Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 04 Oct 2006.

To cite this article: Naotake Nakamura , Tatsuya Oida , Mami Shonago , Hidekazu Onoi & Tomonori Hanasaki (1995): Syntheses and Physical Properties of Ferrocene Derivatives(V) a Study on the Phase Transition of Liquid Crystals Containing Ferrocene by x-ray PSPC System, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 265:1, 1-8

To link to this article: http://dx.doi.org/10.1080/10587259508041672

Mol. Cryst. Liq. Cryst. 1995, Vol. 265, pp. 1–8
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SYNTHESES AND PHYSICAL PROPERTIES OF FERROCENE DERIVATIVES(V) A STUDY ON THE PHASE TRANSITION OF LIQUID CRYSTALS CONTAINING FERROCENE BY X-RAY PSPC SYSTEM

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Abstract The structure changes with the phase transition of liquid crystalline monosubstituted ferrocene derivatives, [4-[ω-(cholesteryloxycarbonyl)alkoxycarbonyl]phenyl]ferrocene, have been studied using a X-ray PSPC system. The results of the X-ray measurements agreed very closely with those of DSC measurements and polarizing microscopy texture observations. It was suggested that a layer structure existed in a crystal and a liquid crystal phases of the samples. The long spacing values were estimated from the PSPC data. The long spacing value of liquid crystal phase was not so much different from that obtained in our previous work. Consequently, the structure model of the liquid crystal phase previously presented can be applicable to this study. In addition to the liquid crystal structure model, the reasonable models of the crystals will be newly presented in this paper.

INTRODUCTION

Phase transition behavior of monosubstituted ferrocene derivatives containing cholesteryl group as a mesogenic one, [4-[ω-(cholesteryloxycarbonyl)alkoxycarbonyl]phenyl]ferrocene (abbreviated to CAPF-*n*, *n*=1-11, where *n* is a number of carbon atoms in the methylene chain as a flexible spacer), has been investigated in our laboratory[1,2]. Previously, we reported that seven kinds of them (CAPF-2, 4, 6, 8, 9,

10, and 11) exhibited the liquid crystallinity[1,2]. These liquid crystal phases were identified as a smectic one by polarizing microscopy texture observations. Moreover, the smectic structures were studied by X-ray diffraction counter method[3]. Consequently, the tilted double layer (n=2, 4, 6, 8, and 10) and the tilted quasi single layer (n=9, 10, and 11) structures were presented as the liquid crystal structure models[3]. But the study was performed using quenched samples of which structures were kept the liquid crystal ones even if the experiments were performed at room temperature.

In this study, continuous structure changes depending on temperature were investigated using a X-ray PSPC (position sensitive proportional counter) system for even series of the samples, CAPF-2, 4, 6, and 8,of which liquid crystal structure is tilted double layer. The experimental results will be described and the reasonable models of crystal and liquid crystal structures will be presented in this paper.

EXPERIMENTAL

All the samples studied here were synthesized in our laboratory. Details of the synthetic procedures were already described in the previous papers[1,2]. The sample synthesized gave only one spot on the TLC analyses and it was identified as the objective compound by ^{1}H-NMR (JEOL, JNM GX-270) spectra.

Thermal analyses and texture observations were made by a DSC (Perkin Elmer DSC-7) and a polarizing microscope (Nikon XTP-11) equipped with a heating stage (Mettler FP-800), respectively.

The sample for X-ray measurements was placed in a very thin-wall glass capillary. The temperature of the sample was precisely regulated by a gas blow system which was designed in our laboratory[4]. The scanning rate of the temperature for X-ray measurements was 5°C/min, which is the same as those in DSC measurements and texture observations. A small-angle X-ray diffractometer(Rigaku CN203E5) was used. In order to make a quick measurement, the PSPC system was applied as the detector in this experiment. Monochromated CoKα

radiation generated by Rigaku RU-200 was used in order to prevent the influence of the 2nd X-ray from iron atoms included the sample. An intensity of the incident beam was 40kV and 150mA.

