

# Effects of Experimental Variables on the Synthesis of Porous Matrices

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**ABSTRACT:** Macroporous beads, poly(ethylene glycol dimethacrylate-*co*-acrylic acid) [poly(EGDMA-*co*-AAc)], and poly(ethylene glycol dimethacrylate-*co*-hydroxyethyl methacrylate) [poly(EGDMA-*co*-HEMA)] were prepared by the suspension polymerization technique in the presence of a porogen agent. Different experimental conditions such as amount of initiator, porogen type, and temperature were studied to optimize the polymerization systems. These hydrophilic copolymers were characterized by IR spectroscopy, scanning electron microscopy, specific surface area, and swelling in water. A new parameter, H, defined as the ratio between the equilibrium weight swelling ratio ( $q_w$ ) and equilibrium volume swelling ratio ( $q_v$ ), allowed to select the reaction conditions from which matrices with high capacity of water sorption and low stretching degree were reached. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 920–927, 2001

**Key words:** hydrogels; porous materials; equilibrium weight swelling ratio ( $q_w$ ); equilibrium volume swelling ratio ( $q_v$ )

## INTRODUCTION

Macroporous hydrophilic matrices are being widely studied for their possible use as a catalyst, to immobilize enzymes, as HPLC supports, in drug delivery of active substances (pesticides, herbicides, fungicides, etc.), as adsorbents, etc.<sup>1–5</sup> In the agricultural field, formulations of controlled release systems in sandy soils from matrices that present high values of equilibrium weight swelling ratio ( $q_w$ ) are of growing interest. Macroporous hydrophilic matrices can be used with these properties, also keeping a stiff network

in both the swollen and dry state, with a high crosslinking degree and macroporous presence.

These macroporous matrices can be obtained by suspension copolymerization, using monovinyl monomers and crosslinking reagents in the presence of inert diluents or a porogen agent. In accordance with other authors,<sup>6–9</sup> it is known that during the process, crosslinking and phase separation occur, being responsible for the porous structure development that depends on the crosslinking agent concentration, type, and concentration of the porogen and temperature. In the reaction, the products precipitate after they become insoluble in the reaction medium, forming the nuclei as a result of the crosslinking whose size is dependent on the chosen porogen. The nuclei develop to the size of globules during polymerization, and can attach themselves to generating

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microspheres, which at the same time can associate to form particles. The development of microspheres and particles, which constitute clusters, depends on the porogen. The globules and their clusters make up the morphological unit of the porous polymers, defining porous as the gap between the aggregate of globules and clusters. Also, during the suspension copolymerization reactions, products with different properties can be obtained after the nucleation process, depending on the polymerization rate (which influences the speed of phase separation), which is ruled, at the same time by temperature and concentration of the initiator.<sup>9</sup>

On the other hand, it is known<sup>9</sup> that the different product features are derived from the globule size and their aggregates. An increase in the globule size and/or aggregation of the clusters during polymerization promote an increase in porous volume.

The choice of polymerization conditions and experimental optimization must be specific for each chosen monomer system, because there are no general rules for this aim.<sup>7</sup>

This article evaluates, through the new parameter  $H$ , the influence of polymerization conditions on the structure and morphology of poly(EGDMA-co-AAc) and poly(EGDMA-co-HEMA) porous matrices obtained by suspension polymerization using benzoyl peroxide (BPO) as the radical initiator. The polymerization conditions studied were: type of porogen, percentage of initiator, and temperature. The products were studied by IR spectroscopy, SEM, specific surface area, and swelling in aqueous medium.

## EXPERIMENTAL

### Reagents and Methods

The following chemicals were purchased and used: 2-hydroxyethyl methacrylate, HEMA (FLUKA); acrylic acid, AAc (BASF); ethylene glycol dimethacrylate, EGDMA (FLUKA), and benzoyl peroxide, BPO (Riedel de Haen). Porogens and relations in the reactions were selectioned according to the literature<sup>6,10</sup>: cyclohexane (Cyc) and a mixture of cyclohexanol/*n*-butanol (CyOH/BuOH) using a mol ratio of 7.0 : 2.4.

