Shape Memorizing Properties of a Hydrogel of Poly(vinyl Alcohol)

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SYNOPSIS

Hydrogel prepared by repetitive freezing and thawing of poly(vinyl alcohol) aqueous solution was chemically crosslinked with glutaraldehyde. The chemically crosslinked hydrogel hardly changed its physical appearance, and showed good elasticity and strength as original gel. However, after treating in boiling water, it swelled a little, depending on the condition of the chemical treatment. The melted gel thus obtained showed shape memorizing property, that is, it could firmly hold nearly 200% of strain, keeping its original high elasticity. The strain could be released very quickly (< 1 s) in boiling water, and the gel was suggested to be applied to a new type of gel actuator. X-ray diffraction study revealed that the melted gel does not necessarily reform the physical crosslinks in exactly the same manner as the original gel in the process of shape restoring, but the distribution of the physical crosslinks can be restored as they were. It was suggested that the chemical crosslinks which remember the distribution of the physical crosslinks plays a critical roll in the shape restoring process.

INTRODUCTION

It has been known that the highly elastic hydrogel can be prepared from an aqueous solution of poly(vinyl alcohol).[1-4] As the gel has enough strength as a membrane, it has been investigated as a membrane material.[5] It also contracts very quickly in poor solvents like acetone, methanol, etc. The gel has attracted much attention as a material of artificial muscle or a gel actuator because of its quick reaction against environmental change.[6] In order to improve the performance as an actuator, the authors have carried out investigations of the anisotropically contractile hydrogel of PVA.[7,8] The anisotropically contractile hydrogel of PVA was prepared by endowing network orientation in the gel structure. The excellent physical strength of the gel has also been utilized as a strengthening material of physically poor polyelectrolyte gel.[9-11]

The gel is excellent not only in its physical properties, but also in biocompatibility.[12] Particularly, the PVA hydrogel prepared from aqueous solution of dimethyl sulfoxide has excellent transparency, and is expected to have applicability for artificial lens, etc.[13,14]

Despite these excellent properties, the gel is strongly limited in thermal stability,[5] because it has been considered to be constructed by the hydrogen bonds between the PVA polymer chains and cannot hold a stable gel state over 60°C, melting down above 80°C. Although the tacticity and the degree of polymerization of the PVA can profoundly affect the physical properties of the gel, that is, for instance, syndiotactic-rich PVAs have better heat resistance than atactic ones, thermal stability cannot be maintained in boiling water in any way.[15]

In this report, we introduced chemical crosslinks in the gel structure by treating the gel with glutaraldehyde. The gel thus obtained has excellent shape memorizing properties, as will be shown below. The major differences from the so-called shape memorizing plastics are high water (or solvent) content and high elasticity, which are also the characteristics of the original gel.

EXPERIMENTAL

Materials

PVA was Kuraray 117 supplied from Kuraray Co. The degree of polymerization and saponification are 1700 and 99%, respectively. The PVA was fully sa-

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ponified and purified according to the conventional procedure.

Preparation of Physically Crosslinked Gel

The PVA was solubilized in boiling water, and 10% (w/w) aqueous solution was obtained. The solution was cast on a petri dish while it was warm enough. The casted PVA solution was frozen at −20°C for 23 h. Then, the gel was thawed by leaving the petri dish at ambient temperature for 1 h. This freezing-and-thawing cycle was repeated six times. The gel was kept in distilled water at ambient temperature until it was served for measurements. The gel, thus prepared, will be called a "physical gel" for convenience in this paper.

Preparation of Chemically Crosslinked Gel

The physical gel was immersed in an aqueous solution of glutaraldehyde at 5°C for 12 h, and was then kept at 40°C for 1 h in an acidic aqueous solution. The chemically crosslinked gel thus obtained was rinsed in distilled water, and was served for the following measurement. This gel is called *chemical gel* in this paper.

