RADIATION POLYMERIZATION OF 2-HYDROXYETHYL METHACRYLATE–VINYL PYRROLIDONE–WATER SYSTEM

Minoru KUMAKURA and Isao KAETSU

Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, Takasaki, Gunma, Japan

Received June 1st, 1987
Accepted November 23rd, 1987

Radiation polymerization of 2-hydroxyethyl methacrylate–vinyl pyrrolidone–water system at low temperature was studied. The polymerization rate–irradiation temperature curve had a maximum peak at near glass transition temperature, and it was shifted to the site of high temperature with increasing monomer concentration. The polymerization rate in vinyl pyrrolidone at low temperatures was accelerated by the addition of water. The polymers obtained by radiation polymerization of 2-hydroxyethyl methacrylate–vinyl pyrrolidone–water system at low temperatures were a high hydrophilicity and had porous structure.

Hydrophilic polymers such as hydrogels are among the best materials for number of biomedical applications. There is no precise and limiting definition of hydrogels and, as can be seen, problems arise in the use of the term. The most useful description is, however, that hydrogels are water swollen polymer networks of either natural or synthetic origin and of these it is the cross-linked covalently bonded synthetic hydrogels that have grown most dramatically in use. The recent developments and interest in the field can be traced back to the studies of Wichterle and Lim who first indicated the usefulness in biomedical applications of the polymer of 2-hydroxyethyl methacrylate.[1] The polymerization of 2-hydroxyethyl methacrylate and the properties of its polymer have been studied by many workers.[2–4] Recently, Hosaka et al. have studied the properties of the copolymers of methyl methacrylate and vinyl pyrrolidone for the purpose of making soft contact lenses.[5]

In this work, radiation polymerization of 2-hydroxyethyl methacrylate–vinyl pyrrolidone–water system at low temperatures was studied from the aspect of making hydrophilic soft porous gels.

EXPERIMENTAL

Materials. 2-Hydroxyethyl methacrylate (HEMA) and vinyl pyrrolidone (NVP) were obtained from Tokyo Kasei Industry Co., Ltd.

Irradiation. The mixture solution of monomer and water was charged into a glass tube, and used for irradiation. The γ-irradiation with Co 60 source was performed at various temperatures using coolants; temperatures of 0, −24, −45, and −63°C were obtained by the freezing points of water, carbon tetrachloride, monochlorobenzene, and chloroform, respectively, The temperatures of −78 and −196°C were obtained with dry ice–methanol and liquid nitrogen, respectively. The irradiation dose and dose rate were 1 Mrad and 1 MR/hr, respectively. After irradiation, the tube was immediately immersed in liquid nitrogen to prevent the postpolymerization, and then it was crushed in cooled water whereupon the polymer was separated.

Hydrophilicity of polymer. The hydrophilicity of polymer was evaluated by measuring water absorption. Water absorption (wt. %) was determined as the ratio of weight of water to the weight of the polymer at dry state.

RESULTS AND DISCUSSION

Effect of Irradiation Temperature on Polymerization Rate

The polymerization of HEMA–water, NVP–water, and HEMA–NVP–water systems were carried out by γ-ray irradiation at low temperatures, and their polymerization rates were measured. The relationship between polymerization rate and irradiation temperature is shown in Fig. 1. The polymerization rate in HEMA–water system (monomer concentration, c_M 10 vol. %) increased with increasing irradiation temperature. But, NVP–water system (c_M, 10 vol. %) did not polymerize at irradiation temperature range of −100–25°C. On the other hand, the polymerization rate in HEMA–

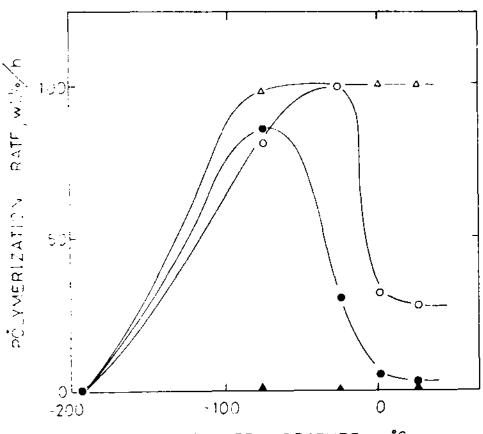

FIG. 1

Effect of irradiation temperature on polymerization rate. Systems: HEMA–water (c_M 10 vol. %) △; NVP–water (c_M 10 vol. %) ▲; HEMA–NVP–water (HEMA : NVP = = 1 : 3), c_M 10 vol. % ●, c_M 30 vol. % ○

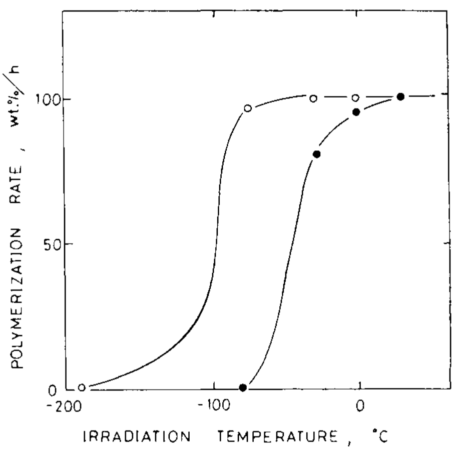

FIG. 2

Effect of monomer composition on polymerization yield in HEMA–NVP–water (irradiation temperature 0°C). Monomer concentration (vol. %): ● 10, ○ 30, □ 70

