Liquid Crystalline Hydrogels. 2. Effects of Water on the Structural Ordering

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ABSTRACT: The effects of water on the liquid crystalline structure of the copolymer poly(11-(4′-cyanobiphenyloxy)undecyl acrylate-*co*-acrylic acid)s (poly(11CBA-*co*-AA)s) were investigated. When the molar fraction of 11CBA, *F*, was higher than 0.26, the copolymers did not dissolve but swelled in water to give the hydrogels, keeping the smectic A ordering. This smectic A phase of the copolymers of $F = 0.37$ and 0.29 transferred to more organized smectic I ordering by further incorporation of water, while the SmA ordering of the copolymer of $F = 0.26$ disappeared to give the amorphous state. The role of water and the mechanism for forming a liquid crystalline structure in the hydrogel have been discussed.

Introduction

In the preceding paper,[1] we have reported that the copolymers consisting of a hydrophobic monomer containing a mesogenic moiety, 11-(4′-cyanobiphenyloxy)undecyl acrylate (11CBA), and a hydrophilic monomer, acrylic acid (AA), show the liquid crystalline structure (smectic A (SmA) with the bilayer structure), in which side chains are arranged perpendicularly to the main chain axis. The copolymer transferred from SmA to isotropic phase at a certain temperature (T_i), which increased with the decrease in the mesogenic component, showing a maximum of 126 °C at $F = 0.29$. The order and spacing of the smectic layer increased with the increase in the AA composition. It seems to be unique that an introduction of AA increased the isotropic temperature and the ordering of the SmA phase because other copolymer samples exhibiting the liquid crystals, such as poly(11CBA-*co*-2-ethylhexyl acrylate),[2] decrease T_i with an increase in the content of the amorphous moiety.[2−8]

This paper is concerned with the effects of water on the structure of the amphiphilic liquid crystalline copolymer. If the water is incorporated into poly(11CBA-*co*-AA)s, the AA component might be preferentially hydrated and increase the molecular mobility due to decreased glass transition temperature, while the organization of hydrophobic and mesogenic moieties might be enhanced by the increased hydrophobic interaction. These two opposite effects of water might strongly affect structures and properties of the liquid crystalline copolymers.

Experimental Section

Syntheses of Monomers and Polymers. 11-(4′-Cyanobiphenyloxy)undecyl acrylate (11CBA)[9,10] and poly(11-(4′-cyanobiphenyloxy)undecyl acrylate-*co*-acrylic acid)s, poly(11CBA-*co*-AA)s, were prepared by the procedures described in the preceding paper.[1] The mole fraction of 11CBA unit, *F*, which is defined as [11CBA]/([11CBA] + [AA]), was determined from ^{1}H NMR spectra of poly(11CBA-*co*-AA)s according to the method described in the preceding paper.[1]

Measurements. ^{1}H NMR spectra were measured in a 4 wt % of chloroform-*d* solution by 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.

The optical observation under a crossed polarizer 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.

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

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

Results and Discussion

1. Solubility of Poly(11CBA-*co*-AA)s in Water. Poly(11CBA-*co*-AA)s were immersed in water, and their swelling properties have been investigated. The copolymers of $F < 0.18$ dissolved in water, while those of $F > 0.26$ did not dissolve but only swelled forming the hydrogels, presumably due to hydrophobic interaction of mesogenic side chains to give a physical cross-linkage. This corresponds well to the formation of liquid crystalline structure in the dry state, that is, the copolymers of $F > 0.26$ showed the liquid crystalline structure while that of $F = 0.18$ was amorphous.[1]

Figure 1 shows the degree of swelling, *q*, as a function of *F*. The copolymer of $F = 0.26$ shows the swelling degree to a value as large as 24, while those of $F > 0.29$ swell only moderately to the extent of 1.23 or lower. This also might correspond to the fact that the isotropization temperature, T_i, of the copolymer in the dry state decreased from 129 to 126 °C with the decrease in *F* from 0.29 to 0.26.[1]

2. Structural Transition of Poly(11CBA-*co*-AA)s in Water. In the preceding paper,[1] the dry copolymers of $F > 0.29$ showed the fan-shaped texture under crossed

