JOURNAL OF MATERIALS SCIENCE 24 (1989) 1809–1813

Characteristics of porous polymer composite columns prepared by radiation cast-polymerization

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Porous polymer composite columns having porous structure were prepared by radiation cast-polymerization of hydrophilic monomers at low temperature and their characteristics were studied. The porosity of the polymer increased with decreasing monomer concentration. The elution time of water in the polymer column increased with increasing monomer concentration and with decreasing irradiation temperature. The elution time was dependent on the degree of hydration of the polymer. The polymer with a degree of hydration of 0.2 to 0.4 gave the minimum elution time. The elution time decreased with the addition of porous inorganic substances.

1. Introduction

The use of solid porous materials in both gaseous and liquid systems is now accepted as a separation and purification method [1–3]. Silica gel, molecular sieves and porous glass beads have been used often as an inorganic adsorbent [4–8], and also hydrophilic gel-like porous polymers have been used as organic adsorbents in various fields such as chemistry, biochemistry and medicine [9, 10]. The separation and purification process using such materials, in general, have been carried out by a column method, in which cylindrical columns packed with the materials in particular form have been used. Recently, porous polymeric gels with a chemical or biofunctional group have been seen to have an important advantage in biotechnology because of a high separation efficiency due to high specific affinity of biological substances such as antibodies and enzymes. We have studied the radiation polymerization at low temperatures and its application for immobilization of biological substances such as antibodies, enzymes and microbial cells [11–13].

In this work, the preparation method of porous polymer composite columns having porous structure by radiation cast-polymerization at low temperature was studied.

2. Experimental procedure

2.1. Materials

Hydroxyethyl methacrylate (HEMA), hydroxyethyl acrylate (HEA), hydroxypropyl methacrylate (HPMA), tetraethylene-glycol dimethacrylate (4G), and diethyleneglycol dimethacrylate (2G) obtained from Shin Nakamura Chemical Co Ltd were used as the monomer. Silica gel, which is a porous inorganic substance, was obtained from Kanto Chemical Co Ltd.

2.2. Preparation of the porous polymer composite column

The monomer solution of a certain concentration consisting of a monomer and water was put into a 20 cm long, 1.8 cm diameter glass tube. This tube was cooled to -78° C and irradiated with 1 Mrad or γ rays from a ^{60}Co source. After irradiation, the polymer composite resulting from radiation polymerization was

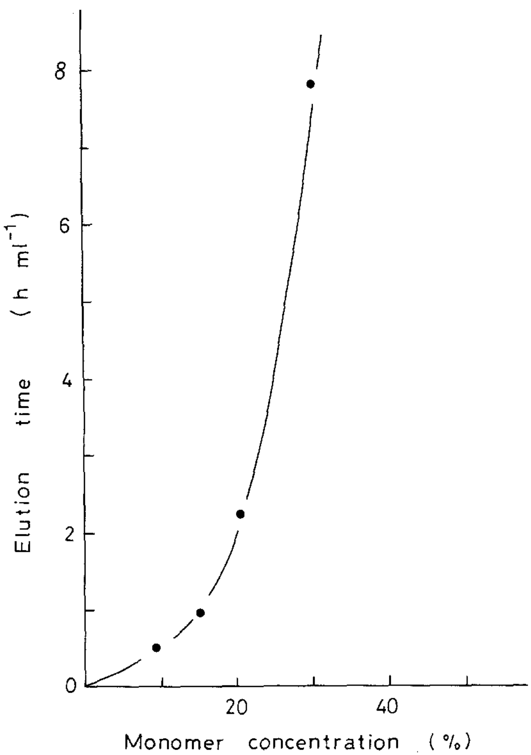

Figure 1 Relation between HEMA monomer concentration and elution time. Length of the polymer composite is 1.0 cm.

