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Hydrophilic polymeric membranes obtained by radiation cast-copolymerization of ethyl acrylate with various monomers

MINORU KUMAKURA, ISAO KAETSU
Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, Takasaki, Gunma, Japan

Hydrophilic polymeric membranes were prepared by radiation cast-copolymerization of ethyl acrylate with various diacrylates and dimethacrylates. The hydration and mechanical properties of the copolymers were studied as a function of copolymerization composition. The degree of hydration, tensile strength, tear strength, elongation at break, and Young's modulus increased with decreasing concentration of the ethyl acrylate component. In a certain copolymerization composition, the hydrophilic polymeric membranes which resemble the mechanical property of the biomedical materials were obtained.

1. Introduction

Hydrophilic materials (hydrogels) such as poly (hydroxyethyl methacrylate) have been used in medical and surgical applications [1, 2]. However, although the principles involved in the formation of hydrogel polymers can not be regarded as of recent origin, it is only during the last ten years or so that the potential of these materials has begun to be realised. By copolymerization of hydroxyethyl methacrylate with hydrophobic monomers such as methyl methacrylate, gels with water contents below 40% are obtained. While, copolymerization with none hydrophilic monomers enables hydrogels having water contents greater than 40% to be produced [3]. Hydrogels are among the best materials for a number of biomedical applications. Unfortunately, the hydrophilic nature of the gel renders it structurally weak, thereby limiting its use as a biomaterial.

This work dealt with hydrophilic polymeric membranes obtained by radiation cast-copolymerization of ethyl methacrylate with various hydrophilic monomers, in which hydration and mechanical properties of the copolymeric membranes were studied. The structural (mechanical) weakness of the hydrogels led to the study of radiation cast-copolymerization of ethyl acrylate with various monomers. The polymeric membranes which do not contain impurity such as polymerization initiator can be obtained by radiation cast-polymerization.

2. Experimental procedure

Ethyl acrylate (EA), tetraethyleneglycol dimethacrylate (4G), nonaethyleneglycol dimethacrylate (9G), nonaethyleneglycol dimethacrylate (P-9G), nonaethyleneglycol diacrylate (A-9G), nonapropyleneglycol diacrylate (AP-9G), and hydroxypentyl methacrylate (HPMA) were obtained from Mitsubishi Gas Chemical Co., Ltd.

Polymeric membranes were prepared by radiation cast-polymerization using a casting flame as follows. The monomer was charged in a casting flame which was constructed by two glass plates, a silicon–rubber gasket, and flame fixing clamps After charging, the casting flame was irradiated (total irradiation dose, $1 \times 10^6\,\mathrm{R\,h^{-1}}$ at room temperature. After irradiation, polymeric membrane was obtained by releasing of the flame fixing clamps. The polymeric membranes having various thicknesses can be obtained by regulation of the thickness of the silicon–rubber gasket.

Tensile strength, Young's modulus, and elongation at break were determined by using specimens

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cut into dumbbell shapes according to ASTMD 638 and, tear strength test was carried out according to ASTMD 1004 with an Instron universal testing instrument (model 1130).

Water content (%) was determined as the ratio of weight of water to the weight of the membrane at swelling equilibrium with at 25° C, and water absorption (%) was determined as the ratio of weight of water to the weight of the membrane at dry state.

3. Results and discussion

3.1. Copolymeric membranes of EA with diacrylates and dimethacrylates

The relation between hydration property and copolymerization composition of EA with diacrylates and dimethacrylates was studied. Relations between the water content and copolymerization composition are shown in Figs. 1 and 2. The water contents of the polymers of A-9G, 9G and 4G were larger than that of EA, and the water contents of the polymers of AP-9G and P-9G were comparable with that of EA. Thus, the degree of hydration in the polymers of the monomers having propyleneglycol units was smaller than those of ethyleneglycol units. As can be seen in Figs. 1 and 2, the degree of hydration of the copolymers of EA with various hydrophilic monomers increased with increasing concentration of the hydrophilic monomers. It was found that the polymers having various hydration properties can be obtained by varying the copolymerization composition in the radiation cast-polymerization. The degree of hydration of the copolymer (1 : 1) of EA with A-9G was larger than that of Calgary lenses which are polymer blend consisting of 50% poly(methyl methacrylate), 40% cellulose acetate butyrate and 10% silicon, and was smaller than that of poly(hydroxyethyl methacrylate) gels [4]. The polymer of EA has hydrophobic and elastic property as well as silicon rubber. The polymer EA can be easily changed to hydrophilic materials keeping slight elastic property by the copolymerization as can be seen in Fig. 1. It is known that the improvement of the property of silicon rubber by polymerization is very difficult though the blending method is possible. The polymeric membrane of EA could be quickly obtained

