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Melting and Crystallization Processes of EBBA
I. Thermal Analysis

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Melting and crystallization processes of EBBA (N-*p*-Ethoxybenzylidene-*p*′-butylaniline) have been studied by the method of thermal analysis and measurement of light transmittance. When the sample is cooled down from the nematic phase at a rapid cooling rate, solid phase (solid S) is formed directly. Solid S contains two solid modifications (solid S_1 and solid S_2). By heating the solid S, some amount of Solid S_1 is transformed into the nematic phase through the process of (melting of solid S_1 → crystallization to solid S_2 → melting of solid S_2). After the melting of solid S_1, some liquid crystalline state appears transiently. Solid S_1 is stabilized by the heat treatment at low temperature. The quantity of solid S_1 in solid S increases with the heat treatment time and/or with cooling at a low temperature.

1 INTRODUCTION

When a liquid crystalline sample in the state of liquid crystalline phase is cooled down, the sample is often crystallized into the solid phase through the supercooled liquid crystalline state. If this solid sample is reheated, lower melting points or multi-melting points are sometimes observed. These observations have often been explained by the meltings of some kinds of solids which have different thermal stabilities, i.e. solid state polymorphism. The study of solid state polymorphism of liquid crystalline materials has already been reported by many authors. It is well known that the solid order obtained is quite dependent on the cool-

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ing rate and the extent of nucleation. This indicates that a different cooling process should bring about different kinds of solids. However, in many experiments on the solid state polymorphism, temperature control at a cooling process has not been generally practiced so far. Consequently it happens that the phase diagram which has been reported by one author is often different from the ones reported by other authors. For example, Lydon and Kessler[1] have reported the disagreement of their DTA data in the heating process of MBBA with those reported by Mayer *et al.*[2] and Petrie *et al.*[3] Then they have supposed that the reason of this discrepancy is perhaps due to the different quenching rates.

The study of solid state polymorphism of EBBA has been reported by Kirov *et al.*,[4] Ogorodnik[5,6] and Sorai *et al.*[7] Kirov *et al.* carried out thermal analysis and Raman spectroscopy and have suggested three kinds of solids. Ogorodnik has suggested four kinds of solids from the Raman spectra and the multi-peaks of his thermogram. Sorai *et al.* measured the specific heat and have indicated the metastable crystalline phase. A high pressure DTA thermogram was obtained by Schneider *et al.*[8,9] They have suggested two kinds of solids (solid 1 and solid 2) and have explained the melting process that solid 1 as well as solid 2 melts into the nematic phase at a low and high temperature respectively. Although the solid order obtained is quite dependent on the rate of cooling and extent of nucleation, in these measurements mentioned above, adjustment of the cooling condition was not employed as an important experimental condition. Consequently these suggestions[4-9] do not agree with each other. Agarwal and Arora[10] carried out the dielectric measurement on "stable" and "metastable" solids which were obtained with slow (0.5 °C/min) and rapid (5 °C/min) cooling rates respectively. It is questionable that the "stable" solid named by them is really a stable one, because even in the slow cooling process stable solid is formed by the accidental crystallization from the supercooled nematic phase.

In the present investigation, thermal analysis and measurement of light transmittance of EBBA are carried out under the adjustment of cooling condition. The melting and crystallization processes of EBBA are clarified, and the explanations of the formation process and characteristics of each solid are examined.

2 EXPERIMENTAL

2.1 Samples

A highly purified EBBA sample was obtained from Fuji Shikiso Co.; therefore the sample was not purified furthermore.

2.2 Apparatus

2.2.1 Thermal analysis Thermal analysis was carried out using low temperature differential scanning calorimetry (Rigaku Denki Co.). By the use of liquid nitrogen, the heating and cooling rate could be easily controlled over the range of $-100 \sim +300$ °C.

2.2.2 The measurement of light transmittance The measurement of the intensity of transmitted light in the sample was carried out. The apparatus is shown in Figure 1. The sample was enclosed in a cylindrical glass capsule which was 4 mm in inner diameter. The incident laser beam entered vertically on the surface of this glass capsule. The intensity of transmitted light was detected by the photo diode. A strong laser beam tends to damage the liquid crystalline sample, therefore a low intensity beam was used as an incident light source. The temperature was measured by means of an alumel chlomel thermocouple placed in the sample. The temperature of the sample could be controlled precisely by the use of a temperature controller (Shinku Riko Model HPC-5000-3064 MLA).

