Liquid Crystalline Hydrogels: Mesomorphic Behavior of Amphiphilic Polyacrylates Bearing Cholesterol Mesogen

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ABSTRACT: Copolymers composed of 5-acryloyloxypentyl cholesterate (Ch5A) and acrylic acid (AA), poly(Ch5A-*co*-AA)s, were prepared changing their molar ratio, and their mesomorphic behaviors were investigated. Wide- and small-angle X-ray diffraction studies showed that poly(Ch5A-*co*-AA)s with a Ch5A mole fraction, F, of 0.20 and larger showed the smectic A phase in which side chains are arranged perpendicularly to the main-chain axis forming bilayers. The structural ordering and the clearing temperature, T_c, increased with decreasing F. The copolymers with F of around 0.10 exhibited a mesophase showing extremely high T_c and longer periodic spacing than the SmA phase. The copolymers of $F = 0.05$ and higher were not dissolved in water but swelled to form hydrogels with mesomorphic properties, presumably due to the physical cross-linking of hydrophobic aggregates of Ch5A side chains. The relationship between the uncommon thermotropic behavior and the mesomorphic structure formed by the specific interaction of chiral Ch5A components was discussed.

Introduction

Liquid crystalline (LC) polymer networks have a variety of unique properties originating both from network structures and from liquid crystals: they may exhibit volume phase transition and elasticity and accompanying changes in Young's modulus and optical properties such as birefringence, color, and light reflection.[1−3] Extensive and systematic studies on structures and properties of LC elastomers[4−11] and LC organogels[12,13] have been made.

We have systematically studied the water-swollen LC gels which were copolymers consisting of a hydrophobic monomer with a mesogenic moiety, 11-(4′-cyanobiphenyloxy)undecyl acrylate (11CBA), and a hydrophilic monomer, acrylic acid (AA). The LC copolymers form the smectic A (SmA) structure in which side chains are arranged perpendicularly to the main-chain axis forming bilayers.[14] These copolymers did not dissolve in water because of their high hydrophobicity of 11CBA but swelled to form LC hydrogels. When the molar fraction of 11CBA, F_{11CBA}, was 0.37 and 0.29, LC hydrogels changed their structure from the SmA to the smectic I (SmI) in which the side chains are tilted to the neighboring side chains and formed a pseudohexagonal packing. This morphological behavior could be associated with the molecular interactions between the hydrophobic mesogenic component (11CBA) and the hydrophilic nonmesogenic component (AA) that eventually cause a phase separation. LC copolymer hydrogels composed of AA and 4′-(11-acryloyloxyundecyloxy)biphenyl-4-carboxylic acid (11ABA) having a carboxyl group at the end of mesogenic component showed a monolayer−bilayer transformation by changing mesogen composition due to selective combination of hydrogen bonding of the carboxyl groups between 11ABA and AA units.[15] In both cases of 11CBA and 11ABA, clearing temperature (T_c) and the structural order increased with an increase in AA molar ratio until showing a maximum. This phenomenon seems to be quite unique since LC copolymers containing other amorphous moieties decrease T_c with an increase in the content of the amorphous moiety.[16−20] The LC copolymers and the hydrogels containing AA and a mesogenic component with the particular interaction may show an unusual mesomorphic behavior.

The cholesterol was widely known as a good mesogen since most of cholesterol esters exhibited LC phase.[21] Another appealing property of the cholesterol mesogen is the optical activity to form the helical mesomorphism.[21−23] However, so far as the authors know, there has been no report on the LC hydrogel with cholesterol mesogen, although the lyotropic behavior of the surfactant having a cholesterol group has been studied.[24] Here we report on the synthesis and the mesomorphic properties of amphiphilic copolymers containing AA and cholesterol mesogen, poly(5-acryloyloxypentyl cholesterate, poly(Ch5A-*co*-AA)s. It is found that the copolymers with a small composition of Ch5A units showed an anomalous increase in transition temperatures and the uncommon mesomorphic behavior.

