

Effect of Degree of Crosslinking on Water Transport in Polymer Microparticles

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Synopsis

The water transport in microparticles of poly(2-hydroxyethyl methacrylate) crosslinked with small amounts of ethylene glycol dimethacrylate was investigated as a function of time. Dynamic swelling curves were obtained and analyzed with a simple, empirical, exponential expression, where the exponent n indicates the mechanism of water transport. It was determined that the mechanism changed from Fickian to non-Fickian transport as the nominal crosslinking ratio increased from $X = 0.007$ to $X = 0.124$ mol EGDMA/mol HEMA. Smaller particles attained their equilibrium swelling value faster. The velocity of the penetrant front was determined with optical microscopy, and it was found to decrease from 22.2 to 11.2 $\mu\text{m}/\text{min}$ as the crosslinking ratio increased.

INTRODUCTION

Transport of penetrants in glassy polymers may be associated with macromolecular relaxations as a result of a transition from the glassy to the rubbery state. Under these conditions, the mechanism of penetrant transport may be Fickian or anomalous (non-Fickian).¹

Of particular interest to our research groups is the transport of water through initially glassy, hydrophilic polymers. Several aspects of the transport mechanism in these systems are not well understood, but it is now believed that hydrogen bonding may be complicating the overall transport mechanism. Recently, several studies of this transport behavior have been published by our group.²⁻⁵ It is now recognized that parameters which affect the macromolecular relaxations influence the transport mechanism as well.² These include the molecular weight and molecular weight distribution (for uncrosslinked polymers), the degree of crosslinking (for crosslinked polymers), and the penetrant activity. One goal of the contribution was to investigate the effect of the degree of crosslinking of hydrophilic polymers on the diffusional mechanism of water.

In addition, it is well known that the magnitude of the characteristic length of the polymer sample is important in the overall transport mechanism.⁶ A simple way of understanding this effect is through the diffusional Deborah number, which is defined as the ratio of the characteristic relaxation time of the polymer/penetrant system to the characteristic diffusion time of penetrant in the polymer. For $De \approx 1$, relaxation controls the trans-

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port process. If the thickness is decreased, then $De \gg 1$ and the transport becomes Fickian.⁷ Use of microparticles of different size is instrumental in proving this point. Therefore, an additional goal of the present work was to examine this effect for hydrophilic, glassy polymers.

In the experimental studies presented here, poly(2-hydroxyethyl methacrylate) (PHEMA) was selected as the model hydrophilic polymer. The polymer was prepared by a suspension crosslinking/polymerization technique by reaction of monomer HEMA with small amounts of its dimer ethylene glycol dimethacrylate (EGDMA), which acts as a crosslinking agent for HEMA. Thus, crosslinked microparticles of desirable crosslinking ratio X were produced.

EXPERIMENTAL

Preparation of Polymer Particles

The preparation of PHEMA particles was done by modification of the recently reported suspension polymerization technique of Mueller et al.⁸

In a typical experiment, 180 g of a 20 wt % aqueous solution of NaCl were mixed with 11.5 g of $MgCl_2 \cdot 6H_2O$ and the mixture was heated under rapid agitation (500–600 rpm) in a three-neck 500 mL flask while the temperature was increased slowly up to 70°C. A sample of 61.5 mL of a 1*N* aqueous solution of NaOH was added dropwise and until formation of a fine gel-like precipitate of $Mg(OH)_2$, at which time the agitation speed was reduced to 300 rpm.

To this the polymerization solution was added consisting of 100 g of HEMA (Fluka, Buchs, Switzerland), 1 g of the crosslinking agent EGDMA (Merck, Hohenbrunn, West Germany) and 0.1 g of the initiator azobisisobutyronitrile (Merck). The mixture was maintained at 70°C for 3 h, and then at 90°C for 1 h. The final product was cooled under agitation and the residual $Mg(OH)_2$ was dissolved by adding 5 mL of 37 wt % HCl solution. The microparticles were obtained by filtration, washed with water and ethanol, and dried at room temperature for a day and then under vacuum at 40°C and 150 mm Hg for 3 days.

In total, six different crosslinked systems were prepared by adding different amounts of crosslinking agent, EGDMA. Thus, the nominal crosslinking ratio X was 0.007, 0.019, 0.032, 0.047, 0.062, and 0.124 mol EGDMA/mol HEMA.

TABLE I
Particle Size Distribution for Crosslinked Particles^a

Particle diameter (μm)	Weight fraction of particles (%)	Cumulative Weight (%)
105–210	17.4	17.4
210–300	47.8	65.2
300–430	18.0	83.2
430–610	16.8	100.0

^a $X = 0.007$ mol EGDMA/mol HEMA.

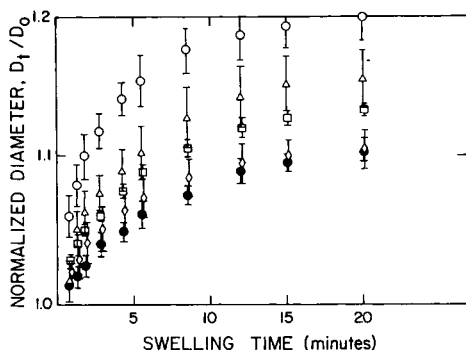


Fig. 1. Normalized diameter of EGDMA-crosslinked PHEMA particles, D_t/D_0 , as a function of swelling time for different crosslinking ratios X : (○) 0.007; (△) 0.019; (□) 0.032; (◇) 0.047; (●) 0.062.

