Hydrogels with the ordered structures

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Abstract

A water-swollen hydrogel with a molecularly-ordered structure was prepared by copolymerizing acrylic acid and acrylic monomer containing hydrophobic long alkyl or mesogenic moiety. The gels with a long alkyl side chain formed the crystalline structure and undergo the reversible order–disorder transition with change in temperature or solvent composition which accompanied a dramatic change in Young’s modulus. These gels exhibited such chemomechanical behaviors as the shape memory and the rotational motility on the water surface. On the other hand, the gels with the mesogenic side chain formed the liquid crystalline structure with polymorphism in water, and mesophase diagram was established by changing copolymer composition and water content. Mechanism of these structural and chemomechanical behaviors has been explained in terms of order–disorder transition. © 2001 Published by Elsevier Science Ltd.

Keywords: Hydrogel; Order–disorder transition; Long alkyl moiety; Mesogenic moiety

1. Introduction

A polymer gel consists of an elastic cross-linked network with a fluid filling the interstitial space of the network, and fundamental studies on the polymer gels have intensively been made [1–3]. Water-swollen hydrogels are generally amorphous in nature and have no particular ordered structure at the molecular level. This might be one of the reasons why the synthetic polymer gels suffer from a lack in mechanical toughness or motility. On the other hand, biological gels usually form well-ordered aggregates in the “junction zones” [4], which allow the living organisms to be of sufficient mechanical toughness and have smooth motility, where the molecularly ordered structure can roughly be classified into crystals and liquid crystals.

In this article, the works on the hydrogels containing chemically bound functional groups forming the crystalline or liquid crystalline structures are reviewed in terms of formation and transition of the ordered phase.

We have attempted to synthesize the water-swollen hydrogels with the molecularly-ordered structure by copolymerizing acrylic acid (AA) with acrylic monomer containing a hydrophobic long alkyl group in the side [5–12]. Their structures and order–disorder transition by changes in temperature, solvent composition, pH, and ionic strength have been investigated. The hydrogels immersed in water-soluble organic solvent such as ethanol and tetrahydrofuran (THF) underwent disorder–order transition when they were placed on a water surface and showed extensive translational and rotational motions [13–15].

In contrast with the crystalline structure, a liquid crystalline structure usually easily transforms into a lower or higher ordered structure with a small change in enthalpy and entropy [16,17], which may allow the gels polymorphism, mechanical, electromagnetical and optical anisotropies. Using these specific characteristics of liquid crystalline compounds, Kishi et al. have synthesized the organogels containing mesogenic side chains and demonstrated that the organogels swollen in the nematic solvent changes their shape and size quickly (order of milliseconds) responding to the electric field [18,19]. However, there is no systematic research of the water-swollen hydrogels with liquid crystalline structure.

We have synthesized the water-swollen hydrogels containing a mesogenic side chains 11-(4′-cyanobiphenyloxy) undecyl group, and investigated the effects of monomer compositions, temperature [20], and water content [21] on the structure. It was found that these hydrogels showed the polymorphism by changing the composition of mesogenic component and swelling degree. In addition, the highly oriented hydrogels which shows the strong birefringence were prepared.

2. Experiment

2.1. Syntheses of monomers

AA (Aldrich) was purified by distillation before use.
Cetyl acrylate (Osaka Yuki Kagaku Kogyo Co, Ltd) and stearyl acrylate (SA; Aldrich) were purified by recrystallization, respectively. 16-acryloyloxyhexadecanoic acid (AHA) was synthesized by the procedure shown in the literature [7]. 11-(4'-Cyanobiphenyloxy)undecyl acrylate (11CBA) was synthesized by esterification of 11-(4'-cyano biphenyl oxy)undecanol (11CB) by acryl chloride in THF. Detailed methods as to how to synthesize 11CB were described in the literature [20,22].

2.2. Syntheses of gels

The copolymers with various composition, \( F (F_i) \) is defined as the mole fraction of the monomer containing a long alkyl or mesogenic side chain to the total monomer), were prepared by a radical polymerization of monomers. Cross-linked copolymer gels were prepared by the same procedure as the copolymers in the presence of a cross-linker. Detailed methods were described in the literatures [5–12].