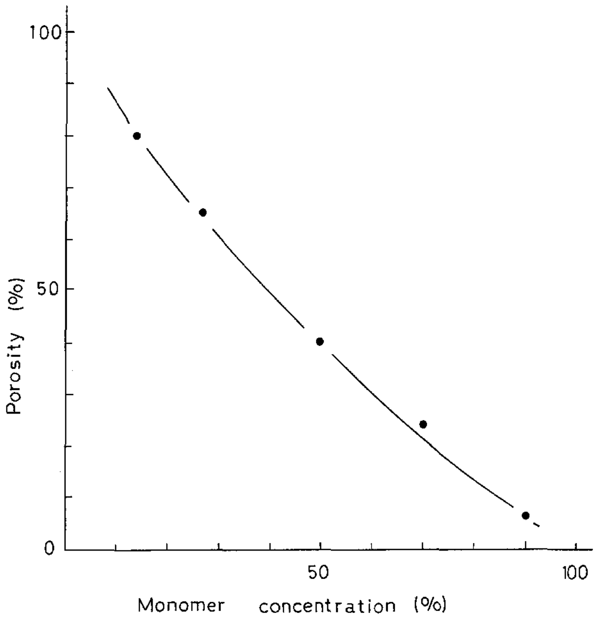

Figure 2 Relation between HEMA monomer concentration and porosity in the polymer composite.

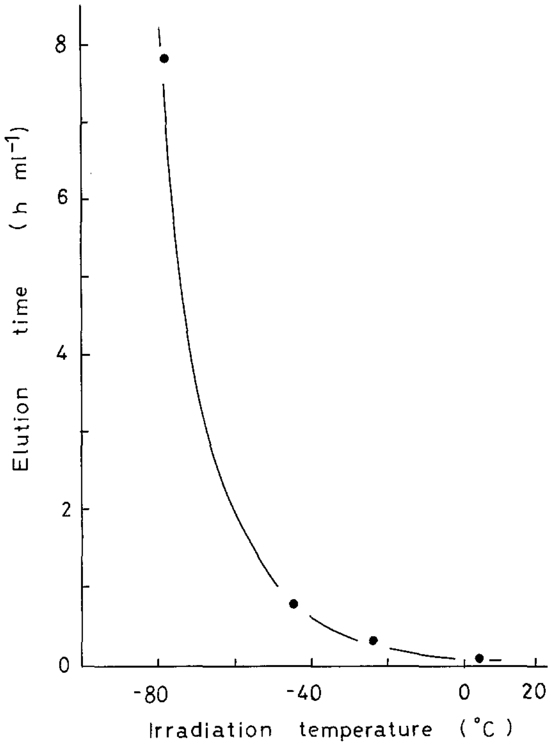

Figure 3 Relation between irradiation temperature and elution time. Length of the polymer composite is 1.0 cm; HEMA monomer concentration is 30%.

removed from the tube at room temperature. The cylindrical polymer composite was cut to a certain length and put into a similar size tube having a stop cock on the bottom.

2.3. Evaluation of elution ability

The elution time of the polymer composite column was evaluated using water. 10 ml of water was put into the polymer composite column and the elution was measured.

2.4. Measurement of porosity

The porosity, which indicates the degree of porous structure of the polymer composite, was obtained by measuring the pore space with an optical microscope.

2.4. Measurement of degree of hydration

The hydrophilicity of the polymer composite was evaluated by measuring the degree of hydration of the polymer. The polymer sample was immersed into distilled water at room temperature for 1 week. The degree of hydration was determined as the ratio of weight of water to the weight of the polymer at swelling equilibrium.

3. Results and discussion

3.1. Effect of HEMA monomer concentration on elution ability

The effect of HEMA monomer concentration on elution ability was studied using a 1 cm polymer composite column, which was obtained by radiation polymerization of HEMA monomer solution. The relationship between HEMA monomer concentration and elution time is shown in Fig. 1. The elution time increased with increasing monomer concentration. This result indicates that the resistance of the elution of water increases due to the increase of the density of the polymer composite. The polymer composite used in this work has a porous structure which is formed by radiation polymerization at low temperature. A polymer composite with a porous structure would have a possible application as a stationary phase in column chromatography. The porous structure in the polymer composite is formed by the following mechanism. In the preparation process of the polymer composite, when the monomer solution containing the monomer and water is frozen at $-78°$C, the whole phase becomes a solid-like one consisting of the mixture of the small ice particles and glassy-state monomer phase. As the polymerization of the monomer phase proceeds by irradiation, the ice particles remain in the polymer phase. After irradiation, the ice particles melt by raising the temperature and change to small sized pores. The pores formed at low temperature below 0° C were cylindrical, while those formed at room temperature were spherical.

