

A Novel Hybrid Material of Polymer Gels and Bilayer-Membranes

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Responsive polymer gels that contain bilayer membranes have been synthesized and characterized as a novel hybrid material. The hybrid gels show some unique properties which cannot be obtained from the individual polymer gels and the bilayer membranes. Iridescent color resulting from the Bragg diffraction of visible light by the periodic structure of bilayer membranes can be changed by controlling the swelling degree of a polyacrylamide gel. Introduction of bilayer membranes strongly affects the volume phase transition behavior of a poly-*N*-isopropylacrylamide gel. By polymerizing a gel while shear flow is imposed upon the solution to be gelled, an anisotropic gel has been synthesized. The hybrid gels show more than seven times larger elastic modulus, and can be extended more than three times before fracture than the simple polymer gel.

Key words: polymer gel, hybrid gel, bilayer membrane, anisotropic gel, iridescence

1. INTRODUCTION

Polymer gels and bilayer membranes are both quite unique soft materials, and have been extensively studied. They show, of course, very different characteristics. Polymer gels undergo volume phase transition in response to a change of surrounding solution conditions. They are used as drug delivery systems and chemo-mechanical devices. Bilayer membranes, on the other hand, are studied as a model of biological membranes, and are also used as drug delivery systems, taste- and/or olfactory-sensors etc. However, hybrid materials made of polymer gels and bilayer membranes have not yet been either developed or studied. One of the present authors (K.T.) and his coworkers studied previously the iridescent

phenomena resulting from periodic structures of bilayer membranes of polymerizable surfactant and the immobilization of the iridescent lamellar structures inside a polyacrylamide gel.¹⁾ The polyacrylamide gel thus obtained containing bilayer membranes in its inside showed interesting properties as a hybrid material.^{2,3)} The present paper is to demonstrate the synthesis, the characterization and the interesting properties of the hybrid gels.

2. EXPERIMENTAL

Dodecylglyceryl itaconate (DGI; $n\text{-C}_{12}\text{H}_{25}\text{OCOCH}_2\text{-C(=CH}_2\text{)-COOCH}_2\text{CH(OH)-CH}_2\text{OH}$) was synthesized.^{1,3)} We use polyacrylamide (AAm) and poly-*N*-

isopropylacrylamide (NIPA) gels to immobilize the bilayer membranes. As shown previously, DGI monomer molecules form an iridescent lamellar liquid crystal in water in the concentration range of 1-2 wt % of DGI in the presence of small amount of ionic surfactant (0.2-2.0 wt % with respect to DGI).¹⁾ In this work, we preferably use sodium dodecyl sulfate as an ionic surfactant. This iridescent structure of DGI is maintained even in the aqueous solution of the monomers of acrylamide, *N*-isopropylacrylamide and *N,N'*-methylene-bis-acrylamide. The iridescent solution of DGI containing any of the above monomer and cross linker was photo-polymerized by UV light, and the lamellar structure of the polymeric DGI was immobilized inside the network of AAm or NIPA gel. The iridescent color shifts to red during the above polymerization process, since the surface area of the bilayer membranes decreases due to the bond-formation between the DGI molecules, thus leading to the increase of the inter-membrane distance.¹⁾ Molecular weight of the DGI polymer was estimated by gel permeation chromatography to be about 100,000 when the DGI was polymerized alone (homo-polymerization).¹⁾

Bilayer membrane systems are essentially anisotropic in their structure. But the anisotropic domains are randomly oriented in bulk, and the entire solution in a vessel shows isotropic properties. We were able to align the bilayer membranes in the bulk phase, and to immobilize the anisotropic structure within the polymer gels. The liquid crystal sample of DGI (3.0 wt %) containing the gel-forming monomers as mentioned above was filled into the sandwich-type cell (1mm thickness) under shear flow: One open side of the cell was dipped in the liquid crystal sample, and the N₂ gas in the empty space of the cell was sucked with a syringe from the other side of the cell frame. The sucking rate of the sample solution was 0.5 mm/sec, and the shear rate was roughly estimated to be $\sim 1 \text{ s}^{-1}$. UV irradiation was

started immediately after the sample solution was filled up in the cell. The temperature was kept constant at 40°C during the entire process of preparation. In order to make cylindrical gels, glass capillaries having inner diameters of 1.0 mm and 0.34 mm were used as polymerization cells. The same monomer solution as the gel preparation of rectangular sample was filled from one side of the capillary by suction from the other side. The other conditions for polymerization were the same as above.

Volume phase transition of the gels was observed by essentially the same method as that described elsewhere.⁴⁾ Mechanical properties of the gels were measured with a tensile tester (Orientec, type RTA-100).³⁾ A test piece of 1mm×10mm×50mm was cut from a plate-like gel sample, and set in the chucks of the tensile tester. The sample length between two chucks was 10mm.

