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: 24 Sep 2006.

To cite this article: Tomonori Hanasaki , Mitsunori Ueda & Naotake Nakamura (1993): Syntheses and Physical Properties of Ferrocene Derivatives (II) Liquid Crystallinity and Multiple Melting Behavior of Ferrocene Derivatives, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 237:1, 329-336

To link to this article: http://dx.doi.org/10.1080/10587259308030147

Mol. Cryst. Liq. Cryst., 1993, Vol. 237, pp. 329–336
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Printed in the United States of America

Syntheses and Physical Properties of Ferrocene Derivatives (II) Liquid Crystallinity and Multiple Melting Behavior of Ferrocene Derivatives

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(Received November 17, 1992; in final form February 2, 1993)

Nine kinds of monosubstituted ferrocene derivatives, ω-[4-(4-methoxyphenoxycarbonyl)phenoxycarbonyl]alkyl 4-ferrocenylbenzoate, were prepared. The derivatives containing 4, 6, 10 and 11 carbon atoms in the flexible alkyl chain of the compounds showed liquid crystallinity, and multiple melting behavior was observed in the compounds containing 4, 6 and 11 carbom atoms. An appearance of the liquid crystallinity showed a carbon number dependence on the flexible alkyl chain.

Keywords: ferrocene, liquid crystal, multiple melting behavior, phase transition, transition metal complex

INTRODUCTION

Liquid crystal compounds containing transition metals have come to be of great interest in recent years. It is expected that these compounds exhibit unique optical, electrical and magnetic properties. Furthermore, these properties have the possibility of finding application in imaging devices. Many organic transition metal complexes substituted with long alkyl chains have been synthesized, and their liquid crystallinity has been discussed.[1] Moreover, it was reported that several of these complexes showed multiple melting behavior.[2]

However, there were a few reports in which the liquid crystallinity of the ferrocene derivative was discussed.[3,4,5] Quite recently, it was reported that an appearance of liquid crystallinity was found in monosubstituted compounds which had the methylene flexible spacer between the ferrocenyl group and the mesogenic cholesteryl one.[6] It is rarely found that ferrocene derivatives exhibit multiple melting behavior.[6,7]

In this study, nine kinds of monosubstituted ferrocene derivatives were synthesized. The compounds designed here were ω-[4-(4-methoxyphenoxycarbonyl)phenoxycarbonyl]alkyl 4-ferrocenylbenzoate (abbreviated hereafter to MPAF-*n*, where

n is the number of carbon atoms in the flexible alkyl chain). Thermal analyses and texture observations of MPAF-*n* were made in a wide temperature range. The liquid crystallinity and multiple melting behavior of MPAF-*n* are described in this report.

EXPERIMENTAL

The objective compounds, MPAF-*n* (n = 1–7, 10 and 11) were synthesized by the routes illustrated in Figure 1. The synthetic procedure for MPAF-10: 4-Methoxyphenyl 4-hydroxybenzoate was prepared from 4-hydroxybenzoic acid and 4-methoxyphenol by esterification in benzene containing a catalytic amount of sulfuric acid.[8] After 11-bromoundecanoic acid was converted into its acid chloride using thionyl chloride, the 4-methoxyphenyl 4-hydroxybenzoate was treated with the acid chloride in ether containing pyridine. The terminal bromine atom of the resulting product was converted into an iodine one. Methyl 4-ferrocenylbenzoate was prepared from methyl 4-aminobenzoate by diazotization and coupling. The methyl 4-ferrocenylbenzoate was hydrolyzed by potassium hydroxide. This hydrolyzate was treated with potassium hydroxide and silver nitrate. MPAF-10 was prepared by esterification from the resulting products obtained from previous procedures. MPAF-10 was precipitated from a benzene solution by dilution with methanol after purification by column chromatography. After drying, MPAF-10 was obtained as an orange powder.

MPAF-*n* gave only one sport on the TLC analyses and it was confirmed to be the objective compound using ^{1}H-NMR (JEOL, JNM GX-270) spectra. The thermal analyses were made by a differential scanning calorimeter (Perkin Elmer, DSC-7, abbreviated hereafter to DSC). The scanning rate was 5°C/min. Texture obser-

