

pH-Sensitive Acrylic-Based Copolymeric Hydrogels for the Controlled Release of a Pesticide and a Micronutrient

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ABSTRACT: Acrylic-based copolymers of methyl methacrylate (MMA) and methacrylic acid (MAA) have been prepared by solution and bulk polymerization techniques using benzoyl peroxide (BPO) as an initiator. Three polymers were prepared with a varying ratio of MMA/MAA. In an effort to increase the hydrophilicity of the matrix, one MMA/MAA polymer was prepared by adding an additional amount of 2-hydroxy ethyl methacrylate (HEMA). All the polymers were crosslinked *in situ* by ethylene glycol dimethacrylate (EGDMA). These polymers were characterized by Fourier transform infrared spectroscopy and differential scanning calorimetry. Viscous flow characteristics were determined from solution viscosity and rheological measurements. Dynamic and equilibrium swelling experiments were carried out under varying pH conditions (i.e., 0.1N NaOH, 0.1N HCl, and double-distilled water). Partially crosslinked hydrogels show varying hydrophilicity because of the presence

of carboxylic acid groups making them pH-responsive. Swelling increased with an increasing number of —COOH groups on the polymer backbone and the hydrophilicity varied with changing pH. Cypermethrin, a widely used pesticide, and cupric sulfate, a model micronutrient, were loaded into these pH-sensitive hydrogels to investigate their controlled release characteristics. The *in vitro* release rates of both compounds have been carried out under static dissolution conditions at 30°C. Release data have been fitted to an empirical relation to estimate transport parameters. The release results have been discussed in terms of the varying hydrophilicity of the hydrogel network polymers. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 394–403, 2003

Key words: hydrogels; cypermethrin; cupric sulfate; controlled release; transport properties; microencapsulation; stimuli-sensitive polymers

INTRODUCTION

Hydrogels are polymeric network structures absorbing large quantities of water (an absorption of nearly a thousand-fold water when compared to the dry mass of polymer).¹ In arid areas, the use of hydrogels in sandy soil (macroporous medium) may increase the water-holding capacity, thus improving the quality of plants.^{2,3} Hydrogels in soil applications facilitate an increased water sorption, minimizing the frequency of irrigation and water loss due to evaporation. In recent years, the use of pH-sensitive hydrogels in soil applications is increasing because soil has an alkaline pH and therefore, development of hydrogels that are responsive to alkaline media is important.^{1,2} Additionally, in agricultural areas, it is advantageous to have a hydrogel that can encapsulate a toxic pesticide or mi-

cronutrient so as to regulate its safe release to the environment.^{4,5} Because copper sulfate is highly water-soluble and cypermethrin is almost water-insoluble, their encapsulation using a common hydrogel is advantageous. In the earlier literature, many kinds of superabsorbing hydrogels have been reported for use in soil applications.^{1,5}

In a previous study,⁶ we reported the preparation of pH-responsive polymeric hydrogels for the release of bioactive molecules. In continuation of this work, we now report the synthesis of pH-responsive hydrogels for the encapsulation of a pesticide (cypermethrin) and a micronutrient (cupric sulfate) because these are essential for the growth and yield of agricultural crops.^{7,8} However, their excessive use or handling without proper encapsulation or safety measures might be hazardous to human health and hygiene. To control the release characteristics as well as to vary the rigidity of the hydrogel matrices, we have treated them with organic solvents. In a previous study by Katime et al.,⁹ bulk polymerization was used to produce a similar type of hydrogel by using methacrylic acid (MAA) and methyl methacrylate (MMA) monomers at different ratios in the presence of *N,N'*-methylene-bisacrylamide as the crosslinking agent, but the

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TABLE I
Synthetic Details of the Copolymers

Polymer sample code	Copolymer composition	Crosslinking agent, EGDMA	Nature of polymer sample
I	75% MMA + 25% MMA	0.01%	Less hydrophilic
II	50% MMA + 50% MMA + 0.01% HEMA	0.01%	Medium hydrophilic
III	25% MMA + 75% MAA	0.01%	Highly hydrophilic

study focused more on the mechanical and thermodynamic properties of the matrices instead of their release characteristics. In the present work, we have used ethylene glycol dimethacrylate (EGDMA) as a crosslinking agent to prepare three polymers. However, in one of these, 2-hydroxy ethyl methacrylate (HEMA) was also added to increase the matrix hydrophilicity. Polymers were prepared by both solution and bulk polymerization techniques. Polymers prepared by solution polymerization were fine powders, which were used to encapsulate and release the water-insoluble pesticide and the water-soluble micronutrient. The release characteristics of these hydrogels have been monitored to evaluate their applications in agriculture.

EXPERIMENTAL

Materials

Fluka samples of MMA (purity > 99%), MAA (purity > 98%), EGDMA (purity > 97%), and HEMA (purity > 99%), sodium hydroxide pellets (MCB), and aqueous ammonium hydroxide (Merck, Germany) were used as supplied. Benzoyl peroxide (BPO, purity > 97%, Fluka) was used as an initiator and hydroquinone (purity > 97%, Sigma) was used as an inhibitor. Sulfur-free toluene was used as a solvent. Cupric sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, molecular weight = 250 and purity = 98%, Spectrum) and cypermethrin (CAS 52315-07-8, NEAT, Supelco, Bellefonte, PA) were of ACS reagent grade. Deionized water was used in the preparation of aqueous solutions. AR grade samples of tetrahydrofuran (THF), methanol, acetone, dimethyl sulfoxide (DMSO), and hydrochloric acid were obtained from EM Science (Gibbstown, NJ).

