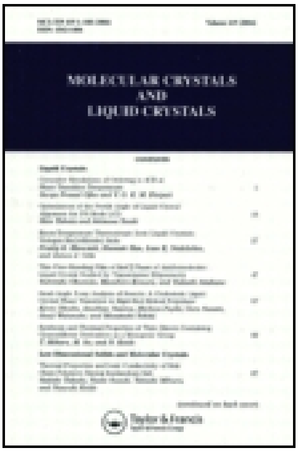

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Syntheses and Physical Properties of Ferrocene Derivatives (I) Liquid Crystallinity of Ferrocene Derivatives Containing Cholesteryl Group

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Syntheses and Physical Properties of Ferrocene Derivatives (I) Liquid Crystallinity of Ferrocene Derivatives Containing Cholesteryl Group

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Nine kinds of ferrocene derivatives, [4-[ω-(cholesteryloxy carbonyl)alkoxy carbonyl]phenyl] ferrocene, were synthesized. Polarizing microscopy observations and differential scanning calorimetry measurements of these compounds were made in a wide temperature range. The liquid crystallinity was observed in the derivatives containing 2, 4, 6, 10, and 11 carbon atoms in the flexible alkyl chain of the compounds. An appearance of the liquid crystallinity was discussed with a conformation of the flexible alkyl chain which exerted a great influence on the molecular shape.

Keywords: ferrocene, liquid crystal, phase transition, transition metal complex, cholesteryl derivative

INTRODUCTION

Ferrocene is one of the typical sandwich compounds, that is constructed with two cyclopentadienyl rings and one iron atom. Ferrocene is a chemically stable compound and exhibits an aromaticity. As one of the characteristic reactions of ferrocene is substitution reaction, many ferrocene derivatives have been synthesized hitherto. These compounds have very interesting optical, magnetic and electrical properties and most of them are colored red or orange. Therefore, if liquid crystalline ferrocene derivatives are synthesized, it is expected that the compounds have great function.

The first example of a liquid crystal containing ferrocene was reported by J. Malthete and J. Billard.[1] Two kinds of ferrocene derivatives, [*N*-4(4′-alkoxybenzoyloxy)-benzylidene] *p*-aminophenyl ferrocenecarboxylates, where the alkoxy groups were octyloxy and decyloxy, exhibited liquid crystallinity and their mesophases were identified as stable nematic phases by texture observations under a polarizing microscope. Besides, J. Bhatt *et al.*[2] found out monotropic liquid crystalline phase transition in three kinds of ferrocene compounds. These compounds were diesters of 1,1'-ferrocene diacid and exhibited smectic A or C phases. In order to probe the influence of the ferrocenyl group on an appearance of liquid crystallinity, two benzoate derivatives and one ferrocenyl compound were examined. The benzoates exhibited liquid crystallinity and the ferrocenyl compound did not, and it was described that the ferrocenyl group attenuated the liquid crystal forming tendency of the mesogenic group. As liquid crystalline molecules are generally rod-like and ferrocene is considerably voluminous, the above consideration may be reasonable. Recently, it was reported that 1,1'-disubstituted ferrocene derivatives[3,4] and co-polyesters of 1,1'-*bis*-(chlorocarbonyl) ferrocene[5,6] showed liquid crystallinity. Both of them are the disubstituted type. Although the molecules contain the voluminous ferrocenyl group, their molecular shapes can be regarded as rod-like. So, it may be possible for liquid crystallinity to appear.

In this study, new type liquid crystalline ferrocene compounds containing cholesteryl groups as the mesogene were designed. These molecules are monosubstituted ferrocene derivatives. And the methylene flexible spacer is located between the ferrocenyl and cholesteryl groups in order to ease a bulk effect of the ferrocenyl group. The compounds designed here was [4-[ω(cholesteryloxy carbonyl)alkoxy-carbonyl]phenyl] ferrocene, (abbreviated hereafter to CAPF-*n*). Where *n* is a number of carbon atoms in the flexible alkyl chain.

