Morphology and structure of highly elastic poly(vinyl alcohol) hydrogel prepared by repeated freezing-and-melting

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Abstract: Morphology and structure of poly(vinyl alcohol) (PVA) hydrogel prepared by the "repeated freezing-and-melting" method have been investigated by X-ray diffraction, scanning electron microscopy, light-optical microscopy, and simple tension test. The PVA aqueous solution gelled highly by using this method to show rubber-like elasticity, reflecting the gel network in which the amorphous chains are physically cross-linked by the crystallites. The gel morphology was characterized by the porous structure, which was originated from the gelation of continuous PVA-rich solution phase segregated around copious ice crystal phases formed upon freezing. The high gelling ability involved in this method was closely related to the segregation mechanism.

Key words: Poly(vinyl alcohol), water, gel.

Introduction

It is well known that aqueous poly(vinyl alcohol) (PVA) solution gels gradually upon standing at room temperature, showing an increment in elasticity [1]. It has been widely accepted that the gelation phenomenon is a result of formation of network in which PVA crystallites work as junction points. Recently, relation between the gelation and the liquid-liquid separation was pointed out and the dynamics at early stage of sol-gel transition was interpreted in terms of the spinodal decomposition [2].

On the other hand, it was recently shown by Nambu [3, 4] that aqueous PVA solution gelled highly when the "repeated freezing-and-melting" method was applied, in contrast to the case where the conventional gelling method was used. The gelling procedures in this newly found method were as follows. Aqueous PVA solution was first frozen and then the frozen state was released at a low temperature above 0 °C; this cycle was repeated. With increasing the freezing cycle number, rubber-like elasticity in the resultant gel was much increased, the stickiness inherent in the original solution being lost and the water-resistance also being increased. The similar PVA hydrogels have been prepared through the "freeze drying" process [5], where

aqueous PVA solution was frozen, semi-dried by evacuation in the frozen state and successively immersed in water at room temperature. Characteristic rheological, mechanical and some physical properties of the gels have attracted our attention [3, 6–10]. It remains to be noted that the high conformity of the gels to a living body as well as stability in vivo allows the development for medical use.

As far as we know, PVA is a unique polymer whose hydrogel prepared through the "freezing" shows rubber-like elasticity. We should reveal why the "freezing" involved in the above preparation methods has a good effect on the gelling enhancement for the PVA-water system and how morphology, structure and properties of the gel are related to one another. With respect to morphology of the PVA hydrogel, we find only the description [11] that when the PVA-water system was once frozen, ice crystals were formed within it and growth traces of the crystals were left as pores in the dried gel prepared by evacuation under the frozen state. The detailed studies have not yet been carried out. In this paper, we deal with the PVA hydrogel prepared by the "repeated freezing-and-melting" method. Morphology and structure of the gel, together with the related gelling mechanism, will be studied by using

such techniques as X-ray diffraction, scanning electron microscopy, light-optical microscopy, and simple tension test.

Experimental

Preparation of PVA hydrogels

The PVA sample used was supplied by Kuraray Co., which had the degree of polymerization 3500, and the degree of saponification 99.8 mol %. All the PVA hydrogels were prepared by Nambu's "repeated freezing-and-melting" method [3], as mentioned below.

A 15 wt % PVA aqueous solution was prepared by standing at about 100 °C for 3 h. The hot solution was poured into a circular aluminium mould with a diameter of 12 mm and a thickness of 1.5 mm and then cooled to room temperature. Successively, it was frozen in an electric freezer maintained at about −15 °C. After 23 h, the frozen state was released at room temperature for 1 h. This freezing cycle, which was the same throughout the experiments in this work, was repeated to give the elastic gels. The gels thus obtained were used for the X-ray photographic measurements. Here, vaporization of water from the specimens during the gelation was avoided by sealing the surfaces with aluminium foil. By the similar procedures, sheets of the gel with a thickness of 1.5 mm were prepared for the simple tension test.

