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Effects of irradiation temperature on swelling and shrinking kinetics of thermo-responsive gels prepared by radiation-induced polymerization

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Abstract

Acryloyl-L-proline methyl ester (A-ProOMe) gels were prepared by γ-ray irradiation of aqueous monomer solutions at temperatures ranging from 0 to 60°C. The gels with heterogeneously and homogeneously crosslinked structures were obtained by irradiation at temperatures higher and lower than the lower critical solution temperature (LCST) of approximately 14°C, respectively. The former gel had a faster shrinking rate than that of the latter gel. In contrast, the swelling rate of the gels changed drastically at irradiation temperatures between 20 and 30°C higher than the LCST. The irradiation temperature dependence of the responsive kinetics of the A-ProOMe gels was elucidated by observing the microscopic homogeneity of the gel network structure with a scanning electron microscope (SEM). These results clearly show that the responsive kinetics of the gels can be controlled by adjusting the irradiation temperature in relation to the homogeneity of the nanoscopically crosslinked structure and the microscopic gel network.

Keywords: Irradiation temperature effect; Thermo-responsive gel; Swelling–shrinking kinetic

1. Introduction

The responsive gels, which exhibit a large volume transition in response to small changes in environmental factors such as temperature, pH, and solvent composition, [1–6] have been successfully investigated for their application to various devices such as sensors, bio-actuators, and drug delivery systems [7–12]. The swelling–shrinking kinetic of the gels is one of the most important characteristics for performance of the devices.

It is well known that the sizes and homogeneity of crosslinked network structures as well as the formation of a layer with the surface barrier in the initial stage of shrinking influence the responsive rate of the gels. Hirasa et al. [13] reported the shrinking rate of thermo-responsive and sponge-like structured poly(vinyl methyl ester) (PVME). In this case, the irradiation for radiation-induced self-bridging is necessary to carry out at different temperatures; that is, pre-irradiation at temperatures below the lower critical solution temperature (LCST) forms a loosely crosslinked network gel followed by a formation of tightly crosslinked network gels by rising the irradiation temperature above the LCST. However, it has not yet been demonstrated why the stepwise irradiation is required to obtain a gel with such a quick response of shrinking.

On the other hand, we reported synthesis of a self-bridged gel by γ-ray irradiation of the monomer in aqueous solutions, in which a monomer was polymerized by γ-ray irradiation, followed by a self-bridging reaction between the two chains of the resulting polymer in the absence of a crosslinker [14]. In this case, the crosslinking network of the gels should be varied with the irradiation temperatures above and below the LCST of the corresponding linear polymer. The linear polymer obtained in the initial stage of irradiation below LCST to form a homogeneous crosslinking network on a nanoscopic scale. Contrary to this, the polymer chains collapse above LCST, and formed a heterogeneous crosslinking network.

In this paper, we report swelling- and shrinking-kinetics of self-bridged gels based on acryloyl-L-proline methyl ester (A-ProOMe) with LCST of 14°C obtained at various irradiation temperatures, and their physical microstructures by means of a scanning electron microscope (SEM) observation.

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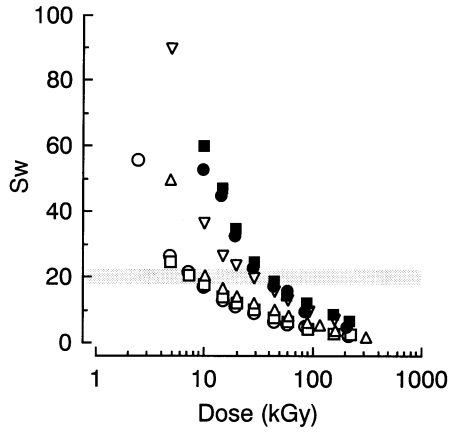

Fig. 1. Equilibrium swelling ratio at 0°C in water for A-ProOMe gels, which were obtained as a function of dose at irradiation temperatures of (○) 0°C, (□) 10°C, (△) 20°C, (▽) 30°C, (●) 40°C, and (■) 60°C.