Experimental Section

Materials. Cholesteryl-6-acryloyloxyhexanate (Ch5A) was prepared according to the procedures described in the literature.[25] Acrylic acid (AA; TCI) was purified by distillation under reduced pressure. N,N'-Methylenebis(acrylamide) (MBAA; WAKO Pure Chemical Industries, Ltd.) and α,α′-azobis(isobutylonitrile) (AIBN; Junsei Chemical Co., Ltd.) were recrystallized from ethanol before use. Dimethylformamide (DMF; Junsei Chemical Co., Ltd.) was dried over calcium hydride and distilled before use.

Polymerization. Poly(Ch5A-*co*-AA)s were prepared by radical copolymerization of Ch5A and AA in DMF. The total monomer concentration was 2.0 M, and the polymerization was carried out in the presence of AIBN (0.01 M) at 60 °C for 24 h under nitrogen. Poly(Ch5A-*co*-AA)s were purified by repeated precipitation from DMF into ethyl acetate. Number-average molecular weights, M_n, were determined by gel permeation chromatography (eluent: THF) using polystyrene standards.

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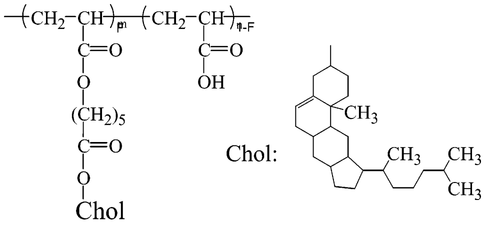

Figure 1. Molecular structure of poly(Ch5A-*co*-AA)s.

The copolymer composition, F, defined as $F = [\mathrm{Ch5A}]/([\mathrm{Ch5A}] + [\mathrm{AA}])$ was simply evaluated from the monomer composition in the feed because the yields were 95−98%.

Poly(Ch5A) was prepared by the analogous procedure as the copolymers, but the reprecipitation was made from DMF to methanol.

Measurements. Wide-angle (WAXD) and small-angle (SAXD) X-ray diffraction measurements and differential scanning calorimetry were carried out by the procedure described before.[14,15,26] Ultraviolet−visible (UV−vis) and circular dichroism (CD) spectra were measured using a quartz cell with an optical path of 0.1 cm by a Hitachi spectrophotometer and a Jasco spectropolarimeter J-725, respectively. The molecular ellipticity $[\theta]$ was evaluated in terms of the Ch5A unit. In the case of hydrogels, the hydrogels were cut 1×2 cm^2 and put in a quartz cell with an optical path of 1 cm. An optical path was decided from the thickness of hydrogels. The degree of swelling (q) of the gel was determined by the weight ratio of a swollen gel to the dried one.

Results and Discussion

1. Mesomorphic Behavior of Poly(Ch5A-*co*-AA)s.

Poly(Ch5A) was a hydrophobic polymer capable of forming the smectic bilayer structure with a spacing of 5.0 nm, and the mesogenic nature of Ch5A unit was confirmed in the literature[25] while polyAA is hydrophilic and amorphous. Poly(Ch5A-*co*-AA)s with various copolymer compositions were prepared by a free radical polymerization. The reactivity of Ch5A may be higher than that of AA since the reactivity of stearyl acrylate (SA) whose electronic environments around the double bond are similar to Ch5A is 6 times as high as that of AA according to the previous paper.[27] Therefore, one can assume that Ch5A and AA monomers may randomly be incorporated to give the randomly sequenced copolymers, if the Ch5A monomer concentration in the feed is low. Number-average molecular weights of the copolymers were in the range 5000−7000, which are relatively lower than the conventional polymers but comparable with the previously reported copolymers with 11CBA and 11ABA mesogens. The poly(Ch5A-*co*-AA)s, when molar fractions of Ch5A, F, were higher than 0.05, were soluble in DMF, tetrahydrofuran, and *N*-methylpyrrolidone but were not soluble in water while the copolymers of $F = 0.01$ and 0.001 were water-soluble.

