flexible polymer chains to which ionizable groups are attached. pH-responsive gels based on acrylic/methacrylic acid derivatives, *N,N*-(dimethylamino)ethyl methacrylate (DMAEMA), have been reported.^{9,10} It is known that piperazine can form complexes with metal ions.^{11,12} In this article, the development of a new piperazine-based hydrogel with metal chelating properties is described. The new gel possesses both hydrophilic and chelating moieties in the same molecule. The swelling and metal ion-uptake behavior under noncompetitive conditions of this new pH-responsive hydrogel are described.

EXPERIMENTAL

Materials

Acryloyl chloride (Acros, Geel, Belgium) and ethylene glycol dimethacrylate (EGDMA: Fluka, Buchs,

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Switzerland) were distilled under a vacuum and stored in the refrigerator. 2,2-Dimethoxy-2-phenylacetophenone (DMPA: Aldrich, Milwaukee, WI), *N,N*-methylenebisacrylamide (MBA: Baker, Phillipsburg, NJ), and *N*-methylpiperazine (Acros) were used as received. All other solvents were used as received unless otherwise mentioned. NaH_2PO_4 – Na_2HPO_4 buffer and acetic acid–sodium acetate buffer solutions were prepared by adjusting a 0.1M NaH_2PO_4 solution with Na_2HPO_4 and 0.1M acetic acid with 0.1M trisodium acetate to the required pH, respectively.

Synthesis

Synthesis of Monomers

The monomer *N*-acryloyl-*N'*-methylpiperazine (AcrNMP) was synthesized from acryloyl chloride and *N*-methylpiperazine as reported earlier.¹³

Synthesis of Hydrogels

AcrNMP (6 g, 38.9 mmol) along with the crosslinker EGDMA (2 wt %) and the photoinitiator DMPA (0.5 wt %) were dissolved in 25 mL of methanol in glass ampules. The mixture was purged by bubbling dry nitrogen gas for about 15 min and the ampule was sealed. Polymerization was carried out by free-radical photoinitiation by placing the ampule in a photochemical reactor (Rayonet, $\lambda > 300$ nm) for about 30 min. The clear, transparent, solid polymer was recovered and placed in diethyl ether for 3 weeks to remove the soluble fractions. It was then swelled in distilled water and cut into small discs (ca. 1–1.5 mm) and dried to a constant weight in a vacuum. The gels are abbreviated as follows: GBE-2 (in bulk with 2 wt % EGDMA), GSE-2 (in solution using 2 wt % EGDMA), and GSB-2 (in solution using 2 wt % MBA).

Measurements

Swelling Experiments

The extent of swelling of the crosslinked polymers was determined gravimetrically. After a soaking period of 48 h, each sample was removed from the respective vials, tapped with a moist Kim-wipe towel to remove the excess surface water, and weighed. The dry weights were measured after the gels were dried in a vacuum at 50°C for 2 days until constant weights were maintained. The weight-swelling ratio (W) is defined as

$$W = (\text{wet weight} - \text{dry weight}) / (\text{dry weight}) \quad (1)$$

Batch Metal-uptake Experiments

The batch metal-uptake experiments were performed using standard metal chloride solutions of 0.20M and acetate buffer solutions. The metal solutions and buffer solutions were prepared from analytical-grade reagents. All the experiments were performed in polyethylene bottles at 25°C. The capacities for Co^{2+} , Cu^{2+} , Ni^{2+} , Zn^{2+} , and Ca^{2+} under noncompetitive conditions were determined as a function of pH (range: 3.5–6.0). Batches of 0.2 g of the polymer gel was soaked and stirred in a solution formed by mixing 25 mL of a 0.2M metal chloride solution and 25 mL of the buffer solutions for 2 days. The polymer was then washed in ethanol and ether and then dried to a constant weight in a vacuum at 50°C.

Regeneration Experiments

In the regeneration experiments, batches of the polymer gels, each 0.20 g, were loaded with 25 mL of the respective metal standard solutions and 25 mL of the HOAc/NaOAc buffer at pH 4.5. The loaded samples were stripped with 1.0M H_2SO_4 .

Atomic Absorption Measurements

The metal ion content was analyzed using a Shimadzu AA-680 atomic absorption spectrophotometer (AAS). Samples for metal analysis were prepared by heating 0.2 g of the dried loaded samples with concentrated H_2SO_4 and concentrated HNO_3 until clear solutions were obtained. The metal content of all these solutions was measured by AAS spectroscopy using a linear calibration curve.

