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Liquid-Crystalline Hydrogels. 1. Enhanced Effects of Incorporation of Acrylic Acid Units on the Liquid-Crystalline Ordering

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ABSTRACT: Copolymers composed of 11-(4′-cyanobiphenyloxy)undecyl acrylate (11CBA) and acrylic acid (AA), poly(11CBA-*co*-AA)s, were prepared by changing their molar ratio, and their structures were investigated under various temperatures. From wide- and small-angle X-ray studies, it was found that poly(11CBA) and poly(11CBA-*co*-AA)s with a mole fraction of 11CBA more than 0.26 showed the smectic A (SmA) phase with a layer spacing (d_2) of 46−58 Å, to which the mesogenic moiety of 11CBA attached perpendicularly with a side-by-side spacing of 4.3 Å (d_1). The ordering as well as the d_2 spacing of the smectic layer increased by incorporating an appropriate amount of AA. At the same time, the isotropic temperature of the copolymer increased with AA content. The enhanced ordering and the thermostability by introducing AA were explained in terms of the cooperative hydrogen interaction between the carboxylic groups of AA.

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 in recent years.[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 lack in mechanical toughness. 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.

Previously we have reported on the water-swollen hydrogels in which a molecularly ordered structure was incorporated by copolymerizing acrylic acid (AA) with crystallizable monomers such as *n*-stearyl acrylate (SA), 16-acryloylhexadecanoic acid (AHA), and hexadecyl acrylate (HA).[5−9] It was found that introduction of an appropriate amount of water increases the crystallinity of the ordered hydrogels owing to the enhanced hydrophobic interaction between long alkyl side chains.[10] Crystalline domains located in these copolymer hydrogels not only enhanced Young's modulus to a value as high as 10^7−10^8 Pa[5] but also underwent reversible order−disorder transition with change in temperature, solvent composition, and pH.[8] On the basis of the order−disorder transition, a solvent-driven rotor moving as fast as 4.0 × 10^2 rpm as well as an electric generator has been constructed.[11,12]

A liquid-crystalline phase can transform from a lower ordered isotropic phase into a higher ordered crystalline state sometimes via other liquid-crystalline phases very easily by change in temperature, accompanied with small transition enthalpy and entropy.[13] Molecules in the liquid-crystalline phase, despite the preferential orientation, still have a high mobility responding cooperatively to electric, magnetic, and mechanical fields.[13,14] Using these specific characteristics of liquid-crystalline compounds, Kishi et al. synthesized cross-linked gels containing cyanobiphenyl mesogen.[15,16] They found that, if these gels are swollen in the nematic solvent, 4-pentyl-4′-cyanobiphenyl, they showed nematic structures and changed their shape and size quickly (order of milliseconds) responding to the electric field.[15,16]

We have synthesized the water-swollen liquid-crystalline hydrogels by copolymerizing AA with a mesogenic monomer, 11-(4′-cyanobiphenyloxy)undecyl acrylate (11CBA), and investigated the effects of monomer compositions, temperature, water content, pH, and salt concentration on the liquid-crystalline structure. We expected that thermotropic liquid-crystalline phase in a hydrogel might effectively be modulated by changing these hydrophilic environments which gives the hydrogels mechanical and optical anisotropy. Although the lyotropic behavior of the thermortropic liquid-crystalline compound in water has been studied by Ringsdorf,[17] so far as the authors know, there has been no report on the hydrogel with thermotropic liquid-crystalline behavior.

In this article, we report on the synthesis and the thermotropic behaviors of the liquid-crystalline copolymers poly(11CBA-*co*-AA)s in the dry state. It was found that the incorporation of AA units to 11CBA sequence not only enhances the organized structure but also thermally stabilizes it. The liquid-crystalline behavior of the copolymer by incorporation of water will be published in a separate paper.

Experimental Section

Materials. Acryloyl chloride (Junsei Chemical Co., Ltd.), triethylamine (Kanto Chem. Co., Ltd.), potassium carbonate (TCI), 4′-cyanobiphenol (TCI), hexane (Junsei Chemical Co., Ltd.), ethanol (Junsei Chemical Co., Ltd.), and 11-bromoundecanol (TCI) were used as received. Tetrahydrofuran (THF; Junsei Chemical Co., Ltd.), dimethylformamide (DMF; Junsei Chemical Co., Ltd), and acrylic acid (AA; TCI) were distilled before use. α,α′-Azobis(isobutyronitrile) (TCI) were recrystallized before use.

