Solute and Penetrant Diffusion in Swellable Polymers. XI. The Dynamic Swelling Behavior of Hydrophilic Copolymers Containing Multiethylene Glycol Dimethacrylates

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SYNOPSIS

Copolymers of 2-hydroxyethyl methacrylate with a number of multiethylene glycol dimethacrylates were prepared by bulk copolymerization in the presence of AIBN as an initiator. The content of the dimethacrylate varied between 30 and 50 mol %. Additional copolymers were prepared by solution polymerization in the presence of water or ethanol. All samples were swollen in water up to thermodynamic equilibrium, and their dynamic swelling behavior was studied as a function of time. It was concluded that the mechanism of water transport in these moderately and highly crosslinked polymers was a coupled relaxation and diffusion and that the relaxational contribution to the overall transport depended on the chain length of the multiethylene glycol dimethacrylate.

INTRODUCTION

PHEMA Copolymer Swelling

Copolymers of 2-hydroxyethyl methacrylate (HEMA) with various difunctional ethylene glycol dimethacrylates (MEGDMA) are very important in biomedical applications.[1-4] Poly(2-hydroxyethyl methacrylate) (PHEMA) hydrogels are usually prepared by the free-radical solution polymerization of HEMA in the presence of a difunctional crosslinking agent. The most widely used crosslinking agents are ethylene glycol dimethacrylate (EGDMA), diethylene glycol dimethacrylate (DEGDMA), and tetraethylene glycol dimethacrylate (TeEGDMA).

The swelling behavior of PHEMA in various swelling agents has been studied due to the importance of swelling in solute diffusion studies. The maximum amount of water that can be maintained in homogenous polymer gels depends on the hydrophilicity of the polymer. Since water is only 45% miscible in HEMA monomer at room temperature, one would expect equilibrium swelling of PHEMA of a comparable amount. Transparent PHEMA gels have equilibrium water volume fraction of 0.35–0.42 depending on the crosslinking agent content.[5]

The kinetics of both the penetrant uptake and the swelling of PHEMA gels have been investigated. The swelling properties of the PHEMA network depend[5] on at least three important parameters:

1. the Flory interaction parameter χ between the polymer and swelling agent;
2. the concentration of crosslinks in the network (as indicated by the number average molecular weight between crosslinks, $\bar{M}_c$, or the crosslinking density, ρ_x); and
3. the degree of swelling with respect to the reference state where the polymer chains exhibit unperturbed end-to-end dimensions.

The degree of swelling of homogenous PHEMA gels in water shows little variation as a function of the degree of crosslinking. Based on the insensitivity of the swelling to changes in the degree of crosslinking and on the anomalous swelling behavior shown in the presence of dilute urea solutions, there seems to exist a secondary noncovalent network structure. It is believed that this secondary structure

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superimposed upon the covalent network results in the very high degree of crosslinking in the polymer and controls the swelling behavior of the hydrogel. The secondary structure proposed consists of hydrogen bonds between pendant hydrogen and carbonyl groups in a hydrophobic environment.[6]

Glassy–Rubbery Transition and Controlled Release

Previous controlled release studies with crosslinked PHEMA and its copolymers have been reported.[5] Good[7] used PHEMA in its glassy form to release tripelennamine–hydrochloride. He observed non-Fickian release but was unable to obtain zero-order release. Good and Mueller[8] and Mueller and Heiber[9] used a wide range of copolymers for swelling–controlled release applications. For certain formulations, experimental results with oxyprenolol–HCl showed quasi-zero-order release for up to 24 h. Lee found zero-order release at low loadings of crosslinked PHEMA beads and thiamine–HCl (vitamin B_1). This constant release disappeared as the loadings increased over 18.67 wt %. Lee[10] has also found an approach to obtain zero-order release from these systems and to eliminate the observed burst effect. He prepared microparticles with 70% HEMA and 30% of a crosslinking agent derived from poly(*n*-butylene oxide) endcapped with 3-isocyanatomethyl-3,5,5-trimethyl-cyclohexyl isocyanate. He incorporated oxyprenolol–HCl at levels of up to 34.4% by soaking the microparticles in a 60 : 40 ethanol–water mixture. He washed the external layer by extraction for 5–30 min. Upon drying, these systems showed zero-order release for up to 3 h. By the method of extraction, Lee created a favorable concentration profile in the polymer that counterbalanced the geometric characteristics of the Fickian diffusion from matrices.[10]

Franson and Peppas[11] examined the possibility of adjusting the hydrophilicity of the glassy polymer carrier by copolymerizing HEMA with methyl methacrylate (MMA) using EDGMA as a crosslinking agent. A copolymer with 90% HEMA was found to deliver theophylline with a mechanism that was close to zero-order release. Davidson and Peppas[12,13] used various diffusion techniques and determined that the diffusion coefficient of theophylline in P(HEMA-*co*-MMA) gels was a function of the hydrophilicity of the number of entanglements. A minimum was seen in the diffusivity of theophylline for the copolymer with 70% HEMA, which is the copolymer with the largest number of entanglements per unit volume.[12,13] Korsmeyer et al.[14] examined copolymers of HEMA and NVP with a wide range of hydrophilicity. Theophylline release close to zero order was obtained over a period of 1–5 h after a small initial burst.

