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A Novel Hybrid Material of Polymer Gels and Bilayer Membranes

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ABSTRACT: 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 the gel. Introduction of bilayer membranes strongly affects the volume phase transition behavior of the gel. By the polymerization of 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 a seven times larger elastic modulus and can be extended more than three times before fracture than the simple polymer gel.

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.[1−4] They are used as drug delivery systems[5] and chemomechanical devices.[6,7] Bilayer membranes, on the other hand, are studied as a model of biological membranes and are also used as drug delivery systems,[8,9] taste- and/or olfactory-sensors,[10,11] 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 collaborators 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 poly(acrylamide) gel.[12] A preliminary investigation suggested that the above poly(acrylamide) gel containing bilayer membranes showed some interesting properties as a hybrid material.[13] The present paper is an extension of the previous work,[13] and deals with synthesis and experimental characterization of the hybrid gels of bilayer membranes and polymer network.

Experimental Section

Materials. Dodecylglyceryl itaconate (DGI; n-$C_{12}H_{25}$-$OCOCH_2C(=CH_2)COOCH_2CH(OH)CH_2OH$) was synthesized by the slightly modified procedure described in the previous work as shown in Figure 1.[12] Itaconic acid anhydride (50.1 g, 0.44 mol) was mixed and reacted with dodecanol (80.0 g, 0.43 mol) at 110−120 °C for 50 min to obtain the dodecyl itaconate. After the reaction was completed, 100 mL of hexane was added to the reaction mixture at 70 °C under a vigorous mechanical stirring, and the crude product of white crystal was precipitated. The crude sample of dodecyl itaconate was recrystallized from ethanol. The melting point of the purified sample was 76−78 °C. The dodecyl itaconate thus obtained (5.0 g, 0.017 mol) was dissolved in toluene (5 mL), and reacted with glycidol (3.75 g, 0.051 mol) at 100 °C in the presence of 10 mg (39.7 μmol) of pyridinium p-toluenesulfonate as a catalyst. The reaction mixture was refluxed with stirring for 5 h at 100 °C. The toluene was evaporated under reduced pressure. The crude product was applied to a silica gel column and eluted with a hexane/ethyl acetate mixture (4/6 by weight). The collected DGI fraction was purified twice by recrystallization from an acetone/hexane mixture (1 /1 by weight). The final product (mp = 62−63 °C) was proven to be more than 99% pure by NMR and HPLC analysis. Decylglyceryl itaconate (DeGI) was also synthesized by the same procedures as above and showed a melting point of 53 °C.

We used poly(acrylamide) and poly-(N-isopropylacrylamide) (NIPA) gels to immobilize the bilayer membranes. The monomers of acrylamide, N-isopropylacrylamide and N,N-methylenebis(acrylamide) (a cross-linker) were purchased from Merck, Kodak, and Kanto Chemical Co., respectively. Irgacure 2959 was obtained from Ciba Geigi as a nonionic initiator of the photopolymerization. NIPA was recrystallized twice from an ether/hexane mixture. All other samples were of guaranteed reagent grade and were used without further purification. Deionized and distilled water was used to prepare the sample solutions.

Preparations of the Bilayer-Membranes-Immobilized Polymer Gels. 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).[12] 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-methylenebis(acrylamide). The iridescent solution of DGI containing any of the above monomers and cross linkers was photopolymerized by UV light, and the lamellar structure of the polymeric DGI was immobilized inside the network of acrylamide 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 intermembrane distance.[12] Molecular weight of the DGI polymer was estimated by gel permeation chromatography to be about 100 000 when the DGI was polymerized alone (homopolymerization).[12]

A monomer solution containing 700 mM of acrylamide, 10 mM of N,N-methylenebis(acrylamide) and 2 mM of Irgacure

