Liquid Crystalline Gels. 3. Role of Hydrogen Bonding in the Formation and Stabilization of Mesophase Structures

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ABSTRACT: Copolymers composed of various amounts of 4′-(11-acryloyloxyundecyloxy)biphenyl-4-carboxylic acid (11ABA) and acrylic acid (AA), poly(11ABA-*co*-AA)s, were synthesized, and their liquid crystalline structures were investigated both in dry and in water-swollen states. Wide- and small-angle X-ray studies revealed that both dry and swollen poly(11ABA-*co*-AA)s show a liquid crystalline structure, which transforms from smectic C with the bilayer ($\mathrm{SmC_2}$) to smectic C with the monolayer ($\mathrm{SmC_1}$), when the 11ABA composition, F([11ABA]/([11ABA] + [AA])), decreases from 0.72 to 0.44. The phase diagram of these copolymers was established by changing F and the temperature. It shows that the samples can build up a liquid crystalline structure for F as low as 0.07 at the elevated temperature of 155 °C. The enhanced ordering of the liquid crystalline structure and the thermostability of the copolymers were explained in terms of hydrogen bonding formed between carboxyls of mesogenic side chains and AA.

Introduction

In the previous papers, we reported that the copolymers consisting of a hydrophobic monomer with a mesogenic moiety, 11-(4′-cyanobiphenyloxy) undecyl acrylate (11CBA), and a hydrophilic monomer, acrylic acid (AA), show the smectic A (SmA) structure in which side chains are arranged perpendicularly to the main chain axis forming bilayers: this structure is formed only when the molar fraction of 11CBA, F_{11CBA}, is 0.26 and higher,[1,2] and the order and spacing of the smectic layer increased with the increase in the AA composition. These copolymers did not dissolve because of their increased hydrophobicity of 11CBA but swelled in water to form hydrogels, still keeping the liquid crystalline ordering (liquid crystalline gels; LCG). LCG of $F_{11CBA} = 0.37$ and 0.29 changed their structure from the SmA to the smectic I (SmI) phase in which the side chains are tilted to the neighboring side chains and formed pseudohexagonal packing. However, LCG of $F_{11CBA} = 0.26$ transformed from the SmA phase to the amorphous state.[2] This morphological behavior could be associated with the molecular interactions between the hydrophobic mesogenic component (11CBA) and the hydrophilic nonmesogenic component (AA) that eventually might cause a microphase separation.

In this paper, we have made structural and morphological studies of the liquid crystalline copolymers prepared from AA and 4′-(11-acryloyloxyundecyloxy)-biphenyl-4-carboxylic acid (11ABA), which has the same chemical structure as 11CBA, except for a carboxyl group replacing the cyano group at the end of the mesogen. This type of copolymer is expected to exhibit the liquid crystalline polymorphism due to selectively combined hydrogen bonding of the carboxyl groups between 11ABA and AA units. The water incorporation could dominate the morphological behavior of the liquid crystalline copolymers similarly to the case of the poly-(11CBA-*co*-AA)s.[2]

LCG have a variety of unique properties originating both from gels and from liquid crystals: they may exhibit volume phase transition and accompanying changes in Young's modulus and optical properties such as birefringence, color, and light reflection.[3−5] The studies on the structural behavior of liquid crystalline copolymers containing hydrophilic units in the dry state have revealed that a structural change occurred by the incorporation of nonmesogenic components.[6−10] Extensive and systematic studies on structures and properties of liquid crystalline elastomers have been made, and it was proved that the mechanical stress was effective on changes of transition temperatures,[11] birefringence,[12,13] and mesophase structures.[14−18] The specific properties such as second harmonic generation,[19,20] piezoelectricity,[21,22] and electro- and magnetomechanical behaviors[23−26] were also investigated. However, so far authors know the liquid crystalline hydrogels had not systematically been studied.

Experimental Section

Materials. 11-(4′-Cyanobiphenyloxy)undecanol (11CB) was prepared by the procedure shown in the previous paper.[1] Acryloyl chloride (Junsei Chemical Co., Ltd.), triethylamine (Kanto Chem. Co., Ltd.), and potassium hydroxide (Junsei Chemical Co., Ltd.), used for monomer synthesis, were used as received. Diethylene glycol (Junsei Chemical Co., Ltd.), used as a solvent for monomer synthesis, was used as received. Hexane (Junsei Chemical co., Ltd.), methanol (Junsei Chemical Co., Ltd.), and acetic acid (Kishida Chemical Co., Ltd.), used for purification of the monomer, were used as received. Acrylic acid (AA; TCI), used as a monomer, was distilled before use. α,α′-Azobis(isobutylonitrile) (AIBN; TCI), used as a radical initiator, was recrystallized before use. Tetrahydrofuran (THF; Junsei Chemical Co., Ltd.) and *N*-methyl-2-pyrrolidone (NMP; Junsei Chemical Co., Ltd.), used as solvents for polymerization, were distilled before use. Chloroform (Junsei Chemical Co., Ltd), used for purification of the polymers, was used as received.

