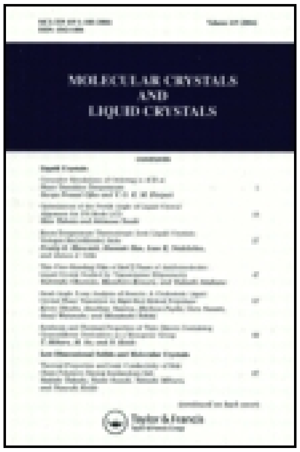

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Melting and Crystallization Processes of EBBA II. X-ray Analysis

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Melting and Crystallization Processes of EBBA

II. X-ray Analysis

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Melting and crystallization processes of EBBA (N-p-ethoxybenzylidene-*p*′-butylaniline) have been studied by the method of X-ray analysis, thermal analysis and Raman spectroscopy. A solid sample obtained by rapid cooling (cooling rate: 40 K/min) from nematic to 5°C (sample A) is composed of imperfect and/or small crystals, and the sample melts without any transformations. The solid sample obtained by quenching (cooling rate: 13 K/s) from nematic to about −100°C (sample B) is also composed of imperfect and/or small crystals. In the heating process (−100 ~ −13°C) sample B transforms to a more stable crystalline form. After the melting of a large part of sample B, some crystalline phase appears at about 35°C. An amorphous phase or a glassy liquid crystal were not formed on quenching, even at the cooling rate of 13 K/s.

Keywords: EBBA, liquid crystals, polymorphism, solids, crystallization, x-ray analysis

1. INTRODUCTION

Solid state polymorphism of EBBA has been studied by thermal analysis,[1–4,6–9] Raman spectroscopy,[5,7,8] radiothermoluminescence,[9] dielectric measurement[10] and the method of thermally stimulated depolarization,[11] and many solid forms of EBBA have been suggested already. The differences among those solid forms are caused by differences in crystal structure and molecular conformation. The crystal structure and the molecular conformation are dependent on thermal history, especially on cooling condition (for example, cooling rate and heat treatment temperature) of the sample. Therefore the author carried out thermal analysis by adjusting the cooling condition of a sample, and has suggested: 1. the existence of two solid modifications (solid S_1 and solid S_2), 2. a transformation process during the heating process of solid S_1 and 3. an adequate cooling condition to obtain those modifications.[12]

Thermal analysis gives information on enthalpy changes of the sample. In contrast, X-ray analysis gives information on the microstructure, especially structure differences between crystalline forms. Although X-ray analyses on molecular packings in the nematic and isotropic phases of EBBA have been made by Leadbetter et al.,[13] the solid state polymorphism of EBBA has not been studied by X-ray analysis.

Formation of an amorphous phase[14] and a glassy liquid crystal[15] have been suggested for a solid sample which was quenched from the nematic phase to liquid nitrogen temperature. The formation of glassy liquid crystals was also suggested for the solid sample obtained by fast cooling (15 ~ 20 K/min).[16] It is an interesting problem whether the amorphous phase or the glassy liquid crystal can be obtained by quenching of a nematic sample or not. However, the formation of the amorphous phase or the glassy liquid crystal of EBBA have not been confirmed by X-ray analysis.

In the present investigation, X-ray analysis, thermal analysis and Raman spectroscopy of EBBA solid sample were carried out. Then the characteristics of the crystal structure of each solid modification and the process of structural change during heating are clarified.

2. EXPERIMENTAL

2.1. Samples

A highly purified EBBA sample (Fuji Shikiso Co.) was used for all experiments. A powdered sample was made of single crystals which were precipitated from ethanol solution.

As mentioned in the previous paper[12] the quantity of solid S_1 in solid S increases with heat-treatment time at a low temperature and/or with cooling to a low temperature. That is, the quantity of solid S_1 in solid S increases with increasing degree of cooling. In the present experiment two types of samples which were obtained with different cooling rates were prepared. The solid samples obtained by rapid cooling and quenching are named samples A and B respectively. Samples A and B, used for X-ray analysis, were obtained by the following processes.