METHODS

Solution polymerization

Partially crosslinked acrylic copolymers of different compositions were synthesized. In the actual procedure, a 500-mL capacity reaction kettle fitted with a flat flange glass cover, equipped with a stirrer, cold water condenser, and 125-mL-capacity glass separating funnel with a pressure equalizing tube for reagent addition was used. The kettle assembly was mounted in a constant temperature water bath set at 30°C. In

this kettle, 150 g toluene, 25–75 mass % distilled MMA, 25–75 mass % distilled MAA, and 0.01 mass % EGDMA were added. In a separate set of experiments, 0.01 mass % HEMA was also added under continuous stirring. Synthetic details and polymer sample identifications are given in Table I.

The reaction temperature was raised to 75°C and 0.1% (0.05 g) BPO previously dissolved in 50 g toluene was added dropwise under continuous stirring. Reaction conditions were maintained for 8 h; the solution was cooled to room temperature, filtered through coarse filter paper under partial vacuum, washed with toluene, dried, and stored in a desiccator. Neutralization was carried out in aqueous alkali solution.

Bulk polymerization

Using bulk polymerization, three polymers were prepared by using the same composition as employed in solution polymerization. Required quantities of monomers, initiator, and crosslinking agents were taken into two test tubes with diameters of 10 and 20 mm. The test tubes were sealed and placed in a water bath maintained at 75°C for 6–8 h. After complete polymerization, the test tubes were broken to access the cylindrical-shaped solid polymers. The samples were heated in a hot-air oven at 150°C for 4 h to ensure complete crosslinking. Samples were cut into disc-shaped pieces of specific thickness and diameter for sorption studies in different pH media.

Polymer characterization

Fourier transform infrared (FTIR) measurements

FTIR (Nicolet, Model Impact 410) was used to characterize the polymer and cypermethrin as well as to study the chemical interactions between cypermethrin, cupric sulfate, and the copolymers before and after loading. FTIR samples were prepared in KBr pellets under a hydraulic pressure of 400 kg. The FTIR spectrum with cypermethrin was taken as a thin film of pesticide pressed between KBr windows. Spectra were scanned in the range of 4000–500 cm^{-1} for neat polymers, cypermethrin, and cupric sulfate loaded polymers.

Differential scanning calorimetric study

Differential scanning calorimetric (DSC) analysis of the polymer samples was carried out on a thermal

analysis system (Rheometric Scientific) to determine the glass-transition temperatures. These experiments were performed at the Institute for Environmental and Industrial Science at Southwest Texas State University, San Marcos, TX. The samples were scanned in a temperature range of 25–250°C at a heating rate of 10°C per minute in argon atmosphere.

Viscosity measurements

Viscosity measurements on polymer solutions in acetone were made by using a Cannon Fenske capillary-type viscometer (No. 50) at 20°C. Solutions were prepared in six different concentrations in the range from 0.01 to 0.035 mass %. The average efflux times of three independent measurements were taken for all the solutions as well as for solvent (acetone). Relative and specific viscosities of the polymer solutions were calculated by applying corrections for the viscometric constant (0.01442) as provided by the manufacturer. The intrinsic viscosity of the polymer solutions was calculated from the plot of specific viscosity versus concentration. The molecular weight of the polymers was then calculated by using the Mark–Houwink–Sakurada (MHS) equation. The values of the MHS constants, $k = 3.4 \times 10^{-3}$ and $a = 0.74$, were taken from Karuta et al.¹⁰

Rheological measurements

Viscosities of polymer dispersions in THF and water mixtures were measured by using a Brookfield rheometer (Model DV-III) taking 8 mL of the sample into the removable sample chamber equipped with a temperature probe. The removable sample chamber was inserted into a water-jacket assembly and an insulation cap was placed on the chamber to minimize heat loss during measurements.

We selected the SC-21 spindle (supplied with the instrument) based on the % torque, which varied from 10 to 90 (i.e., within the recommended optimum range). Before taking the actual readings, the rheometer scale was autozeroed and data were collected at 30, 35, and 40°C. The bath temperature was kept constant within $\pm 0.01^\circ\text{C}$ by circulating water into the jacket by using a stirred circulator bath (Grant, Model Y14, U.K.). To maintain the bath temperature at 30°C, we used an immersion cooler probe (Julabo, Model FT-200, Germany). Before actual measurements, the rheometer was calibrated by using the standard fluid No. 1000 supplied with the instrument.

The viscosity of the solution of polymer I in THF (10.034% w/v) was found to be 80.7 mPa s when measured at a shear rate of 200/s at 30°C, but at 35 and 40°C, the same polymer solution showed viscosities of 75.3 and 70.3 mPa s, respectively. Such a decrease in viscosity at higher temperatures follows es-

tablished principles. In the case of polymer II solution (12.52% w/v) in THF, the observed viscosity of 147.9 mPa s at a shear rate of 200/s at 30°C showed a sudden drop to 41.9 and 13.5 mPa s at 35 and 40°C, respectively. This may be due to the collapse of the polymer chain. Polymer III did not form a clear solution over the permissible concentrations of the rheometer and hence rheological properties of polymer III could not be measured.