3. Results and discussion

3.1. Hydrogels with the crystalline ordering

There are two methods of giving the hydrogels the crystalline structure: one is the complexation of the hydrogels with the molecules capable to form the crystalline structures through intermolecular interaction, and the other is the synthesis of the hydrogels containing chemically bound functional groups forming the crystalline structures. A number of studies on the structure of the complex of the polyelectrolyte gels with oppositely charged surfactants with a long alkyl tail or a planar component have been made. Complexes of natural polyelectrolytes [23,24] with surfactants formed well-organized structures. Kabanov et al. have reported that the structure of the stoichiometric complexes formed between cross-linked poly(acrylic acid) (PAA) and cationic surfactants; cetyltrimethyl ammonium bromide form a layer structure. The layer structure [25] and its function for many other complexes were also investigated [26–30]. The complex of polycation gels with anionic phthalocyanine formed a hexagonal columnar structure [31]. In contrast, so far authors know, there has been no report describing the synthesis, structure, and properties of water-swollen hydrogels containing chemically-bound crystalline structure.

3.1.1. Structures of dry and wet gels

3.1.1.1. Dry state. To study the molecular structure of the chemically cross-linked copolymer networks in the dry state, a wide angle X-ray diffraction (WAXD) pattern of the poly(SA-co-AA) networks of various \( F_{SA} \) (\( F_{SA} = [F_{SA}] / ([F_{SA}] + [AA]) \)) has been taken by Ni-filtered Cu\( \alpha \) radiation (40 kV, 40 mA) in transmission geometry. WAXD pattern of the poly(AA) and poly(SA-co-AA) networks with \( F_{SA} \) of 0.05, 0.05, and 0.1 showed no diffraction peak through \( 2\theta = 5–40^\circ \) (\( \theta \) diffraction angle). This indicates that the poly(AA) and these copolymer networks are amorphous. When \( F_{SA} \) is 0.25, a diffraction pattern appeared at \( 2\theta = 21.0^\circ \), which is equivalent to a lattice-spacing \( (d_i) \) of 4.2 Å. The copolymer networks of \( F_{SA} = 0.25 \) and higher showed the same diffraction and the lattice-spacing hardly changed when \( F_{SA} \) changed from 0.25 to 1.0. The crystallinity of the network was estimated from the value of the peak height to the width of the diffraction at \( 2\theta = 21.0^\circ \) and proved that the crystallinity of the \( F_{SA} = 0.25 \) network was the highest of all. According to the literature [32], this diffraction is attributed to an interplanar spacing (100) of crystalline state formed by the long alkyl side chain of poly(SA). The (100) interplanar spacings of the dry network as well as the dry un-cross-linked copolymer with various copolymer compositions were found to be 4.2 Å, indicating the side-by-side spacing between the long alkyl side groups of the network.

A small angle X-ray diffraction (SAXD) pattern was taken in a similar manner as WAXD. The SAXD pattern of the poly(SA-co-AA) network of \( F_{SA} = 0.25 \) showed a diffraction peak at \( 2\theta = 1.42^\circ \) corresponding to a spacing \( (d_i) \) of 49.9 Å. Assuming the stearyl group is in the extended \( \beta \)-sheet conformation and aligned perpendicularly to the main chain, the length of octadecyl group is calculated as 25.7 Å by the molecular model. These results suggest that the long alkyl side chains form a lamellar structure with a thickness of about 50 Å making a tail-to-tail alignment perpendicularly to the main chains as illustrated in the left side (a) of Fig. 1.

3.1.1.2. Water-swollen state. The degree of swelling, \( q \), which is defined as the weight ratio of a swollen gel to the dried one strongly depends on \( F_{SA} \). Poly(AA) gel showed \( q \) as high as 1280, while \( q \) of the poly(SA-co-AA) gel rapidly decreased with increase in the SA content: \( q \) of the gel with \( F_{SA} \) of 0.05, 0.10, 0.15 and 0.25 became as low as 80, 8.1, 1.9 and 1.6, respectively. The copolymer gels of \( F_{SA} > 0.5 \) showed no swelling practically. This is obviously due to extensive aggregate formation of hydrophobic long alkyl side groups in water.