3 RESULTS AND DISCUSSION

3.1 Crystallization process

Figure 2 shows thermograms which were obtained in the cooling process from the nematic phase. In any cooling rate the liquid crystalline phase is transformed into solid through supercooled nematic phase. When the nematic sample is cooled at a rapid cooling rate more than 10 K/min (run 1), a single broad exothermic peak appears on the thermogram. This broad peak indicated that the sample is crystallized into a solid which is partly similar to the frozen state of the liquid crystalline phase. This solid is named solid S. When the nematic sample is cooled at a slow cooling rate of less than 3.2 K/min (run 3), two stepped crystallization can be observed. The crystallization curve shows a broad exothermic

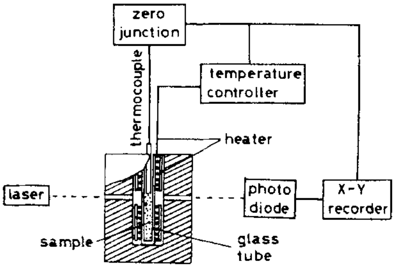

FIGURE 1 Apparatus for measuring light transmittance.

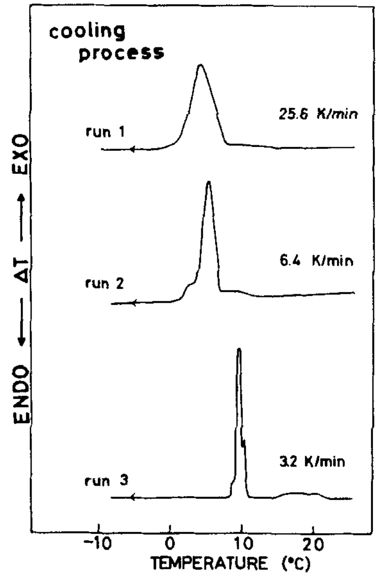

FIGURE 2 DSC thermograms of EBBA in the cooling processes. Cooling rates are indicated in the figure.

peak in the range of 21 ~ 12 °C and a sharp exothermic peak at 10 °C.

In order to clarify the cause of appearance of the broad exothermic peak of run 3, the measurement of light transmittance was carried out. As the intensity of the transmitted light fluctuates with the lapse of time, Figure 3 shows the averaged intensity of transmitted light. Then the intensity in Figure 3 is not corrected by other experimental conditions (for example, refractive index of the sample). In the cooling process the intensity of transmitted light does not decrease abruptly over the temperature range where the broad peak of DSC thermogram appears. If a small number of large-sized crystals is formed through the processes of nucleation and growth of crystals, the degree of the scattering of the laser beam may be small, (i.e. the intensity of transmitted light in the transformation process from the nematic phase to solid does not perhaps de-

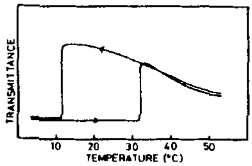

FIGURE 3 Averaged intensity of transmitted light in the sample. The heating and the cooling rates are 0.8 K/min.

crease abruptly). From these suppositions a two-stepped crystallization process with the slow cooling rate can be considered as follows. In the first place, in the temperature region of the broad exothermic peak of run 3 a small amount of the sample is transformed into large-sized crystals. Subsequently in the temperature region of sharp exothermic peak the residual sample crystallizes around the crystals which are formed in the first place. By the microscopic observation the confirmation of these suppositions will be given in the near future.

As shown in Figure 2, the DSC thermogram, obtained at 6.4 K/min (run 2), is an intermediate one which was obtained between rapid (run 1) and slow (run 3) cooling rates. So it is supposed that in this cooling rate the crystallization process is the one mixed with the rapid and slow cooling rates.