Transport Studies

Upon drying the particles were sieved, and the individual fractions were stored in dessicators until further use. The transport of water was measured in an optical microscope at $T = 24 \pm 1^\circ\text{C}$ with regular and polarized light by determining the change of particle diameter as a function of time. In some experiments, the position of the water front was determined as a function of time and the velocity of the penetration front was calculated.

RESULTS AND DISCUSSION

The particles produced by the suspension copolymerization/crosslinking technique were spherical and of size between 105 and 800 μm depending on the surface tension between the two phases and the rate of agitation. Table I presents a typical particle size distribution of a crosslinked PHEMA with $X = 0.007$, as prepared by this reaction.

The dynamic swelling behavior of crosslinked PHEMA particles was followed by measuring the change of the particle diameter D_t , in an optical microscope as a function of time. Figure 1 presents the effect of the degree of crosslinking, as indicated by the nominal crosslinking ratio X , on the dynamic swelling behavior of the PHEMA particles. The equilibrium swelling value of the particle diameter D_∞ normalized with respect to the original diameter D_0 dropped significantly, namely by about 100% from 1.189 to 1.089 as the crosslinking ratio increased from 0.007 to 0.124 (see Table II).

TABLE II
Characteristics of Crosslinked PHEMA Microparticles

Nominal crosslinking ratio, X (mol/mol)	Theor. \bar{M}_c , $M_{c\text{theor}}$	Equilibrium normalized diameter, D_∞/D_0	Equilibrium degree of swelling, Q	Exponent n of eq. (1)	Penetrant front velocity, v ($\mu\text{m}/\text{min}$)
0.007	9,975	1.189	1.681	0.53	22.2
0.019	3,350	1.150	1.521	0.46	15
0.032	2,050	1.131	1.447	0.52	14.1
0.047	1,400	1.105	1.349	0.60	13.3
0.062	1,050	1.102	1.338	0.80	11.9
0.124	525	1.089	1.291	0.85	11.2

This expected behavior is the result of more tightly crosslinked networks which do not expand in water as much as the loosely crosslinked ones.

The same table presents the theoretical value of the molecular weight between crosslinks as calculated from the nominal crosslinking ratio. It must be noted that the values of $\bar{M}_{c, \text{theor}}$ are accurate for the loosely crosslinked networks. As the crosslinking ratio increases above 0.062 steric hindrances and the unfavorable reactivity of EGDMA could create problems of effective formation of the network. In that, a system with $X = 0.124$ may have a value of \bar{M}_c which is substantially higher than the theoretical value of 525.

The shape of the dynamic swelling curves does not show the characteristic overshoot response that is sometimes observed in anomalous transport^{2,9} of penetrants in glassy polymers, and which has been attributed to macromolecular rearrangements and change of the penetrant solubility in the swollen polymer as a result of the relaxations. This, however, is not a unique characteristic of relaxation controlled transport.⁹ Therefore, non-Fickian transport may be observed, as will be shown below, without having an overshoot response.

Analysis of the transport mechanism of water using the empirical equation (1) was achieved by calculating the values of the exponent n , using the first 60% of the adsorption/transport curves of Figure 1:

$$\frac{D_t}{D_\infty} = kt^n \quad (1)$$

Table II presents the results of this analysis. The value of n increases as the crosslinking ratio increases, indicating departure from Fickian diffusion at high degrees of crosslinking. For values of $X = 0.062$ the exponent n has a value of 0.80 which is characteristic of highly non-Fickian diffusion approaching Case-II transport ($n = 1.0$).⁷

These results present some interesting new aspects of the mechanism of non-Fickian transport. It is evident that, as the degree of crosslinking increases, the mechanism of transport becomes non-Fickian, for two reasons: (i) Due to the considerable effect of crosslinking on the relaxation time, the

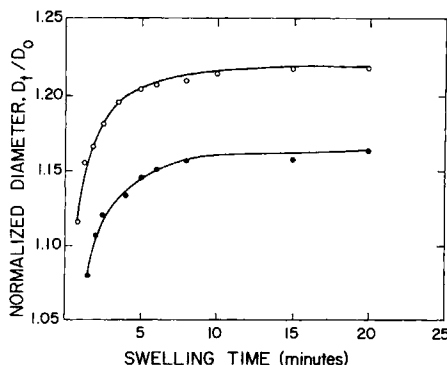


Fig. 2. Normalized diameter of EGDMA-crosslinked PHEMA particles, D_t/D_0 , as a function of time for two particle sizes, 275 (○) and 383 (●) μm ($X = 0.007$).