RESULTS AND DISCUSSION

pH-Dependent Swelling Studies

Figure 1 shows the effect of the solution pH on the swelling of the hydrogel GSE-2 at 25°C. The swelling was extensive at low pH but low at high pH. This is attributed to the protonation of the tertiary amino nitrogen of the piperazine moiety at low pH. The protonation leads to electrostatic interactions, thus creating a difference in the osmotic pressure between the gel interior and the external solution. The swelling ratios of the gels GSE-2 and GBE-2 at pH 2.6 were 59 and 9, re-

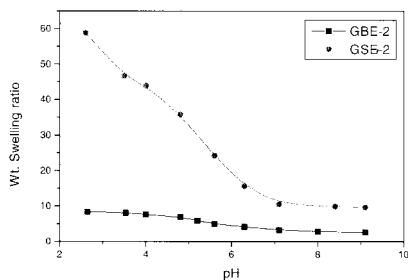


Figure 1 Effect of pH on the equilibrium swelling of GSE-2 and GBE-2 at 25°C.

spectively. It can also be seen from Figure 1 that the swelling of the polymer prepared under bulk conditions exhibits much poorer swelling behavior. This is due to the glassy nature of the polymers as a result of additional crosslinking of the monomers.¹⁴

Water-sorption Kinetics

Figure 2 shows the water-sorption kinetics of the gels GBE-2 in pH 2.6 and in pure water. It can be seen that the swelling ratio of the gel increases with time and reaches a maximum after ~100 min. Two different processes can generally describe the diffusion of a solvent into a polymer matrix, namely, the diffusion of the solvent into the swollen matrix and the advancement of the swollen–unswollen boundary as a result of polymer relaxation. The initial swelling data were fitted to the following equation¹⁵ in the range of $M_t/M_\infty \leq 0.6$:

$$M_t/M_\infty = kt^n \quad (2)$$

where M_t and M_∞ are the mass of water taken up at time t and infinite time, respectively; k , a characteristic constant of the gel; and n , a characteristic exponent of the mode of transport of the

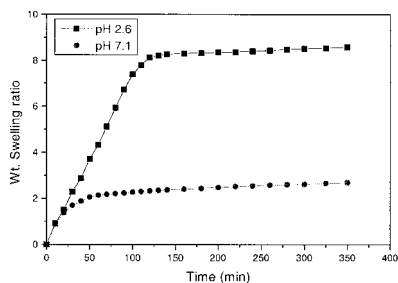


Figure 2 Water-sorption kinetics of GBE-2 in acidic (pH 2.6) and neutral media at 25°C.

Table I Diffusion Parameters of GBE-2 at 25°C

pH	n	k	$D \times 10^7$ (cm ² /s)
2.6	0.833	0.0152	2.08
7.0	0.5227	0.0774	5.00

penetrant. The values of n and k were calculated from the slopes and intercepts, respectively, of the plot of $\log(M_t/M_\infty)$ versus $\log(t)$. For Fickian kinetics, in which the rate of diffusion of the solvent is rate-limiting, $n = 0.5$, while values of n between 0.5 and 1 indicate the contribution of non-Fickian processes such as polymer relaxation.¹⁶

The collective diffusion coefficients of the gels were determined from the gradient of the plot of the initial swelling rate versus the square root of time, using the following equation, within the same range of $M_t/M_\infty \leq 0.6$:

$$M_t/M_\infty = 4/l \times (D \times t/\pi)^{1/2} = W_t/W_\infty \quad (3)$$

where W_t and W_∞ are the weight swelling ratios at time t and time infinity, respectively; t , the time; and l (0.11 cm), the initial thickness of the dry gel. The results are summarized in Table I. The diffusion of water in the gels followed a non-Fickian behavior or Case II transport due to the dominance of polymer relaxation under acidic conditions. However, in pure water, the diffusion approached Fickian behavior. Schott proposed the following equation for describing the extensive swelling of the polymer:¹⁷

$$t/W = A + Bt \quad (4)$$

where W is the water uptake at time t ; $B = 1/W_\infty$, the inverse of the maximum swelling; and $A = 1/(dW/dt)_0$, the reciprocal of the initial swelling rate. By applying the present swelling data to eq. (4), it was found that plots of t/W against t gave straight lines with good correlation coefficients.