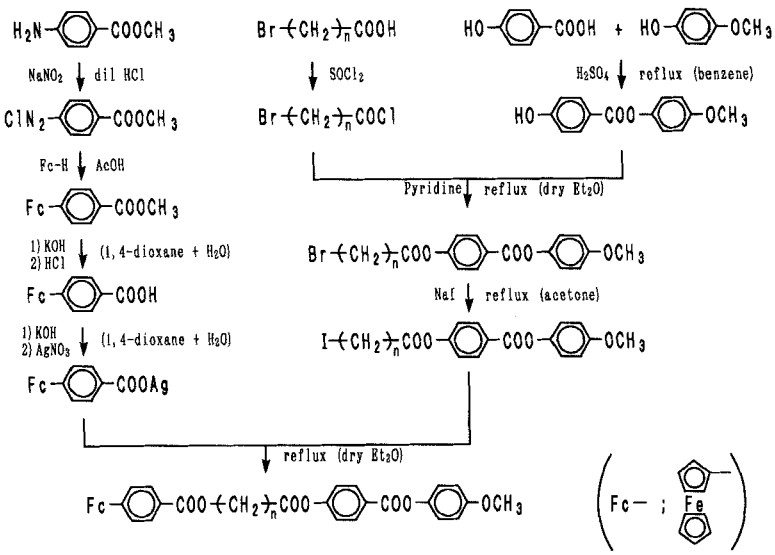

FIGURE 1 Scheme of synthetic process. *n*: the number of carbon atoms in the alkyl chain.

vations were carried out using a polarizing microscope (Nikon XTP-11) equipped with a heating stage (Mettler FP-800).

RESULTS AND DISCUSSION

The DSC curves of MPAF-6 are shown in Figure 2. On the first heating of as grown sample, small endothermic (A) and exothermic (B) peaks were continuously observed at 117°C and 120°C, respectively. Although texture change was not observed appreciably around these temperatures under the polarizing microscope, it was considered that the sample once melted and immediately recrystallized. So, it is assumed that the as grown sample is a metastable crystal and it transforms to a stable one accompanied by the melting. This crystal showed an endothermic peak (C) at 123°C. This temperature was confirmed to be the melting point by polarizing microscopy observations. During the heating up to 140°C from the melting temperature, no peak and texture change were observed. On the first cooling from 140°C, the sample showed two small exothermic peaks (D and E) and a little shift of the base line to the endothermic side just below peak E temperature. Peak D is a clearing point, because the texture observed below this transition temperature was the characteristic liquid crystalline one. This phase is denoted by L.C.1. Photo 1 shows the texture of L.C.1 taken at 47°C. No texture changes were observed around peak E. It may be understood that a phase transition from L.C.1 to other liquid crystalline phase (denoted by L.C.2) occurred at peak E and a glass transition happened just after the phase transition. On the second heating from 0°C, the broad peak F and the endothermic peak G were observed at 21°C and 24°C, respectively. Peak F was identified as the glass transition point owing to the typical shape of the DSC curve. Peak G may be the transition point from L.C.2 to L.C.1. Two broad exothermic peaks (H and I) and three endothermic peaks (J, K, and L) were observed after peak G. These peaks are explained as follows. Peak

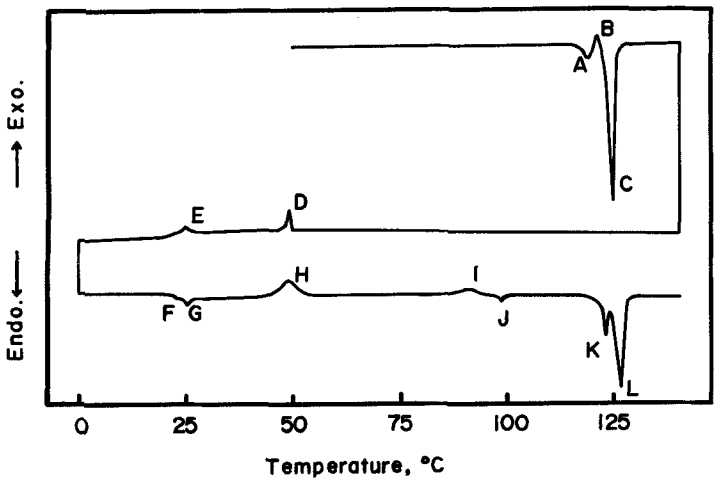

FIGURE 2 DSC curves of MPAF-6. Scanning rate: 5.0°C/min.

