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# Syntheses and Physical Properties of Ferrocene Derivatives (III) Liquid Crystallinity of Disubstituted Ferrocene Derivatives

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# Syntheses and Physical Properties of Ferrocene Derivatives(III) Liquid Crystallinity of Disubstituted Ferrocene Derivatives

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A new series of 1,1′-disubstituted ferrocene derivatives, 1,1′-bis[ω-[4-(4′-methoxyphenoxycarbonyl)phenoxy]-alkoxycarbonyl]ferrocene, incorporating a variable carbon number of methylene chain units has been prepared. The thermal behavior of these compounds has been examined by polarizing microscopy observations and differential scanning calorimetry measurements. Four of five kinds of samples synthesized here showed liquid crystallinity near the ambient temperature. Furthermore, these compounds have a fairly wide temperature range of liquid crystalline states.

*Keywords: Ferrocene, liquid crystal, 1,1′-disubstituted derivatives, transition metal complex, phase transition*

## INTRODUCTION

Many liquid crystalline compounds containing transition metals have been synthesized hitherto,[1] because it is expected that these compounds exhibit unique optical, electrical, and magnetic properties. For the same reason, the liquid crystallinity of ferrocene derivatives has been investigated by many workers in recent years.[2–15] Although monosubstituted[2,13–15] and 1,3-disubstituted[6,10] ferrocene derivatives which show liquid crystallinity have been synthesized, the majority of ferrocene containing liquid crystalline compounds were 1,1′-disubstituted derivatives.[3–9,11,12] These compounds are classified into two types from the viewpoint of the molecular structure, as follows.

a) The mesogenic group is directly introduced into the cyclopentadienyl ring of the ferrocene, and it has a flexible alkyl chain as a terminal group.

b) A methylene chain as a flexible spacer is located between the ferrocenyl and mesogenic groups.

Many reports have been published on the liquid crystalline 1,1′-disubstituted ferrocene derivatives of type a).[3–6,9,11,12] The temperature ranges of the liquid crystalline state of these compounds were far higher than the ambient temperature. On the other hand, there were few reports in which the liquid crystallinity of the type b) compounds was discussed.[7,8] These type b) compounds exhibited the liquid crystalline phase near the ambient temperature in comparison with that of type a). It may be

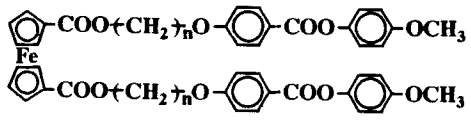


FIGURE 1 General structure of bMAF-$n$($n = 2, 3, 5, 10$ and 11). $n$: the number of carbon atoms in the methylene chain.

favorable for applied studies that the liquid crystalline temperature range is near the ambient temperature.

The objects of this study were syntheses of 1,1′-disubstituted ferrocene derivatives which show the liquid crystallinity in the ambient temperature and the elucidation of the thermal behavior of these compounds. The compounds designed here were 1,1′-bis[$\omega$-[4-(4′-methoxyphenoxycarbonyl)phenoxy]alkoxycarbonyl]ferrocene (abbreviated hereafter to bMAF-$n$, where $n$ is the number of carbon atoms in the methylene chain units. Figure 1 shows the general structure of bMAF-$n$. These compounds are of the type b), and the terminal group is a methoxy one whose molecular interaction is not very strong.

## EXPERIMENTAL

The objective compounds, bMAF-$n$ were synthesized according to the scheme shown in Figure 2. The synthetic procedures for bMAF-3: 1,1′-diacetylferrocene was prepared by a reaction of acetyl chloride with aluminum chloride and ferrocene.[16] 1,1′-Ferrocenedicarboxylic acid was derived from the 1,1′-diacetylferrocene by treatment with sodium hypochlorite. The 1,1′-ferrocenedicarboxylic acid was further converted into its