Gel specimens with the thickness of 1.5 mm were similarly prepared from solutions containing 5, 10, and 15 wt % PVA. For scanning electron microscopic observations, they were transformed into xerogels by the removal of water in methanol for one day and successive drying under vacuum.

For light-optical microscopy, 2.5 wt % solutions were directly frozen several times between slide and cover glasses to obtain the gels.

Measurements

Wide-angle X-ray diffraction photographs of the hydrogels were taken with Cu K_α radiation monochromated by graphite. During the measurements, surfaces of the samples were sealed by aluminium foil in order to prevent drying.

The xerogels were fractured at liquid nitrogen temperature. The fractured surfaces were decolated by gold and observed by scanning electron microscope.

The light-optical microscopic observations for the hydrogels were carried out by a polarization microscope with parallel polarizers.

Stress-strain curves for the gel strips of 3 mm width, cut from the hydrogel sheets, were recorded at room temperature, using an extension tester, with an extension speed of 40 mm/min and 20 mm between the clamps.

Results and discussion

In Figure 1 we show the X-ray diffraction patterns of the 15 wt % PVA hydrogels with freezing cycle numbers, $N = 7, 14$, together with that of the hydrogel before freezing $(N = 0)$, obtained by holding the solution at room temperature for one day. All the gels commonly
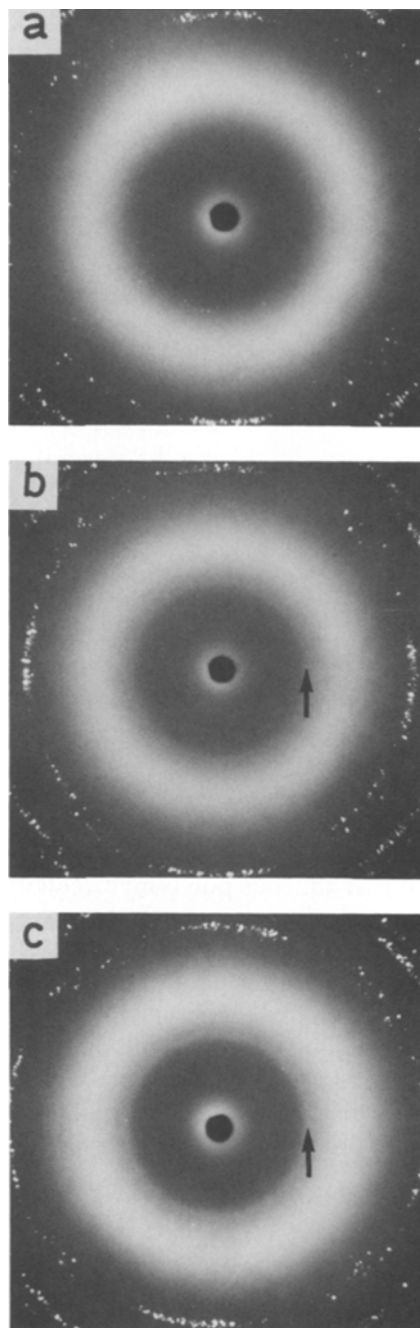

Fig. 1. Wide angle X-ray diffraction patterns of 15 wt % PVA hydrogels: (a) $N = 0$; (b) $N = 7$; (c) $N = 14$. In (b) and (c) the arrow denotes a diffraction ring of $(10\bar{1}) + (101)$ of PVA crystals. Outer diffraction spots arise from aluminium foils used for the sealing of the specimens

have a broadly diffused scattering, which is mainly originated from principal component of liquid water. The gel of $N = 0$ had an elasticity, but was mechanically so
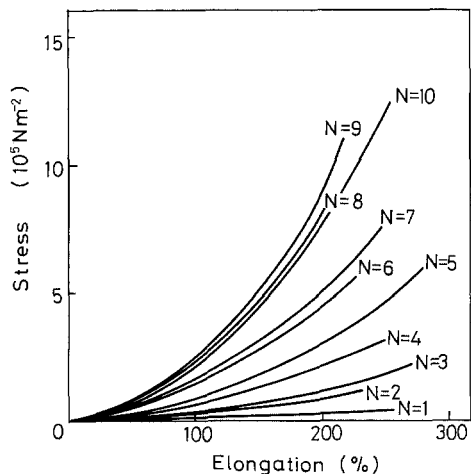
Fig. 2. Stress-strain curves for 15 wt % PVA hydrogels