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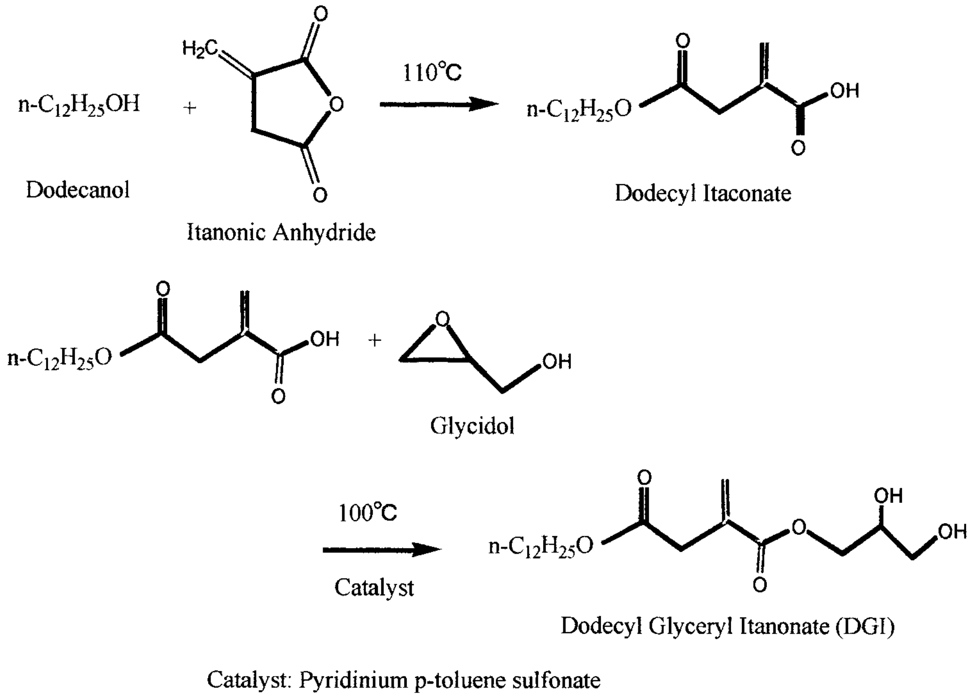

Figure 1. Synthetic procedure for DGI.

2959 (as an initiator) was bubbled with nitrogen gas at the flow rate of 0.5 mL/min for 20 min. The DGI powder and an anionic surfactant, sodium dodecyl sulfate, of 0.5 mol % with respect to DGI were dissolved into the above monomer solution in the N_2 gas atmosphere, and the sample solution was left to stand in a water bath at 50-55 °C for more than 3 h until the homogeneous iridescent color appeared. The monomer solution thus prepared was gently transferred with a pipette to a polymerization cell under the N_2 gas atmosphere. Two kinds of polymerization cells were used to prepare a platelike gel and a thin cylindrical gel. A rectangular frame of silicone rubber of a thickness of 1 or 2 mm was sandwiched between two glass plates for platelike gel preparation. One side of the frame is detachable, and used for sample injection. The polymerization was performed by irradiating UV light with a mercury lamp of 450 W at ca. 50 °C. The sample cell was set at the distance of 15 cm from the lamp and rotated at 7 rpm to be irradiated homogeneously. The polymerization reaction was completed within about 20 min. A thin glass capillary with an inner diameter of 140 μm was utilized as a cell for cylindrical gels.

N-Isopropylacrylamide (NIPA) gel bearing the bilayer membranes of DeGI or DGI was made by procedures similar to the above. An aqueous solution of the monomer (NIPA, 800 mM), the cross-linker (*N*,*N*-methylenebis(acrylamide), 20 mM) and the initiator (Irgacure 2959, 1 mM) was bubbled with N_2 gas at the flow rate of 0.5 mL/min for 20 min. The surfactant solution of bilayer membranes was separately prepared by dissolving the required amount of DeGI or DGI and sodium dodecyl sulfate (0.5 mol % for the surfactant) into pure water under N_2 gas atmosphere, and the sample solution was left to stand in a water bath at 50-55 °C for more than 3 h to obtain the homogeneous iridescent color. The surfactant solution was cooled down to 25 °C for DeGI or 31 °C for DGI, and then mixed with the same volume of monomer solution separately prepared as above. The iridescent solution containing monomers was gently injected into the sandwich-type polymerization cell having a thickness of 2 mm. The polymerization temperature was essentially important to maintain the metastable solution state even below the Krafft points (=35 °C for DeGI and =43 °C for DGI) of the surfactants, and was kept at 25 °C for DeGI and 31 °C for DGI during the polymerization procedures. All the experimental conditions not mentioned here were the same as those of the poly(acrylamide) gel preparations described above.

