# Preparation and Swelling of Polymeric Hydrogels

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## Synopsis

Hydrogel polymers find extensive biomedical applications combining the properties of hydrophilic and crosslinked materials. In this work, poly(methacrylic acid) hydrogels were prepared by the copolymerization of methacrylic acid with varying amounts of 1,4-butanediol dimethacrylate. The polymerization reaction was followed by viscometric measurements and the swelling properties of the samples prepared were also investigated. Alkaline treatment of the hydrogels was performed, to define the changes induced. Finally, a correlation between swelling data, derived from loosely crosslinked samples, led to the determination of the interaction parameter of the system poly(methacrylic acid)–water.

## INTRODUCTION

Polymeric hydrogels have been thoroughly investigated[1-7] for of their importance in biomedical applications, such as soft contact lenses and controlled release membranes. Hydrogel polymers combine glassy behavior in dry state with elasticity when they absorb sufficient amounts of water. In both cases, the material's behavior is influenced, to a great extent, by the network prepared, that is, by the crosslinking reaction.

It is known that the network characteristics (crosslink density, etc.) are influenced not only by the crosslinking agent concentration, but also by its chemical structure.[8] For example, short-chain crosslinkers give reduced crosslinking efficiency compared with the larger chain agents. On the other hand, the network characteristic parameters control the behavior of the polymer in the glassy state and especially, predict its swelling characteristics, when water or other penetrants are absorbed. The swelling characteristics are critical, for example, when hydrogels are used as drug carriers in the controlled release of pharmaceuticals.[4,9]

The sorption of water by glassy hydrogels, has been discussed by P. I. Lee[4] and anomalous behavior ranging from Fickian to Case II extremes is referred to generally, depending on the experimental temperature in relation to the glass transition temperature $(T_g)$ of the polymer.

In our work, a series of gels based on methacrylic acid were prepared, with varying amounts of crosslinking agent. The swelling characteristics of these samples were studied and the influence of sodium hydroxide treatment was determined. In addition, an attempt was made to correlate the swelling data for hydrogels characterized by low crosslink density. These materials, pre-

CCC 0021-8995/89/082121-09$04.00

pared with small amounts of crosslinking agents, have been considered as
nearly ideal networks, and allow the calculation of interaction parameters of
the system, poly(methacrylic acid)–water. The interaction parameter, in turn,
is very useful for fast determination of the crosslink density from swelling
data.

This analysis should be of great importance for the practice because, as
mentioned above, the swelling behavior of the hydrogels is controlled by the
network parameters. For the definition of the influence of technical parame-
ters (such as crosslinking agent concentration or chemical composition) on the
hydrogel structure, it is necessary to characterize the network prepared: to
determine some critical values such as the average molecular weight between
crosslinks ($M_c$).

## EXPERIMENTAL

### Materials and Methods

For preparation of the hydrogel, methacrylic acid (chemical pure, Fluka
A.G.) was used. The crosslinking agent was a multifunctional methacrylate
ester, 1,4-butanediol dimethacrylate (for synthesis, Merck-Schuchardt).
Sodium thiosulfate and potassium persulfate were the components of the
initiator redox system. For the preparation of the methacrylic acid solutions,
deionized water was used, and finally, ethyl alcohol was used to promote
compatibility of 1,4-butanediol dimethacrylate with the methacrylic acid-
water mixture.

The methacrylic hydrogel was prepared by solution polymerization. The
percentage of the components used for the preparation of various samples are
listed in Table I. In all cases, polymerization was carried out at 25°C.

TABLE I
Composition and Presentation of Hydrogel Samples

| Component | Sample | | | | | | |
|---|---|---|---|---|---|---|---|
| | A | B | C | D | E | I | II |
| | | | | Weight (g) | | | |
| Methacrylic acid | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| $H_2O$ | 20.25 | 20.25 | 20.25 | 20.25 | 20.25 | 20.25 | 20.25 |
| Ethanol | 4.75 | 4.75 | 4.75 | 4.75 | 4.75 | 4.75 | 4.75 |
| 1,4 BGDMA | 0.4 | 0.5 | 0.6 | 0.8 | 1.0 | 0.05 | 0.1 |
| $Na_2S_2O_5$ | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| $K_2S_2O_8$ | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| Sample presentation after alkaline treatment | NA | NB | NC | ND | NE | — | — |

## Viscosity Measurements

The copolymerization reaction was followed by viscosimetry, using a Brookfield viscometer, at 20 rpm, and equipped with an RVT head and spindle No. 1. The indications on the centigrade scale were recorded every three seconds. The viscometer head, spindle number, and rotation speed correspond to a coefficient which transforms the scale indications to viscosity values, in cP. In our case, where the viscosity changes are related with the reaction propagation, it is rather useless to transform the indications (arbitrary units) to viscosity units.