weak as to be broken by a minimal force. In this gel, stickiness inherent in the original viscous solution remained, which became weaker and disappeared with increasing N, as already found [3]. This indicates that the gel network before freezing is not fully developed. In its X-ray photograph, it was difficult to recognize crystalline reflections of PVA.

The elasticity and tenacity of the gel increased with N, as indicated in the stress-strain curves in Figure 2; the trend in the elasticity is consistent with that found in the dynamic modulus, E' [3]. In parallel with the phenomenon, the crystalline reflection situated just inside the diffuse scattering, as seen in Figure 1, becomes more discrete with N. On the basis of monoclinic unit cell dimensions of PVA crystal given by Bunn [12], the reflection was identified as the superposition of equatorial $(10\bar{1})$ and (101), which is known as the strongest reflection of the crystal. It is expected from the above results that with N, the PVA crystallites as physical cross-linking sites in the network increase in number and may also develop larger in size. However, it seems that intensity of the crystalline reflection for the gel of $N = 14$ is yet weaker than expected when provisionally most of the PVA chains in the PVA-water system are crystallized. The crystallinity of PVA component in the system is probably low. The atactic poly(vinyl alcohol) sample used here is a highly crystalline material. However, owing to a strong hydrogen bonding interaction between hydroxyl groups in PVA chains and water molecules, a large amount of amorphous chains remain in the gel system, being associated with water. Entropy elasticity of the gel,

i. e., negative temperature dependence of the specimen length [3] or positive temperature dependence of the dynamic modulus E' [7], which was observed up to a higher temperature region, can be considered to reflect such rubberlike structure in which the flexible amorphous chains are physically cross-linked by the rigid crystallites.

In Figure 3, we show the scanning electron micrographs of fracture surfaces of xerogels which were obtained from 15 wt % hydrogels. We find that in the case of $N = 2$ only a simple surface is exposed by fracture and that by one more freezing the resultant xerogel is led to the micro porous structure. The pore sizes are about $\sim 1\ \mu$ in diameter. It is expected that in the former case, the porous structure, if originally formed in the hydrogel, is disrupted by self-adhesion during transformation into the xerogel, since the hydrogel skeleton is mechanically very weak, as found from Figure 2. With increasing N, the original hydrogel with a thickness of 1.5 mm became more cloudy and almost non-transparent above $N = 3$, suggesting the development of structure with a micro-phase separation. Further more repeated freezing did not result in an essential change in the xerogel morphology. Now, the similar morphology was found in the xerogel obtained from 10 wt % hydrogel, as shown in Figure 4; the pore sizes are estimated to be a few microns. It appears that there is a tendency for the pore size to increase with lowering the concentration.

It is common knowledge that the gelation is very sensitive to the degree of saponification, i. e., the bulkiness and lower water-resistance of unsaponificated acetyl groups in the chains prevent the growth and propagation of PVA crystallites in the water environment, and then the gelation is very retarded. Based on this, the following fact and the corresponding one given in Figure 3 do not conflict with each other; the use of a slightly lower saponificated PVA sample (98.7 mol %) than the sample used here (99. 8 mol %) needed a considerably larger cycle number of freezing, $N > 20$ where the porous structure in the xerogel began to be observed [13].