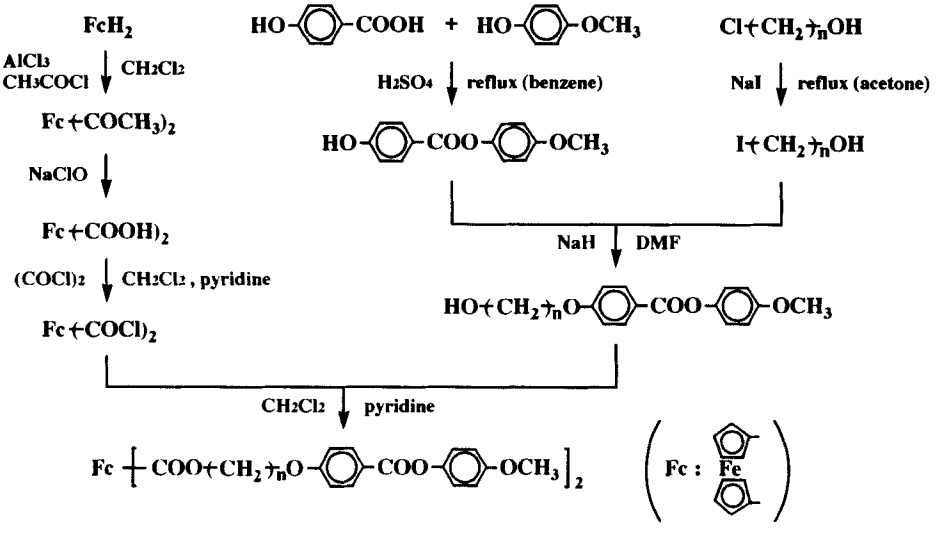


FIGURE 2 Scheme of synthetic process. $n$: the number of carbon atoms in the methylene chain.

acid chloride using oxalyl chloride in dichloromethane containing pyridine.[17] 4-Methoxyphenyl 4-hydroxybenzoate was prepared from 4-hydroxybenzoic acid and 4-methoxyphenol by esterification in benzene containing a catalytic amount of sulfuric acid.[18] A terminal chlorine atom of 3-chloropropanol converted into an iodine one before the next reaction. After the 4-methoxyphenyl 4-hydroxybenzoate was treated with sodium hydride, it was made to react with the 3-iodopropanol in DMF. The objective product, bMAF-3, was prepared by esterification from the products obtained from previous procedures. The product was purified by column chromatography and precipitated from dichloromethane by dilution with hexane. After drying, bMAF-3 was obtained as an orange powder. The product gave only one spot on the TLC analyses and it was confirmed to be the objective product using $^1$H-NMR(JEOL, JNM GX-270) spectra.

Other homologues, that is, bMAF-2, 5, 10 and 11 were synthesized by a manner similar to the above. So, five kinds of bMAF-*n* were prepared.

Thermal measurements were made by a differential scanning calorimeter (Perkin Elmer DSC-7, abbreviated hereafter to DSC), and the scanning rate was 5.0°C/min.

Texture observations were carried out using a polarizing microscope (Nikon XTP-11) equipped with a heating and cooling stage (Mettler FP-800). The scanning rate was 5.0°C/min, in analogy with DSC measurements.

## RESULTS AND DISCUSSION

Figure 3 shows the DSC curves of bMAF-3. On the 1st heating of as grown sample, two endothermic peaks (A and B) were observed at 103°C and 116°C, respectively.