2. Experimental

2.1. Preparation of A-ProOMe gels

Acryloyl-L-proline methyl ester (A-ProOMe) used as a monomer was synthesized in the same manner as previously reported [15]. The preparation of poly(A-ProOMe) gels with a characteristic self-bridged network structure is as follows. An aqueous solution with 30% (v/v) A-ProOMe after bubbling a dry nitrogen was transferred into a 5 mm inner diameter glass ampoule. The ampoules were irradiated under a nitrogen atmosphere with doses of 2.5 to 440 kGy using γ-rays from a ^{60}Co source at temperatures of 0, 10, 20, 30, 40 and 60°C. The resulting gels were separated from the ampoule and cut off to the same length as the diameter. The gels were then immersed in an excess amount of acetone, and gradually replaced into a distilled-deionized water to remove unreacted monomer.

2.2. Swelling ratio of A-ProOMe gels

The swelling ratio (Sw) of A-ProOMe gels was calculated from the following equation,

$$\mathrm{Sw} = \frac{W_\mathrm{s} - W_\mathrm{d}}{W_\mathrm{d}},$$

where W_s is the weight of a swollen gel at a certain temperature and W_d is the weight of dried one. The weight of the gel was measured gravimetrically after wiping excess water at the surface of gel.

2.3. Swelling and shrinking rates of A-ProOMe gels

In order to investigate swelling- and shrinking-kinetics of A-ProOMe gels, the monomer in an aqueous solution was irradiated with doses of 7.5, 7.5, 10, 30, 45 and 60 kGy at temperatures of 0, 10, 20, 30, 40, and 60°C, respectively. The conversion of the gels were determined by weight ratio of the ethanol-insoluble fraction to the feed monomer, and those of the gels prepared at 0, 10, 20, 30, 40, and 60°C were 95–98%. The obtained gels were first swollen at 0°C (an ice water system) until the equilibrium is reached. Then, the swollen sample was transferred in water kept at 40°C. At a prescribed time interval, the sample was taken out from water and weighed after wiping the excess water at the surface of gel. The swelling- and shrinking-kinetics for A-ProOMe gels were measured by repeating between the two temperatures, 0 and 40°C. In this study, the temporal change of gel swelling was evaluated by using the normalized Sw. The normalized Sw is expressed as following equation:

$$\text{Normalized Sw} = \frac{\mathrm{Sw}_t - \mathrm{Sw}_{40}}{\mathrm{Sw}_0 - \mathrm{Sw}_{40}},$$

where Sw_t is the swelling ratios of the samples at time t after jumping to 0 and 40°C, respectively, and Sw_0 and Sw_{40} are swelling ratios of the samples treated at temperatures of 0 and 40°C, respectively, when the equilibrium is reached.

2.4. Microscopic observation

The physical structure of the gels in the swollen state and in the shrunken state at given temperatures were observed by using SEM. For this purpose the treated gels were frozen in refrigerator kept at −85°C and lyophilized. The cross-section of the gel after coating with gold was observed with a JEOL JXA-733 SEM.

3. Results and Discussion

3.1. Swelling profiles of A-ProOMe gels

A-ProOMe gels with self-bridged networks were obtained with irradiation doses ranging from 2.5 to 440 kGy at irradiation temperatures of 0, 10, 20, 30, 40, and 60°C. The dose dependence of the swelling ratio (Sw) of the gels treated with water at 0°C is shown in Fig. 1 as a function of the irradiation temperature. The Sw of the obtained gels gradually decreased with an increase of irradiation dose and greatly depended on the degree of cross-linking [14]. Fig. 1 also shows that a higher irradiation dose is required as the irradiation temperature increases to obtain the A-ProOMe gel with a constant Sw value.

Since it is well known that the swelling and shrinking rates of thermo-responsive gels are proportional to the square of the diameter, [16] we chose gels of the same size to compare the responsive rate of the gels prepared at different irradiation temperatures. We employed irradiation doses of 7.5, 7.5, 10, 30, 45, and 60 kGy for irradiation temperatures of 0, 10, 20, 30, 40, and 60°C, respectively, to obtain gels with the same Sw of approximately 20 and the diameter of about 9 mm at 0°C in water.