Syntheses of 4′-(11-Acryloyloxyundecyloxy)biphenyl-4-carboxylic Acid (11ABA). 4′-(11-Acryloyloxyundecyloxy)-biphenyl-4-carboxylic acid (11ABA) was synthesized as follows. The cyano group of 11CB was hydrolyzed in a mixed solvent, diethyleneglycol (400 mL)/water (100 mL), in the presence of

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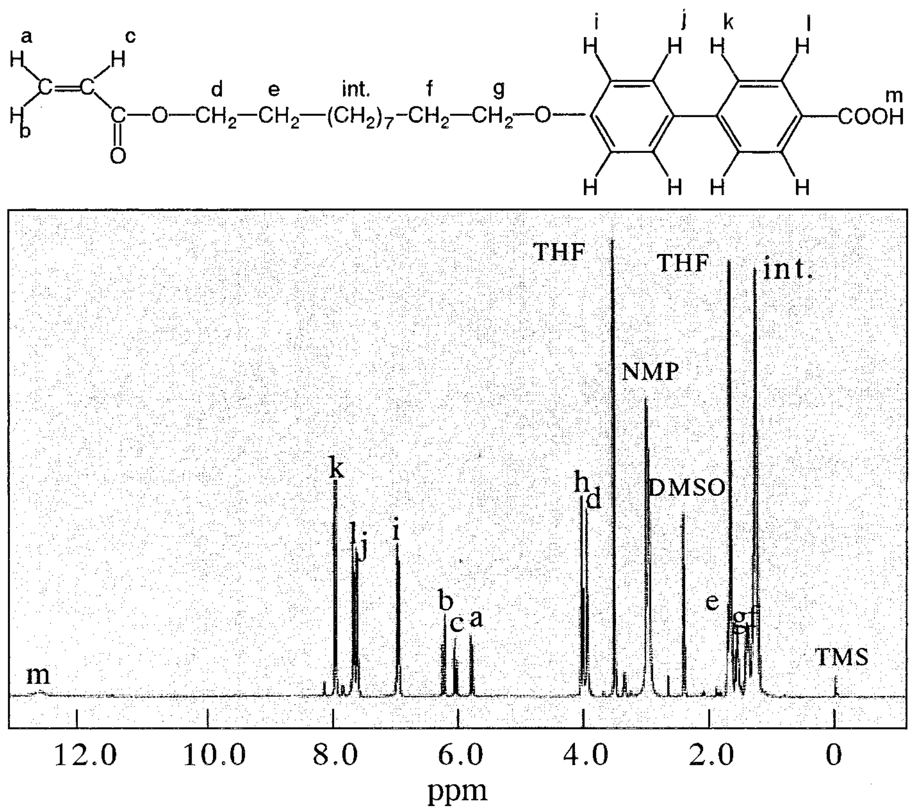

Figure 1. ^{1}H NMR spectrum of 11ABA monomer.

potassium hydroxide (0.089 mol) with stirring at 200 °C for 18 h. The reaction solution was poured into diluted hydrochloric acid (pH = 1) to give the white powder that was recrystallized from acetic acid/methanol to obtain the white crystal of 4′-undecyloxybiphenyl-4-carboxylic acid (11AB) (yield: 90%; melting point: 151 °C; isotropic point 195 °C). The IR spectrum confirmed the transformation from the cyano group (2270 cm^{-1}) to the carboxylic group (1695 cm^{-1}).

A NMP solution (150 mL) of 11AB (0.010 mol) and triethylamine (4 mL) was added dropwise under nitrogen to a NMP solution (50 mL) of acryloyl chloride (0.012 mol) with stirring over several hours at 0 °C and then at room temperature for 24 h. Triethylamine hydrochloride salt, generating as a result of reaction, was removed by filtration, and then the reaction solution was poured into distilled water to give a white powder, which was dried in vacuo. The product was recrystallized from THF/hexane to give the white crystal of 11ABA (yield: 25%; melting point: 243 °C). The structure of 11ABA was confirmed by the ^{1}H NMR spectrum (Figure 1).