3.2. Relationship between porosity and HEMA monomer concentration

The degree of the porous structure in the polymer composite was evaluated by measurement of the porosity. The relationship between porosity and HEMA monomer concentration is shown in Fig. 2. The porosity decreased markedly with increasing of monomer concentration, indicating that the pore space reduces with increasing monomer concentration. The porous polymer composites obtained by the present method were sponge like gels because a hydrophilic HEMA monomer was used, in which the mechanical strength of the polymer obtained at HEMA monomer concentration above 15% were available for the column. The size of the pore in the porous polymer composites, of course, varied with monomer concentration, and it decreased with an increase of monomer concentration. The diameter of the pore in the polymer composite

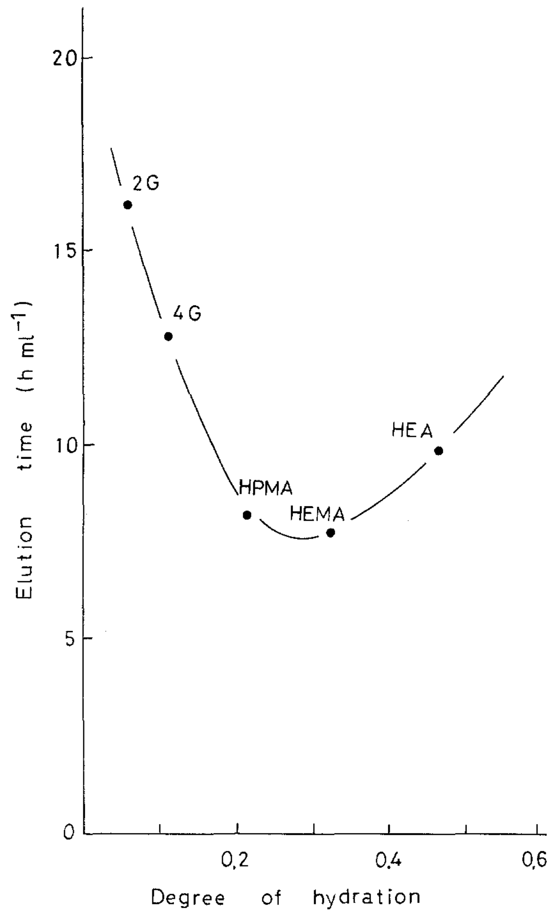

Figure 4 Relation between degree of hydration and elution time in the polymer composites obtained by use of various monomers. Monomer concentration is 30%; length of the polymer composite is 1.0 cm.

obtained from 30% HEMA monomer concentration was 10 to 40 μm. Thus, although the size of the pore in the polymer composites obtained from 30% HEMA monomer concentration was relatively large compared to the molecular size of water, the elution ability in the polymer composite column appeared to be low; the elution time was about 8 h ml^{-1} as seen in Fig. 1. This means that water flows out mainly through the membrane between the pores in the polymer composite by a diffusion mechanism to that occurring inside the pore.

3.3. Effect of irradiation temperature on elution ability

The relationship between elution time and irradiation temperature in 30% HEMA monomer concentration is shown in Fig. 3. The elution time decreased with increasing irradiation temperature. Thus, the elution ability in the polymer composite obtained at an irradiation temperature above $-25°$ C was high. A drastic change of elution time by irradiation temperature suggests that the porous structure varies markedly with irradiation temperature. However, the shape of the pore formed at temperatures below 0° C was different from that formed at temperatures above 0° C as mentioned above. This is caused by the mechanism of polymer formation, that is, at temperatures below $-24°$ C the polymerization of HEMA monomer proceeds almost by homogeneous reaction in the supercooled (glassy) state and at temperature above 0° C at