Sample A: A nematic sample was cooled rapidly to 5°C with a rate

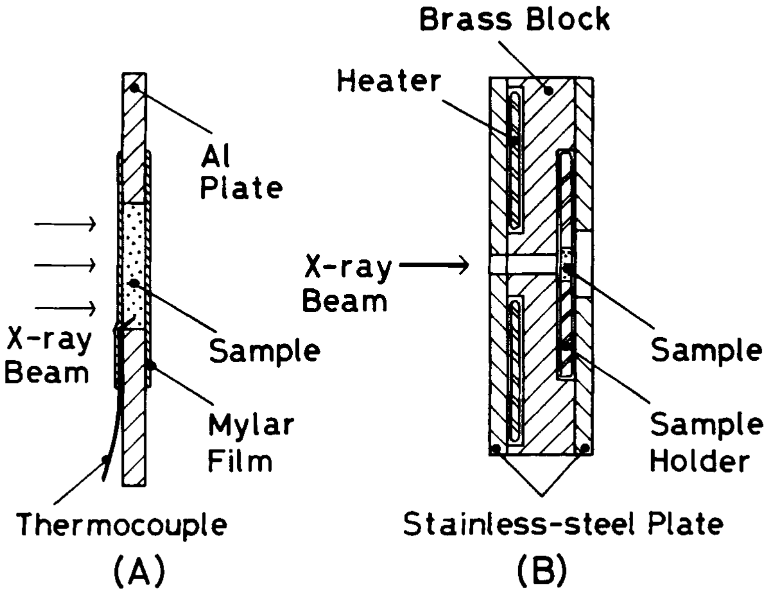

FIGURE 1 Heating apparatus used for X-ray measurement. (A) Cross-section of sample holder (side view). (B) Cross-section of heating block (top view).

of about 40 K/min, and then it was heat treated for 5 seconds at 5°C. Sample B: A nematic sample was quenched to −100°C with a rate of about 13 K/s (800 K/min), and then it was heat treated for 30 seconds at −100°C.

Samples A and B, used for Raman spectroscopy, were obtained by almost the same processes described above.

2.2. Apparatus

Figure 1(A) and (B) shows cross-sections of the sample holder and heating block for X-ray measurement respectively. The EBBA sample was sandwiched between thin mylar films (25 μm in thickness). The thickness of the sample was about 1 mm. A nematic sample contained in the sample holder was cooled rapidly by pressing the sample holder against a copper block which had been cooled before. The heating block was cooled to the same temperature as the sample holder, and the sample was heated by a heater in the heating block. The temperature of the sample was measured by a thermocouple inserted in the sample. The temperature of the sample could be controlled above 20°C.

A Rigaku Rotaflex RU-200 (60 kV, 200 mA) was used as X-ray generator. Nickel filtered CuKα radiation was used as an incident

X-ray beam. The intensity of the scattered X-rays from the sample was measured by a scintillation counter. The diffractometer was controlled by a microcomputer system, and successive diffraction patterns during the heating process could be obtained automatically. The diffractometer was scanned over a range of $5° < 2\theta < 30°$ with the scanning speed of 32°/min. It took only 46 seconds to obtain one diffraction pattern.

3. RESULTS AND DISCUSSION

3.1. Sample A: solid sample obtained by rapid cooling

Figure 2 shows an X-ray diffraction patterns of sample A during the heating process. The heating rate was lower than 0.2 K/min. Three high intensity reflections appear in the angle range of 21° ~ 22° and many weak reflections are observed at other diffraction angles at a temperature of 33.0°C. The diffraction angle and reflection intensity for each peak scarcely change with temperature up to about 33°C. Then the reflection intensities decrease monotonously from 33.5°C to 35.0°C, though the diffraction angle of each reflection does not move. At about 35°C the intensities of all reflections decrease abruptly, and a broad peak which corresponds to the diffuse X-ray scattering by nematic materials appears around 22°. It can be concluded from these results that structural change does not occur in the heating process of sample A up to 35°C, and the melting temperature of sample A occurs at about 35°C.