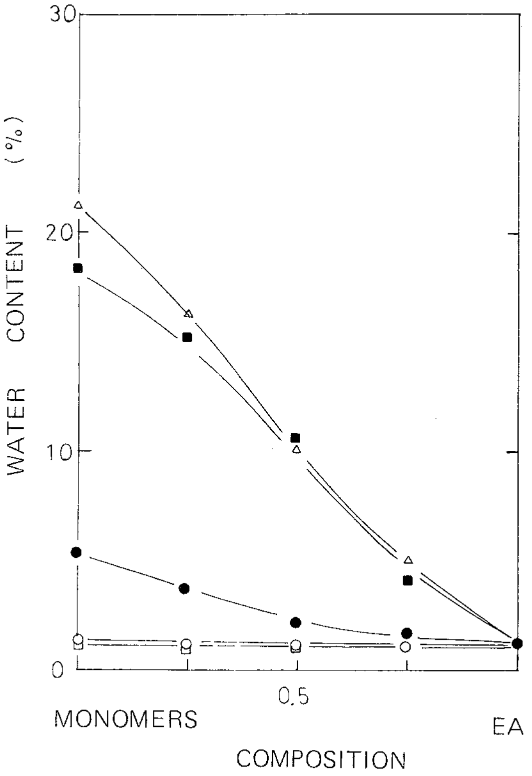

Figure 1 Relation between water content and copolymerization composition. ● 4G, ○ AP-9G, ■ 9G, △ A-9G, □ P-9G.

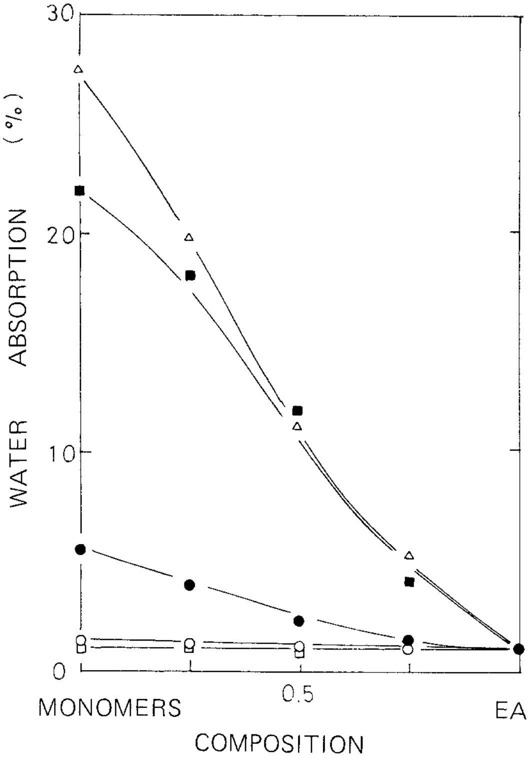

Figure 2 Relation between water absorption and copolymerization composition. The comonomers are the same as those in Fig. 1.

by radiation cast-copolymerization with bifunctional monomers such as diacrylates and dimethylacrylates though the polymerizability of EA is relatively low. In this work, the bifunctional monomers having a large number of the ethyleneglycol and propyleneglycol units were used because the monomers of the large number of the ethyleneglycol or propyleneglycol unit have usually hydrophilic property. The water content and absorption of the polymer of 9G was larger than that of 4G in Figs. 1 and 2, indicating that the hydrophilic property is markedly dependent on the number of ethyleneglycol units. The hydrophilic property of the polymer of polyethyleneglycol methacrylates would be based on the absorption ability of the polar group such as the ether bond and the configuration of the polar group in the polymer chain. In the copolymerization of EA with these monomers, it is considered that the reaction proceeds by alternate polymerization. The polymers obtained by such a reaction would provide a reasonable configuration for accessibility of water. Indeed, the water content and absorption of the copolymers increased monotonously with the increasing component of EA.

