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Structures in optically isotropic and bluish colored cubic phases formed by enantiomeric association in an (*R*,*S*) dichiral compound and a stereoisomeric (*R*,*R*) and (*S*,*S*) mixture

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The structures of an optically isotropic cubic phase and a bluish colored phase exhibited in an (*R*,*S*) dichiral compound with fluorines have been investigated. Not only the bluish colored phase but also the cubic phase exhibit circular dichroism, being confirmed to be chiral phases. Based on the analysis of several X-ray diffraction peaks observed in the small angle range, we find that the optically isotropic chiral cubic (IsoX) phase belongs to the symmetry group *I*432. It is also found that the cubic phase emerging in the equimolar mixture of (*R*,*R*) and (*S*,*S*) stereoisomers also has *I*432 symmetry, suggesting the formation of the cubic phase due to chiral recognition between chiral end chains. The molecular recognition upon forming the IsoX phase is also discussed by mixing (*R*,*R*) and (*S*,*S*) stereoisomers in the crystalline phase. The other important finding is the exotic phase with a blue colored and foggy texture below the isotropic liquid. X-Ray diffraction results in this phase clearly show a diffraction ring corresponding to a layer structure with a quite long correlation length. We assigned this phase to a smectic blue phase (BP_{sm}).

1. Introduction

Liquid crystals are anisotropic media, which exhibit a variety of anisotropic structures. As for positional orders, one-dimensional and two-dimensional orders are well known to exist as smectic phases and columnar phases, respectively. In addition, three-dimensional positional order also emerges in a variety of liquid crystalline materials. Higher order smectic phases such as smectic G (SmG) and SmB_{cryst} with hexagonal order within each layer are good examples. Among liquid crystals with such an anisotropic nature, there exist two classes of phases that appear to be isotropic. They are the Blue phase (BP) and the Cubic (Cub) phase, both of which have cubic symmetries. The Blue phase appeared in the first discovered liquid crystalline material[1] and the Cub phase was also found quite a long time ago,[2] though both of the structures were not clarified for a long time after their discovery. The subject of this paper is these two cubic phases.

Chirality in liquid crystals becomes more and more attractive. The introduction of chirality to molecules causes a spontaneous twist in the molecular orientation. In some cases, particularly when chirality is very strong, three-dimensional orders emerge due to structural frustration of the twist. BP appearing between the isotropic liquid (IsoLiq) and chiral nematic (N*) phases has such complex three-dimensional helical structures with cubic lattices of body-centered or simple cubic types.[3] Because of the Bragg reflection due to the helical pitch, this phase usually exhibits a bluish colored texture. This phase emerges since molecules have the chance to form a helix in any directions perpendicular to the molecular rod when the cholesteric helix emerges in the isotropic phase. A similar situation could be imagined to appear in forming helices at the phase transition from IsoLiq to chiral smectic C* (SmC*) phases. This phase might display a similar appearance to that of the usual (cholesteric) BP. This type of BP was actually discovered by Li *et al.*[4] and Pansu *et al.*[5] in 1997. However, the correlation length of the smectic order was estimated not to be so long, *i.e.*, at most 100 nm.[5] This phase is now designated as BP_{sm} to distinguish it from the cholesteric BP.[6–8] In many cases, the materials that exhibit the BP and BP_{sm} phases also show twist grain boundary (TGB) phases[8] in the phase sequences, IsoLiq–BP–N*–TGB_A–TGB_C–SmC* and IsoLiq–BP_{sm}–TGB–SmC*. The TGB phase appears as another type of frustrated chiral system in materials having strong chirality. In this phase, smectic blocks form a helix with the helical axis parallel to the smectic layer and with an array of screw dislocations in between.[9]

On the other hand, optically isotropic cubic phases emerge in many compounds that have strong intermolecular interactions through hydrogen bonds, ionic metals and many long alkyl chains.[10–11] Cub phases sometimes appear together with the SmC phase in the following phase sequences; IsoLiq–(SmA)–Cub–SmC and IsoLiq–SmC–Cub. Hence there may be a chance for SmC* materials with strong chirality to exhibit both cubic phases, *i.e.*, BP (BP_{sm}) and Cub. As far as we know, only one type of material, 6-deoxy-β-L-*erythro*-hexapyranosides,

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exhibits both phases; IsoLiq–BP–Ch–(Cub)–Crystal, though the emergence of Cub is monotropic and the structures have not been identified.[12] In this paper, we report for the first time the stable appearance of two cubic phases, BP$_{sm}$ and Cub, in a dichiral compound.