The preceding overview indicates that little research has been done in investigating the effects of degree of crosslinking on the swelling and drug release characteristics of crosslinked HEMA systems. In the work of Franson and Peppas,[15] it was noted that some crosslinking may have occurred with the P(HEMA-*co*-MMA) systems due to radical chain transfer mechanisms to the growing copolymer chain. In addition, impurities of the crosslinking agent EGDMA are usually found in the HEMA. However, the degree of crosslinking or average molecular weight between crosslinks was not determined in that work. Walker and Peppas[15] investigated the importance of crosslinking and average molecular weight between crosslinks. They prepared polymers for swelling–controlled release applications by bulk, free-radical polymerization reaction at 60°C from EGDMA, DEGDMA, TrEGDMA, and TeEGDMA comonomers with up to 50 mol % HEMA comonomer. Equilibrium and dynamic swelling studies with the prepared polymers were carried out at 25°C in buffered solutions with pH 7. Both the initial penetrant uptake rates and the equilibrium volume degree of swelling increased with increasing HEMA mole fraction in the polymer. Initial penetrant uptake rates and equilibrium volume degrees of swelling also increased with increasing number of glycol groups in the EGDMA crosslinking agent. The mechanism of solvent uptake approximated that of Fickian diffusion and was therefore non–relaxation controlled but approached zero-order kinetics with HEMA mole fractions of 0.5. Highly crosslinked PHEMA polymers exhibited low volume degrees of swelling with uptake rates dependent on the molecular weight of the crosslinking agent and the mole fraction of the hydrophilic agent.

The objectives of this research study were to investigate the importance of the molecular weight of the crosslinking agent and mole fraction of the hydroxyethyl methacrylate (HEMA) and methacrylic acid (MAA) on the relaxational behavior of highly crosslinked polymeric networks. The objectives were (i) to prepare highly crosslinked copolymers of HEMA and MAA with different molecular weight ethylene glycol dimethacrylates (EGDMA), both with and without drug incorporated during polymerization; (ii) to determine the dynamic and equilibrium characteristics of these polymers in water; and (iii) to determine the transport characteristics

exhibited by these polymers, which would, in turn, indicate the rate-limiting step of penetrant uptake.

EXPERIMENTAL

Preparation of Polymers

The polymers for the swelling studies were prepared by free-radical bulk polymerization. The HEMA was copolymerized with ethylene glycol dimethacrylate (EGDMA), diethylene glycol dimethacrylate (DEGDMA), triethylene glycol dimethacrylate (TrEGDMA), tetraethylene glycol dimethacrylate (TeEGDMA), hexaethylene glycol dimethacrylate (HeEGDMA), or dodecaethylene glycol dimethacrylate (DoEGDMA) (see Table I). All monomers were obtained from Polysciences, Warrington, PA. Solution copolymerizations of HEMA with the various multiethylene glycol dimethacrylates (MEGDMA) in the presence of water or ethanol (20 wt %) were also conducted.

In summary, the following copolymers were prepared with two different HEMA molar compositions, 50 and 70 mol %, by both bulk and solution polymerizations: P(HEMA-*co*-EGDMA), P(HEMA-*co*-DEGDMA), P(HEMA-*co*-TrEGDMA), P(HEMA-*co*-TeEGDMA), P(HEMA-*co*-HeEGDMA), and P(HEMA-*co*-DeEGDMA).

Methacrylic acid (MAA) was also copolymerized with the various molecular weight MEGDMA by bulk or solution polymerization. The following copolymers were prepared with 50 and 70 mol % MAA: P(MAA-*co*-EGDMA), P(MAA-*co*-DEGDMA), P(MAA-*co*-TrEGDMA), P(MAA-*co*-TeEGDMA), P(MAA-*co*-HeEGDMA), and P(MAA-*co*-DoEGDMA). These copolymers were also prepared by solution copolymerization in the presence of 20 wt % ethanol.

In all reactions, 2,2-azobis(2-methylpropionitrile) was used as the free-radical initiator in amounts of 1 wt %. The reaction was carried out in sealed 7-mL polypropylene vials that were placed and agitated in a water bath at 40°C for 6 h and 12 h at 60°C. The resulting transparent polymer cylinders were sliced into disks of diameters ranging from 12 to 14 mm and thicknesses ranging from 0.8 to 1.9 mm.

Swelling Studies

The dynamic and equilibrium swelling studies were carried out at 25 ± 2°C. The dry samples were initially weighed in air and *n*-heptane. They were then placed in separate vials of a buffered pH 7 solution and swollen; they were removed at regular time intervals, blotted dry, weighed in air, and then replaced in the vials. These swelling studies were conducted over a 2-week time period. At the end of the study, the samples were air dried for 24 h and then dried in a vacuum oven at 40°C for an additional 2 days. They were then weighed in both air and *n*-heptane to obtain the final dry weights.