That traces of crystal growth of ice are left as pores in the hydrogel is suggested by scanning electron micrographs of the xerogel obtained from 5 wt % hydrogel, as shown in Figure 5. It is seen that the pores which are in the order of 10 μ are linearly linked together, along the direction nearly normal to the freezer plate. Development of such an oriented texture was frequently observed in the case where the PVA concentration was lowered to 5 wt % applied here. It is
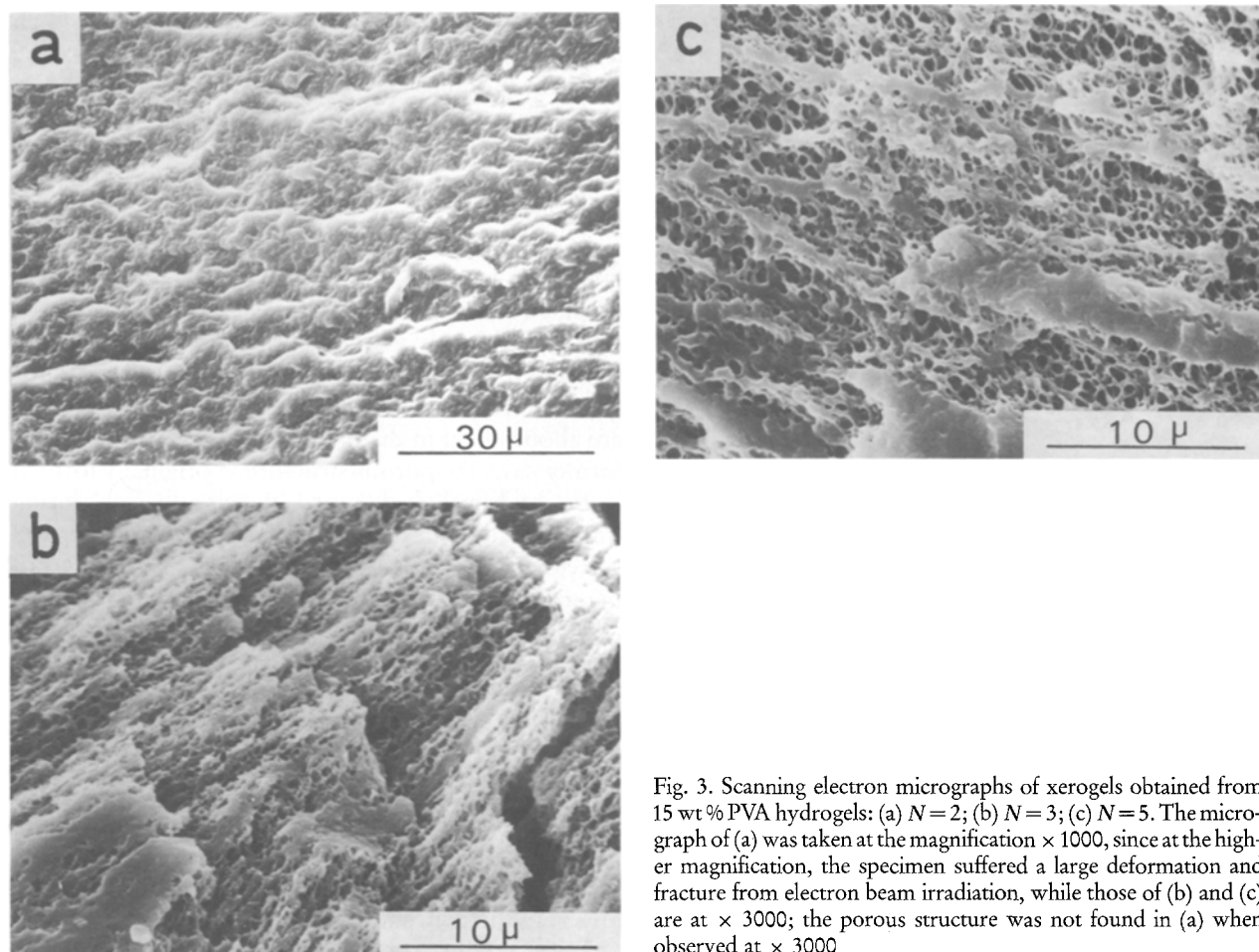
Fig. 3. Scanning electron micrographs of xerogels obtained from 15 wt % PVA hydrogels: (a) $N = 2$; (b) $N = 3$; (c) $N = 5$. The micrograph of (a) was taken at the magnification × 1000, since at the higher magnification, the specimen suffered a large deformation and fracture from electron beam irradiation, while those of (b) and (c) are at × 3000; the porous structure was not found in (a) when observed at × 3000

deduced that under freezing, the ice crystals grow along the direction of temperature gradient, the more PVA-rich solution phases being segregated around them, and that the gelation proceeds in the segregated solution phases, which consequently form the continuous porous gel skeleton.