EXPERIMENTAL

The typical synthetic scheme is shown in Figure 1. First, *p*-ferrocenyl benzoic acid was prepared from methyl-*p*-aminobenzoate by diazotization, coupling, and hydrolysis, and it was converted to its silver salt. Second, an ω-bromoalkanoic acid ($n = 1 - 7$, 10, and 11) and cholesterol was treated with a catalytic amount of *p*-toluenesulfonic acid. In the case of CAPF-10, the 11-bromoundecanoic acid was converted to its acid chloride using thionyl chloride before an esterification with cholesterol, because 11-bromoundecanoic acid didn't react with cholesterol directly. The terminal bromine atom was converted to an iodine before the final reaction. Objective compound, CAPF-*n* was purified by column chromatography and it gave only one spot on TLC analysis. It was identified to be the objective compound using ^{1}H-NMR (JEOL, JNM GX-270). Phase transition points were measured by differential scanning calorimeter (Perkin Elmer, DSC-7, abbreviated hereafter to DSC), and the scanning rate was 5°C/min. Texture observations were made using a polarizing microscope (Nikon XTP-11) equipped with a heating stage (Mettler, FP-800).

RESULTS AND DISCUSSION

Figure 2 shows the DSC curves of CAPF-3 as an example. On the 1st heating, as grown sample exhibited endothermic (A) and exothermic (B) peaks at 122 and 127°C, respectively. So, the sample once melted and immediately recrystallized. It is considered that the as grown crystal is metastable crystal (K1) and it transforms

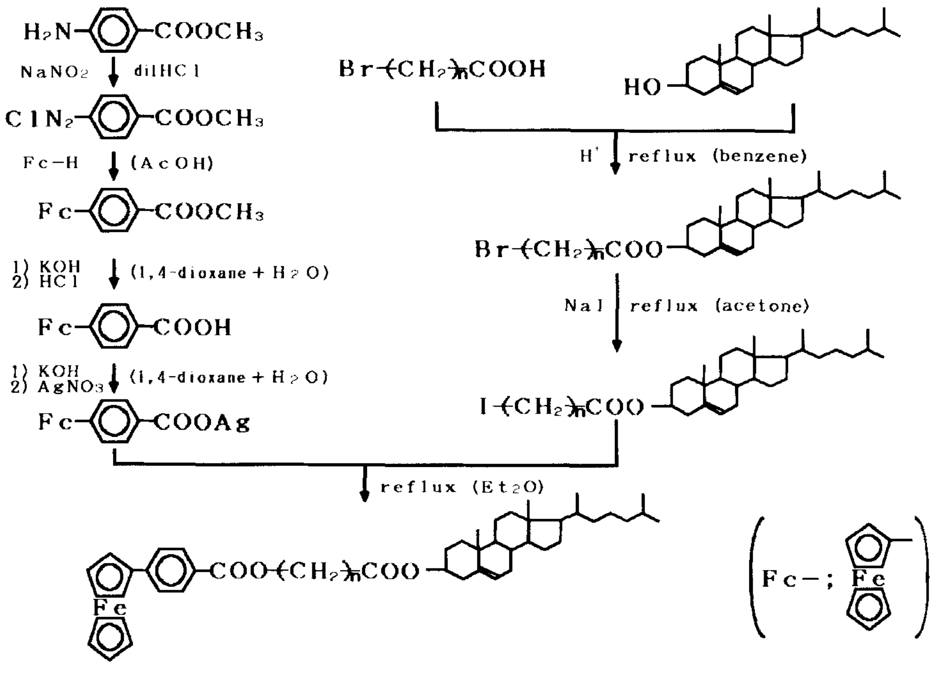

FIGURE 1 Scheme of synthetic process. *n*: the number of carbon atoms in the alkyl chain.