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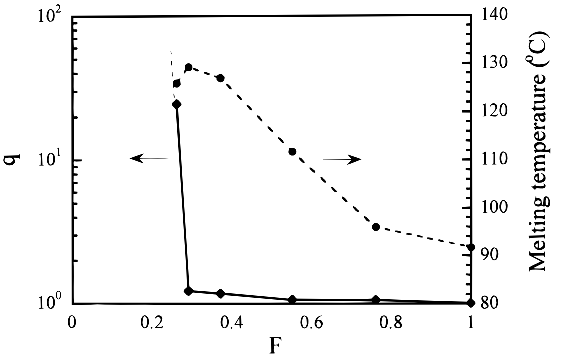

Figure 1. Swelling degree q of poly(11CBA-*co*-AA)s and their isotropic temperatures T_i in the dry state as a function of F.

polarizing microscope which is characteristic of the SmA phase. The fan-shaped texture is still observed for the samples of $F = 0.76$ and 0.55 equilibrated in water ($q = 1.05$ and $q = 1.08$, respectively). An interesting result is the fact that the broken fan-shaped texture is observed for the water-swollen samples of $F = 0.29$ and 0.37, which is usually observed in a smectic phase with a higher ordered structure than the SmA phase.[7] The dry sample of $F = 0.26$ showed the birefringence[1] which disappeared in the equilibrated water-swollen state.

The liquid crystalline structures of these gels have been investigated changing F and q. X-ray diffraction of poly(11CBA-*co*-AA)s of $F = 0.55$ ($q = 1.08$) and 0.76 ($q = 1.05$) showed a similar pattern as those of dry samples, but a dramatic structural change was observed for the samples of lower F and larger q. Figure 2 shows the wide-angle X-ray diffractions (WAXD) pattern of the oriented fibrous samples of $F = 0.37$ copolymer with $q = 1.0-1.18$. (The fiber axis corresponding to the main chain axis was placed in the vertical direction of the figure.) The WAXD pattern of the dry sample of $F = 0.37$ showed strong diffractions of the halo on the meridian line at around $2\theta = 20.6°$ (θ = diffraction angle), which corresponds to a spacing of side-by-side packing of mesogenic groups, d_1, of 4.3 Å (Figure 2a). This indicates that mesogenic side chains are loosely packed side by side and arranged perpendicularly to the main chain, indicating this sample takes the SmA structure as illustrated in Figure 8 (SmA gel).[1] Since the same SmA structure was observed for the sample of $q = 1.10$, indicating that incorporation of less than 10% of water does not induce any change of side-by-side packing of mesogenic groups. The strong diffraction on the meridian line was somewhat broadened for the sample of $q = 1.12$ as shown in Figure 2b, and the halo completely disappeared for the sample of $q = 1.18$; instead, two sharp diffractions appeared at $2\theta = 35°$ ($d_1 = 3.8$ Å) on the meridian line (mark A), and four sharp diffractions appeared at $2\theta = 27°$ ($d_1 = 5.0$ Å), laying symmetrical to the meridian line (mark B). According to the literature,[11] the WAXD pattern showing two diffractions on the meridian line and four diffractions symmetrical to the meridian line in Figure 2c is characteristic of the SmI phase in which the mesogenic side chains aligned quasi-hexagonally and tilted toward a neighboring side chain. A narrow distribution of diffractions A and B indicates that side chains are well-organized side by side. The side chains in the SmI state which is a kind of liquid crystalline state have the short structural order range but a larger positional order than those in the SmA state. The tilt of side chains was confirmed by the presence of diffractions B, and the angle of diffraction B to the meridian line, ψ (shown in Figure 2c), was 23°. The tilted angle, ϕ (shown in Figure 8), of the side chains to the main chain in the SmI phase was calculated using the equation[11]

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

and found to be 27°. The WAXD pattern of the SmI phase was also observed for the samples of $q = 1.13$ and 1.18 (equilibrated swelling), and the tilt angle was independent of the water content. The broadened diffraction of the halo observed in the WAXD pattern of $q = 1.12$ (Figure 2b) can now be concluded as the transient state from the SmA to SmI phase.