Water-uptake properties

Water absorption by the polymer was measured in terms of gram of water uptake per 100 g of dry polymer. To do this, 100 mg of polymer was placed on a 30-mL-capacity sintered crucible, which was placed in a 150-mL beaker. A small amount of water was added to the beaker until it touched the crucible disk. The beaker was covered with a lid and an increase in mass of the polymer was measured after 4 h. From these measurements, gram of water absorbed per 100 g of the polymer was calculated.

Sorption experiments

The disc-shaped bulk-polymerized polymer samples were cut from large cylindrical samples. Their initial diameter, thickness, and initial dry mass were measured and the samples were placed in different airtight glass bottles containing 0.1N NaOH, 0.1N HCl, and double-distilled water, respectively. The flasks were maintained at a constant temperature of 30°C in a temperature-controlled oven (WTB Binder, Germany); the swollen samples were periodically removed, blotted to remove the surface-adhered water droplets using smooth tissue paper, weighed on a Mettler analytical balance (model AE 240, Switzerland, accuracy, ± 0.01 mg), and placed back into liquid media. These measurements were made until the samples attained constant mass, signifying complete equilibration. From the gravimetric data, % mass uptake (M_t), equilibrium % mass uptake (M_∞), and diffusion coefficients (D) were calculated, respectively, by using eqs. (1)–(3):

$$M_t = \frac{W_t - W_0}{W_0} \times 100 \quad (1)$$

$$M_\infty = \frac{W_\infty - W_0}{W_0} \times 100 \quad (2)$$

$$\frac{M_t}{M_\infty} = \frac{4}{h} \left[\frac{Dt}{\pi} \right]^{1/2} \quad (3)$$

In the above equations, W_0 is initial dry mass of the polymer disc; W_t and W_∞ are, respectively, the mass at time, t , and equilibrium mass during sorption experi-

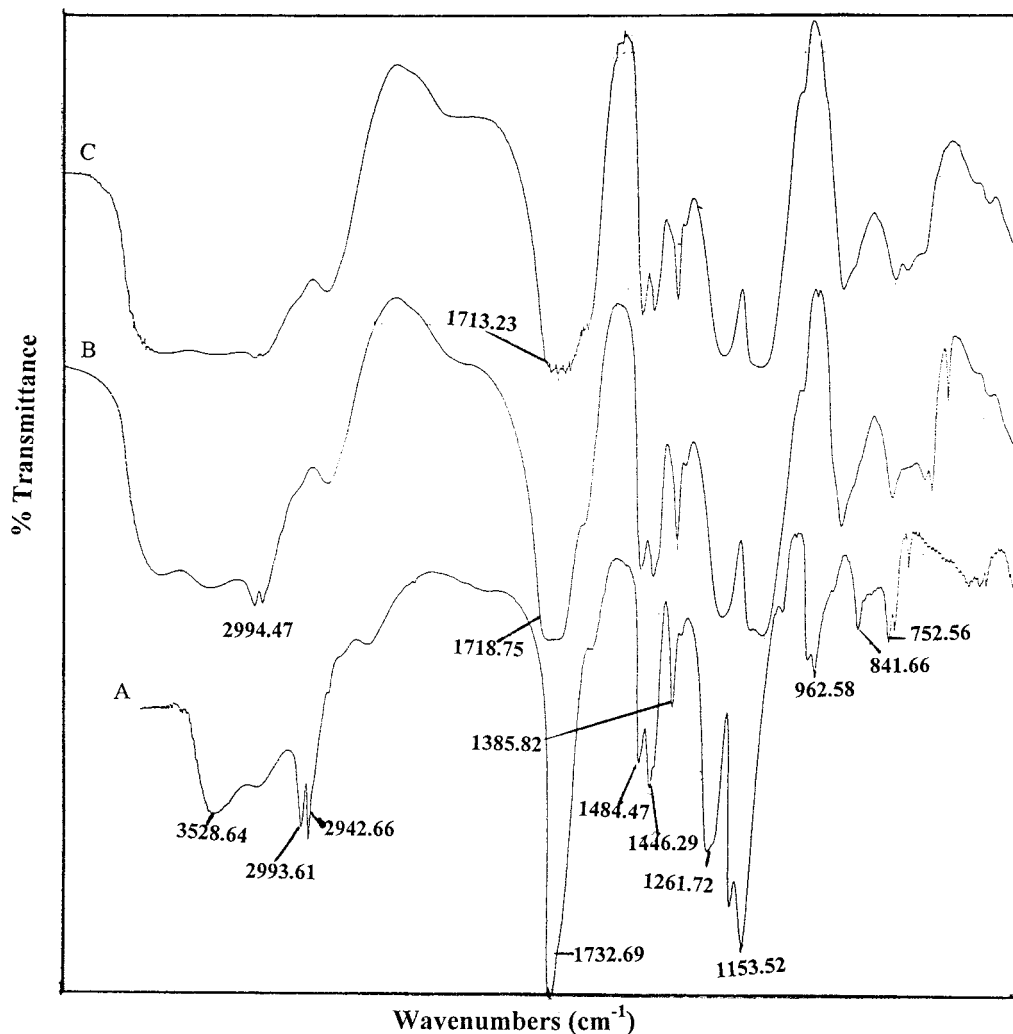


Figure 1 FTIR spectra of (A) Polymer I, (B) Polymer II, (C) Polymer III.

ments; and h is the thickness of the disc-shaped samples. Diffusion coefficients were calculated as per published procedures.^{11,12}

Encapsulation of cupric sulfate and cypermethrin

The polymer was treated with acetone or DMSO before encapsulation. The polymer was then mixed with a known amount of cupric sulfate and subsequently swollen in alkali solution. The swollen hydrogel was dried at room temperature and stored in a desiccator. For loading cypermethrin, the dry polymer powder was treated with acetone only and the pesticide was loaded.