RESULTS AND DISCUSSION

Preparation of Copolymers for Swelling Studies

Of the HEMA-containing copolymers prepared using 50 mol % HEMA, only P(HEMA-*co*-TeEGDMA), P(HEMA-*co*-HeEGDMA), and P(HEMA-*co*-DoEGDMA) resulted in clear polymer samples without defects or cracks; these samples were useful for further experimental studies. The copolymers prepared using the lower molecular weight dimethacrylates (EGDMA, DEGDMA, and TrEGDMA) resulted in highly crosslinked, cracked polymers. This cracking phenomenon was probably due to the extremely high crosslinking in the polymeric networks.

Table I Comonomers Used in Experimental Work

Comonomer	Structure	Molecular Weight
EGDMA	$CH_2=C(CH_3)COOCH_2CH_2OOCC(CH_3)=CH_2$	198
DEGDMA	$CH_2=C(CH_3)COO(CH_2CH_2O)_2OCC(CH_3)=CH_2$	242
TrEGDMA	$CH_2=C(CH_3)COO(CH_2CH_2O)_3OCC(CH_3)=CH_2$	286
TeEGDMA	$CH_2=C(CH_3)COO(CH_2CH_2O)_4OCC(CH_3)=CH_2$	330
HeEGDMA	$CH_2=C(CH_3)COO(CH_2CH_2)_6OCC(CH_3)=CH_2$	418
DoEGDMA	$CH_2=C(CH_3)COO(CH_2CH_2O)_{12}OCC(CH_3)=CH_2$	682
HEMA	$CH_2=C(CH_3)COOCH_2CH_2OH$	130
MAA	$CH_2=CCH_3COOH$	86

Due to the shorter chains of the lower molecular weight dimethacrylates (EGDMA, DEGDMA, TrEGDMA), these copolymerization reactions resulted in more crosslinked structures than the copolymerizations of the longer chain, higher molecular weight dimethacrylates (TeEGDMA, HeEGDMA, DoEGDMA). Of the copolymers prepared using 50 mol % MAA, only P(MAA-*co*-DoEGDMA) resulted in an uncracked, clear polymer useful for further study.

To reduce the degree of crosslinking, copolymers were also prepared using a decreased concentration of MEGDMA or an increased amount of HEMA (70 mol %). However, the results were not much better. Most of the samples were still very highly crosslinked and cracked. Phase segregation seemed to be also a problem. Most of the polymers prepared using 70 mol % MAA resulted in white, ceramiclike polymers. Only the P(MAA-*co*-TeEGDMA) and P(MAA-*co*-DEGDMA) samples were useful for further swelling studies.

To avoid the nonuniformity problem, a solvent (20 wt % ethanol) was added to the reacting comonomer system. The resulting HEMA-containing copolymers (with 70 mol % HEMA) were clear and initially glassy copolymers; however, many cracked upon air drying. Only the P(HEMA-*co*-DEGDMA), P(HEMA-*co*-TrEGDMA), and P(HEMA-*co*-TeEGDMA) samples remained uncracked. The copolymers P(MAA-*co*-DEGDMA), P(MAA-*co*-TrEGDMA), and P(MAA-*co*-TeEGDMA) using 70 mol % MAA were also obtained without defects upon drying. Rapid evaporation of ethanol from the samples was the cause of the cracking.

The copolymers prepared by solution polymerization of the HEMA with the greater molecular weight dimethacrylates [e.g., P(HEMA-*co*-HeEGDMA) and P(HEMA-*co*-DoEGDMA)] resulted in rubbery copolymers that were sometimes fragile. The solvent incorporated with the long chains of the crosslinking agent during polymerization may have resulted in the formation of a loosely crosslinked polymeric network.

Swelling Experiments

Analysis of the equilibrium and dynamic swelling characteristics of all copolymer compositions was performed. The ratio of the mass of water at any time, M_t, to the mass of the dry polymer, M_p, was plotted as a function of time. Most of the data showed good reproducibility. Figure 1 illustrates the dynamic swelling behavior of the copolymers P(HEMA-*co*-TeEGDMA), P(HEMA-*co*-HeEGDMA), and P(HEMA-*co*-DoEGDMA) with 50 mol % HEMA. The P(HEMA-*co*-DoEGDMA) samples exhibited the highest equilibrium water uptake in swelling experiments. In general, as the molecular weight of the crosslinking agent within the copolymer increased, the equilibrium water uptake increased. This could be explained by the lower degree of crosslinking of the networks when higher molecular weight ethylene glycol dimethacrylates were used in the copolymerization. The longer chains present in the P(HEMA-*co*-DoEGDMA) also enabled the polymeric structure to expand more and absorb more water. The P(HEMA-*co*-DoEGDMA) samples had a visible increase in diameter due to swelling and became very rubbery.

