Studies on Irradiation of Agar–Agar in the Solid State: On the Changes of Thermal Property of Agar–Agar Hydrogel Produced by Irradiation*

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SYNOPSIS

Solid agar–agar was irradiated with ^{60}Co gamma-rays, and effects of radiation on the crosslinks of agar–agar molecule were studied by measuring the melting and setting points of the agar–agar hydrogel at different radiation dose and elapsed time after irradiation.

INTRODUCTION

It is well known that many molecules are rendered less stable if they are irradiated,[1,2] and also that some polysaccharides, such as cellulose and carrageenans, form a thermoreversible gel.[3,4] However, the thermal property changes which accompany a change of crosslinks of polysaccharide chains in a gel are not clear. It was, therefore, considered desirable to study the effects of radiation on the crosslinks of agar–agar molecule. The effects of radiation on agar–agar are also of interest to those who study the effects of radiation on organisms grown in this biomaterial.

Changes of the crosslinks can be followed conveniently by measuring the melting and setting points of agar–agar hydrogel as functions of radiation dose and elapsed time after irradiation.

EXPERIMENTAL

Material

Agar–agar used in this work was a commercial material produced by the Junsei Chemical Co., Ltd.

Apparatus and Procedure

In irradiation, the solid agar–agar was put into an irradiation bottle and irradiated with ^{60}Co gamma-rays in air at room temperature at dose rate of 1.3×10^5 rad/h.

In thermometry, at same time or different times after irradiation, the irradiated solid agar–agar was dissolved in distilled water at about 100°C, after gelling the agar–agar solution at 20°C for 24 h the melting point was measured, or after holding the agar–agar solution at 30°C for 1 h and cooling the setting point was measured.

In calculation of heat of reaction for crosslinking processes, the heat energy required to dissociate or associate crosslinks of agar–agar hydrogel was calculated using the melting or setting point given by the equation of Eldridge and Ferry,[3]

$$\log_{10} C = \Delta H_{m,s}/2.303RT_{m,s} + \text{const} \qquad (1)$$

where C is the agar–agar concentration (g/L), $\Delta H_{m,s}$ is the heat of reaction for the crosslinking processes of the agar–agar hydrogel (kcal/mol of crosslinks), or the agar–agar hydrosol (kcal/mol of crosslinks), R is the gas constant, and $T_{m,s}$ is the melting point of the agar–agar hydrogel (K) or the setting point of the agar–agar hydrosol (k). Equation (1) is converted to

$$\Delta H_{m,s} = (k \log_{10} C_1/C_2)(1/T_1 - 1/T_2)$$
$$k = 2.303 \times R \qquad (2)$$

RESULTS AND DISCUSSION

The changes in melting and setting points of agar–agar hydrogel at various radiation doses were studied

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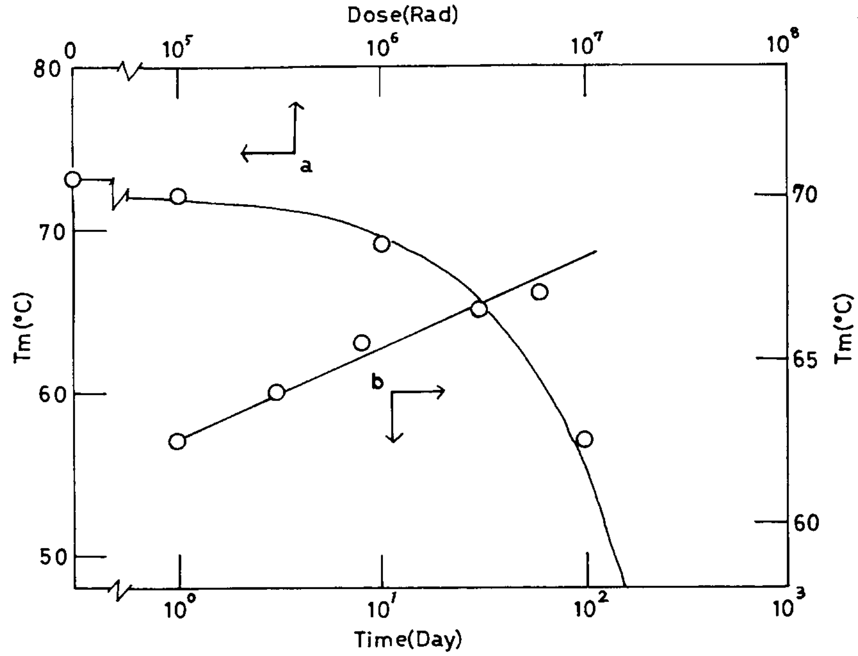