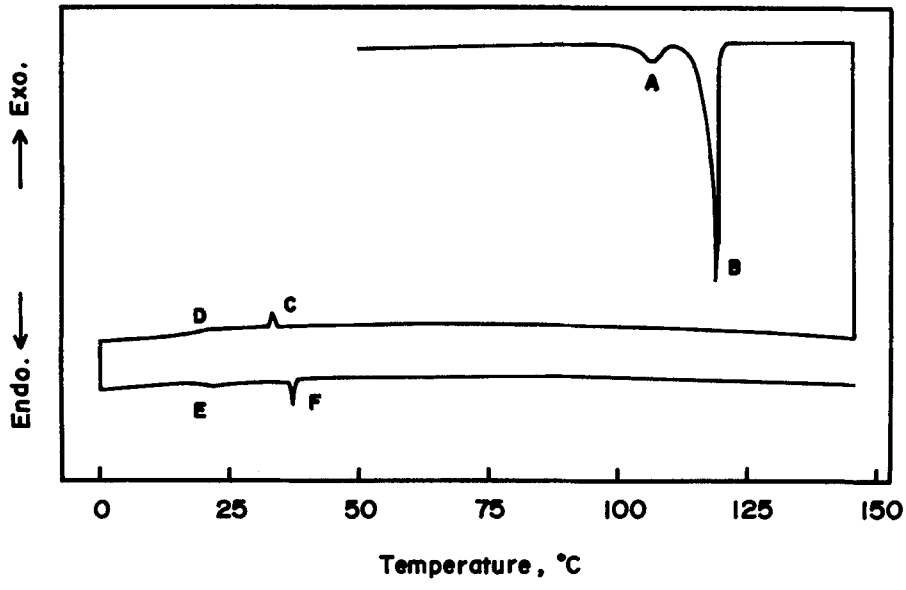



FIGURE 3 DSC curves of bMAF-3, Scanning rate: 5.0°C/min.

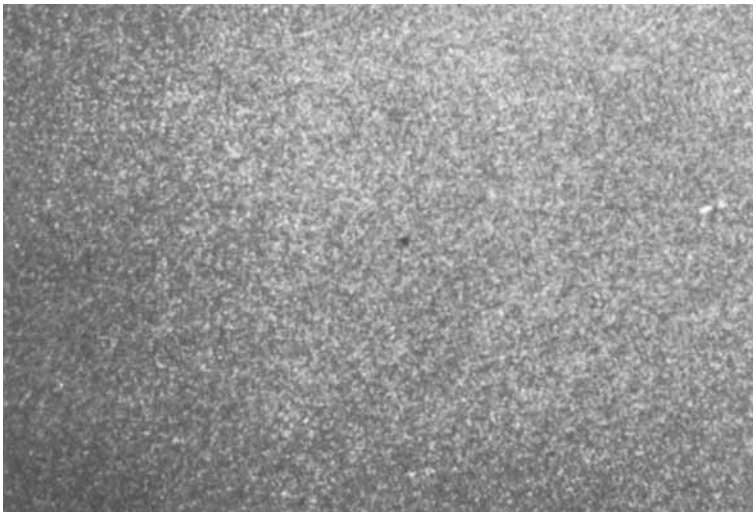


PHOTO 1 Texture of L.C.1 phase of bMAF-3 taken at 33°C. See Color Plate VI.

Although a texture change was not observed appreciably around the peak A temperature under a polarizing microscope, it may be considered that it corresponded to a solid–solid phase transition. The peak B temperature was confirmed to be the melting point of this sample by polarizing microscopy observations. During the heating up to 145°C from the melting temperature, no phase changes were observed. On the first cooling from an isotropic melt, the sample exhibited a small but sharp peak (C) and a baseline shift (D) at 34°C and 18°C, respectively. The peak C was identified as a clearing point, since a characteristic liquid crystalline texture was observed under the peak C temperature by the polarizing microscope. This liquid crystalline phase is denoted by L.C.1. Photo 1 shows the texture of the L.C.1 phase taken at 23°C. Although the texture change was not seen around the temperature of baseline shift D, this shift was determined to be a glass transition because of the typical shape of the DSC curve. On the second heating from 0°C, the glass transition (baseline shift E) and the clearing point (peak F) were observed at 19°C and 35°C, respectively. After the second heating, the running cycle gave the same results mentioned above within the experimental error.

