pH-Sensitive Dimethylaminoethyl Methacrylate (DMAEMA)/Acrylamide (AAm) Hydrogels: Synthesis and Adsorption from Uranyl Acetate Solutions

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ABSTRACT: A random copolymer of dimethylaminoethyl methacrylate (DMAEMA) and acrylamide(AAm) [poly(DMAEMA/AAm)], with a pH-sensitive character, was prepared by a redox polymerization method. Increasing the DMAEMA content of the gel, the pH, and the ionic strength of the solution decreased the swelling ratios of the hydrogels. The adsorption of poly(DMAEMA/AAm) hydrogels from uranyl acetate (UA) solutions was studied at different pHs. The adsorption capacity of hydrogels increased from 200 to 1200 mg of UA per gram of dry hydrogel with increasing pH of the adsorption solution. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2028–2031, 2003

Key words: hydrogels; adsorption

INTRODUCTION

Hydrogels that are crosslinked hydrophilic polymers have been widely used in application fields from agriculture to controlled drug delivery systems. Gels undergo reversible and discontinuous volume changes in response to changes in environmental conditions, such as solvent composition, temperature, salt concentrations, and pH.[1–4] The pH-responsive hydrogels are those containing one or more ionic or ionizable monomer in the polymeric backbone, side groups, or crosslinks. Examples of common polyelectrolytes include poly(acrylic acid),[5, 6] poly(methacrylic acid),[7, 8] poly(acrylamide-co-itaconic acid),[9] poly(vinylamine),[19] and poly(4-vinyl pyridine).[11] These gels contain pendant acidic or basic groups that change ionization in response to changes in pH. Temperature- and pH-sensitive gels have recently been of increasing interest in the fields of controlled drug delivery, immobilization of enzymes and cells, and dewatering of protein solutions.[12–17] In this study, we describe the synthesis and adsorption capacity of a pH-sensitive copolymer of dimethylaminoethyl methacrylate (DMAEMA) and acrylamide (AAm).

EXPERIMENTAL

Chemicals

Acrylamide (AAm) and dimethyaminoethyl methacrylate (DMAEMA) monomers were from Merck and used without further purification. *N*,*N*′-Methylenebisacrylamide (MBAAm), a crosslinking agent from BDH, and potassium persulfate (KPS), an initiator from Merck, were used to form the copolymeric hydrogels. $HNa_2O_4P.2H_2O$ and H_3PO_4 from Merck and KH_2PO_4 from BDH were used to prepare phosphate buffer solutions.

Preparation of pH-sensitive hydrogels

The preparation of the gel began by combining two monomers, AAm [a small organic molecule that terminates in an aminocarbonyl (—$CONH_2$) group] and DMAEMA (a hydrophobic hydrogel containing cationic groups) with the crosslinker MBAAm, which consists of two acrylamide monomers that are linked through their aminocarbonyl groups. Then, potassium persulfate (KPS) was added to initiate a chain reaction of polymerization. Hydrogels of different copolymer compositions were prepared by using the same amount of AAm monomer in each case (i.e., 0.20 g) and varying the amount of DMAEMA (i.e., 0.20, 0.25, and 0.30 mL) Constant quantities of MBAAm (0.1 mL of 5 mg/mL solution) and KPS (0.6 mL of 0.05 g/mL solution) were also used. Gelation took 2.5–3 h. Fresh hydrogels, which were obtained in long cylindrical shapes, were cut into 4-mm-long pieces and washed for 1 week with distilled water for removal of unreacted monomers. Finally, the washed hydrogel pieces were dried in air.

Determination of swelling ratio

Dried crosslinked copolymers were weighed and transferred into buffer solutions of different ionic

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strengths at 25°C to determine the hydrogel swelling ratio. The dynamic swelling kinetics of hydrogels with time was investigated gravimetrically. Swollen gels were removed from the buffer solutions baths at regular intervals and were dried superficially with filter paper, weighed, and placed in the same baths as quickly as possible until they reached to their equilibrium states.

Dried hydrogels were glassy and very hard, but swollen hydrogels were very soft. The swollen hydrogels kept their cylindrical shapes, but with enormous dimensions, had good mechanical sounds, and showed no evidence of dissolution, deformation, dispersion, or damage.

The ratio of mass swelling was calculated from the following equation:

$$\text{Swelling Ratio} = [(m_t - m_0)/m_0] \quad (1)$$

where m_0 is the mass of the dry gel at initial of experiment and m_t is the weight of the swollen gel at time t.