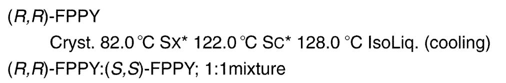
We discovered an optically isotropic liquid crystal phase in dichiral ferroelectric liquid crystal compounds containing fluorines in 1998.[13] At the phase transition from SmC* to the optically isotropic phase on cooling, the extraordinary endothermic peak was observed in the DSC measurement.[13] The appearance of this optically isotropic phase (called IsoX) depends on chirality;[13,14] (*R*,*R*) and (*S*,*S*) stereoisomers alone do not exhibit IsoX, but in the binary mixtures of (*R*,*R*) and (*S*,*S*) stereoisomers, IsoX appears in the central region of the binary phase diagram. From these results, the emergence of this phase is seemingly organized by molecular aggregation due to intermolecular chiral recognition. As such this molecular system seems to have a strong chiral interaction, so that the necessary condition for forming BP is satisfied. As we expected, the existence of the BP$_{sm}$ phase was confirmed below the isotropic liquid based on texture observation, X-ray analysis and circular dichroism. The characterization of this BP$_{sm}$ is another purpose of this paper. We found that the present BP$_{sm}$ phase is quite distinct from the previous ones in view of the long correlation length of the smectic order such as 1 µm. The other purpose is to unambiguously determine the cubic structure of the IsoX phase. Since circular dichroism is observed in this cubic phase, we assign this phase to a new chiral cubic phase with a symmetry *I*432. Molecular recognition upon forming the IsoX phase is also discussed by mixing (*R*,*R*) and (*S*,*S*) stereoisomers in the crystalline phase.

2. Experimental

The sample used was 2-{4-[(*R*)-2-fluorohexyloxy]phenyl}-5-{4-[(*S*)-2-fluoro-2-methyldecanoyloxy]phenyl}pyrimidine ((*R*,*S*)-FPPY),[13–15] as shown in Fig. 1. For comparison, we also used the stereoisomers of (*R*,*S*)-FPPY, *i.e.*, (*R*,*R*)-FPPY and (*S*,*S*)-FPPY and their mixtures. The phase sequences of these compounds are also shown in Fig. 1.

X-Ray diffraction measurements were conducted using two setups; a commercial X-ray system (Rigaku, RU-200) and a synchrotron radiation system of Photon Factory in Tsukuba. Samples were placed in 1 mm diameter capillary tubes. Only preliminary data were acquired by the former system, since diffraction profiles changed on sample preparation and repeated measurements. For the measurements, on the other hand, the latter system is preferable, since the data acquisition is made in a short time because of the strong light source. Additionally, in order to analyze the structure of a uniform domain, we used an X-ray microbeam[16,17] on the beam line 4A. The X-ray energy was monochromated to 8 keV (λ = 1.55 Å) and the incident beam was collimated using a Si/W multilayer mirror with an angular divergence of 0.5 mrad, and the spatial resolution was 2.5×3 µm^2. The detail of the optical geometry was illustrated in previous papers.[16,17] Since the system is equipped with a polarizing microscope, each phase transition is clearly recognized. Using an imaging plate (IP) instead of a one-dimensional scintillation counter, we could rapidly obtain a two-dimensional diffraction pattern. The exposure time was 5–30 s. Camera length was calibrated using the lattice constants of stearic acid measured under the same conditions.

Circular dichroism measurements were carried out using a spectropolarimeter (Jasco J720). Samples were sandwiched between 1 mm thick quartz plates and their cell gaps were controlled to be 50 µm using PET films.



(*R*,*S*)-FPPY

Cryst. 67.9 °C S$_X$* 97.4 °C IsoX 107.0 °C S$_C$* 116.7 °C IsoLiq. (cooling)

(*R*,*R*)-FPPY

Cryst. 82.0 °C S$_X$* 122.0 °C S$_C$* 128.0 °C IsoLiq. (cooling)

(*R*,*R*)-FPPY:(*S*,*S*)-FPPY; 1:1mixture

Cryst. 50.0 °C S$_X$* 97.0 °C IsoX 123.0 °C S$_C$* 124.0 °C IsoLiq. (cooling)

Fig. 1 Chemical structure of the dichiral compound with fluorines, FPPY, and phase sequences of its (*R*,*S*)-, (*R*,*R*)-, (*S*,*S*)-forms and their mixture.