3.2 Melting process

Solid S follows a simple crystallization process, and so it is supposed that the structure of solid S is simple rather than that of the solid obtained by slow cooling processes. Therefore, in the first place, the melting process of solid S is clarified (Figure 4). Solid S was obtained by the cooling at the rate of 12.8 K/min from the nematic phase to −25 °C (run 1 in Figure 4). The melting thermogram of solid S (1.6 K/min) shows two endothermic peaks (run 2 in Figure 4). Two endothermic peaks corre-

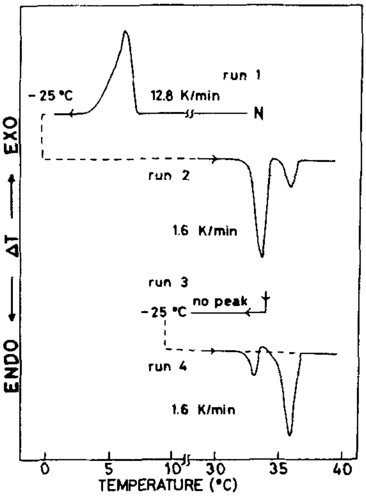

FIGURE 4 Heat treatment effect on the melting process. Run 2 is the melting thermogram of solid S. Run 4 is the melting thermogram of heat treated solid S which is heated up to 34 °C and cooled down to −25 °C (run 3). Heating rates are indicated in the figure.

spond to the meltings of two kinds of solids. Those solids are named S_1 and S_2 which correspond to a low and a high temperature peak, respectively. Ogorodnik[6] and Schneider *et al.*[8,9] have also reported two similar endothermic peaks as proof of the existence of some kinds of solids. However, they have not made further investigation of the melting process. By obtaining the details of the melting process of solid S, solid S was heated up to 34 °C where the larger part of the solid S_1 melts, and immediately the sample was cooled down. As the solid S was heated at the slow heating rate (1.6 K/min), the temperature of the sample could be controlled perfectly in the above heating and cooling processes. In spite of the cooling of the sample to −25 °C the exothermic peak which corresponds to the peak shown in Figure 2 did not appear. When this sample was reheated at the rate of 1.6 K/min (run 4), small endothermic, small exothermic and large endothermic peaks appeared successively. Generally an exothermic peak is caused by the crystallization of a melted material, so the small exothermic peak of run 4 is due to the crystallization into solid S_2. Accordingly, it can be considered that some amount of the solid S is transformed into the nematic phase in the process of the melting of the solid S_1 → crystallization to solid S_2 → melting of solid S_2. This type of exothermic peak and/or the result which corresponds to this exothermic peak appears in the lower temperature; therefore, in the ordinary experimental condition the small exothermic peak is covered with these two peaks and disappears from the melting curve as shown in the run 2. Several authors[4-9] have already suggested a different phase diagram and several kinds of solids. However, their suggestion has been based on thermograms on which no exothermic peak appears. The result of the present thermal analysis conflicts with their explanation concerning the melting processes.

In order to confirm the melting process of the solid S, the light transmittance measurement has been carried out. Generally a solid phase of a liquid crystalline material is opaque and a liquid crystalline phase is turbid. Figure 5 shows the light intensity (arbitrary scale) in the melting process of solid S. In the first place the intensity increases at about 31 °C, which shows the melting of solid S. Then the intensity turns into zero at about 33 °C, which shows the formation of the solid. Finally, the intensity increases at about 35 °C by the melting of the solid. The melting process obtained by the measurement of light transmittance coincides fairly well with the one obtained by the thermal analysis. Therefore, it can be concluded that some amount of solid S is transformed into the nematic phase through the process of melting of the solid S_1 → crystallization to solid S_2 → melting of solid S_2. After

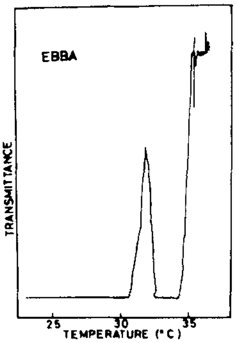

FIGURE 5 Intensity of transmitted light (arbitrary scale) in the melting process of solid S. Heating rate is 0.8 K/min.

the melting of the solid S_1, liquid crystalline state appears transiently. The characteristics of this liquid crystalline state can not be obtained in the present investigation.