Preparations of the Anisotropic Poly(acrylamide) Gels. 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 before in the poly(acrylamide) gel preparation method 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 N_2 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/s, and the shear rate was roughly estimated to be $\sim 1\ s^{-1}$. 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 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.

Experimental Procedures for the Measurement of the Gel Properties. Light reflection spectra of the monomer solutions of DGI and the iridescent gels were measured with a spectromultichannel photodetector (Ohtsuka Electronics, type MCPD-110A) and detected in normal direction with respect to the incident white light. The intensity of the reflected light from the sample solution was calibrated by that from a TiO_2 white board.

Volume phase transition of the gels was observed by essentially the same method as that described elsewhere.[14] We prepare a thin cylindrical gel having diameter of 140 μm. It was inserted into a glass capillary and set in a water bath. The pure water surrounding the gel was always flushed through the capillary during the measurement. The phase-contrast microscopic image of the gel was monitored on a TV display, and the diameter of the gel was measured with a microscaler. The temperature of the water bath was varied stepwise after the equilibrium diameter of the gel was measured.

Anisotropic poly(acrylamide) gels were characterized with a polarizing microscope (Nikon, Optiphot-Pol). A gel slab was

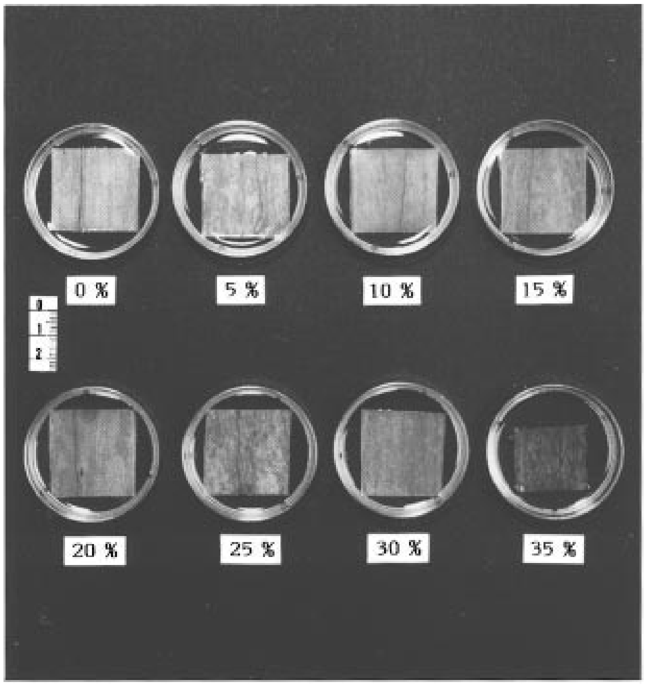

Figure 2. Photographs of the hybrid poly(acrylamide) gels with bilayer membranes (700 mM acrylamide, 10 mM *N*,*N*-methylenebis(acrylamide), 2.0 wt % DGI) immersed in water/ethanol mixtures of various ratios. The ethanol concentrations in wt % are denoted in the figure. The gels were immersed in the solvent for 2 weeks to attain the equilibrium. The iridescent color appears to result from the periodic structure of bilayer membranes and the shift to blue is due to the shrinkage of the gel with an increasing concentration of ethanol.