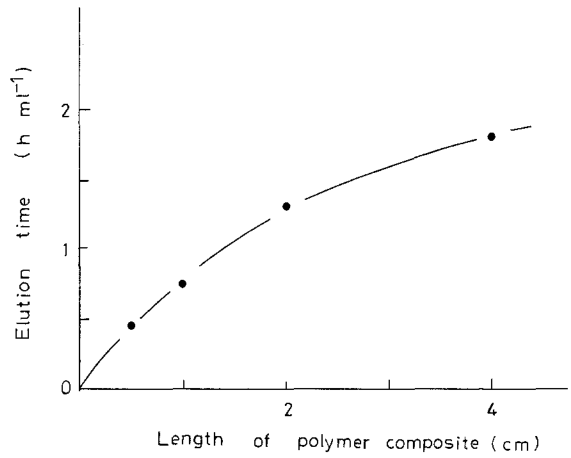

Figure 5 Relation between length of polymer composite and elution time. HEMA monomer concentration is 30%; irradiation temperature is $-45°$ C.

which the monomer and water a homogeneous aqueous solution, the polymerization is a heterogeneous precipitation reaction forming a polymer which is isolated from the monomer phase due to the lower solubility of the polymer in water. The pore formed at temperatures above 0° C was a discontinuous (independent) spherical shape. On the other hand, at lower temperatures, homogeneous, almost bulk polymerization took place in the supercooled phase due to good compatibility of the polymer with monomer, forming almost continuous pore structure owing to dispersed ice. It is proposed that the pores formed at irradiation temperature above 0° C are in partial contact with each other so that the thickness of the membrane between the pores is thin and the elution ability increased. The present preparation method has a characteristic which makes it possible to obtain porous polymer composites having pores of various shapes. The porous polymer composites obtained in the present method are clearly different from porous materials such as polyurethane sponge.

3.4. Effect of hydrophilicity of polymer on elution ability

Polymer composites having various hydrophilicities were prepared by using various monomers, and the relationship between elution time and degree of hydration was studied (Fig. 4). The elution time decreased at first and then increased with increasing degree of hydration, indicating that elution ability is affected by the hydrophilicity of the polymer. The polymer composites obtained from 2G and 4G monomers having a hydrophobic property gave a particle polymer shape and those obtained from HPMA, HEMA and HEA monomer having a hydrophilic property a block polymer with a porous structure. Consequently, the elution in the column charging the particles is different from that charging the block polymer composites. The flow of water in the columns charging the particles proceeds through a gap between the particles, therefore, the elution ability is high. The formation of polymeric particles in a hydrophobic monomer solution containing a monomer and water results in the radiation polymerization of the suspended

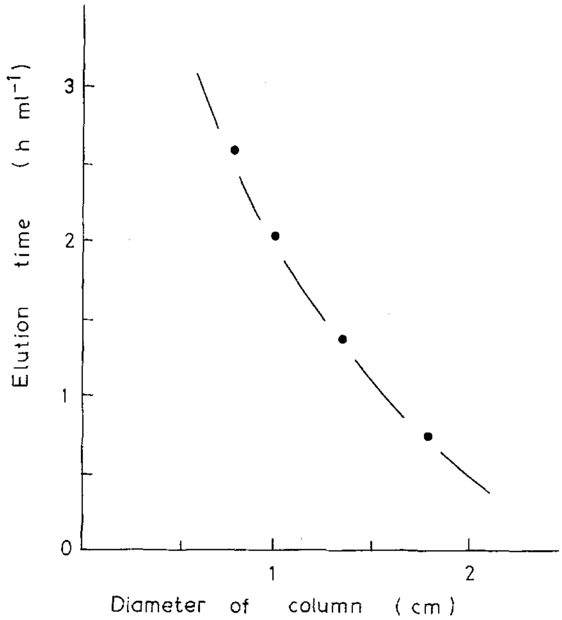

Figure 6 Relation between size of column and elution time. HEMA monomer concentration is 30%; irradiation temperature is $-45°$ C; length of the polymer composite is 1.0 cm.

system, in which the size of the particle obtained depends on the monomer concentration, hydrophilicity of monomer, and irradiation temperature. The size range of the particles obtained from 2G and 4G monomers was 50 to 200 μm. In general, the size of the particles obtained from a low degree of hydration was smaller than those obtained from a high degree of hydration. The elution ability in the particles from 2G monomers was higher than that from 4G monomers in Fig. 4, although the size of the particles from the 2G monomer was smaller than that from the 4G monomer in which packing density of the particles differs between both systems.