The microscopic textures of poly(Ch5A) and poly(Ch5A-*co*-AA)s with various F were observed by a crossed-polarizing microscope. The poly(Ch5A) showed the batonet texture (Figure 2a) characteristic of the smectic phase.[23] The texture disappeared at 125 °C by heating and solidified at 5 °C by cooling. When F of the copolymers was 0.01 and higher, the birefringence with fluidity was observed in a certain temperature range, although the texture characteristic of the LC phase was not observed (Figure 2b,c). The birefringence disappeared at an elevated temperature which referred to the clearing temperature, T_c, and solidified at a reduced temperature which referred to the glass transition temperature, T_g. These findings indicate that the copolymers of $F = 0.01$ and higher exhibited the mesophases. It is quite unique that the copolymers composed of amorphous and mesogenic units with such a low mesogen composition are still able to show the mesophase, since the mesogen molar ratio of less than 0.5 is difficult to form the mesophase structure according to the previous reports,[16−20] except for ours.[14,15] It can be considered that this phenomenon may be the special feature of the mesogenic copolymers with AA units since the copolymers with 11CBA and 11ABA mesogens also exhibited the mesophase at the low molar ratios of 0.26 and 0.07, respectively, as reported previously. The present copolymers exhibited the mesophase at the mesogen composition of only 0.01, strongly suggesting that the mesophase inducing capability of Ch5A is excellent.

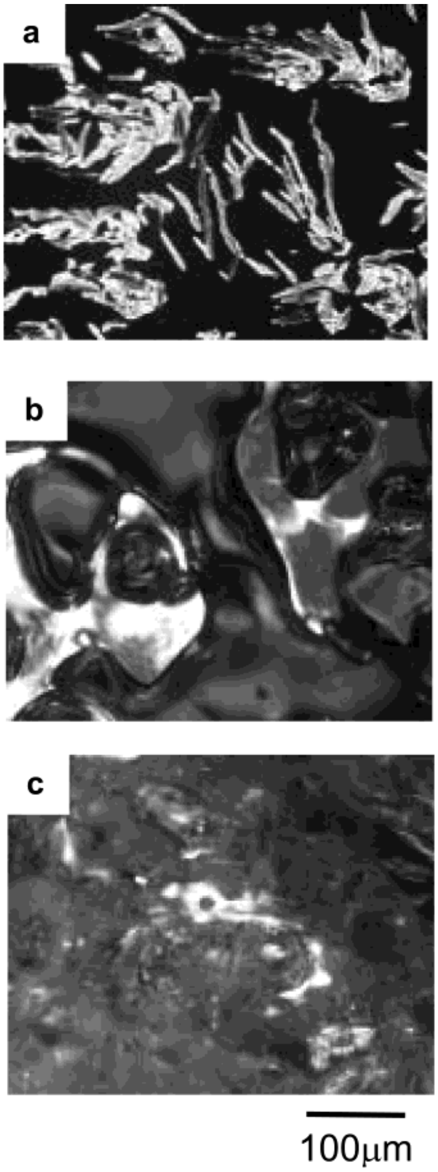

Figure 2. Microscopic textures of polymers taken under a crossed polarizer: (a) poly(Ch5A) taken at 100 °C; (b) poly(Ch5A-*co*-AA) of $F = 0.5$ taken at 200 °C; (c) poly(Ch5A-*co*-AA) of $F = 0.05$ taken at 200 °C. Scale bar: 100 μm.

The structures of the copolymers were investigated by X-ray diffraction. The WAXD image of the copolymer with F of 0.50, which was fibrized at a spinning ratio of about 5 cm s^{-1} in the mesophase state, is shown in

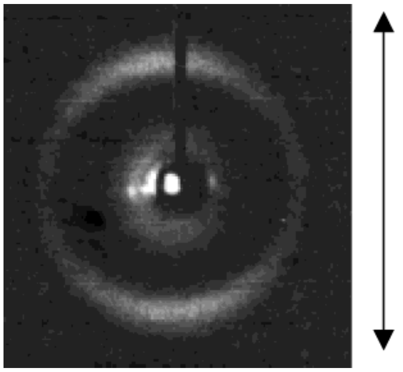

Figure 3. Wide-angle X-ray diffraction image of poly(Ch5A-*co*-AA) of $F = 0.50$ in the dry state taken at 20 °C. The sample was fiberized from the liquid crystalline state at 100 °C. Arrow shows a fiber axis.