Measurements

Swelling and Contraction Processes

The contraction and swelling process of the gel was investigated in methanol. The gel membrane was cut out in rectangular of size of 1 × 3 cm, and was fixed by clipping both of the ends. The clipped gel was suspended in a thermostated measuring cylinder in which a solvent was filled. The change of the gel size in vertical direction was followed with cathetometer.

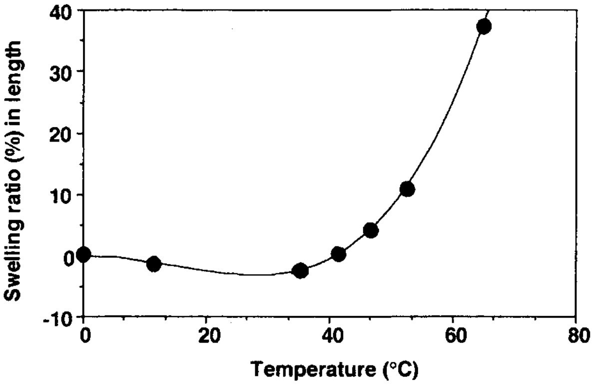

Figure 1 Temperature dependence of swelling ratio of freeze-and-thaw PVA hydrogel.

Table I Effect of GA Concentration and Heat Treatment in Boiling Water on the Swelling Degree[a] of Chemically Crosslinked PVA Hydrogel

	GA Concentration (%)				
	0.05	0.06	0.07	0.10	0.20
	Swelling Degree (%) in Length				
Right after boiling in water	106	104	107	101	110
After 12 h immersion in water at 20°C	133	130	124	103	110

[a] Swelling degree was defined as the percent value of the ratio of gel length after treatment to that of original gel. Experimental error encountered reaches 5% at maximum in these particular measurements, particularly in the case of low GA concentration, since the gel size (originally ca. 3 cm) was measured by placing the melted gel on a glass plate and by reading the meniscus under the plate.

X-Ray Diffraction Pattern

X-ray diffraction was measured using Ni-filtered Kα radiation of Cu from Geigerflex Rad IIA (Rigaku Electric Co.). The instrument attached with proportional counter was operated at 40 kV and 20 mA.

RESULTS AND DISCUSSION

Effect of Boiling on the Shape of the Gel

In Figure 1, the effect of temperature on the gel size is shown on a physical gel. It is shown that the gel began swelling over 50°C by losing crosslinking points in the gel, and cannot hold a gel state over 80°C. When a physical gel was immersed in hot water, it melted quickly, and a homogeneous aqueous solution was obtained.

On the other hand, the chemically crosslinked gel did not dissolve even in boiling water when treated properly with GA, as shown in Table I. The result shows that the crosslinks in the physical gel is composed by only physical interaction (such as hydrogen bond) and not by covalent bonding, but that of the chemical gel is made by covalent bond together with physical interaction.

As the PVA is a crystalline polymer, the crosslinking points are considered to be made up by microcrystallite, in which the polymer chains mainly binds together by hydrogen bonds.[16] The crosslinking points in the physical gel are also considered to have originated from hydrogen bonds between polymer chains. However, the detailed structure of the crosslinking points in the physical gel is not necessarily clarified yet.[17] In this report, the crosslinking points in the physical gel will be denoted as "physical crosslinks," and those in the melted chemical gel will be denoted as "chemical crosslinks," which are equivalent to covalent crosslinks.

In Table I, the effect of heat treatment in boiling water was shown on the appearance of chemical gel. Right after the heat treatment, the gel changed its appearance from white to semitransparent, and the size of the gel swelled slightly. However, the gels prepared in diluted GA solution ([GA] < 0.1% in Table I) continued swelling when left in water, and reached equilibrium in 12 h at ambient temperature. While in the case [GA] > 0.1%, the gel hardly changed its size by prolonged immersion in water. These swollen gels will be called "melted gels" in this paper. The melted gel thus obtained still kept enough strength for strain fixing, as will be shown below.

