Polymeric materials having a porous structure prepared by radiation polymerization

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Polymeric materials having a porous structure were prepared by radiation polymerization of 2-hydroxyethyl methacrylate–water system at various temperatures, and its nature was studied. The materials prepared at low irradiation temperatures below about $-20°$ C had a cylindrical (continuous) pore structure, and those at high irradiation temperatures 0° C had a noncontinuous pore structure. The pore size varied with radiation polymerization conditions such as monomer concentration, irradiation temperature etc. The orientation of the pore in the materials prepared at low irradiation temperatures was observed.

1. Introduction

Porous polymeric materials continue to be the object of intensive research in the fields of polymer chemistry, biology, medicine, and physiology [1]. Synthetic porous membranes are being applied to the solution of process engineering separation problems in the pharmaceutical and chemical industry [2, 3]. Furthermore, porous polymeric gels have been used for the separation of the substances of high molecular weight in biological and chemistry [1]. The preparation of porous polymeric materials have been carried out by various methods, such as evaporation of solvents, emulsion, elongation of polymer, etc. [3]. Initially, virtually all synthetic porous polymers were cast from cellulose derivatives which were known to be film-forming substances [4]. Microporous filters have been produced from the blends of cellulose nitrate and cellulose acetate [5]. On the other hand, hydrophilic polymeric gels such as hydrogels have been prepared by catalystic chemical reactions of 2-hydroxyethyl methacrylate, vinyl alcohol, acrylamide monomer, etc. [1, 6].

In this work, we deal with a new preparation method of polymeric materials having a porous structure by radiation polymerization and with the nature of the porous structure.

2. Experimental procedure

2-Hydroxyethyl methacrylate (HEMA) monomer was obtained from Shin Nakamura Chemical Industry Co., Ltd.

The monomer and water were mixed, put into a glass tube (20 cm in length and 1.8 cm in diameter), and irradiated at low temperatures. The irradiation (1.0 Mrad) was carried out by γ-ray from ^{60}Co source at a dose rate of 1.0 Mrad h^{-1}. The irradiation temperatures of 0, -24, -45, and $-63°$ C were obtained by the freezing points of water, carbon tetrachloride, monochlorobenzen, and chloroform, respectively. The temperature of $-78°$ C was obtained with dry ice–methanol. After irradiation, the polymer sample was taken out from the tube, elevating the temperature of the tube to room temperature.

The polymer material samples obtained were cut with a microtome at low temperatures, and its porous structure was examined with a light microscope (Olympus Model FHF). The cutting positions (A, B, and C sectional planes) of the sample with microtome is shown in Fig. 1.

3. Results and discussion

3.1. Formation of porous structure

Radiation polymerization of HEMA–water system at low temperatures was studied to obtain poly-

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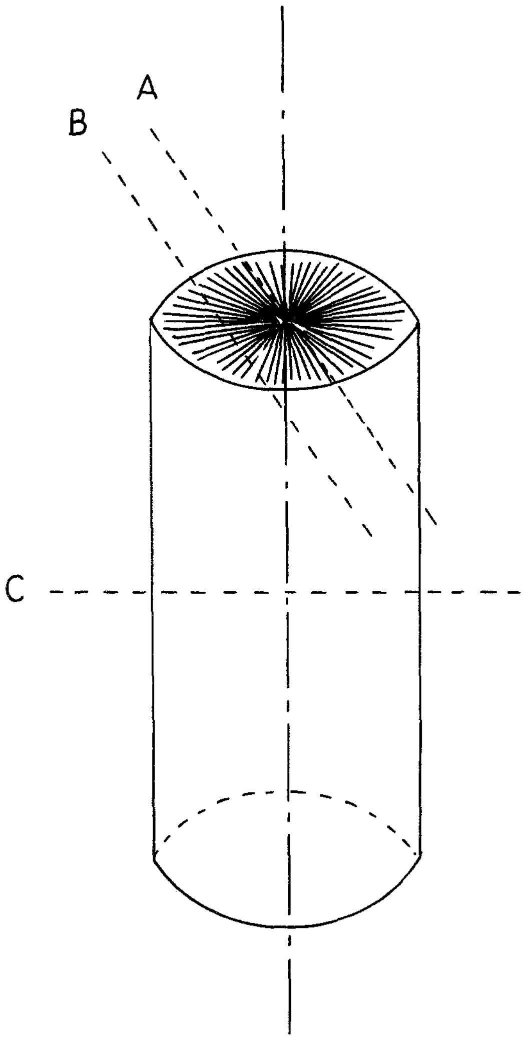

Figure 1 Cutting position (sectional plane) of sample with microtome.