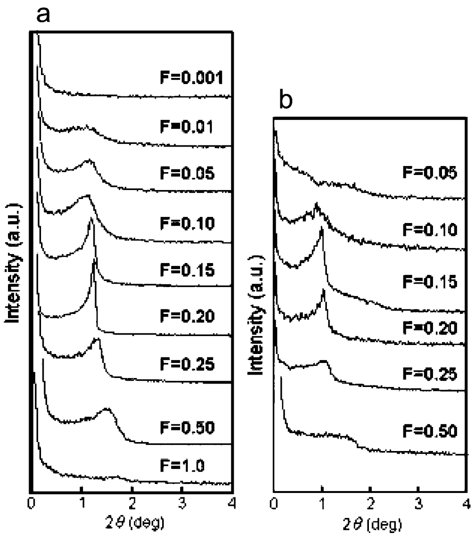

Figure 4. Small-angle X-ray diffraction patterns of poly(Ch5A-*co*-AA)s taken at 20 °C. (a) The samples quenched from the liquid crystalline state were dried in vacuo. (b) The water-swollen hydrogels prepared by cast from a methanol/tetrahydrofuran (v/v 1/1) solution and successive immersion in the pure water at 20 °C for a week.

Figure 3 where the fiber axis (presumably corresponding to the main chain) is placed vertically. This image shows two broad diffraction spots at $2\theta = 16.4°$ (θ: diffraction angle) corresponding to the spacing of 0.54 nm on the meridian line, indicating that mesogenic side chains are aligned side by side with a spacing of 0.54 nm (d_1) but perpendicularly to the main-chain axis. The d_1 spacing of the copolymers was almost constant regardless of F and equal to that of mesogenic polymer of poly(Ch5A) but somewhat bigger than those of poly(11CBA)[14] and poly(11ABA).[15] Small-angle diffraction spots faintly appearing on the equatorial line in this WAXD pattern may originate from the smectic layer structure and indicate that the layers align along the fiber axis.

SAXD patterns of poly(Ch5A) and poly(Ch5A-*co*-AA)s were taken to evaluate the layer spacing and the long-range ordering (Figure 4a). In poly(Ch5A) ($F = 1.0$), a small peak is detected at $2\theta = 1.8°$ corresponds to a spacing of 50 Å, d_2, which agrees with the bilayer thickness shown in the literature.[25] The peak shifted toward the smaller angle with a decrease in F and increased its sharpness until $F = 0.20$, indicating that incorporation of an appropriate amount of AA units into the poly(Ch5A) enhanced the structural ordering, but reduced its sharpness below that. On the other hand, the copolymer of $F = 0.001$ showed no diffraction, denying the formation of the long-range structure. It is notable that the copolymer of $F = 0.01$ showed the broad SAXD peak at $2\theta = 1.0°$, indicating that incorporation of Ch5A into polyAA, even if the amount was very small, enhanced the formation of the long-range structure. The sharpest peak in the $F = 0.20$ copolymer should be attributed to the cooperative effects of Ch5A and AA units on the enhancement of the structural ordering.

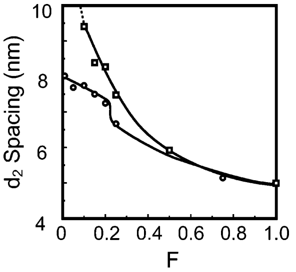

Figure 5. Changes in d_2 spacing as a function of F. Circular marks refer to the samples in the dry state prepared by the procedure shown in Figure 4a. Square marks refer to the water-swollen hydrogels prepared in the procedure shown in Figure 4b.