Dissolution experiments

Cupric sulfate

A 100-mg sample of cupric sulfate encapsulated in the polymer was taken in an envelope of Whatman filter paper No. 4. The envelope was then placed in a

125-mL Erlenmeyer flask; 50 mL distilled water was added, and then the flask was placed in a water bath at 30°C. The aqueous samples were withdrawn periodically and analyzed for Cu^{2+} by using an atomic absorption spectrophotometer (AAS) (Perkin-Elmer, Model 2280) set at 324 nm with a copper source. The gas-flow rates of acetylene and air were maintained at 20 and 45 mL/min, respectively.

A calibration plot was established by measuring the absorbance of eight standard solutions. A stock solution of 102.25 ppm was made by diluting 0.4018 g of cupric sulfate pentahydrate with 1000 mL of deionized (DI) water. A straight line was obtained for the plot of absorbance versus concentration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ with a correlation coefficient of 0.998. All data points were based on measurements in triplicate.

Cypermethrin

Static dissolution experiments were carried out in 250-mL conical flasks containing 40% (w/v) solution

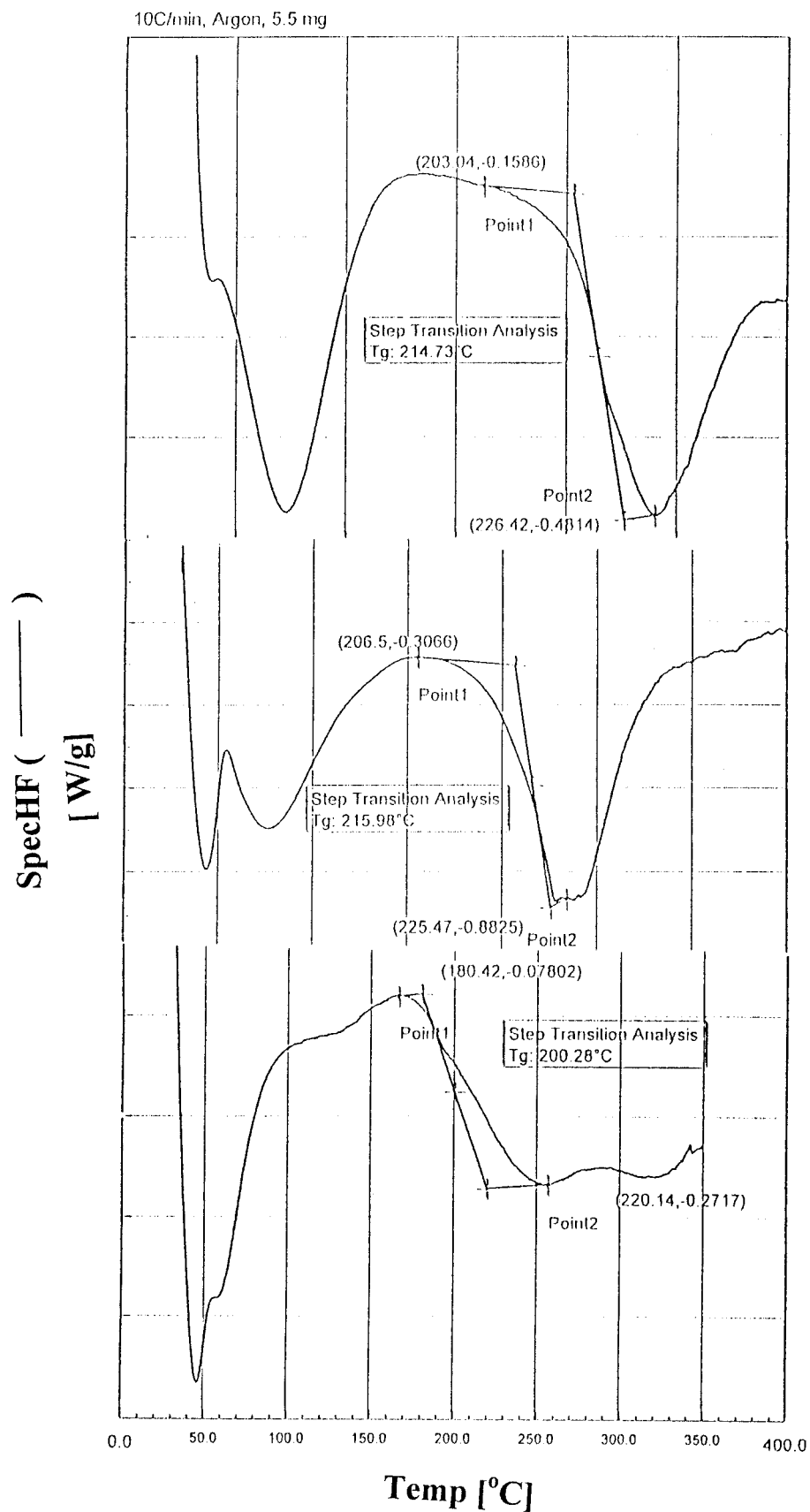


Figure 2 DSC thermograms of (A) Polymer I, (B) Polymer II, (C) Polymer III, for the first heating cycle.