Synthesis of Poly(11ABA-*co*-AA)s. Poly(11ABA-*co*-AA)s with various 11ABA-AA compositions were obtained by radical polymerization in THF varying 11ABA composition in feed, $f_{11ABA} = 1.0$, 0.75, and 0.50, or in NMP, $f_{11ABA} = 0.25$, 0.10, and 0.05 (monomer concentration: 0.2−0.76 mol L^{-1}) at 60 °C for 3 days in vacuo; 0.5 mol % of AIBN was used as an initiator. The polymerization proceeded homogeneously and poly(11ABA-*co*-AA)s were obtained with yields of 20−59% as white powder by repeatedly precipitating with chloroform. The mole fraction of the 11ABA unit in poly(11ABA-*co*-AA)s, F_{11ABA}, was determined by the analysis of ^{1}H NMR spectra from the ratio of the peak areas of biphenyl protons (7.01−7.96 ppm) and α-protons (2.24 ppm) (Table 1). Number-average molecular weights, M_n, respectively, were determined by gel permeation chromatography (GPC; Tohso RI8020; column, Tohso G5000H, G4000H, G3000H;eluent, THF) calibrated with standard polystyrenes (Tohso). The results are summarized in Table 1.

Measurements. ^{1}H NMR spectra of 4 wt % 11ABA were measured in THF-d_8/dimethyl sulfoxide-d_6 solution were measured with a NMR spectrometer (JEOL GSX-400) at 400 MHz. ^{1}H NMR chemical shifts in parts per million (ppm) were recorded downfield from 0.00 ppm using tetramethylsilane (TMS) as an internal reference.

Table 1. Monomer Composition and Molecular Weight of Poly(11ABA-*co*-AA)s

f_{11ABA}[a]	1.0	0.75	0.50	0.33	0.25	0.10	0.05
F_{11ABA}[b]	1.0	0.72	0.44	0.28	0.22	0.07	0.04
M_n ($\times 10^{-3}$)[c]	4.0	3.4	3.2	3.4	3.4	3.8	3.8

[a] Mole composition in feed. [b] Mole composition in the copolymer. [c] Number-average molecular weight.

Infrared (IR) spectra were recorded on a microsampling infrared spectrometer (JASCO, MSX-2000) after 64 scans (4-cm^{-1} resolution) over the range from 4600 to 600 cm^{-1}. The samples were mixed with potassium bromide and pressed to give transparent pellets.

The optical microscopic observation was performed on a polarizing microscope (Olympus, BH-2) equipped with a Mettler FP-80 hot stage. The film as a sample was prepared by casting between two glass plates in the isotropic state.

The thermotropic behavior was measured on a differential scanning calorimeter, DSC (DSC22C, Seiko), at a scanning ratio of 5 °C min^{-1} from 0 to 250 °C in nitrogen. The samples (about 10 mg) were dried thoroughly at a temperature higher than 100 °C for 3 h in vacuo before being hermetically sealed in aluminum pans.

Wide-angle X-ray diffraction (WAXD) patterns were taken with a flat-plate camera mounted on a Shimazu X-ray generator (XD-610) emitting Ni-filtered Cu Kα radiation (40 kV, 40 mA) in transmission geometry. The distance from the sample to the film was determined by calibration with the silicon powder. Small-angle X-ray diffraction (SAXD) patterns were recorded on a Rigaku X-ray diffractometer (RINT-2000) (40 kV, 200 mA) in transmission geometry. A 2θ (θ: diffraction angle) scanning speed of 1° min^{-1} with a sampling interval of 0.01° was used. The samples were quenched from the liquid crystalline state at 160 °C.

The degree of swelling (q) was defined as the weight ratio of a swollen gel to the dried one.

Results and Discussion

1. Structure of Poly(11ABA). The microscopic texture of poly(11ABA) was observed with crossed polarizers to confirm the presence of liquid crystals. When the solid sample is heated, the fanlike texture characteristic to the smectic phase[27] with the layer structure appeared at 120 °C (Figure 2a), which disappeared at 240 °C by further heating.

This sample was drawn at a spinning ratio of about 5 cm s^{-1} at 146 °C and the molecular structure was investigated by WAXD. The WAXD pattern in Figure 3, where the fiber axis (presumably corresponding to the main chain) is placed vertically, shows four broad diffractions with $2\theta = 20.3°$ (θ: diffraction angle) corresponding to the spacing of 4.4 Å located at symmetrical positions with an angle ($\psi = 40°$) to the meridian line. This diffraction pattern indicates that mesogenic side chains are aligned side by side with a spacing of 4.4 Å (d_1), but tilted to the normals of the main chain axis by an angle of approximately $\psi = +40°$ or $\psi = -40°$. d_1 spacing of this polymer, 4.4 Å, is equal to that of a liquid crystalline polymer, poly(11CBA).[1] Small-angle diffractions appearing on the equatorial line in this WAXD pattern should originate from the layer structure as suggested from microscopic observation and indicate that the layers align along the fiber axis.