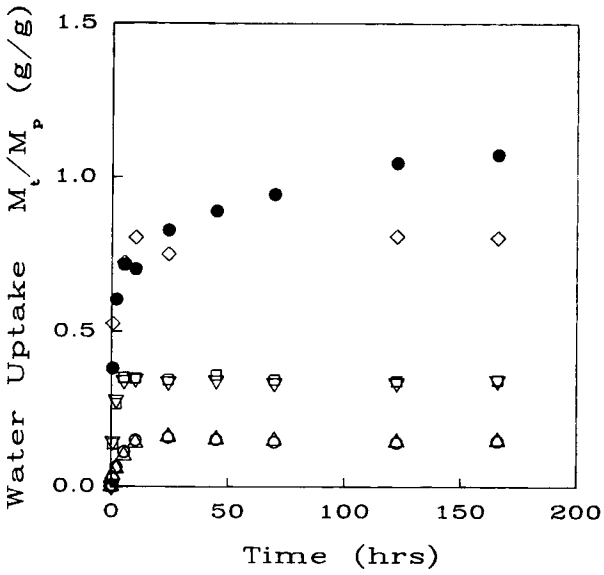

Figure 1 Dynamic swelling behavior of copolymers at 25°C as a function of the number of ethylene glycol units in the multiethylene glycol dimethacrylate comonomers, keeping the HEMA fraction constant at 50 mol % and copolymerizing in bulk: (○) P(HEMA-*co*-TeEGDMA); (△) P(HEMA-*co*-TeEGDMA); (□) P(HEMA-*co*-HeEGDMA); (▽) P(HEMA-*co*-HeEGDMA); (◇) P(HEMA-*co*-DoEGDMA); (●) P(HEMA-*co*-DoEGDMA).

Figure 2 demonstrates the dynamic behavior of the more loosely crosslinked P(MAA-*co*-DoEGDMA) networks containing 70 mol % MAA, which exhibited higher water uptake than the more crosslinked network P(MAA-*co*-TeEGDMA) with 70 mol % MAA. Figure 3 shows that the equilibrium swelling behavior of the P(MAA-*co*-DoEGDMA) with 70 mol % MAA exhibited higher water uptake than the P(MAA-*co*-DoEGDMA) with 50 mol % MAA. The copolymers with compositions of higher

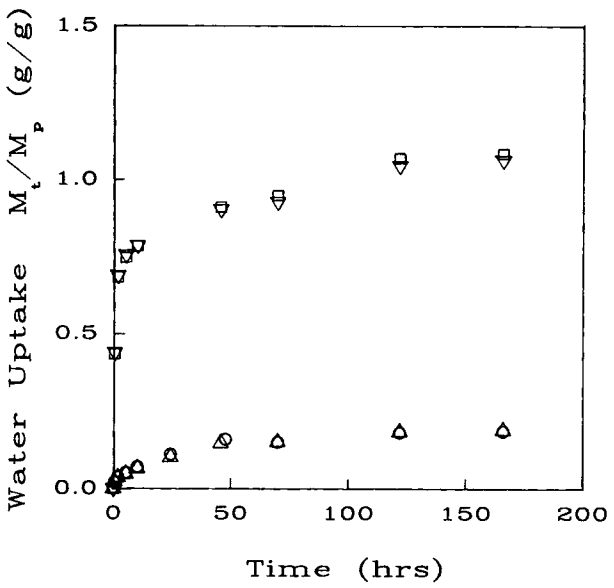

Figure 2 Dynamic swelling behavior of copolymers at 25°C as a function of the number of ethylene glycol units in the multiethylene glycol dimethacrylate comonomers, keeping the MAA fraction constant at 70 mol % and copolymerizing in bulk: (○) P(MAA-*co*-TeEGDMA); (△) P(MAA-*co*-TeEGDMA); (□) P(MAA-*co*-DoEGDMA); (▽) P(MAA-*co*-DoEGDMA).

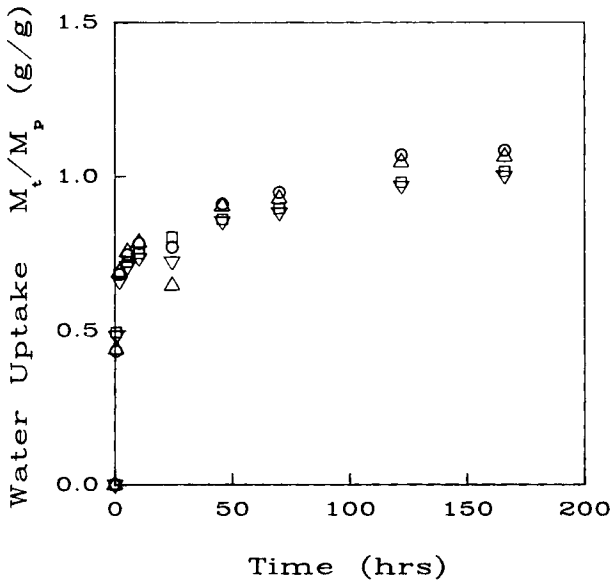

Figure 3 Dynamic swelling behavior of copolymers at 25°C as a function of MAA mole fraction, keeping the number of ethylene glycol units in the multiethylene glycol dimethacrylate comonomers constant and copolymerizing in bulk: (○) P(MAA-*co*-DoEGDMA) with 70 mol % MAA; (△) P(MAA-*co*-DoEGDMA) with 70 mol % MAA; (□) P(MAA-*co*-DoEGDMA) with 50 mol % MAA; (▽) P(MAA-*co*-DoEGDMA) with 50 mol % MAA.