Howard et al. carried out X-ray analysis on EBBA single crystals precipitated from 60/40 petroleum ether and have reported the crystalline parameters.[17] Their crystallographic data indicate the existence of many high intensity reflections. On the other hand, only three high intensity reflections appear in Figure 2. In addition, the angle range of these reflections (21° ~ 22°) coincides with the peak position of the broad peak of the diffraction from the nematic phase. This can be explained by assuming that sample A is a crystalline phase whose molecular packing lost long-range regularity, and that the intermolecular distance perpendicular to the molecule axis is similar to that of the nematic phase.

Run 1 in Figure 3 shows a DSC melting curve (3.2 K/min) of a single-crystal sample. The peak temperature of the endothermic peak is 37.5°C. After melting, this single crystal sample was cooled with the same process as for sample A, and then another DSC melting

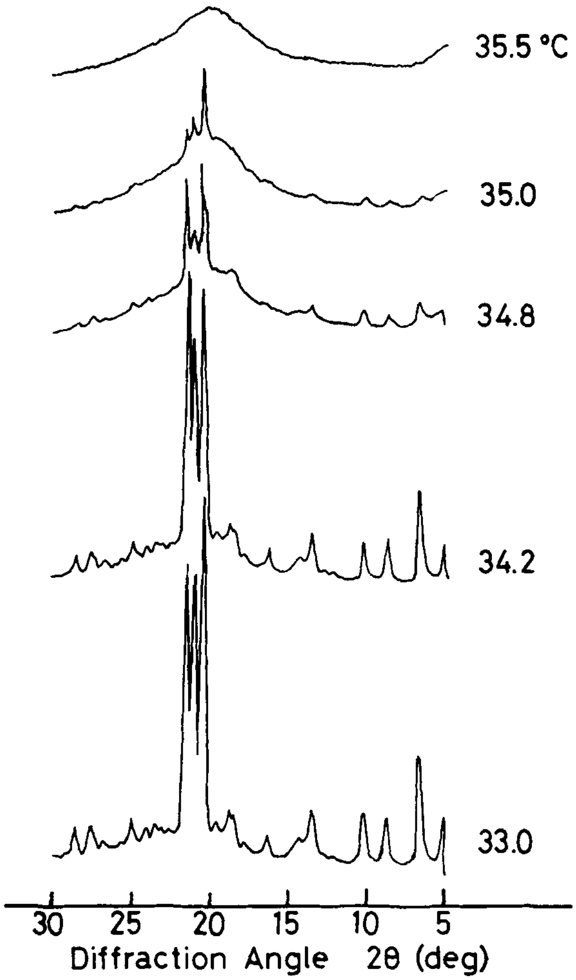

FIGURE 2 X-ray diffraction patterns of sample A during the heating process.

curve was obtained (run 2). The peak temperature of run 2 is 37.0°C and is slightly lower than that of run 1. The peak area of run 2 is about half of run 1. These results indicate that sample A is of low crystallinity and/or consists of imperfect crystal.

3.2. Sample B: solid sample obtained by quenching

3.2.1. Transformation process Figure 4 shows the change of the X-ray diffraction pattern of sample B during the heating process. The heating rate was less than 10 K/min. The diffraction pattern changes

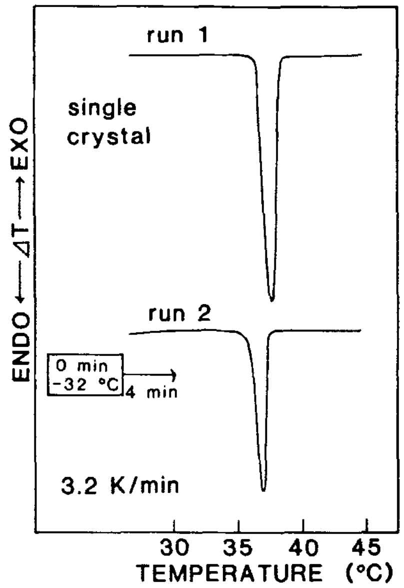

FIGURE 3 DSC melting curves of EBBA. Run 1: single crystal sample. Run 2; solid sample obtained by the same cooling process as sample A.

drastically with increasing temperature. Three high intensity reflections appear at the diffraction angles of 5.8°, 21.0° and 21.9° in the diffraction pattern at −70°C. With increasing temperature the intensities of those reflections decrease. In addition, several new reflections appear over a wide diffraction angle as shown in the diffraction pattern at −13°C.