Mechanical properties of the polymeric membranes from the copolymerization of EA with diacrylates and dimethacrylates were studied. The relation between the tensile strength and copolymerization composition is shown in Fig. 3. The tensile strength of EA polymer increased markedly with copolymerization, in which the addition of 4G was the predominant effect. Though the tensile strengths of both 4G and P-9G polymers were comparable with each other, the tensile strengths of the copolymer (1 : 1) of EA with these monomers show a large difference. The tensile strength dependency curve by copolymerization composition in the 4G–EA system was a linear one, while that in the P-9G–EA system was convex. This result suggests that the polymer structure makes a difference between both copolymers. The curve shape in the 9G–EA, A-9G–EA, and AP-9G–EA systems, suggesting that the polymer structure of these copolymers are similar each other. The tensile strength of P-9G polymer was larger than that of AP-9G polymer, and also, the tensile strength of the 9G polymer was larger than that of the A-9G polymer, indicating that the tensile strength of the polymers is considerably affected by the presence of methyl group. Furthermore, the tensile strength of the copolymers in the 9G–EA system was smaller than that in the 4G–EA system, though both 9G and 4G are dimethacrylate monomers, suggesting that the tensile strength of the polymers decreased with the increasing number of ethyleneglycol units. The tensile strength of the copolymer (1 : 1) of EA with 4G was comparable with that of medical grade poly(vinyl chloride) [5].

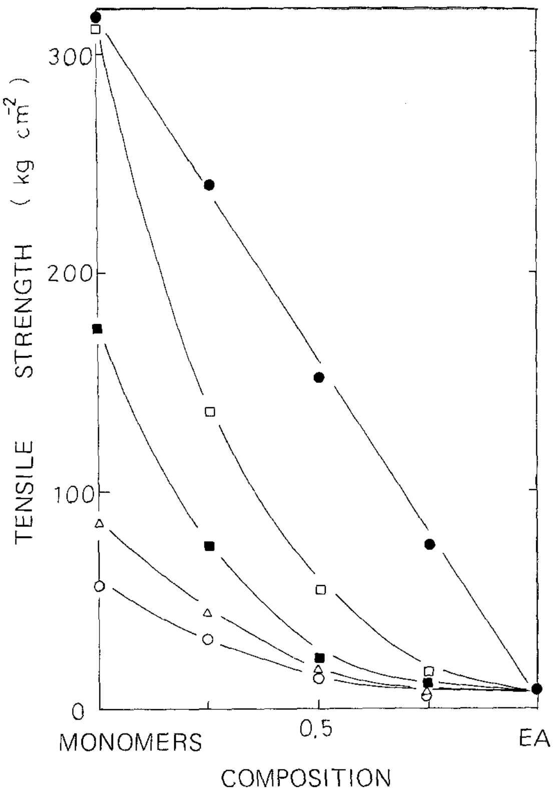

Figure 3 Relation between tensile strength and copolymerization composition. The comonomers are the same as those in Fig. 1.

The relation between elongation at break and copolymerization composition is shown in Fig. 4. The elongations of 4G, 9G, A-9G, P-9G, and AP-9G were small, so that the polymers having a flexible property could be obtained in the high concentration of EA. The elongation of EA polymer was large and was larger than that of medical grade silicon rubber [5]. This elongation of EA polymer decreased with the increasing concentration of diacrylates or dimethacrylates. The elongations of the copolymer (3 : 1) of EA with diacrylates or dimethacrylates were comparable with that of poly(hydroxyethyl methacrylate), of which their tensile strengths were

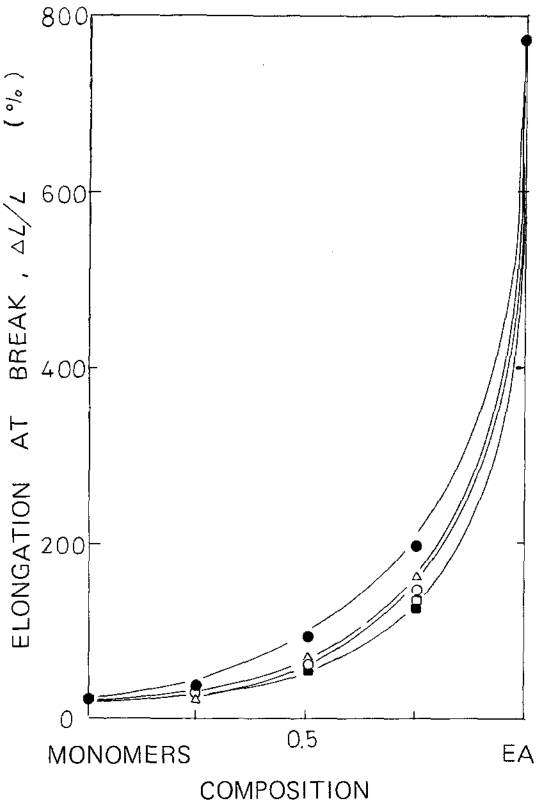

Figure 4 Relation between elongation at break and copolymerization composition. The comonomers are the same as those in Fig. 1.