MAA had swelling characteristics with higher equilibrium values.

Figures 4 and 5 show the dynamic swelling response over time of the copolymers prepared using ethanol or water as a solvent. In all cases, the P(HEMA-*co*-TeEGDMA) and P(MAA-*co*-TeEGDMA) with 70 mol % HEMA showed the swelling behavior with the highest equilibrium water uptake.

In a comparison of the HEMA-containing copolymers and the MAA-containing copolymers, the MAA-containing copolymers exhibited swelling dynamics with initial higher water uptake and higher equilibrium water uptake level. This is because the MAA-containing copolymers are more hydrophilic than the HEMA-containing polymers. Figure 6 shows the relevant results for TeEGDMA-containing systems.

The method of polymerization may also have an effect on the equilibrium swelling behavior of the copolymers. The P(MAA-*co*-TeEGDMA) with 70 mol % MAA made in the presence of the solvent ethanol showed swelling characteristics with higher initial water uptake than the swelling behavior of the P(MAA-*co*-TeEGDMA) with 70 mol % MAA made by bulk polymerization (as shown in Fig. 7). The polymers made in the presence of a solvent may

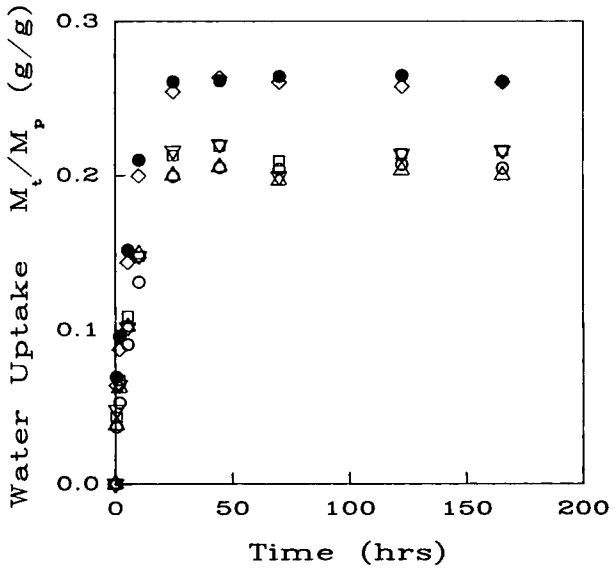

Figure 4 Dynamic swelling behavior of copolymers at 25°C as a function of the number of ethylene glycol units in the multiethylene glycol dimethacrylate comonomers, keeping the HEMA fraction constant at 70 mol % and copolymerizing with ethanol as a solvent: (○) P(HEMA-*co*-DEGDMA); (△) P(HEMA-*co*-DEGDMA); (□) P(HEMA-*co*-TrEGDMA); (▽) P(HEMA-*co*-TrEGDMA); (◇) P(HEMA-*co*-TeEGDMA); (●) P(HEMA-*co*-TeEGDMA).

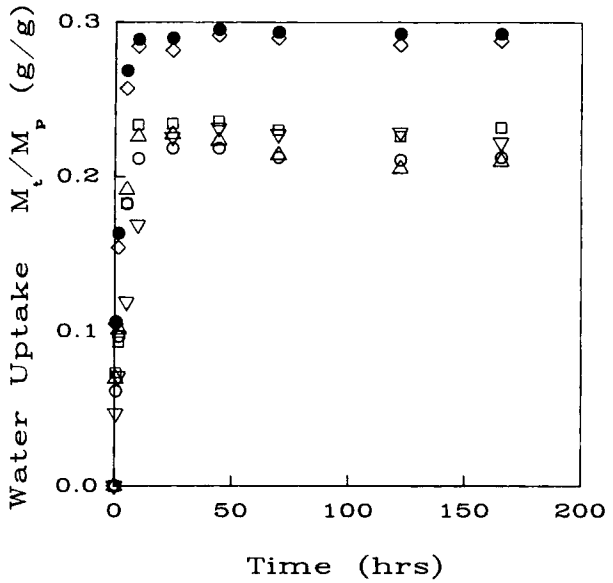

Figure 5 Dynamic swelling behavior of copolymers at 25°C as a function of the number of ethylene glycol units in the multiethylene glycol dimethacrylate comonomers, keeping the MAA fraction constant at 70 mol % and copolymerizing with ethanol as a solvent: (○) P(MAA-*co*-DEGDMA); (△) P(MAA-*co*-DEGDMA); (□) P(MAA-*co*-TrEGDMA); (▽) P(MAA-*co*-TrEGDMA); (◇) P(MAA-*co*-TeEGDMA); (●) P(MAA-*co*-TeEGDMA).