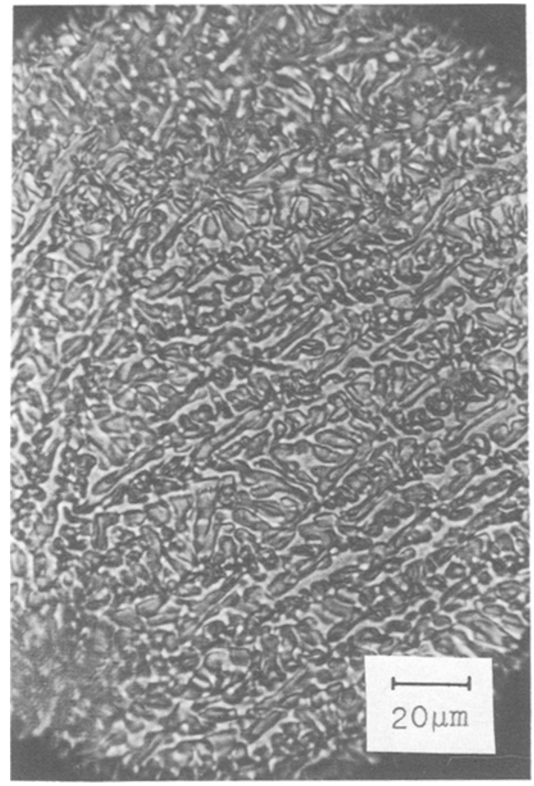

Figure 2 Microphotograph of porous structure. Monomer concentrations: 50%; irradiation temperature: $-78°$ C; cutting position of sample: B plane.

meric materials having a porous structure. A typical photograph of the sectional plane of the sample from the HEMA–water system is shown in Fig. 2. As can be seen in Fig. 2, the polymer matrix had a porous structure. Furthermore, the sample exhibited a sponge-like soft state. The formation of the porous structure was based on the melting of ice in the polymer matrix after radiation polymerization. This formation of the porous structure was the most characteristic feature in the polymer matrix obtained by radiation polymerization of hydrophilic glass-forming monomers at low temperatures. HEMA used in this work was a typical hydrophilic glass-forming monomer, giving an amorphous supercooling state near a glass transition temperature (T_g). The phase diagram in HEMA–water system has been studied previously [7]; the melting peak of the eutectic composition at the eutectic point (above $-24°$ C) could hardly, or only slightly, be distinguished and that the change of apparent specific heat corresponding to T_g could clearly be observed. This fact shows that, in the temperature region below $-24°$ C, most of the water has crystallized to ice, while all eutectic compositions consisting mainly of monomer with a small amount of water have undergone supercooling. Thus, the monomeric system was a suspension of ice in supercooled monomer, acting as the dispersion medium at low temperatures. In HEMA–water system, the polymerization phase, the mechanism, and the porous structure in the polymer matrix were different at temperatures above and below $-24°$ C. At lower temperatures below $-24°$ C, 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 the dispersed ice. Of course, the porous structure changes by monomer concentration.