Syntheses of 11-(4′-Cyanobiphenyloxy)undecyl Acrylate (11CBA). 11-(4′-Cyanobiphenyloxy)undecyl acrylate (11CBA) was synthesized as follows.[18] 4′-Cyanobiphenol (0.051 mol) was

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

f^a	1	0.75	0.50	0.33	0.25	0.20
F^b	1	0.76 ± 0.005	0.55 ± 0.005	0.29 ± 0.01	0.26 ± 0.01	0.18 ± 0.01
M_n ($\times 10^{-3}$)	4.4	5.2	3.4	3.0	2.4	2.6
M_w ($\times 10^{-3}$)	5.0	5.8	4.0	3.6	2.6	2.7
M_w/M_n	1.14	1.13	1.19	1.21	1.08	1.04

[a] 11CBA in feed. [b] 11CBA in copolymer.

reacted with 11-bromoundecanol (0.051 mol), in the presence of potassium carbonate (0.051 mol) in DMF solution (130 mL) at 155 °C for 24 h. After potassium bromide precipitated was removed, the reaction solution was poured into water to give the white powder, which was recrystallized from methanol/water to obtain the white crystal of 11-(4′-cyanobiphenyloxy)-undecanol (11CB) (yield 45%, melting point 94 °C, isotropic point 98 °C).

A THF solution (150 mL) of 11CB (0.024 mol) and triethylamine (4 mL) was added dropwise under nitrogen to a THF solution (50 mL) of acryloyl chloride (0.029 mol) with stirring over several hours at 0 °C and then at room temperature for 24 h. After the triethylamine hydrochloride that formed as a result of reaction was removed, THF was evaporated and the solid material was repeatedly washed with water and dried under vacuum. The product was then recrystallized from THF/hexane to give the white crystal of 11CBA (yield 42%, melting point 94 °C). The structure of 11CBA was confirmed by ^{1}H NMR and IR spectra.

Synthesis of Poly(11CBA-*co*-AA)s. Poly(11CBA-*co*-AA)s with various 11CBA-AA compositions, *f*, were synthesized by the radical polymerization. The polymerization was carried out in a 20 wt % monomer concentration of THF at 60 °C for 24 h under nitrogen. A 1 mol % sample of α,α′-azobis(isobutyronitrile) was used as an initiator. Poly(11CBA-*co*-AA)s were purified by reprecipitating from THF into water for several times. The yield was 64−82%. Number and weight-average molecular weights, M_n and M_w, 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 were measured in a 4 wt % of chloroform-*d* solution by 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.

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}. 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 texture was recorded on a digital camera after annealed for 12 h at 80 °C.

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 150 °C in nitrogen. The samples (about 10 mg) were dried thoroughly at temperature higher than 100 °C for 5 h in vacuo before being hermetically sealed in aluminum pans. The thermogram on cooling was recorded in the second scan after the temperature was kept at 150 °C for 10 min. Transition enthalpy and entropy were calculated with respect to 11CBA units.

Wide-angle X-ray diffraction 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 silicone powder. Small-angle X-ray diffraction patterns were recorded on a Rigaku X-ray diffractometer (RINT-2000) (40 kV, 200 mA) in transmission geometry. A 2θ scanning speed of 1° min^{-1} with a sampling interval of 0.01° was used.

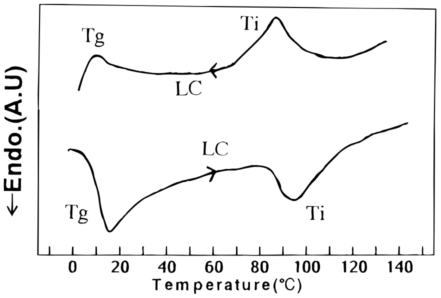

Figure 1. DSC thermogram of poly(11CBA) in the second scan. Scanning rate: 5 °C min^{-1}.