Contraction Behavior of Melted Gel

Contraction in methanol and swelling in water were repeated, and the time courses are shown in Figure 2 on the melted gel. It is noteworthy that the melted gel which was served for contraction process could not restore its melted state in water unless the heat treatment was carried out again on the gel, and this hysteresis was particularly remarkable in the first contraction process. By repetition of the contraction-and-swelling process, the gel size approached that of the chemical gel, which was nearly the same size as that of the physical gel. In other words, the melted gel almost restored its original size and elasticity by one contraction treatment, suggesting that the physical crosslinking points in the original chemically crosslinked physical gel were memorized in the melted gel through chemical crosslinking points.

Shape Fixing Methods

The chemically crosslinked physical gel was set in a particular shape and was deswollen in a poor solvent like methanol. The deswollen solid gel held the particular shape set before the deswelling. The deswollen gel restored its original physical shape and properties when immersed in water. This is the first method of shape fixing by deswelling. In this method, the shape could only be held in deswollen solid form, and not in the elastic gel form. We did not investigate this method in this report.

The second method is based on the breaking down of the hydrogen bonds in the physical gel, that is, the heat-treated transparent gel, or "melted gel," was a starting state. The melted gel was deswollen in methanol after being set in a particular shape. The deswollen solid gel held the shape as it was set, and the shape was stably fixed even in water in contrast to the case of the chemically crosslinked physical gel. This method was mainly investigated in this paper.

The third method is removing water from the melted hydrogel by drying. The film thus obtained have an appearance almost the same as the oridinal transparent PVA film.

Shape Fixing by Deswelling under Elongation

As has been suggested in the section before the above, if the physical crosslinking points could be

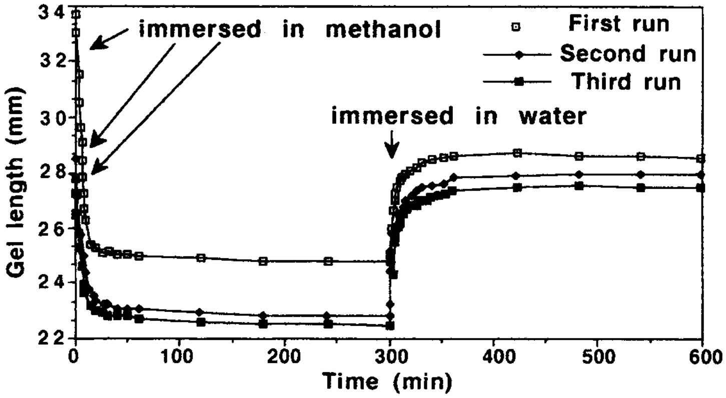

Figure 2 Shape recovering process in repetitive swelling-and-contraction treatment, started from melted gel [gel (4) in Fig. 6]. Contraction and swelling processes were carried out in methanol and water, respectively. The gel restored the size of the gel before melting, that is, gel (3) is nearly equal to that of gel (6) in appearance.