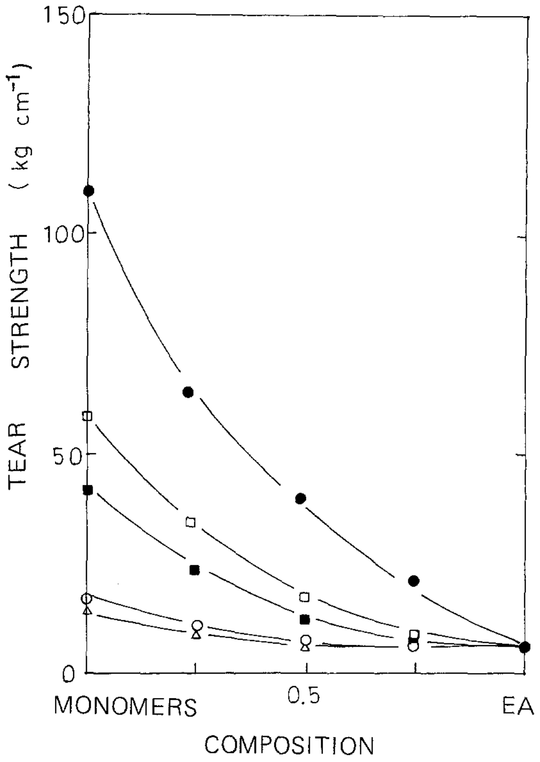

Figure 5 Relation between tear strength and copolymerization composition. The comonomers are the same as those in Fig. 1.

larger than that of poly(hydroxyethyl methacrylate) [6]. Though the degree of hydration of the flexible copolymers resulting from high AE content is slightly small in comparison with that of poly(hydroxyethyl methacrylate), various biomedical applications can be considered.

The relation between tear strength and copolymerization composition is shown in Fig. 5. The tear strength of 4G polymer was larger than those of 9G, A-9G, and AP-9G polymers. This trend was the same as that in tensile strength. The tear strengths of the copolymers in the 4G–EA system of 1 : 1 and 3 : 1 mixtures were comparable with those of silicon rubber and polyurethane used for medical purposes [7]. Furthermore, the tensile strengths of these copolymers were relatively large, as described above. Thus, the copolymers of EA with diacrylates or dimethacrylates obtained in this work appeared to be hard flexible materials. This characteristic was different from the materials (acrylates) resulting from ethyl and butyl methacrylates (2.5%) with methylmethacrylate (7.5%), which has been studied by Person and Jones [8].

3.2. Copolymeric membranes of EA with HPMA

The polymer of HPMA having the five numbers of the methylene unit was measured by copolymerization with EA. The relation between the degree of hydration and copolymerization composition is shown in Fig. 6. The degree of hydration of HPMA polymer was smaller than that of poly(hydroxyethyl methacrylate), but was larger than that of EA polymer. However, it is expected that the mechanical property of the copolymers is larger than that of poly(hydroxyethyl methacrylate) and these copolymers have a flexible property without swelling with water. The water content and absorption of the copolymers increased with increasing concentration of HPMA, and the water absorption of the copolymer (1 : 1) was comparable with those of natural rubber and poly(vinyl chloride). The mechanical properties such as tensile strength and Young's modulus of the copolymers were tested as shown in Figs. 7 and 8. The tensile strength of HPMA polymer was the same order with those of P-9G and 4G polymers and tensile strength dependency curve shape by

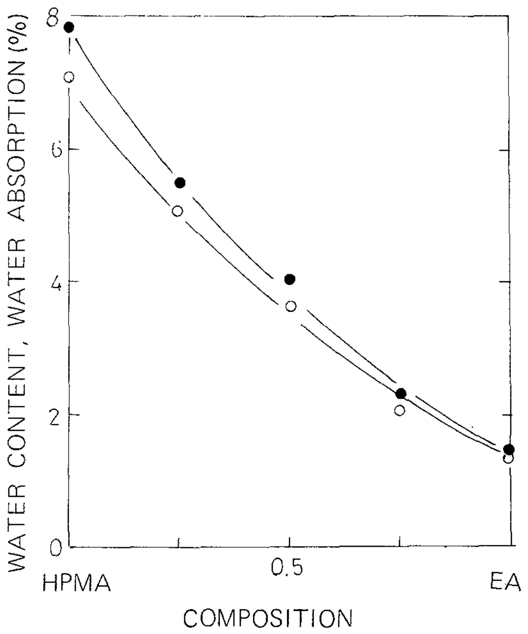

Figure 6 Relation between water content or water absorption and copolymerization composition in HPMA–EA system. ○ water content, ● water absorption.