A SAXD pattern of poly(11ABA) was taken to evaluate the layer spacing and the long-range ordering (Figure 4). Two peaks are detected at $2\theta = 2.1°$ and 4.2° corresponding to spacings of 42.1 and 21.0 Å, respectively, which are obviously first- and second-order diffractions of the layer structure. If the mesogenic side chains with the length of 26.5 Å as calculated from a molecular model are tilted as much as 40° to the normal direction of the layer, the bilayer thickness of 41 Å is obtained, which agrees well with the layer spacing, d_2 (42.1 Å), derived from the SAXD pattern. Thus, one can conclude that poly(11ABA) exhibits the smectic C phase with the bilayer structure in which the side chains are allowed to tilt as much as 40° (SmC_2). As reported in the previous paper,[1] the poly(11CBA-*co*-AA)s exhibit the SmA structure with the bilayer structure in which the side chains are arranged parallel to the layer normal, which leads to a spacing d_2 of 46.0 Å. Thus, the smaller d_2 in the SmC_2 structures of poly(11ABA) than that in the SmA structure of poly(11CBA) is explained by the tilting of mesogenic side chains. The SmC phase has two directors: long axis (*n*-director) of mesogen and the projection of the *n*-director onto the layer plane (*c*-director)[27] while SmA has only the *n*-director. This indicates that the substitution of the cyano group of the mesogenic side chain end by a carboxyl group enhanced the liquid crystalline ordering.

A DSC measurement was carried out and was found that the glass transition temperature (T_g) of poly(11ABA) is 160 °C and the transition temperature from the SmC_2 phase to the isotropic phase (T_i) is 230 °C, respectively. These transition temperatures are substantially higher than those of poly(11CBA) ($T_g = 5$ °C, $T_i = 94$ °C) and indicate an enhanced stability of the liquid crystalline structure of poly(11ABA) presumably because of the hydrogen bonding between carboxyl groups at the mesogenic side chain ends.

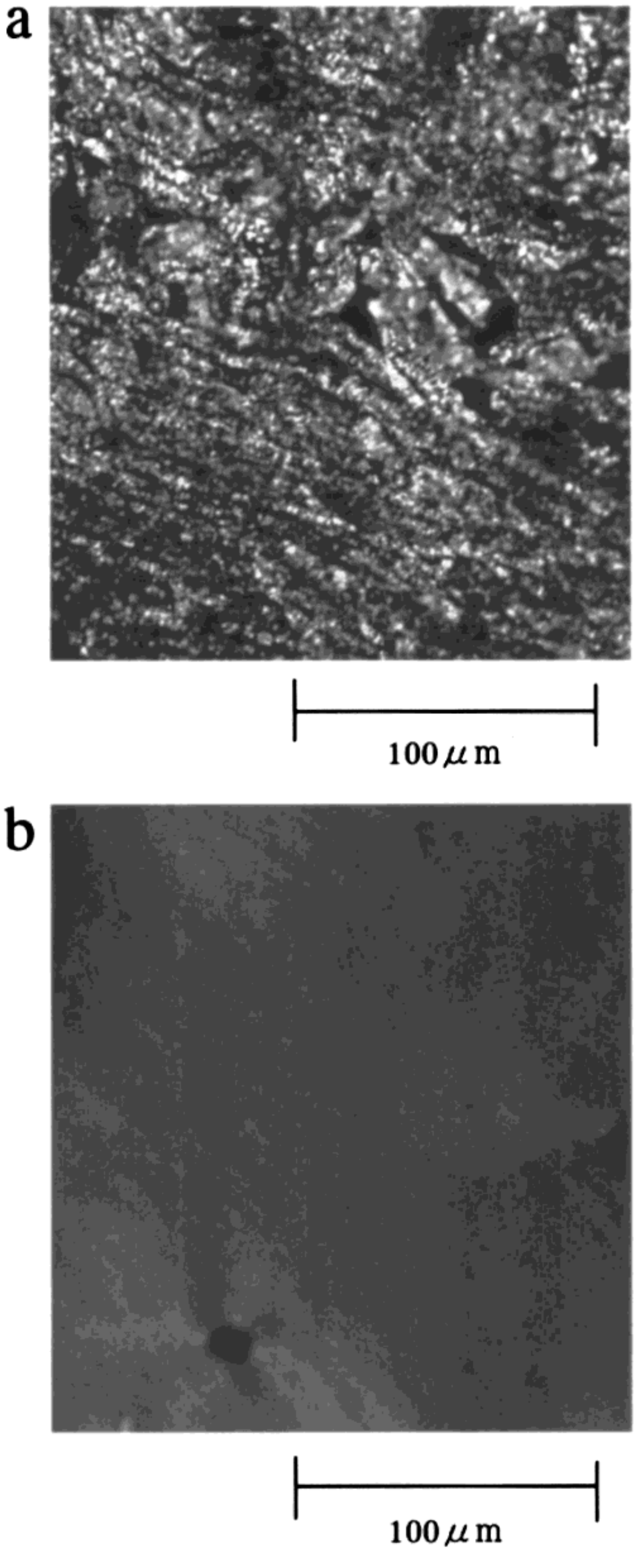

Figure 2. Microscopic textures of polymers under a crossed polarizer: (a) poly(11ABA), 230 °C; (b) poly(11ABA-*co*-AA) of $F_{11ABA} = 0.07$, 130 °C.