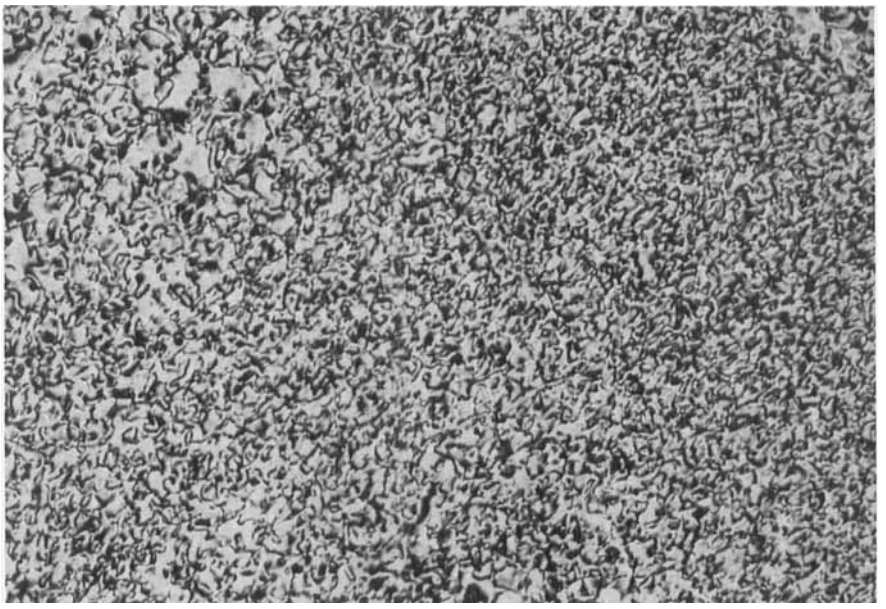

PHOTO 1 Texture of L.C.1 phase of MPAF-6 taken at 47°C. See Color Plate XV.

H corresponds to a crystallization from L.C.1, because an appearance of nuclei of a new crystal was distinctly observed under the polarizing microscope. This crystal is denoted by K1. K1 grew gradually with increasing temperature. Such phenomenon, that is, crystallization from the liquid crystalline phase in the heating process, has been observed on the DSC measurements.[9] Photo 2 shows the texture of K1 taken at 48°C. K1 transformed into two individual crystals at peak I temperature. The textures of these crystals were distinct from that of K1. This transformation was very slow. Before the transformation was completely finished, K1 melted at peak J. Photo 3 shows the texture of the crystals taken at 110°C. In Photo 3, the left side crystal is denoted by K2, and the one on the opposite side is denoted by K2′. K2′ and K2 melted at peaks K and L, continuously. The temperatures of peak K and L were nearly equal to that of the melting point observed on the first heating. Taking into account these results, it is considered that the K1, grown at peak H, is a metastable crystal, and this crystal transforms to the two other crystals (K2′ and K2) at peak I. It may be considered that K2′ and K2 do not so much differ from one another in thermal stability, because the melting points of the K2′ and K2 were nearly the same temperature. In the result, the melting behavior was observed three times on the second heating. After the second heating, the continuous cooling and heating cycles gave the same results obtained on the first cooling and the second heating, respectively.

The result of MPAF-10 on the first heating was nearly equal to that of MPAF-6. That is, the as grown sample of MPAF-10 was a metastable crystal. In the case of MPAF-*n*, except for MPAF-6 and 10, the as grown samples were stable crystals, because no peak and texture change were observed on the first heating up to the melting temperature.

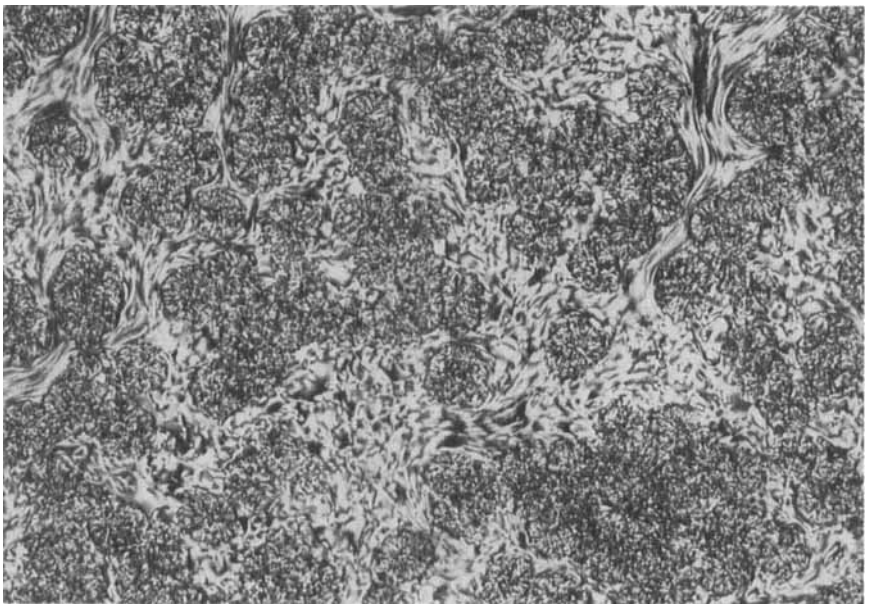

PHOTO 2 Texture of K1 crystal of MPAF-6 taken at 48°C. The remaining L.C.1 phase is observed around K1. See Color Plate XVI.