The peak positions at 21.0° and 21.9° correspond to the angle-range where the diffuse scattering of the nematic phase appears. Consequently, as explained in the case of sample A, it can be also assumed for sample B that the crystalline phase lost range regularity in its molecular packing, and that the intermolecular spacing perpendicular to the molecular axis is similar to that of the nematic phase. In addition, it can be concluded from the successive changes of the diffraction pattern that the crystalline structure of sample B transforms to another, more stable one, in the heating process.

The formation of an amorphous phase[14] and a glassy liquid crystal[15,16] have been suggested for the EBBA solid samples which were obtained by quenching of a nematic sample to liquid nitrogen temperature or by fast cooling. However, the formation of these has not been confirmed by X-ray analysis. When the present sample holder in which

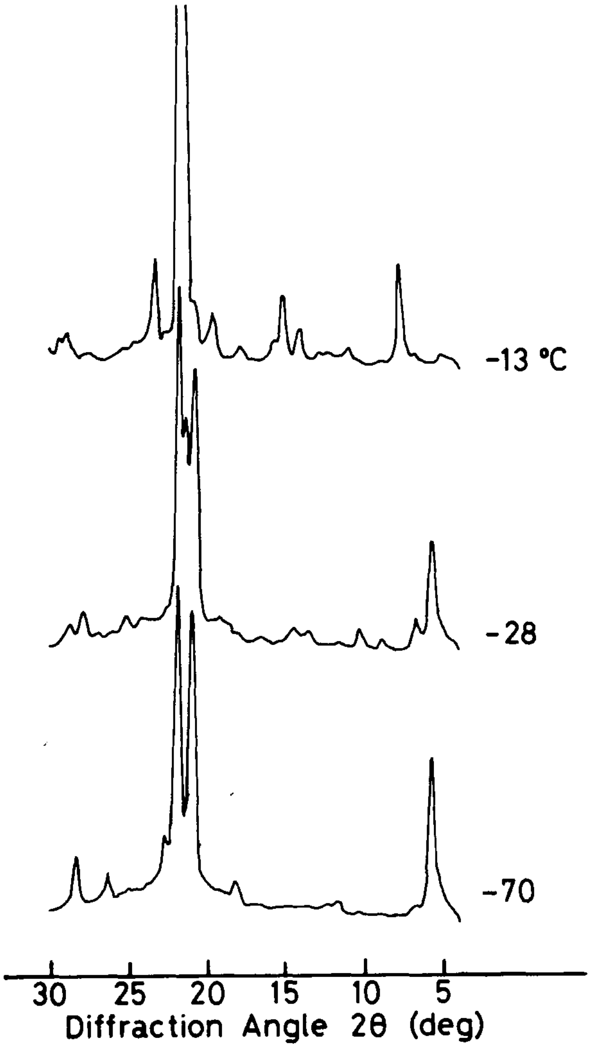

FIGURE 4 X-ray diffraction patterns of sample B during the heating process (− 100 ~ − 13°C).

a nematic sample was enclosed was immersed in a liquid nitrogen bath, rapid cooling of the sample was prevented by the nitrogen gas which was generated on the surface of the sample holder. Accordingly in the present experiment the solid sample was cooled by putting the sample holder against a copper block that was cooled in liquid nitrogen. Although sample B was cooled with a high cooling rate (13 K/

s) by this procedure, the diffraction pattern at −70°C in Figure 6 is different from that of the nematic phase, but close to the crystalline solid. Therefore, it is reasonable to consider that the amorphous phase and the glassy liquid crystal are not formed by such quenching (~13 K/s), although the possibility of the formation of an amorphous phase or a glassy liquid crystal in a small part of the sample can not be excluded.