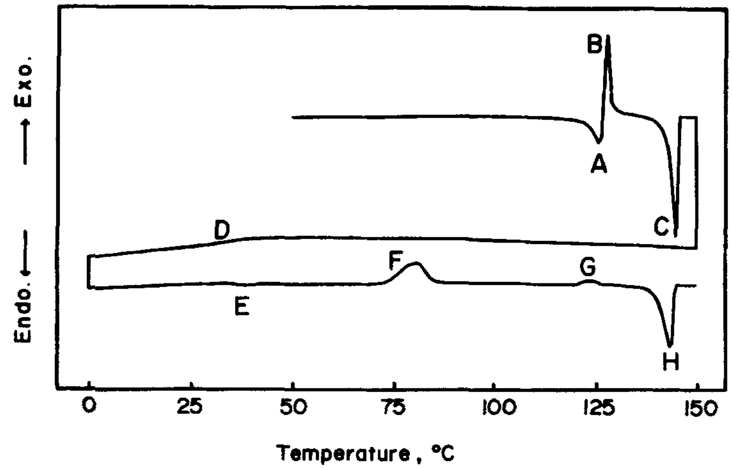

FIGURE 2 DSC curves of CAPF-3. Scanning rate: 5.0°C/min.

to stable one (K2). This crystal exhibited the endothermic peak (C) at 144°C. This temperature is decided as that of the melting by the polarizing microscopy observations. Just above the melting point, the texture of the sample was not perfectly black. This state is very viscous and slimy whereas the sample is in a molten state. So, a little ordered state exists in this state. When the heating was continued from the melting point, the sample decomposed at about 220°C. During the heating, no texture changes were observed. On the 1st cooling from 150°C, one very broad peak (D) was observed at 37°C. As mentioned above, this sample is very viscous and slimy in the molten state. Moreover, no texture changes were observed by the microscopy observations around the peak (D). Therefore, the peak (D) may be considered to be a glass transition to a frozen state of a supercooled sample of which only small parts are a little ordered. On the 2nd heating from 0°C, four peaks (E,F,G, and H) were observed. Owing to the typical shape of glass transition on the DSC curve, it is considered that the small peak (E) is glass transition one. No texture changes were observed around the peak (E) temperature. That is, the texture was dark. The sample crystallized at the exothermic peak (F). The sample of this state crystallized at the peak (F) transformed to other crystal state at the exothermic peak (G). And this crystal melted at the peak (H). The temperature of the peak (H) was nearly equal to that of peak (C). This fact suggests that the crystal just below the peak (H) is stable crystal (K2) observed on 1st heating. As the peak (G) is small, the phase change may be attributed to rearrangements of a little order formed at the peak (F). This behavior is different from that on 1st heating. So, the state below the peak (G) is similar to stable crystal (K2) rather than metastable crystal (K1). Therefore, this state is denoted by K2′. Photo 1 shows the K2′ crystalline texture taken at the temperature between the peaks (F) and (G). After the 2nd heating, the running cycle gives the same results mentioned above.

The DSC curves for CAPF-4 is shown in Figure 3. On the 1st heating, the as grown sample showed only one endothermic peak (I). This point was confirmed to be the melting one by polarizing microscopy observations. No phase changes were observed on the 1st heating up to the melting temperature. So, the as grown sample is stable crystal (K2). This sample is also very viscous and slimy in the molten state. On the 1st cooling, small but sharp exothermic peak (J) was observed

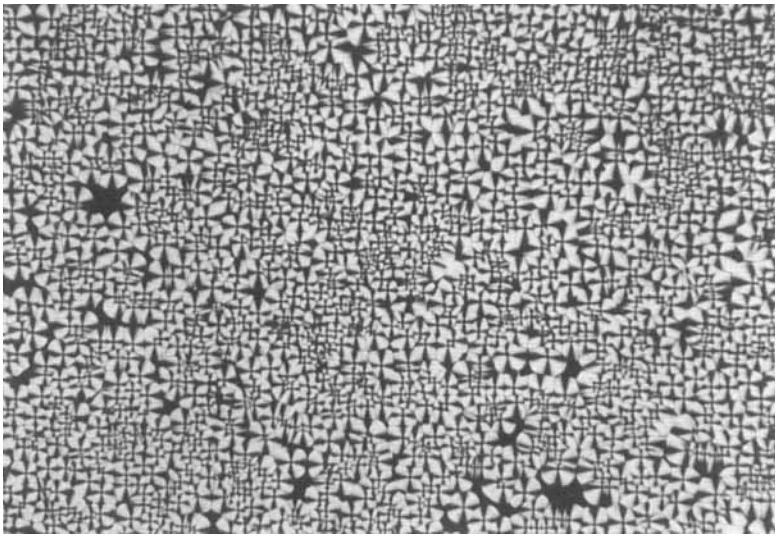

PHOTO 1 Texture of the crystal phase of CAPF-3 taken at 89°C. See Color Plate IX.