### Polymerization Reactions

Copolymerization reactions were performed using a mol ratio of (3.0 : 1.0 : 9.3: 2.5 10<sup>2</sup>) of monovi-

nylic monomer (HEMA or AAc), crosslinking reagent, porogen, and water respectively. In all cases, EGDMA was used as the crosslinking reagent and BPO as the initiator. Poly(vinylpyrrolidone) (PVP) was used as the stabilizer of the suspension using a proportion of 10 mg/mL with respect to total mixture. The reactions were kept under stirring for 2 h. The temperatures assayed were 70 and 85°C, and the BPO values (%) used were 0.60, 2.44, and 5.00, referred to total mol of the reagents.

Once obtained, the beads were exhaustively washed with distilled water and ethanol. Then they were dried in a stove at 70°C up to constant weight. The yield of each reaction was calculated through the percentage of dry matrix obtained vs. total grams of reagents used.

### Characterization

Swelling studies were carried out by placing portions (50–100 mg) of each product in distilled water (pH = 6.5) in a special funnel (with a very small hole in a closed chamber) for 24 h followed by a 24-h drainage in the same closed chamber. Then, the wet samples were weighed in an analytical scale and the weights were measured at different evaporation times (each 15 s for 7–8 min after the sample was removed from the chamber). Then data was processed using a plot of weight of wet sample (g) vs. evaporation time (s), taking the weight of the sample in swollen state ( $W_{sw}$ ) at time zero, which is achieved by extrapolation. Subsequently, the samples were dried in a stove at 70°C, for 48 h and weighted to obtain the weight of the dry sample ( $W_{dry}$ ). Once  $W_{sw}$  and  $W_{dry}$  were attained, the equilibrium weight swelling ratio,  $q_w$ , was determined:

$$q_w = W_{sw}/W_{dry} \quad (1)$$

The equilibrium volume swelling ratio,  $q_v$ , [Eq. (2)] was calculated by the ratio of the volume of samples in the swelling equilibrium state ( $V_{sw}$ ) and the volume of samples in the dry state ( $V_{dry}$ ). It was performed using graduated tubes after the samples have been soaked for 24 h in an excess of distilled water.

$$q_v = V_{sw}/V_{dry} \quad (2)$$

Adsorption isotherms of CO<sub>2</sub> at 273 K were carried out on a Micromeritics Model Gemini

**Table I** Conditions and Results of Suspension Polymerization of HEMA and EGDMA

Porogen	Temp. (°C)	Initiator (%)	Yield (%)	$q_w$	$q_v$	$H$	$A_{1635\text{ cm}^{-1}}/A_{1730\text{ cm}^{-1}}$	$S_s$ (m <sup>2</sup> /g)
CyOH/BuOH	85	0.60	100	2.9	2.0	1.45	0.053	37.7
CyOH/BuOH	85	2.44	98	3.3	2.1	1.57	0.113	4.1
CyOH/BuOH	85	5.00	100	3.3	2.3	1.43	0.126	7.8
CyOH/BuOH	70	2.44	100	2.8	2.0	1.40	0.149	26.1
Cyc	85	0.60	100	6.3	1.5	4.20	0.019	28.5
Cyc	85	2.44	100	4.8	1.9	2.52	0.025	44.8
Cyc	85	5.00	100	4.2	2.0	2.10	0.035	23.9
Cyc	70	0.60	100	5.9	1.5	3.93	0.060	25.9
Cyc	70	2.44	93	7.3	1.5	4.87	0.029	39.0
Cyc	70	5.00	100	5.1	1.5	3.40	0.029	33.9