RESULTS AND DISCUSSION

As was already reported in our previous paper[1], CAPF-2 showed simple phase transition behavior in the 1st heating and cooling processes. Under the polarizing microscope, only melting behavior of the as grown sample was observed at 146°C on the 1st heating. And on the 1st cooling, the molten sample changed into the liquid crystal phase at 75°C. A typical texture of liquid crystal was observed at lower than this temperature. After that, no texture change was observed by the polarizing microscope down to 0°C, although a baseline shift corresponded to a glass transition was detected on DSC curve at 46°C. On the 2nd heating, however, a little complicated phase transition

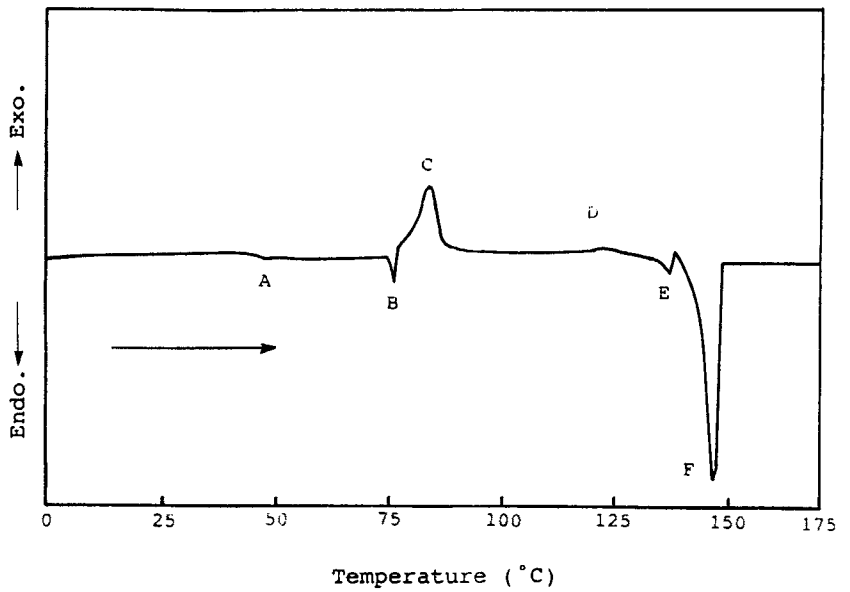

FIGURE 1 DSC curves of CAPF-2 on the 2nd heating.

phenomenon was observed. Figure 1 shows DSC curve of CAPF-2 on the 2nd heating. A baseline shift(A) observed at 46°C was identified as the grass transition owing to the shape of DSC curve. A small endothermic peak(B) and a relatively large exothermic peak(C) were observed at 74 and 80°C, respectively. And a very broad and small exothermic peak(D) was detected in the temperature range of about 100 to 130°C. After that, small and large endothermic peaks(E and F) were successively observed at 133 and 144°C. The results observed in the 2nd heating process were explained as follows with the results of polarizing microscopy texture observations. After the glass transition, the liquid crystal phase disappeared at the small endothermic peak(B), namely it was clearing point. Just after the clearing point, a crystal(a) appeared around the relatively large exothermic peak(C). This crystal grew gradually with increasing temperature. Furthermore, another crystal(b) appeared around the small exothermic peak(D) and grew gradually with increasing temperature. These crystals(a and b) were melted at individual their melting points (E and F), respectively. Figure 2 shows the phase transition temperatures of CAPF-2 on the 2nd heating determined by DSC measurements. As is shown in Figure 2, each phase above the glass transition temperature is called (I)-(VI) with increasing temperature.