Effects of water content on the short-range and long-range structures of the gels have been studied by WAXD and SAXD studies. The water-swollen samples of poly(SA-co-AA) of \( F_{SA} = 0.25 \) showed the same diffraction peak of \( d_i \) as those of dry gels. We have evaluated the crystallinity of the gel from the sharpness of diffraction peak at a spacing of 4.1 Å and its change was investigated as a function of \( q \). It was found that the gel showed a maximum crystallinity at around \( q = 1.2 \), indicating that the introduction of water into the gels first enhances the crystalline ordering, and then lowers it. This result was presumably due to the enhanced hydrophobic interaction between the long alkyl side chains by incorporation of an appropriate amount of water.
The SAXD pattern of this copolymer gel also showed a diffraction peak which shifted to a lower angle with increasing $q$. The lattice spacing of $d_1$ was constant, while $d_2$ increased from 49.9 to 55.0 Å. In other words, when the network polymer absorbs water up to $q = 1.6$, it increases the long-range organization ($d_2$) as much as 5 Å while keeping a constant short-range ordering of 4.0 Å. One should notice here that the lamellar distance ($d_2$) of the swollen gels is nearly 5 Å larger than that of their dry state. This indicates that the water molecules are preferentially adsorbed in the main chain moiety due to the hydrophilic carboxyl group of AA units as shown in the right side (b) of Fig. 1.

When the number of carbon atoms of the long alkyl side chain decreased from 18 (stearyl group) to 16 (hexadecyl group), $q$ of the copolymer gel in the equilibrated water swollen state increased from 1.6 to 3.5, apparently due to the decrease in hydrophobicity of the side chain of the gel. However, if the carboxyl group is incorporated into the hexadecyl side chain end (AHA), $q$ further increased to 5.5 due to the hydrophilicity of carboxyls. From the WAXD and SAXD study, these hydrogels formed the crystalline domain with $d_1 = 4.1$ Å but without the long-range ordering in the equilibrated water-swollen state.

3.1.2. Order–disorder transition

3.1.2.1. Temperature. In order to investigate the thermal behavior of the poly(SA-co-AA) gels, we have measured differential scanning calorimetry (DSC) thermogram at a scanning ratio of 5°C min$^{-1}$ under nitrogen. DSC thermograms of the poly(SA-co-AA) gels showed the endothermic and exothermic peaks at 48 and 42°C upon heating and cooling, respectively, which was confirmed to be the reversible order–disorder transition together with the results of X-ray study. In every poly(SA-co-AA) gel, hysteresis was observed wherein the melting temperature was higher than the crystallization temperature, but the transition temperature was independent of the copolymer composition.

Young’s modulus, $E$, of the poly(SA-co-AA) gel was determined as the slope of the stress–strain curve where the strain rate was 1.0 mm min$^{-1}$. Temperature dependence of $E$ is shown in Fig. 2. $E$ decreased gradually with increasing temperature from 30 to 47°C and decreased abruptly from $1.7 \times 10^7$ to $2.2 \times 10^5$ Pa above 49°C. The temperature at which $E$ decreased abruptly coincides with the order–disorder transition temperature of the gel obtained by a

![Fig. 2. Temperature dependence of Young’s modulus ($E$) of the poly(SA-co-AA) gel of $F_{AA} = 0.25$.](image-url)
DSC measurement. The gel showed a typical jelly-like softness above the temperature. The drastic change observed in mechanical property is reversible and cyclically reproduced by repeated temperature changes.

3.1.2.2. Medium. The gels also showed the order–disorder transition by change in the composition of the solvent: water–ethanol or water–THF. As shown in Fig. 3, the swelling degree of the poly(SA) gel remained as low as 2.0 in a low THF concentration, but suddenly swelled when THF concentration becomes 90% when the concomitant volume increased several times. On the contrary, an abrupt shrinkage of the THF-swollen gel occurred if only a small amount of water was introduced, which in turn produced a large hydrostatic pressure and ejected the THF most efficiently. The collapse of the gel could be related to the order–disorder transition by the presence of water; time dependence of the crystallization of the gel was studied by a polarizing microscope under crossed nicols as shown in Fig. 4. Only a dark image of the gel was seen on the photograph at the beginning indicating the gel is entirely amorphous while it became clear from the outer to inner part of the gel with time, meaning that the crystallization progresses from the outer surface toward the inner part of the gel at 60 s.