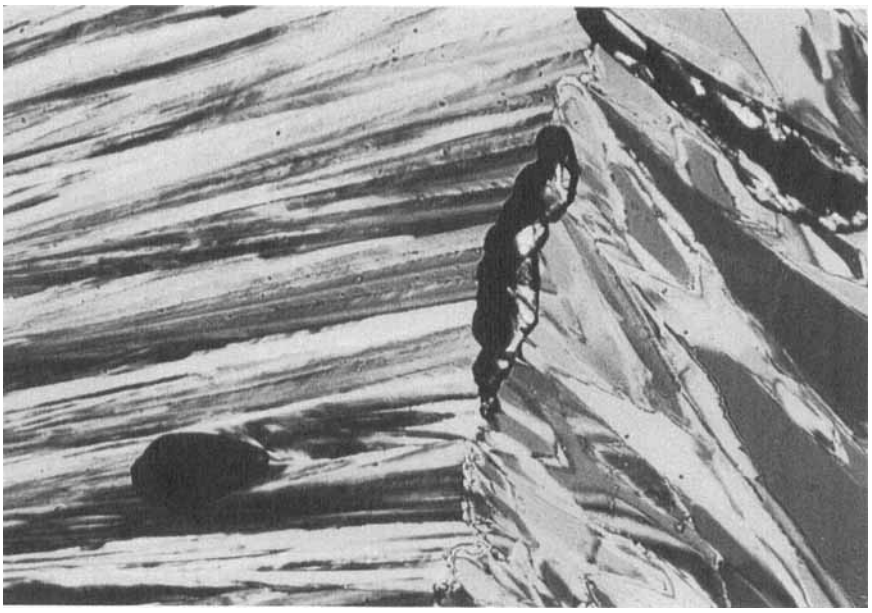

PHOTO 3 Textures of K2 (left side) and K2′ (right side) crystals of MPAF-6 taken at 110°C. See Color Plate XVII.

Just above the melting point, the textures of all MPAF-*n* were not perfectly black under the polarizing microscope. This fact suggests that a little ordered state may remain after the melting, because MPAF-*n* was very viscous and slimy whereas the sample was in the molten state. And this result was quite similar to that of the ferrocene derivatives containing cholesteryl group as a mesogenic one.[6]

The phase transition behavior of MPAF-*n* on the first cooling and second heating is summarized in Table I. In Table I, crystal phases are roughly classified into two categories. One is a stable crystal phase (K2) which does not show any phase transition up to the melting temperature in the heating process. The other is met-

TABLE I

Phase transition temperatures of MPAF-*n*

n	Phase Transition Temperatures (°C)
1	G 43 L / 42
2	G 27 L 72 K2 151 L in part → decomposed / 25
3	G 28 L / 27
4	G 28 L.C.2 33 L.C.1 40 L 47 K1 64 K1' 116 K2 138 L / 26 / 34 / 126 L 127 / 40
5	G 18 L / 17
6	G 21 L.C.2 24 L.C.1 45 K1 86 K2 124 L / 20 / 27 / 86 / 97 L K2' 121 / 50
7	G 11 L 70 K2 105 L / 10
10	G 17 L.C.2 19 L.C.1 27 K1 79 K2 106 L / 14 / 19 / 45
11	G 22 L.C.1' 25 L 30 K2 87 L / 19 / 23 L.C.1 / K2' 87 / 24 / 28

→ heating process
⇢ cooling process

G : glass state
L : liquid
L.C.1 : liquid crystal
L.C.2 : liquid crystal
L.C.1' : liquid crystal

K1 : metastable crystal
K1' : metastable crystal
K2' : metastable crystal
K2 : stable crystal

astable crystal phase (K1) which transforms to another more stable crystal at higher temperature range and the texture of K1 is different from that of K2 under the polarizing microscope. In the case that liquid crystal-liquid crystal phase transition was observed, higher temperature liquid crystalline phase is denoted by L.C.1, and lower one is denoted by L.C.2. These symbols (K1, K2, and so on) in Table I are defined independently on each MPAF-*n*. Therefore, for example, it is not yet confirmed whether K2 of all MAPF-*n* is the same structure or not in crystallographic point of view.