2. Effects of AA Incorporation on the Structure (Dry State). The results in Table 1 show that 11ABA is sufficiently reactive in radical polymerization and almost equivalently incorporated into the copolymer. Therefore, the copolymers should be randomly sequenced and can partially have the short sequence with excess 11ABA or AA units. Number-average molecular weights 3200−4000 were not high enough when compared with those of common polymers but are in the same order as those of poly(11CBA) in the literature

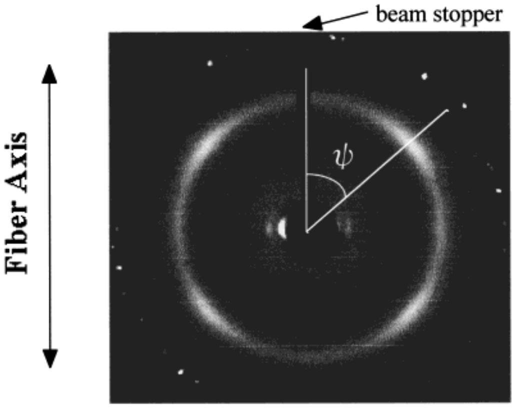

Figure 3. Wide-angle X-ray diffraction pattern of poly(11ABA) in the dry state taken at 20 °C.

(Table 1).[1,2,28,29] The copolymers of $F_{11ABA} = 0.22$ and larger were soluble in THF and NMP but were not soluble in water or DMSO.

The microscopic texture of poly(11ABA-*co*-AA)s with various copolymer compositions, F_{11ABA}, was observed with crossed polarizers. When the F_{11ABA} of the copolymers were 0.07 and higher, the birefringence with fluidity was observed in a certain range, although no texture characteristic of the liquid crystalline phase was observed. The birefringence disappeared upon heating and its fluidity disappeared upon cooling. The birefringence also disappeared by applying a shear stress to the samples by sliding two glass plates. All these findings indicate that the copolymers of $F_{11ABA} = 0.07$ and higher have liquid crystalline phases, and then transition temperatures observed by heating and cooling correspond to T_i and T_g. It is of interest that the copolymers of such a low value of F_{11ABA} are still able to show the liquid crystalline phase. This is in strong contrast with the case of poly(11CBA-*co*-AA)s, which formed the liquid crystalline structure only at $F_{11CBA} = 0.26$ and higher. Again, the mesogenic structure formed by the hydrogen bond bridging between carboxyls of the mesogenic side chains with their likes or with AA is considered to stabilize the liquid crystalline structure.

The effects of AA units on the structure was investigated by WAXD using fibrous samples of poly(11ABA-*co*-AA)s. Similarly to poly(11ABA), every copolymer sample of $F_{11ABA} = 0.22$ or higher showed four broad diffractions with $2\theta = 20.3°$ ($d_1 = 4.4$ Å) and $\psi = 40°$ and indicated that the mesogenic side chains are aligned side by side having a tilt angle of $+40°$ or $-40°$ (SmC). The SAXD pattern of the $F_{11ABA} = 0.72$ sample was quite similar to that of poly(11ABA) (Figure 4a), indicating the formation of a bilayer structure with the same spacing (42.1 Å). However, interestingly, the copolymers of $F_{11ABA} = 0.44$, 0.28, and 0.22 show one intense diffraction peak with d_2 spacings of 22.7, 27.6, and 28.5 Å ($2\theta = 3.9°$, 3.2°, and 3.1°), respectively. These spacings correspond approximately to the length of the mesogenic side chain (25.5 Å) and suggest the formation of a monolayer structure. The copolymer of $F_{11ABA} = 0.44$ also shows a very small diffraction peak at $2\theta = 1.95°$. This peak indicates that the small domain of the bilayer structure was partially formed by the short copolymer sequence with excess 11ABA units. Then, the bilayer structure in the SmC phase (SmC_2) transforms to the monolayer structure (SmC_1) at $F_{11ABA} = 0.44$. Although the copolymer of $F_{11ABA} = 0.07$ did not show any diffraction by WAXD and SAXD, the birefringence with fluidity under crossed polarizers (Figure 2b) was observed. Moreover, the clearing temperature was observed at 155 °C where a DSC thermogram showed the endothermic peak. These experimental facts demonstrate that the $F = 0.07$ sample exhibits the liquid crystalline phase. However, we failed to identify the kind of liquid crystalline phase since the liquid crystalline domain was too small.