3. Results and discussion

3.1 Structure of the cubic phase

Let us first show the X-ray profiles obtained using a commercial X-ray diffraction system. Fig. 2 shows the diffraction profiles obtained using a sample in a 1 mm diameter capillary tube. Each profile was obtained for twenty minutes, and we repeated the measurements 10 times continuously. It is seen that the peak positions and intensities change for every measurement. This is a characteristic of the cubic phase; the domain temporally and spatially grows and changes due to the rapid molecular motion, the orientation of the lattice changes, and its lattice constant slightly fluctuates due to the domain growth. At this stage we realized that the measurements should be made quickly and an irradiated area should be either uniform or perfectly random. Levelut and Clerc have already proposed similar conditions for the structural analysis of the cubic phase.[18]

As mentioned above, quick data acquisition from uniform domains is important. One of the solutions for this problem is the use of synchrotron radiation. For this reason, we measured the X-ray microbeam diffraction from quite uniformly oriented samples. The two-dimensional X-ray diffraction patterns obtained are shown in Fig. 3. On the heating process from the crystal, many spots were detected in the IsoX phase as shown in Fig. 3(a), indicating that the domains grown from the crystal phase are still small and powder-like. Just above 129 °C, the phase transition from IsoX to a higher temperature phase (afterwards the existence of BP$_{sm}$ between IsoX and IsoLiq will be discussed), a clear but broad ring pattern appears as observed in the smectic phase, as shown in Fig. 3(b). The intensity of this ring diffraction gradually decreases with the increase of temperature.

On cooling from IsoLiq (165 °C), a sharp ring pattern indicating SmC* was observed at 126 °C (Fig. 3(c)). At 125.5 °C, the phase transition to IsoX occurs during the exposure, as shown in Fig. 3(d). Fig. 3(e) and 3(f) show the diffraction patterns in IsoX on cooling. The diffraction patterns are rather simple, which suggests that the diffraction is obtained from domains comparable with or larger than the beam spot size. In

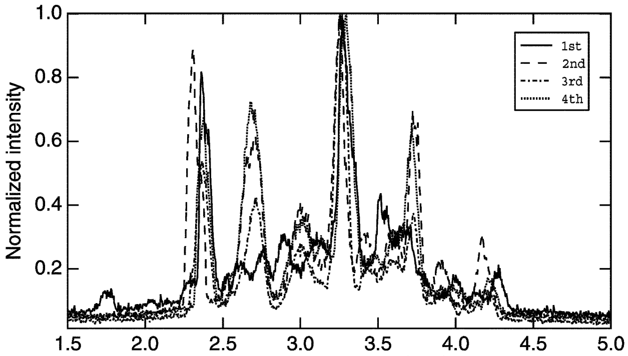


Fig. 2 Diffraction profiles obtained from a 1 mm diameter capillary sample at 110 °C. These profiles were obtained repeatedly 10 times.