Polyethylene takes a similar melting process to EBBA under a pressure of more than 4000 kg/cm^2.[11-13] For example, when a high density polyethylene sample is cooled down from the melt at the pressure of 3000 kg/cm^2, the sample is crystallized into a chain-extended crystal and chain-folded crystal. A chain-folded sample has more amorphous concentration than the chain-extended sample and the crystal size of the chain-folded crystal is considerably smaller than that of the chain-extended crystal. So the chain-extended crystal has a higher melting point than chain-folded crystal, although the crystal structure of the chain-folded crystal is the same as that of the chain-extended crystal. When the sample crystallized at the pressure of more than 3000 kg/cm^2, is heated at the pressure of more than 4000 kg/cm^2, the sample is transformed into the isotropic phase. Through the process of melting of chain-folded crystal → crystallization to chain-extended crystal → melting of chain-extended crystal and formation of liquid crystalline phase → isotropic phase. It can be considered from these transformation processes that solid S_1 and solid S_2 closely correspond to the chain-folded crystal and chain-extended crystal respectively. It is supposed from this correspondence that the solid S_1 contains many defects and that the crystal size is smaller than that of solid S_2. The correctness of this supposition has been confirmed from the microscopic observation of these samples. The result of microscopic observation will be given in the near future.

The melting thermogram of the sample which was cooled down from

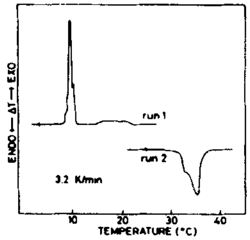

FIGURE 6 Melting thermogram (run 2) of the sample which was cooled down from the nematic phase at slow cooling rate (run 1).

the nematic phase at a slow cooling rate is shown in Figure 6. Two peaks appear on the thermogram, but these peaks are broader than those obtained by rapid cooling. This broad thermogram indicates that the slow cooling sample contains solid S_1 and solid S_2 as mixtures. As the quantity of solid S_1 or solid S_2 can not be obtained easily in the present investigation, the explanation of the melting process of the slow cooling sample is complicated. In the following section (Section 3.3) characteristics of solid S_1 and solid S_2 are given.

3.3 Characteristics of each solid

Figure 7 shows the melting thermograms of the samples which are cooled down to −32 °C and −69 °C. The low and the high temperature peaks on these curves correspond to the melting of solid S_1 and solid S_2,

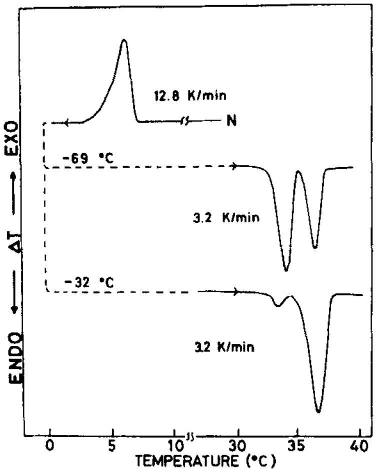

FIGURE 7 Melting thermograms of the samples which are cooled down to −32 °C and −69 °C.

respectively. As the melting process of the solid S is not simple, the quantity of solid S_1 or solid S_2 in the solid S can not be obtained precisely from these thermograms. However, the estimation of the quantities can be deduced from the area of those peaks. As shown in Figure 7 by the cooling to lower temperature (−69 °C) the area of the low temperature peak increases and that of high temperature peak decreases. This shows that the solid S sample contains solid S_1 and solid S_2 as mixtures, and that the ratio of S_1/S increases with cooling temperature.

Figure 8 shows the heat treatment effect of solid S on the melting process. Run 1 and run 2 are the melting thermograms (3.2 K/min) of solid S treated at (−32 °C, 30 min) and at (−32 °C, 0 min) respectively. The peak area of solid S_1 is comparable with that of solid S_2 in run 1. When the peak areas of run 1 are compared with those of run 2, the high temperature peak area decreases and low temperature peak area increases with increasing the time of heat treatment at low temperature (−32 °C). After the cooling of solid S to −32 °C, solid S is immediately reheated to 30 °C for 4 minutes and then the melting thermogram (3.2 K/min) is obtained (run 3). The low temperature peak of this thermo-

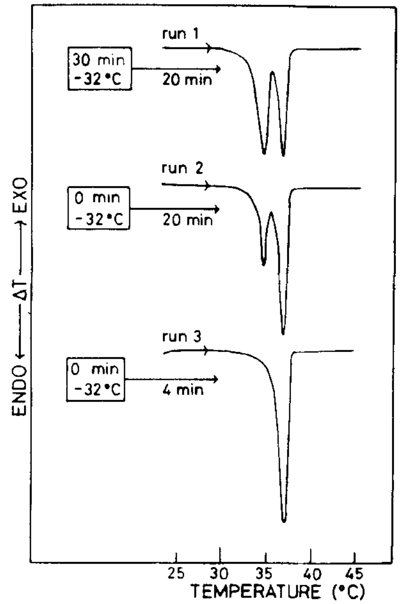

FIGURE 8 Heat treatment effect of solid S on the melting process. Run 1 and run 2 are the melting thermograms (3.2 K/min) of solid S treated at (−32 °C, 30 min) and at (−32 °C, 0 min) respectively. Run 3 is the melting thermogram (3.2 K/min) of the sample obtained by the rapid heating (16 K/min) from −32 °C to 30 °C.