Figure 5 shows d_2 spacing as a function of F. The d_2 spacing gradually decreased with increasing F but showed an abrupt dip at $F = 0.20$ where the SAXD peak is sharpest. There may be the mesomorphic difference in the copolymers above and below $F = 0.20$. One can guess that the copolymers above $F = 0.20$ formed the bilayer whose thickness gradually decreased with increasing F since the smooth curve could be drawn on the plots containing the spacing of the poly(Ch5A) bilayer. Ch5A and AA units should form separate domains in the copolymer since poly(Ch5A) is not miscible with polyAA (Figure 6a,b). Then the increase in the bilayer thickness can be explained by the increased size of AA domains similarly as the case of 11CBA copolymers. IR spectra of the copolymers showed an intense peak at around 1700 cm^{-1} assigned to an aliphatic carboxylic dimer[28] (hydrogen bonding between AA carboxyls) with overlapped peaks of acrylate ester, demonstrating the formation of the hydrogen bonding of AA units. The domains containing an appropriate amount of AA might supplementarily stabilize the LC organization through forming the cooperative hydrogen bonding between carboxylic groups, but too much AA might disturb the organization inversely. These effects of copolymerization of AA monomer with the mesogenic monomer on the enhancement of the structural ordering of the bilayers were also found in the copolymers of 11CBA[14] and 11ABA.[15] In the system of 11CBA mesogen, the composition showing the sharpness maximum was 0.26, which is higher than that in the case of the present copolymer having Ch5A mesogen (0.20). On the basis of the finding that the monomers can be randomly copolymerized in these compositions, we can estimate that the hydrogen bonding of about 4 units of AA existing between neighboring Ch5A mesogens can organize the mesomorphic structure most effectively while about 3 units of AA existing between neighboring 11CBA mesogens the mesomorphic structure most effectively. A WAXD study confirmed that the side-by-side space between Ch5A mesogens (0.54 nm) was 1.2 times as wide as that between 11CBA mesogens (0.44 nm). The mesomorphic structure with the wider spacing