–NVP–water system (c_M 10 and 30 vol. %) increased, reached a maximum, and then decreased with increasing irradiation temperature. This result indicated that the polymerization of HEMA–NVP–water system proceeds at low temperatures only. The peaks of the polymerization rate in HEMA–NVP–water system (c_M 10 and 30 vol. %) appeared at the temperatures of about −80 and −25°C, respectively, indicating that the position of the peak was shifted to the side of high temperature with increasing monomer concentration. HEMA is glass-forming monomer, which gives an amorphous glassy state at low temperatures. We have studied the effect of water in the radiation polymerization of HEMA–water, and it presented that the polymerization rate of HEMA at low temperatures was accelerated by addition of water[6]. The glass transition temperature (T_g) of HEMA was −96°C, at which the polymerization rate in HEMA–NVP–water system was considerably large as seen in Fig. 1. NVP is non glass-forming monomer, so that NVP and water at about −100°C are crystallized each other. At low temperatures of HEMA–NVP–water system (HEMA : NVP = 1 : 3), the glass phase of HEMA and crystals for NVP and water are mixed. However, it is proposed that most of NVP becomes to be glass state by the presence of glass forming monomer such as HEMA, forming an eutectic composition at low temperatures, and it leads to copolymerization of HEMA and NVP. In fact, the polymerization rate in HEMA–NVP–water system at near T_g was

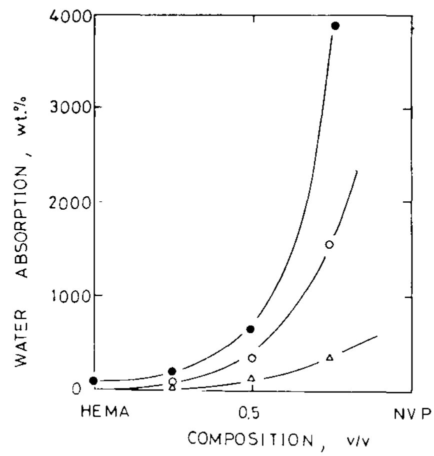

FIG. 3

Relationship between polymerization rate and irradiation temperature: NVP–water (c_M 30 vol. %) ○; NVP ●

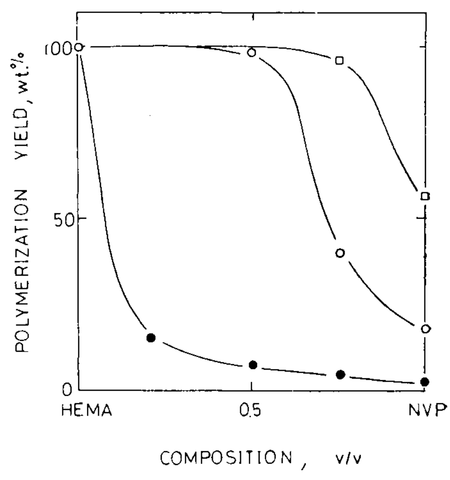

FIG. 4

Relationship between water absorption and monomer composition in the polymers from HEMA–NVP–water (irradiation temperature −78°C). Monomer concentration (vol. %): ● 10, ○ 30, △ 70 very large in which the polymerization yield was a maximum, though the polymerization of NVP–water system did not occur.

Effect of Monomer Composition on Polymerization Yield

The effect of monomer composition on polymerization at 0°C in HEMA–NVP–water system was studied. The relationship between polymerization yield and monomer composition is shown in Fig. 2, as a function of monomer concentration. The polymerization yield in low monomer concentration below 30 vol. % increased with increasing HEMA component. This indicated that the polymerization in HEMA–NVP–water system at low temperatures is intimately related on the content of glass-forming monomer.

Effect of Water on Polymerization of NVP

The effect of water on the polymerization of NVP at low temperatures was examined. The polymerization rate curve in NVP–water system (c_M 30 vol. %) was shifted to the side of low temperature in comparison with that in NVP system as shown in Fig. 3. This suggested that the polymerization of non glass-forming monomer such as NVP at frozen state was accelerated by the presence of water. This acceleration of the polymerization seems to be the contribution of the species resulting from the degradation of water.

Effect of Monomer Composition on Hydrophilicity

The hydrophilicity of the polymers from HEMA–NVP–water system at low temperatures was examined. The relationship between water absorption and monomer composition is shown in Fig. 4. The water absorption of the polymers increased markedly with increasing NVP composition, in which the water absorption in low monomer concentration was larger than those in high monomer concentrations. From this result, it was found that high hydrophilic polymers having a porous structure can be obtained by radiation polymerization of HEMA–NVP–water system at low temperatures. The formation of porous structure in the polymers results in the melt of ice within the polymer matrix after radiation polymerization. Therefore, the nature such as pore size and porosity in the porous polymers varies with monomer concentration, irradiation temperature et al. A large value of the water absorption in low monomer concentrations was due to a high porosity and large pore size. The hydrophilic porous polymers obtained could utilize for various biological and biomedical applications.

REFERENCES

1. Wichterle O., Lim D.: Nature *185*, 117 (1960).
2. Migliaresi C., Nicodemo L., Nicolais L., Passerini S.: J. Biomed. Mater. Res. *15*, 307 (1981).
3. Pinchuk L., Eckstein E. C.: J. Biomed. Mater. Res. *15*, 183 (1981).
4. Andrede J. D.: *Hydrogels for Medical and Related Applications.* ACS Symp. Ser., No. 31, Washington 1976.
5. Hosaka S., Yamada A., Tanzawa H., Momose T., Magatani H., Nakajima A.: J. Biomed. Mater. Res. *14*, 557 (1980).
6. Kumakura M., Fujimura T., Kaetsu I.: Eur. Polym. J. *19*, 621 (1983).