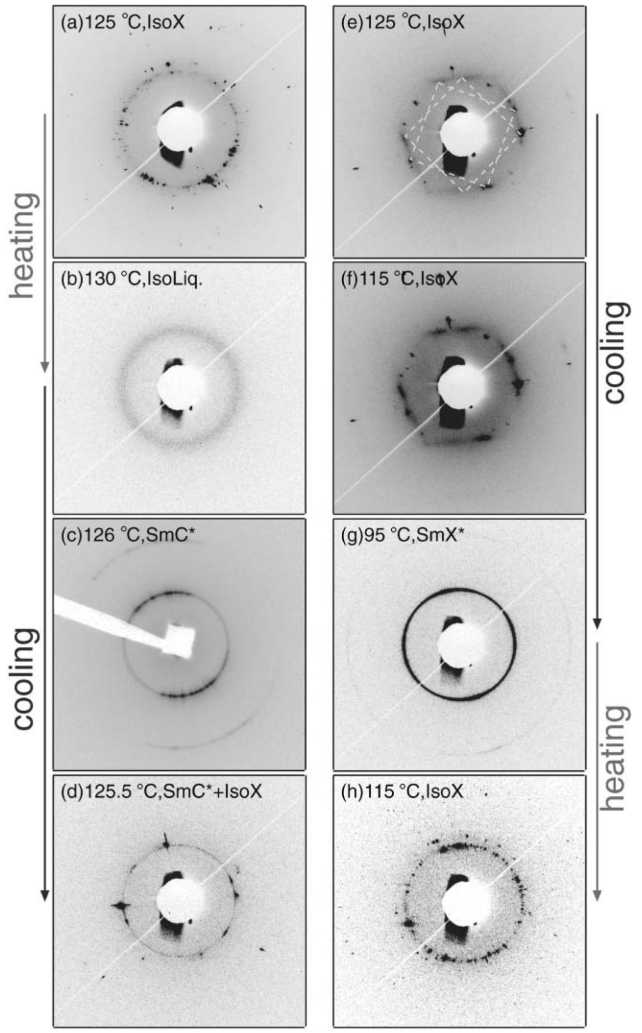


Fig. 3 2-Dimensional X-ray diffraction pattern of (*R*,*S*)-FPPY using an X-ray microbeam. (a) 125 °C (IsoX), (b) 130 °C (low temperature side of IsoLiq; BP_{sm}), (c) 126 °C (SmC*), (d) 125.5 °C (SmC* + IsoX), (e) 125 °C (IsoX), (f) 115 °C (IsoX), (g) 95 °C (SmX*) and (h) 115 °C (IsoX). Diffraction spots corresponding to (222) on two broken lines belong to the same cubic domains, respectively. Exposure time is about 5–30 s.

the temperature range of the IsoX phase, the diffraction pattern does not change drastically except that the number of spots slightly increases to appear at the lower temperature side. When the phase transition from IsoX to SmX* occurs, a sharp single ring pattern appears at $2\theta \approx 3.16°$ again, as shown in Fig. 3(g). Afterwards when temperature increases until IsoX appears again, the diffraction pattern changes to Fig. 3(h), indicating the diffraction from powder-like domains of IsoX, as observed in Fig. 3(a).

From these results, we calculated the reciprocal distances of IsoX. The obtained data are listed in Table 1. As far as analyzed observable peaks concerned, the space group of the IsoX phase belongs to *Im*3*m* or *I*432[18] with a unit lattice constant of 93.9 Å. *Im*3*m* and *I*432 cannot be distinguished by X-ray analysis alone because they obey the same extinction rule. Later the assignment to *I*432 is concluded. The highest intensity was observed at the diffraction peak corresponding to (321). In this compound, the layer thickness in SmC* is 28.0 Å, and it is very close to the reciprocal constant of the (222) plane, which is different from other compounds as reported in ref. 18. Assuming a density of 1 g cm^{-3}, there are *ca.* 900 molecules per cubic unit cell. The simplified model structure suggested by these X-ray results is shown in Fig. 4, where all the (222) planes are shown. This quite simple structure would actually relax to the Schwarz P surface structure.

Table 1 The reciprocal distances experimentally obtained in IsoX of (*R*,*S*)-FPPY at 110 °C. The assignable indices and corresponding reciprocal distances calculated assuming *Im*3*m* or *I*432 with a lattice constant *a* = 93.88 Å are also shown

Experimental *d*/Å	Calculated (*a* = 93.88 Å)	Indices
46.0	46.9	200
38.3	38.33	211
33.4	33.50	220
29.7	29.69	310
27.1	27.10	222
25.0	25.32	321
23.5	23.46	400
22.2	22.13	411
21.2	20.99	420
13.65	13.55	444

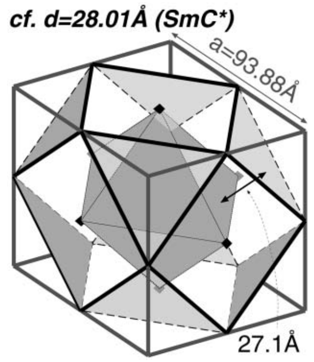


Fig. 4 Cubic *I*432 structure of IsoX in (*R*,*S*)-FPPY determined by X-ray diffraction. This figure was quite simply drawn, and it is considered that it would actually relax to the Schwarz P surface structure as shown in Fig. 6 of ref. 9.