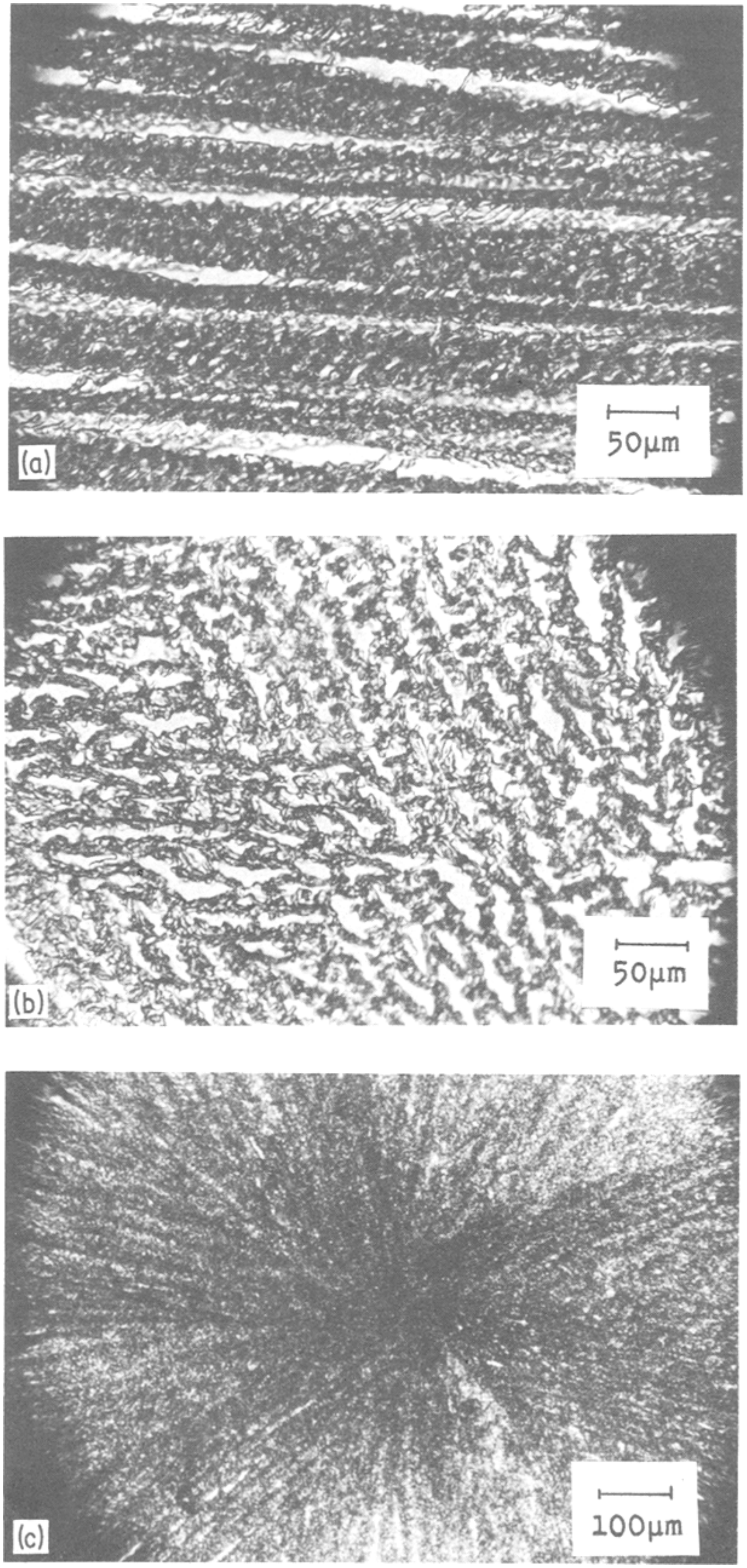

Figure 3 Microphotographs of porous structure in various positions of sample. Monomer concentration and irradiation temperature are 30% and -78° C, respectively. (a): A plane, (b): B plane, (c): C plane.

3.2. Orientation of pore in various positions of sample

The orientation of the pore in various positions of the sample was examined by cutting the sample at various positions and its microscopic observation. The microphotographs of the porous structure at A, B, and C position of the sample are shown in Fig. 3. Fig. 3c is a photograph taken near the centre of the sample. From this photograph, it is found that the pores are radially orientated. As can be seen in Fig. 3a, the shape of the pore appeared to be a cylindrical structure. These results show that the formation of the cylindrical pore structure in HEMA–water systems is based on the growth of ice in needle-shaped state. According to Fig. 3b, the pore size (diameter) can be estimated though the sectional plane of the pore is not a circle and is considerably deformed. This shape of the pore varies with the polymerization conditions such as monomer concentration, irradiation temperature, etc.

The orientation of the pore in the sample changes by the shape of the sample tube. In the polymerization using a thin box case, the cylindrical pore is horizontally orientated and porous polymeric membranes could be utilized for various separation filters.

3.3. Effect of monomer concentration on pore size

The relationship between the size of the pore and monomer concentration is shown in Figs. 4 and 5.

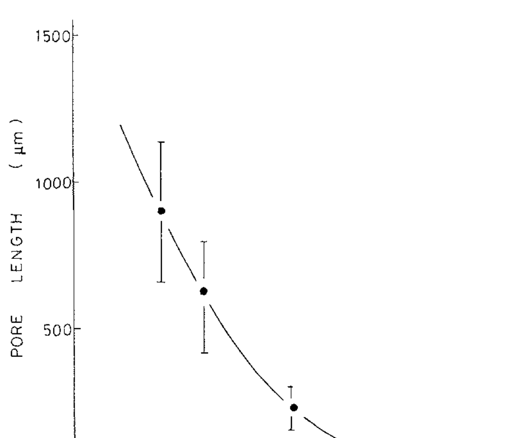

Figure 4 Relationship between pore length and monomer concentration at low irradiation temperature (– 78° C).