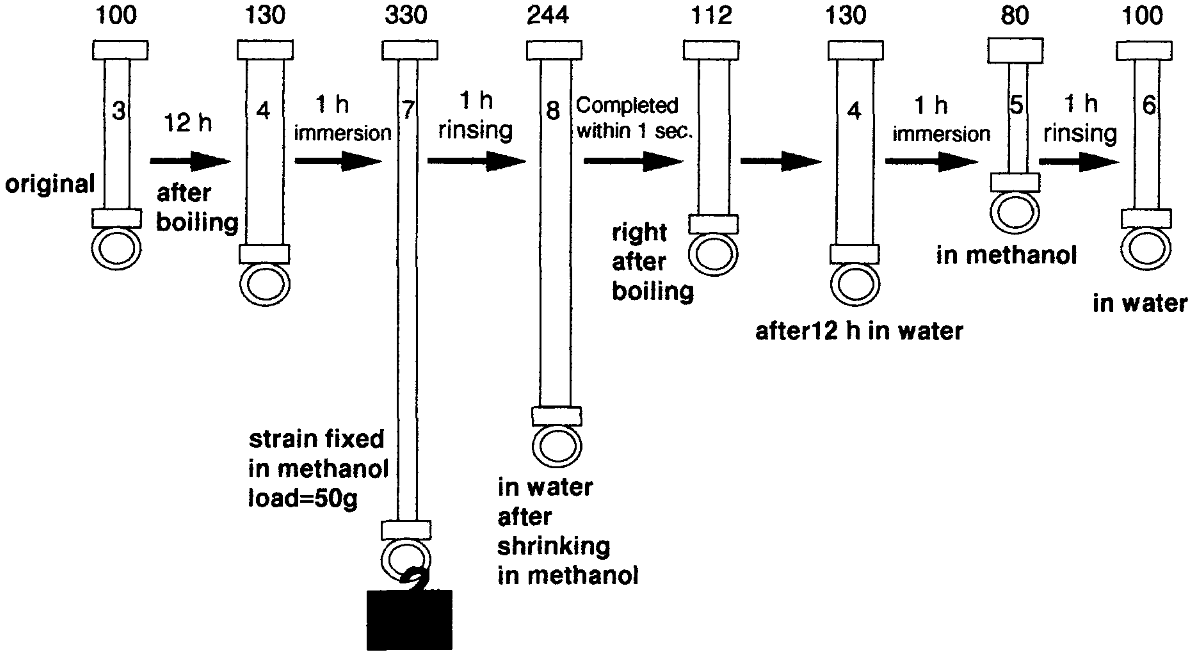

Figure 3 Processes of shape fixation and recovery of chemically crosslinked elastic PVA hydrogel by using desolvation. Physical gel was chemically crosslinked with glutaraldehyde (GA) of 0.06 wt %. Gel numbers denoted in this figure showed corresponding states to those shown in Figure 6, though the gel in that figure was the one prepared at [GA] = 0.07 wt %. Gel (6) is nearly the same to gel (3). The figures shown top of each gel means the relative gel size measured with cathetometer.

restored in the first deswelling (or contraction) process, being triggered by the chemical crosslinking points, it will also be expected that the shape under elongation can be fixed by deswelling. The effect of elongation on the shape fixing by deswelling was investigated on the gel chemically crosslinked in [GA] = 0.06%. An example is shown in Figure 3.

First, the melted gel was elongated with a load in water, and the elongated gel was immersed in methanol for deswelling. The deswollen gel turned into white solid gel, remaining a huge strain in its structure and shape. When the solid gel was immersed in water at ambient temperature, it swelled without losing the shape endowed by deswelling under elongation. It did not take back its original shape of transparent melted gel, but did the character of white elastic physical gel or original chemically crosslinked physical gel, except holding a huge strain of ca. 200% in its structure. The elongated gel thus obtained was stable and reversible under further swelling-and-contraction processes. This gel can also be expected to show anisotropic contraction behavior, as suggested in our previous paper.[9]

When the elongated gel was immersed in boiling water, it contracted instantly to its original size, which is smaller than that of the melted gel. The contracted gel swelled gradually to the size of melted gel in water at ambient temperature. As the contracted gel had the value of water content nearly equal to that of original gel, the contracting process does not relate to the deswelling, but solely to the release of the strain endowed in the gel structure. The process is, therefore, considered to be originated completely by an entropic elasticity of the gel. This property is also in agreement with the fact that the gel hardly loses water by elongation or squeezing.[18]

Heating in the boiling water caused a breakdown of the physical crosslinking, and the strain in the gel was released instantly, causing quick entropic contraction. The slow swelling, which followed after the quick contraction, can be explained by the slow osmotic swelling, which resulted from the increase of the polymer chains liberated from physical crosslinking. In other words, by melting, the physically restricted region in the polymer chain (or the polymer chain in solid phase in the gel) began behaving freely, causing an increase of osmotic pressure. Then, the gel swelled slowly to reach osmotic equilibrium. Similar behavior was also observed on the gel, which is chemically crosslinked in a GA solution of 0.07%.

