# Swelling of Poly(glycidyl Methacrylate) Gel Particles by Organic Solvents

TAKESHI FUKUDA,* NORIYUKI KOHARA, YOSHIHIKO ONOGI, and HIROSHI INAGAKI

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan

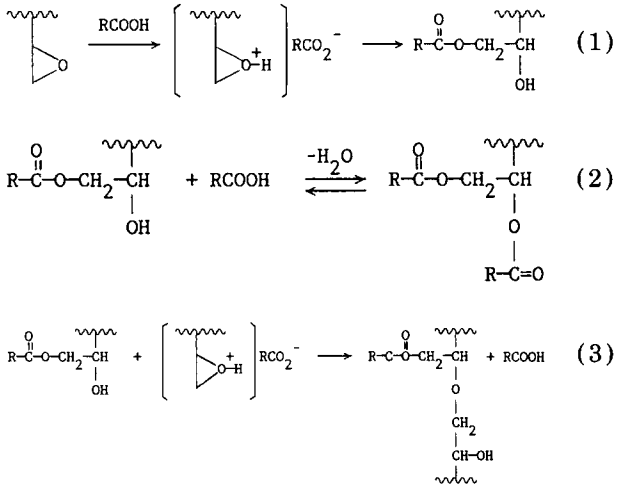
SYNOPSIS

Fine particles of poly(glycidyl methacrylate) (PGMA) were prepared by suspension polymerization and crosslinked via the ring-opening reaction of the epoxide group with formic acid. A fraction of the spherical gel particles averaging about 70 $\mu$m in diameter was examined under an optical microscope with its swelling behavior in a number of solvents. Equilibrium degrees of swelling were established with accuracy to show that this polymer gel has rather unusual affinities for solvents: (i) It is swollen (and, without the crosslinks, soluble in most cases) in many types of solvents, (ii) it cannot be represented by a single value of solubility parameter, and (iii) it is not swollen at all in water nor in aliphatic alcohols, in spite of the presence of hydroxy groups in the chain.

## INTRODUCTION

Poly(glycidyl methacrylate) (PGMA) has a reactive epoxide ring in the side chain, by use of which various functional groups can be introduced on the polymer[1]: For example, carboxyl groups can be easily introduced by the reaction with *N,N*-dicarboxymethylamine. Treatment with a secondary amine followed by quarternarization gives a polymer with cationic groups. Starting with a crosslinked PGMA, we thereby obtain both cationic and anionic ion-exchanging resins. Also possible is introduction of thiol groups by the reaction with mercaptocarboxylic acid. Thus PGMA has potential utility as, e.g., stationary phases in liquid chromatography, carriers of enzymes, and selective adsorbents for biochemical substances.[1-3] In these applications, the polymer is insolubilized by use of a multifunctional crosslinking agent, and hence the product is virtually a copolymer.

In the coatings area, a number of examples of the thermosetting type reactions of GMA polymers with carboxylic acids can be found.[1] Generally, epoxide is ring-opened in the presence of an acid or a base. The treatment with a base, however, may cause unfavorable hydrolysis of acylate groups as well as the ring-opening of epoxide groups. A strong acid will hydrolyze the epoxide to a diol. When a milder acid, a carboxilic acid is used, the following three reactions possibly occur[1]:




Reaction 1 is an addition-type esterification, while reaction 2 is a condensation-type esterification. The latter being an equilibrium reaction, this esterifi-

* To whom correspondence should be addressed.

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cation should hardly occur in the presence of a large amount of water, as in our case (see below). Reaction 3 is a crosslinking reaction, which is the basis for the above-mentioned thermosetting type PGMA systems.

Our ultimate goal is to develop high-performance and economical GMA-based polymer gels for aqueous and nonaqueous chromatographic stationary phase to separate organic compounds and simple salts. As a first step to this end, we in this paper have studied the affinity for water and other organic solvents of PGMA microparticles insolubilized by crosslinking according to the above method. It will be shown below that the PGMA gel has characteristic affinity for several classes of solvents.