The DSC curves of bMAF-10 are shown in Figure 4. Only the melting point was observed at 93°C (peak G) on the first heating. The small but sharp two exothermic peaks (H and I) were detected on the first cooling. Furthermore, in the temperature range of about 62°C to 30°C, a very broad exothermic peak (J) was found on the DSC curves. The results of texture observations were as follows. The appearance of the nuclei of a crystal was observed at 62°C. This crystal is denoted by K1. K1 grew gradually with decreasing temperature. However, the rate of the growth of the K1 crystal was very slow. The remaining portion, namely, the molten part, changed into the liquid crystalline phase at the peak H temperature (58°C). This liquid crystalline phase is denoted by L.C.1. So, K1 and L.C.1 coexisted in this state. Photo 2 shows the texture of

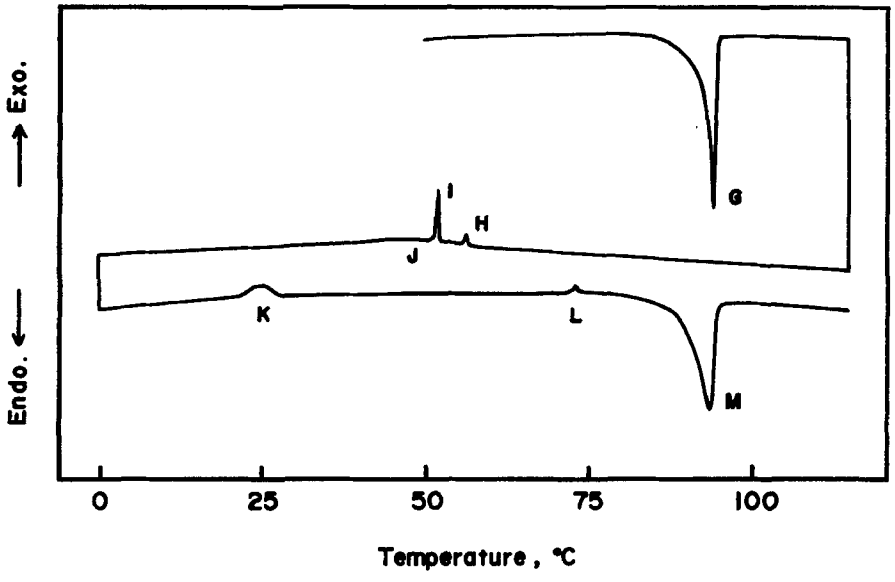



FIGURE 4 DSC curves of bMAF-10, Scanning rate: 5.0°C/min.

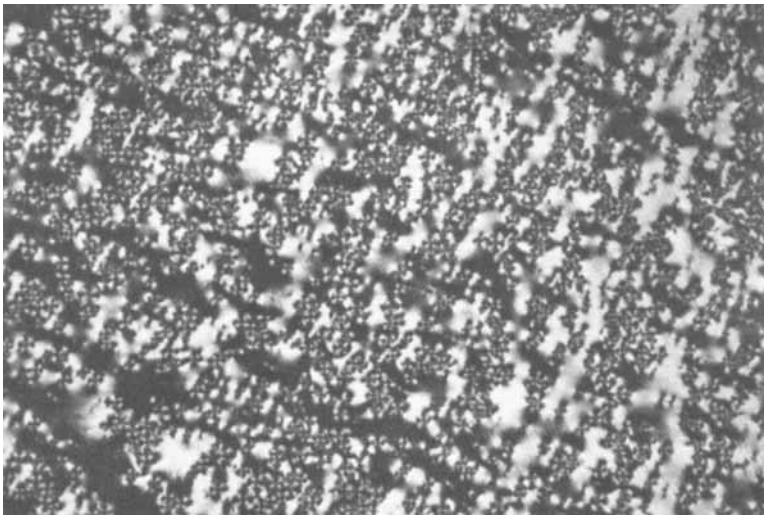


PHOTO 2 Texture of K1 and L.C.1 phases of bMAF-10 taken at 56°C. See Color Plate VII.

