Synthesis and Formation Mechanism of Porous 2-Hydroxyethyl Methacrylate–Ethylene Glycol Dimethacrylate Copolymer Beads

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SYNOPSIS

Porous poly(2-hydroxyethyl methacrylate) (PHEMA) beads cross-linked with ethylene glycol dimethacrylate (EGDM) were prepared by the suspension polymerization of the monomers in the presence of cyclohexanol or toluene as the diluents. A 20% aqueous NaCl solution containing $MgCl_2 \cdot 6H_2O$, bentonite, and gelatine was used as the water phase. In this way, spherical, highly swellable, and/or porous copolymer beads of sizes 0.1–1.0 mm could be synthesized at EGDM contents higher than 20 mol %. The copolymers formed in cyclohexanol, compared to those prepared in the absence of a diluent, exhibit a larger degree of volume swelling in water, indicating that most of the diluent remains in the gel phase throughout the copolymerization. Contrarily, toluene induces porous structures even at a very low degree of cross-linking (41% porosity at 2 mol % EGDM). An interesting feature of HEMA–EGDM copolymerization in toluene is that the pore volume of the networks increases with increasing EGDM concentration up to 20 mol %, but it decreases again as the EGDM concentration further increases. The results can be explained with the differences in the solvating conditions of the copolymers depending on their EGDM contents.

INTRODUCTION

Particles of hydrophilic copolymer networks, called hydrogels, are widely used as specific sorbents and as support carriers in biomedical engineering. These particles are prepared mainly by an inverse suspension polymerization technique, by which the water-soluble monomers are suspended in an organic phase and polymerized therein to give copolymer beads having a controlled size.[1-5] Another approach to synthesize such particles is the classical suspension polymerization technique using water-insoluble derivatives of the monomers and subsequent hydrolysis or aminolysis of the formed beads.[6-10] Attention has recently been devoted to the direct synthesis of hydrophilic particles by use of this technique.[11-18] For this purpose, various salts were added into the water phase in order to diminish the water solubility of the monomers.

Galina and Kolarz reported the synthesis of cross-linked polymethacrylic acid beads in an aqueous phase containing calcium chloride.[11] Horak et al. used an aqueous solution of polyvinylpyrrolidone as the water phase and a mixture of higher-boiling alcohols as the diluent of the monomer phase for obtaining cross-linked poly(2-hydroxyethyl methacrylate) (PHEMA) beads.[17] They pointed out that the diluent in the monomer phase reduces the water solubility of the HEMA monomer. Mueller et al.,[13] and, later on, Peppas et al.[14-16] and Jayakrishnan et al.[18] described the synthesis of cross-linked PHEMA particles in an aqueous phase containing sodium chloride and a magnesium hydroxide precipitate. By this technique, the magnesium hydroxide precipitate is produced *in situ* by addition of sodium hydroxide in an aqueous solution of magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) and it acts as a suspension stabilizer. The presence of the sodium chloride in the aqueous phase reduced the monomer solubility and allowed the formation of spherical, hydrophilic beads.

The present study deals with the synthesis and formation mechanism of porous PHEMA beads

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Journal of Applied Polymer Science, Vol. 46, 401-410 (1992)
CCC 0021-8995/92/030401-10$04.00

cross-linked with ethylene glycol dimethacrylate (EGDM). For this purpose, a number of porous HEMA–EGDM copolymer particles were prepared. In the preliminary experiments, the suspension polymerization technique of Mueller et al.[13] was adopted as the method of synthesis. However, the size and the size distribution of the copolymer particles thus obtained were found to be very sensitive to the composition of the monomer phase, i.e., to the EGDM and diluent concentrations and to the kind of diluent. This is probably due to the inhibitory effect of the magnesium hydroxide on the reaction.[18] In addition, this technique seems to have the disadvantage that the stabilizer magnesium hydroxide is difficult to remove from the beads after synthesis so that a posttreatment of the bead suspension with an acid solution was necessary. Therefore, a new procedure was developed to synthesize spherical, porous HEMA–EGDM copolymer beads. Similar to Mueller et al., a 20% aqueous sodium chloride solution containing $MgCl_2 \cdot 6H_2O$ was used as the water phase. But, instead of producing a magnesium hydroxide precipitate, bentonite in combination with gelatine was added into the water phase as the suspension stabilizer. In this way, spherical HEMA–EGDM copolymer particles of sizes 0.1–1.0 mm with various porosities could be prepared at EGDM contents higher than 20 mol %. This stabilizer system has also been successfully applied by us in the synthesis of hydrophobic, cross-linked polymer beads.[19] The formation of porous structures was induced by using two different diluents, namely, cyclohexanol and toluene.