Results and Discussion

Polymerization proceeded homogeneously, and poly(11CBA-*co*-AA)s were obtained with high yields of 64−82% as white high-viscous liquids for the samples of high 11CBA content or white powders for the samples of low 11CBA content at room temperature. The mole fraction of 11CBA unit in poly(11CBA-*co*-AA)s, *F*, was determined from the ratio of the peak area for biphenyl protons of 11CBA side chains (6.9−7.8 ppm) to the alkylene protons of 11CBA side chains and main chains (1.2−4.2 ppm) in ^{1}H NMR spectra. *F* values of individual copolymers were calculated several times in order to estimate their errors, and it was proved that the errors were sufficiently small (Table 1). *F* values were almost the same as the monomer composition in feed, *f*, indicating both monomers were almost equally incorporated into the copolymer (Table 1). We could roughly estimate that the reactivity of 11CBA may be higher than that of AA, supporting the result that the reactivity of stearyl acrylate (SA) whose chemical structure around the double bond is similar to 11CBA is 6 times as reactive as AA according to the previous paper.[5] Therefore, one can assume that 11CBA and AA monomers may randomly be incorporated to give the randomly sequenced copolymers, if the 11CBA monomer concentration in feed is low. Average molecular weights were not high enough comparing with those of common polymers showing (2−6) × 10^3 but in the same order as those of poly(11CBA) in the literature;[18,19] the distribution of molecular weights was sufficiently narrow (Table 1). Any copolymers of poly(11CBA-*co*-AA)s were soluble in THF and chloroform but were insoluble in water except for $F = 0.18$.

Liquid-Crystalline Structure of Poly(11CBA). The thermotropic behavior of poly(11CBA) ($F = 1.0$) was examined by DSC measurement, and the thermograms in the second scan are shown in Figure 1, in which two peaks were detected at 5 and 94 °C on heating and at 2 and 92 °C on cooling. Between these two temperatures, poly(11CBA) was a white viscous liquid, suggesting the liquid-crystalline state. The microscopic observation under the crossed polarizer was made at 80 °C after the