copolymerization composition in HPMA–EA system was similar to that in P-9G–EA system. However, the tensile strength of the copolymer (1 : 1) in HPMA–EA system was smaller than that in P-9G–EA system, suggesting that the polymer structure of the copolymer in HPMA–EA system is different from that in P-9G–EA system owing to the difference of methacrylate and dimethacrylate. The tensile strength of the copolymer (3 : 1) in HPMA–EA system was slightly larger than that of silicon rubber and smaller than that of polyurethane, though the Young's modulus of the copolymer (3 : 1) in HPMA–EA system was larger than that of silicon rubber and was the same as that of polyurethane for medical use [7]. Thus, it was found that the copolymeric membranes in HPMA–EA system were slightly hydrophilic materials having flexible property compared with those in diacrylates–EA and dimethacrylates–EA systems. The copolymeric membranes obtained in this work were transparent, which was differed from other materials such as silicon rubber and polyurethane.

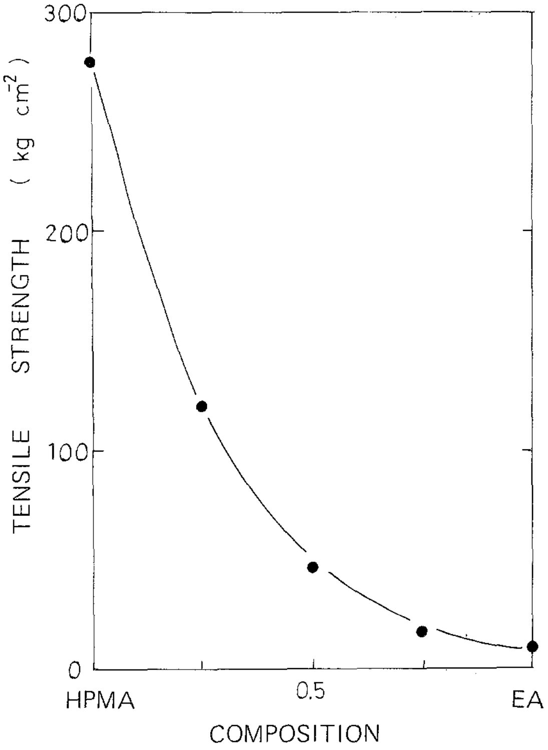

Figure 7 Relation between tensile strength and copolymerization composition in HPMA–EA system.

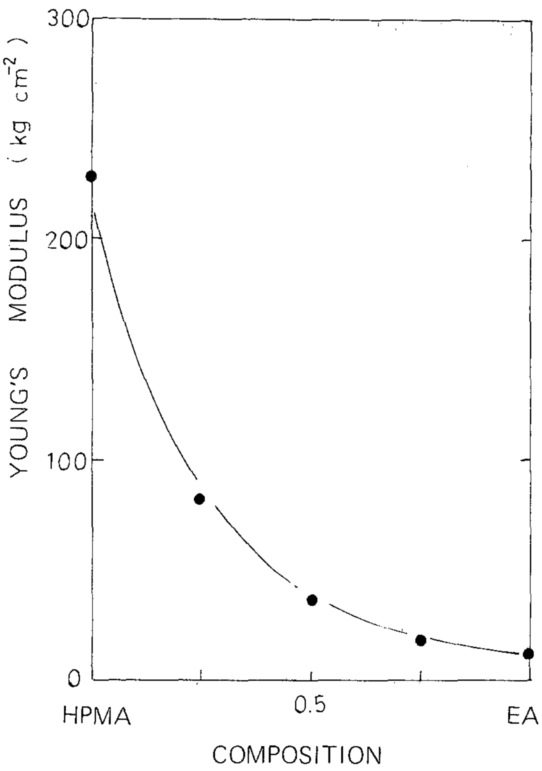

Figure 8 Relation between Young's modulus and copolymerization composition in HPMA–EA system.

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