In the case of MPAF-1, only glass transition was observed by DSC measurements in the heating and cooling processes. No texture change was observed by the polarizing microscope during these processes.

The thermal behavior of MPAF-3 and 5 was nearly the same as that of MPAF-1, as only the glass transition happened in the heating and cooling processes.

The results of DSC measurements and texture observations of MPAF-2 and 7 were nearly equal to one another. Namely, the results obtained in the cooling process were quite similar to those of MPAF-1. In the heating process, after the glass transition, the sample crystallized from the molten state and this crystal (K2) melted. Only the sample of MPAF-2 partially decomposed after the melting.

In the case of MPAF-4, the liquid crystalline phase (L.C.1) appeared at 40°C from the molten state in the cooling process. After the phase transition from L.C.1 to the other liquid crystalline phase (L.C.2) happened, the glass transition was observed. In the heating process, the glass transition point, the phase transition point from the L.C.2 to L.C.1, and the clearing point were observed. At 47°C, K1 was crystallized from the molten state. Such phenomenon was observed on the DSC measurements of the ferrocene derivatives containing cholesteryl group.[6] This crystal is metastable, because more stable crystal was observed at higher temperature range. K1 transformed to the other metastable crystal at 64°C. The exothermic peak corresponding to this transformation was very small on the DSC measurement. Moreover, a little change of the texture was observed by polarizing microscopy observations at 64°C. This metastable crystal may be not so much different from that of previous metastable one. So, this crystal is denoted by K1′. K1′ transformed into a stable crystal (K2) at 116°C. The melting behavior of K1′ was not seen by polarizing microscopy observations. From the results of the precise DSC measurements, however, it may be explained that K1′ melted before the transformation from K1′ to K2 was completely finished. K2 melted at 138°C. This sample showed double melting behavior.

The thermal behavior of MPAF-10 was nearly equal to that of MPAF-6. But in this case, K2′ crystal and the melting behavior of K1 crystal were not observed.

In the case of MPAF-11, a small portion of the molten sample crystallized to K2′ crystal, and this crystal did not change any more through the cooling process. The remaining portion transformed into the liquid crystalline state (L.C.1) in the cooling process. After the clearing point, small exothermic and glass transition peaks were observed on the DSC measurements. It may be considered that the small exothermic peak corresponds to the rearrangements in L.C.1, because only clearing point was detected in the continuous heating process by DSC measurements and no texture changes were observed around the exothermic peak under the

polarizing microscope. The low temperature phase of the liquid crystalline state is denoted by L.C.1′. In the heating process, although the glass transition and the clearing point were continuously observed, K2′ remained. Above the clearing point, the other crystal (K2) appeared. However, the texture of K2 was different from that of K2′, which crystallized in the cooling process. Thus, two distinct crystals (K2 and K2′) coexisted just below the melting point. It was observed that K2 melted immediately after the melting of K2′ by polarizing microscopy observations. So, it may be considered that the K2 and K2′ do not so much differ from one another in thermal stability. MPAF-11 showed double melting behavior.

As can be seen from Table I, four kinds of samples showed liquid crystallinity. Three of them have even-carbon atoms in the flexible spacer (n = 4, 6 and 10). MPAF-11 has the longest alkyl chain (n = 11) in the odd-carbon number series studied here. These results are explained by a conformation of the flexible alkyl chain between the ferrocenyl and mesogenic groups, as was already reported in our previous paper.[6] The previous compound has the cholesteryl group as a mesogenic one. That is, although the characteristics (polarizability, geometry, etc.) of the mesogenic group of MPAF-n are different from those of the previous compounds, the flexible alkyl chain carbon number dependence on the appearance of liquid crystallinity was nearly equal to the previous results. Therefore, it is clear that the liquid crystallinity of these monosubstituted ferrocene derivatives is more influenced by the molecular shape of the compounds than by the characteristics of the mesogenic group.

Three kinds of the samples (MPAF-4, 6 and 11) exhibited multiple melting behavior, as can be seen in Table I. Taking into account the melting behavior of these compounds observed in this study, it seems that this behavior is classified into two types, as follows.

(i) The metastable crystal transforms to a stable one. However, before the finish of the transformation, the metastable crystal melts itself, and the stable one grows from the molten state.

(ii) Two crystals coexist up to the melting point and these crystals show their own melting point.

The double melting behavior of MPAF-4 is classified as type (i). MPAF-11 shows the behavior of type (ii). MPAF-6 exhibits both types (i) and (ii).

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