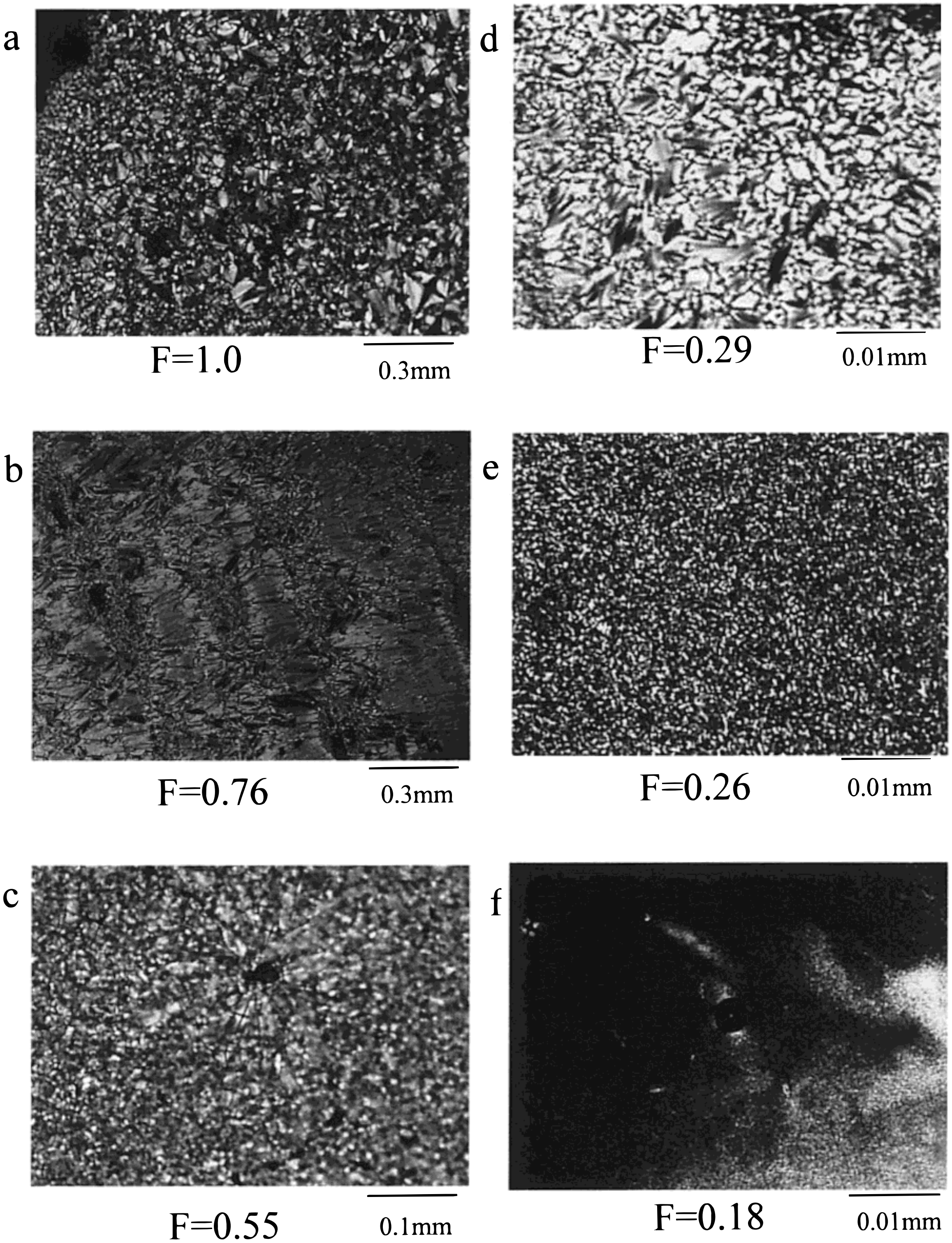

Figure 2. Microscopic textures of poly(11CBA-*co*-AA)s under crossed polarizer at 80 °C: (a) $F = 1.0$, (b) $F = 0.76$, (c) $F = 0.55$, (d) $F = 0.29$, (e) $F = 0.26$, (f) $F = 0.18$.

sample was annealed at the same temperature for 12 h. The fan-shaped texture showing fluidity which is characteristic of the liquid-crystalline phase with the layer structure was observed as shown in Figure 2.[13] The fan shape did not change its form in the temperature range between 4 and 93 °C, while it disappeared above 93 °C or froze below 4 °C, indicating that the two peaks observed at 4 and 93 °C in Figure 1 could be assigned to the glass transition (T_g) and isotropization (T_i), respectively. Thus, it was found that poly(11CBA) exhibits the liquid-crystalline phase between 4 and 93 °C, which is in good agreement with the literature.[18] Although Shibaev et al.[19] reported that poly(11CBA) exhibited the liquid-crystalline phase with the layer structure between 30 and 145 °C, the increased transition temperatures might originate from the increased molecular weight of poly(11CBA), as reported in ref 18.

Shibaev et al. also confirmed from the X-ray diffraction patterns that poly(11CBA) has a smectic phase with spacings of 4.5 and 44 Å. However, no further detailed structural information on poly(11CBA) has been reported.