Lydon and Kessler[18] have suggested that the diffraction pattern of quenched nematic material of MBBA (N-p-methoxybenzylidene-p′-butylaniline) coincides with that of nematic material and suggested the formation of nematic glass. The difference between EBBA and MBBA on the formation of the glassy liquid crystal, both have similar molecular structure, may be caused by the difference in the molecular packing of their nematic phases.[13]

3.2.2. Melting process Figure 5 shows X-ray diffraction patterns taken during melting process of sample B. The heating rate was less than 0.2 K/min. Since the X-ray diffraction pattern at −13°C in Figure 4 is nearly equal to that of 31.0°C of Figure 5, it is obvious that the crystalline structure did not change from −13°C to 31°C. Then, with increasing temperature (32.0°C ~ 33.5°C) the intensities of all reflections decrease except for that of 19.3°. This result suggests that in the temperature range from −13°C to 32°C sample B contains two solids whose crystalline structures are different from each other.

At 35.0°C the peak of 19.3° almost disappears, and a new, sharp peak at 21.4° and small peak at 20.8° appear suddenly. However, these peaks have disappeared completely by the next scan (35.2°C). Then new, small peaks appear at about 25° at 35.2°C, and these peaks disappear completely at 35.4°C. Only a broad peak remains at 35.4°C. That is, all of the sample has changed to the nematic phase at this temperature.

Diffuse scattering of the X-ray beam by noncrystalline parts in a sample results in a broad peak. A broad peak in Figure 5 was obtained by subtraction of the sharp peak, which is attributed to the reflection from the crystalline part, from the X-ray diffraction pattern. Figure 6 shows the temperature-dependence of the diffraction intensity of this broad peak at a diffraction angle of $2\theta = 19°$, where the broad peak shows maximum. The curve of Figure 6 shows a distinct mini-the sample decreases at this temperature. On the other hand, the sharp peak and the small peaks which correspond to formation of new crystalline phases appear at 35.0°C and 35.2°C respectively. It can be concluded on the basis of these results that some crystalline

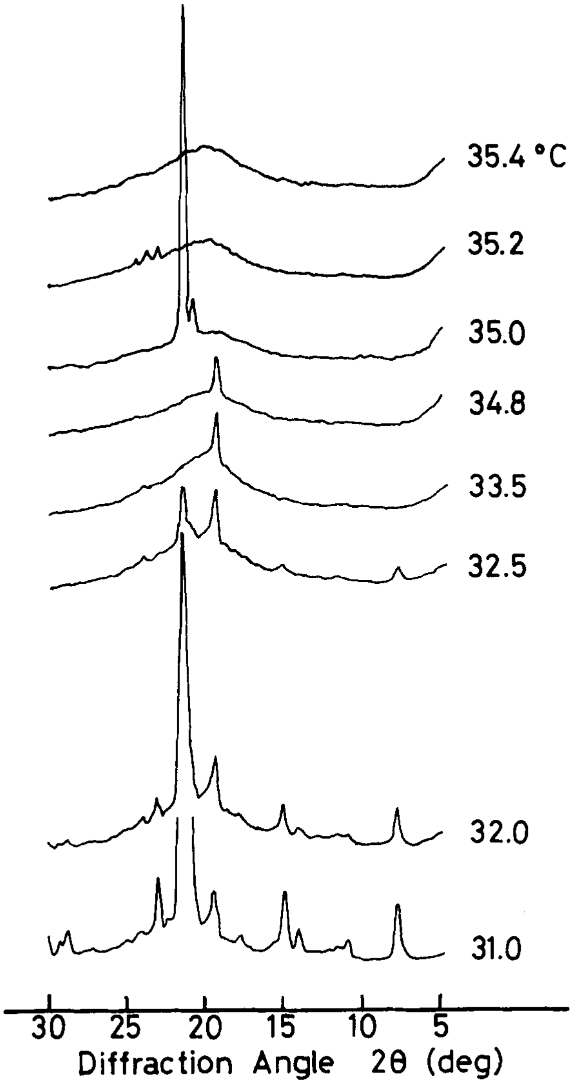

FIGURE 5 X-ray diffraction patterns of sample B during the melting process (31 ~ 36°C).