## EXPERIMENTAL

### Preparation of PGMA Particles

Suspension polymerization of GMA was carried out by almost exactly following the method and recipe employed by Švec et al.,[2] except that ethyleneglycol dimethacrylate, a commonomer/crosslinking agent, was not used. A particularly vigorous stir was applied to the polymerization system to obtain fine particles. After the reaction, the suspended polymer particles were repeatedly washed with water and then methanol to remove soluble components. The particles were then immersed in a 50%-aqueous solution of formic acid, allowed to react with the acid at 100°C for 1 h, then thoroughly washed with water, and dried. The gel particles thus obtained were fractionated by wet screening, and those between 200 and 250 mesh (between 63 and 74 $\mu$m in diameter) were used for the following experiments.

### Swelling Experiments

Swelling experiments of the PGMA gel were made with ca. 30 different solvents including water, alcohols, esters, ketones, nitriles, amides, and hydrocarbons. A vacuum-dried particle was placed on a slide glass along with a few drops of solvent to immerse it, and observed under an optical microscope to determine the diameter as a function of time. The degree of swelling at equilibrium, $\alpha_e$, was evaluated with

$$\alpha_e = (d_e/d_0)^3 \qquad (4)$$

where $d_0$ and $d_e$ are the diameters of the particle at time zero and at swelling equilibrium, respectively. It was confirmed that $\alpha_e$ was independent of the original size, i.e., $d_0$, of the particle. Figure 1 shows

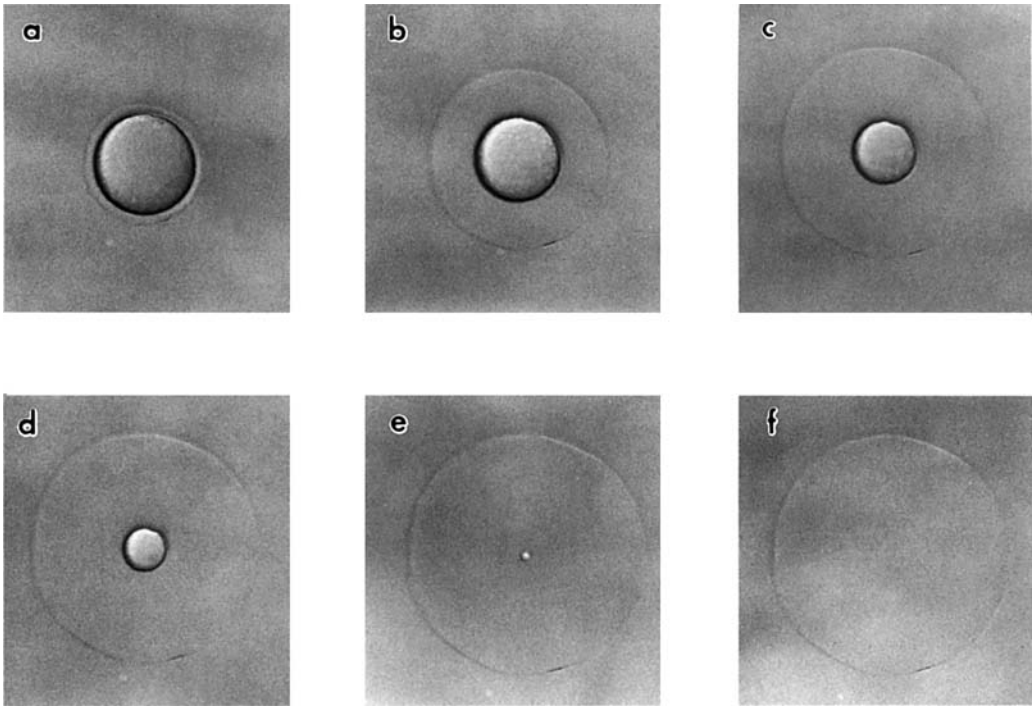


**Figure 1** Optical micrographs of a crosslinked PGMA particle upon swelling in benzyl alcohol. $t$ (min): (a) 1; (b) 5; (c) 10; (d) 15; (e) 23; (f) 30.

examples of photomicrographs of a PGMA particle upon swelling. The penetrant front separating the swollen and unswollen portions of the particle can be clearly seen.