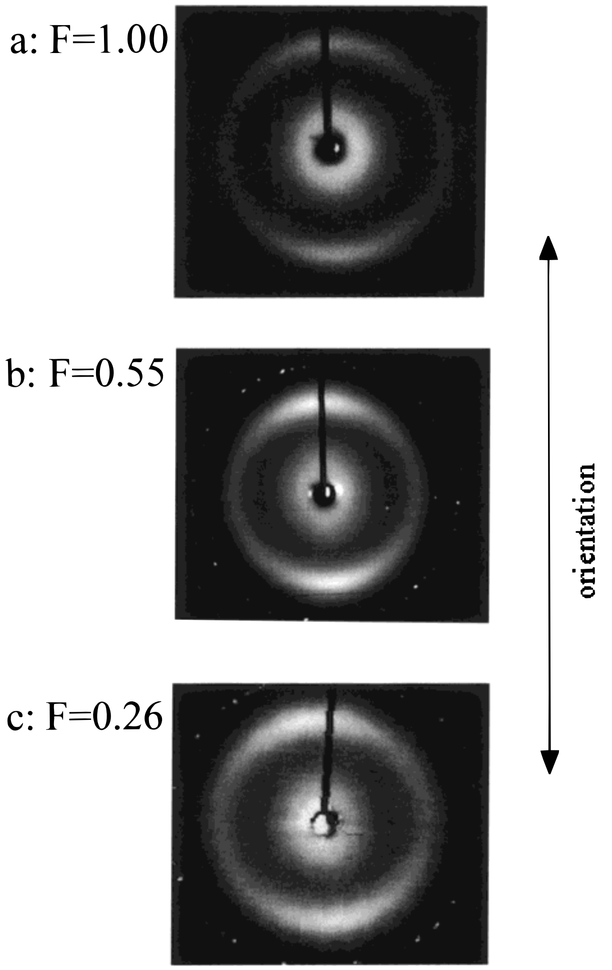

Figure 3. Wide-angle X-ray diffraction images of poly(11CBA-*co*-AA)s at 80 °C: (a) $F = 1.0$, (b) $F = 0.55$, (c) $F = 0.29$.

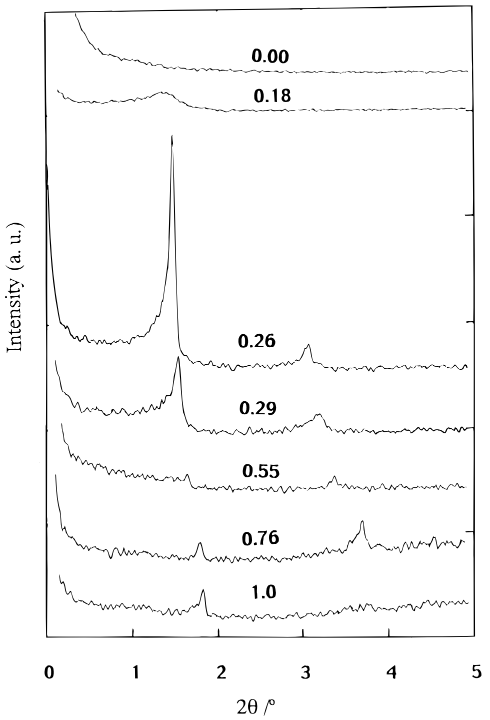

Figure 4. Small-angle X-ray diffraction patterns of poly(11CBA-*co*-AA)s. Numbers in the figure denote *F*.

We have further analyzed the structure of poly(11CBA) by wide-angle X-ray diffraction (WAXD) patterns in detail using an oriented sample especially to establish the relative position and angle of the side chain to the main chain. The oriented fiber of poly(11CBA) was obtained by spinning the liquid-crystalline state at 90 °C without further stretching. Figure 3a shows the WAXD pattern of the oriented fiber of poly(11CBA). One can see that the fiber axis corresponding to the main chain is placed in vertical, and a broad halo with an average spacing of 4.3 Å is on the meridian line. This spacing satisfactorily agrees with the value of the side-by-side packing of the mesogenic group in the liquid-crystalline phase.[19] Since no peak with a spacing longer than 40 Å was detected in this WAXD pattern owing to the screening by the direct beam stopper, a small-angle X-ray diffraction (SAXD) pattern experiment was carried out (Figure 4; $F = 1.0$). A weak peak was clearly detected at $2\theta = 1.9°$ corresponding to a spacing of 46 Å, which is in good agreement with the value of layer spacing reported by Shibaev et al.[19] As shown in Figure 3, the WAXD pattern shows the strong diffractions on the meridian line, indicating that the side chains are arranged perpendicularly to the main-chain axis. Besides, the SAXD pattern shows the layer diffraction with the spacing of 46 Å, which is a bit shorter than twice the length of the side chain (25.5 Å), supposing the side chain take the all-trans conformation. However, the spacer (undecyl group) of the side chain does not necessarily take the all-trans conformation in the liquid-crystalline phase, and if a part of the spacer of the side chain takes the double-gauche conformation, one can calculate that the length of side chain becomes 23 Å to give the bilayer spacing of 46 Å, which corresponds with the spacing observed from SAXD pattern. In other words, poly(11CBA) forms the smectic A (SmA) phase with a bilayer structure, in which side chains are perpendicularly arranged to the main-chain axis without positional ordering within the layer, as shown in Figure 7a.