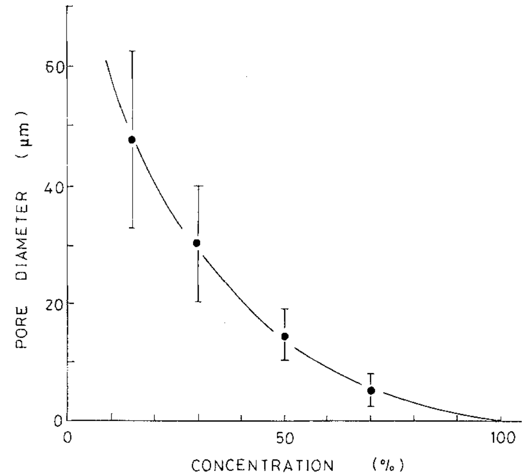

Figure 5 Relationship between pore diameter and monomer concentration at low irradiation temperature (– 78° C).

The length and diameter of the pore decreased with increasing monomer concentration, indicating that the size of the pore is markedly depended on monomer concentration. In high monomer concentrations above 50%, ice is certainly dispersed in the monomeric system and its shape changes with crystallization conditions. The surface structure of the pore is very complex and this indicated that water or ice is intimately interacted. Certainly, since HEMA is a hydrophilic monomer having a hydroxyl group, the interaction of HEMA with water is proposed.

The microphotograph of the sample with a high monomer concentration (70%) is shown in Fig. 6. According to this photograph, it is found that cylindrical pores are cubically orientated. This indicated that the nucleus of ice is regularly formed with a relatively slow crystallization rate. On the other hand, in lower monomer concentrations below 30%, the many nuclei of ice, which are formed near the surface of the tube, would grow becoming more concentrated toward the centre of the tube. Therefore, a porous structure as shown in Fig. 3 is formed.

3.4. Effect of irradiation temperature on pore size

The effect of irradiation temperature on pore size was examined. The relationship between particle diameter and irradiation temperature is shown in Fig. 7. As irradiation temperature increases, the pore diameter increased markedly, reached a maximum, and then decreased. Thus, it was found

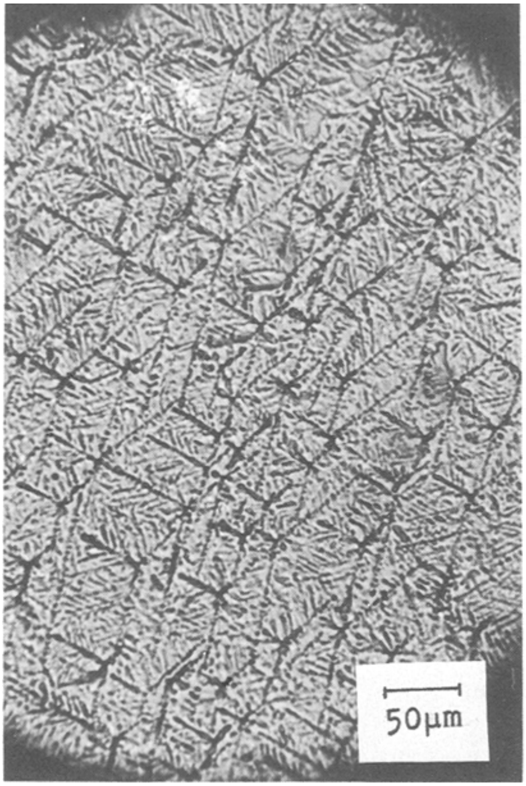

Figure 6 Microphotograph of porous structure in sample from high monomer concentration (70%). Irradiation temperature: $-78°$ C.