2370 Apparatus, and the specific surface area ( $S_s$ , m<sup>2</sup>/g) evaluation was done by means of the BET method. Scanning electron microscopy (SEM) was performed on a Philips SEM 501 B instrument. IR spectra of both copolymers were recorded on a Nicolet 5-SXC spectrometer on KBr disks. Also, the ratios of absorbances corresponding to the double-bond signal and the ester absorption signal ( $A_{1635\text{ cm}^{-1}}/A_{1730\text{ cm}^{-1}}$ ) were compared in products poly(EGDMA-*co*-HEMA) to confirm the disappearance of double bonds. The double-bond stretching at 1635 cm<sup>-1</sup> and carbonyl stretching (ester) at 1730 cm<sup>-1</sup> were the absorption bands used to calculate the ratio. Two straight lines that linked the points of the spectrum at 1850, 1660, and 1600 cm<sup>-1</sup> were regarded as the baselines for peak intensity standards to correct the background.<sup>11</sup>

## RESULTS AND DISCUSSION

The variables studied to obtain poly(EGDMA-*co*-HEMA) and poly(EGDMA-*co*-AAc) products were: concentration of initiator; type of porogen, and temperature. These insoluble water products were obtained with yields between 80 and 100%.

Different techniques to determine the swelling capacity, in most cases, use methods that probably lead to important mistakes in weights, for example, using tissues or blotting paper to eliminate the rests of unadsorbed water by the sample. In this work, a new method to measure swelling in water, which allows reaching conclusions about experimental variables, is shown. It is based on an adaptation of a technique reported by Errede et al.,<sup>12</sup> which was especially useful to

determine  $q_w$  without the need of a preliminary dryness of the remaining unadsorbed water.

According to the results obtained by Okay et al.,<sup>6</sup> it is known that  $q_v$  is closely related with the stretching of the network as a function of the crosslinking density. Moreover,  $q_w$  of highly crosslinked matrices is a consequence of the gap filling by the liquid, depending on the network porosity. It would indicate that an optimal highly crosslinked macroporous bead would be that which possesses a high  $q_w$  value and a small  $q_v$ . Therefore, in this work the swelling parameters  $q_w$  and  $q_v$  were used to obtain the parameter  $H$ , expressed as follows:

$$H = q_w/q_v \quad (3)$$

$H$  reflects the balance between water sorbed and polymer network expansion of hydrogel beads. High value of  $H$  would be indicative of a high retention of water with a low stretching degree, which is the ideal condition for macroporous beads with a rigid network. So, the new parameter  $H$  is useful for the comparative studies of the different products obtained as a function of the variables of synthesis used. Experimental conditions and results are summarized in Tables I and II.

## IR Spectroscopy

The IR spectra (cm<sup>-1</sup>) of poly(EGDMA-*co*-AAc) products showed the following characteristic signals: 1705 (carboxyl of acid group); 1730 (stretching vibration of C=O of ester group), 1320–1250 and 1200–1150 (stretching vibrations of C—O—C) and

**Table II** Conditions and Results of Suspension Polymerization of AAc and EGDMA

Diluent	Temp. (°C)	Initiator (%)	Yield (%)	$q_w$	$q_v$	$H$	$S_s$ (m <sup>2</sup> /g)
CyOH/BuOH	85	0.60	96	4.3	2.7	1.59	82.1
CyOH/BuOH	85	2.44	86	5.3	1.8	2.94	58.7
CyOH/BuOH	85	5.00	94	5.1	2.3	2.22	54.9
Cyc	85	0.60	83	3.8	2.0	1.90	55.5
Cyc	85	2.44	85	6.9	1.8	3.83	29.7
Cyc	85	5.00	86	5.3	1.8	2.94	32.1
Cyc	70	0.60	85	4.8	2.2	2.18	44.1
Cyc	70	2.44	97	8.3	2.5	3.32	72.7
Cyc	70	5.00	83	6.9	1.3	5.31	35.2

3100–2900 and 1635 (stretching vibrations of =C—H and C=C, respectively). The IR spectra of poly(EGDMA-*co*-HEMA) products showed the signals corresponding to the ester group and double bond C—C, previously assigned and the absorption signals (cm<sup>-1</sup>) at 3650–3590 (stretching vibration of the —OH group), 1350–1260 (bending vibration of the —OH group) and 1050 (stretching vibrations of —C—O of —COH).