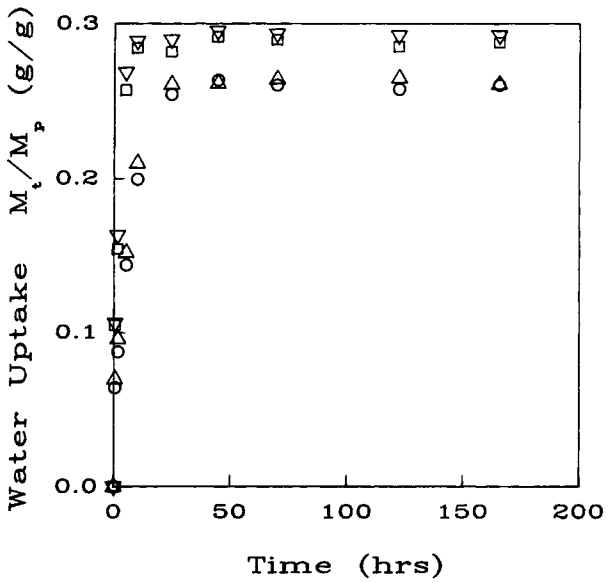

Figure 6 Dynamic swelling behavior of copolymers at 25°C as a function of comonomer, HEMA or MAA, keeping the comonomer fraction constant at 70 mol % and copolymerizing with ethanol as a solvent: (○) P(HEMA-*co*-TeEGDMA); (△) P(HEMA-*co*-TeEGDMA); (□) P(MAA-*co*-TeEGDMA); (▽) P(MAA-*co*-TeEGDMA).

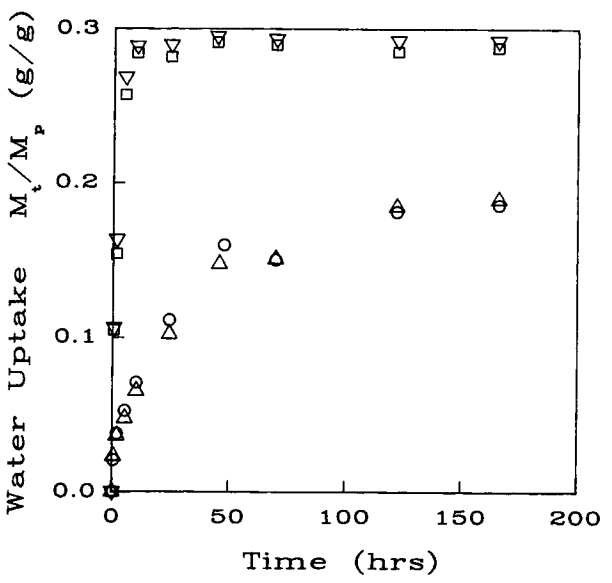

Figure 7 Dynamic swelling behavior of copolymers at 25°C as a function of the type of polymerization, bulk or solution, keeping the MAA fraction constant at 70 mol %: (○) P(MAA-*co*-TeEGDMA) prepared without solvent; (△) P(MAA-*co*-TeEGDMA) prepared without solvent; (□) P(MAA-*co*-TeEGDMA) prepared with ethanol; (▽) P(MAA-*co*-TeEGDMA) prepared with ethanol.

have a more open and relaxed structure due to the solvent being incorporated in the structure during the polymerization. Therefore, during the swelling studies, the equilibrium value of water uptake was attained faster by these copolymers.

The choice of solvent used during the solution polymerization process may also have an effect on the swelling characteristics of the copolymers. The P(HEMA-*co*-TeEGDMA) with 70 mol % HEMA made with ethanol showed swelling dynamics with a higher initial water uptake rate and higher levels of equilibrium swelling, as shown in Figure 8. This was the result of the favorable thermodynamic interaction of ethanol with the HEMA-containing networks, which led to a more open polymer network structure.

Since the thicknesses of the samples varied from 0.8 to 1.9 mm, an analysis of the water uptake, M_t/M_p, versus the swelling time divided by the square of the thickness was also carried out for all the swelling studies. Typical results are shown in Figure 9, which exhibits the same trends as before. The more loosely crosslinked structures showed swelling behavior with higher equilibrium water uptake, and polymers prepared in the presence of a solvent showed dynamics with higher initial water uptakes.