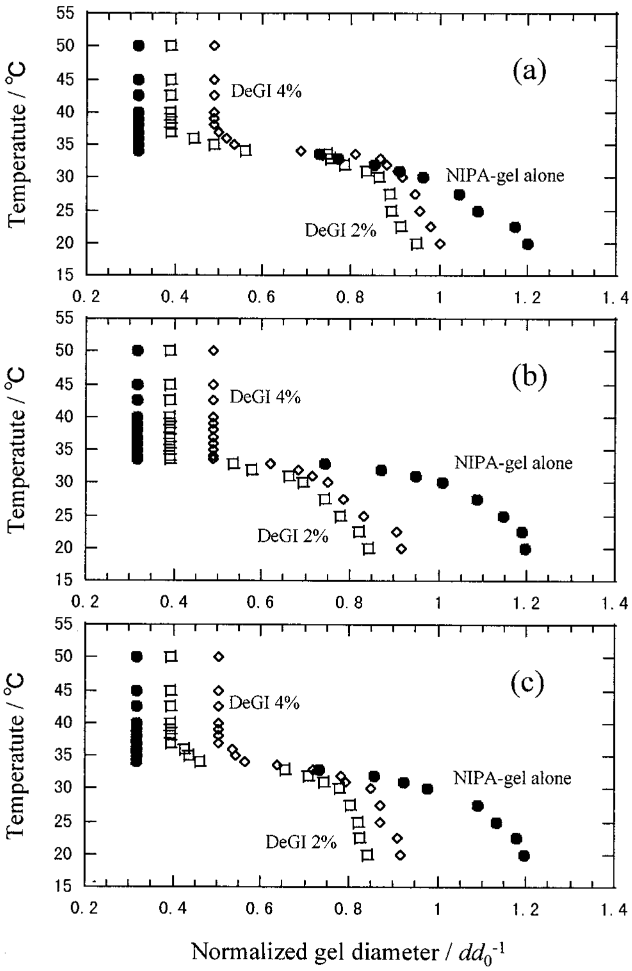

Figure 3. Effect of the immobilized bilayer membranes of DeGI on the phase transition behavior of NIPA gel (800 mM NIPA, 20 mM *N*,*N*-methylenebis(acrylamide), 0−4 wt % DeGI). The diameter of a cylindrical gel normalized by the initial (as synthesized) one, d/d_0, was plotted against temperature. The first experimental run of the temperature-elevating process (a), the temperature-descending process (b), and the second temperature-elevating process (c) are shown from top to bottom in the figure.

cut as a small rectangular post along with and perpendicular to the flow direction of the monomer solutions at the time of the sample preparation. Microscopic observations were made under crossed polarizers for all three of cross sections of the gel post. A cylindrical gel was also cut perpendicularly to the cylinder axis and observed from the surface and the cross section. The gel was rotated on the sample stage and observed at two crossing angles between the flow direction and the direction of detecting polarizer. One was 0° and the other was 45° in the counterclockwise direction. An anisotropic cylindrical gel (0.34 mm diameter, ~1 mm length) was employed to investigate the anisotropy in the swelling/shrinking behaviors. Both the length and the diameter of the cylindrical gel were measured at 25 °C with the same microscopic apparatus as that used in the phase transition experiments. Water/ethanol mixed solvents were utilized to control the swelling degree of the gel. A water/ethanol mixture of a certain ratio was flowing through the sample cell. The mixing ratio of the solvent was changed after the equilibrium length and diameter of the gel were obtained. The same experiments were done as a reference for the simple poly(acrylamide) gel.

Mechanical properties of the gels were measured with a tensile tester (Orientec, type RTA-100). A test piece of 1 mm × 10 mm × 50 mm was cut from a platelike gel sample, and set in the chucks of the tensile tester. The sample length between two chucks was 10 mm. The stress was recorded, while the sample gel was extended at constant rate of 10 mm/min. For the hybrid anisotropic gels with oriented membranes, the tensile test was carried out in directions parallel and perpendicular to the flow direction during the sample preparation.

Freeze−fracture transmission electron microscopy was carried out by exactly the same way as that employed in the previous work.[15]

Results

Change of the Iridescent Color Accompanied by the Gel Shrinkage. The poly(acrylamide) gel incorporating the 2.0 wt % DGI bilayer membranes shows an iridescent red color as already reported previously.[12] 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 some extent depending on the shrinking degree of the gel as exhibited in Figure 2. The volume of the poly(acrylamide) 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 which affect the volume of the polymer gels.