Transparent Film Obtained by Drying the Melted Gel

A transparent film was obtained by drying a melted gel which was chemically crosslinked in [GA] = 0.07% in sheet form. This transparent film kept its film state in water, and did not change into either melted gel form or white physical (or chemical) gel form. The wet film was then immersed in methanol. After deswelling in methanol, it kept transparent film form and did not change into original gel form.

When the film was heat treated in boiling water, it changed into a melted gel. The melted gel had the same properties described above, suggesting that the transparent film can be considered to have the same chemical crosslinks or network structure. The difference among the physical gel, the chemical gel, the melted gel, and the transparent film treated in this paper can be considered to originate from that in the existence, the amount, or the distribution of the physical crosslinks in the gel which can be endowed in the process of deswelling and are removed by heat

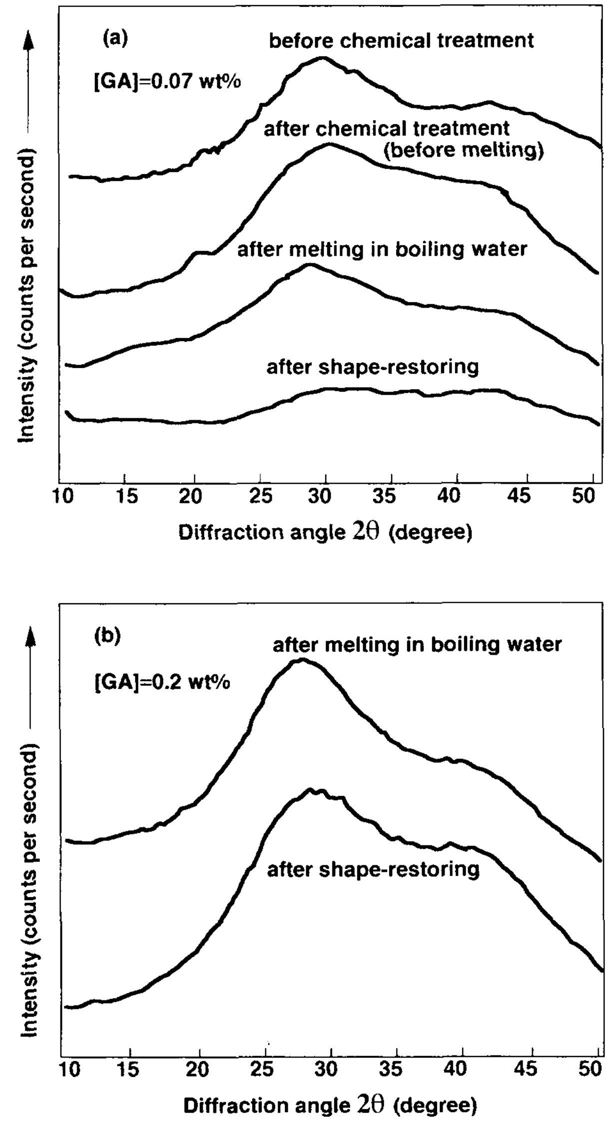

Figure 4 X-ray diffraction pattern of PVA hydrogel covalently crosslinked at (a) [GA] = 0.07 wt % and (b) [GA] = 0.2 wt %. Scale of intensity was the same in all cases.