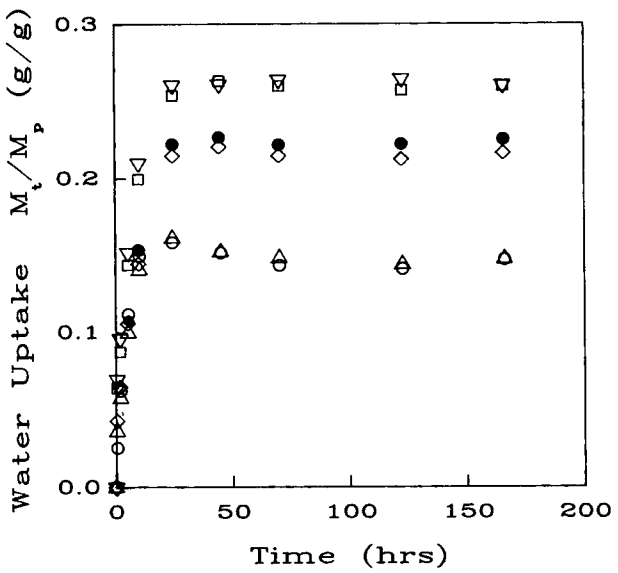

Figure 8 Dynamic swelling behavior of copolymer at 25°C as a function of type of solvent used in polymerization: (○) P(HEMA-*co*-TeEGDMA) with 50 mol % HEMA polymerized in bulk; (△) P(HEMA-*co*-TeEGDMA) with 50 mol % HEMA polymerized in bulk; (□) P(HEMA-*co*-TeEGDMA) with 70 mol % HEMA polymerized in bulk; (▽) P(HEMA-*co*-TeEGDMA) with 70 mol % HEMA polymerized in bulk; (◇) P(HEMA-*co*-TeEGDMA) with 70 mol % HEMA polymerized in bulk; (●) P(HEMA-*co*-TeEGDMA) with 70 mol % HEMA polymerized in bulk.

The fractional water uptake, the ratio of the mass of penetrant uptake at any time, M_t, to the mass of penetrant uptake at any time, M_t, to the mass of penetrant uptake at equilibrium, M_∞, was also analyzed as a function of time. The dynamics of the P(HEMA-*co*-TeEGDMA) with 50 mol % HEMA, as shown in Figure 10, exhibited a slight water overshoot over the equilibrium value, which is a similar result to that obtained by Walker and Peppas.[15] This can be attributed to molecular relaxations. The water diffuses into the network before the chains of the molecule have had time to relax (diffusion is faster than the relaxation), and the fractional uptake curve reaches a maximum, the overshoot value. When the chains do finally relax, water is forced out of the network, and the water uptake eventually reaches its equilibrium value. The dynamic swelling behavior of P(HEMA-*co*-TeEGDMA) exhibited an overshoot, whereas the other copolymers did not indicate overshoot because the chains in the P(HEMA-*co*-TeEGDMA) were long enough to have increased relaxational freedom.

The penetrant-uptake-versus-time curves of most of the dynamic swelling experiments exhibited a "burst" effect, which is an abrupt and fast initial uptake. Burst effects have been reported by Korsmeyer and Peppas[14] for water penetration in P(HEMA-*co*-NVP) copolymers and by Urdahl and Peppas.[16] The burst effect is probably due to the presence of a thin layer formed during the polymerization that is morphologically different from the bulk of the polymer. Since the penetrant diffusion coefficient in a polymer is dependent upon the degree of crosslinking, an initial jump in the uptake would be expected if the crosslinking density of the polymer was significantly lower in a thin, outer layer of the sample.

As a result of this burst effect, analysis of the swelling behavior can be essentially done by shifting each of the fractional uptake curves upward based upon the magnitude of the burst effect apparent in the plot. The shifting of the curve can be expressed as[16]

$$M_t/M_\infty - \alpha = kt^n \qquad (1)$$

where α is a shift factor indicative of the initial burst effect during sorption.

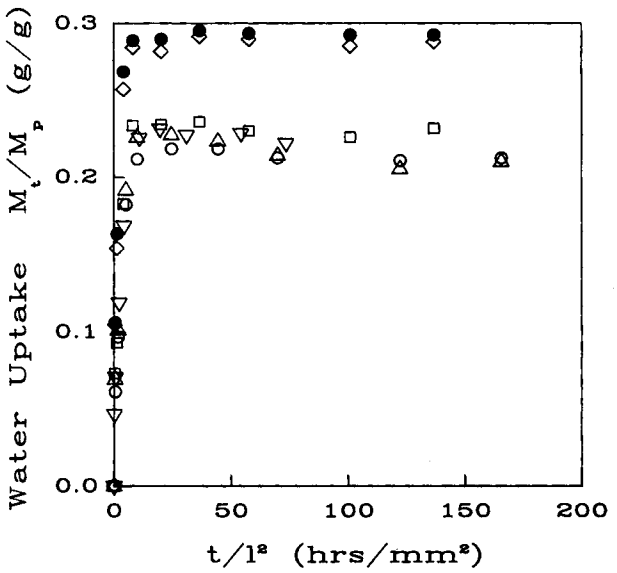

Figure 9 Dynamic swelling behavior of copolymers at 25°C as a function of the number of ethylene glycol units in the multiethylene glycol dimethacrylate comonomers, keeping the MAA fraction constant at 70 mol % and using ethanol as a solvent: (○) P(MAA-*co*-DEGDMA); (△) P(MAA-*co*-DEGDMA); (□) P(MAA-*co*-TrEGDMA); (▽) P(MAA-*co*-TrEGDMA); (◇) P(MAA-*co*-TeEGDMA); (●) P(MAA-*co*-TeEGDMA).