K1 and L.C.1 taken at 56°C. The phase transition from L.C.1 to the other liquid crystalline phase (L.C.2) was observed at 53°C. The growth of the K1 crystal was continued until about 30°C. Nevertheless, the L.C.2 phase was observed under 30°C. That is, K1 and L.C.2 coexisted below this temperature (30°C). On the second heating from 0°C, two exothermic peaks (K and L) and endothermic peak(M) were observed at 21°C, 72°C,

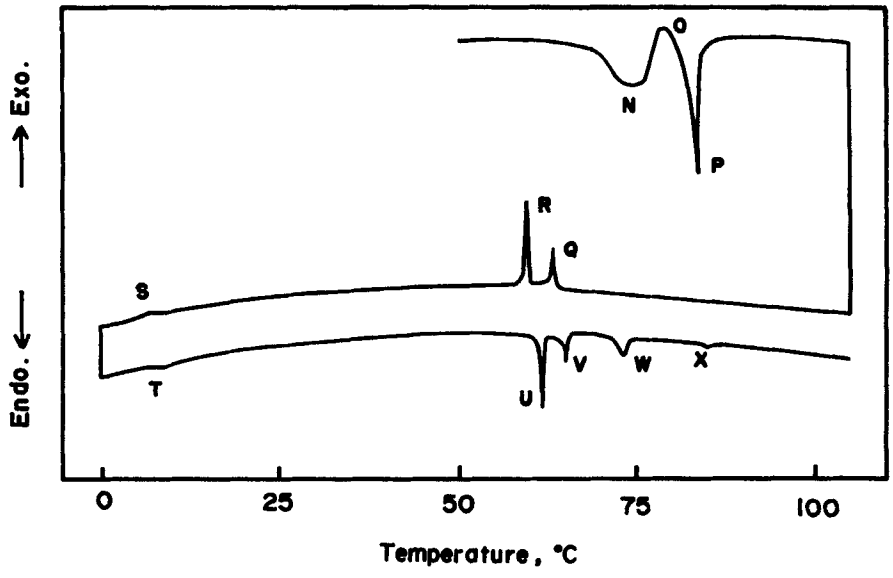



FIGURE 5 DSC curves of bMAF-11, Scanning rate: 5.0°C/min.

and 95°C, respectively. From the peak K temperature, K1 grew gradually with increasing temperature once again, and all of the portion eventually crystallized. It was considered that the phase transition from K1 to the other crystal one occurred at the peak L temperature, although the texture change was not observed appreciably by polarizing microscopy. This crystal phase is denoted by K2. The K2 crystal melted at 95°C. Because the melting temperature of K2 was the same as that of the as grown sample observed on the first heating, and also since the peak L was the exothermic peak, K2 is the stable crystal and K1 is the metastable one.

Figure 5 shows the DSC curves of bMAF-11. On the first heating, broad endothermic(N), small exothermic(O) and sharp endothermic (P) peaks were continuously observed in the range of about 70°C to 83°C. Under the polarizing microscope, a little change in the texture was observed at about peak O temperature. It was considered that the as grown sample once melted and immediately recrystallized. So, the as grown sample may be a metastable crystal and it transformed into a stable one after melting. The endothermic peak P was the melting point of bMAF-11. On the first cooling from 105°C, the molten sample changed into the liquid crystalline state at peak Q temperature, and a phase transition from this liquid crystalline phase to other one was observed at peak R temperature. The high temperature phase of the liquid crystalline state is denoted by L.C.1, and the low one is denoted by L.C.2. Photo 3 and 4 show the textures of L.C.1 and L.C.2, respectively. No texture change was observed around the temperature of baseline shift S by microscopy. Owing to the shape of the DSC curve, this shift was identified as the glass transition point. On the second heating from the glass state, the sample showed four endothermic peaks (U, V, W, and X) after the glass transition (baseline shift T). These peaks were explained as follows by the results of polarizing microscopy observations. Peak U and V corresponded to the phase transition from