## RESULTS AND DISCUSSION

The GMA polymer before the treatment with formic acid showed IR absorbances at 850 and 910 $cm^{-1}$, characteristic of epoxide ring. It was readily soluble in acetone, tetrahydrofuran, dimethyl formamide, and some other solvents, but insoluble, for example, in water and methanol. After the acid treatment, the polymer turned out to be soluble in no solvent, while the epoxide ring absorbances disappeared, the hydroxy absorbance near 3500 $cm^{-1}$ newly emerged, and the ester-carbonyl peak around 1720 $cm^{-1}$ became significantly broadened (Fig. 2). These confirm that the addition-type esterification (reaction 1) and the crosslinking-type etherification (reaction 3) have taken place, but the condensation-type esterification (reaction 2) has not, at least to an important degree.

Figure 3 shows the time dependence of swelling degree of a gel particle in benzyl alcohol and *N,N*-dimethyl acetamide. In both cases, equilibrium swelling is reached in a few tens of minutes. That this is real equilibrium was confirmed by observing the diameter not to change after 2 weeks. Figure 4 gives the position of the penetrant front from the center of the sphere as a function of time. It shows that the front moves at an approximately constant

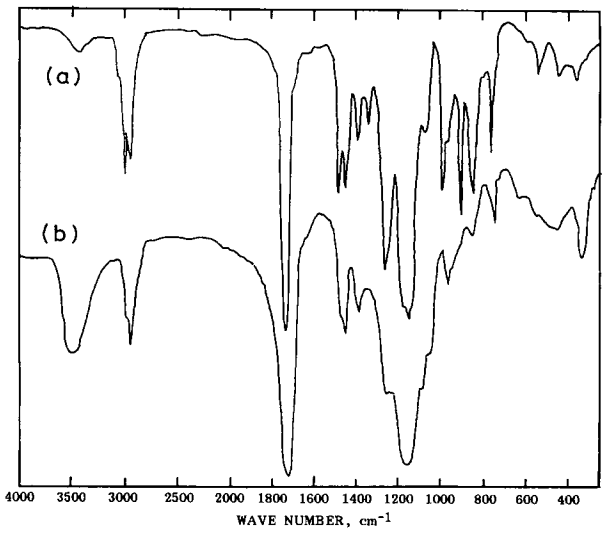


**Figure 2** IR spectra of PGMA, (a) before and (b) after the treatment with formic acid.

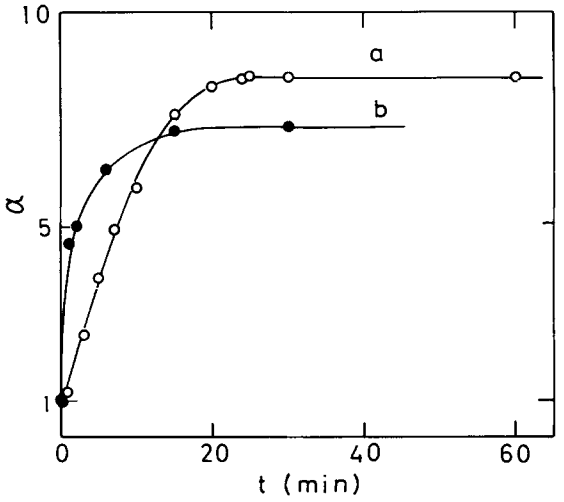


**Figure 3** Degree of swelling $\alpha$ plotted against time $t$ for a crosslinked PGMA particle immersed in: (a) benzyl alcohol; (b) *N,N*-dimethyl acetamide.

velocity to arrive at the center in about 25 min, in this example, when swelling equilibrium is also achieved (compare Figs. 3 and 4). Similar behavior was observed with other solvents. Time to reach equilibrium differed for differing solvents and differing sizes of the particles, but it was on the order of tens of minutes in all cases, quite short as compared with that required in conventional swelling experiments. For example, Graham et al.,[4] who made careful swelling experiments with a piece of crosslinked poly(ethylene oxide) weighing about 10 mg, noted that the sample took approximately 1 week to reach a constant weight, i.e., equilibrium. A PGMA particle of ours weighs only about $2 \times 10^{-4}$