Porous structures in polymer networks are known to be formed as a result of a phase separation during their formation process.[20] The phase separation is promoted, i.e., the total volume of voids (pores) in the network increases as the concentration of the divinyl monomer or that of the diluent increases, or as the solvating power of the diluent decreases. Relationships between the synthesis conditions and the porous structure of hydrophobic copolymers such as styrene–divinylbenzene copolymers have been studied for many years.[20,21] However, very few studies in the literature deal with the formation of porosity in HEMA–EGDM copolymers and these studies were concerned mainly with loosely cross-linked networks. Dusek and Sedlacek observed the appearance of a turbidity in PHEMA gels prepared in the presence of water or butanol as the diluents.[22–24] Ilavsky and Prins found an abrupt change in the mechanical and optical properties of PHEMA gels if the degree of dilution with water during copolymerization exceeds 45%.[25,26] Recent studies of Horak et al.[17] and Jayakrishnan et al.[18] demonstrated the formation of porous structures with alcohols as the diluent. However, there is no systematic study in the literature showing the relationships between the synthesis variables and the morphology of the resulting material.

In this investigation, the pore volume of HEMA–EGDM copolymers as well as their equilibrium degree of volume swelling in water were examined as a function of the EGDM concentration and of the solvating power of the reaction medium. Taking into account the extent of polymer–solvent interactions during the course of the copolymerization, the experimental results allow us to describe the conditions of the porosity formation in HEMA–EGDM copolymers, depending on the degree of cross-linking and on the solvating power of the diluent.

EXPERIMENTAL

Materials

2-Hydroxyethyl methacrylate (HEMA, Merck) was distilled under reduced pressure over copper(I) chloride. Ethylene glycol dimethacrylate (EGDM, Merck) was freed from the inhibitor by shaking with 10% aqueous KOH, washing, and drying over sodium sulfate. It was then distilled under reduced pressure over copper(I) chloride. Various batches of HEMA and EGDM monomer solutions were used and they were analyzed by gas chromatography (GC) before polymerization. The GC analysis of the monomers gave the following results: HEMA solution contains 98.2–98.5% HEMA and 0.4–0.6% EGDM; and EGDM solution contains 98% EGDM and 1% HEMA. The rest of about 1% in both solutions was not characterized and taken as nonpolymerizable compounds (diluents) during calculations.

All the other materials were used without further purification, including dibenzoyl peroxide (Merck), toluene (Merck), cyclohexanol (Aldrich), NaCl (Merck), $MgCl_2 \cdot 6H_2O$ (Merck), bentonite (Doksan), and gelatine (Merck).

Copolymerization

Copolymerization was conducted in a 500 mL roundbottom, four-neck flask, fitted with a mechanical stirrer, argon inlet, condenser, and pipette outlet. All reactions were carried out at 80 ± 1°C. A mixture of 70 mL of 20% aqueous NaCl solution containing $MgCl_2 \cdot 6H_2O$ (4.0 g), bentonite (0.1 g), and gelatine (0.2 g) was first introduced into the reactor, heated to the reaction temperature, and stirred at 250 rpm for 1 h. A mixture of the monomers (14 mL) and the diluent (14 mL), containing dibenzoyl peroxide as the initiator (0.22 g; 1.5 wt % in relation to the monomers), was then added to the reactor under argon atmosphere and the reaction was allowed to proceed for 4 h at 80°C. After polymerization, the copolymer beads were first washed with water and then extracted with acetone for 8 h in a Soxhlet apparatus and finally dried *in vacuo* at 70°C. The particles were sieved using ASTM sieves and those of 0.250–1.000 mm in diameters were used for further treatment and characterization.

Solvent Treatment

It is known that the dry porosity of heterogeneous networks does not necessarily correspond to the swollen-state porosity, i.e., to the situation after network formation.[21,27–31] To preserve the swollen-state porosity in the dried state, the copolymer beads were first swollen to equilibrium in methanol. Then, they were successively washed with methanol–toluene mixtures containing increasing amounts of toluene and, finally, with pure toluene. Using this procedure, called solvent-exchange,[30] the good solvent methanol in the swollen gel is replaced successively by the nonsolvent toluene and, thus, the gel is transferred from the rubbery to the glassy state before the drying process. The copolymer beads after treatment with toluene as a final solvent were dried *in vacuo* at room temperature.

Methods

GC analyses of the monomers were performed on a United Technologies Packard Model 439 GC with a 10% OV-17 column (oven temperature 120–200°C programmed, detector temperature 250°C, injection temperature 200°C).

The apparent density of the copolymers, d_0, was determined by the mercury pycnometric method. Porosity, $P\%$, and pore volume, V_p, were calculated from d_0 as

$$P\% = (1 - d_0/d_2) \times 100\% \qquad (1)$$

$$V_p = 1/d_0 - 1/d_2 \qquad (2)$$

where d_2 is the density of homogeneous HEMA–EGDM copolymers.