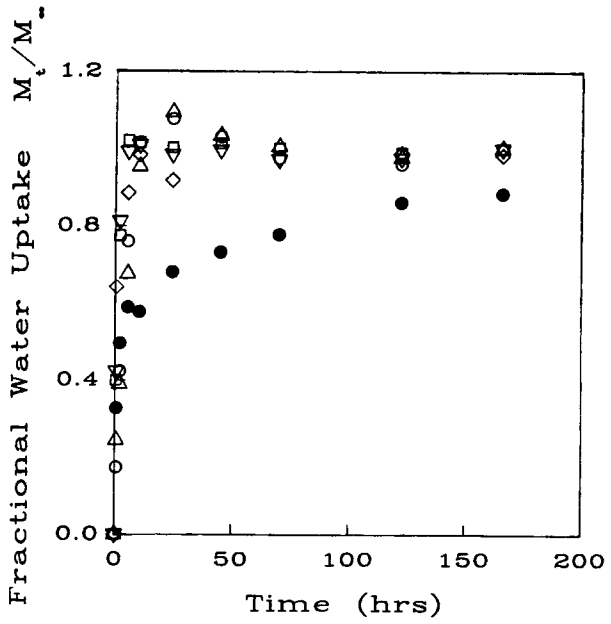

Figure 10 Dynamic swelling behavior of copolymers at 25°C as a function of the number of ethylene glycol units in the multiethylene glycol dimethacrylate comonomers, keeping the HEMA fraction constant at 50 mol %; no solvent (temperature 25°C): (○) P(HEMA-*co*-TeEGDMA); (△) P(HEMA-*co*-TeEGDMA); (□) P(HEMA-*co*-HeEGDMA); (▽) P(HEMA-*co*-HeEGDMA); (◇) P(HEMA-*co*-DoEGDMA); (●) P(HEMA-*co*-DoEGDMA).

In the current study, the values of α, k, and n were determined by fitting the experimental data to Eq. (1) using statistical analysis regression. The values of n obtained by this analysis are reported in Table II.

Most of the values of n are around 1, indicating that case II transport was the rate-limiting step of the penetrant during the dynamic swelling studies. Therefore, for most of the copolymers prepared, the uptake of penetrant was relaxation controlled. Only the P(HEMA-*co*-DoEGDMA) with 50 mol % HEMA exhibited transport behavior controlled by both relaxation and diffusion. Finally, supercase II transport was observed with some samples.

These studies indicate the importance of the difunctional comonomer in copolymerization–crosslinking reactions and the type of crosslinked structures formed.

CONCLUSIONS

From the work completed in this study, the following conclusions can be made:

1. It is possible, but difficult, to prepare uniform copolymers from the reaction of HEMA or MAA with large amounts of various multiethylene glycol dimethacrylates.
2. The copolymers swell in water, and equilibrium water uptake values are relatively low, indicating not very swellable systems, i.e., highly crosslinked networks. The less crosslinked copolymers exhibited swelling characteristics with higher equilibrium water uptake. The copolymers prepared by solution polymerization showed dynamic swelling with faster initial water uptake.

Table II Analysis of Transport Mechanism of Water Transport in MEGDMA-Containing Swelling–Controlled Release Systems Using Equation (1)

Copolymer Sample	Composition	Solvent During Copolymerization	Exponent n	Mechanism
P(HEMA-*co*-TeEGDMA)	50 mol % HEMA	None	1.11	Super-Case II
P(HEMA-*co*-DoEGDMA)	50 mol % HEMA	None	0.95	Non-Fickian
P(HEMA-*co*-DEGDMA)	70 mol % HEMA	Ethanol	1.06	Case II
P(HEMA-*co*-TrEGDMA)	70 mol % HEMA	Ethanol	1.05	Case II
P(HEMA-*co*-TeEGDMA)	70 mol % HEMA	Ethanol	1.05	Case II
P(HEMA-*co*-TrEGDMA)	70 mol % HEMA	Water	1.10	Super-Case II
P(HEMA-*co*-TeEGDMA)	70 mol % HEMA	Water	0.98	Case II
P(MAA-*co*-TeEGDMA)	70 mol % MAA	None	1.05	Case II
P(MAA-*co*-DoEGDMA)	50 mol % MAA	None	0.98	Case II
P(MAA-*co*-DoEGDMA)	70 mol % MAA	None	1.08	Case II
P(MAA-*co*-DEGDMA)	70 mol % MAA	Ethanol	1.14	Super-Case II
P(MAA-*co*-TrEGDMA)	70 mol % MAA	Ethanol	1.48	Super-Case II
P(MAA-*co*-TeEGDMA)	70 mol % MAA	Ethanol	0.98	Case II

3. Penetrant transport in the copolymers approaches case II transport.

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