The X-ray analysis was also made for IsoX in the 1 : 1 mixture of (*R*,*R*)-FPPY and (*S*,*S*)-FPPY. The two-dimensional X-ray diffraction patterns on (a) heating and (b) cooling are shown in Fig. 5. Obtained diffraction patterns are very similar to those in IsoX of (*R*,*S*)-FPPY. The reciprocal lattice constants determined from the diffraction pattern are listed in Table 2. Although some expected peaks, that were observable in IsoX of (*R*,*S*)-FPPY, were not observed, the space group of IsoX in the mixture is found to also be *Im*3*m* or *I*432.

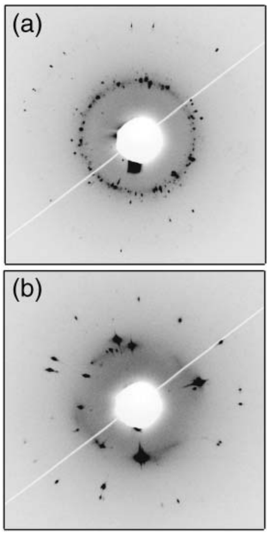


Fig. 5 2-Dimensional X-ray diffraction pattern of IsoX (110 °C) in a 1 : 1 mixture of (*R*,*R*)-FPPY and (*S*,*S*)-FPPY using an X-ray microbeam on heating (a) and cooling (b).

Table 2 The reciprocal distances experimentally obtained in IsoX′ of a 1 : 1 mixture of (*R*,*R*)-FPPY and (*S*,*S*)-FPPY at 110 °C. The assignable indices and corresponding reciprocal distances calculated assuming *Im*3*m* or *I*432 with a lattice constant $a = 91.8$ Å are also shown

Experimental *d*/Å	Calculated ($a = 91.8$ Å)	Indices
45.5	45.9	200
–	37.48	211
32.0	32.46	220
29.2	29.03	310
26.5	26.5	222
24.4	24.53	321
22.9	22.95	400
–	21.64	411
–	20.52	420
–	19.57	332
–	18.73	422
17.8	18.00	431
16.5	16.76	521
16.2	16.23	440
–	15.74	433
15.2	15.3	442
14.8	14.89	532
13.4	13.25	444

A calculated unit lattice constant is 91.8 Å, slightly smaller than that in (*R*,*S*)-FPPY. The fact that the same cubic structure is formed in the equimolar mixture of (*R*,*R*)-FPPY and (*S*,*S*)-FPPY as well as in (*R*,*S*)-FPPY supports the idea that this cubic phase is constructed due to chiral recognition between chiral end chains.

3.2 Smectic blue phase

Through texture observation, a new phase is clearly observed in the higher temperature range of SmC*. Fig. 6 shows microphotographs at various temperatures in a 100 μm thick glass sandwich cell of (*R*,*S*)-FPPY. In the higher temperature range than the IsoLiq phase (Fig. 6(b)) and in the IsoX phase (Fig. 6(d)), a completely dark view was observed under crossed polarizers. However, in the lower temperature range (from 130 °C to 140 °C on heating, and from 121 °C to 117 °C on cooling) than IsoLiq, a blue-colored and foggy texture was observed, as shown in Fig. 6(c). This texture is quite similar to that in the Blue III phase.[3] Although a clear DSC peak was observed at the phase transition between the usual Blue phase and the IsoLiq phase in *e.g.* cholesteryl nonanoate,[19] (*R*,*S*)-FPPY did not exhibit any clear peaks in this temperature region.[14] According to high sensitivity AC calorimetry, however, a very small and broad peak was observed in a wide temperature range over more than 20 °C. Details of this thermal analysis will be reported in a separate paper.[19] This kind of thermal behavior is similar to those in the chiral compound showing the blue and TGB phases, as reported by Pansu *et al.*[5]

In this blue-colored phase, a broad ring pattern shown in Fig. 3(b) was observed in the X-ray diffraction measurements. From the intensity profiles of this pattern shown in Fig. 7(a), the long range periodicity and the correlation length along the layer normal were determined using the following Lorentzian equation,

$$I(Q) \approx I_0/\{(Q - Q_0)^2 + (1/\xi)^2\} + \text{background}$$

where Q_0 and ξ are a reciprocal distance and a correlation length along the layer normal, respectively, and the calculated results are shown in Fig. 7(b). The periodicity is similar to the SmC* layer spacing, and the correlation length is much larger than those in the BP_{sm} phase in the compounds reported by Pansu *et al.*[5] Although we cannot determine the structure in this blue-colored texture, we can safely say that the blue-colored phase observed in (*R*,*S*)-FPPY has a longer smectic layer correlation, being assigned to BP_{sm}. This BP_{sm} phase is distinct from the BP_{sm} phase previously reported in view of a long-range layer correlation.