### Effect of Variation of the Porogen

#### Swelling Studies

As can be observed in Tables I and II, the results of  $H$  corresponding to products poly(EGDMA-*co*-AAc) and poly(EGDMA-*co*-HEMA), respectively, show the influence of the porogen on the pore formation. The  $H$  values of both copolymers obtained with Cyc were higher than CyOH/BuOH compared with the respective percentages of the initiator (0.60, 2.44, and 5.00%) at 85°C. This finding would be related to the different solubility parameters of the porogens that affects the phase separation, pointing out that Cyc is a better porogen than CyOH/BuOH to obtain these porous beads by suspension polymerization. In general, the  $q_w$  values depend on the kind of porogen used, which influences the pore morphology.<sup>6</sup>

Also, it was observed that the effects of the porogens and the polymerization kinetics on the parameter  $H$  is more important in the poly(EGDMA-*co*-HEMA) than those found for the poly(EGDMA-*co*-AAc).

#### IR

The ratios of the absorbances  $A_{1635\text{ cm}^{-1}}/A_{1730\text{ cm}^{-1}}$  (C=C/C=O) from poly(EGDMA-*co*-HEMA) spectra

were compared in the products obtained at different temperatures and initiator concentrations (see Table I). In all instances the  $A_{1635\text{ cm}^{-1}}/A_{1730\text{ cm}^{-1}}$  values obtained using Cyc were lower than those obtained with CyOH/BuOH, which means a low relative amount of double bonds, which would imply a high conversion of reaction. Therefore, the low  $q_v$  values and high  $q_w$  values found for the products obtained with Cyc showed that these products would display a higher crosslinking density as well as higher water uptake than those obtained using CyOH/BuOH. This would suggest that Cyc acted as a precipitating agent of the nuclei of the polymer in an early phase separation, previous to the gel point, probably due to the incompatibility of the polymer-porogen system forming pores among the microspheres and their aggregates (particles) yielding high porosity. On the other hand, the CyOH/BuOH system would act as a better solvating agent for the poly(EGDMA-*co*-HEMA) polymer. It may be accounted for by the occurrence of the hydroxyl groups in both (polymer and porogen), with a latter phase separation forming pores corresponding to the spaces between the globules yielding a lower porosity of the products.<sup>6</sup>

#### Specific Surface Area

Beads of poly(EGDMA-*co*-HEMA) obtained from Cyc as porogen, show in general higher  $S_s$  values than those obtained from CyOH/BuOH (see Table I). These data are in agreement with previous reports, confirming that Cyc acts as a poor solvent for the polymer. It also increased the phase separation forming microspheres and their aggregate (particles), which in turn, would increase the surface area and the pore volume. Also, this again is in agreement with the high values reported for  $H$ .

**Table III Values of  $S_s$  of Poly(EGDMA-co-AAc) and Poly(EGDMA-co-HEMA) Under Different Experimental Conditions**

Monomer	$S_s$ (m <sup>2</sup> /g) <sup>a,b</sup>			$S_s$ (m <sup>2</sup> /g) <sup>a,c</sup>			$S_s$ (m <sup>2</sup> /g) <sup>d</sup>			
HEMA	25.9 <sup>e</sup>	39.0 <sup>f</sup>	33.9 <sup>g</sup>	28.5 <sup>e</sup>	44.8 <sup>f</sup>	23.9 <sup>g</sup>	37.7 <sup>c,e</sup>	4.1 <sup>c,f</sup>	7.8 <sup>c,g</sup>	26.0 <sup>b,f</sup>
AAc	44.1 <sup>e</sup>	72.7 <sup>f</sup>	35.2 <sup>g</sup>	55.5 <sup>e</sup>	29.7 <sup>f</sup>	32.1 <sup>g</sup>	82.1 <sup>c,e</sup>	58.7 <sup>c,f</sup>	54.9 <sup>c,g</sup>	77.8 <sup>b,f</sup>

<sup>a</sup>Diluent: Cyc.<sup>b</sup>Temperature: 70°C.<sup>c</sup>Temperature: 85°C.<sup>d</sup>Diluent: CyOH/BuOH.<sup>e</sup>Initiator: 0.60%.<sup>f</sup>Initiator: 2.44%.<sup>g</sup>Initiator: 5.00%.