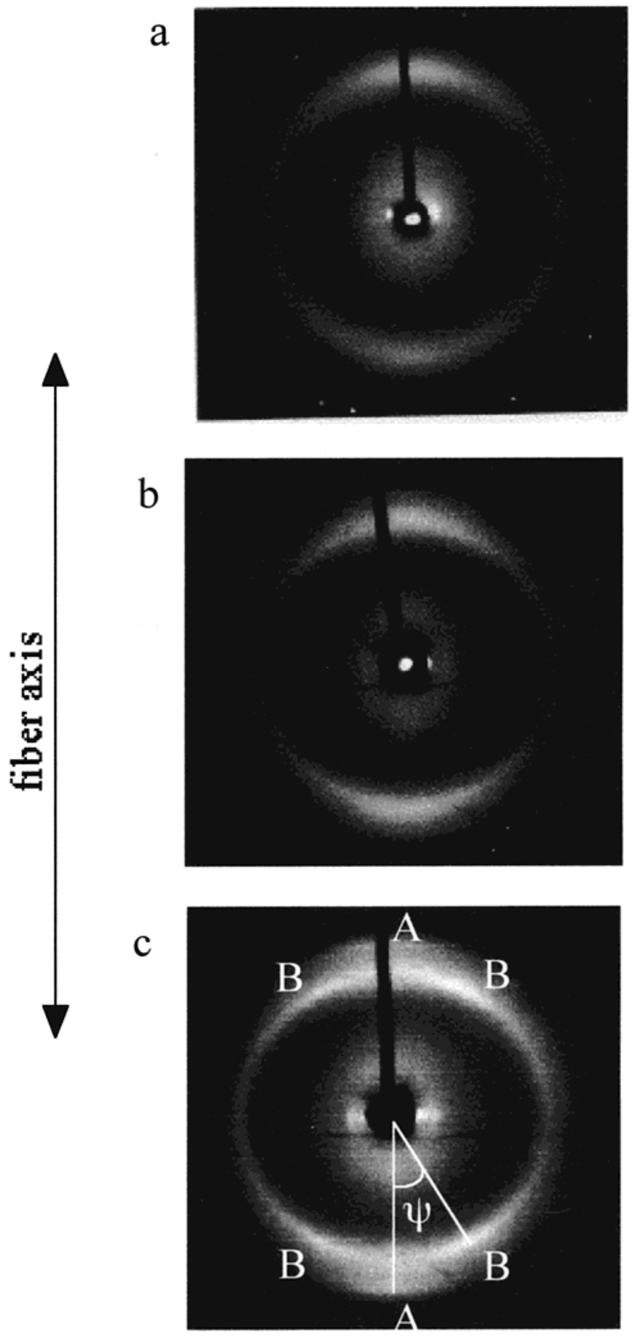

Figure 2. Wide-angle X-ray diffraction patterns of poly(11CBA-*co*-AA)s of $F = 0.37$. (a) $q = 1.0$, (b) $q = 1.12$, and (c) $q = 1.18$.

Long-range ordering (d_2) of the copolymer ($F = 0.37$) was investigated using SAXD as a function of q (Figure

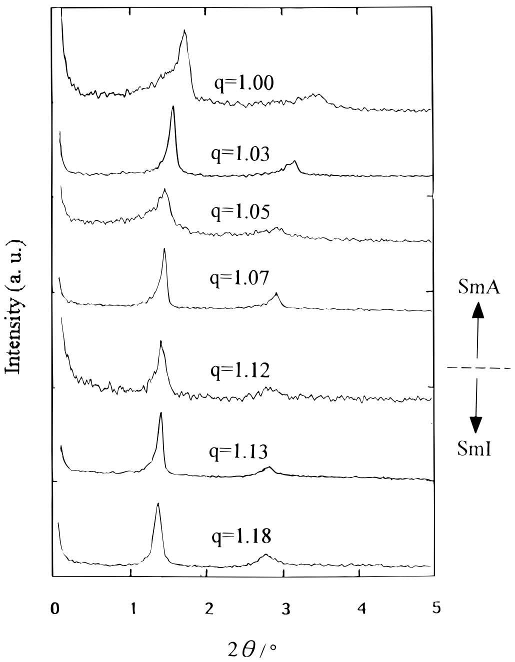

Figure 3. Small-angle X-ray diffraction patterns of poly(11CBA-*co*-AA)s of $F = 0.37$ with various q.