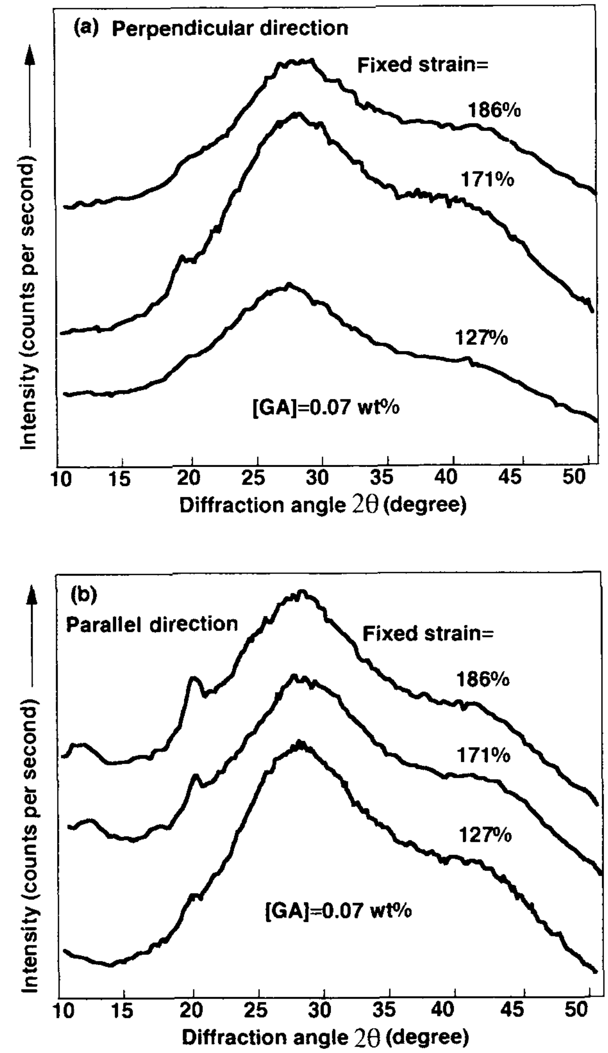

Figure 5 Effect of stain fixing on the diffraction pattern of covalently crosslinked PVA hydrogel. Covalently crosslinked in [GA] = 0.07 wt %. (a) Scanned in perpendicular direction; (b) scanned in parallel direction.

treatment. Actually, the extent of the strain fixing decreased with GA concentration in the chemical treatment, and we could not fix strain in the gel treated at [GA] = 0.2 wt %. The results suggest that the strain could not be fixed as the large amount of chemical crosslinks disturbed new arrangements of the physical crosslinks under elongation.

X-Ray Diffraction Pattern of the Gel

As has been shown, it is clear that the covalently crosslinked hydrogel of PVA has excellent shape-memorizing properties, although the properties are just in appearance and not clear if the shape recovery concerns about the microscopic structure change or not. In this section, we show some results on X-ray diffraction patterns of the shape-memorizing PVA hydrogels chemically crosslinked in [GA] = 0.07%, and discuss on the relation between the microstructure change and the shape memorizing property.

As shown in Figure 4(a), it is clear that the chemical treatment does not affect the structure of the freeze-and-thaw gel of PVA, although a slight increase of relative intensity at about $2\theta = 40°$. By melting, the small diffraction peak at $2\theta = 19°$ disappeared. When the gel restored its shape by immersing in water after deswelling in methanol, the characteristic diffraction pattern was lost. In Figure 4(b), the results show that the shape-restored hydrogel showed actually the same pattern as that of the melted gel, which is covalently crosslinked in higher GA concentration than that in Figure 4(a). These results suggest that: (1) Chemical treatment with GA of low concentration can affect slight loosening of higher order structure without serious deformation of the gel structure. (2) By treating in boiling water, the crystallites, which can be considered to be physical crosslinking points, disappeared by melting. (3) Shape restoring does not necessarily mean the re-formation of the crystallites as they were there, but rather the formation of smaller aggregates of PVA chains which is different from original gel. The higher the GA concentration or the denser the covalent crosslinking, the easier shape restoring can be expected.