Table I Composition and Properties of HEMA–EGDM Copolymers[a]

Series	EGDM (mol %)	d_0 (g/cm^3)	$P\%$	V_p (mL/g)	q_v
I	2	1.320	0	0	1.75 (14; 0.14)
	10	1.322	0	0	1.22 (16; 0.08)
	20	1.306	0	0	1.16 (16; 0.04)
	40	1.292	0	0	1.11 (10; 0.04)
	60	1.267	0	0	1.06 (15; 0.01)
	98	1.20	0	0	—
II	2	1.27	3.8	0.030	2.04 (10; 0.15)
	20	1.234	5.5	0.045	1.89 (19; 0.14)
	40	1.142	11.6	0.102	1.79 (9; 0.10)
	50	1.075	16.3	0.152	1.85 (10; 0.10)
	70	0.852	32.1	0.377	1.41 (10; 0.06)
	89	0.741	39.0	0.526	1.37 (40; 0.09)
III	2	0.774	41.4	0.534	—
	5	0.772	41.5	0.538	2.04 (15; 0.10)
	10	0.730	44.8	0.613	1.49 (14; 0.04)
	20	0.645	50.6	0.785	1.16 (10; 0.08)
	40	0.678	47.5	0.701	1.05 (50; 0.03)
	60	0.715	43.6	0.609	1.08 (10; 0.05)
	80	0.758	38.6	0.510	1.14 (10; 0.03)

[a] d_0 = apparent density, $P\%$ = total porosity, and V_p = pore volume of copolymers, q_v = equilibrium volume swelling ratio of copolymers in water at room temperature (numbers in parentheses are the number of measured particles and the geometric standard deviation, respectively). The copolymers in series I were prepared without using a diluent, in series II with cyclohexanol, and in series III with toluene as the diluents.

The equilibrium volume swelling ratio of copolymers, q_v, was determined by measuring the diameter of the beads, with an optical microscope (Leitz Dialux 20) using calibrated granicules, both before and after swelling the samples in a large excess of water for 1 week. q_v was calculated as

$$q_v = D/D_0 \tag{3}$$

where D and D_0 are the swollen and initial diameters of the beads, respectively. The q_v values and their sample standard deviations were determined by measuring 9–50 particles for each run (see Table I).

The apparent volume swelling ratio, $q_{v,a}$, was determined by placing the copolymer beads in a graduated cylinder and reading the volume. An excess of a solvent was then added, and the volume was read at the swelling equilibrium. $q_{v,a}$ was calculated as

$$q_{v,a} = \text{final volume}/\text{initial volume} \tag{4}$$

RESULTS AND DISCUSSION

Formation of Porous HEMA–EGDM Copolymer Beads

The composition of HEMA–EGDM copolymers and their properties are collected in Table I. The copolymers in series I were prepared without using a diluent, which we shall call hereafter "standard copolymers," and in series II, with cyclohexanol, and in series III, with toluene as the diluents. The monomer concentration in the organic phase was constant at 50% by volume in series II and III, whereas the EGDM concentration was varied over a wide range.

The suspension polymerization technique gave spherical particles of sizes 0.100–1.000 mm when the EGDM concentration was higher than 20 mol %. Figure 1 shows a typical size distribution of the copolymer particles with 40 mol % EGDM content. An increase in the EGDM concentration or addition of the diluent toluene or cyclohexanol into the monomer phase caused only a slight reduction in the particle sizes and a slight shift in the particle-size distribution. Odd-shaped particles appeared at 20 mol % EGDM content and their number increased as the EGDM concentration further decreases. The appearance of odd-shaped particles with decreasing EGDM concentration may be due to the increase in the interactions between water and organic phases through hydrogen bonding.

As seen in Table I, the density of standard copolymers decreases from 1.320 to 1.20 g/cm^3 as their EGDM contents increase from 2 to 98 mol %. For the following calculations, the standard copolymers