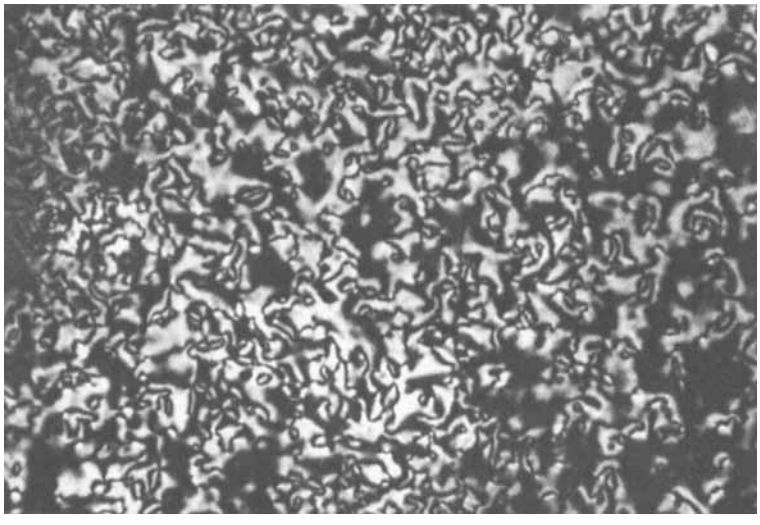


PHOTO 3 Texture of L.C.1 phase of bMAF-11 taken at 62°C. See Color Plate VIII.

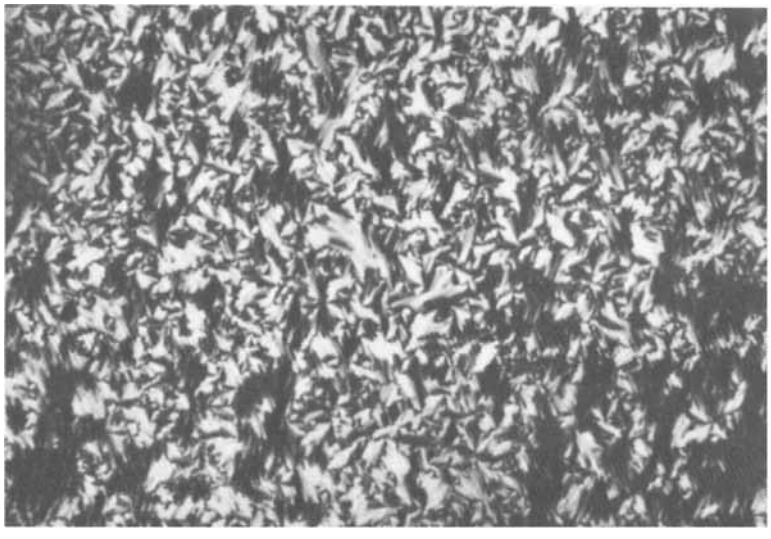
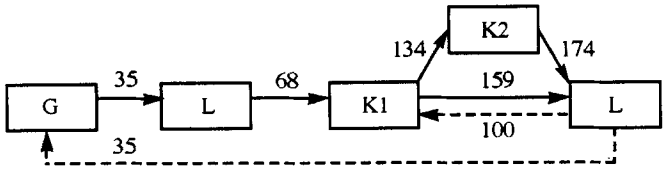
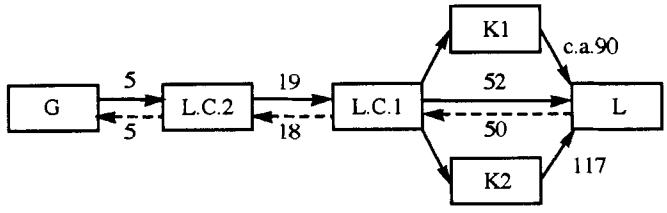
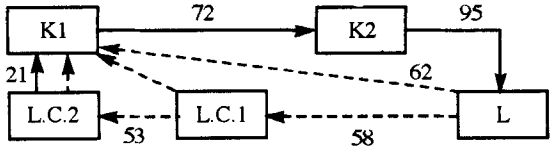
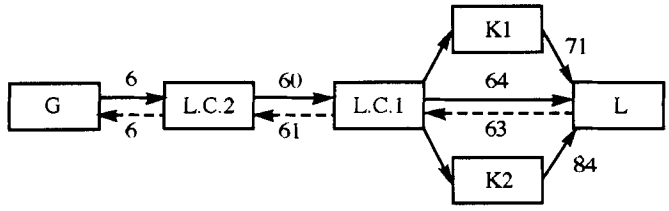


PHOTO 4 Texture of L.C.2 phase of bMAF-11 taken at 25°C. See Color Plate IX.

