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Synthesis and Physical Properties of Ferrocene Derivatives (XXII): Monosubstituted Ferrocene Derivatives Containing Biphenyl Group in the Mesogenic One

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The monosubstituted ferrocene derivatives containing biphenyl group in mesogenic one, ω-[4-(4-methoxybiphenoxy carbonyl) phenoxycarbonyl] alkyl 4-ferrocenylbenzoate, have been synthesized by changing the carbon atoms number of the flexible spacer. The analogous compounds in which phenyl group was contained instead of biphenyl one have been prepared and reported previously. Their phase transition behavior has been studied by a differential scanning calorimeter and a polarizing microscope. The effect of an existence of the biphenyl group on their phase transition behavior and a comparison of the phase transition phenomena with that of ω-[4-(4-methoxyphenoxy carbonyl) phenoxycarbonyl] alkyl 4-ferrocenylbenzoate will be discussed.

Keywords Crystal structure; ferrocene; liquid crystal; metallomesogen; monosubstituted ferrocene derivative

1. Introduction

If a transition metal is introduced into an organic compound containing mesogenic group, it may be expected that the molecule show not only liquid crystallinity but also interesting physical properties. To introduce the transition metal into the

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organic molecule, it is convenient to use metallocene such as ferrocene, The ferrocene easily causes substitution reaction as well as benzene.

Liquid crystalline ferrocene derivative had firstly observed in monosubstituted one [1]. After that, many different kinds of monosubstituted derivatives and disubstituted ones have been synthesized from a viewpoint of liquid crystals. Many papers on liquid crystalline ferrocene derivatives are reviewed recently [2].

Disubstituted ferrocene derivatives can be classified into three types, 1, 2-, 1, 3-, and 1, 1′-disubstituted ones according to the position of the substituents. The liquid crystalline monosubstituted ferrocene derivatives are further classified into two types in accordance with their molecular structure as shown in Figure 1.

Type 1, the mesogenic group is directly introduced into a cyclopentadienyl ring of the ferrocene, and the mesogenic group has a flexible alkyl chain as a terminal group (Fig. 1a).

Type 2, methylene chain as a flexible spacer is located between the ferrocenyl moiety and the mesogenic one (Fig. 1b).

Type 1 exhibited enentiotropic liquid crystalline phase, while Type 2 showed monotropic one. Many reports have been published on the type 1 [2].

A series of monosubstituted ferrocene derivatives, ω-[4-(4-methoxyphenoxy carbonyl) phenoxycarbonyl] alkyl 4-ferrocenylbenzoate (abbreviated hereafter as MPAF-*n*, $n = 1 \sim 11$, where *n* is the number of carbon atoms in the flexible methylene unit) which belongs in type 2 (Fig. 1(b)) were prepared in our laboratory [3,4]. The general chemical structure of MPAF-*n* is shown in Figure 2(a). Five members, these are MPAF-4, 6, 8, 9, 10, and 11, exhibited monotropic nematic and smectic liquid crystalline phases [3,4].

In the present study, we synthesized the type 2 compounds (Fig. 2(b)), which contain the biphenyl group in the mesogenic one instead of phenyl group in MPAF-*n*. The reason why is that the compounds synthesized here are expected to exhibit enantiotropic liquid crystalline phase, because a promotion ability of an appearance of liquid crystallinity of the biphenyl group is stronger than that of the phenyl group. Name of the newly designed compounds is ω-[4-(4-methoxybiphenoxy carbonyl) phenoxycarbonyl] alkyl 4-ferrocenylbenzoate (abbreviated hereafter as MBPAF-*n*, where *n* is the number of carbon atoms in

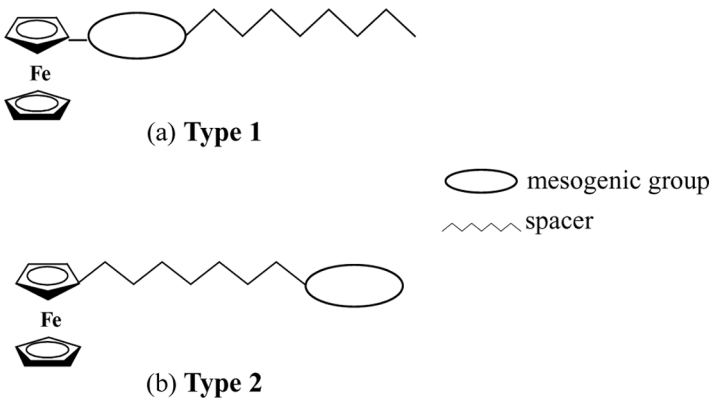


Figure 1. General structures of liquid crystalline mono-substituted ferrocene derivative.