The gels prepared at temperatures below and above the LCST exhibited a similar equilibrium swelling ratio at temperatures ranging from 0 to 40°C, and they had a volume phase transition temperature (VPTT) of around 14°C as

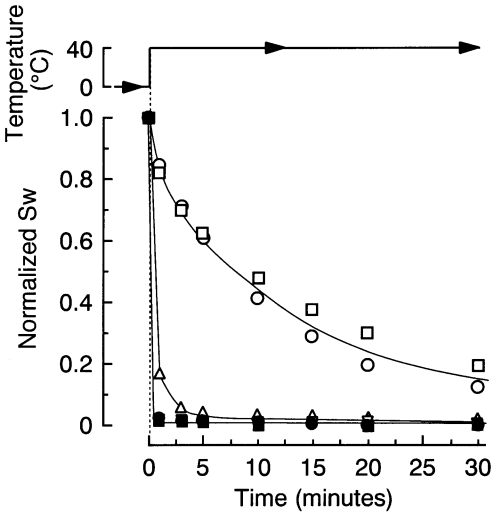

Fig. 2. Shrinking profile as a function of time after a temperature jumping to 40°C from 0°C for A-ProOMe gels obtained with a dose of 7.5, 7.5, 10, 30, 45 and 60 kGy at (○) 0°C, (□) 10°C, (△) 20°C, (▽) 30°C, (●) 40°C, and (■) 60°C, respectively.

previously reported [15]. Therefore, it is clear that irradiation conditions such as dose and temperature affect the formation of the network structure that govern their Sw of the gels but not the hydrophobic characteristics of the gels which govern their VPTTs.

3.2. Shrinking and re-swelling kinetics

We investigated the shrinking kinetics of the gels prepared at 0, 10, 20, 30, 40, and 60°C. Fig. 2 shows the change in the normalized Sw of the gels as a function of time when the swollen gels equilibrated at 0°C are quickly immersed in water at 40°C (above LCST). The shrinking rate was greatly dependent on the irradiation temperature. The gels prepared at 0 and 10°C gradually shrank and reached in the equilibrium states after 2 h. In contrast, the gel prepared at 20°C, above the LCST, shrank very quickly to reach in the equilibrated state less than 5 min. The gels prepared at 30, 40 and 60°C shrank much faster than that prepared at 20°C. The shrinking rates were too fast to determine the exact time in which the gels reached equilibrium (less than 1 min). From these results it is clear that the shrinking rate of the gels prepared at temperatures higher than the LCST drastically increase with increases of irradiation temperature up to 60°C.

The swelling kinetics of the shrunken gels was also affected by the irradiation temperatures at which these gels were prepared. Fig. 3 shows the plots of the normalized Sw versus the time after the shrunken gels equilibrated at 40°C were quickly immersed in water at 0°C (below LCST). The gels prepared at 0 and 10°C gradually swelled and reached in the equilibrium states more than 5 days. The gel prepared at 20°C reached in the equilibrated state one day, which was about 5 times faster than the rates of gels

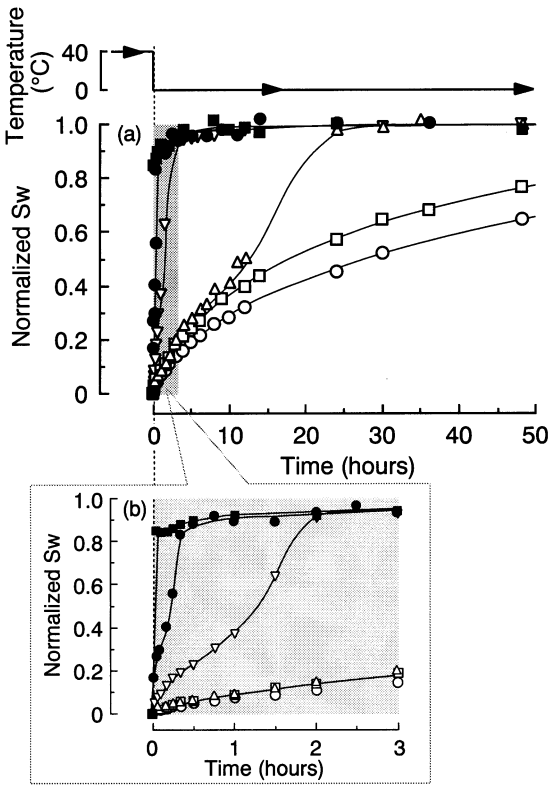

Fig. 3. Swelling profile as a function of time after a temperature jumping to 0°C from 40°C for A-ProOMe gels obtained with a dose of 7.5, 7.5, 10, 30, 45 and 60 kGy at (○) 0°C, (□) 10°C, (△) 20°C, (▽) 30°C, (●) 40°C, and (■) 60°C, respectively.

prepared at 0 and 10°C but much slower than the shrinking rates of the gels prepared at more than 30°C, which swelled and quickly reached the equilibrated state in less than a few hours. Contrary to the shrinking kinetics, there is no clear boundary around the LCST (14°C) for the shrinking rate (the periods required to reach equilibrated states), as shown in Fig. 3(a).