In the agar-ice composites prepared by freezing agar-water gel using a zone-crystallization apparatus, it was reported by Tong et al. [14] that a cylindrical shape of pores developed along the direction of temperature gradient. The origin of the porous morphology was explained by the mechanism in which agar molecules are segregated around ice crystal phases formed by freezing; formation of the porous structure was accomplished by only one freezing. Woessner et al. [15] showed from pulsed NMR measurements for
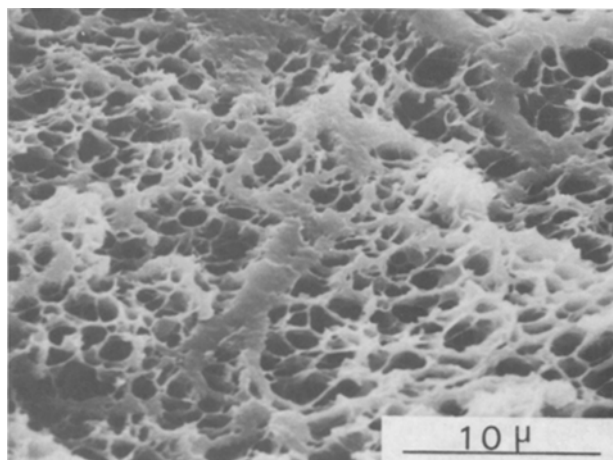

Fig. 4. Scanning electron micrograph of xerogel obtained from 10 wt % PVA hydrogel ($N = 10$)
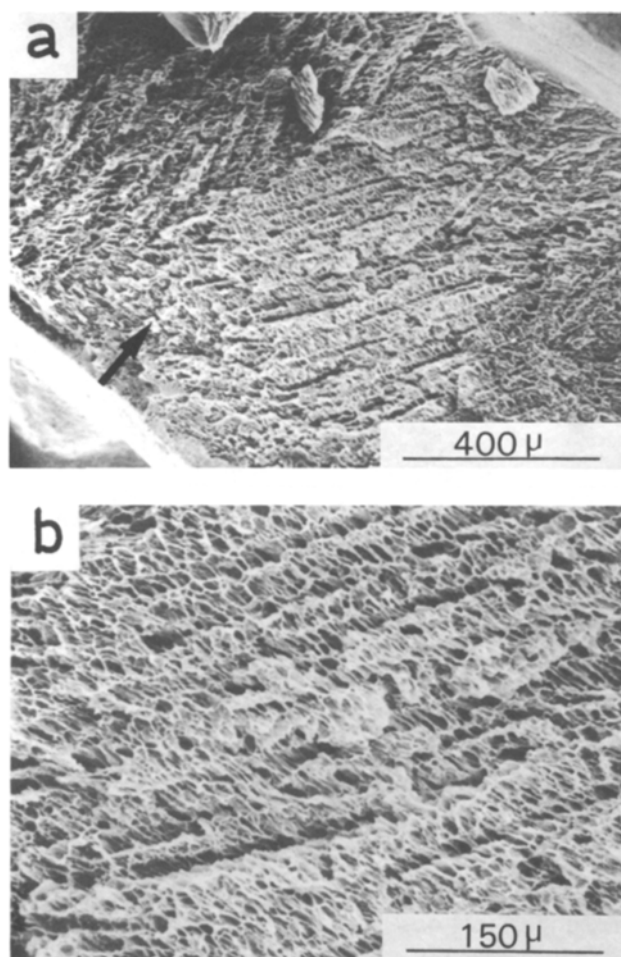
Fig. 5. Scanning electron micrographs of xerogel obtained from 5 wt % PVA hydrogel ($N = 10$). In (a) the arrow denotes the direction of the sample thickness, i. e., the direction normal to the freezer plate. (b) is a magnification of a section in (a)