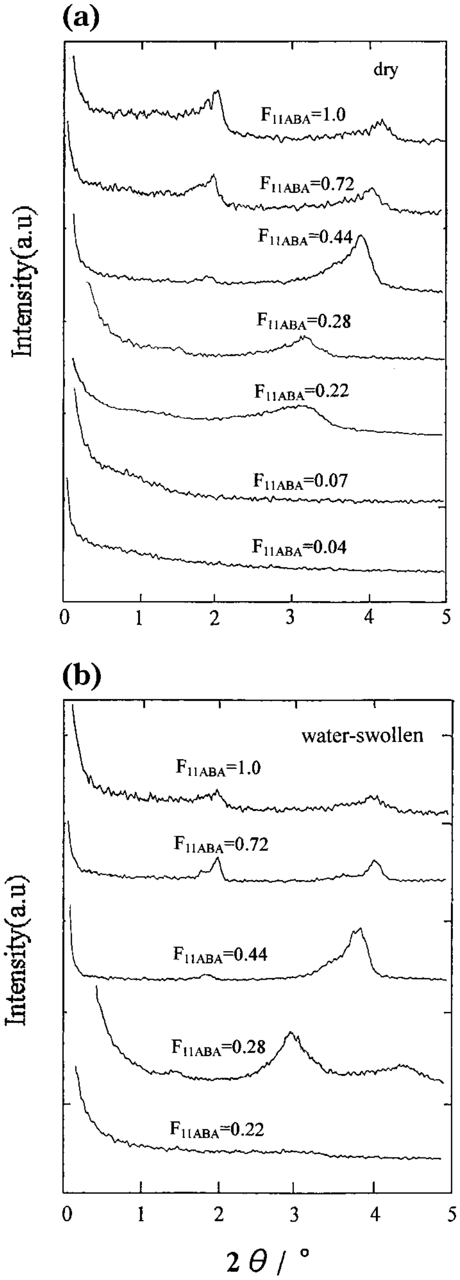

Figure 4. Small-angle X-ray diffraction patterns of poly(11ABA-*co*-AA)s taken at 20 °C: (a) dry state; (b) water-swollen state.

Figure 5 shows d_2 spacing as a function of F_{11ABA}. d_2 spacing abruptly decreased from 44 to 23 Å when F_{11ABA} decreases from 0.72 to 0.44 because of SmC_2 to SmC_1 transition, while d_1 spacing, corresponding to the side-by-side packing, is 4.4 Å through the F_{11ABA} range of 1.0−0.22. This can be explained well if the combination of hydrogen bonding is changed: in the case of the bilayer structure, the hydrogen bond is formed between 11ABA units and their likes (Figure 6a), while in the case of the monolayer structure, the hydrogen bond is

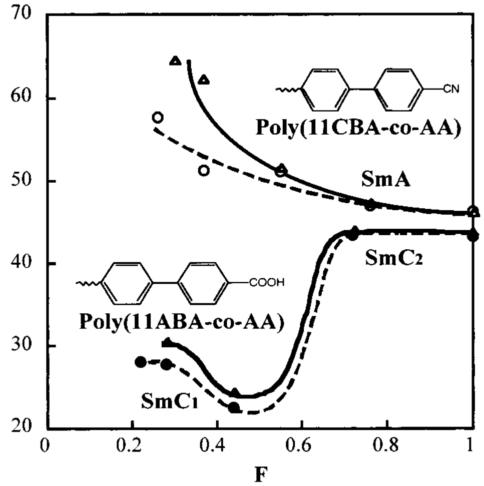

Figure 5. Schematic illustration of liquid crystalline structures of poly(11ABA-*co*-AA)s: (a) bilayer, $F_{11ABA} = 1.0, 0.72$; (b) monolayer, $F_{11ABA} = 0.44, 0.28$, and 0.22.

formed between 11ABA and AA units as shown in Figure 6b. d_2 increased with a decrease in F_{11ABA} from 0.44 to 0.28. One possible reason for this is that the AA units unable to participate in the monolayer formation were present between the monolayers and increased the distance between them.