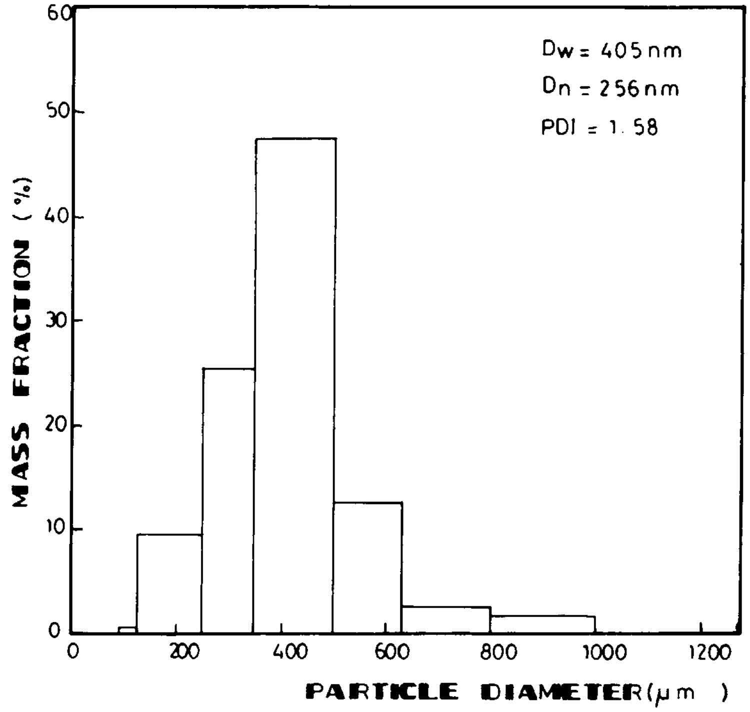

Figure 1 Particle-size distribution of HEMA–EGDM copolymer beads with 40 mol % EGDM content.

are assumed to be nonporous and their densities and swelling degrees are taken as equal to those of homogeneous HEMA–EGDM copolymers. However, it must be pointed out that the diffusion of small amounts of water into the monomer phase may induce, especially at high EGDM contents, heterogeneities in the network structure. Indeed, Peppas et al. observed that, although the HEMA monomer is sparingly soluble in the aqueous phase as a result of the salting-out effect, water is present in the monomer phase.[16] If, alternately, the porosity calculations using eq. (1) are repeated by adhering to a homogeneous copolymer density $d_2 = 1.32$ g/cm^3, the porosity of standard copolymers will increase up to 9% at 98 mol % EGDM. However, equivalent calculations for other series of copolymers showed that the deviations do not affect the results about the porosity formation in the presence of the diluents.

In Figures 2 and 3, the pore volume, V_p, and the equilibrium volume swelling ratio of the networks in water, q_v, are plotted against the EGDM concentration, respectively. The dashed curves in Figure 2 were calculated using the equation[32]

$$V_p = \frac{v_d}{q_v} - \frac{1}{d_2}\left(1 - \frac{q_{v,0}}{q_v}\right) \tag{5}$$

where v_d is the volume of the diluent added per gram of the monomer (0.95 mL/g), and d_2 and $q_{v,0}$ are, respectively, the density and the equilibrium volume swelling ratio of homogeneous (standard) copolymers.