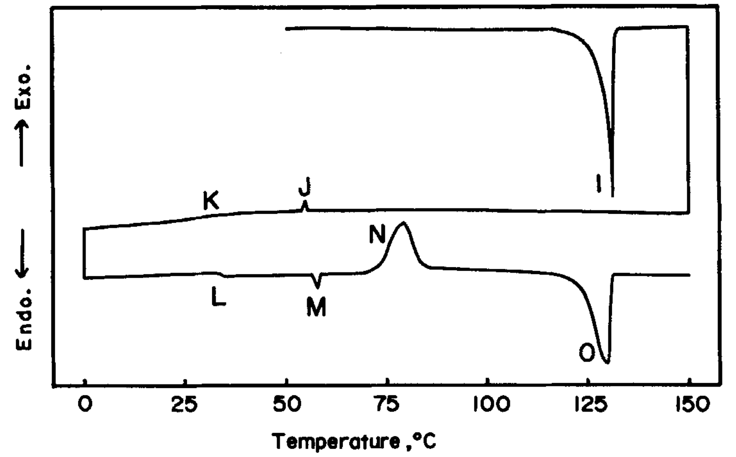

FIGURE 3 DSC curves of CAPF-4. Scanning rate: 5.0°C/min.

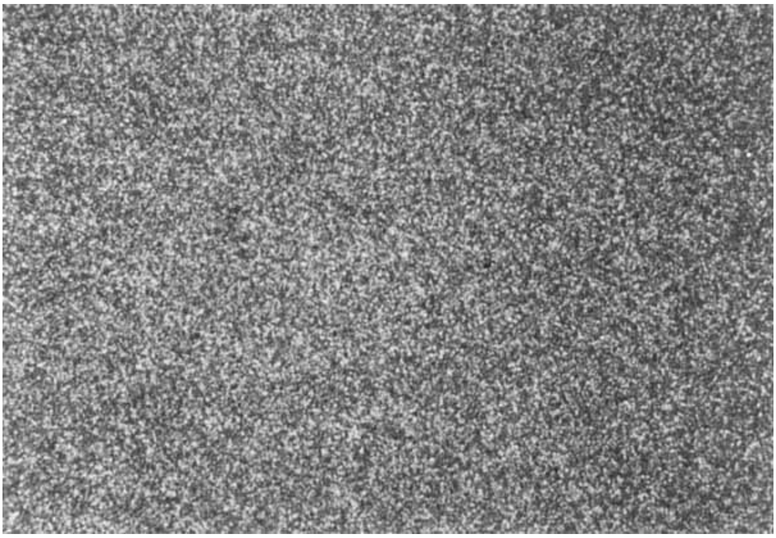

PHOTO 2 Texture of the liquid crystal phase of CAPF-4 taken at 16°C. See Color Plate X.

at 56°C. This is a clearing point because the microscope texture is the characteristic of liquid crystalline state. And the liquid crystalline phase appeared below this transition point. The color of the sample was beautiful yellowish green. Photo 2 shows the texture of the liquid crystal taken at 16°C. The glass transition underwent at very broad peak (K). After the transition point, no peaks and texture changes were observed in the cooling process down to 0°C. On the 2nd heating, the phase change behavior was different compared with that of CAPF-3. There were four peaks (L,M,N, and O). Owing to the typical curve of the DSC, peak (L) was the glass transition, as was already observed in the 1st cooling of this sample. Peak (M) was observed at 57°C and was identified as the clearing point of the liquid crystal by polarizing microscopy observations. The exothermic peak (N) observed at 73°C corresponded to a crystallization of crystal from the liquid state, because an appearance of the crystal was distinctly observed by polarizing microscope. This crystal melted at the endothermic peak (O) of which temperature was 124°C. Comparing the peak (O) temperature with that of the peak (I), it is considered that the sample crystallized at peak (N) is stable crystal (K2). The result obtained on the 2nd cooling was the same as that on the 1st cooling. And on the 3rd heating, it gave the same result as that on 2nd heating.