X-ray study showed that the hydrogels containing the long alkyl side chains with the end group of carboxyls, poly(AHA-co-AA) gel, also showed the reversible order–disorder transition by pH change at around pH = 10 as well as temperature change (68°C), accompanying with the increase in q from 5.5 to 70 and the decrease in E from 10^7 to 10^5. From the pH titration, it was proved that this result was attributed to the ionization of carboxyls of the side chain end. The recrystallization and shrinkage of the gel occurred by adding the salt as much as the ionic strength of 10^{-1}–10^{-2} M.

3.1.3. Chemomechanical behaviors

3.1.3.1. Shape memory. A material is said to show shape memory if it can be deformed to a new shape (which it retains), only to revert to its original shape when heated above a certain critical temperature. Perhaps the most famous example of such a material is titanium–nickel alloy, produced by a reversible martensitic structural transformation [33]. The mechanism in our polymer gels is very different.
The mechanical properties of the water-swollen gels containing a long alkyl side chain drastically changed due to a reversible order–disorder transition, which allowed us to expect “shape memory” behaviors. If the gel is heated above the transition temperature (50°C) under its ‘soft’ state, it can be readily deformed to a new shape. As far as the gel is kept cooled in its deformed state, it is rigid and retains its new shape.

The crystalline aggregates formed among the side chains lock and keep the new shape. If the gel is then once again heated above the transition, it spontaneously recovers its original size and shape in a few seconds. This behavior is illustrated in Fig. 5. The hydrogels containing the long alkyl side chain with the ionizable group, poly(AHA-co-AA) gels, show the similar shape memory effect by changing temperature and also pH.

Based on the shape memory effect, we have constructed the gel valve. As illustrated in Fig. 6a, the load was placed on the plate of the poly(SA-co-AA) gel which has a slit at the center. The gel was tough enough to support the loads at 25°C. When the gel is heated up to 40°C, the gel plate became soft and is not able to hold the load any more and it opens the slit to drop the load (Fig. 6b). The gel plate automatically closes by the shape memory effect when all the glass beads used as a load has been dropped (Fig. 6c).

3.1.3.2. Chemical motor. We have constructed a new class of motor and generator system using order–disorder transition. The driving force of the motion of the gel is originated from the surface tension of spreading organic fluid, which is pumped out of the gel due to high osmotic and hydrostatic pressures in the gel. If the poly(SA) gel swollen in the THF, which is in amorphous state, is placed on the water surface, it transfers to ordered state
from the surface and simultaneously undergoes translational and rotational motions for a long time (more than 2 h). The process of a prolonged motion of the gel on the water surface was related to two steps: the first step is the releasing of organic solvent from the gel by osmotic pressure and hydrostatic pressure. When the gel swollen in THF is placed on water, it quickly forms a crystalline skin layer and an osmotic pressure is produced between the inside and outside of the gel. Since the formation of the crystalline surface skin layer additionally produces a large hydrostatic pressure difference, the organic solvent was ejected for a long period. The organized layer behaves as a permselective membrane, which allows the organic solvent to diffuse out but does not allow the water to come in. The formation of organized structure of the gel starts from the outer surface of the gel and develops into its inner part. By virtue of this, the skin layer keeps “pumping out” the organic solvent for a prolonged period of time. Here, an important fact is that the crystalline skin layer formed at the gel–water interface can act as a “molecular orifice” through which the organic solvent in the gel flows out.

The second step is the spreading of the organic solvent on the surface of the water and imparting motion to the gel. Once the organic solvent is ejected out of the gel, it rises up

Fig. 7. Schematic illustration and photographs of the poly(SA) gel: (a) translational motion; (b) rotational motion.