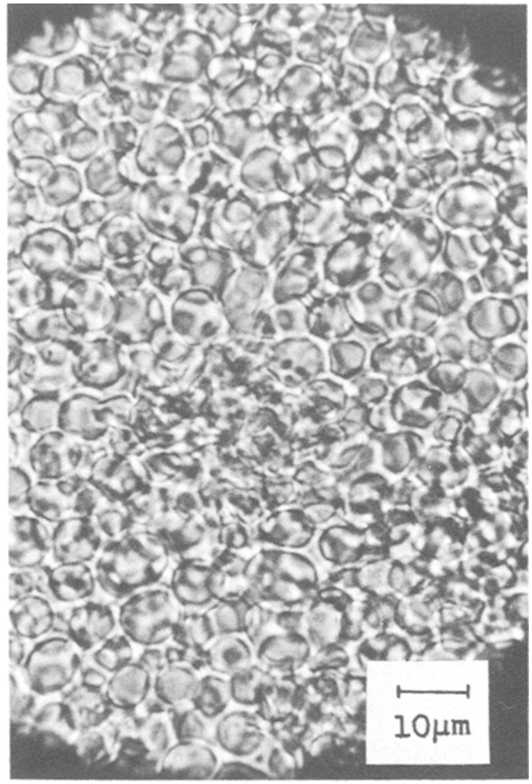

Figure 8 Microphotograph of porous structure in sample obtained at high irradiation temperature (25° C). Monomer concentration: 30%.

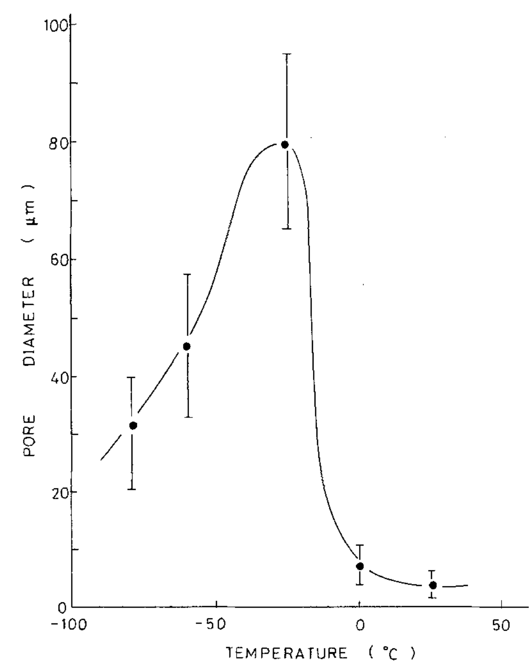

Figure 7 Relationship between pore diameter and irradiation temperature. Monomer concentration: 30%.

that the pore diameter–irradiation temperature curve has a maximum near $-20°$ C. In low temperatures below $-24°$ C, the polymerization of HEMA proceeds almost by homogeneous reaction in the supercooled state as mentioned above. However, in high irradiation temperatures above 0° C where the monomer and water are a homogeneous aqueous solution, the polymerization is a heterogeneous precipitation reaction forming a polymer which is isolated from the monomeric phase due to the lower solubility of the polymer in water. In this case, the shape of the pore formed was an uncontinuous (independent) pore such as the spherical pore shown in Fig. 8. Thus, the mechanism of the pore was different between the low (frozen state of water) and high (non-frozen state of water) temperatures. The pore diameter in high temperatures above 0° C is very small, though monomer concentration is low as seen in Fig. 8. The size of the pore formed with a non-frozen state appeared not to be affected by the increase in temperature. The decrease of the pore diameter by further decrease of the tempera-

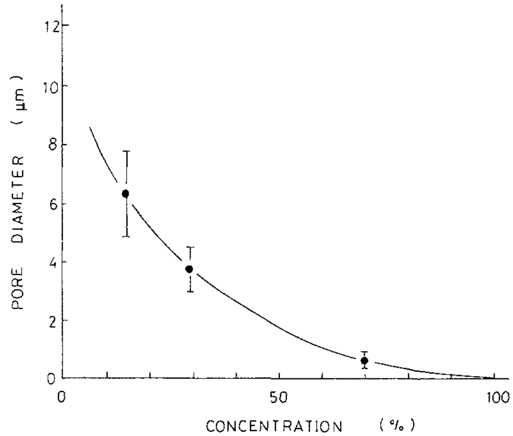

Figure 9 Relationship between pore diameter and monomer concentration at high irradiation temperature (25° C).

ture is due to a greater formation of small ice nuclei at lower temperatures. The growth of ice at temperature region of near -20° C is relatively slow, in which a eutectic composition is slightly formed. This would lead to the appearance of the peak of the pore diameter.

Effect of monomer concentration on pore size in the radiation polymerization at room temperature was examined. The pore diameter increased with increasing monomer concentration, but the size of the pore obtained at room temperature was smaller than that at low temperatures. The polymeric materials having various pore sizes, which were obtained by radiation polymerization of the HEMA–water system, could be used for chemical and biomedical applications. The polymers obtained by the radiation polymerization technique do not contain impurities such as catalysts, and furthermore are sterilized by the radiation. In this work, it was found that porous polymeric materials having various pore sizes have been prepared by choosing a certain polymerization condition.

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