TABLE II
Glass Transition Temperatures, Intrinsic Viscosities, and Molecular Masses of Polymers

Polymer sample code	T_g (°C)		Intrinsic viscosity (mL/g)	Viscosity average molecular mass, M_v
	1st Heat	2nd Heat		
I	200.3	133.1	7.1	30,471
II	216.0	150.5	7.5	32,987
III	214.7	149.2	8.1	36,135

of methanol in distilled water as the dissolution media by using closer caps and kept in an incubator (WTB Binder, Germany) set at 30°C. Polymer samples containing the pesticide, weighing about 150 mg, were taken in dissolution media and the flasks were thoroughly shaken. Each time, 10-mL-aliquot samples were removed at regular time intervals and analyzed for cypermethrin by using a UV spectrophotometer (Anthellie, Secomam, France) at the λ_{\max} of 272 nm. Experiments were performed in triplicate and the average value was considered for data treatment and plotting.

RESULTS AND DISCUSSION

Polymer characterization

FTIR spectra of the neat polymers are presented in Figure 1. Polymer I contains a broad band at 3528 cm^{-1} , which corresponds to hydroxyl stretching (intermolecular hydrogen bonding). Two strong bands appear at 2993 and 2943 cm^{-1} that correspond to the symmetrical and antisymmetrical aliphatic stretching modes of a CH_3 group. A sharp band appearing at 1732 cm^{-1} corresponds to a $\text{C}=\text{O}$ stretching vibration associated with an ester group. The CH_2 and CH_3 group vibrations appear at 1484 cm^{-1} . The CH_2 deformation is observed at 1446 cm^{-1} , whereas the asymmetrical CH_3 deformation appears at 1450 cm^{-1} . A sharp band appearing at 1385 cm^{-1} corresponds to a symmetrical deformation mode of hydrogens in a methyl group. The bands appearing at 1261, 1205, and 1153 cm^{-1} are due to $\text{C}=\text{O}$ vibrations in methyl esters of long-chain acids. Among these three bands, the peak at 1153 cm^{-1} is the strongest. In polymer sample II (Fig. 1B), because of the addition of HEMA, the hydroxyl-stretching peak broadens. Similarly, the characteristic peak of the ester appearing at 1732 cm^{-1} slightly broadens and shifts to 1719 cm^{-1} . This is due to a decreasing amount of MMA content in the polymer. The same is true for polymer III [Fig. 1(C)]. The band at $\text{C}=\text{O}$ shifts to a lower frequency.

The FTIR spectra of the three polymers loaded with cupric sulfate did not change, indicating no chemical interactions between the polymer and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. This indicates that Cu^{2+} is physically entrapped in the hydrogel network. The characteristic peaks in the FTIR of cypermethrin appearing at 3221, 1586, and

1407 cm^{-1} as well as in the range of 963 to 522 cm^{-1} did not change in the FTIR spectra of cypermethrin-loaded polymeric matrices, indicating the absence of chemical interactions between cypermethrin and these polymers.

Glass transition temperatures (T_g) of the polymers were measured by DSC. Typical DSC thermograms for two successive heat runs are shown in Figure 2. The T_g values obtained for the three polymers for the first and second heating cycles are given in Table II. It is evident that the T_g are higher for polymer II and polymer III when compared to polymer I, indicating a higher hydrophilicity. The hydrophilic nature increases with an increasing amount of MAA as well as HEMA in the matrix.

Viscosity measurements

The viscosity-average molecular mass was calculated from the intrinsic viscosity data and the results are given in Table II. These data show that the mass increases with an increasing amount of MAA in the copolymer.

In vitro release kinetics

Figures 3-5 show the % cumulative release of Cu^{2+} as a function of time for the samples treated with NH_4OH , acetone, and DMSO, respectively. It should be noted that the release greatly depends upon the nature of the solvent used in treating the polymer

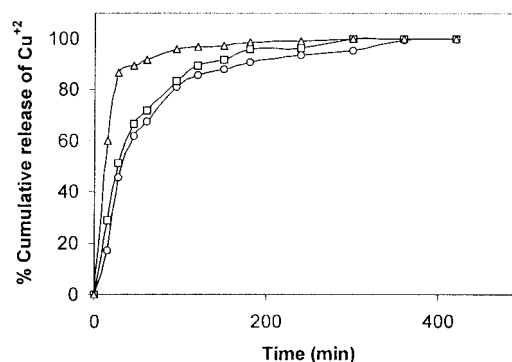


Figure 3 The % cumulative release versus time for Cu^{2+} loaded in Polymer I (\circ), Polymer II (\square), and Polymer III (\triangle), all treated with NH_4OH .

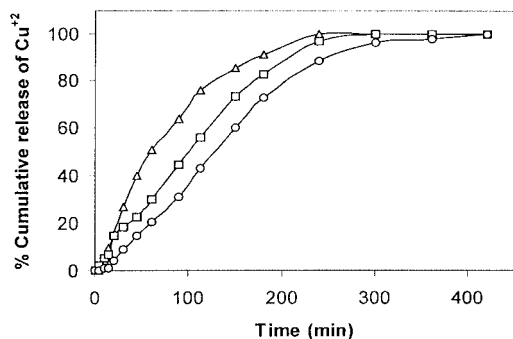


Figure 4 The % Cumulative release versus time for Cu^{2+} loaded in Polymer I (○), Polymer II (□), and Polymer III (△), all treated with acetone.

during encapsulation. For instance, with NH_4OH -treated hydrogels, release follows a burst effect (i.e., a sudden release is observed and completed within the first 40–50 min in all these polymers). Such large burst effects are generally attributed to the presence of particles of active agent on the surface of the hydrogel. A higher amount of Cu^{2+} is released in the case of polymer III when compared to polymers I and II (see Fig. 3). On the other hand, the acetone-treated polymers showed release over an extended period of up to 300 min (see Fig. 4). For the DMSO-treated hydrogels, the % cumulative release data are higher for polymers II and III than for polymer I (see Fig. 5). It is observed that % cumulative release curves for polymers II and III vary almost identically.