The sample of CAPF-2 gave similar DSC results as that of CAPF-4. But, on the 2nd heating, very small continuous exothermic and endothermic peaks were observed just under the melting point in addition to the peaks corresponding to the peaks (L,M,N, and O) of CAPF-4 (Figure 3). This phenomenon may be understood as follows. The crystal grown at 80°C (Table I) is metastable crystal (K1), and it melts at the endothermic peak temperature (133°C). This liquid immediately recrystallized to stable crystal (K2). The reason why this crystal is stable crystal (K2) is that the melting temperature of this crystal is nearly the same as that of as grown crystal, which is stable crystal (K2).

In the case of CAPF-1, DSC results are explained as follows. On the 1st heating, small endothermic, exothermic and exothermic peaks were continuously observed over the temperature range from about 70°C to 95°C. These peaks are not yet understood. But the crystal melted at 170°C. So, as grown sample is metastable crystal (K1) and the crystal transforms to stable crystal (K2) via complicated phase transition process. On the 1st cooling, the DSC results were nearly same as those of CAPF-3. On the 2nd heating, the metastable crystal (K2′) was grown at 88°C, but a new crystal (K2″) was observed at 106°C. And this crystal transformed to stable crystal (K2) at 125°C. The exothermic peak at 125°C was very small. Therefore, this crystal is not so much different compared with stable crystal (K2). So, it is denoted by K2″.

The DSC results of CAPF-5 and 7 were nearly equal to one another. Namely, the results obtained on the 1st heating of these samples were quite similar to that of CAPF-4, but the results observed on the 1st cooling were nearly the same as that of CAPF-3. On the 2nd heating, only glass transition was observed in both samples, and no other peaks were obtained in the DSC measurements. Therefore, only the dark screen was observed throughout the 1st cooling and the 2nd heating runs under polarizing microscope. Viscosity and slime of these samples in the molten state are similar to that of CAPF-3. This high viscosity may prevent an arrangement of molecules at a freezing temperature on 1st cooling. Therefore, the results obtained on 1st cooling and 2nd heating may be attributed to the high viscosity of the samples.

The DSC curves of CAPF-6 were nearly the same as that of CAPF-4 except the result on the 2nd heating in which only glass transition and the clearing point were observed.

In the case of CAPF-10, the DSC curves were similar to those of CAPF-2 as was shown in Figure 4. For an explanation of the phase transition phenomenon, a vertical axis in the Figure 4 is elongated about 10 times compared with those in Figures 2 and 3. These peaks are understood as follows. Peak (P) is glass transition,

TABLE I

Phase transition temperatures (°C).