phase appears during the melting process of sample B. The reflection peaks which correspond to the new crystal growing above 35°C appear transiently, and the peaks are few. Therefore, the detailed formation process of the new crystal and its melting process are difficult to analyze from the present experiment. The relation between the solid

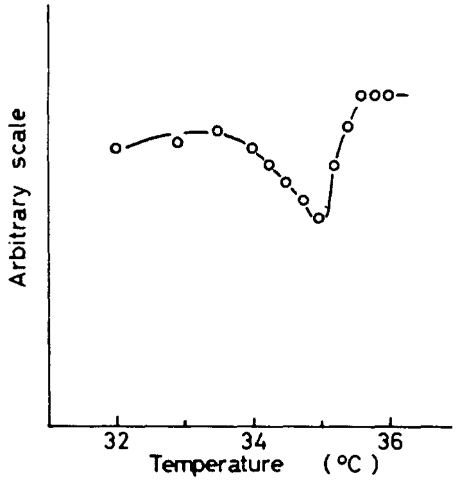

FIGURE 6 Temperature dependence of the scattering intensity which is caused by the noncrystalline part in the sample. The intensity is obtained at a diffraction angle of $2\theta = 19°$.

which corresponds to the diffraction peak at 19.3° and the new crystal is also difficult to clarify.

As mentioned above, a new crystal is formed by recrystallization of nematic material at about 35°C. Accordingly, the following melting process can be suggested for the sample obtained by quenching. Initially a large amount of solid sample melts and the residual solid sample remains unchanged in the temperature range from 32.0°C to 33.5°C. Then some part of the nematic sample recrystallizes at about 35°C. Finally, all of the sample melts at 35.4°C. This melting and recrystallization process is consistent with the conclusion obtained by thermal analysis.[12]

3.3 Raman spectroscopy

Raman spectra of powdered initial sample, sample A, sample B and nematic and isotropic phase samples are shown in Figure 7. The spectra of the powdered sample, samples A and B were obtained at room temperature, and those of the nematic and isotropic phases were obtained at 45°C and 85°C, respectively. Since the powdered sample was obtained by breaking a solution grown single crystal sample into fine pieces, the spectrum of the powdered sample corresponds to that of a single crystal.

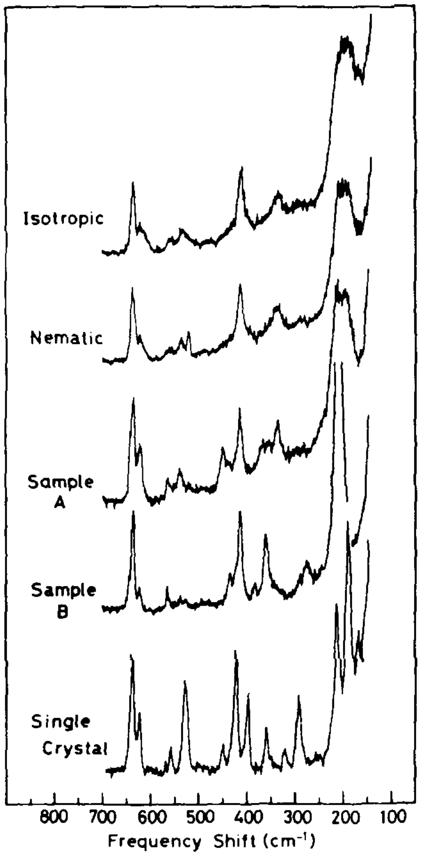

FIGURE 7 Raman spectra of the powdered sample, sample A, sample B and nematic and isotropic phase samples. The spectra of sample A and sample B were obtained at room temperature. Those of the nematic and isotropic samples were obtained at 45°C and 85°C respectively.