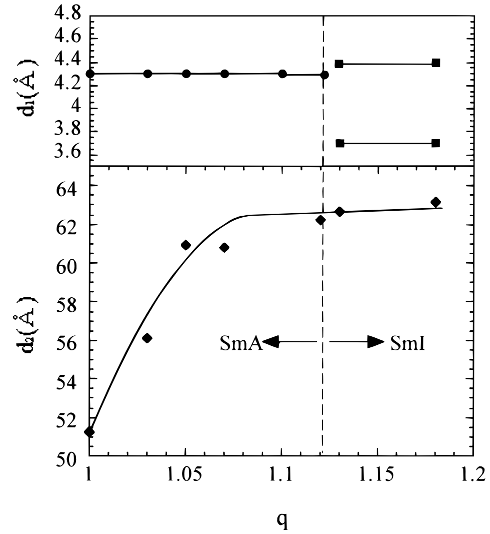

Figure 4. Short-range (d_1) and long-range (d_2) spacings of poly(11CBA-*co*-AA)s of $F = 0.37$ as a function of q.

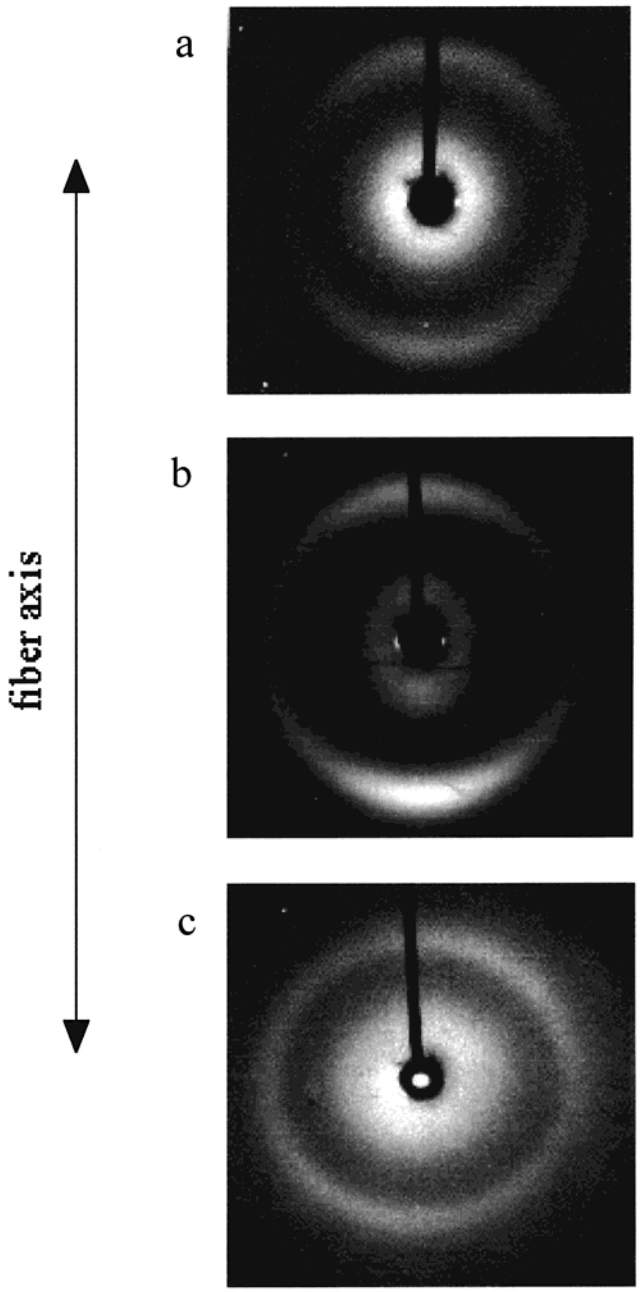

Figure 5. Wide-angle X-ray diffraction patterns of poly(11CBA-*co*-AA)s of $F = 0.26$. (a) $q = 1.00$, (b) $q = 1.13$, and (c) $q = 1.77$.