Figure 1 (a) Melting point vs. radiation dose (0.5% agar–agar hydrogel). (b) Melting point vs. time after irradiation (0.5% agar–agar hydrogel and 3×10^6 rad).

with 0.5–3.0% agar–agar. Figures 1(a) and 2(a) show the relations between the values of the melting and setting points and the radiation dose. The $T_{m,s}$ value of the agar–agar hydrogel was found to follow

$$T_{m,s} = a \exp(-kr) \tag{3}$$

where r is the absorbed dose (rad) and a and k are adjustable constants, whereas the changes in melting

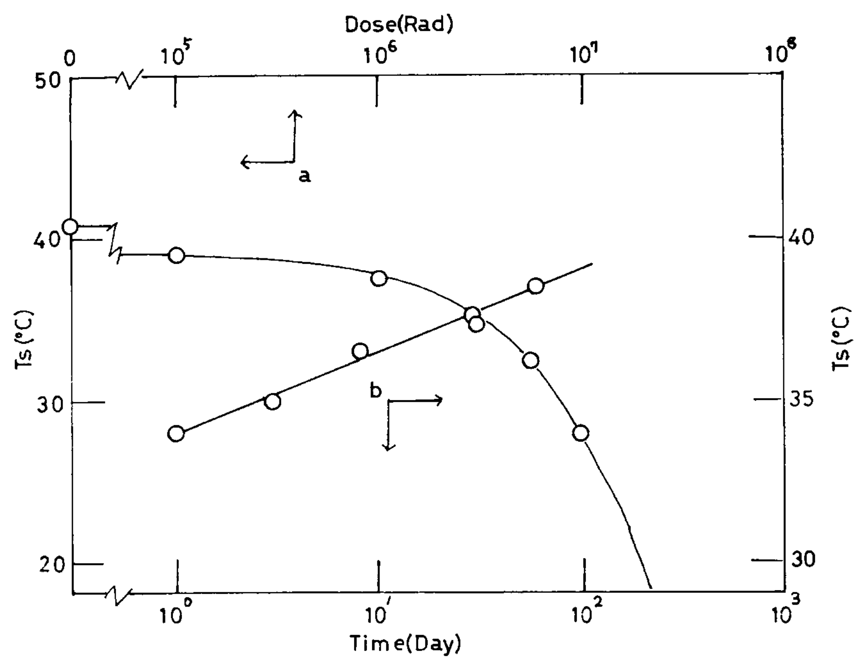

Figure 2 (a) Setting point vs. radiation dose (0.5% agar–agar hydrosol). (b) Setting point vs. time after irradiation (0.5% agar–agar hydrosol and 3×10^6 rad).

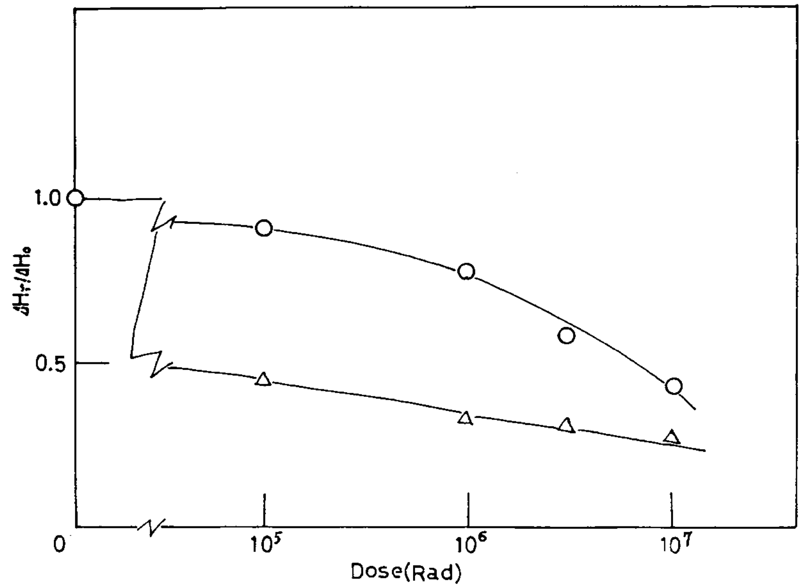

Figure 3 Heat of reaction vs. radiation dose for various crosslinking processes: (○) Gel_I; and (△) Gel_{II}.