The presence of CyOH/BuOH produces a latter phase separation, promoting globules without collapses and lower values in the  $S_s$ . The behavior observed with both porogens was in accordance and that corroborated by the IR studies.

In general, products poly(EGDMA-co-AAc) show low values of  $S_s$  (corroborated by high H values) with Cyc over CyOH/BuOH, probably due to a large globule size. The  $S_s$  from poly(EGDMA-co-AAc) products (see Table III) were higher than those of poly(EGDMA-co-HEMA) in both porogens, because each monovinyllic monomer (AAc or HEMA) have different polymerization kinetics and solubility in porogens, which affect the phase separation.

### Effect of the Temperature and Initial Concentration of the Initiator

#### Swelling Studies

By varying the initiator concentration, it was observed that the maximum values of H for poly(EGDMA-co-HEMA) matrices were reached using 2.44% of the initiator at 70°C and 0.60% of the initiator at 85°C (see Table I). For poly(EGDMA-co-AAc) matrices, the ideal values occurred at 5.00% at 70°C and 2.44% of the initiator at 85°C (see Table II). In these cases, this behavior may be attributed to the effect of the temperature and initiator concentration on the kinetic polymerization. These values are relevant to find the optimal conditions (temperature and initiator concentration) to achieve the optimal polymerization rate (optimum velocity,  $V_{op}$ ), at which large size pores are developed.

In general, for both copolymers, the H values are higher at 70°C than at 85°C with Cyc. This is probably due to the fact that a low reaction temperature produces a minor number of free radicals, which generates a minor number of nuclei

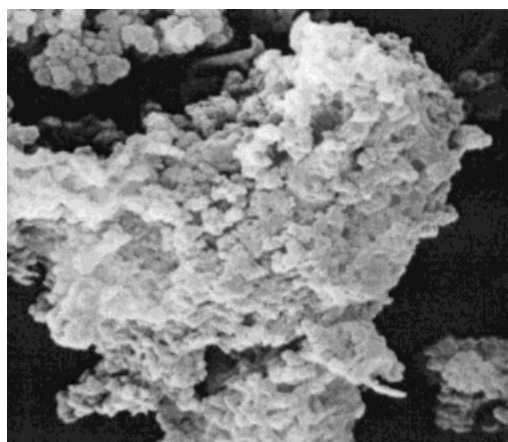
and globules with a higher size, because in each polymerization system the quantity of monomers is the same.<sup>7</sup>

#### IR

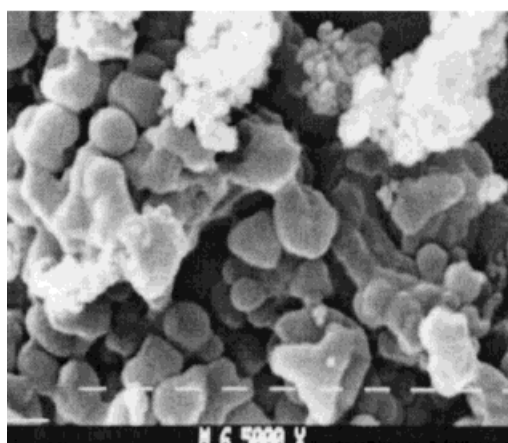
The  $A_{1635\text{ cm}^{-1}}/A_{1730\text{ cm}^{-1}}$  ratios for the poly(EGDMA-co-HEMA) products at different initiator concentrations (at 85°C) and different porogens were compared. It is noticed that an increase of this ratio is observed (see Table I) as the percentage of initiator rises, as could also be observed with  $q_v$ . This would indicate a relative decrease in crosslinking density. Also, as can be seen from Table I, a decrease in  $A_{1635\text{ cm}^{-1}}/A_{1730\text{ cm}^{-1}}$  value with an increase in temperature would promote a higher double-bond conversion.<sup>11,13</sup>