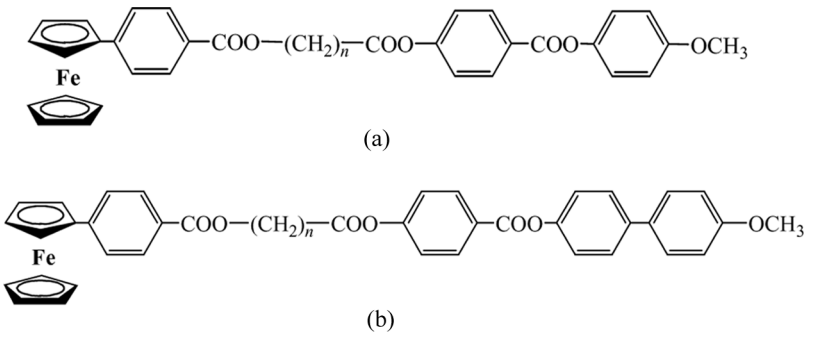


Figure 2. General structures of (a) MPAF-*n* and (b) MBPAF-*n*.

the flexible methylene unit), and the general chemical structure of MBPAF-*n* is shown in Figure 2(b). Using these compounds, studies on the phase transition phenomena were made.

2. Experimentals

Figure 3 shows a synthetic route of MBPAF-6 as an example. After purification, the compounds were identified by ^{1}H-NMR (JEOL, ALPHA-400 (400 MHz)) spectrometer using $CDCl_3$ and DMSO as a solvent. We mentioned ^{1}H-NMR data of MBPAF-n synthesized in this study below.

MBPAF-6

^{1}H-NMR data of MBPAF-6 in δ(ppm): 0.88(t, 2H), 1.26(quin, 2H), 1.83(quin, 4H), 2.64(t, 2H), 3.86(s, 3H), 4.08(s, 4H), 4.35(t, 2H), 4.40(t, 4H), 4.72(t, 2H), 6.99(d, 2H), 7.25(d, 2H), 7.27(d, 2H), 7.51(d, 2H), 7.54(d, 2H), 7.60(d, 2H), 7.97(d, 2H), 8.26(d, 2H).

MBPAF-7

^{1}H-NMR data of MBPAF-7 in δ(ppm): 1.49(quin, 6H), 1.80(quin, 4H), 2.62(t, 2H), 3.86(s, 3H), 4.08(s, 4H), 4.27(t, 2H), 4.40(t, 4H), 4.72(t, 2H), 6.99(d, 2H), 7.25(d, 2H), 7.27(d, 2H), 7.51(d, 2H), 7.54(d, 2H), 7.60(d, 2H), 7.97(d, 2H), 8.26(d, 2H).

MBPAF-8

^{1}H-NMR data of MBPAF-8 in δ(ppm): 1.25(t, 2H), 1.48(quin, 8H), 1.79(quin, 2H), 2.61(t, 2H), 3.86(s, 3H), 4.08(s, 4H), 4.33(t, 2H), 4.40(t, 4H), 4.72(t, 2H), 6.99(d, 2H), 7.25(d, 2H), 7.27(d, 2H), 7.51(d, 2H), 7.54(d, 2H), 7.60(d, 2H), 7.97(d, 2H), 8.26(d, 2H).

MBPAF-9

^{1}H-NMR data of MBPAF-9 in δ(ppm): 1.45(quin, 10H), 1.48(quin, 8H), 1.79(quin, 4H), 2.60(t, 2H), 3.86(s, 3H), 4.08(s, 4H), 4.32(t, 2H), 4.40(t, 4H), 4.72(t, 2H), 6.99(d, 2H), 7.25(d, 2H), 7.27(d, 2H), 7.51(d, 2H), 7.54(d, 2H), 7.60(d, 2H), 7.97(d, 2H), 8.26(d, 2H).