Effects of the Immobilized Bilayer Membranes upon the Phase Transition Behaviors of the NIPA Gel. The 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 Figures 3 and 4. The simple NIPA gel behaves similarly as found in the previous work,[14] where it was shown that the transition between

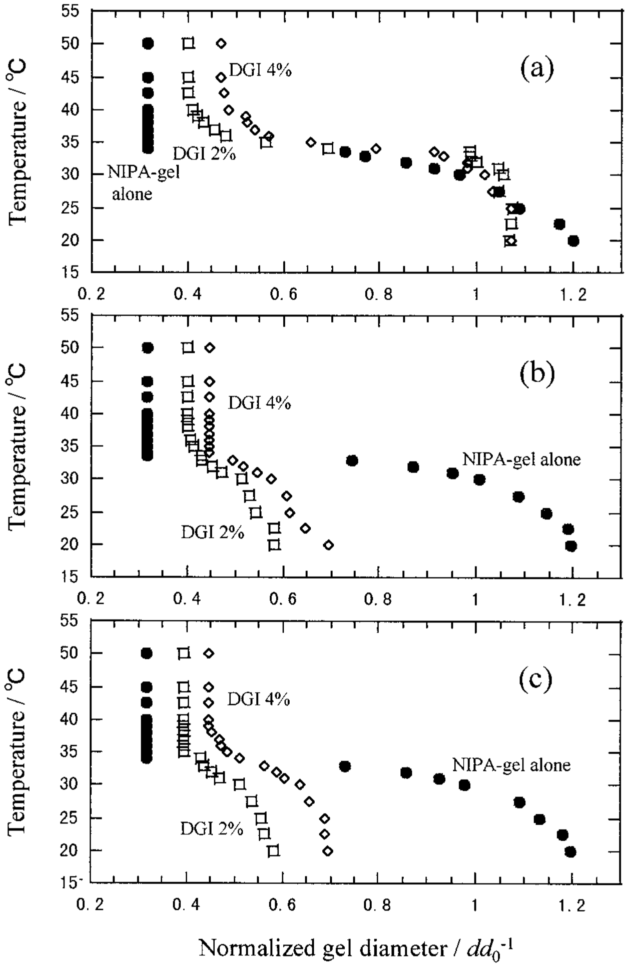

Figure 4. Effect of the immobilized bilayer membranes of DGI on the phase transition behavior of NIPA gel (same gel composition as that of DeGI). The meaning of the parts a–c from top to bottom is the same as that in Figure 3.