3. RESULTS AND DISCUSSION

3.1 Change of the iridescent color accompanied with the gel shrinkage

The polyacrylamide gel incorporating the 2.0 wt % DGI bilayer membranes shows the iridescent red color as already reported previously.¹⁾ This color is due to Bragg diffraction of visible light resulting from periodic structure of the bilayer membranes. The iridescent color is found to shift to blue to an extent depending on the shrinking degree of the gel. The volume of the AAm gel decreases with increasing the concentration of ethanol, and the spacing between the bilayer membranes immobilized in the gel networks also results in the smaller distance being accompanied by the gel shrinking. This result indicates that the iridescent color can be controlled by the environmental conditions that affect the volume of the polymer gels.

3.2 Effects of the immobilized bilayer membranes upon the phase transition behaviors of the NIPA gel

NIPA gel undergoes volume phase transition from a

swollen state to a collapsed one at about 34°C when the temperature is raised. One can suppose that the bilayer membranes incorporated inside the gel will affect the phase transition behavior. The phase transition behaviors of the simple NIPA gel and the hybrid NIPA gels are shown in Figure 1. The simple NIPA gel behaves similarly as found in the previous work,⁴⁾ where it was shown that the transition between the swollen and the collapsed states is reversible. In the cases of DGI-immobilized gels, however, the bilayer membranes give some remarkable effects on the phase transition behavior of the NIPA gel. The volume change between swollen and collapsed phases is much reduced by introducing the

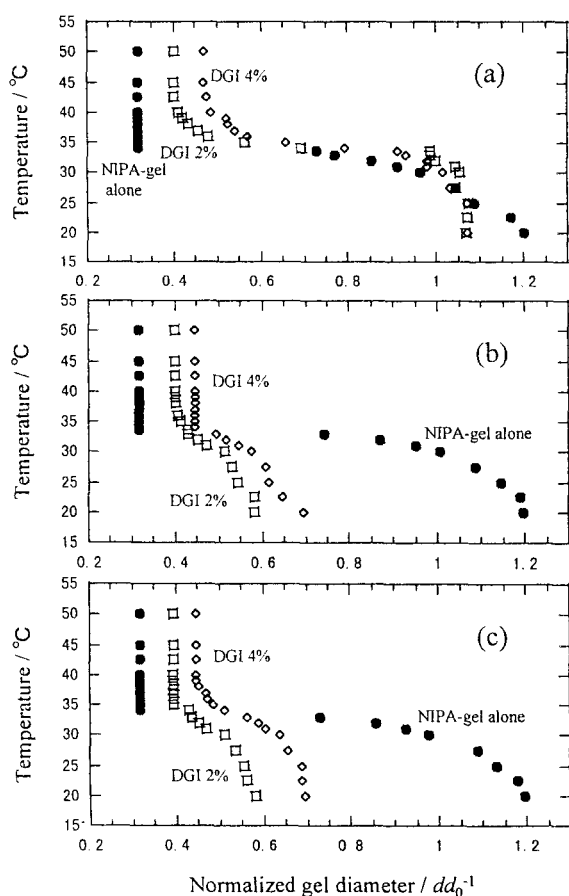


Fig.1: Effect of the immobilized bilayer membranes of DGI on the phase transition behavior of NIPA gel. First run of temperature elevation (a), temperature decrease (b), and second temperature-increasing process (c).

bilayer membranes. Furthermore, the diameter of the gel does not return to the initial value but becomes smaller when the temperature decreases back (compare the plots of the top figure (a) with the middle (b) in Figure 1), and the same swollen and collapsed diameters are recovered in the second run. Interestingly the initial diameter was recovered when sodium dodecyl sulfate was added to the surrounding medium of the gel. (Not shown in the figures.)

3.3 Anisotropy in the Hybrid Polyacrylamide Gels

The polarizing microscopic photographs show the anisotropy in the hybrid AAm gels prepared under shear flow. In the rectangular pillar sample, two cross sections parallel to the flow direction during the gel preparation showed similar textures, and the texture seemed to be in one-dimensional alignment. The cross section perpendicular to the flow direction, on the other hand, showed no aligned texture. In the cylindrical gel, the cross sectional view showing the big cross-like pattern is particularly interesting. This pattern covers the entire cross section of the gel sample indicating that the anisotropic orientation takes place in the whole gel of 1 mm diameter. These observations in both rectangular and cylindrical shaped anisotropic gels were very much different from those of the homogeneous gels that were prepared without flow treatment for orientation.