the agar-water gel that motions of the great majority of water molecules are unaffected by the presence of agar molecules. It is suggested that a very large fraction of water is the bulk water or free water. They showed further [16] that bound water molecules which interact strongly with the polymer molecules amount to a very small fraction, lower than 1 % in a 10 % agar-water gel. It is supposed that these facts they presented are related to the ease of segregation of the agar-water system upon freezing, since interaction between the components is an important factor influencing the segregation. Here, it is unquestionable that water molecules which are classified into the category of free water are directly related to the formation of ice crystal phases. The situation in the PVA-water system is somewhat

different from that in the agar-water system; in PVA hydrogel prepared by γ-ray cross-linking, a considerable amount of water molecules interact strongly with PVA molecules, as recognized by Hatakeyama and Yamauchi [17] using DSC, i. e., several moles of water including 1–1.5 moles of non-freezing water are bound to each hydroxy group of PVA. Assuming that these estimates are applied to the PVA-water system studied here, it is inferred that the clear segregation as realized in the agar gel cannot be achieved by only one freezing. Then, in the early stage of freezing cycle, the isolated bulk water phases (equal to ice crystal phases) strictly speaking should be called the PVA-poor solution phases. However, on the other hand, taking into account that the repeated freezing is nothing but the repeated recrystallization or regarded as a kind of refinement process for ice crystals, it is expected that polymer chains as impurity will be rejected from the growing ice crystals whenever the PVA-water system is frozen. Thus, with the freezing cycle number, the concentration of PVA in the PVA-rich solution phases will be increased and that in the PVA-poor solution phases will be decreased. Consequently, the latter phases approach water more, giving rise to the porous structure.

In Figure 6 the light-optical micrographs for 2.5 wt % hydrogels are shown. Only by one freezing-and-melting, the starting solution is transformed into a kind of modulated structure with a concentration fluctuation, as observed in (a); the denser domains are considered to correspond to PVA-rich solution phases built up by segregation at ice grain boundaries. It looks as if they develop larger to form more continuous gel skeletons by repeated freezing, as seen in (b). At the same time, it is visible from (b) and (c) that the gel skeletons become denser and the appearance more distinct, suggesting that the polymer concentration in them is more and more increased by the repeated segregation. Then, the formation of the PVA crystallites which act as the junction points is much facilitated in the segregated solution phases and consequently the gelation is much enhanced.