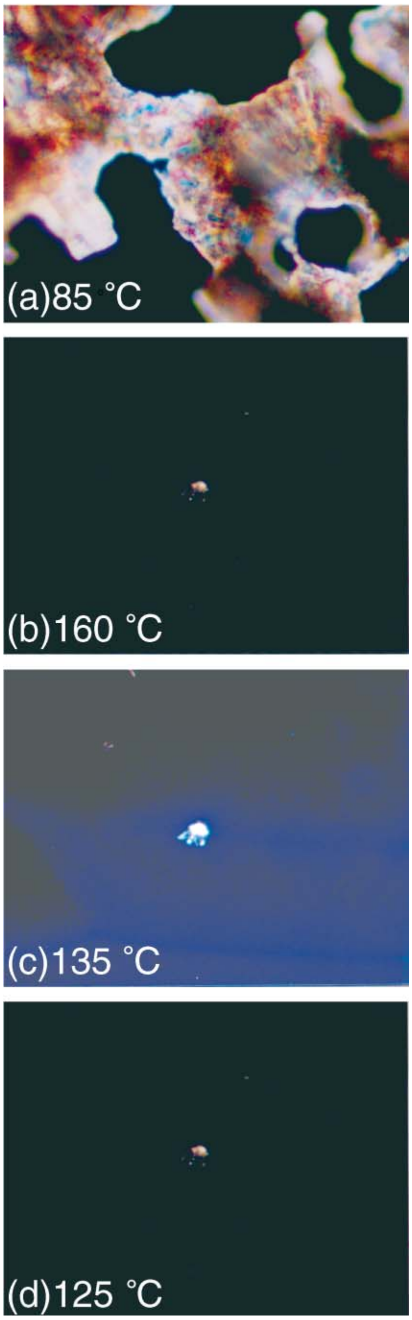


Fig. 6 Microphotographs of a 100 μm thick sandwich cell of (*R*,*S*)-FPPY in the vicinity of the IsoLiq and IsoX (or SmC*) phase transitions. (a) 85 °C, SmX–IsoX phase transition, (b) 160 °C, IsoLiq, (c) 135 °C on cooling, blue colored texture and (d) 125 °C, IsoX.

3.3 Circular dichroism

In order to investigate the chirality of the Cub phase as well as the BP_{sm} phase, circular dichroism (CD) measurements were carried out. Fig. 8 shows the temperature dependence of the CD spectra in the transition sequence of IsoLiq–BP_{sm}–SmC*–Cub on cooling. A CD peak was observed near 300 nm when entering the BP_{sm} phase (122 °C) and scarcely changes its peak wavelength throughout the temperature range down to 110 °C in the SmC* and Cub phases. The CD intensity increases with decreasing temperature in the BP_{sm} and then decreases in the SmC* phase after reaching a maximum just above the BP_{sm}–SmC* phase transition at 118 °C. In the Cub phase, the CD

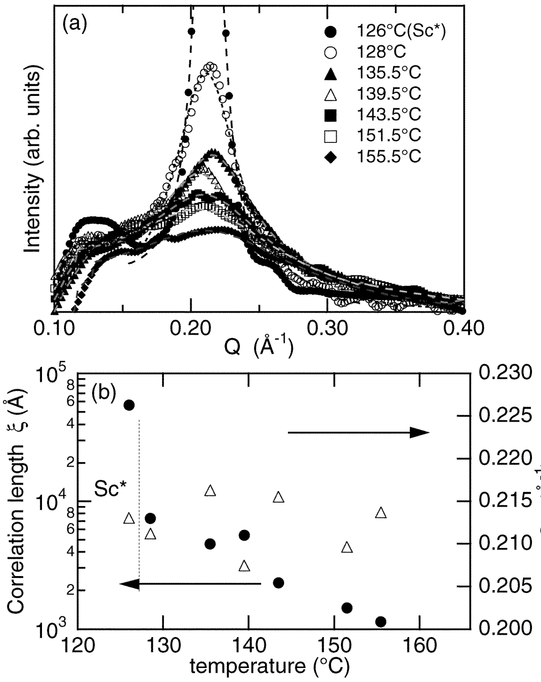


Fig. 7 Intensity profiles of X-ray diffraction of (*R*,*S*)-FPPY in the temperature range observed in the blue-colored texture (a) and the temperature dependence of the correlation length ξ (b).