L.C.2 to L.C.1 and the clearing of L.C.1, respectively. Under the polarizing microscope after the clearing point, two individual crystals were observed in a very small portion of the sample. It could not be confirmed by polarizing microscopy observations when the sample crystallized. It seems that the crystallization occurred almost simultaneously with the clearing of the L.C.1 phase, since the baseline immediately after peak V shifted

TABLE I

| n | Phase Transition Temperatures |
|---|---|
| 2 |  |
| 3 |  |
| 5 |  |
| 10 |  |
| 11 |  |



n;the carbon atoms in the methylene chain

2nd heating process

1st cooling process

L.C.1;liquid crystal
L.C.2;liquid crystal
K1 ;metastable crystal
K2 ;stable crystal
G ;glass state
L ;liquid

to the exothermic side on the DSC curves. These two crystals grew gradually with increasing temperature. But the growth rate of these crystals was very slow. So, only a small portion crystallized up to the melting points. These crystals melted at 71°C (peak W) and 84°C (peak X) independently. The crystal which melted at 71°C is denoted by K1, and the another one which melted at 84°C is denoted by K2.

The thermal behavior of bMAF-*n* on the first cooling and second heating is summarized in Table I. The phase transition temperatures were determined by the DSC. However, the melting temperature of the K1 crystal of bMAF-5 was determined by microscopy observations. The temperatures of crystallization of bMAF-5 and 11 in the heating process were not noted in Table I because these temperatures could not be identified by DSC measurements or polarizing microscopy observations. In all samples, the running cycle after the second heating gave the same results obtained on the first cooling and the second heating, respectively. In Table I, the symbols (K1,

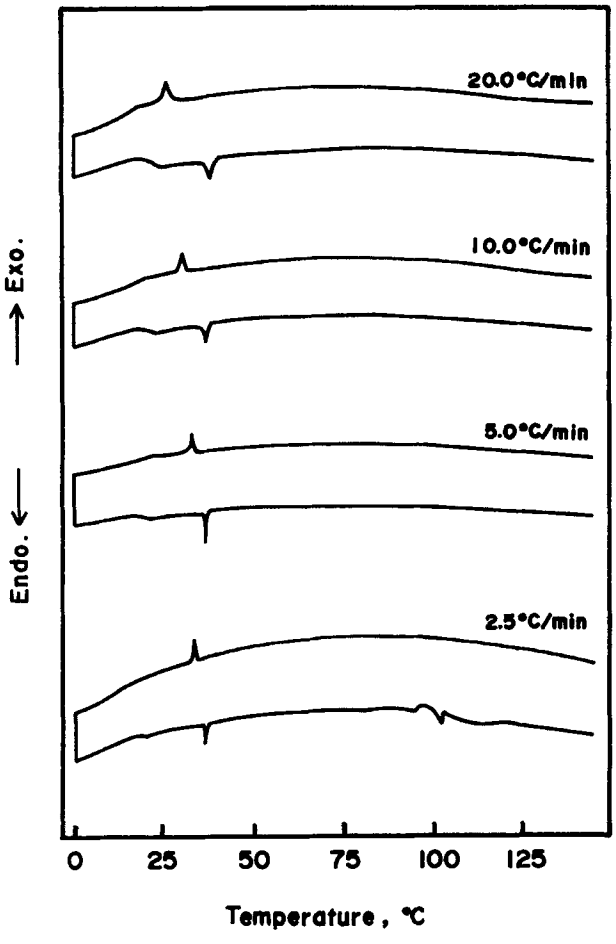



FIGURE 6 Dependence on the scanning rate of the thermal behavior of bMAF-3.

L.C.1, and so on) are defined independently for each sample. So, for example, it is not yet confirmed whether K1 of all bMAF-*n* has the same structure or not from a crystallographic point of view.