The changes in the normalized Sw of the gels at the initial stage of swelling process are shown in Fig. 3(b). The gels prepared at 0 and 10°C showed very slow responses; the normalized Sw was less than 0.2 even after 3 h. The swelling profile of the gels prepared at 20°C was similar to that of gels prepared at 0 and 10°C, even though the former gels reached the equilibrium states five times faster than the latter gels. This difference resulted from the increase in swelling rate of the gel prepared at 20°C after 10 h, which was not observed in the gels prepared at 0 and 10°C. As the result, the swelling profile shows a sigmoidal shape. The gels prepared at temperatures higher than 30°C reached the equilibrium state much faster than those prepared at temperatures lower than 20°C, and the swelling rate of the gels gradually increased with increases of irradiation temperature up to 60°C. The gels prepared at 30 and 40°C were also swollen by two steps with a sigmoidal shape. Compared with the shrinking kinetics, in which there is a clear boundary of irradiation temperature at which the

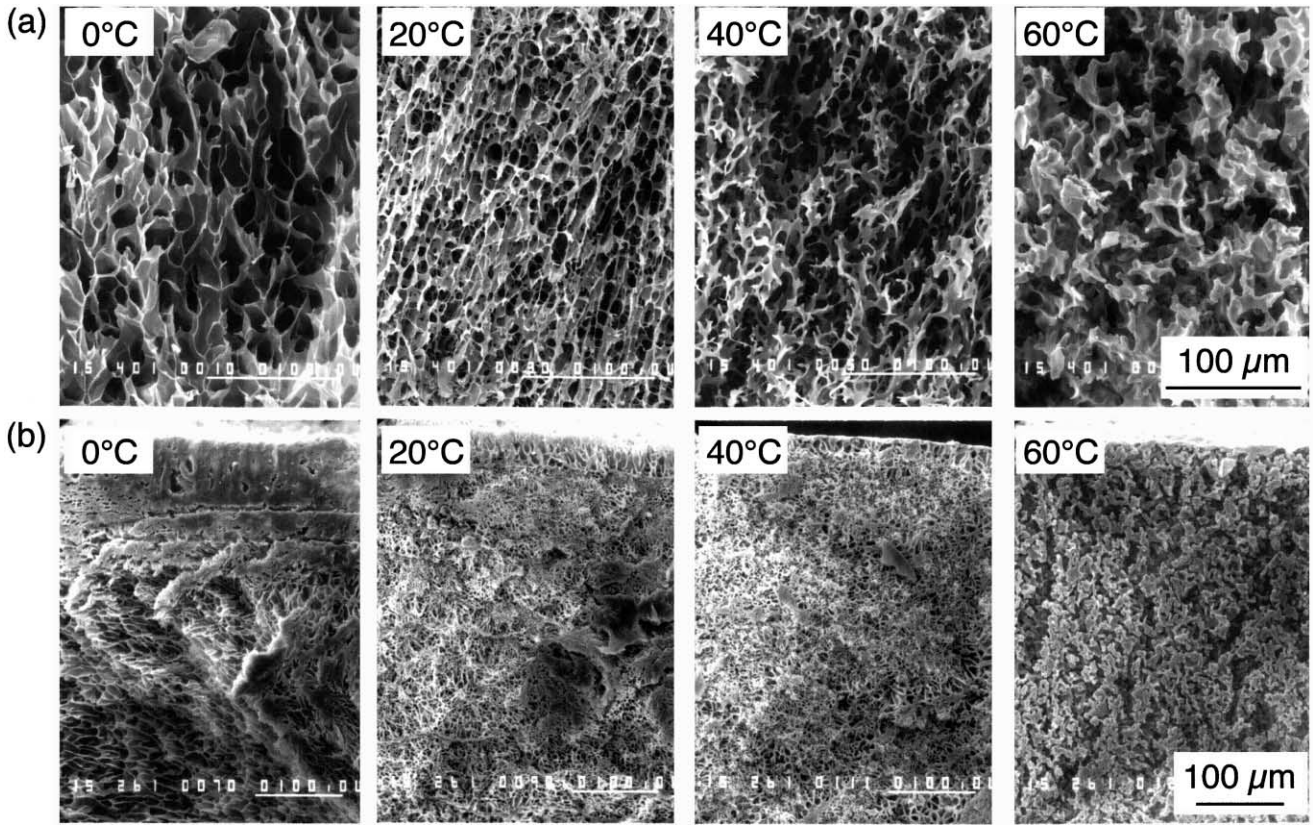

Fig. 4. Cross-sectional SEM views of A-ProOMe gels (a) swollen state with water at 0°C and (b) shrunken up to a normalized Sw of 0.5 at 40°C (see Fig. 2). Gels were prepared at irradiation temperature given in figure with a dose of 7.5, 10, 45, 60 kGy.

shrinking rate changes, the dependence of the swelling kinetics on the irradiation temperature is more complicated. However, the effect of irradiation temperatures on the shrinking and swelling kinetics of the A-ProOMe gels can be elucidated by observation of cross-sections of the gels during the shrinking and swelling processes by means of SEM (vide infra).

A similar dependence of the preparation temperatures on the shrinking- and swelling-kinetics were also observed in *N*-isopropylacrylamide (NIPAAm) or diethyl acrylamide gels prepared by radical polymerization using a crosslinker, initiator, and accelerator [17]. Even though such additives have been used for the