Figure 6 displays the % cumulative release of cypermethrin in all the hydrogels treated with acetone. For polymers II and III, the initial release of cypermethrin is fast. On the other hand, the release of cypermethrin is much slower and prolonged for Polymer I approaching an extended release of up to 100 h. Release from the acetone-treated hydrogel (i.e., polymer I) is much slower than that from polymers II and III.

A close observation of the initial release curves given in Figures 3 to 6 are indicative of the fact that a large amount of solute molecules will be released from

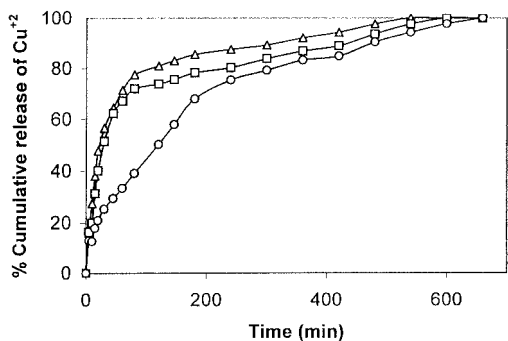


Figure 5 The % cumulative release versus time for Cu^{2+} loaded in Polymer I (○), Polymer II (□), and Polymer III (△), all treated with DMSO.

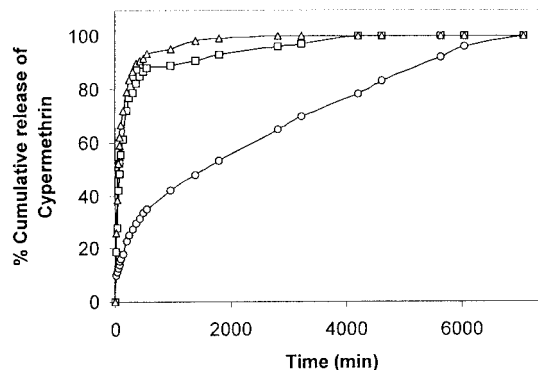


Figure 6 The % cumulative release versus time for cypermethrin-loaded in Polymer I (○), Polymer II (□), and Polymer III (△), all treated with acetone.

the hydrogels. Such a burst release depends upon the nature of the solute as well as the rigidity of the polymeric matrix. In addition, it is also dependent upon the solubility of the active ingredient in the external medium (i.e., the greater the solubility, the faster the release rates). Such burst effects can be effectively reduced or even avoided by increasing the ingredient loading and/or by increasing the matrix rigidity by crosslinking.

In all cases, the nature of the % cumulative release curves depends upon the water-uptake capacities of the matrices. FTIR spectral data show that incorporation of Cu^{2+} does not alter the polymer structure, indicating that encapsulation is more of a physical phenomenon than a chemical interaction. In general, the % cumulative release depends upon the hydrophilicity of the matrix, which decreases in the order: polymer III > polymer II > polymer I. Release of Cu^{2+} occurs because of polymer chain relaxation after complete water absorption by the hydrogel. The DMSO-treated polymers are more rigid and have a fibrouslike structure; release of Cu^{2+} occurs over about 8 h. The release of Cu^{2+} from the acetone-treated polymer is faster (i.e., it is completed in about 6 h). Finally, release from the aqueous NH_4OH -treated polymers is the fastest (i.e., release occurred in 5 h).

The % cumulative release data of Cu^{2+} or cypermethrin from the hydrogels have been fitted to the empirical equation proposed by Peppas and Peppas¹³:

$$\left(\frac{M_t}{M_\infty}\right) = kt^n \quad (4)$$

Here, M_t and M_∞ represent the amount of active agent released at time t and at infinite time, k is a proportionality constant representing the interaction of the active ingredient with the polymer, and n is the exponent characteristic of the mode of transport of the active ingredient through the polymer matrix. The release parameters n and k were calculated from the

TABLE III
Analysis of Release Kinetics of the Loaded Hydrogels

Polymer sample code	Polymer treated with	Active agent encapsulated	k (min ⁻ⁿ) 10 ⁻³	n	Corr. coeff. r
I	NH ₄ OH	Cu ²⁺	34.32	0.57	0.989
II	NH ₄ OH	Cu ²⁺	19.31	0.81	0.987
III	NH ₄ OH	Cu ²⁺	2.76	0.87	0.990
I	Acetone	Cu ²⁺	0.22	1.65	0.982
II	Acetone	Cu ²⁺	2.25	1.36	0.988
III	Acetone	Cu ²⁺	7.00	0.89	0.983
I	DMSO	Cu ²⁺	11.56	1.03	0.989
II	DMSO	Cu ²⁺	0.07	1.85	0.980
III	DMSO	Cu ²⁺	20.63	0.90	0.980
I	Acetone	Cypermethrin	29.91	0.38	0.982
II	Acetone	Cypermethrin	38.00	0.58	0.984
III	Acetone	Cypermethrin	62.30	0.51	0.990

least-squares method at a 95% confidence limit by using eq. (4). When solvent diffusion through the gel region is much slower than the rate at which the gel-glassy polymer interface moves into the glassy core, Fickian transport results in a value of $n = 0.5$. When the chain relaxation at the gel-glassy polymer interface is much slower than the solvent diffusion rate in the swollen gel region, this interface advances at a constant velocity, resulting in non-Fickian diffusion, for which n lies between 0.5 and 1.0. In such cases, diffusion and relaxation rates are comparable.^{14,15} Super Case II transport is characterized by n values > 1 .