As can be seen from Table I, the thermal behavior of bMAF-5 was nearly equal to that of bMAF-11. In the case of bMAF-2, double melting behavior was observed in the heating process, but the sample did not show liquid crystallinity. It can be noted from Table I that liquid crystallinity was observed in four kinds of sample. These compounds exhibited a wide liquid crystalline temperature range near the ambient temperature, compared with that of the other 1,1′-disubstituted ferrocene derivatives already reported by other researchers.[3–9,11,12] The clearing points of these compounds increase with the increasing number of carbon atoms in the methylene chain units. Although the number of samples studied here is not large enough to discuss the even–odd effect with regard to the thermal behavior, it seems that the compounds of odd carbon number series are liable to exhibit liquid crystallinity.

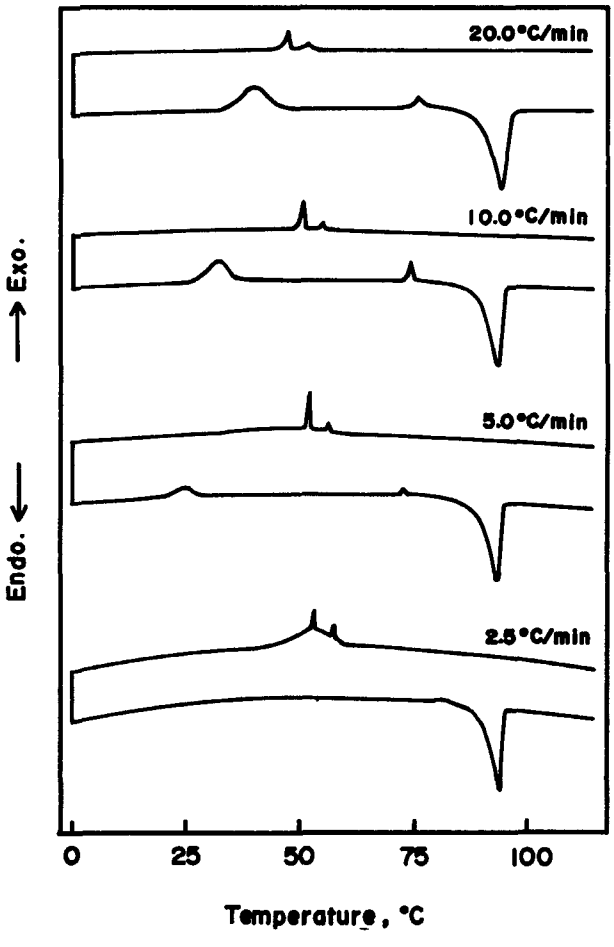



FIGURE 7 Dependence on the scanning rate of the thermal behavior of bMAF-10.

The dependence on the scanning rate of the thermal behavior of bMAF-3 and 10 was investigated by the DSC. Figures 6 and 7 show the DSC curves of the first cooling and second heating (scanning rate; 20.0, 10.0, 5.0 and 2.5°C/min) of bMAF-3 and 10, respectively. As shown in Figure 7, in the case of 20.0°C/min, the exothermic peak, which is based upon the crystallization corresponding to peak J in Figure 4, was not observed in the cooling process. So, all portion of the molten sample changed into the liquid crystalline state. In the case of 2.5°C/min, all portions of the sample, although the molten sample changed into the liquid crystalline state in part, eventually crystallized in the cooling process. Therefore, it was appreciated that the liquid crystalline phase of this sample was unstable and dependent on the scanning rate. On the other hand, it is understandable from Figure 6 that the crystallization from the liquid crystalline state did not happened in the cooling or heating process, although several peaks corresponding to the crystallization and melting of a part of the sample were observed in the range of about 75°C to 125°C in the heating process. That is, the liquid crystalline phase of this sample was stable in these scanning rates.

Taking into account the thermal behavior of the previous compounds reported by the other researchers,[7,8] compared with the type a) compounds, the type b) one seems to show the tendency that the molten sample changes into the liquid crystalline phase at a far lower temperature than its melting point in the cooling process and this liquid crystalline phase is not necessarily the stable one. Although this reason has not been clarified, it may be ascribed as follows. It is considered that the orientation of the mesogenic groups of the type b) compound is apt to be influenced by a thermal motion and a little conformation change of the methylene chain in comparison with that of type a). Therefore, it may be that the type b) compounds show the tendency mentioned above.

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