As shown in Figure 7 the spectrum of sample A is similar to those of the nematic and isotropic phases and is largely different from that of the powdered sample. It is concluded from this result that sample A has a disordered molecular conformation which is similar to that of the nematic and isotropic phases. However, this conclusion does not mean that the molecular packing of sample A is the same as in the state of the amorphous phase or the nematic glass, because X-ray analysis is a more adequate method for the determination of the molecular packing than Raman spectroscopy. That is, as mentioned in 3.1.2 it is concluded from X-ray analysis that sample A is a crystalline phase, though the molecular packing in the crystalline phase lost higher-order regularity. The conclusion of the disordered conformation of sample A obtained by Raman spectroscopy is consistent with the conclusion of the molecular packing which lost long-range regularity obtained by X-ray analysis.

Many and sharp peaks appear in the spectrum of the powdered sample. The spectrum of sample B lacks some of these peaks that appeared in the powdered sample. However, in the low frequency region (150 ~ 300 cm^{-1}) the spectrum of sample B is intermediate between the spectra of the nematic state and the powdered samples. The band associated with the accordion-mode vibration of the end butyl chain of EBBA molecule has been assigned to the band at 280 cm^{-1}.[19] The peak height of the band at 280 cm^{-1} is obviously intermediate between those of the nematic state and the powdered samples. In contrast, the band at 280 cm^{-1} of sample A has disappeared. Although sample B was obtained by higher cooling rate than sample A, the spectrum of sample B is more similar to that of the powdered sample than that of sample A. This fact confirms the suggestion, which is obtained by X-ray analysis and microscopic observation, that sample B transforms to more perfect crystalline solid in the heating process up to room temperature.

3.4 Solid state polymorphism

The nematic liquid crystal has a high degree of long-range orientational order of the molecules, but no long-range positional order. The molecules in the nematic phase are spontaneously oriented with their long axes approximately parallel. The crystalline phase has a high degree of long range positional and orientational order. In the phase transition process from the nematic to the crystal a molecule has to move from the position in the nematic phase to its lattice position in the crystal. Since an EBBA molecule is long (ca. 20 Å) and has two bulky benzene rings, the molecule is supposed to have large steric hinderance to translational and rotational motion. Therefore it is rational to consider that a stable crystal which is like a solution grown crystal is not formed instantaneously, and that a solid sample obtained by rapid cooling takes an intermediate molecular packing, one between the nematic and crystalline phases. With increasing cooling rate, the molecular packing of the solid sample is supposed to be closer to the nematic phase, and the difference of the molecular packing of the solid sample from that of the crystalline phase increases. That is, the instability of the solid sample increases with increasing cooling rate, and the solid sample obtained by high cooling rate transforms to a more stable one whose molecular packing is closer to the crystalline phase.

The above discussion of the formation and transformation processes of solid samples are consistent with the present experimental results obtained for samples A and B. The formation and transformation processes of sample A and B can be explained as follows: Samples A and B were obtained by rapid cooling and quenching from the nematic phase, therefore the molecular packings are intermediate between nematic and crystalline. This supposition is confirmed by the experimental evidences, i.e. small numbers of high intensity reflections and coincidence of the diffraction angle range between high intensity reflections from the solid samples and diffuse scattering from the nematic phase, as shown in the X-ray diffraction patterns in Figures 2 and 4.

As sample B was made with a higher cooling rate than sample A, the molecular packing of it is closer to the nematic phase and sample B is more unstable than sample A. Accordingly, transformation to another, more stable solid form, should occur during the heating process. The transformation is confirmed by the change of the diffraction pattern, as shown in Figure 4. In constant in sample A the transformation does not occur during the heating process. However, sample A transforms slowly to the crystalline phase at room temperature, as clarified by microscopic observation and X-ray analysis.[20]

Acknowledgments

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