n	1st heating	1st cooling	2nd heating
1	$\mathrm{K1}\overset{70\sim95}{\text{——}}\mathrm{K2}\overset{170}{\text{——}}\mathrm{L}$	$\mathrm{L}\overset{45}{\text{——}}\mathrm{G}$	$\mathrm{G}\overset{48}{\text{——}}\mathrm{L}\overset{88}{\text{——}}\mathrm{K2'}\overset{106}{\text{——}}\mathrm{K2''}\overset{125}{\text{——}}\mathrm{K2}\overset{165}{\text{——}}\mathrm{L}$
2	$\mathrm{K2}\overset{146}{\text{——}}\mathrm{L}$	$\mathrm{L}\overset{75}{\text{——}}\mathrm{L.C.}\overset{46}{\text{——}}\mathrm{G}$	$\mathrm{G}\overset{46}{\text{——}}\mathrm{L.C.}\overset{74}{\text{——}}\mathrm{L}\overset{80}{\text{——}}\mathrm{K1}\overset{133}{\text{——}}\mathrm{L}\overset{138}{\text{——}}\mathrm{K2}\overset{144}{\text{——}}\mathrm{L}$
3	$\mathrm{K1}\overset{122}{\text{——}}\mathrm{L}\overset{127}{\text{——}}\mathrm{K2}\overset{144}{\text{——}}\mathrm{L}$	$\mathrm{L}\overset{37}{\text{——}}\mathrm{G}$	$\mathrm{G}\overset{38}{\text{——}}\mathrm{L}\overset{74}{\text{——}}\mathrm{K2'}\overset{121}{\text{——}}\mathrm{K2}\overset{141}{\text{——}}\mathrm{L}$
4	$\mathrm{K2}\overset{129}{\text{——}}\mathrm{L}$	$\mathrm{L}\overset{56}{\text{——}}\mathrm{L.C.}\overset{35}{\text{——}}\mathrm{G}$	$\mathrm{G}\overset{35}{\text{——}}\mathrm{L.C.}\overset{57}{\text{——}}\mathrm{L}\overset{73}{\text{——}}\mathrm{K2}\overset{124}{\text{——}}\mathrm{L}$
5	$\mathrm{K2}\overset{96}{\text{——}}\mathrm{L}$	$\mathrm{L}\overset{26}{\text{——}}\mathrm{G}$	$\mathrm{G}\overset{29}{\text{——}}\mathrm{L}$
6	$\mathrm{K2}\overset{59}{\text{——}}\mathrm{L}$	$\mathrm{L}\overset{51}{\text{——}}\mathrm{L.C.}\overset{27}{\text{——}}\mathrm{G}$	$\mathrm{G}\overset{27}{\text{——}}\mathrm{L.C.}\overset{52}{\text{——}}\mathrm{L}$
7	$\mathrm{K2}\overset{119}{\text{——}}\mathrm{L}$	$\mathrm{L}\overset{20}{\text{——}}\mathrm{G}$	$\mathrm{G}\overset{22}{\text{——}}\mathrm{L}$
10	$\mathrm{K2}\overset{96}{\text{——}}\mathrm{L}$	$\mathrm{L}\overset{53}{\text{——}}\mathrm{L.C.}\overset{19}{\text{——}}\mathrm{G}$	$\mathrm{G}\overset{20}{\text{——}}\mathrm{L.C.}\overset{51}{\text{——}}\mathrm{L}\overset{58}{\text{——}}\mathrm{K1}\overset{74}{\text{——}}\mathrm{L}\overset{80}{\text{——}}\mathrm{K2}\overset{95}{\text{——}}\mathrm{L}$
11	$\mathrm{K2}\overset{77}{\text{——}}\mathrm{L}$	$\mathrm{L}\overset{40}{\text{——}}\mathrm{L.C.}\overset{12}{\text{——}}\mathrm{G}$	$\mathrm{G}\overset{13}{\text{——}}\mathrm{L.C}\overset{40}{\text{——}}\mathrm{L}$

n ; the carbon atoms in the methylene chain
L ; liquid
L.C. ; liquid crystal
G ; glass state

K1 ; metastable crystal
K2 ; stable crystal
K2' ; metastable crystal
K2" ; metastable crystal

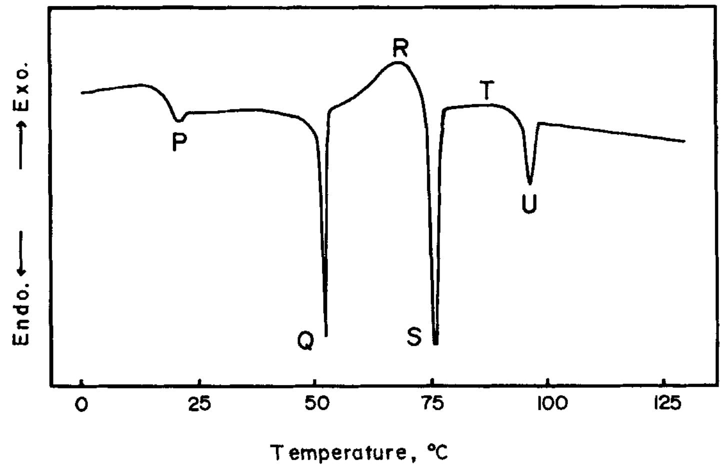

FIGURE 4 DSC curve of CAPF-10 on the 2nd heating. Scanning rate: 5.0°C/min.