Adsorption of uranyl acetate

The uptake of uranyl acetate (UA) by DMAEMA/AAm hydrogels in acetate buffer solutions at different pHs (3.6, 4.3, 5.3) was studied. At pH values >5.3, the UA precipitated. Acetate buffer solutions were prepared with 0.1 g of UA, acetic acid, and sodium hydroxide in a total solution volume of 30 mL. About 0.05 g of dry hydrogels was put into these solutions. The hydrogels swelled until they reached their equilibrium. During the adsorption studies, 0.5-mL samples of solutions were deposited onto aluminium disks at defined time intervals. The UA remaining in the disc after the solutions evaporated was the amount that was not absorbed (unadsorbed amount) by the hydrogel in 0.5 mL of solution. Using this quantity, the adsorbed amount of UA can be calculated.

The samples prepared according to the procedures just described were counted for 1 h with a multichannel α-counting system. The counts obtained from the samples were related to adsorbed UA in the following way: Initially,

$$0.1 \text{ g of UA}/30 \text{ mL} = 0.00333 \text{ gof UA}/1 \text{ mL of solution} \quad (2)$$

$$(\text{count}/0.5 \text{ mL}) \times 2 = \text{count}/1 \text{ mL of solution} \quad (3)$$

$$(\text{count}/1 \text{ mL})/(0.00333 \text{ g of UA}/1 \text{ mL}) = \text{count/g of UA} \quad (4)$$

At time t,

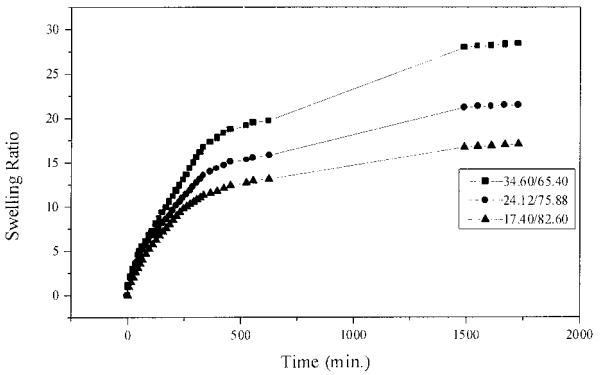

Figure 1 Effect of copolymer DMAEMA/AAm on the swelling behavior of the hydrogels in buffer solution at pH 3.0 and ionic strength of 0.05.

$$(\text{count}/1 \text{ mL})/(\text{count/g of UA}) = \text{g of UA}/1 \text{ mL at time t} \quad (5)$$

$$\text{Initial g of UA}/1 \text{ mL} - \text{time } t \text{ g of UA}/1 \text{ mL} = \text{adsorbed g of UA}/1 \text{ mL of solution} \quad (6)$$

$$[\text{Adsorbed g of UA/g of gel}] \times 30 \text{ mL}/m_{\text{jel}} = \text{adsorbed g of UA}/30 \text{ mL of solution/g of gel} \quad (7)$$

RESULTS AND DISCUSSION

Effect of the hydrogel composition on swelling

The effect of various DMAEMA/AAm mole ratios on the swelling of the produced gels was studied. The concentration of AAm in the polymerization medium was fixed at 200 mg/0.7 mL. Swelling studies were performed in phosphate buffer solution (pH 3.0; total ionic strength, 0.05) with the gels in the form of short cylinders. These experiments were conducted in a thermostatic water bath. The effect of gel composition on the swelling behavior of the gels produced with different DMAEMA/AAm mole ratios is shown in Figure 1. Higher equilibrium swelling ratios were obtained by increasing the DMAEMA content of the gel structure. An increase in the DMAEMA/AAm ratio increases the concentration of ionizable groups and therefore increases the extent of swelling of these copolymer gels. In other words, an increase in AAm content decreases the concentration of ionizable amine groups, thereby lowering the osmotic pressure that can be generated by the counterions.

Effect of pH of buffer solutions on swelling

The swelling ratios of poly(DMAEMA/AAm) hydrogels at 25°C in aqueous buffers, with varying pH

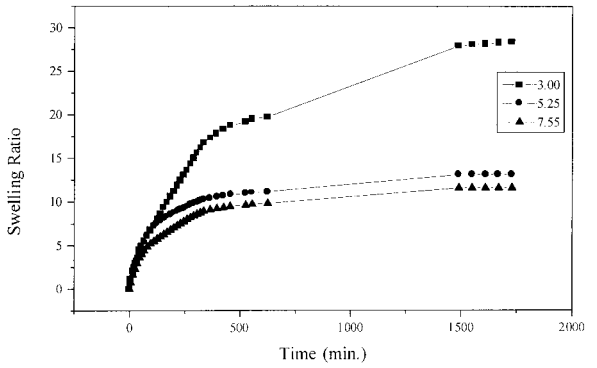

Figure 2 Effect of pH on the swelling behavior of the hydrogels at 25°C. the initial DMAEMA/AAm mole ratio was 34.60/65.40, and the ionic strength was 0.05.