#### Morphology

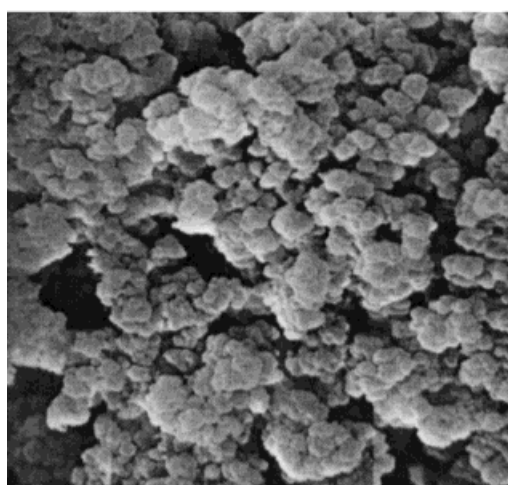
The morphology on the surface of poly(EGDMA-co-HEMA) and poly(EGDMA-co-AAc) samples using 70 and 85°C with Cyc as porogen was examined by SEM (5000×). Figures 1(A)–(C) and 2(A)–(C) show the photographs obtained from poly(EGDMA-co-HEMA) samples at 70 and 85°C, respectively. Figures 3(A)–(C) and 4(A)–(C) were obtained from poly(EGDMA-co-AAc) samples at 70 and 85°C, respectively. (A)–(C) sequences refer to percentage of the initiator (%): 0.60, 2.44, and 5.00, respectively. In general, the surface of all matrices shows porous materials and the presence of macroporous materials. As it can be seen in Table III, the poly(EGDMA-co-HEMA) matrices show in almost all cases low specific surface area compared to values obtained for poly(EGDMA-co-AAc). This could be verified by SEM, because in Figures 1–2, more partly fused microspheres can be noticed [poly(EGDMA-co-HEMA) matrices] than in Figures 3–4 [poly(EGDMA-co-AAc) matrices] using Cyc as porogen.



(A)

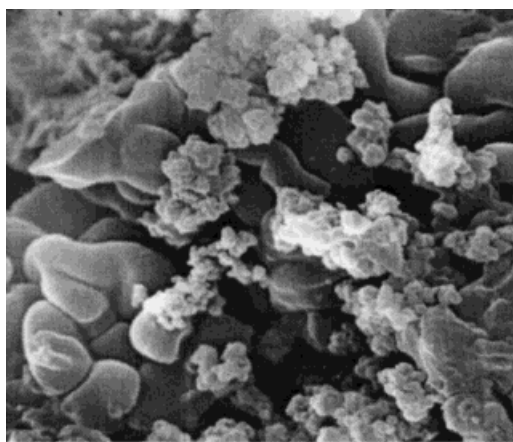


(B)

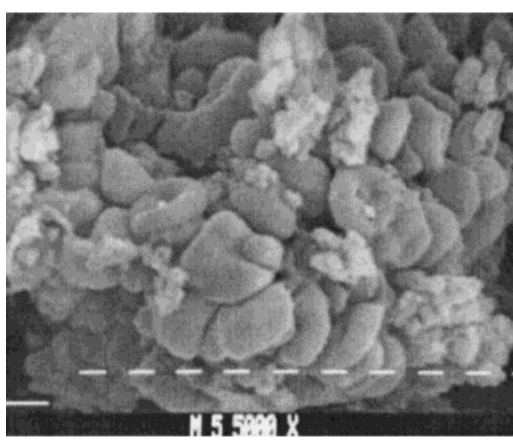


(C)