Effects of AA on Liquid-Crystalline Structure. The liquid-crystalline structure of the copolymer poly(11CBA-*co*-AA)s was investigated by changing the AA content. DSC thermograms (second scan) of poly(11CBA-*co*-AA)s were similar to that of poly(11CBA), showing two peaks at elevated temperatures and indicating that they have the liquid-crystalline phase.

The microscopic texture of poly(11CBA-*co*-AA)s with various *F* was observed under the crossed polarizer to confirm the liquid-crystalline phase. Figure 2b–f shows the liquid-crystalline textures of the copolymers taken at 80 °C after being annealed at the same temperature for 12 h. The fan-shaped texture was again observed in all poly(11CBA-*co*-AA)s samples except for $F = 0.18$, but the domain size of the fan-shaped texture decreased with the decrease in *F*, indicating that the growth of liquid-crystalline domain was suppressed by incorporating AA. These textures disappeared above the higher peak temperature (T_i) and frozen below the lower peak temperature (T_g) of the DSC curves. Thus, it was confirmed that copolymers of $F = 0.26$ or larger exhibited a similar liquid-crystalline phase with the layer structure as that of poly(11CBA). It is quite interesting that poly(11CBA-*co*-AA)s of $F = 0.26$ is able to form the liquid-crystalline phase despite the low concentration of 11CBA. On the other hand, no DSC peak and no particular texture were observed for the copolymer of $F = 0.18$.

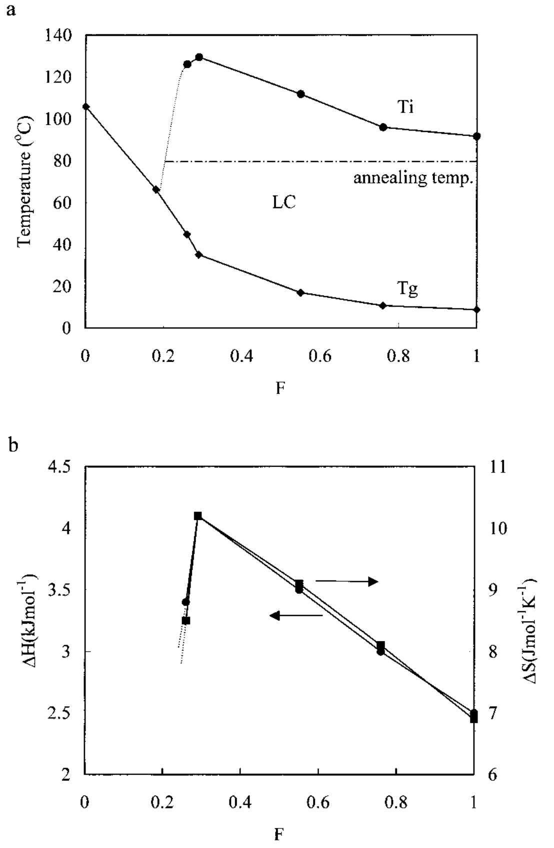

Figure 5. (a) Glass transition temperature, T_g, and isotropic temperature, T_i, of poly(11CBA-*co*-AA)s as a function of *F*. (b) Transition enthalpy and entropy of poly(11CBA-*co*-AA)s from SmA to isotropic phase as a function of *F*.

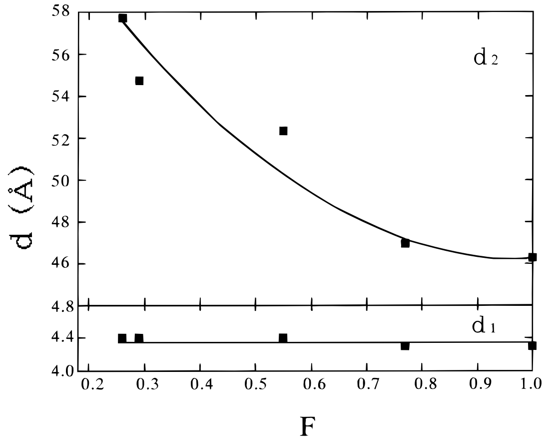

Figure 6. Changes in d_1 and d_2 spacings as a function of *F*.