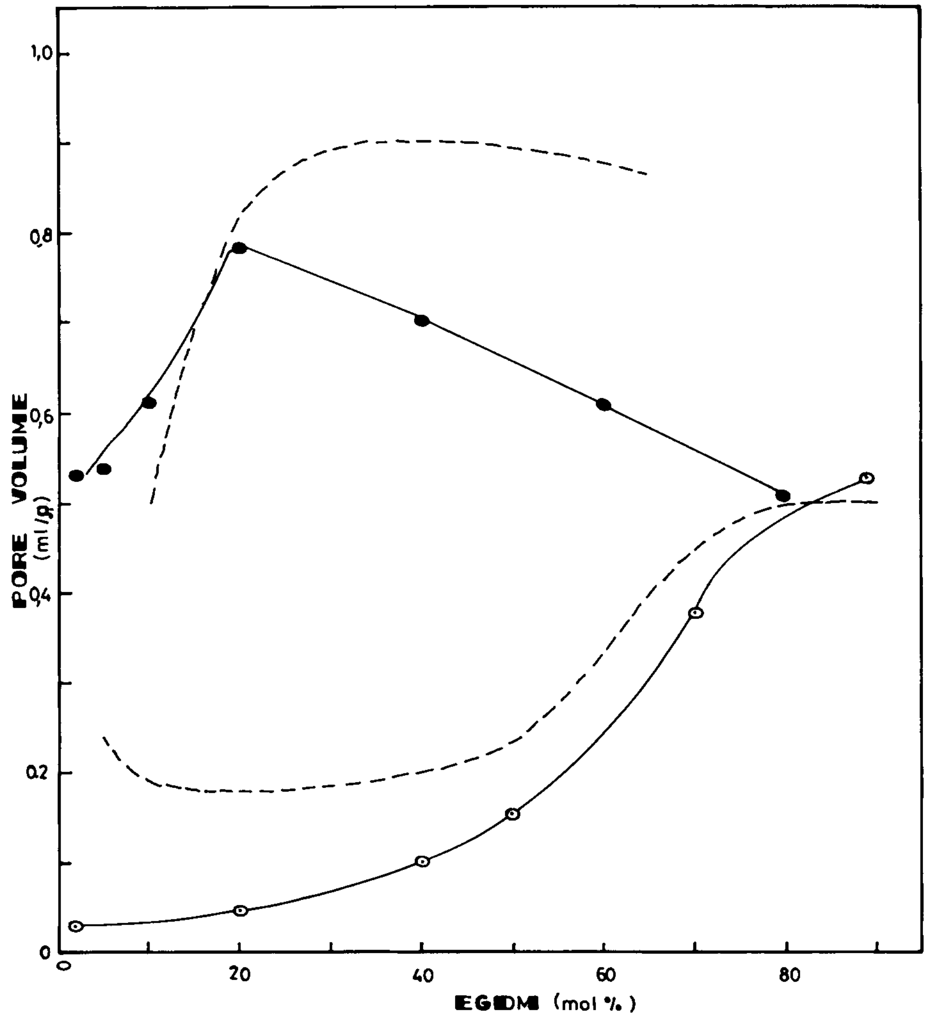

Figure 2 Dependence of the pore volume, V_p, on the EGDM concentration for copolymer beads prepared in cyclohexanol (○) and in toluene (●) as the diluents. The dashed curves were calculated using eq. (5).

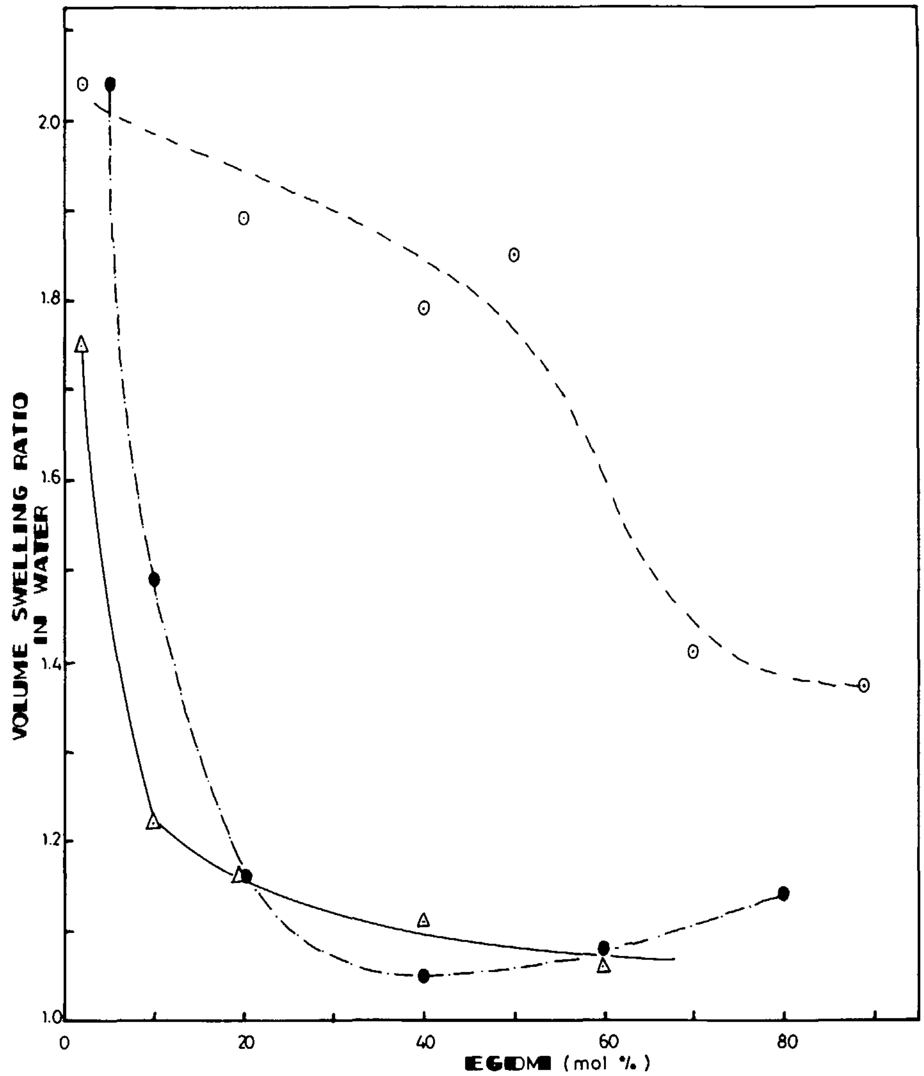

Figure 3 Dependence of the equilibrium volume swelling ratio in water, q_v, on the EGDM concentration for copolymer beads prepared without using diluent (△), in cyclohexanol (O), and in toluene (●) as the diluents.