preparations of the gels, no detailed studies have been performed on the influence of the gelation temperature with the reactivity between these additives and monomers that affected the gel properties such as transition temperature and responsive kinetics. Contrary to the case of a gel prepared by a radical polymerization, it is not necessary to take into account the effect of the preparation temperature on the reactivity in self-bridged gels prepared by a radiation-induced reaction of monomers without any additives, when we choose the monomers that processed polymerization and crosslinking preferentially compared with degradation, such as NIPAAm and A-ProOMe.

3.3. Microscopic structures observed by means of SEM

The microscopic structures of the gels prepared at 0, 20, 40, and 60°C were compared during the shrinking of the gels. The gels were removed from a 40°C-water bath during the shrinking of the gels and then lyophilized at −85°C, and the cross-sectional structures were examined. Fig. 4(a) shows SEM photographs of the swollen gels equilibrated at 0°C (the starting point of the shrinking process). All the gels prepared at different temperatures had microscopic pore structures; in this respect, there was no difference among these gels. However, we found the difference in the microscopic structures at the midpoint of the shrinkage (the normalized Sw ∼ 0.5), as shown in Fig. 4(b), where the top and the bottom of the pictures correspond to the surface and the inside of the gels, respectively. Only the gel prepared at 0°C, which is lower than the LCST, formed a dense shrinking layer at the surface,[1] whereas the gels prepared at temperatures higher than 20°C had porous structures throughout the entire regions of the gels without any surface layer. Furthermore, above the LCST, the porous structure of the gels gradually increase with increases of

[1] We reported the skin layer formation of A-ProOMe gels prepared with crosslinker during shrinking process. However, we have not conducted SEM observation of the self-bridged gel of A-ProOMe.