3). One can see two peaks for every sample at the relative 2θ position (1.72−1.41° and 3.43−2.82°) with a corresponding spacing of 2:1 (51.3−62.6 and 25.7−31.3 Å). Taking account of the fan-shaped texture observed by the microscope, the appearance of the second-order diffraction of d_2 indicates that these samples may form the layer structure. With the increase in q, these peaks shifted to a lower angle, i.e., to the increased layer spacing, d_2, and became constant ($2\theta = 1.41°$, $d_2 = 62.6$ Å) at $q = 1.10{-}1.18$. If d_1 and d_2 are plotted as a function of q, one can get Figure 4. d_1 is 4.3 Å and is constant until $q = 1.12$ but showed two spacings of 3.7 and 4.4 Å when q becomes larger than 1.12 (Figure 4a). On the other hand, d_2 substantially increased from 51.3 to 62.6 Å with an increase in q from 1.00 to 1.07 and then almost constant (62.6 Å) for the samples of $q > 1.07$.

According to our previous analysis, the layer spacing, d_2, is the sum of the sublayer length of the mesogenic side chains, d_s, and that of the main chain, d_m. If the side chain changes its orientation from perpendicular (SmA) into a tilted direction (SmI), d_s should decrease to give a decreased total layer spacing, d_2. Nevertheless, Figure 4 shows that d_2 continuously and moderately increases around this transition. This result indicates that the splitting of d_1 (4.3 Å) to two spacings 3.7 and 4.4 Å could be associated with the structural change due to the phase transition from SmA to SmI.

The SmI phase was also observed in the more swollen sample of $F = 0.29$ copolymer with $q = 1.23$. We further investigated the structure of the $F = 0.26$ sample with a larger equilibrium swelling ($q = 24$) to investigate the effect of water on the liquid crystalline structure. Figure 5 shows the WAXD patterns of the oriented sample of poly(11CBA-*co*-AA) of $F = 0.26$ with various q. A similar halo was observed at a center spacing of 4.3 Å ($2\theta = 20.6°$) on the meridian line for the sample of $q = 1.0$

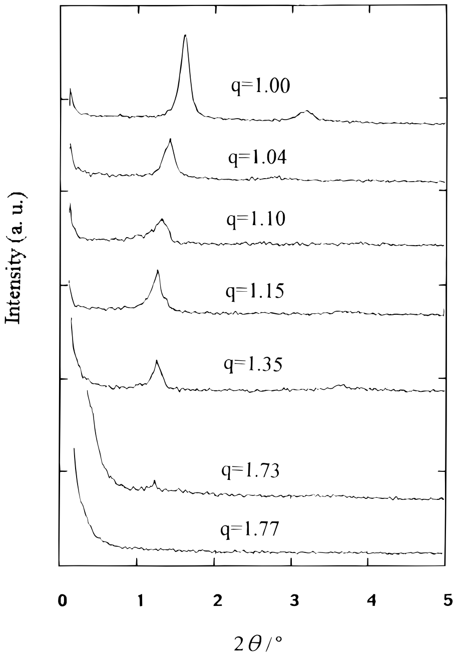

Figure 6. Small-angle X-ray diffraction patterns of poly(11CBA-*co*-AA)s of $F = 0.26$ at various q.

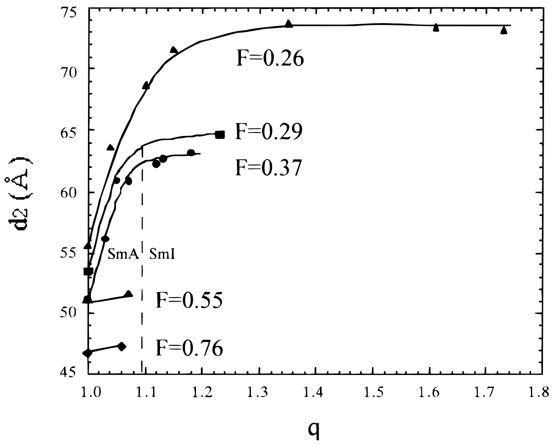

Figure 7. d_2 spacings of poly(11CBA-*co*-AA)s as a function of q.