## Swelling and Deswelling Measurements

The swelling of samples was followed by immersion in deionized water at room temperature. The water absorbed was determined by weighing the samples, after wiping, at various time intervals. Since the water desorption rate is rather slow for the samples tested, at normal atmospheric conditions, it was not judged necessary to carry out the weighing by putting the samples into a vessel with ground closure.

After reaching equilibrium swelling, the samples were exposed at 25°C and 50% relative humidity (RH) and deswelling was followed by weighing. These deswelling measurements can lead to more reliable data compared with those derived from swelling measurements. Some deviations observed can be attributed to the fact that, as the gel swells it loses strength. As a result, the stresses imposed during wiping, transportation for weighing, etc., produce hydrogel fragments leading to erratic results.

An additional series of specimens, for the determination of swelling characteristics, was treated with aqueous sodium hydroxide. The solution used contained 5 g of sodium hydroxide in 1 L of deionized water. The specimens were immersed for 36 h in 25°C. In all cases, the specimens were immersed in sufficient amount of solution, in order to exceed stoichiometric proportion.

## Density Measurements

The density of the dried hydrogel specimens was determined by weighing in air and then in deionized water. The density value can be calculated using the formula:

$$\rho_s = \frac{B_a \rho_w}{B_a - B_w} \tag{1}$$

where: $\rho_s$ The sample density, $B_a$ the weight in air, $B_w$ the weight in water, and $\rho_w$ the density of water.

The weighing of the immersed samples was continued to ensure that absorbed water did not affect the density measurements.

## RESULTS AND DISCUSSION

The viscosity measurements for samples containing 4–10% 1,4-butanediol dimethacrylate (BGDMA) are shown in Figure 1. The curves of Figure 1

Fig. 1.   Viscosity measurements for hydrogel mixtures. ●: A; □: B; ▲: C; ■: D; ○: E.



Fig. 2.   Incubation time for various polymerization mixtures.

TABLE II
Equilibrium Swelling for Hydrogel Specimens

| Specimen | Dry weight (g) | Weight at equilibrium swelling (g) | Swelling (%) |
|---|---|---|---|
| A | 1.345 | 5.514 | 310 |
| B | 1.208 | 4.433 | 267 |
| C | 1.153 | 4.104 | 256 |
| D | 1.006 | 2.970 | 195 |
| E | 0.943 | 2.546 | 170 |
| I | 0.862 | 4.301 | 399 |
| II | 0.750 | 3.603 | 380 |
| NA | 1.232 | 38.561 | 3030 |
| NB | 1.018 | 23.159 | 2175 |
| NC | 0.980 | 18.816 | 1820 |
| ND | 0.642 | 7.030 | 995 |
| NE | 1.030 | 10.815 | 950 |

express the reaction rate, and it is evident that as the crosslinking agent concentration increases, the network is formed more rapidly. It must be noted that the curves of Figure 1 show the viscosity changes after an incubation period, which differs for various samples. The incubation time, as a function of BGDMA content, is presented in Figure 2, where the curve is in agreement with the conclusion already drawn, that higher amounts of crosslinker favor the fast network formation.

The ultimate swelling for the samples of Table I are presented in Table II. A nearly linear decrease of swelling at equilibrium with increasing BGDMA concentration is observed, but the most interesting fact is that the swelling increases dramatically after alkaline treatment. This is a result of the introduction of sodium ions into the network and the subsequent development of negatively charged carboxyl groups. These groups set up an electrostatic repulsion which tends to expand the network.[10] It must be noted of course, that the presence of some other ions (such as sodium cations) acts as an opposite factor for an exceedingly large electrostatic repulsion. For this reason, the use of deionized water during the preparation and handling of the hydrogels studied, is basic to obtaining reliable results. On the other hand, the presence of ions such $Na^+$ is unavoidable, since electrostatic charge balance must be fulfilled. Furthermore, the presence of ions derived from the water itself ($H^+$ and $OH^-$) can affect the magnitude of the electrostatic repulsion. Similar results have been reported by Katchalsky et al.,[11] who studied poly(methacrylic acid) gels crosslinked with divinyl benzene. In our case, of course, the crosslinker used has a considerably longer chain than divinyl benzene. As a result, lower swelling ratios are observed since, for equivalent amounts, the network density is higher with a more drastic crosslinking agent.