In the presence of cyclohexanol as the diluent and up to 50 mol % EGDM content, the increase in V_p is slow and the q_v values, compared to those of the corresponding standard copolymers $q_{v,0}$, are relatively high, indicating that most of the diluent cyclohexanol remains in the network (gel) phase throughout the copolymerization. As the EGDM content further increases from 50 to 70 mol %, V_p increases and q_v decreases rapidly, showing the separation of cyclohexanol out of the network phase (Figs. 2 and 3). Moreover, as q_v values are considerably higher than those of $q_{v,0}$ in the whole concentration range of EGDM, the precipitated copolymers during the network formation process are more or less swollen with the diluent–monomer mixtures.

In contrast to cyclohexanol, toluene induces a heterogeneous structure even at a very low degree of cross-linking (Table I and Fig. 2). At 2 mol % EGDM, d_0 was found to be 0.774 g/cm^3, which corresponds to a total porosity of 41%. The syneresis by the copolymer precipitation in toluene can be seen in Figure 3; q_v decreases rapidly, i.e., the copolymer deswells significantly with increasing EGDM content from 2 to 20 mol %. Simultaneously, the pore volume of the networks, V_p, increases and it reaches to a maximum value at 20 mol % EGDM. At this point, the swelling degree of the network is same as that of the homogeneous network with the same EGDM content, i.e., $q_v = q_{v,0}$, indicating that the diluent toluene separates totally out of the network phase and the network phase is largely unswollen. It is interesting to note that a further increase in the EGDM concentration leads to a decreasing porosity and increasing swelling of the copolymers, which is opposite to the known relationships between the porosity, swelling, and divinyl monomer concentration. As will be seen in the following section, this discrepancy could be explained as a result of the deteriorating solvating power of the diluent–monomer mixtures with increasing EGDM concentration.

The dashed curves in Figure 2 show the calculated V_p vs. % EGDM dependencies for toluene and cyclohexanol as the diluents, respectively. Although the maximum observed in toluene as well as the abrupt increase in V_p between 50 and 70 mol % EGDM contents in cyclohexanol can also be detected from the theoretical curves, the agreement with the experimental data points is only qualitative. This is believed to be primarily due to the uncertainty in the determination of the q_v values of the copolymer beads as well as the possible solubility of water in the monomer phase. Experiments are in progress to check the validity of eq. (5) using HEMA–EGDM copolymer samples prepared under bulk polymerization conditions.

Polymer–Solvent Interactions during Copolymerization

Figures 2 and 3 also show that, depending on the type of the diluent used, the networks at the same EGDM content exhibit different degrees of swelling and porosities. This is due to the differences in the solvating conditions of the growing copolymers during the network formation process. To provide correlation between the network properties and the type of the diluent, we have calculated the extent of polymer–solvent interactions during the course of the copolymerization by using the solubility parameter, δ, of the reaction components.

To estimate the solubility parameter of HEMA polymers, δ_{PHEMA}, a loosely cross-linked PHEMA gel was prepared and its apparent volume swelling ratio, $q_{v,a}$, was determined in a series of solvents. In Figure 4, $q_{v,a}$ is plotted against the δ of the solvents. In poorly hydrogen-bonded solvents (filled circles), the swelling ratio of the PHEMA gel increases only slightly with increasing δ of the solvent. In strongly hydrogen-bonded solvents such as alcohols (empty circles), $q_{v,a}$ increases as the number of carbon atoms in the alcohol molecules decreases and reaches to a maximum value in methanol; thereafter, on passing from methanol to water, it decreases again. Thus, the maximum solvating power occurs in methanol and its solubility parameter[33] $\delta = 14.5\ (\mathrm{cal/cm^3})^{0.5}$ can be taken as that of loosely cross-linked PHEMA networks. This value is in good agreement with the values reported previously for PHEMA gels.[34,35]

Because of the highly cross-linked structure of EGDM networks, PEGDM, their solubility parameter cannot be estimated from the swelling experiments. But dilute solution properties of reactive EGDM microgels[36,37] showed that these intramolecularly cross-linked polymers are well soluble in solvents such as toluene, chloroform, and dioxane with δ values between 8.9 and 10 $(\mathrm{cal/cm^3})^{0.5}$. Their average of 9.4 $(\mathrm{cal/cm^3})^{0.5}$ can thus be taken as an approximate δ of PEGDM.

Furthermore, the apparent swelling ratio of the PHEMA gel in HEMA was found to be 1.6, nearly equal to the value found in cyclohexanol. On the contrary, no swelling could be detected in toluene as well as in EGDM monomer. For the following calculations, the values δ for HEMA and EGDM monomers were assumed to be equal to those of cyclohexanol and toluene, respectively (Table II).