signal remains without showing temperature dependence. Since the linear absorption spectra were almost independent of temperature, this large peak is caused by the induced CD signal due to the macroscopic helical structure. Thus, some helix-related structures do exist in all the phases.

The existence of the CD signal in two phases, Cub and BP_{sm} is important to assign or confirm these phase structures. (1) The Cub phase must not be *Im*3*m* and is assigned to *I*432. This is the first well-defined chiral Cub phase. (2) The bluish colored phase is actually a cubic phase (BP) mediated by a three-dimensional helical structure. Because of the existence of a layer structure in this phase and the SmC* phase below this phase, this phase should be the one occurring as a kind of pretransitional cybotactic cluster of the SmC* phase with a layer structure. In this respect, this blue-colored phase is similar to the blue phase appearing between IsoLiq and Ch phases but is different in the sense that it appears between IsoLiq and SmC* and thus possesses a layer correlation. All these results strongly support the assignment of the BP_{sm} phase. The details of this blue-colored phase will be reported in the near future.

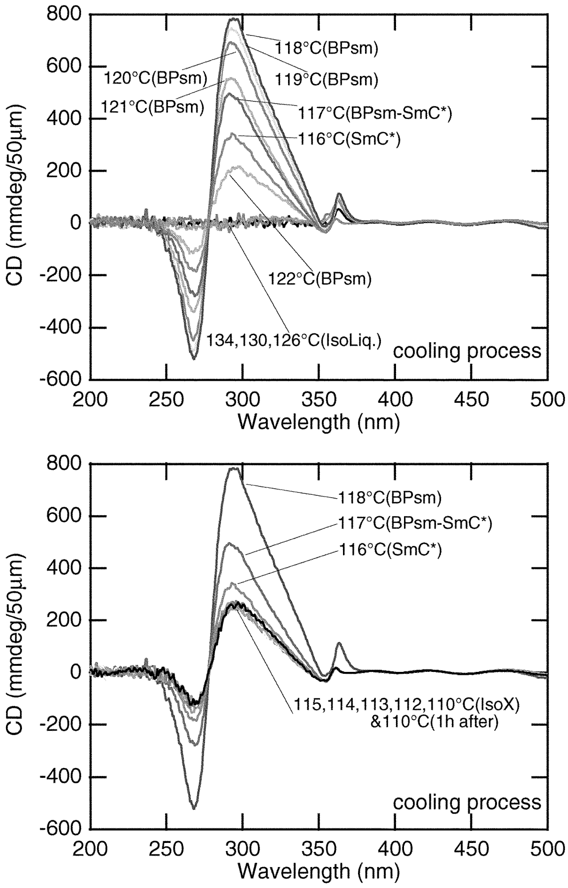


Fig. 8 Temperature dependence of the circular dichroism spectra in a 50 µm thick sandwich cell of (*R*,*S*)-FPPY.

3.4 Molecular recognition in the smectic and crystal phases

Finally, we discuss the experimental fact that is considered to be related with the molecular recognition in the higher-ordered smectic and crystal phases. Fig. 9 shows a series of microphotographs displaying the temporal change of the texture in a 1 : 1 mixture of (*R*,*R*)-FPPY and (*S*,*S*)-FPPY keeping the temperature at 110 °C. This mixture was made only by stirring them with a spatula at room temperature, not by using a