The deswelling of hydrogel samples, as well as the samples after alkaline treatment, is plotted in Figures 3 and 4. As the curves of Figure 3 indicate, there is a nearly linear desorption behavior for the hydrogels and the deswelling rate seems not to be affected by the crosslinking agent concentration (the network density). The same is true for the treated specimens, at least for concentrations from 4 to 6%. For more dense network structures, the linearity

Fig. 3.   Desorption curves for hydrogel specimens at 25°C and 50% RH. ○: A; ■: B; ▲: C;
□: D; ●: E.

is no longer valid, and desorption rate lowers as well. This peculiar behavior is in agreement with the anomalies reported by Lee.[4] The weight measurements in deionized water are presented in Figure 5, as a function of time. As the curve of Figure 5 indicates, during the initial immersion period, a weight increase is evident, which leads to the determination of higher density values, however, after a short time the measurements reach a constant value. This behavior can be explained considering the swelling process of the dried acrylate gel. As a matter of fact, the dry, glassy specimen contains micro-cracks and voids which cannot be immediately filled by the penetrating medium (the water). As the specimen swells, the above-surface defects are expanded, wetting is facilitated, and apparent density increases.

The determination of average molecular weight between crosslinks ($M_c$), is of great importance, since this value is a characteristic parameter of the network. The $M_c$ could be determined through the modulus of elasticity of a specimen, in the rubbery state, using Eqs. (2) and (3):

$$G = \rho RT/M_c \tag{2}$$

$$G = E/3 \tag{3}$$

where $G$ is the equilibrium shear modulus, $\rho$ the density of the polymer, $R$ the gas constant, $T$ the absolute temperature, $E$ the Young's modulus, and $M_c$ the average molecular weight between crosslinks.[12]

In our case, the elevated glass transition temperature of poly(methacrylic acid) gels[13] makes it difficult to perform mechanical tests because, under

Fig. 4. Desorption curves for alkali-treated hydrogel specimens, at 25°C and 50% RH. ○: NA;
■: NB; ▲: NC; □: ND; ●: NE.

normal atmospheric conditions, the specimens begin to disintegrate in the vicinity of 230°C. For this reason, an attempt for the indirect determination of $M_c$ was made, using data derived from very loosely crosslinked gels. For the gels prepared using 0.5 and 1% BGDMA, we assumed that in both cases the total amount of the crosslinking agent was consumed for the intermolecular reaction (crosslinking). As a matter of fact, Loshaek and Fox,[8] who studied the crosslinking of methyl methacrylate with divinyl compounds such as glycol dimethacrylate, report that crosslinking efficiency decreases sharply as the crosslinker concentration increases from 0 to about 5% by weight, and thereafter, an equilibrium effect is essentially evident. An additional reason to justify the assumption already adopted is the high crosslink density of our samples, as mentioned in our discussion of our results with reference to those of Katchalsky et al.[11] The $M_c$ values for specimens I and II must then satisfy the following relation:

$$M_{c,\,\mathrm{I}}/M_{c,\,\mathrm{II}} = 2/1 \qquad (4)$$

Thus, inserting in the Flory-Huggins equation:[14]

$$\rho/M_c = -\left[\ln(1 - v_2) + v_2 + \chi v_2^2\right]/V v_2^{1/3} \qquad (5)$$

the swelling characteristics of specimens I and II (the $v_2$ value for each case),

Fig. 5.   The weight in water as a function of immersion time. Weight in air: 5.2067 g; density: 1.35 g/mL.

and taking into account the relation (4), we obtain:

$$\chi = 0.5987 \tag{6}$$

The symbols in Eq. (5) represent: $\rho$ the density of the unswollen polymer, $v_2$ the volume fraction of the polymer at the equilibrium swelling, $\chi$ the interaction parameter, and $V$ the molar volume of the solvent.

The interaction parameter obtained above can be inserted in Eq. (5) allowing the determination of $M_c$ values for the specimens under investigation in this work. These values are listed in Table III, presenting a gradual decrease as the crosslinking agent concentration increases. However, it must

TABLE III
Calculated $M_c$ Values for Various Hydrogels

| Sample | 1,4 BGDMA (%) | $M_c$ |
|--------|-----|-------|
| I | 0.05 | 50,800 |
| II | 0.1 | 25,500 |
| A | 0.4 | 3,700 |
| B | 0.5 | 1,630 |
| C | 0.6 | 1,250 |
| D | 0.8 | 398 |
| E | 1.0 | 220 |

be noted that the application of the above obtained interaction parameter value, in the case of dense networks of poly(methacrylic acid) is questionable, since the determination was based on swelling data derived from loosely crosslinked samples. In addition, the $M_c$ in Eq. (5) should rather be the effective crosslinks density, however, since the $M_c$ ratio was used [Eq. (4)], this approximation was considered allowable.

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