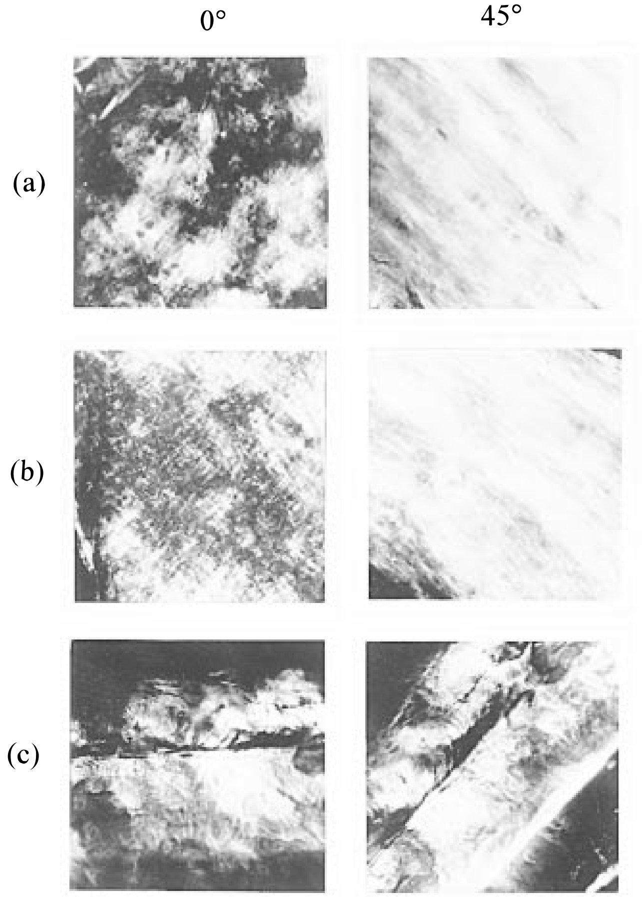

Figure 5. Microscopic photographs (magnification: ×100) under crossed polarizers of an anisotropic poly(acrylamide) gel of rectangular pillared shape (700 mM acrylamide, 10 mM *N*,*N*-methylenebis(acrylamide), 3.0 wt % DGI). The top and the side view of the cross section parallel to the flow direction are shown in the top (a) and middle (b) figures. The bottom photo (c) shows the cross section perpendicular to the flow direction. The three photos in the left-hand column were taken at a crossing angle of 0° between the flow direction and the direction of detecting polarizer, and those in the right-hand column at 45° in the counterclockwise direction.

the swollen and the collapsed states is reversible. In the cases of both DeGI- and DGI-immobilized gels, however, the bilayer membranes have 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 bilayer membranes. Furthermore, the diameter of the gel does not return to the initial value (particularly in the DGI-immobilized gel) but becomes smaller when the temperature decreases back (compare the plots of the top figure (a) with the middle (b) in Figures 3 and 4), 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).

Anisotropy in the Hybrid Poly(acrylamide) Gels. Figures 5 and 6 show microscopic photographs of the anisotropic poly(acrylamide) gels under crossed polarizers. In the rectangular pillar sample (Figure 5), two cross sections parallel to the flow direction during the gel preparation showed similar textures and strong contrast in brightness when observed at crossing angles of 0 and 45°. Furthermore, 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, and almost the same brightness at the crossing angles of 0 and 45°. The strong contrast in the top view between the crossing angles of 0 and 45° was also observed in the cylindrical shaped gel (Figure 6). In the cylindrical gel, the cross-sectional view showing the big crosslike 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 which were prepared without flow treatment for orientation.

There is an indication of swelling anisotropy of the cylindrical gel in Figure 7. 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 poly(acrylamide) 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.

Mechanical Properties of the Hybrid Gels. Figure 8 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

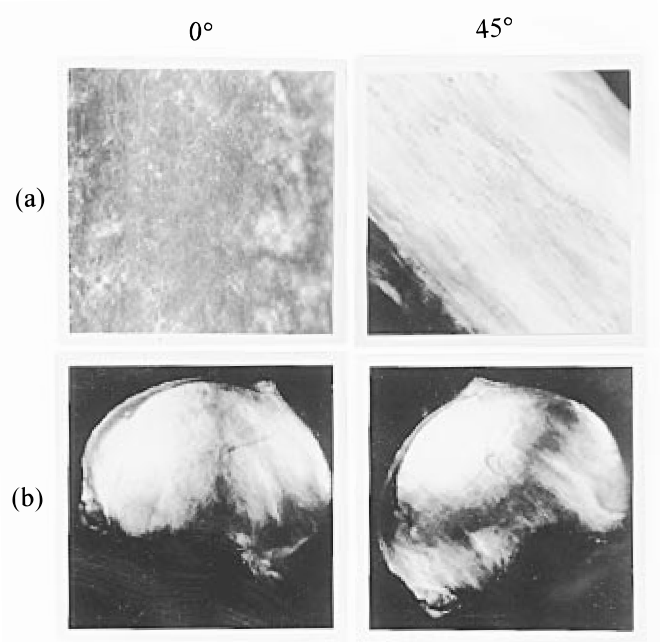

Figure 6. Microscopic photographs (magnification: ×100) under crossed polarizers of an anisotropic poly(acrylamide) gel of cylindrical shape (same gel composition as that shown in Figure 5). The top and the cross-sectional views of the cylindrical gel are exhibited in the top (a) and bottom (b) figures. The photos in the left-hand column were taken at a crossing angle of 0° between the flow direction and the direction of detecting polarizer, and those in the right-hand column at 45° in the counterclockwise direction.