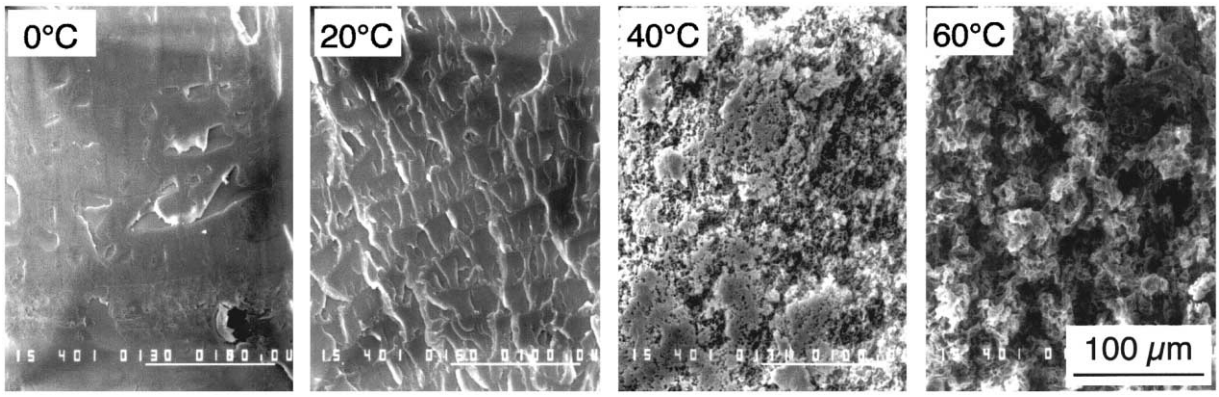

Fig. 5. Cross-sectional SEM views of A-ProOMe gels shrunken completely with at 40°C. Gels were prepared at irradiation temperature given in figure with a dose of 7.5, 10, 45, 60 kGy.

irradiation temperature up to 60°C. These SEM photographs indicate that two factors affect the shrinking kinetics. (1) The size of the porous structure of the gels, which can be obtained by higher irradiation temperatures, increases the shrinking rate. (2) The skin layer that appears during the shrinking of the gel prepared at a temperature lower than the LCST brings about a drastic slowdown of the shrinking rate.

The complicated swelling profiles of the gels prepared at the different temperatures in Fig. 3 are elucidated by the different microscopic porous structures of the gels. Fig. 5 shows SEM photographs of the shrunken gels equilibrated at 40°C (the starting point of the swelling). The gels prepared at 0 and 20°C possess homogeneous wall-like texture, whereas the gels prepared at 40 and 60°C have a microscopic porous structure. Therefore, the slower permeation of water into the homogeneous wall-like texture is expected in the gels prepared at the temperatures lower than 20°C, resulting in the slower swelling kinetics. Among the slow swelling gels, only the gel prepared at 20°C showed the acceleration of swelling after about 10 h (see, Fig. 3a); as the result, the swelling profile of the gel exhibits a sigmoidal shape. This sigmoidal swelling profile is elucidated by taking in account of the change of the microscopic structure during the swelling process. Namely, when the gel prepared at 20°C swelled to some extend, the gel becomes more porous structure, which might be similar to that of the gel at the midpoint (Sw ~ 0.5) of the shrinking, as shown in Fig. 4b; this porous gel structure should be effective to