The relatively high diffusion coefficients observed in the present systems are due to the hydrophilic nature of this gel. Under acidic conditions (pH 2.6), the diffusion coefficients of the gels increased due to the protonation of the amines. In addition to the solvent diffusion and polymer relaxation, the diffusion of ions and ionization of the fixed-charge groups also play a role in the swelling process. A close observation of the initial sorption curve of the present system shows a similar

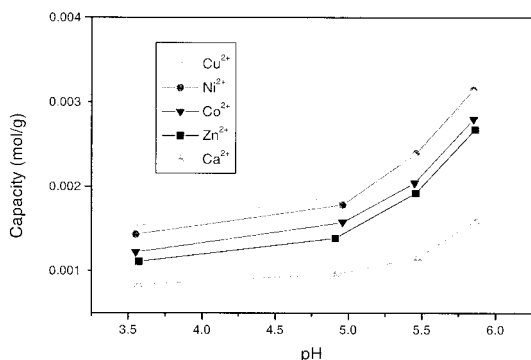


Figure 3 Metal-uptake capacity of GSE-2 under non-competitive conditions at 25°C as a function of pH in 0.1M of MCl_2 solutions.

sigmoidal pattern, which has been observed for certain hydrophilic gels of DEAEMA¹⁸ and NIPAM.¹⁹ This is attributed to the formation of a swelling front during the initial swelling process as explained by Siegel.¹⁸

Effect of pH on the Metal-uptake Capacity of the Gel

Figures 3 and 4 show the metal-uptake capacity of GSE-2 and GSB-2, respectively, for some divalent metal ions as a function of pH. The metal-uptake capacity of the gels GSE-2 and GSB-2 for Zn^{2+} , Co^{2+} , Ca^{2+} , Ni^{2+} , and Cu^{2+} were found to increase with increasing pH of the solution. The pH effect is obviously related to the fraction of free amine available for metal ion complex formation. Owing to the extensive protonation of the amine groups at low pH, the number of amine groups available for complex formation is reduced—hence, less uptake of metal ions. The gel GSE-2 showed a maximum capacity (in the pH

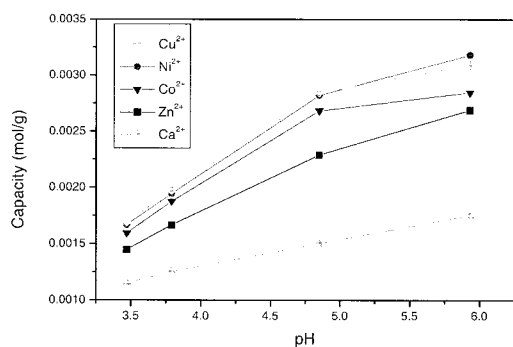


Figure 4 Metal-uptake capacity of GSB-2 under non-competitive conditions at 25°C as a function of pH in 0.1M of various MCl_2 solutions.

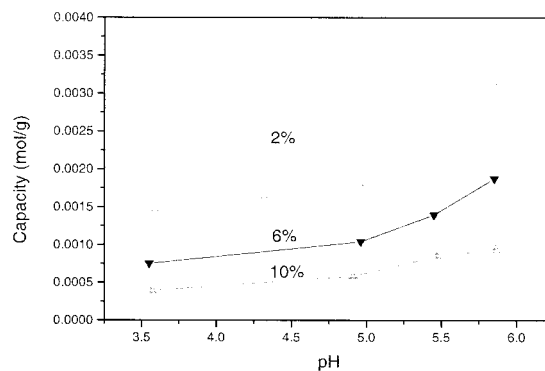


Figure 5 Effect of crosslinker on Ni^{2+} -uptake capacity of GSE gels at 25°C as a function of pH in 0.1M $NiCl_2$ solution.

range tested) of about 0.003 mol/g at pH 5.9 for both Cu^{2+} and Ni^{2+} . A similar maximum capacity was also observed for the GSB-2 gel. It is interesting to note that the plot of the uptake of metal ions as a function of pH for GSE-2 follows a concave profile, whereas the plot of the uptake of metal ions as a function of pH for GSE-2 follows a convex profile. The uptake capacity of GSE-2 and GSB-2 decreases in the order $Ni^{2+} \approx Cu^{2+} > Co^{2+} > Zn^{2+} > Ca^{2+}$ for the pH range studied. The higher uptake observed for Ni^{2+} and Cu^{2+} is due to the formation of a more stable metal ion complexes with piperazine.^{20,21}

Effect of Crosslinker on the Uptake Capacity of the Gels

The effect of the crosslinker concentration with 2, 6, and 10 wt % on the uptake of Ni^{2+} by GSE gels was studied and the results are shown in Figure 5. The swelling of the gels and the metal-uptake capacity decreased with increasing crosslinker content due to the formation of more rigid polymer networks.