Figure 3 illustrates PSPC data of CAPF-2 measured at various temperatures. As a reflection located at the lower-side accompanied with the 2nd order higher-angle side reflection in (I), (III), (IV), and (V) phases, a layer structure existed in these four phases. As can

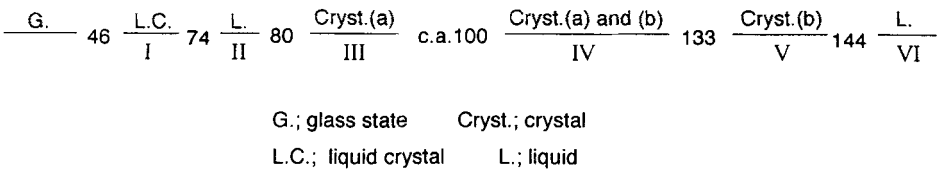

FIGURE 2 Phase transition temperatures of CAPF-2.

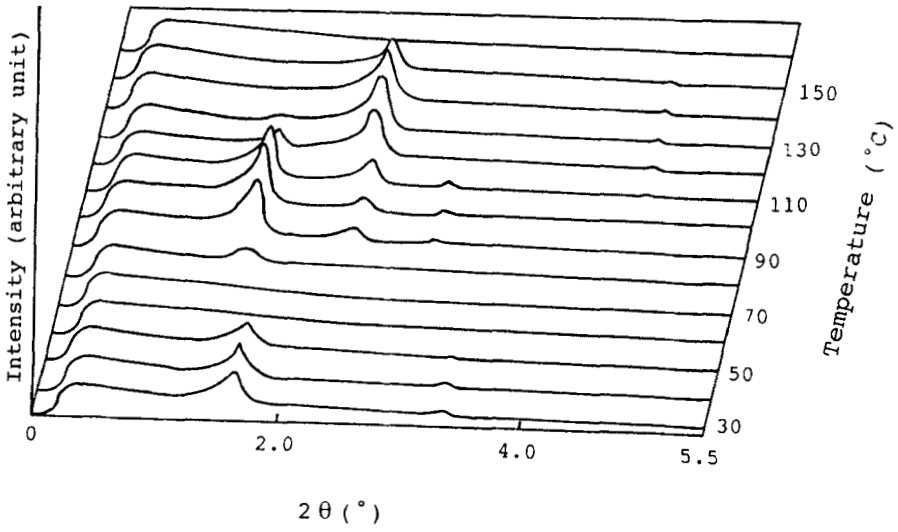

FIGURE 3 PSPC data of CAPF-2 on the 2nd heating.

be seen from Figure 3, a reflection corresponded to the long spacing of liquid crystal phase(I) is observed at about $2\theta=1.7$ from 30 to 50°C. This long spacing value was estimated to be 62 Å, which was not so much different compared with that obtained in our previous work(58.6 Å)[3]. A little difference between the two may be attributed by the sample preparation, that is, the quenched sample was used in the previous work, while the sample in this work was prepared by gradual cooling. Therefore, the same structure model presented in our previous paper is also applicable in this case. The intensity of the reflection was gradually decreased with increasing temperature. And at the clearing point, the reflection disappeared. From 60 to 70°C, there were no peak. This result is quite reasonable, because the sample was in liquid phase(II). At about 80°C, the reflection corresponded to the long spacing of a crystal(a) was detected and its long spacing value was 68 Å. The intensity of this peak increased with increasing temperature. This result shows that the crystal grow gradually with increasing temperature, and this result coincides with that of