peak (Q) is the clearing point, peak (R) corresponds to the crystallization for the metastable crystal (K1). This metastable crystal (K1) melted immediately at peak (S). As the crystallization and melting were happened continuously, the crystal and the liquid were coexisted between peaks (R) and (S). After the melting, a few nuclei of new crystal were appeared quickly in the liquid state. This phenomenon was easily observed by polarizing microscope. These nuclei grew gradually with increasing temperature. It is considered that the peak (T) corresponds to this crystallization. Before the crystallization was completely finished, the crystal melted at peak (U) temperature (95°C). Therefore, the liquid and the crystal coexisted between peaks (T) and (U). Since the temperature of the peak (U) is nearly equal to that of stable crystal (K2) observed on 1st heating of as grown sample, the new crystal appeared after the peak (T) is identified with stable crystal (K2). Two exothermic peaks (R) and (T) were very broad. Therefore, it is considered that the crystallization has happened quite slowly in order to high slime of the sample. It should be noted that this phenomenon is one of a typical double melting one which is observed in other organometallic compounds.[7]

Figure 5 shows only the 2nd heating DSC curve of CAPF-11, because the DSC curves of the 1st heating and 1st cooling are similar to those of CAPF-6. The vertical axis in Figure 5 is elongated about 10 times as similar to that in Figure 4. Peak (V) is the glass transition and peak (W) is the clearing point. The texture of the sample just above the peak (W) was not completely black under polarizing microscope. As already described above, these samples are quite viscous even in molten state. The quite small endothermic peak (X) observed at about 68°C is not yet fully understood. No remarkable texture changes were observed around this temperature.

The phase transition temperatures observed in this study are summarized in Table I. The liquid crystallinity was observed in five kinds of samples. Four of them have even carbon atoms in the flexible spacer ($n = 2$, 4, 6, and 10), so, the sample of $n = 8$, namely CAPF-8, may exhibit the liquid crystallinity. The re-

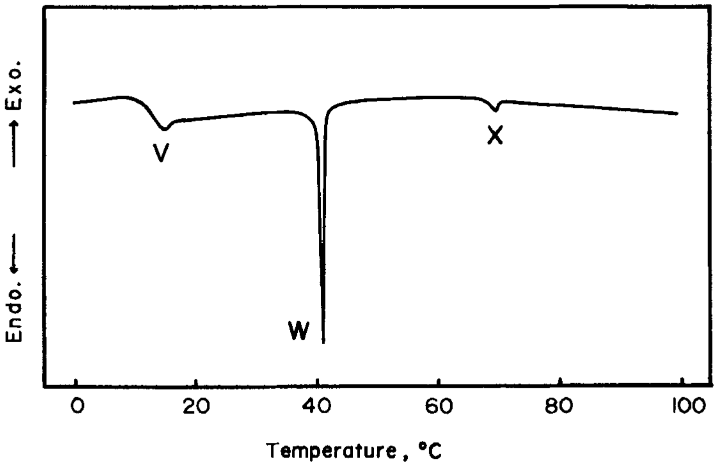

FIGURE 5 DSC curve of CAPF-11 on the 2nd heating. Scanning rate: 5.0°C/min.

maining sample, CAPF-11 has odd carbon atoms in the spacer ($n = 11$). These compounds studied here have two bulky groups, that is, ferrocenyl and cholesteryl ones in both sides of the molecules. When the flexible spacer has even carbon atoms and all of them locate themselves in *trans* positions, the molecule is regarded as rod-like because the two terminal bulky groups lie in *trans* positions to each other. This molecular shape is convenient to show the liquid crystallinity. On the other hand, in the odd carbon number series, the shape of the samples of which the spacer is rather short may be far from rod-like. But, the longer the spacer becomes, the more moderate the *cis-trans* effect is. Therefore, it may be considered that the molecular shape of CAPF-11 is regarded as rod-like and exhibits the liquid crystallinity.

Acknowledgment

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