The values of n and k estimated by the method of least-squares at a 95% confidence limit are given in Table III. The values of n for the release of Cu²⁺ for the hydrogels treated with NH₄OH vary between 0.57 and 0.87, indicating that the release is non-Fickian. However, in the case of Cu²⁺-loaded hydrogel treated with acetone and Cu²⁺-loaded hydrogel treated with DMSO, n values vary between 0.89 and 1.65, and 0.9 and 1.85, respectively, indicating the transport is predominately Super Case II. Values of k did not show any systematic trend, because the hydrogel has varying hydrophilicity. In the case of cypermethrin-loaded matrices treated with acetone, the n values vary around 0.5, indicating transport follows Fickian-type diffusion.

Swelling of hydrogels depends upon the extent of water uptake, which decides the equilibrium sorption.

The rate of approach to equilibrium is used to estimate the diffusion coefficient of the solvent molecules through the hydrogel network polymer. However, the kinetic response of the hydrogels depends on both the history and the chemical composition of the hydrogel. The release of pesticide or micronutrient depends upon the macromolecular chain relaxation in addition to transport of pesticide or micronutrient. Both compounds used in this study are different in nature (i.e., cupric sulfate is a water-soluble salt, whereas cypermethrin is a water-insoluble organic compound). Thus, the pesticide release will be different than the release of micronutrient.

Sorption experiments

For a polymer containing ionic groups, swelling forces are greatly enhanced as a result of localization of charges on the polymer backbone. Upon neutralization with alkali (either partially or completely), the negatively charged carboxyl groups are converted into the sodium salt of the corresponding acid with the solvated sodium ions. To understand the effect of pH on the swelling of these polymers, dynamic swelling experiments were carried out with the aim to obtain % equilibrium water uptake. These data are fitted to eqs. (1)–(4); the results are presented in Tables IV–VI.

It is observed that water uptake increases with increasing pH of the solution. Because the pK_a of car-

TABLE IV
Dynamic and Equilibrium Swelling Data of Acrylic-Based Copolymers in 0.1N NaOH at 30°C

Polymer sample code	n	k (h ⁻ⁿ) × 10 ²	Corr. coeff. r	$D \times 10^{13}$ (m ² s ⁻¹)	% Equilibrium water uptake
I	0.51	2.45	0.998	4.88	1340 ± 136
I A ^a	0.71	1.97	0.999	3.72	1120 ± 121
II	0.66	1.43	0.999	2.45	1470 ± 61
II A	0.53	1.47	0.997	1.39	1558 ± 86
III	0.77	1.48	0.999	3.01	2104 ± 100
III A	0.78	0.90	0.998	4.39	4080 ± 122

^a The same polymer prepared by bulk polymerization sample with higher diameter.

TABLE V
Dynamic and Equilibrium Swelling Data of Acrylic-Based Copolymers in 0.1N HCl at 30°C

Polymer sample code	n	$k (h^{-n}) \times 10^2$	Corr. coeff. r	$D \times 10^{12} (\text{m}^2 \text{s}^{-1})$	% Equilibrium water uptake
I	0.59	2.35	0.987	1.11	3.58 ± 0.21
I A ^a	0.58	3.19	0.987	1.50	2.92 ± 0.12
II	0.58	4.16	0.972	2.77	9.62 ± 0.58
II A	0.51	2.45	0.997	4.35	12.06 ± 0.61
III	1.02	4.32	0.988	13.48	26.11 ± 1.21
III A	—	—	—	—	316.7 ± 10.3

^a The same polymer prepared by bulk polymerization sample with higher diameter.

boxylic acid containing polymer⁶ is 4.6 and at a pH > 4.6 (i.e., changing from 0.1N HCl to 0.1N NaOH) the carboxyl groups of hydrogels tend to dissociate, the osmotic pressure inside the hydrogel increases. This results in higher water-uptake values. Water uptake at higher pH depends upon the available free volume of the expanded polymer matrix, polymer chain relaxation, and availability of ionizable functional groups such as —COOH for water to form hydrogen bonds. Water-uptake values are presented in Tables IV–VI. For polymer I in 0.1N NaOH solution, the % equilibrium water uptake is 1340 at 30°C, but in water, its value is 4.43, whereas in 0.1N HCl, the uptake is still smaller (i.e., 3.58). The same trend is observed in all three polymers. For polymers I, II, and III, the % water uptake in 0.1N NaOH solution are 1340, 1470, and 2104, respectively. The same trend is observed in water as well as in 0.1N HCl solutions. Generally, the more hydrophilic the polymer, the greater the water uptake. Polymer discs with higher diameters designated with the letter A, shown in Tables IV–VI, show the same trend as those observed for small diameter samples. The actual photographs of the swollen polymer samples are compared in Figure 7 with the unswollen samples.