The elution ability in the polymer composites obtained from HPMA, HEMA and HEA monomers increased with increasing degree of hydration. Since the feature of the porous structure in the polymer composites is not markedly affected by the hydrophilicity of the polymer, the increase of the elution ability with the degree of hydration is due to an increase of the diffusion of water in the membrane swelled by water. Thus, it was found that the polymer composite column can regulate the elution time by the selection of the monomer.

3.5. Effect of size and length of polymer composite column on elution ability

The relationship between elution time and the length of the polymer composite is shown in Fig. 5. The elution time increased with the length of polymer composite column, indicating that the diffusion resistance increases with increasing length of polymer composite column. The elution time did not increase linearly with the length of the polymer composite column. This indicated that water does not only flow through the membrane but also between the pores. The relationship between elution time and size of the polymer composite column is shown in Fig. 6. The elution time decreased with increasing size of the polymer composite column. This decrease is reasonable due to the increase of surface area of the polymer composite column.

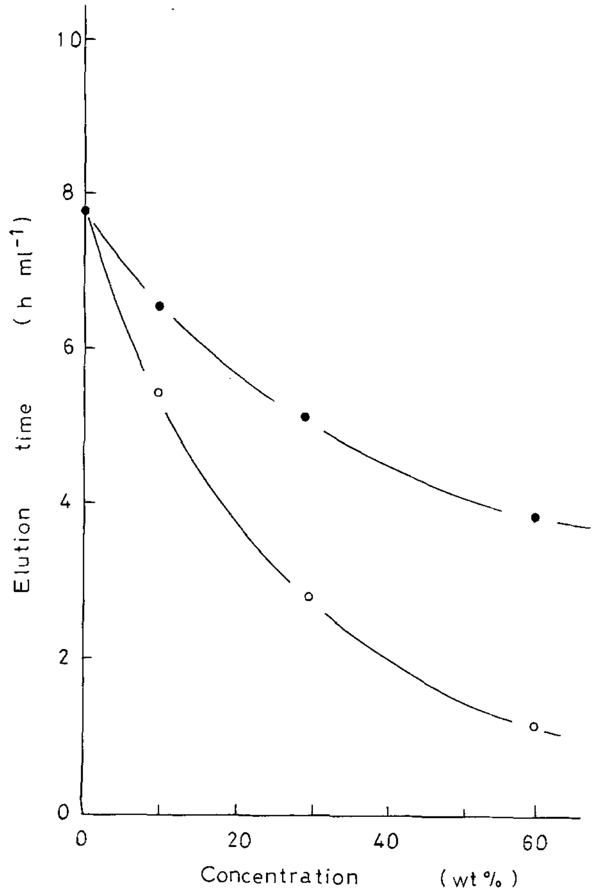

Figure 7 Relation between concentration of porous substance and elution time. HEMA monomer concentration is 30%; length of the polymer compositie is 1.0 cm; (●), silica gel; (○) cellulose powder (200–300 mesh).

3.6. Effect of addition of porous substances on elution ability

The effect of addition of porous substances such as silica gel and cellulose powder on elution ability was studied. The relationship between elution time and concentration of porous substance is shown in Fig. 7. The elution time decreased with the addition of the porous substances. The addition of the porous substances effectively decreased the elution time in the polymer composite columns. Since the porous substances were added to the monomer solution in the preparation process of the polymer composite before irradiation, they were homogeneously mixed in the polymer composites in which the polymer of HEMA was included in the inner side of the porous substance particle. In the case of the addition of cellulose powder, its elution time was shorter compared to that in silica gel.

From these results, it was found that elution time can be controlled by the choice of the preparation conditions of the polymer composite. The present method can be used to obtain porous polymer composites with controllable pore size without impurities such as a catalyst. Furthermore, the present method has the merit that a polymer composite immobilizing various biological substances can be added at the preparation stage before irradiation. Biological substances can be immobilized in the polymer composites without decreasing the biological activity because of radiation polymerization at low temperatures [11–13]. Such porous polymer biological substance columns could be applied to affinity chromatography.

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Received 10 May
and accepted 12 September 1988