(Figure 5a) and $q = 1.13$ (Figure 5b). Only the homogeneous Debye–Sherrer ring of the halo was observed for the sample of $q = 1.77$ (Figure 5c), indicating that the destruction of organization and orientation occurred by incorporating water due to the lower liquid crystallinity of the copolymer of $F = 0.26$, as shown in the dry state.[1]

Long-range ordering of this copolymer ($F = 0.26$) has been investigated by SAXD patterns using various q samples (Figure 6). One of two peaks corresponding to 55.6 Å ($2\theta = 1.59°$) observed for the $q = 1.00$ sample shifted to a lower angle and weakened with the increase in q and disappeared at $F = 1.77$. Another peak corresponding to 27.8 Å ($2\theta = 3.18°$) disappeared by introduction of a small amount of water ($q = 1.04$). These results indicate that the layer structure gradually transfers to the disordered state by incorporating water to give finally the amorphous phase.

Figure 7 shows the layer spacings, d_2, of poly(11CBA-*co*-AA)s of various F as a function of q. All the samples show an increased d_2 with increase in water content. d_2 in the copolymers of $F = 0.76$ and 0.55 slightly increased with increasing q from 1.0 to 1.08 due to the strong hydrophobic interactions between side chains. On the other hand, d_2 in the copolymers of $F = 0.37$, 0.29, and 0.26 substantially increased in the same increasing range of q. The $F = 0.26$ sample increased its d_2 as much as 17.6 Å, and that of $F = 0.29$ increased 8.0 Å. Such q dependence could be associated with the weak interaction between mesogenic side chains in the copolymer of $F = 0.26$ due to the low 11CBA composition and the large hydration. Assuming that the density of water is 1.0 and all of water incorporating into the copolymer of $F = 0.26$ is localized in the hydrophilic AA region to give the hydrogel of $q = 1.73$, d_2 is simply be calculated as 62.6 Å, which is much smaller than the experimental result (73.2 Å). This may be associated with the increased free volume due to enhanced segmental motion of hydrated AA units.

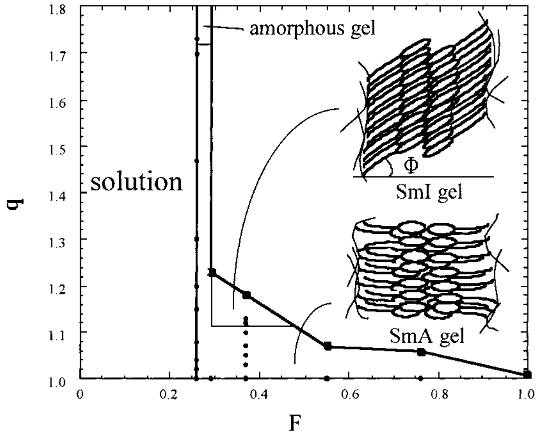

Figure 8. Liquid crystalline phase diagram of poly(11CBA-*co*-AA)s on the basis of q.

Figure 8 shows the phase diagram of poly(11CBA-*co*-AA)s for various q. As mentioned before, poly(11CBA-*co*-AA)s except for $F = 0.18$ formed the hydrogels by physical cross-linkage of liquid crystalline domains. The SmA phase of some samples transferred into the SmI phase by incorporating an appropriate amount of water. For example, the $F = 0.37$ sample exhibited the SmI phase when $q = 1.13-1.23$. This means that more than 3.5 water molecules per 1 unit of 11CBA are necessary to form the SmI structure. This is why we observed only SmA phase for the samples of $F = 0.55$ and 0.76, since, in these cases, only 1.5 and 2.1 water molecules per 1 unit of 11CBA can be incorporated in the copolymers even in the equilibrated swelling state, respectively. In the copolymer of $F = 0.26$, the SmA phase transfers to the amorphous phase at $F = 1.77$, indicating that the SmA phase is observed even in the presence of 820 water molecules per 1 unit of 11CBA. However, it is destroyed by the presence of water more than 820 molecules per 1 unit of 11CBA. Thus, poly(11CBA-*co*-AA)s are able to take three forms of states SmA, SmI, and amorphous structures depending on copolymer composition and water content.

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