(3.00–7.55) and fixed ionic strength (0.05), are presented in Figure 2. For weakly ionizable gels, such as poly(DMAEMA/AAm), the extent of ionization of the ionizable monomers varies with pH. This variation of ionization results in pH-dependent swelling equilibria. The degree of swelling of the poly(DMAEMA/AAm) gels decreases with pH. The hydrogel becomes positively charged in solutions of low pH. The protonation of amino group of hydrogels becomes easier in acidic medium than basic medium. Because positively charged tertiary amine groups are incorporated into the polymer network, the gel swells in the low pH region, due to the ionic repulsion of the protonated amine groups, and collapses in the high pH region, due to unprotonated amine groups. Swelling capacities of hydrogels increase as the acidity of medium increases, and the highest swelling ratios were obtained at the lowest pH of 3.0.

Effect of ionic strength of buffer solution on swelling

In the swelling experiments, the ionic strength of the buffer solution was changed by fixing the composition of DMAEMA/AAm hydrogel at pH 3.0. The variation of the swelling ratio of the produced gel with the ionic strength is given in Figure 3. The equilibrium swelling ratio of the gels decreased with increasing ionic strength. This inverse relationship occurs because of the increased counterion concentration, shielding of charges on the polymer chain, and high ion concentration outside the gel that accompany the increase in ionic strength. As the concentration of ions outside the gel increases, the concentrations of ions inside and outside the gel becomes equal, and the osmotic pressure inside the gel decreases, which also decreases the degree of swelling of the hydrogel.[18]

Adsorption of UA by the poly(DMAEMA/AAm) hydrogel

To observe the uptake of UA by DMAEMA/AAm, hydrogels were studied in acetate buffer solutions at

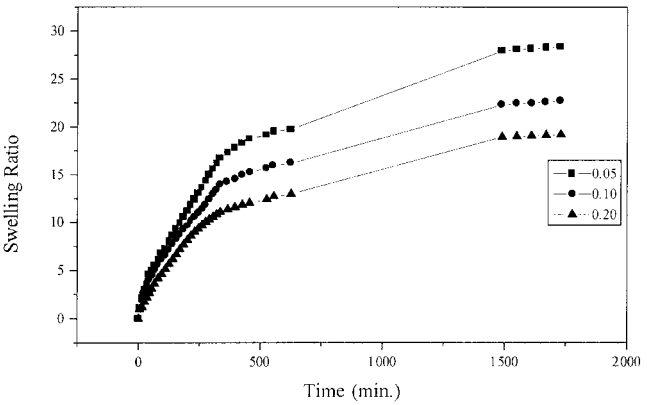

Figure 3 The effect of the change of ionic strength of pH 3.0 buffer solutions on the swelling behavior of hydrogels. The initial DMAEMA/AAm mole ratio was 34.60/65.40.

different pHs (3.6, 4.3, 5.3). Variations of the adsorbed UA per unit mass of gel with time at different pHs are given in Figure 4. According to the results, the uptake of UA by the DMAEMA/AAm hydrogel is much greater in the buffer solution at pH 5.3 than in buffer solutions at lower pHs. The reason for the increase of uptake at high pH values is the existence of —NH— groups in the hydrogel structure. The nitrogen atoms in the —NH— groups become protonated at low pH values, forming —N^+H_2 RA^- groups, where A^- is an anion (acetate in this case). In these protonated groups, the nitrogen atom do not have a free-electron pair capable of forming coordination bonds with transition metals. At higher pH values, however, nitrogen was deprotonated, and the gel could thus bind uranyl ions. Lehto and co-workers examined the uptake of zinc, nickel, and chromium by *N*-isopropyl acrylamide polymer gels and some other copolymeric structure that can take up metal cations by both ion exchanging to the carboxylic group and by coordination to the nitrogen.[19]

The α-energy spectra of uptake of UA by DMAEMA/AAm hydrogel (34.60/65.40) at pH 5.3 are