If the glass transition temperature, T_g, and the isotropic temperature, T_i, of the copolymers are plotted as a function of *F*, one can get Figure 5a. T_g increased monotonically with a decrease in *F*, due to the higher T_g of polyAA. Ti also increased with the decrease in *F* until $F = 0.29$, indicating that the thermostability of the liquid-crystalline structure was enhanced by incorporating AA units. This is in contrast with the behaviors of other copolymer systems in which T_i decreases with the increase in the amorphous component.[20-22] For example, T_i of the smectic phase in poly(11CBA-*co*-2-ethylhexyl acrylate)s decreases with an increase in 2-ethylhexyl acrylate units, and the liquid-crystalline phase disappears when the 11CBA content is less than 0.40.[20] A similar result was also observed in poly(methylhydrogen-*co*-dimethylsiloxane) with a mesogenic side chain.[21]

Figure 5b shows enthalpy and entropy changes of isotropization as a function of *F*. Values of enthalpy and entropy were about 3 kJ mol^{-1} and 9 J mol^{-1} K^{-1}, respectively, which are well in agreement with those of the common liquid-crystalline polymer with the SmA phase. The enthalpy and entropy changes of isotropization also increased with the decrease in *F* until $F = 0.29$. Since the isotropic temperature also increases with the decrease in *F*, these results indicate that the introduction of AA enhances the ordering of molecular packing.

The effect of AA units on the molecular structure was investigated more in detail by WAXD using oriented fibers of poly(11CBA-*co*-AA)s (Figure 3). All the poly(11CBA-*co*-AA) samples except for $F = 0.18$ showed the broad halo with a spacing of 4.3 Å, and no distinct difference in their WAXD patterns from that of poly(11CBA) was observed, meaning that 11CBA side chains align in perpendicular to the main-chain axis without any particular ordering with the layer, the same as poly(11CBA).

However, the weak but clear peak at $2\theta = 1.9°$ corresponding to 46 Å in the SAXD pattern for the sample of $F = 1.0$ shifted toward smaller diffraction angles when AA is incorporated, and d_2 for the sample of $F = 0.26$ increased to 58 Å (Figure 4). Figure 6 shows the layer spacing d_2 and the side-by-side spacing d_1 of the SmA phase as a function of *F*. The layer spacing increased with AA composition at $F \geq 0.26$, while the spacing of the side-by-side packing for 11CBA side chain was constant of 4.3 Å. As described before, the layer spacing corresponds to the long-range ordering roughly twice the length of the fully extended side chain, forming a bilayer structure. Thus, poly(11CBA-*co*-AA)s also form the SmA phase with a bilayer structure, as shown in Figure 7b,c, except for the copolymer of $F = 0.18$ which shows no particular peak.

As shown in Figure 4, besides the peak of the bilayer structure, a new peak appeared at $2\theta = 3.8-2.9°$ in the copolymers, which also shifted toward smaller angles with the increase in AA composition. The new peak corresponds to 23−29 Å, which is half of the bilayer lengths and should be assigned to the second-order diffraction of the bilayer structure. This result indicates that an ordering with a half period of the bilayer is formed with the incorporation of AA, as shown in Figure 7b.

Figure 4 also shows that SAXD peak of the copolymer of $F = 0.26$ at $2\theta = 1.5°$ not only shifted toward the lower angle but also substantially increased its sharpness by incorporating AA units. This result indicates that incorporation of AA enhances the ordering of the bilayer structure in the smectic phase to give well-organized packing of the main chains in the copolymers. The intense layer peak of the $F = 0.26$ sample is not unusual since the weight percent of the 11CBA units was still high (68%). As shown in Figure 5, the transition enthalpy and entropy as well as the transition temperature of the copolymer of $F = 0.26$ decreased in comparison with those of $F = 0.29$. This indicates that the molecular packing of the liquid-crystalline domain became less ordered, although the sample showed a highest order in terms of the bilayer structure.