gram completely disappears. These indicate that with increasing the treated time at a low temperature the quantity of solid S_1 in solid S increases. It is supposed that solid S_1 is stabilized by the heat treatment of solid S at low temperature.

Solid S was cooled down to -32 °C and then the thermograms of different heating rates were obtained (Figure 9). In spite of the same cooling and heat treatment condition of these samples, a different heating rate gives different thermogram. Heating of the sample at the slow heating rate is equivalent to the heat treatment of the sample for a long time at a low temperature. Therefore, the peak area of the low temperature peak increases with decreasing the heating rate. At the rapid heating rate thermograms of run 4 and run 5 result in a broad one, because the phase transition can not follow the temperature change completely. This also supports the above suggestion as to the stabilization of solid S_1.

From these thermal analysis characteristics of solid S can be explained as follows.

(1) Solid S is composed of mixtures of solid S_1 and solid S_2.

(2) Solid S_1 is stabilized by the heat treatment at low temperature.

(3) The quantity of solid S_1 in solid S increases with increasing the heat treatment time and/or with cooling to a low temperature.

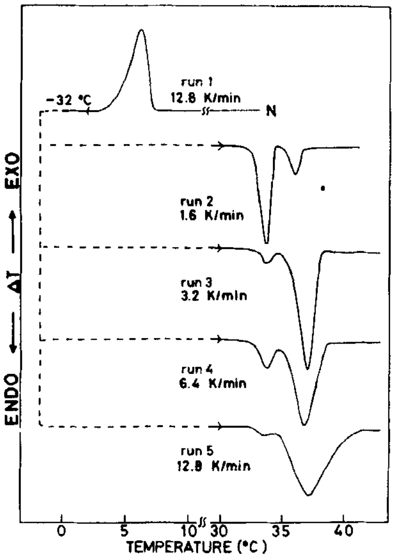

FIGURE 9 Heating rate effect on the melting process. Run 2–5 are the melting thermograms of solid S. Heating rates are indicated in the figure.

The microscopic differences of these solids are to be shown furthermore by means of polarizing microscopy, Raman scattering studies and X-ray analysis.

References

1. J. E. Lydon and J. O. Kessler, *J. Physique Colloq.*, **36**, C1–153 (1975).
2. J. Mayer, T. Waluga and J. A. Janik, *Phys. Lett.*, **41A**, 102 (1972).
3. S. E. B. Petrie, H. K. Bucher, R. T. Klingbiel and P. J. Rose, *Eastmen Organik Chemical Bulletin*, **45**, 1 (1973).
4. F. Cavatorta, M. P. Fontana and N. Kirov, *Mol. Cryst. Liq. Cryst.*, **34** (Letters), 241 (1977).
5. K. Z. Ogorodnik, *Sov. Phys. Solid State*, **17**, 1851 (1976).
6. K. Z. Ogorodnik, *Mol. Cryst. Liq. Cryst.*, **42**, 53 (1977).
7. M. Sorai, T. Nakamura and S. Seki, *Bull. Chem. Soc. Japan*, **47**, 2192 (1974).
8. W. Spratte and G. M. Schneider, *Ber. Bunsenges. Physik. Chem.*, **78**, 843 (1974).
9. R. Sandrock, M. Kamphausen and G. M. Schneider, *Mol. Cryst. Liq. Cryst.*, **45**, 257 (1978).
10. V. K. Agarwal, V. P. Arora and A. Mansingh, *Mol. Cryst. Liq. Cryst.*, **45**, 117 (1978).
11. M. Yasuniwa, C. Nakafuku and T. Takemura, *Polym. J.*, **4**, 526 (1973).
12. M. Yasuniwa and T. Takemura, *Polymer*, **15**, 661 (1974).
13. M. Yasuniwa, R. Enoshita and T. Takemura, *Jpn. J. Appl. Phys.*, **15**, 1421 (1976).