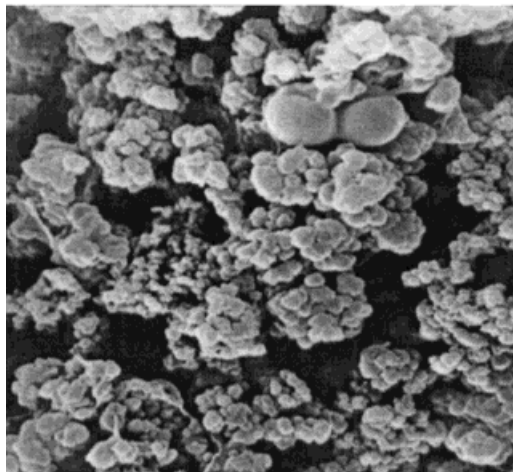
**Figure 1** SEM micrographs (5000 $\times$ ) of poly(EGDMA-co-HEMA) products at 70°C and 0.60 (A); 2.44 (B) and 5.00 (C) % of initiator.



(A)

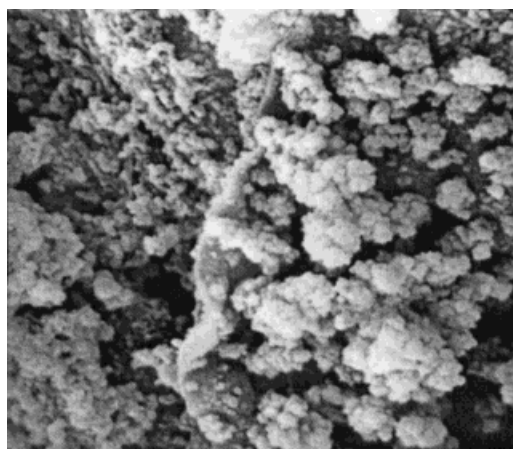


(B)

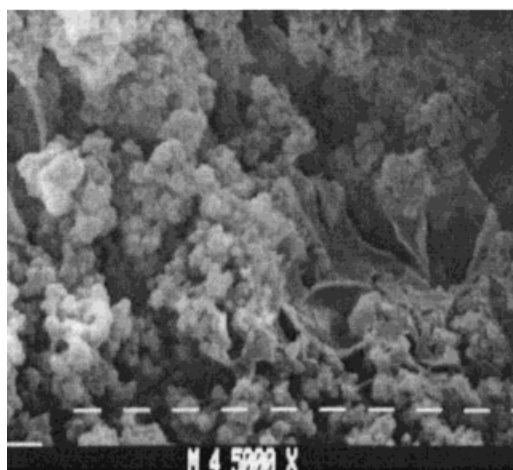


(C)

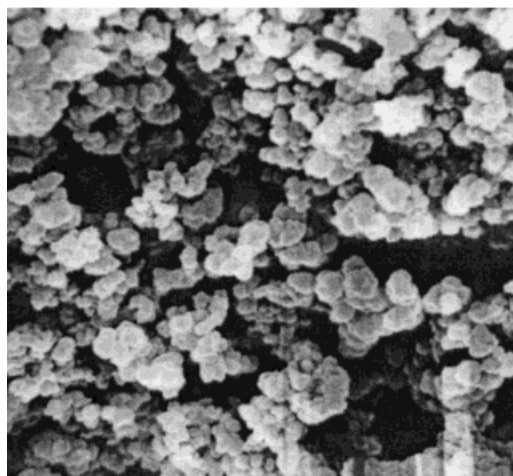
**Figure 2** SEM micrographs (5000 $\times$ ) of poly(EGDMA-co-HEMA) products at 85°C and 0.60 (A); 2.44 (B), and 5.00 (C) % of initiator.