The above results show that incorporation of an appropriate amount of AA enhances the thermostability of SmA phase with increased layer spacing. As has been

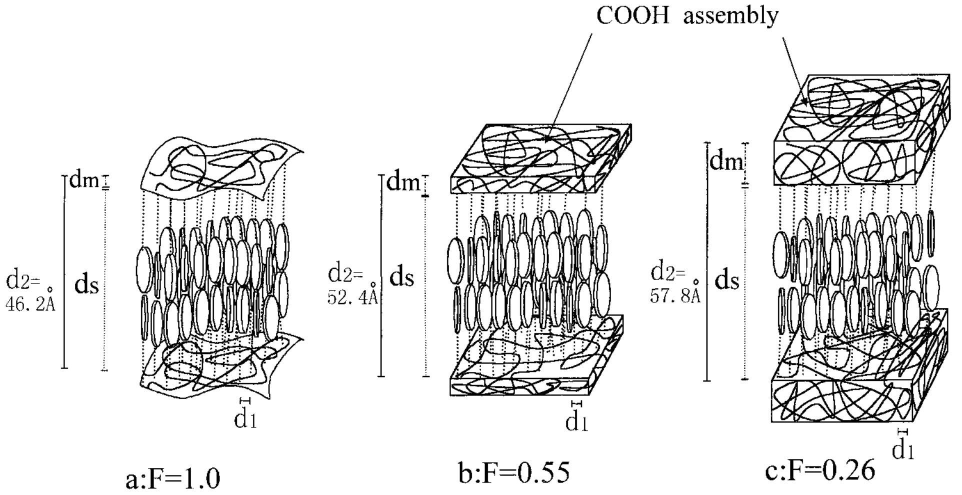

Figure 7. Schematic illustration of structures in SmA phase of poly(11CBA-*co*-AA)s: (a) $F = 1.0$, (b) $F = 0.55$, (c) $F = 0.29$.

pointed out previously, an opposite phenomenon has been reported in the system of poly(methylhydrogen-*co*-dimethylsiloxane) with a mesogenic side chain;[21] i.e., the isotropization temperature of the liquid-crystalline phases decreased with a decrease in the concentration of the mesogenic side chain, although the smectic layer spacing was increased, according to the authors, due to the folding of flexible siloxane main chains.

These effects on the structure by incorporation of AA might be attributed to the strong microphase separation between 11CBA groups and AA groups. As predicted from the fact that monomeric 11CBA is not miscible with AA, 11CBA and AA units may have a strong tendency to form separate domains in the copolymer and the domains of AA might supplementarily stabilize the liquid-crystalline organization through forming the cooperative hydrogen bridge between carboxylic groups. The high T_g of polyAA ($T_g = 106$ °C) is another reason why the copolymer is able to form the liquid-crystalline structure even at such a low F value as 0.26.

As seen from the weak peak at $2\theta = 1.9°$ in Figure 4, the bilayer structure of the sample $F = 1.0$ was less organized. When AA is incorporated, the ordering of the liquid-crystalline structure is enhanced as seen from the intensive and sharp peaks of the SAXD pattern in Figure 4, and the increased spacing might be due to AA units which, as described above, form separate domains through their hydrogen bonding. The incorporation of AA units not only gave the free spacing to 11CBA unit for increased organization because of its relatively short side group but also increased the bilayer spacing through intra- and interchain hydrogen bridges. As shown in Figure 7, the layer spacing d_2 is the sum of the sublayer thickness of the amorphous main chain, d_m, and the sublayer thickness of liquid-crystalline side chain, d_s. This two-phase model of the layer structure was also proposed in the system of poly(methylhydrogen-*co*-dimethylsiloxane) with a mesogenic side chain.[21] The increase in AA would increase d_m through formation of hydrogen bridges (Figure 7b,c) but not d_s, although an appropriate amount of it increases the organization with half-spacing of bilayer for the sample of $F = 0.55$ (Figure 7b). Thus, strong microphase separation formed between the short carboxylic acids and the long liquid-crystalline side groups enhances the ordering of the layer structure.

As pointed out before, the copolymer at $F = 0.26$ showed the most sharp and intensive layer peak, but with less isotropic enthalpy than that of $F = 0.29$. This enhanced layer structure should apparently be attributed to the strong association between carboxylic groups, which might hinder the interaction between the ends of the mesogenic groups and disturb the thermostability.

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