According to the Hildebrand theory,[38] the solvating power of a polymer–solvent medium can be estimated from $(\delta_1 - \delta_2)^2$, where δ_1 and δ_2 are the solubility parameters for the solvent and the polymer, respectively. Thus, the solubility of a polymer in a solvent is favored when $(\delta_1 - \delta_2)^2$ is minimized, i.e., when the solubility parameters of the two components are most closely matched. The values δ_1 and δ_2 during the course of HEMA–EGDM copolymerization can be calculated as follows:

$$\delta_1 = \frac{v_2^{00}(1-x)[f(\delta_{\mathrm{EGDM}} - \delta_{\mathrm{HEMA}}) + \delta_{\mathrm{HEMA}}] + (1 - v_2^{00})\delta_{\mathrm{diluent}}}{1 - x v_2^{00}} \tag{6}$$

$$\delta_2 = f(\delta_{\mathrm{PEGDM}} - \delta_{\mathrm{PHEMA}}) + \delta_{\mathrm{PHEMA}} \tag{7}$$

where v_2^{00} is the initial volume fraction of the monomers in the monomer–diluent mixture, x is the monomer conversion, δ_i is the solubility parameter for the reaction component i, and f is the volume (or weight) fraction of EGDM in the initial monomer mixture. In the derivation of eqs. (6) and (7), an equal reactivity for the monomers is assumed during the course of the copolymerization and cross-linking reactions. Moreover, the concentration of water in the monomer phase is neglected and the effect of temperature on the δ values is ignored.

Figure 5 shows how the value $(\delta_1 - \delta_2)^2$ varies depending on the EGDM concentration (f) and on the monomer conversion (x). It can be seen that increasing EGDM concentration changes the solvating conditions of the polymerization system and these changes are drastic in toluene. For instance,

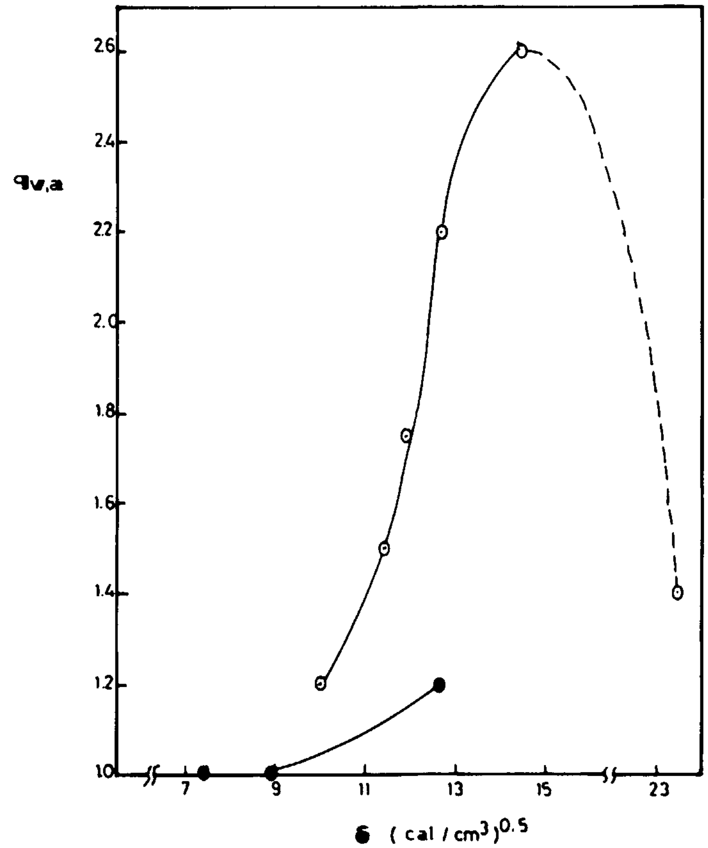

Figure 4 Dependence of the apparent volume swelling ratio, $q_{v,a}$, of a PHEMA gel cross-linked with 2 mol % EGDM on the solubility parameter of the swelling agent (δ). The polymer was prepared in cyclohexanol at an initial monomer concentration of 50% by volume. The used solvents and their δ values in units of $(\text{cal/cm}^3)^{0.5}$ are [33] *i*-amyl alcohol, 10.0; cyclohexanol, 11.4; *n*-propanol, 11.9; ethanol, 12.7; methanol, 14.5: water, 23.4; *n*-heptane, 7.4; toluene, 8.9; and nitromethane, 12.7.

at low EGDM contents, the residual monomer–toluene mixture is a nonsolvent for the growing copolymer chains, whereas it becomes a good one as the EGDM concentration increases. At higher EGDM contents, δ_1 and δ_2 are closely matched so that a phase separation during the copolymerization may only occur due to the increasing cross-link density of the copolymer chains.