Figure 2 shows the anisotropic swelling behavior of a cylindrical AAm gel prepared under shear flow. Water/ethanol mixed solvents were utilized to control the swelling degree of the gel. There is an indication of swelling anisotropy of the cylindrical gel in Figure 2. The ordinate and abscissa denote the normalized length (l/l_0) and diameter (d/d_0) of the gel, respectively. The changes in length and diameter are the same in the simple AAm gel, but are different from each other in the anisotropic hybrid gel since the plots deviate from the straight diagonal line. This result indicates the anisotropic

swelling behavior of the hybrid gel with immobilized membranes. Anisotropic gels are in crucial importance for practical application of polymer gels. For example, one-dimensional swelling-shrinking behavior is essential in the applications for artificial muscles. Our hybrid gels provide us with guiding principles how to synthesize anisotropic polymer gels.

3.4 Mechanical Properties of the Hybrid Gels

Figure 3 shows the stress-strain curves of the simple acrylamide and the anisotropic hybrid acrylamide gels. For the anisotropic gels, the tensile experiments were done in both directions: parallel with (a) and perpendicular to (b) the flow direction at the time of sample preparation. One can clearly see that the bilayer membranes in the gel have a strong effect on the mechanical properties of the hybrid gel. The elastic moduli (initial slope of the stress-strain curves) as well as the stress and the strain at the breakdown point of the hybrid gels are much greater than that of the simple polymer gel. The mechanical strength is one of the weakest points of polymer gels in their practical applications. As shown in Figure 3, the mechanical properties of the gel are much improved by the immobilized bilayer membranes. Furthermore these mechanical properties show the anisotropy in the tensile directions. The gel seems stronger when elongated parallel to the flow direction although the anisotropy is small.

4. REFERENCES

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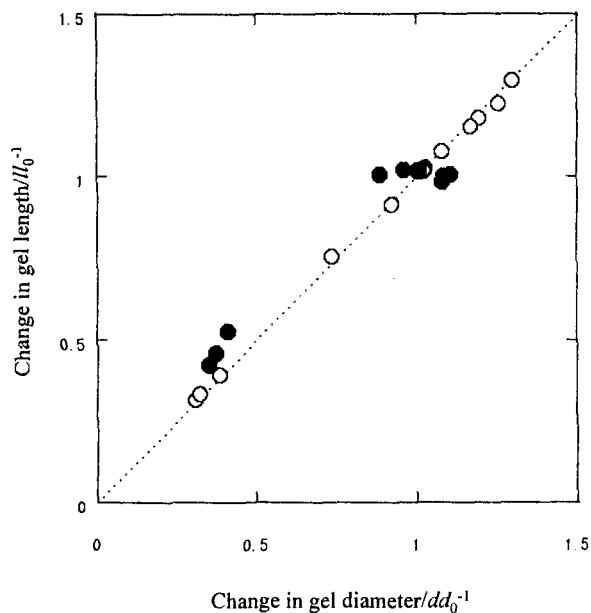


Fig.2: Anisotropic swelling behavior of hybrid AAm gel. Simple AAm gel (○) and anisotropic hybrid gel (●). The swelling degree was changed in the mixed solvent of ethanol/water with various mixing ratios.

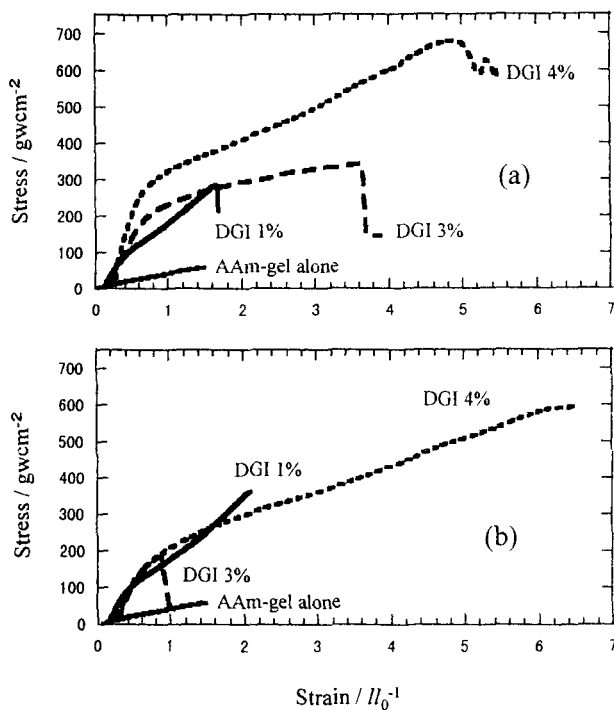


Fig.3: Stress-strain curves of the simple AAm gel and the hybrid gels. The hybrid gels are extended in parallel with (a) and perpendicular to (b) the flow direction of the monomer solution at the time of sample preparation.