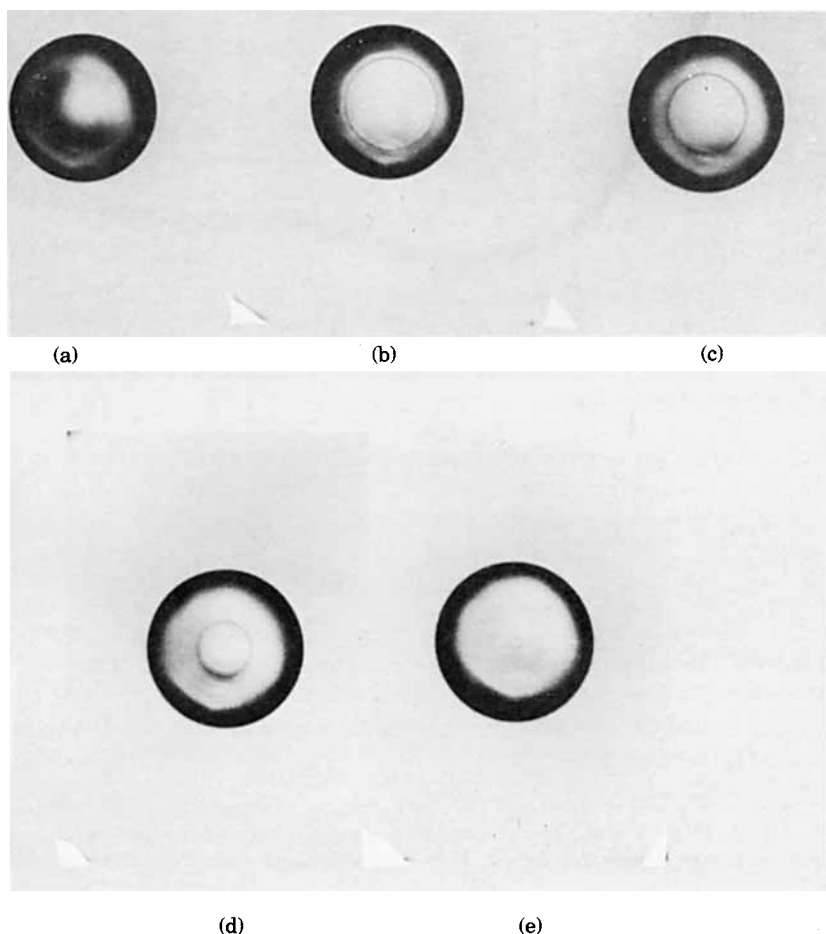


Fig. 3. Optical micrographs of penetration front as a function of time for an EGDMA-crosslinked PHEMA particles with $X = 0.124$: (a) $t = 0$; (b) $t = 8.5$ min; (c) $t = 12$ min; (d) $t = 15$ min; (e) $t = 19$ min.

values of the diffusional Deborah number are shifted towards the value of one. (ii) Diffusion of the penetrant in the crosslinked structure decreases more rapidly than the relaxation time as a function of the degree of crosslinking. Thus, coupling of diffusion and relaxation is observed. The last observation has been seen recently in the case of cyclohexane transport in slabs of crosslinked polystyrene.¹⁰

The effect of particle size on the dynamic swelling is presented in Figure 2 for two particle sizes, 275 and 383 μm for $X = 0.007$. The equilibrium value is attained much faster for the smaller size particles due to the favorable size/volume ratio.

The position of the penetrant front was determined by optical microscopy. Figure 3 shows a typical sequence of pictures of a particle swollen in water. In most cases the position of the front increased linearly with time as shown in Figure 4 for values with $X = 0.007$. However, some samples, especially the highly crosslinked, showed a front velocity which increased with time. Results of the penetrant front position were plotted as a function of time, and the initial velocity of the front was determined as varying from 11.2

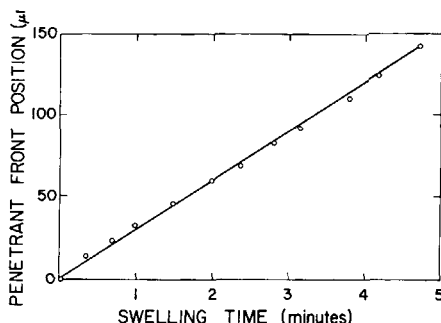


Fig. 4. Penetrant front position in an EGDMA-crosslinked PHEMA particle with $X = 0.007$, as a function of time.

to $22.2 \mu\text{m}/\text{min}$ depending on the crosslinking ratio as shown in Table II. As the crosslinking ratio increases the velocity of the front decreases considerably due to the highly crosslinked structure.

CONCLUSIONS

The degree of crosslinking of hydrophilic, glassy polymer may be used as a means of achieving non-Fickian diffusion, and eventually Case-II transport of water in these polymers. In turn, this behavior may be used to design microparticle controlled release systems which can deliver bioactive agents at constant rates.²

This research was supported in part by a grant from Zyma S.A., Nyon, Switzerland. One of us (N. A. P.) thanks the Zyma Foundation for the Advancement of Medical and Biological Sciences for their financial support during his sabbatical stay at the University of Geneva.

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Received March 14, 1984

Accepted May 10, 1984