Effect of Metal Ion on the Swelling Behavior of the Hydrogel

Figure 6 shows the effect of pH on the swelling of GSE-2 in solutions of various metal ions. It can be seen that the pH has opposing effects on the swelling and metal ion uptake, that is, as the uptake of the metal ions increases, the swelling decreases. High metal ion uptake leads to more physical crosslinking formed by the interchain metal complex formation. The swelling thus decreases.

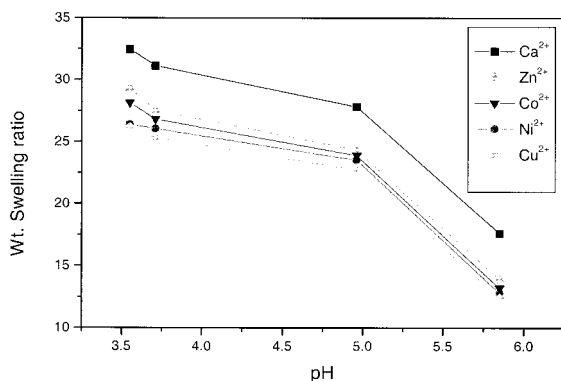


Figure 6 Equilibrium swelling of GSE-2 at 25°C as a function of pH in 0.1M MCl₂ solutions.

Effect of Metal Ion Concentration on the Uptake Capacity

The uptake capacities of GSE-2 for various concentrations of NiCl₂ at pH 5 are presented in Table II. The results are roughly consistent with an equilibrium process for the complex formation between the piperazine and the metal ion. Assuming that the complex formed is a 2:1 adduct with two piperazine units to one metal ion, a rough estimate of the equilibrium constant of $\sim \text{dm}^3 \text{mol}^{-1}$ was obtained for a low metal ion concentration of 0.02M. Obviously, the value should only be treated as an estimate, as other factors such the ionic strength effect should also be taken into consideration. More importantly, it should be noted that no true solution equilibrium should be expected because of the heterogeneous nature of the system.

Regeneration Experiment

The results for the regeneration study using 1M H₂SO₄ are presented in Table III. The removal of the metal ions from the loaded gel was almost complete, with the capacity being unaffected.

Table II Ni²⁺ Uptake Capacity of GSE-2 at pH 5.0 at 25°C

[NiCl ₂] (mol dm ⁻³)	Uptake Capacity (mol g ⁻¹)
0.02	0.00079
0.1	0.00194
0.2	0.00259
0.5	0.00287
1.0	0.00301

Table III Metal Uptake and the Stripping Data of GSE-2 in 1M H₂SO₄ at 25°C

Metal Ion	Amount Loaded (mol g ⁻¹)	Amount Stripped (mol g ⁻¹)
Cu ²⁺	0.00311	0.00286
Ni ²⁺	0.00314	0.00298
Co ²⁺	0.00280	0.00265
Ca ²⁺	0.00159	0.00146
Zn ²⁺	0.00268	0.00254

This indicates that there is no acid-induced decomposition during the process of stripping.

CONCLUSIONS

A new piperazine-based hydrogel containing both hydrophilic and chelating moieties within the same molecule was synthesized. By varying the solutions' pH conditions, the protonation of the tertiary amine of piperazine can be altered, leading to swelling and deswelling of the gel. The water transport in the gels under acidic media was non-Fickian, while in neutral media, it approached almost Fickian behavior. This gel was more selective to Cu²⁺ and Ni²⁺ ions in aqueous solutions, and the uptake capacity increases with increasing pH. The gels could be stripped successfully with 1M H₂SO₄ and regenerated without any loss in their uptake capacity. These hydrophilic gels would therefore be a good candidate for the removal of Cu²⁺ and Ni²⁺ ions.

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