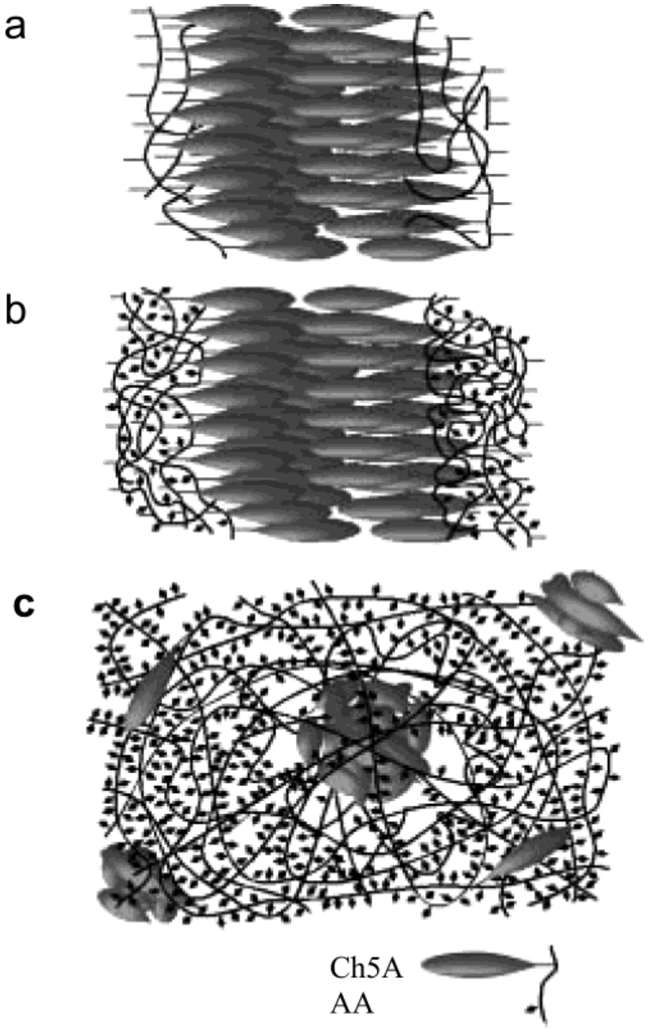

Figure 6. Schematic illustration of mesophase structures of poly(Ch5A) and poly(Ch5A-*co*-AA)s: (a) poly(Ch5A); (b) $F =$ 0.50−0.20; (c) $F =$ 0.15−0.01.

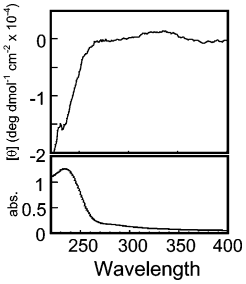

Figure 7. Circular dichroism (top) and ultraviolet−visible absorption (bottom) spectra of the aqueous solution of poly(Ch5A-*co*-AA) with F of 0.10.

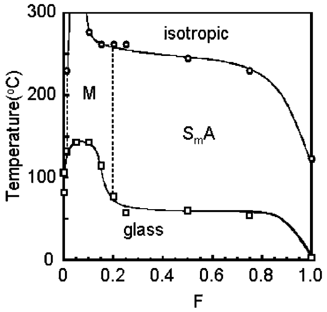

Figure 8. Phase diagram of poly(Ch5A-*co*-AA)s on the basis of temperature and F. M refers to a mesophase.

of mesogens may require the larger amount of AA units for the enhancement of the bilayer structural ordering. On the other hand, in the copolymers having the 11ABA mesogen which has a carboxyl group at the mesogen end, the sharpness maximum appeared when 11ABA was equally incorporated with AA. As shown in the previous paper, this fact suggests that the carboxyl groups of the mesogen end interact with AA carboxyls. This case is different from the present Ch5A copolymers in terms of the orientation of the hydrogen bonding. As for the copolymers below $F = 0.20$, the SAXD peaks of the long-range ordering were small and broad, and d_2 spacing showed a sudden change at $F = 0.20$ (Figure 5). These findings did not confirm the layer structure but another kind of aggregated structure locating with a distance of 7.2−8.0 nm. Besides, there was the difference in the solubility in alkaline solution; the copolymers below $F = 0.15$ were soluble in alkaline solution of pH = 12 while the copolymers above $F =$ 0.20 were insoluble, suggesting that ionization is strongly restricted presumably due to the strong multiple hydrogen bonding of AA units supported by the Ch5A stacking forming the bilayer. The alkaline solution of the copolymers below $F = 0.15$ no longer showed the SAXD peaks but a circular dichroism (CD). Figure 7 shows the CD spectrum of the alkaline solution (pH = 12) of the $F = 0.10$ copolymer at a concentration of 0.02 unit M together with UV spectrum of the same sample. CD peaks with a molecular ellipticity, $[\theta]$, of less than -2000 deg cm^2 dmol^{-1} with the negative Cotton effect in the wavelength range below 270 nm appeared while the UV spectrum showed the absorbance peak ($\lambda_{\max} =$ 235 nm) which can be assigned to the n−π^* electronic transition of carbonyl group and the absorption was low enough to justify the CD spectrum. The same Cotton effects of CD also appeared in the copolymers of $F = 0.15$, 0.05, and 0.01. Since the alkaline solutions of polyAA and the copolymer of $F = 0.001$ showed no CD, we presume that CD of the copolymers may be associated with the formation of some optically active structure although the assignment was not made. If this kind of structure was assumed to form in the dry state, the SAXD peak might be assigned to the distance among the optically active structure as shown in Figure 6c.