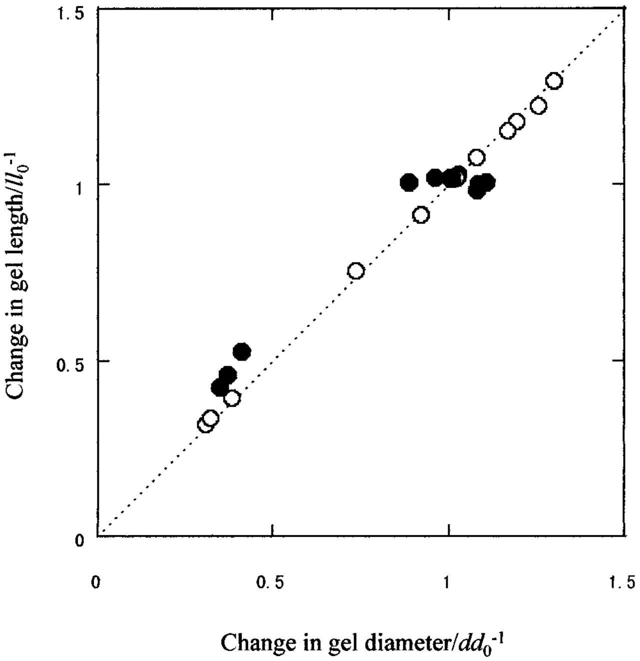

Figure 7. Normalized length (l/l_0) of the anisotropic bilayer-membranes-immobilized (●) and simple (○) poly(acrylamide) gel of cylindrical shape plotted against the normalized diameter (d/d_0) measured in the water/ethanol mixed solvents of various mixing ratios, where l_0 and d_0 are the initial (as synthesized) length and the diameter of the gel, respectively. The gel composition is 700 mM acrylamide, 10 mM *N*,*N*-methylenebis(acrylamide), and 3.0 wt % DGI.

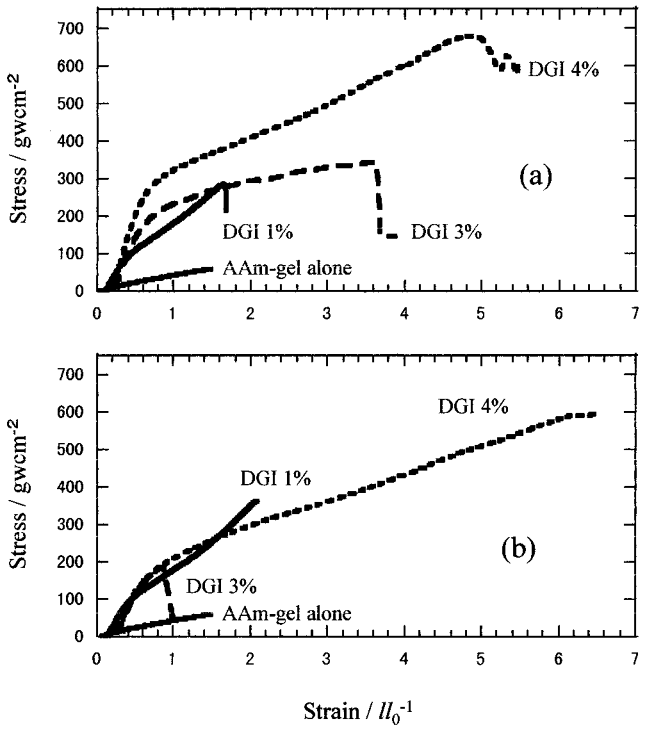

Figure 8. Stress–strain curves of the simple poly(acrylamide) gel and the hybrid gels with membranes. The hybrid gels are extended in parallel with (a) and perpendicular to (b) the flow direction of the monomer solution at the time of sample preparation. The gel composition is 700 mM acrylamide, 10 mM *N*,*N*-methylenebis(acrylamide), and 0–4 wt % DGI.