To investigate the detailed structure of hydrogen bonding between 11ABA and/or AA units, IR spectra of the copolymers were measured (Figure 8). The copolymer samples with F_{11ABA} of 1.0, 0.72, and 0.44 gave three sharp peaks at 1720, 1690−1680, and 1600 cm^{-1} assigned to the vibration of acrylate ester, aromatic carboxylic dimer (hydrogen bonding between mesogenic carboxyls), and phenyl groups,[30] respectively. On the other hand, copolymers with F_{11ABA} of 0.28 and lower gave one intense peak at around 1700 cm^{-1} assigned to an aliphatic carboxylic dimer[30] (hydrogen bonding between AA carboxyls) with overlapped peaks of acrylate ester and aromatic carboxylic dimer. Since no intense peak at around 1700 cm^{-1} is detected, there is no hydrogen bonding formed between two AA units in the copolymers with F_{11ABA} of 0.44 and higher. Thus, the copolymers with $F_{11ABA} = 0.44$ and higher preferentially form hydrogen-bonding bridges between 11ABA units and their likes, yielding a bilayer structure, while copolymers with F_{11ABA} of 0.28 and lower preferentially form hydrogen bonding between 11ABA and AA. To demonstrate the role of hydrogen bonding to form the liquid crystalline structure, we tried to dissolve the copolymers in alkaline solution. However, even the copolymer of $F = 0.22$ did not dissolve below pH = 12, suggesting that ionization is strongly restricted because of hydrogen bonding formed by 11ABA and/or AA units. The copolymers of $F_{11ABA} = 0.28$ and 0.72 dissolved only in NMP containing 1 M sodium hydroxide. The dissolved samples were then precipitated in methanol and IR spectra were taken. These copolymers showed one intensive peak at 1440 cm^{-1} assigned to ionized carboxyls[30] and showed no peak at 1720 and 1690−1680 cm^{-1} corresponding to hydrogen bonding. Both samples showed no melting or birefringence under a crossed polarizer up to 250 °C. In addition, the WAXD pattern showed only a glassy halo and SAXD pattern showed no diffraction. These results indicate that the hydrogen bonding between carboxylic groups of 11ABA and AA units is crucially important for the formation of the SmC structures and their stabilization.

T_i and T_g of poly(11ABA-*co*-AA)s obtained by DSC thermograms are shown in Figure 7 as a function of F_{11ABA}. Those of poly(11CBA-*co*-AA)s are also shown in Figure 7 for comparison. T_i and T_g of poly(11ABA-*co*-AA)s monotonically increases with the increase in F_{11ABA}, just like in many other liquid crystalline polymers.[6−8] Despite the structural change from SmC_2 to SmC_1, there was no distinct discontinuity in T_i and T_g between $F = 0.72$ and 0.44

3. Effects of Water on the Structure. Although the copolymers of $F_{11ABA} = 0.07$ and lower dissolved in water, the copolymers of $F_{11ABA} = 0.22$ and higher were not dissolved but swelled, forming hydrogels. This means the copolymers capable of forming the layer structure in the dry state can form the hydrogels but those of amorphous copolymers dissolve in water—whereupon the hydrogen bridging of mesogenic moieties behaves as a physical “cross-linking” junction. The crossed polarizing microscopic observation of the water-swollen copolymers of $F_{11ABA} = 0.22$ and higher showed the birefringence with fluidity and confirmed the formation of liquid crystalline gels (LCG). Figure 9 shows changes in the degree of swelling, q, as a function of F_{11ABA}. Note poly(11ABA-*co*-AA)s with F_{11ABA} lower than

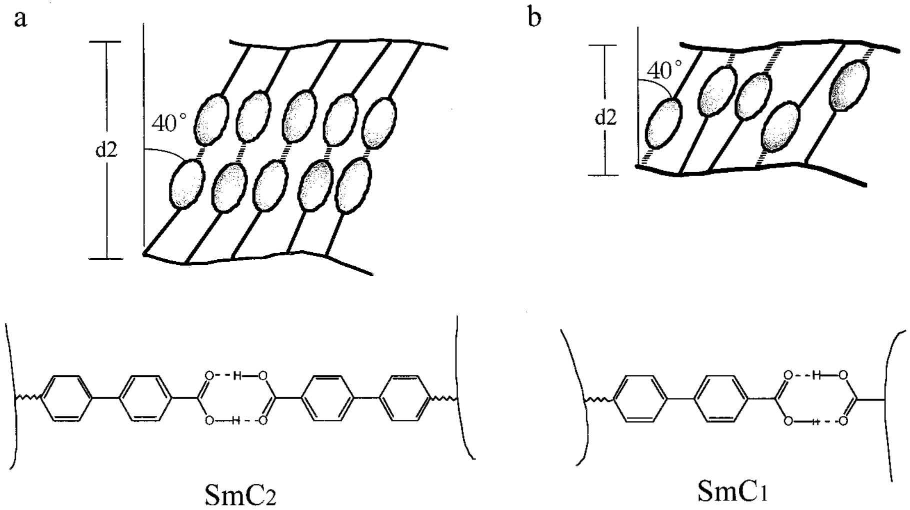

Figure 6. Changes in d_2 as a function of F. Broken lines: dry state. Solid lines: water-swollen state.