Figure 8 showed the phase diagram of the polymers in the dry state as a function of F. T_c and T_g of poly(Ch5A-*co*-AA)s were determined by DSC thermograms. Transition temperatures of poly(Ch5A) were lower than those shown in the literature,[25,29] presumably due to the lower molecular weight, but were comparable with those of poly(11CBA).[14] Transition temperatures of poly(Ch5A-*co*-AA)s gradually increased with decreasing F down to 0.20, which is also similar phenomenon as the case of poly(11CBA-*co*-AA)s.[14] In the range of $F = 0.20$−0.05, T_g drastically increased and showed a maximum of 149 °C, which is 144 °C higher than T_g of poly(Ch5A); besides, T_c showed an anomalous increase and became undetectable in $F = 0.05$. T_c of poly(11CBA-*co*-AA)s showed a maximum of 126 °C at the mesogen molar composition of 0.29.[14] On the contrary with the similarity of transition temperatures of poly(Ch5A) with poly(11CBA), the copolymers of C lower than 0.15 showed a strong contrast. The anomalous thermotropic behavior in poly(Ch5A-*co*-AA)s may be attributed to the thermally stable mesophase structure (marked as M in

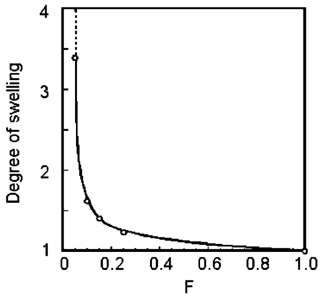

Figure 9. Swelling degrees of poly(Ch5A-*co*-AA) hydrogels with various F.

Figure 8) formed by Ch5A and AA, which are estimated to be randomly sequenced in the copolymer chains.

2. Mesomorphic Behavior of Hydrogels. Although polyAA and poly(Ch5A-*co*-AA) of $F = 0.01$ and 0.001 dissolved in water, the copolymers of $F = 0.05$ and higher were not dissolved but swelled forming hydrogels. We can guess that the hydrogels should be physically cross-linked by the hydrophobic aggregates of Ch5A side chains supported by the hydrogen-bonding bridges of AA. When the mesogen molar composition was 0.05, neither copolymers composed of 11CBA[14] or 11ABA[15] formed hydrogels, indicating that the Ch5A interaction such as hydrophobic interaction and steroid stacking force was very strong. Figure 9 shows changes in the degree of swelling, q, as a function of F. q values increased with decreasing F but below $F = 0.2q$ increased largely. The bilayer structure interfere the swelling in the hydrogels containing 11CBA mesogen.[26] In the present case, the optically active secondary structure does not interfere the swelling very much. The crossed polarizing microscopic observation of the water-swollen copolymers of $F = 0.20$ and higher showed the birefringence with fluidity and confirmed the formation of LC hydrogels while the copolymers below $F = 0.15$ showed no birefringence. WAXD patterns of the copolymer hydrogels were essentially the same as those of dry samples showing the same d_1. On the other hand, SAXD patterns of the copolymer hydrogels showed the broader peaks at smaller diffraction angles than those of dry samples (Figure 4c), especially $F = 0.05$ sample shows no peak, suggesting that the water was intruded into the AA domains breaking the hydrogen-bonding support of the mesophase structure. Figure 5 shows the F dependence of the d_2 spacings in the water-swollen state. On the contrary of the dry state, d_2 showed a smooth change, suggesting the presence of the water make a difference in d_2 spacing ambiguous. Although the hydrogels of $F = 0.15$ and 0.10 showed no birefringence, they clearly showed the SAXD peak. These experimental facts suggest that this sample may form the mesophase structure forming the cross-linking domain small enough not to scatter the visible light.