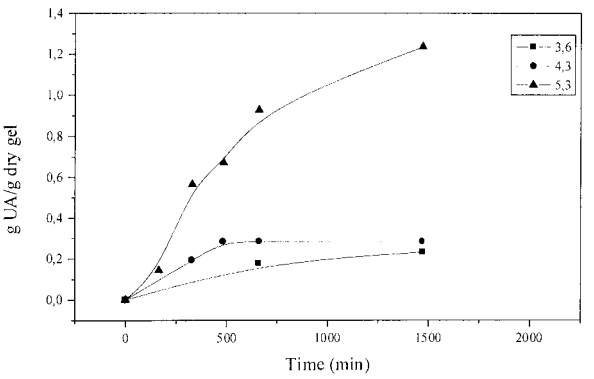

Figure 4 The variation of the adsorbed uranyl acetate per unit mass of dry hydrogel with time. The initial DMAEMA/AAm mole ratio was 34.60/65.40 % at three different pHs.

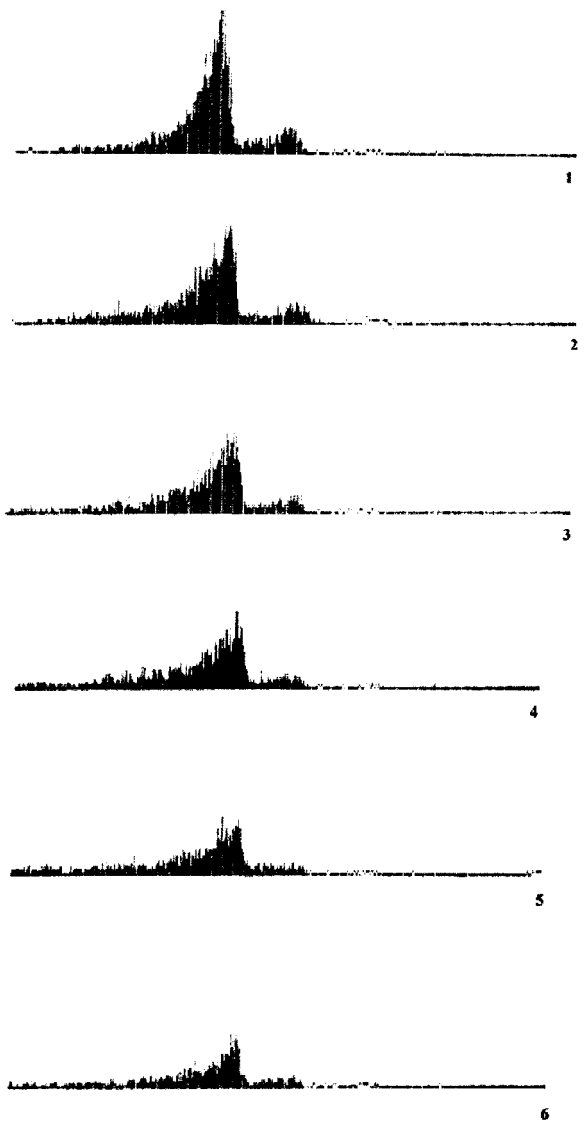

Figure 5 α-Energy spectrum of uptake of uranyl acetate by DMAEMA/AAm hydrogel at a mole ratio of 34.60/65.40 at pH 5.3: (1) sample prepared from the original solution (there is no gel), (2) sample prepared after 165 min, (3) sample prepared after 330 min, (4) sample prepared after 485 min, (5) sample prepared after 660 min, and (6) sample prepared after 1470 min.

shown in Figure 5 for samples prepared from the original solution (with no gel) and gels in solution prepared after 165, 330, 485, 660, and 1470 min. The energy of uranium-238 is ~4200 KeV. The second small energy peak in the upper end of the spectrum corresponds to 4700 KeV and comes from the daughter elements uranium-234, thorium-230, and radium-226. Only the counts from the first peaks of the spectra were used. The thickness of the UA samples caused broadening of peaks because of self-absorption of the α-particles. Although poly(DMAEMA/AAm) hydrogel has a very strong structure with respect to mechanical strength, its network binding energy was overcome in the long-term adsorption studies. The energy that was released by α-decaying uranyl is greater than the hydrogel three-dimensional network structure binding energy, so the mechanical strength of the hydrogel becomes weaker. Insoluble hydrogel was destroyed and dissolved in 0.1 g of UA per 30 mL during the adsorption studies when the hydrogel was left for a long time in the solutions. For the desorption studies, highly swollen hydrogel with UA was put into water. After 20 h, the energies of α-particles from adsorbed UA within the very big volume of hydrogel softened the hydrogel and broke down its mechanical strength.

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