To understand the nature of transport in the polymer samples under different pH conditions, we have fitted the initial dynamic swelling data to eq. (4). These data are also presented in Tables IV–VI. The values of n vary between 0.51 and 0.78 in 0.1N NaOH, indicating that the mechanism of water transport deviates from Fickian to non-Fickian (referred to as anomalous) with increasing hydrophilicity of the hydrogel matrix.

In double-distilled water and 0.1N HCl, the n values are close to 0.5 in all cases but one, indicating that a Fickian trend is present. However, for polymer III in 0.1N NaOH, $n = 1.03$, indicating the presence of Case II transport. The same sample in double-distilled water reaches equilibrium rapidly; hence, it was not possible to calculate the value of n for this system. The parameter k of eq. (4) is a measure of polymer–solvent interaction and this varies in no obvious way with n values.

Apparent diffusion coefficients, D , of solvent molecules have been calculated under different pH conditions by using eq. (3); these data are presented in Tables IV–VI. The values of D in 0.1N NaOH vary from 1.39×10^{-13} to $4.88 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$. The solvent transport in these polymers is quite slow (i.e., it took nearly 15 days to convert the glassy region of the polymer into the rubbery region). On the other hand, in double-distilled water and 0.1N HCl, diffusion coefficients are higher (0.89×10^{-12} to $4.35 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$), in all cases but one, by one order of magnitude, than those observed in 0.1N NaOH. For polymer III, the D values are high, ranging between 9.06×10^{-13} and $13.48 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$, probably because the polymer reaches equilibrium quickly. Such observed higher values of D than those found in 0.1N NaOH are due to a rapid solvent uptake (equilibrium is attained within 7 days).

CONCLUSION

The present study addresses the preparation of three acrylic-based copolymers of MMA and MAA by solu-

TABLE VI
Dynamic and Equilibrium Swelling Data of Acrylic-Based Copolymers in Double Distilled Water at 30°C

Polymer sample code	n	$k (h^{-n}) \times 10^2$	Corr. coeff. r	$D \times 10^{12} (\text{m}^2 \text{s}^{-1})$	% Equilibrium water uptake
I	0.48	4.77	0.966	0.89	4.43 ± 0.27
I A ^a	0.55	3.46	0.991	1.32	3.46 ± 0.21
II	0.56	3.81	0.999	2.06	10.45 ± 0.32
II A	0.47	6.40	0.997	2.51	13.13 ± 0.18
III	—	—	—	9.05	32.00 ± 1.12
III A	—	—	—	—	42.79 ± 2.16

^a The same polymer prepared by bulk polymerization sample with higher diameter.

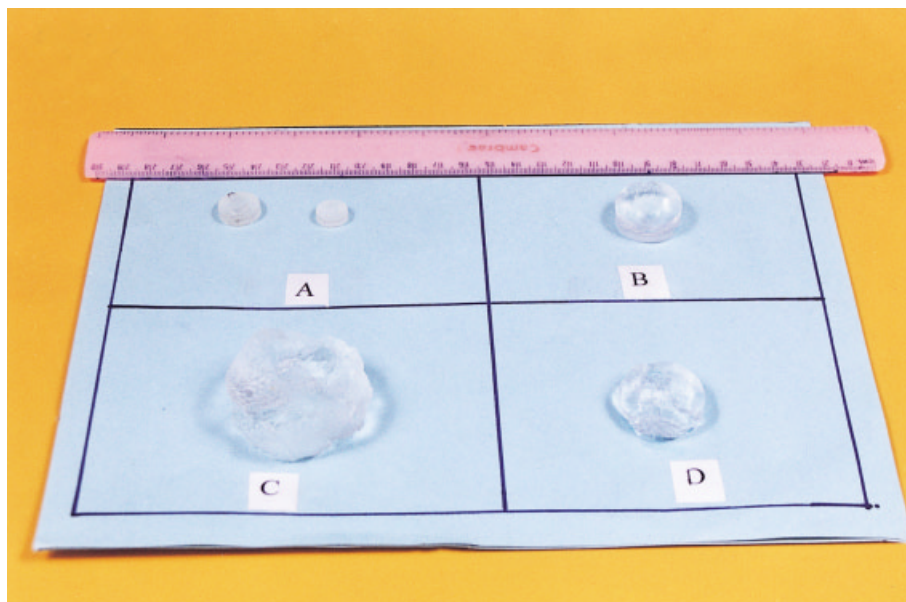


Figure 7 Photographs showing different hydrophilicities at 30°C in 0.1N NaOH: (A) polymer samples in their dry state, (B) Polymer I, (C) Polymer III, and (D) Polymer III. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tion and bulk polymerization techniques by using different ratios of the monomers. In an effort to increase the hydrophilicity, one of the polymers was prepared by adding additional HEMA. Dynamic swelling and equilibrium studies under varying pH conditions indicated a pH dependency of water uptake properties. Swelling was higher in alkaline medium than in water or acidic media. Encapsulation of cypermethrin and cupric sulfate was possible in all the hydrogels synthesized. Release of the active agents through the hydrogels will be beneficial to farmers cultivating in dry lands where there is an acute scarcity of water. The water-absorbing hydrogels of the type developed here will help to reduce the loss of water by evaporation, and thus, help to improve the life span and quality of plants in dry arid areas.

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