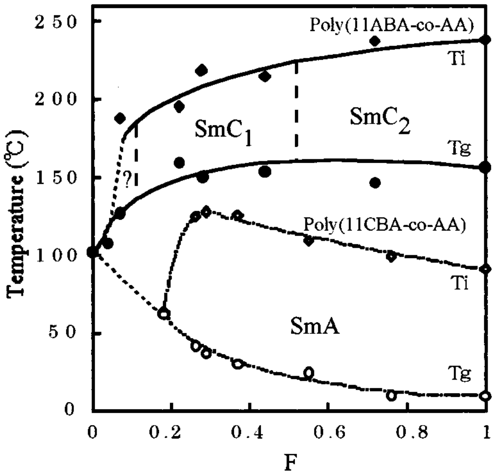

Figure 7. Transition temperatures of poly(11ABA-*co*-AA)s and poly(11CBA-*co*-AA)s. The data of poly(11CBA-*co*-AA)s were cited from ref 1.

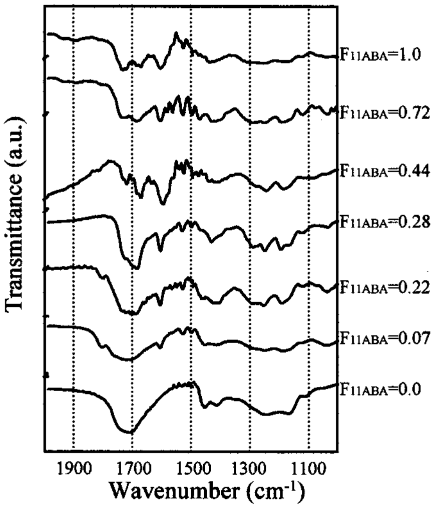

Figure 8. IR spectra of poly(11ABA-*co*-AA)s in the dry state.

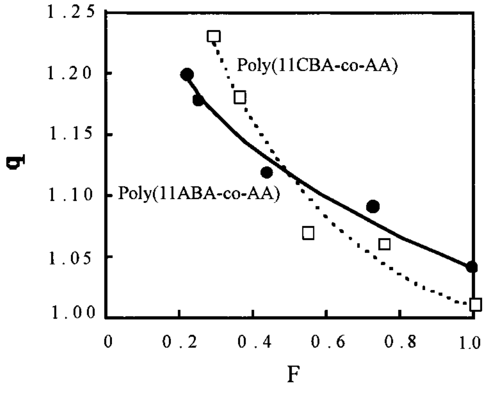

Figure 9. Changes in *q* as a function of *F*. The data of poly(11CBA-*co*-AA)s were cited from ref 2.

0.44 show the decreased *q* despite the presence of carboxyls. The presence of hydrogen bonding in the water-swollen state was confirmed by the IR absorption peak of carboxyl groups at around 1700 cm^{-1}.[30]

WAXD patterns of the more swollen copolymers were essentially the same as those of dry samples showing the same d_1 and ψ, which indicates that the mesogenic groups stay aligned in the same manner as the $\mathrm{SmC_1}$ or $\mathrm{SmC_2}$ structure. SAXD patterns of the copolymer gels of $F_{11\mathrm{ABA}} = 1.0$ and 0.72 were almost the same as those of dry samples, indicating the formation of a bilayer structure with the same d_2 spacing (42.1 Å) (Figure 4). However, d_2 spacings of the copolymers of $F_{11\mathrm{ABA}} = 0.44$ and 0.28 increased by water incorporation from 22.7 to 23.7 Å and from 27.6 to 30.1 Å, respectively. Especially, the layer diffraction of the $F_{11\mathrm{ABA}} = 0.28$ copolymer became more intensive and sharper, indicating that the ordering of the monolayer structure is enhanced by the incoporation of water. Figure 5 shows the *F* dependence of the d_2 spacings. Just like in the case of the dry state, d_2 showed a discontinuous transition between $F_{11\mathrm{ABA}} =$ 0.72 and 0.44 due to the structural transition from $\mathrm{SmC_2}$ to $\mathrm{SmC_1}$. Although the hydrogel of $F_{11\mathrm{ABA}} = 0.22$ did not show any X-ray diffractions, they clearly showed the birefringence with fluidity under crossed polarizers. These experimental facts suggest that this sample may exhibit the liquid crystalline phase similar to the dry copolymer of $F_{11\mathrm{ABA}} = 0.07$.

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