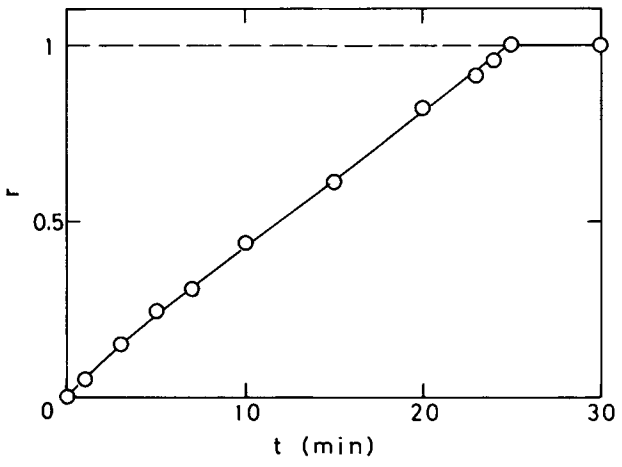


**Figure 4** Penetrant front position $r$ normalized by the particle radius $d_0/2$ at time zero. The solvent is benzyl alcohol.

mg, and this small sample size is obviously the main reason for the quick achievement of equilibrium.

Interestingly, a PGMA sample of a similar size, which was prepared in the presence of a small amount (ca. 9 wt % of total monomer) of ethylene glycol dimethacrylate (EGDMA) followed by the formic acid treatment, reached equilibrium even much more quickly, typically in several to tens of seconds, yet showing equilibrium values of swelling degree similar to those of the EGDMA-free system. Presumably, this gel has a porous structure through which the solvent migrates faster into the particle; thus the effective thickness of the polymer phase to be swollen decreases dramatically. Recently, Robert et al.[5] discussed water transport in a particle of poly(hydroxyethyl methacrylate) (PHEMA) crosslinked with EGDMA. They noted a decrease in penetrant front velocity with an increase in the EGDMA/HEMA ratio or crosslinking density. This result combined with the above-mentioned observation of ours suggest that the front velocity in the GMA–EGDMA copolymer system, treated with the acid, may go through a maximum at a characteristic value of EGDMA/GMA ratio.

The equilibrium degrees of swelling, $\alpha_e$, of the EGDMA-free gel in various solvents are listed in Table I. These values of $\alpha_e$, if plotted as a function of solubility parameter[6] $\delta$, appear to be peaked at three different values of $\delta$, being about 9.3, 11.0, and 12.2 $(\text{cal/cm}^3)^{1/2}$. Solvents relevant to the 9.3 peak include chloroform and benzene derivatives. Second peak around 11.0 $(\text{cal/cm}^3)^{1/2}$ consists of methyl ethyl ketone and nitriles, and the last peak includes strongly hydrogen bonded (H-bonded) solvents such as dimethyl formamide and benzyl alcohol. In Figures 5(a)–5(c), $\alpha_e$ is plotted against $\delta$ by classifying the solvents, according to Burrel,[6] into three groups, i.e., poorly, moderately, and strongly H-bonded solvents. The first group of solvents include hydrocarbons and their halo-, nitro-, and cyano-substitution products, the second group, esters, ethers, ketones, and glycol monoethers, and the last group, alcohols, amines, acids, amides, and aldehydes.[6] For each group of solvents, a clear peak can be seen (Fig. 5), indicating that our gel cannot be represented by a single value of $\delta$. The peaks for the poorly and strongly H-bonded groups are sharp, while that for the middle group is fairly broad. The closed and open circles in the figure indicate that the PGMA untreated with the acid is soluble and insoluble, respectively, in the relevant solvent, while the half-filled circle indicates that the polymer is insoluble but swollen. Good correlation exists between the swellability of the acid-treated polymer and the solubility of the untreated polymer, excepting the case with chlorobenzene which dissolves the untreated polymer but does not swell the treated polymer at all.

Our gel has hydroxy groups and some oxyethylene-like units (cf. reaction schemes 1 and 3), which are expected to afford some hydrophilicity to the basically hydrophobic polymethacrylate structure.