Fig. 8. Photograph of experimental set up to produce an electric power and a lighting of a photodiode array. The size of the rotor is 40 mm long, 6 mm wide, 2 mm thick, and the total weight of the rotor is 434 mg. The flux density of the permanent magnet is equal to 2300 Oe. The stator was made of a copper wire. The solenoid coil was wound with $5 \times 10^5$ turns/m. (For the lighting of the photodiode, the output signal was amplified about 1500 times.)
onto the water surface because of its lower density and rapidly spreads on it because of the large difference in their surface tensions. The surface spreading of the organic solvent imparts a reaction force to the gel and makes the gel move. In order to control the motion, the gel is wrapped up in an aluminum foil, and the spouting hole is prepared. For example, when the spouting hole is prepared at the rear of the model, the gel shows a translational motion as shown in Fig. 7a. Maximum velocity reaches 77 mm s⁻¹. When the two gels are wrapped by an aluminum foil and two spouting holes are settled at opposite sides of the rotor to generate the torque, a rotational motion is seen (Fig. 7b). The gels rotated with a maximum velocity of 400 rpm for nearly 30 min and the rotation continued for more than 2 h with the low velocity.

Using the rotational motion, a generator to produce an electric power has been constructed using the amphiphilic gel equipped with a pair of permanent magnet, solenoid coil, stator and a petri plate filled with water (Fig. 8). When the rotor rotates clockwise on the surface of water, the magnetic flux in the solenoid coil changes to give an electromotive force. Fig. 8 demonstrates a lighting of photodiode array by this amphiphilic gel generator. The numbers of photodiode to be lighted is determined by the rotation velocity of the gel-rotor. The instantaneous electromotive force reached a maximum of about 15 mV if four pieces of coils is used. The instantly induced current was 83 μA and the electric power by the electromagnetic energy was 0.2 μW.

3.2. Hydrogels with the liquid crystalline ordering

3.2.1. Mesophase structure

3.2.1.1. Dry state. We have investigated the structure of the homo- and copolymers derived from AA and 11CBA.

Fig. 9. Microscopic textures of poly(11CBA-co-AA)s under crossed polarizer at 80°C: (a) F₁₁CBA = 1.0; (b) F₁₁CBA = 0.76; (c) F₁₁CBA = 0.55; (d) F₁₁CBA = 0.29; (e) F₁₁CBA = 0.26; and (f) F₁₁CBA = 0.18.
Results of X-ray diffraction studies and microscopic observation showed that poly(11CBA) formed the liquid crystalline smectic A (SmA) structure with the bilayer (layer spacing: 46.2 Å), in which the side chains were perpendicularly arranged to the main chain axis without positional ordering within the layer. Fig. 9 shows microscopic photographs of poly(11CBA) and poly(11CBA-co-AA)s with various compositions, $F_{11CBA} = [11CBA]/([11CBA] + [AA])$, under the crossed polarizer. The fan-shaped texture with fluidity which is characteristic of the smectic structure [16] was observed in all the copolymers except for $F_{11CBA} = 0.18$ as well as poly(11CBA). WAXD and SAXD studies demonstrated that the copolymers of $F_{11CBA} = 0.26$ and larger formed the SmA structure with a bilayer whose thickness $d_2$ was 46.2–57.8 Å and the side-by-side spacing of side chain $d_1$ is about 4.3 Å as shown in Fig. 10. The phase diagram based on changes in $F_{11CBA}$ and temperature was obtained from the results of DSC study (Fig. 11). The glass transition temperature, $T_g$, and the isotropic temperature, $T_i$, increased with a decrease in $F_{11CBA}$ from 1.0 to 0.29, indicating that the thermostability of the liquid crystalline structure was enhanced by incorporating AA units.

3.2.1.2. Water-swollen state. The poly(11CBA-co-AA)s of $F_{11CBA}$ less than 0.18 dissolved in water, while those of $F_{11CBA}$ larger than 0.26 did not dissolve but swelled to form the physical hydrogels, presumably due to hydrophobic interaction of mesogenic side chains. From microscopic observation, the equilibrated water-swollen samples of $F_{11CBA} = 0.76$ and 0.55 still showed the fan-shaped texture as observed in the dry state, while the samples of $F_{11CBA} = 0.29$ and 0.37 showed the broken fan texture characteristic to a smectic phase with a higher ordered structure than SmA structure [16]. The water-swollen sample of $F_{11CBA} = 0.26$ showed no birefringence, suggesting the amorphous state.