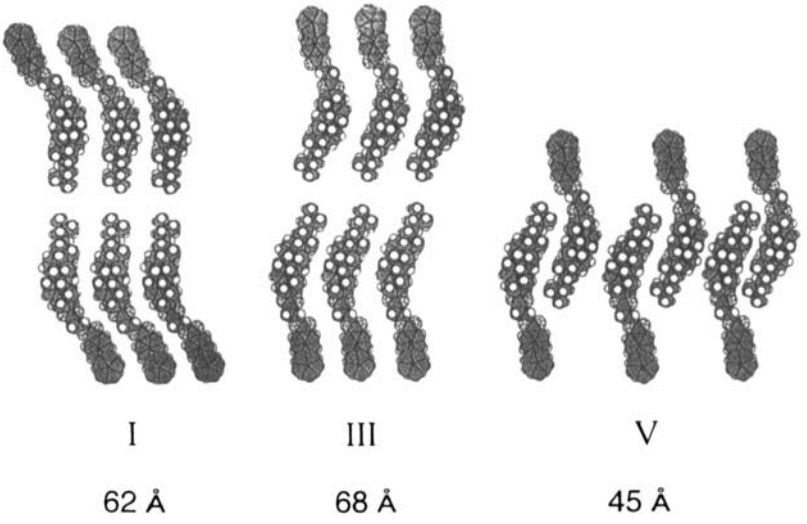

FIGURE 4 Model structures of phase(I), (III), and (V).

polarizing microscopy observations. Another new peak corresponded to the long spacing of a new crystal(b), of which long spacing value(68Å) was quite different from that of previously observed crystal(a), appeared at 100°C in spite of the existence of that of crystal(a). And the intensity of this peak increased little by little with increasing temperature. This peak vanished at 160°C. As the sample was in liquid phase in this temperature, this result is reasonable. Figure 4 shows reasonable structure models corresponded to the phase(I), (III), and (V) with the long spacing values of these phases. In the phase(IV), two kinds of the crystals, that is, crystal(a) and (b), coexisted. In Figure 4, the structure model of phase(I) is the tilted double layer structure previously reported in our paper[3], as already mentioned. In the crystal structure model of phase(III), the two molecules exist in the layer as a head to head fashion and exist vertically to the layer plane. And in the crystal of phase(V), it is considered that one of the molecules in the structure of phase(III) is slipped to the long axis direction and the cholesteryl group are overlapped with each other, as can be seen from

Figure 4. Similar structure models were already reported by T.Yamaguchi *et al.* in liquid crystal phases of side-chain polymers containing cholesteryl group as the mesogenic one[5]. Accordingly, it is considered that these models presented here are reasonable.

The phase transition behavior of CAPF-4 in the 1st heating and cooling process was the same as that of CAPF-2. On the 2nd heating, the glass transition was observed at 35°C, and the liquid crystal phase disappeared at 57°C. The long spacing value of the liquid crystal phase of CAPF-4 obtained from PSPC data(61Å) was nearly equal to that of our previous work(59.9Å)[3]. So, the structure model previously presented is also adapted to this structure in analogy with CAPF-2. After the clearing point, the sample crystallized at about 73°C and this crystal melted at 124°C. The long spacing value of this crystal phase estimated from PSPC results was 57 Å. Taking into account this value, it is considered that the structure model of this crystal may be almost the same as that of phase(V) of CAPF-2 shown in Figure 4. However, the overlapping moiety may be only the tail part of cholesteryl group, not the whole of the group.

In the case of CAPF-6 and 8, the phase transition behavior on the 1st heating and cooling of these samples was the same as those of CAPF-2. The long spacing values of liquid crystal phases of CAPF-6 and 8 were 65 and 68Å, respectively. These values are almost the same values obtained from corresponding samples in the previous work(64.4 and 69.8Å)[3]. Therefore, the model structure previously presented is also applicable to this case. There were no peaks above the clearing temperature on the PSPC data. This result is in good agreement with those of DSC measurements and polarizing microscopy observations.

In conclusion, continuous structure changes depending upon temperature of CAPF-2, 4, 6, and 8 were clearly observed by X-ray measurements using PSPC system. And these PSPC results were closely consistent with those of DSC measurements and polarizing microscopy observations. Moreover, as the long spacing values of liquid crystal phases of these samples obtained in this work were not so much different from those of our previous work.

This study was partially supported by Izumi Science and Technology Foundation.

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