and setting points of agar–agar hydrogel at different times after irradiation (3×10^6 rad) were studied with 0.5–3.0%. Figures 1(b) and 2(b) show the relations between the values of melting and setting points and the time after irradiation. The $T_{m,s}$ value of the agar–agar hydrogel was found to follow

$$T_{m,s} = a + b \log t \quad (4)$$

where t is the time (day) after irradiation and a and b are adjustable constants.

From these results, it seems that the depression of $T_{m,s}$ value is concerned to a decrease of the crosslinks due to destruction of the agar–agar molecule caused by gamma irradiation, whereas the increase of $T_{m,s}$ value by recovery of the crosslinks of the irradiated agar–agar molecule depends on the elapsed time after irradiation to a certain extent.

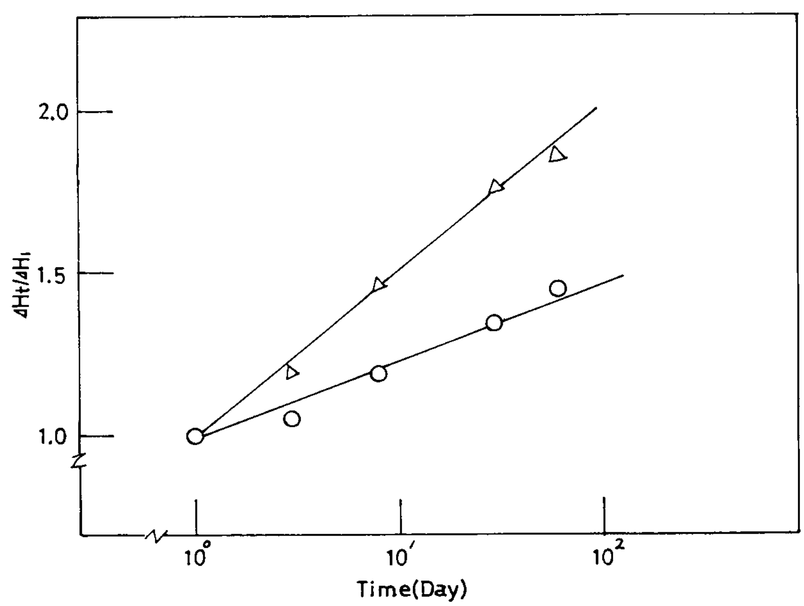

Figure 4 Heat of reaction vs. time after irradiation (3×10^6 rad) for various crosslinking processes: (○) Gel_I; (△) Gel_{II}.

Also, the changes in heat energy required to dissociate or associate crosslinks of agar–agar hydrogel with the irradiation were estimated by the equation of Eldridge and Ferry. If such changes in melting point and heat of reaction are compared to changes in setting point and heat of reaction, then the changes in the crosslinking processes of agar–agar are obtained by the combination of the melting point and setting point data, since the melting point or the setting point in a crosslinking system is considered to be the point at which a 3-dimensional network disappears or first appears, respectively. In the case of this particular agar–agar sol–gel transition the 3-dimensional networks must be entrapped in considerable amounts of water and formed by crosslinks between polysaccharide chains. Suppose that on cooling agar–agar hydrosol (Sol) the polysaccharide chains in the random coil state associate in the double helices to crosslink the chains in a 3-dimensional network (Gel_I) and, subsequently or simultaneously, the double helices could combine into a large aggregates (Gel_{II}). Then the relations between the values of heat of reactions (of setting and of difference of melting − setting) and the radiation dose are obtained for Gel_I and Gel_{II}, and shown in Figure 3. Figure 4 shows the relations between the values of heat of reactions (of setting and of difference of melting − setting) and the time after irradiation for Gel_I and Gel_{II}. With increasing the radiation dose or the elapsed time after irradiation, the heat of reaction of Gel_{II} is lower or higher than that of Gel_I, respectively. It is understood that radioresistance or radiorecovery of crosslinks in the Junction zone system (Gel_{II}) is lower or higher than that in the double helix system (Gel_I), respectively. This conclusion is supported by our previous experiment on X-ray diffractiometry.[5]

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