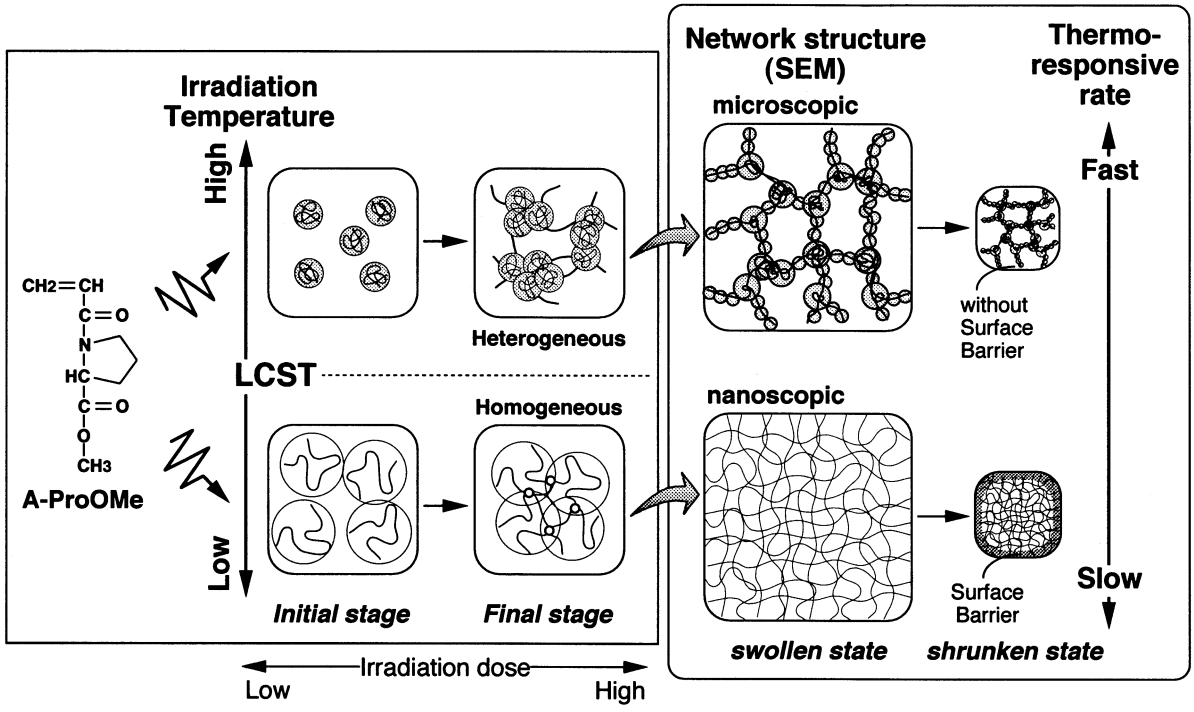

Fig. 6. Proposed model for illustrating the effect of irradiation temperature on the crosslinked network structure of A-ProOMe gels: irradiation at temperatures, (a) above the LCST and (b) below the LCST.

absorb water. The similar sigmoidal swelling profiles observed in the gels prepared at 30 and 40°C are also explained by the fact that these gels possess some homogeneous wall-like texture, which becomes porous during the swelling process.

3.4. Schematic illustration of the relationship between irradiation temperature and responsive kinetics

The effect of the irradiation temperature on the responsive kinetics of the gels is summarized in Fig. 6. The effect is closely related to the homogeneity of the nanoscopic crosslinking and microscopic gel networks. The gel containing the heterogeneous crosslinking was obtained with irradiation at a temperature higher than the LSCT because of nanoscopic phase separation with an aggregation of the initially formed polymers. In contrast, the gel prepared at a temperature lower than the LSCT had an expanded structure due to a high solubility of the initially formed polymer, resulting in the homogeneous crosslinking structure. The aggregation of the initially formed gels can be confirmed by observation of clouding in the solution as well as by a light scattering method [18]. The light scattering of the corresponding linear polymer obtained at the initial stage of gelation showed that the radius of gyration of the initial polymers drastically changed around LCST. Further crosslinking of the gels should proceed homogeneously at temperatures lower than the LCST, resulting in gels consisting of a homogeneous crosslinking structure. In contrast, at temperature higher than the LCST, further crosslinking of the gels should proceed heterogeneously, resulting in gels consisting of a heterogeneous crosslinking structure.

On the other hand, the microscopic gel networks can be observed by means of SEM, as mentioned in the previous section. Namely, the gels consisting of the nanoscopic heterogeneous crosslinking structure have a microscopic heterogeneous gel network without any skin layers and show a very fast shrinking rate. In contrast, the gels consisting of nanoscopic homogeneous crosslinking structures have a microscopic homogeneous gel network with the skin layer and have a very slow shrinking rate. Though the internal structures of gels have been observed by means of laser scanning confocal microscopy as well as SEM, [19] the nanoscopic crosslinking structure cannot be directly observed by spectroscopic measurements. Therefore, we have not yet obtained direct evidence that proves how the nanoscopic crosslinking of the gel develops the formation of microscopic gel network during the preparation of the gels. However, it should be noted that the responsive kinetics of gels can be controlled by changing the irradiation temperature, which has an effect on the homogeneity of the nanoscopic crosslinking structures and the microscopic gel network.

4. Conclusion

All the A-ProOMe gels prepared at different temperatures ranging from 0 to 60°C showed the same volume phase transition, whereas thermo-responsive rates of the gels varied with the irradiation temperature. The gel consisting of heterogeneous and homogeneous nanoscopic crosslinking structures can be prepared by irradiation at temperatures lower and higher than the LCST, respectively. The former gels have faster shrinking rates than those of the latter gels. In contrast, the swelling rates of the gels changed drastically at an irradiation temperature between 20 and 30°C higher than the LCST. The dependence of the responsive kinetics of the gels on the irradiation temperature was elucidated by the microscopic homogeneity of the gel network with a SEM. The responsive kinetics of gels can be controlled by adjusting the irradiation temperature, which has an effect on the homogeneity of the nanoscopic crosslinking structures and the microscopic gel network. Therefore, the radiation-induced gelation technique would be useful in the development of an intelligent material with thermo-responsive properties.

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