The liquid crystalline structures of the copolymer gels have been investigated changing $F_{11CBA}$ and $q$. From WAXD and SAXD patterns of the fibrous gels oriented by spinning in the liquid crystalline melt, it was found that the copolymer gels of $F_{11CBA} = 0.55$ ($q = 1.08$) and 0.76 ($q = 1.05$) still formed the SmA structure in the equilibrated water-swollen state. On the other hand, from the X-ray

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Fig. 10. Schematic illustration of structures in SmA phase of poly(11CBA-co-AA)s.

Fig. 11. Phase diagram of poly(11CBA-co-AA)s on the basis of $F_{11CBA}$ and temperature. $T_g$: glass transition temperature, $T_i$: isotropic temperature.

Fig. 12. Wide angle X-ray diffraction patterns of poly(11CBA-co-AA)s of $F_{11CBA} = 0.37$: (a) $q = 1.0$, (b) $q = 1.18$.

Fig. 13. Changes in short-range ($d_1$) and long-range ($d_2$) spacings of poly(11CBA-co-AA)s of $F_{11CBA} = 0.37$ as a function of $q$. 
diffraction patterns of the gels of $F_{11CBA} = 0.37$ and 0.29, it was confirmed that the water incorporation induced the transformation from SmA to SmI structures. As shown in Fig. 12a, the WAXD pattern of the $F_{11CBA} = 0.37$ sample of $q < 1.13$ showed the halo at $2\theta = 21^\circ$ ($d_1 = 4.3$ Å) on the meridian line and the weak diffractions in the small angle region on the equatorial line, indicating that the formation of the SmA structure. When $q$ increased up to 1.18, the halo completely disappeared, instead, two sharp diffractions appeared at $2\theta = 35^\circ$ ($d_1 = 3.8$ Å) on the meridian line (mark A) and four sharp diffractions appeared at $2\theta = 27^\circ$ ($d_1 = 5.0$ Å) lying symmetrical to the meridian line (mark B) (Fig. 12b). According to the literature [16], this WAXD pattern can indicate the SmI structure in which the mesogenic side chains aligned quasihexagonally and tilted toward a neighboring side chain. The tilt angle, $\phi$ (shown in Fig. 14), of the side chains was calculated to be $27^\circ$ using the equation [16]:

$$\phi = \sin^{-1}(2/3^{1/2}\sin\psi),$$

where $\psi$ is the angle of diffraction B to the meridian line ($23^\circ$; shown in Fig. 12c). SAXD patterns of the copolymer gels of $F_{11CBA} = 0.29$ and higher shows layer diffractions at $2\theta = 1.72 - 1.41^\circ$ corresponding to spacings of 51.3–62.6 Å ($d_2$). If $d_2$ of the copolymer gels are plotted against $q$, one can get Fig. 13. All the samples show an increased $d_2$ with the increase in $q$. $d_2$ in the copolymer gels of $F_{11CBA} = 0.76$ and 0.55 slightly increased with increasing $q$, while $d_2$ in the samples of $F_{11CBA} = 0.37$, 0.29, and 0.26 increased largely.

Fig. 14 shows the phase diagram of the copolymer gels based on $F_{11CBA}$ and $q$. As mentioned above, poly(11CBA-$co$-$AA$)s except for $F_{11CBA} = 0.18$ formed the hydrogels by physical cross-linking of liquid crystalline domains. The SmA structure of the samples of $F_{11CBA} = 0.29$ and 0.37 transformed into the SmI structure at a certain $q$. In the copolymer of $F_{11CBA} = 0.26$, the SmA structure transformed into the amorphous state at $q = 1.77$. Thus, poly(11CBA-$co$-$AA$)s are able to take three forms of states SmA, SmI, and amorphous depending on the copolymer composition and water content.

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