(A)

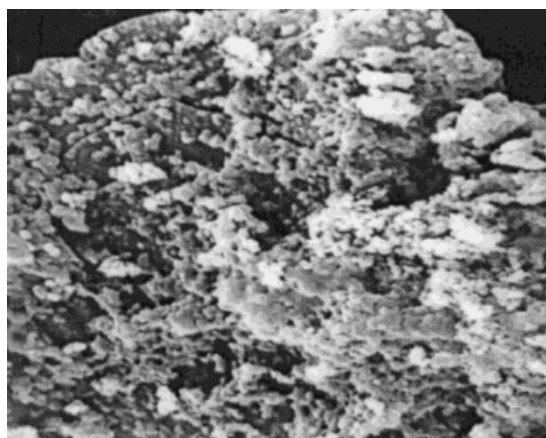


(B)

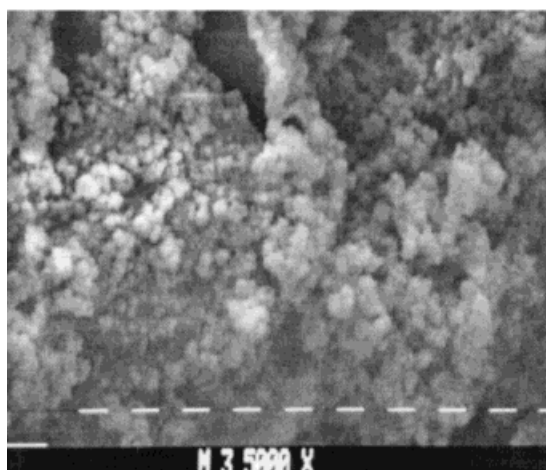


(C)

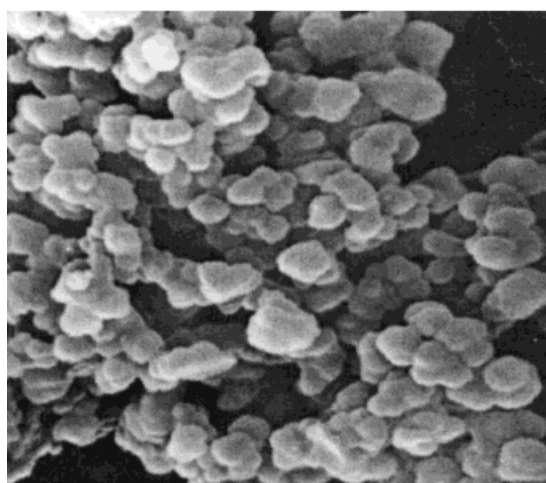
**Figure 3** SEM micrographs (5000 $\times$ ) of poly(EGDMA-co-AAc) products at 70°C and 0.60 (A); 2.44 (B) and 5.00 (C) % of initiator.



(A)



(B)



(C)

**Figure 4** SEM micrographs (5000 $\times$ ) of poly(EGDMA-co-AAc) products at 85°C and 0.60 (A); 2.44 (B) and 5.00 (C) % of initiator.

## CONCLUSIONS

A new parameter,  $H$ , defined as the ratio between the equilibrium weight swelling ratio ( $q_w$ ) and equilibrium volume swelling ratio ( $q_v$ ), allowed selection of the reaction conditions from which matrices with a high capacity of sorption of water and a low stretching degree were reached. These swellable matrices with these properties can be used in agricultural applications as supports, especially in formulations of controlled release systems applicable in sandy soils.

This parameter,  $H$  (which takes in account the stretching of the network), constitutes a useful tool for the characterization of porous matrices, resulting in low cost.

An important effect of the porogen and the polymerization kinetics (temperature, initiator percentage) on the formation of polymeric porous matrices was found. For poly(EGDMA-*co*-AAc) and poly(EGDMA-*co*-HEMA) products, Cyc turned out to be the best porogen. Thus, for poly(EGDMA-*co*-HEMA) matrices, it was observed that the best products were reached using 2.44% of the initiator at 70°C and 0.60% of initiator at 85°C. For poly(EGDMA-*co*-AAc) matrices, the ideal values occurred at 5.00% at 70°C and 2.44% of the initiator at 85°C.

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