Table II Solubility Parameter, δ, of the Monomers, Polymers, and Diluents

Component	δ $(\text{cal/cm}^3)^{0.5}$
HEMA	11.4
EGDM	8.9
PHEMA	14.5
PEGDM	9.4
Cyclohexanol[a]	11.4
Toluene[a]	8.9

[a] From Ref. 32.

A comparison of the results given in Figures 2 and 5 indicates that the porous structures formed in toluene and at low EGDM contents are due to the polymer- (diluent + monomer) incompatibility in the polymerization system (χ-induced syneresis), whereas at higher EGDM contents, to the increasing degree of cross-linking (ν-induced syneresis). The maximum observed in Figure 2 at 20 mol % EGDM can be taken as the transition point between the two regions where χ- and ν-induced syneresis are operative. Compared to toluene, cyclohexanol is a better solvent for HEMA–EGDM copolymers and the phase separation during the network formation is induced mainly by an increase in the degree of cross-linking.

CONCLUSIONS

Depending on the reaction conditions, the suspension polymerization technique described above leads

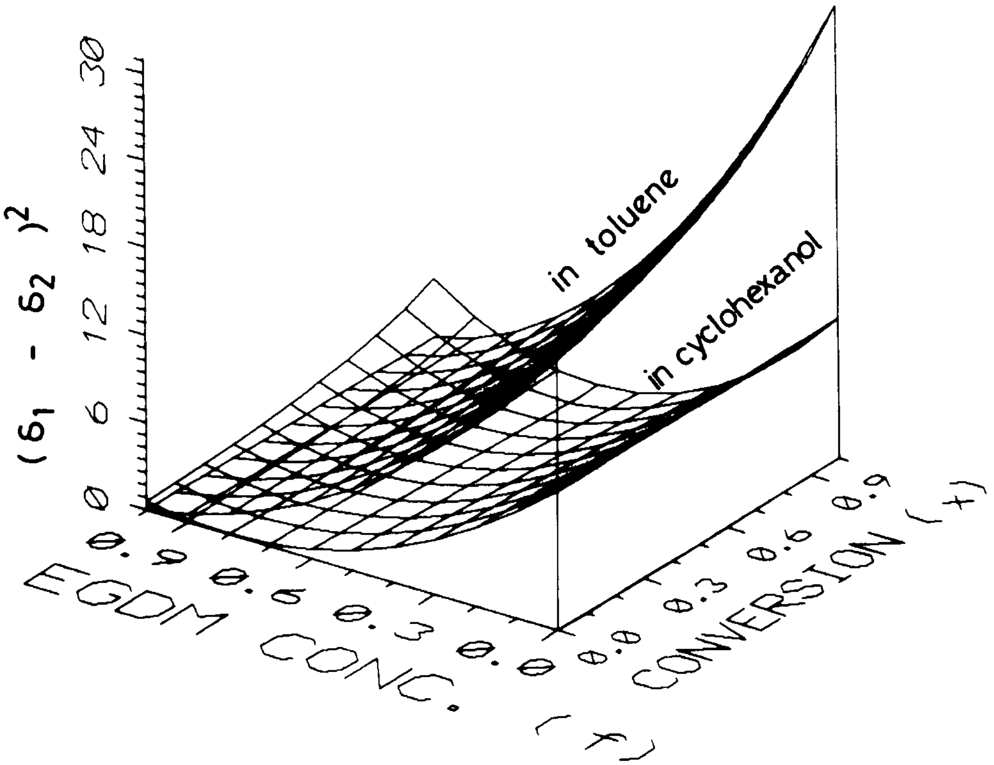

Figure 5 Variation of $(\delta_1 - \delta_2)^2$ during the course of HEMA-EGDM copolymerization depending on the initial EGDM concentration (f) and on the monomer conversion (x).

to the formation of highly swellable and/or porous HEMA-EGDM copolymer beads of sizes 0.1–1.0 mm. The particles thus obtained are spherical at EGDM contents higher than 20 mol %.

The copolymers formed in cyclohexanol as a diluent exhibit, compared to the standard copolymers, a larger degree of swelling in water, indicating that most of the diluent remains in the gel phase throughout the copolymerization. Contrarily, toluene induces porous structures even at a very low degree of cross-linking, i.e., at 2 mol % EGDM. The porosity of the copolymers formed in toluene increases with increasing EGDM content up to 20 mol %, but it decreases again as the EGDM concentration further increases. Calculations performed using the solubility parameter, δ, of the reaction components indicate that the solvating conditions of the polymerization system change depending on the EGDM concentration due to the different solvating powers of the monomers as well as of their homopolymers. These changes are drastic in toluene, which may cause to a transition from χ- to ν-induced syneresis as the EGDM concentration increases.

The authors wish to thank Mr. Ayhan Mesci from TUBITAK Marmara Research Center for technical assistance during this work.

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Received June 17, 1991
Accepted November 19, 1991