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. 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.

Freeze–Fracture Transmission Electron Microscopy. A freeze–fracture transmission electron microscopic photograph is shown in Figure 9. The periodic structure of bilayer membranes is clearly observed inside the poly(acrylamide) gel. The iridescent color appears resulting from the Bragg diffraction of visible light by the above regular structure.

Discussion

Bilayer-Membranes-Immobilized Polymer Gel as a Novel Hybrid Material. A novel soft material developed in this work consists of the bilayer membranes of polymeric surfactant stacked periodically in the chain networks of the polymer gel as demonstrated in Figure 9. The hybrid material must show some coupling effects in its properties of the bilayer membranes and the polymer gels. The iridescent color controlled by the gel shrinking is a typical example of the above coupling effect. There have been reported so far more than 10 surfactant systems which show the iridescent phenomena.[12,15–26] The color, however, can be changed only by the surfactant concentration in most of the systems with only one exception.[15] The iridescent material controlled by the swelling degree of the gel is, of course, first synthesized and characterized in this work.

The mechanical strength is one of the weakest points of polymer gels in their practical applications. As shown in Figure 8, the mechanical properties of the gel are much improved by the immobilized bilayer membranes.

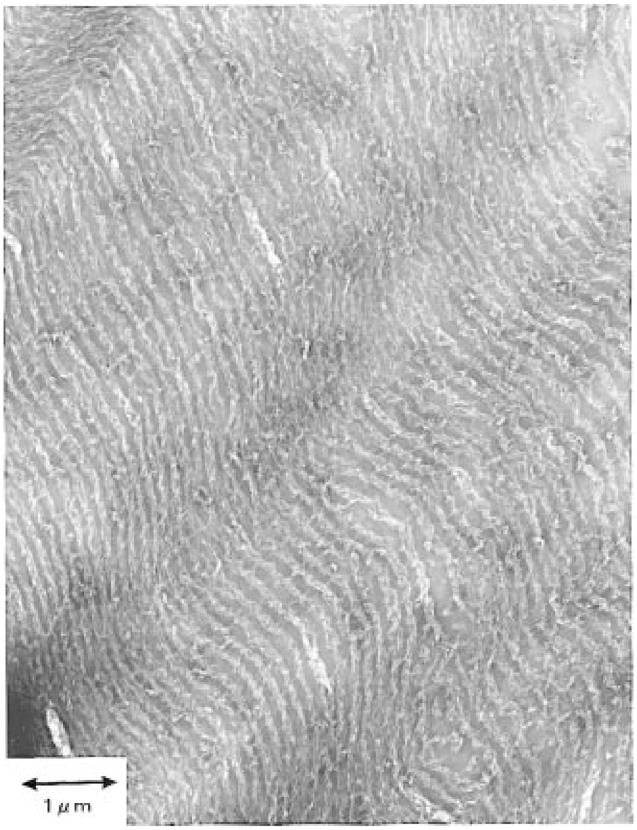

Figure 9. Freeze–fracture transmission electron microscopic photograph of the hybrid poly(acrylamide) gel. The gel composition is the same as that shown in Figure 7.

Swelling and shrinking behaviors of the polymer gel are also modified by the bilayer membranes (Figures 3 and 4).

Formation of Anisotropic Polymer Gels and Their Properties. 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. An anisotropic gel in organic solvents has been reported,[27] but no hydrogel with this behavior has been developed so far. The hybrid gels with bilayer membranes prepared by the polymerization just after shear flow of the monomer solutions showed actually clear anisotropy in the optical, swelling and mechanical properties as shown in Figures 5–8. Our hybrid gels are still far from perfect anisotropy but provide us with guiding principles how to synthesize anisotropic polymer gels which are useful and important in the practical applications of hydrogels.

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