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References and Notes

(1) Hikmet, R. A. M.; Keperman, H. *Nature (London)* **1998**, *392*, 476.
(2) Kikmet, R. A. M.; Lub, J. *Prog. Polym. Sci.* **1996**, *21*, 1165.
(3) Broer, D.; Lub, J.; Mol, G. N. *Nature (London)* **1995**, *378*, 467.
(4) Schätzle, J.; Kaufhold, W.; Finkelmann, H. *Makromol. Chem.* **1989**, *190*, 3269; **1991**, *192*, 1235.
(5) Kaufhold, W.; Finkelmann, H.; Brand, H. R. *Makromol. Chem.* **1991**, *192*, 2555.
(6) Küpfer, J.; Nishikawa, E.; Finkelmann, H. *Polym. Adv. Technol.* **1994**, *5*, 110.
(7) Kundler, I.; Finkelmann, H. *Makromol. Chem. Rapid Commun.* **1995**, *16*, 679.
(8) Talroze, R. V.; Gubina, T. I.; Shibaev, V. P.; Plate, N. A.; Dakin, V. I.; Schmakova, N. A.; Sukhov, F. F. *Makromol. Chem. Rapid Commun.* **1990**, *11*, 67.
(9) Sigel, R.; Stille, G.; Strobl, G.; Lehnert, R. *Macromolecules* **1993**, *26*, 4226.
(10) Disch, S.; Finkelmann, H.; Ringsdorf, H.; Schumacher, P. *Makromol. Chem. Rapid Commun.* **1995**, *28*, 2424.
(11) Zubarev, E. R.; Talroze, R. V.; Yuranova, T. I.; Plate, N. A.; Finkelmann, H. *Macromolecules* **1998**, *31*, 3566.
(12) Kishi, R.; Suzuki, Y.; Ichiro, H.; Hirasa, O. *Chem. Lett.* **1992**, 1855.
(13) Matsuoka, Y.; Kishi, R.; Shishido, M. *Chem. Lett.* **1994**, 2257.
(14) Kaneko, T.; Yamaoka, K.; Gong, J. P.; Osada, Y. *Macromolecules* **2000**, *33*, 412.
(15) Yamaoka, K.; Kaneko, T.; Gong, J. P.; Osada, Y. *Macromolecules* **2001**, *34*, 1470.
(16) Poths, H.; Zentel, R. *Liq. Cryst.* **1994**, *16*, 749.
(17) Ringsdorf, H.; Schmidt, H.-W. *Makromol. Chem.* **1987**, *188*, 1355.
(18) Barmatov, E. B.; Pebalk, D. A.; Barmatova, M. V.; Shibaev, V. P. *Liq. Cryst.* **1997**, *23*, 447.
(19) Shibaev, V. P.; Barmatov, E. B.; Pebalk, D. A.; Barmatova, M. V. *Colloid Polym. Sci.* **1998**, *276*, 662.
(20) Barmatov, E. B.; Bobrovsky, A. Y.; Barmatova, M. V.; Shibaev, V. P. *Liq. Cryst.* **1999**, *26*, 581.
(21) Demus, D. In *Handbook of Liquid Crystals*; Goodby, J., Gray, G. W., Spiess, H.-W., Vill, V., Eds.; Wiley-VCH: Weinheim, 1998; Vol. 1.
(22) Reinitzer, F. *Monatsh. Chem.* **1888**, *9*, 421.
(23) Collings, P. J.; Hird, M. *Introduction to Liquid Crystals*; Tayor & Francis: London, 1997.
(24) Decher, G.; Ringsdorf, H. *Liq. Cryst.* **1993**, *13*, 157.
(25) Freidzon, Ya. S.; Kharitonov, A. V.; Shibaev, V. P.; Plate, N. *Mol. Cryst. Liq. Cryst.* **1982**, *88*, 87.
(26) Kaneko, T.; Yamaoka, K.; Gong, J. P.; Osada, Y. *Macromolecules* **2000**, *33*, 4422.
(27) Matsuda, A.; Sato, J.; Yasunaga, H.; Osada, Y. *Macromolecules* **1994**, *27*, 7695.
(28) Nakanishi, K. *IR Absorption Spectroscopy—Practical,* Nankodo, 1960.
(29) Freiden, Y. S.; Kharitonov, A. V.; Shibaev, V. P.; Platé, N. A. *Eur. Polym. J.* **1985**, *21*, 211.

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