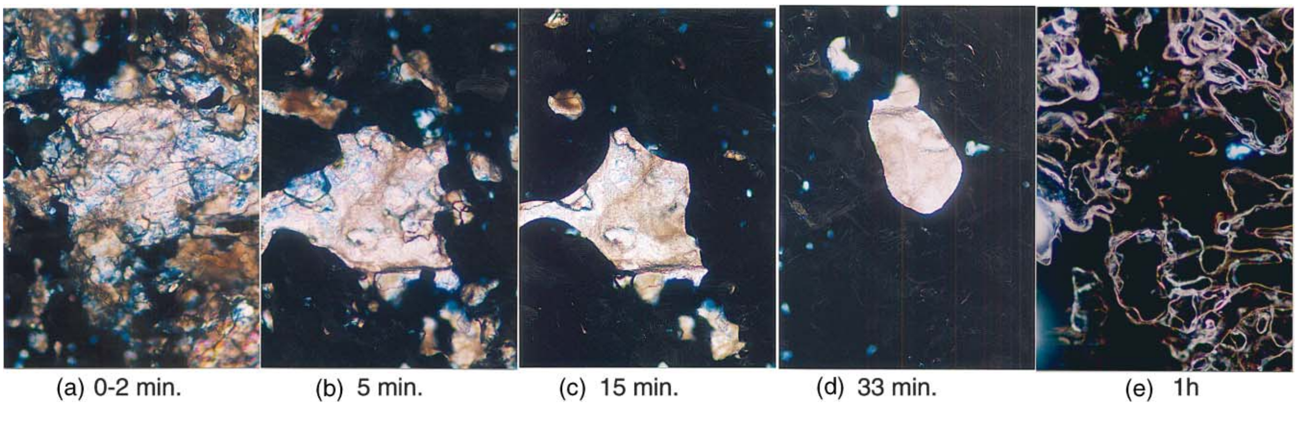

(a) 0-2 min. (b) 5 min. (c) 15 min. (d) 33 min. (e) 1h

Fig. 9 Microphotographs of a 1 : 1 mixture of (*R*,*R*)-FPPY and (*S*,*S*)-FPPY at 110 °C. (a) 0 min after heating up to 110 °C, (b) 5 min later, (c) 15 min later, (d) 33 min later and (e) 1 h later. The isotropic-like texture is not caused by homeotropic alignment, but is due to the appearance of the IsoX phase. This is clear because (*R*,*R*)-FPPY itself never shows such a change even if we monitor the texture under a polarizing microscope for long time. Such a change is possible only when another stereoisomer (*S*,*S*)-FPPY coexists together with the (*R*,*R*)-FPPY. Since this phase emerges only if (*R*) and (*S*) groups coexist, (*R*,*R*)-FPPY and (*S*,*S*)-FPPY must meet and recognize each other.

solvent nor heating up to higher temperatures than the melting point. At 110 °C, each pure compound exhibits SmX*, while the mixture shows IsoX, as mentioned in our previous paper.[15] Since the powder crystals of this mixture was made only by stirring at room temperature, however, the texture immediately after heating up to 110 °C indicates SmX* (see Fig. 9(a)). As time goes by, the texture gradually becomes isotropic (Figs. 9(b)–9(d)) and finally changes to the IsoX phase after 50 min, though the final texture shown in Fig. 9(e) still has many defects due to insufficient mixing. This phenomenon suggests the following process. Immediately after the mixing, (*R*,*R*)-FPPY and (*S*,*S*)-FPPY exist separately, and then they come to recognize each other due to thermal diffusion even in the higher-ordered SmX* phase as time goes by.

This tendency of molecular recognition may occur even in the crystal phase; when heating up to 110 °C just after stirring it at room temperature, it takes about 40 min to change from SmX* to IsoX, but after incubating the mixed substances at room temperature for two weeks, the time needed for the process is shortened to *ca.* 15 min. This fact clearly suggests that the molecular recognition and aggregation occurs to some extent even in the crystal.

4. Conclusion

The structures in the optically isotropic liquid crystalline phase (IsoX) exhibited in the novel dichiral compounds with fluorines, FPPY, were investigated. The results in the X-ray microbeam diffraction together with the existence of the circular dichroism clearly indicate a kind of chiral cubic phase belonging to *I*432. It is also found that IsoX observed in a 1 : 1 mixture of (*R*,*R*)-FPPY and (*S*,*S*)-FPPY has the same space group as that in (*R*,*S*)-FPPY. Moreover, the blue colored and foggy texture was observed in the lower temperature range of isotropic liquid. This phase has a long range density correlation compared with the normal BP and TGB phases, and exhibits a large CD signal due to the macroscopic helical structure, suggesting a new type of the BP_{sm} phase. It is also noteworthy that this is the first example where the two chiral cubic phases, BP_{sm} and Cub, coexist stably.

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