**Table I Equilibrium Degrees of Swelling, $\alpha_e$, of Crosslinked PGMA Microparticles**[a]

| Solvent | $\alpha_e$ | Solvent | $\alpha_e$ |
|---|---|---|---|
| *n*-Hexane | 1.0 | Acrylonitrile | 10.75 |
| Methyl isobutyl ketone | 1.0 | *t*-Butanol | 1.0 |
| *n*-Butyl acetate | 1.12 | Epichlorohydrin | 12.67 |
| Carbon tetrachloride | 1.0 | *i*-Propanol | 1.0 |
| *n*-Decane | 1.0 | *n*-Propanol | 1.0 |
| Xylene | 1.12 | Acetonitrile | 9.08 |
| Ethyl acetate | 1.0 | Dimethyl sulfoxide | 2.79 |
| Tetrahydrofuran | 8.00 | Benzyl alcohol | 8.53 |
| Benzene | 2.00 | Dimethyl formamide | 13.31 |
| Chloroform | 15.09 | Diethylene glycol | 1.0 |
| Methyl ethyl ketone | 6.35 | Diethyl sulfone | 4.28 |
| Chlorobenzene | 1.0 | Ethanol | 1.0 |
| *N,N*-Dimethylacetamide | 7.32 | Methanol | 1.0 |
| Nitrobenzene | 10.98 | Ethylene glycol | 1.0 |
| *o*-Dichlorobenzene | 1.0 | Formamide | 1.43 |
| *n*-Octanol | 1.0 | Water | 1.0 |

[a] Solvents are in order of increasing solubility parameter values.[6]

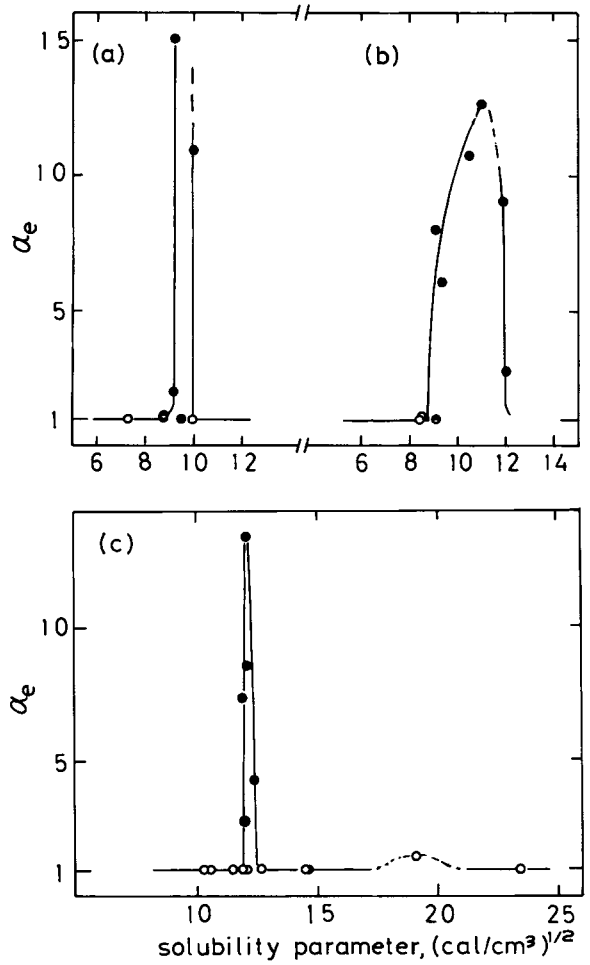


**Figure 5** Equilibrium degree of swelling $\alpha_e$ as a function of solvent solubility parameter: (a) poorly hydrogen bonded (H-bonded) solvents; (b) moderately H-bonded solvents; (c) strongly H-bonded solvents.

Polymers of similar structure such as PHEMA and poly(glyceryl methacrylate) and its monoformic acid ester are known to be highly hydrophilic. Unexpectedly, however, our gel is not at all swollen by water, and, in this respect, it is a hydrophobic polymer. We have no explanation for this. Except for this point, its swelling behavior is rather similar to that of poly(ethylene oxide) gel, which also has affinity towards many types of solvents.[4]

## CONCLUSIONS

Fine particles of PGMA were prepared and crosslinked via the epoxide ring-opening reaction with formic acid. Optical microscopic observation of the particle immersed in a solvent proved to be an accurate and speedy method to study the swelling behavior of the polymer.

The swelling behavior of the PGMA gel is rather unusual in that it is swollen in many types of solvents, but not at all in water in spite of the presence of hydroxy groups on the chain.

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