Now, from Figures 3c, 4 and 5b, we see that the pore size in the xerogel increases with lowering the concentration of PVA. It is considered that also in the original hydrogel the pore size or the size of ice crystal increases with lowering the concentration; for all these cases, shrinkages of the gels ($N \geq 3 \sim 4$) with a disk shape were the same, about 40 % in diameter, when the hydrogels were transformed into the xerogels. It seems that this trend in the pore size is consistent with the
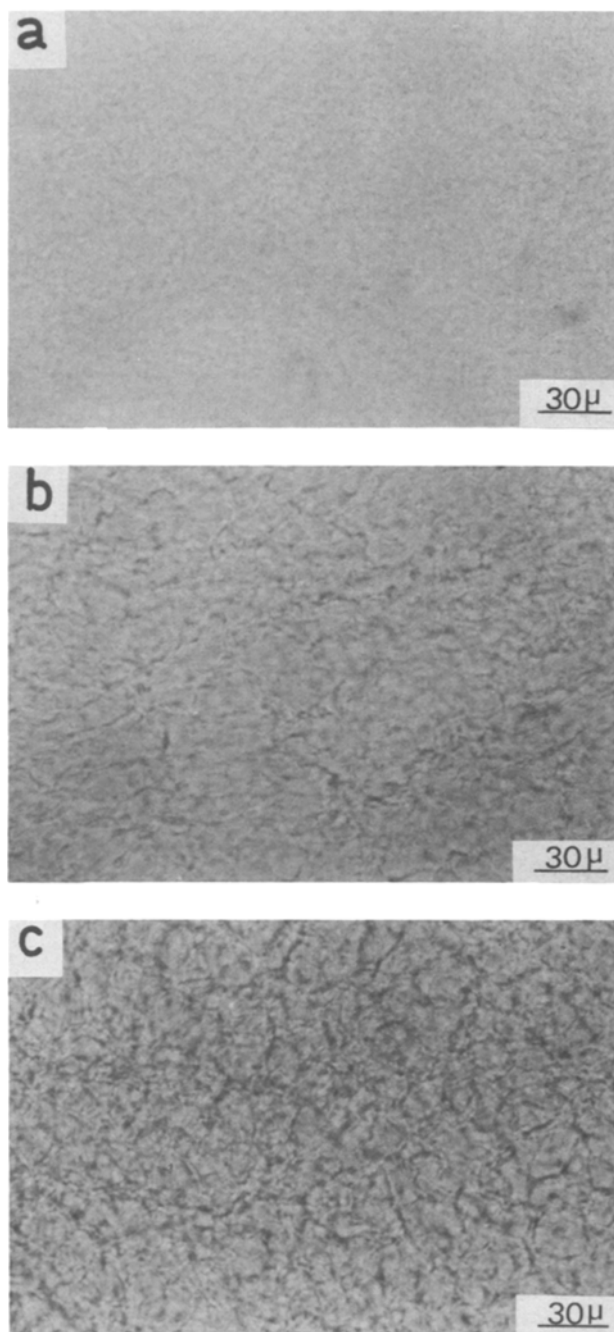
Fig. 6. Light-optical micrographs for 2.5 wt % PVA hydrogels: (a) $N = 1$; (b) $N = 3$; (c) $N = 7$
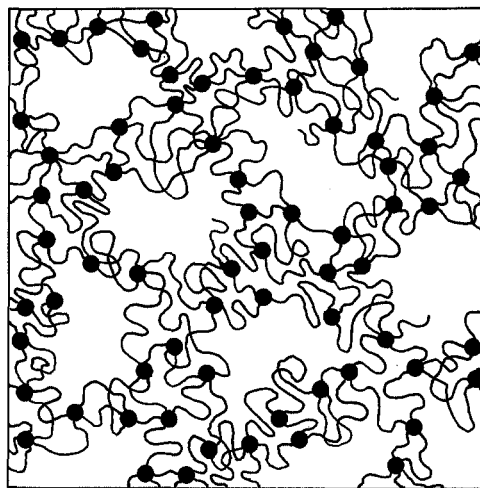

Fig. 7. Schematic representation of structural model for PVA hydrogel prepared by the "repeated freezing-and-melting". Solid circles represent PVA crystallites

As indicated above, the phase separation accompanying the formation of ice crystals has a good effect on the gelling enhancement for the PVA-water system. On the other hand, in hydrogels of several natural polymers including agar, the elasticity was affected by freezing, otherwise the freezing effect, if present, was very small [3]. The reason for this constractive effect of freezing is now obscure.

In the present study, structural model for the highly elastic PVA hydrogel which is prepared by the "repeated freezing-and-melting" can be postulated as shown in Figure 7. The model shows that the hydrogel is composed of the following three kinds of phases: water phases or solution phases with a very low concentration of PVA, which in the frozen gel correspond to the crystal phases of ice; amorphous phases, in which every PVA chain is associated with water; PVA crystal phases, which restrain gross mobility of the amorphous chains. Our views for the gel structure and the gelling mechanism should be confirmed by further examination.

mechanism in which diffusion plays a major role, since with lowering the concentration of PVA, exclusion of the chains from the growth front of an ice crystal will become easy and then the formation of a larger size of the ice crystal is expected.

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