Effect of strain fixing and structural anisotropy on the diffraction pattern was shown in Figures 5(a) and 5(b). Figure 5(a) shows the diffraction pattern when the strain fixed gel was scanned perpendicularly to the oriented direction. Figure 5(b) shows the pattern when the gel was scanned parallel to the oriented direction. In the perpendicular direction,

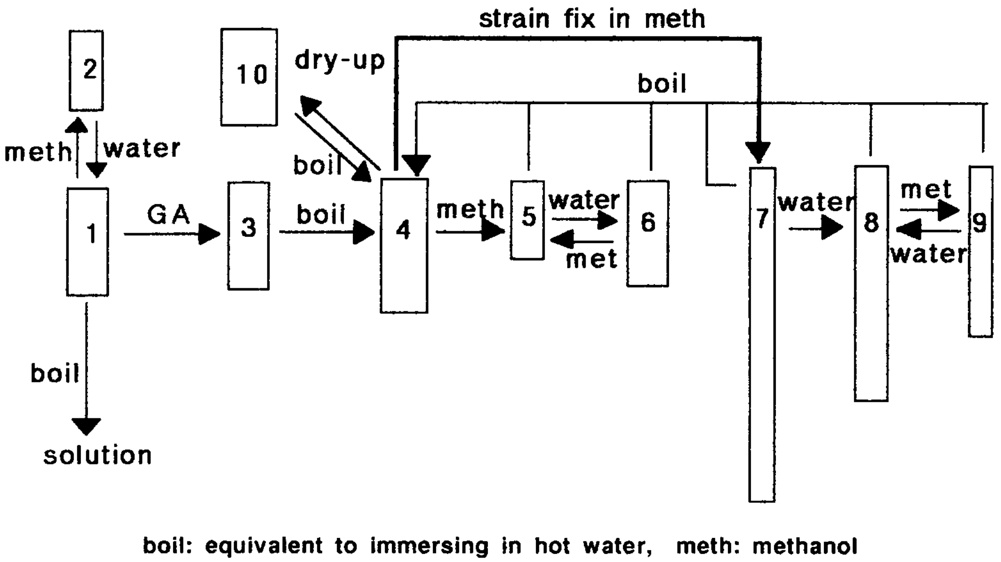

Figure 6 Summary of shape memorizing properties of chemically crosslinked PVA hydrogel: boil = equivalent to immersing in hot water (>80°C), meth = methanol. Chemical crosslinking was carried out at [GA] = 0.07 wt %. Gels 1, 3, and 6 are the same not only in size but also in physical properties. Gels 2 and 5 are also the same in size. Gels 1, 3, 4, 6, and 8 are elastic hydrogels. Gel 4 is denoted as a melted gel in this paper. Gel 10 is a solid transparent film whose shape was fixed before drying. Gels 2, 5, and 7 are stiff methanol gels, and can be converted into xerogel by evaporating methanol. Size of rectangular shows relative size obtained by measurement at 30°C.

the strain fixing did not seriously affect the diffraction pattern. On the contrary, the effect of strain fixing was remarkable in the parallel direction, that is, the diffraction peaks at $2\theta = 19°$ and $2\theta = 11°$ increased with the fixed strain, suggesting that the crystallite formation proceeded, and the fibril of polymer chain was effectively oriented and fixed in elongated direction. The effect of elongation of the elastic hydrogel not covalently crosslinked was investigated on the diffraction pattern, and the crystalline peak at $2\theta = 19°$ was also observed by elongation of the elastic hydrogel of PVA.[19] Taking the measurements in the previous papers into account, the results shown in this paper suggest that the shape-memorizing properties of the covalently crosslinked freeze-and-thaw gel of PVA originate in the combination of chemical and physical crosslinks; particularly, the physical crosslink which can be reversibly formed plays a critical role. The chemical crosslinks have the role of memorizing of location and distribution of the physical crosslinks, and have the function to restore the physical crosslinks at the loci where they were. This is possible as the chemical crosslinks can localize around the surfaces of the crystallites as physical crosslinks.[20]

CONCLUSIONS

All the results obtained on the gel chemically crosslined in [GA] = 0.07% are summarized in Figure 6. As can be seen in the figure, the chemical gel is revealed to take some states that are different to each other. One of the typical examples is the shape-memorizing property of the melted elastic gel. It could hold nearly 200% of strain in gel state, and could release the strain very quickly. The possibility of developing a new type of hydrogel material as an actuator is suggested, which utilizes a strain endowed in the gel network as a source of energy of actuation.

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