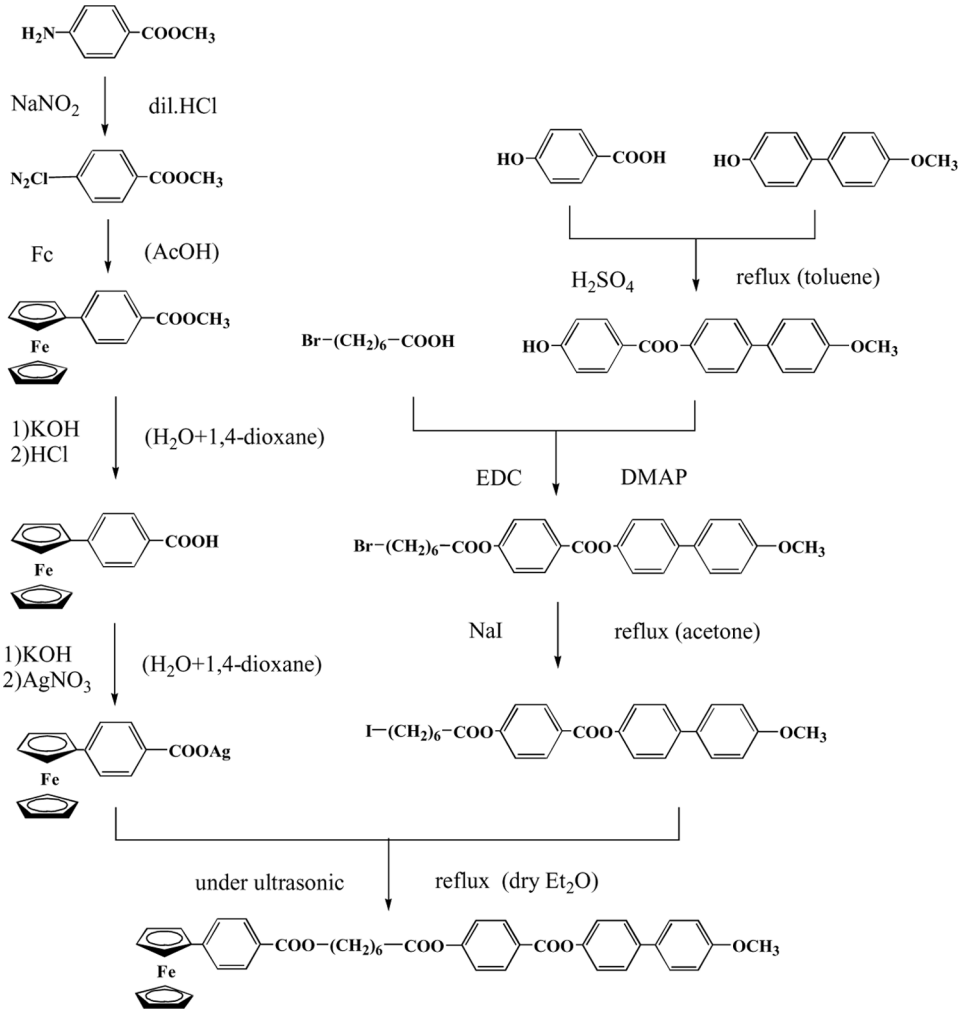


Figure 3. Synthetic route of MBPAF-6.

MBPAF-10

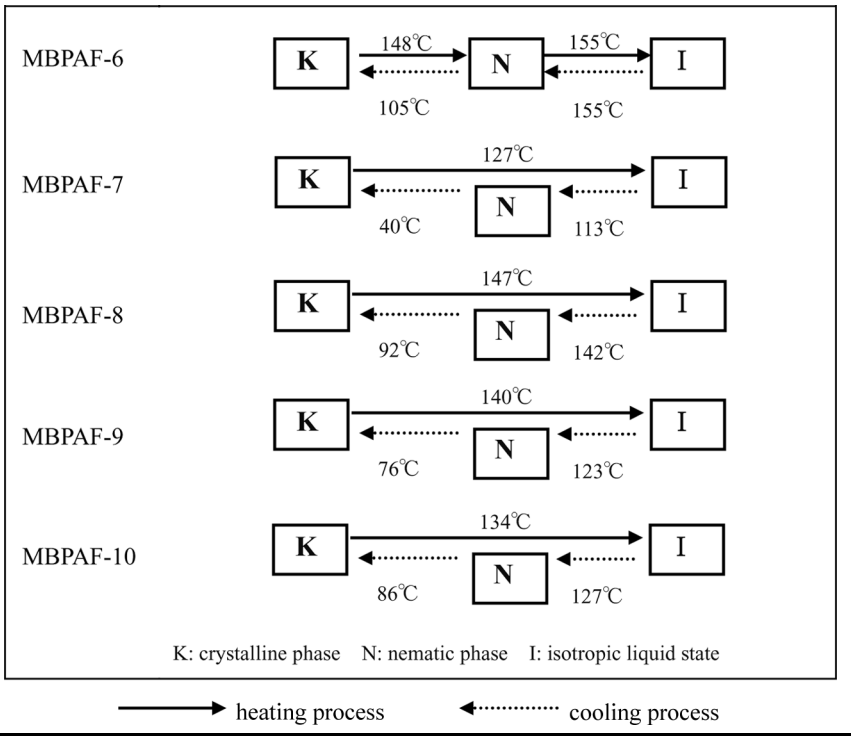
^{1}H-NMR data of MBPAF-10 in δ(ppm): 1.37(quin, 12H), 1.78(quin, 4H), 1.79(quin, 2H), 2.60(t, 2H), 3.86(s, 3H), 4.08(s, 4H), 4.30(t, 2H), 4.40(t, 4H), 4.72(t, 2H), 6.99(d, 2H), 7.25(d, 2H), 7.27(d, 2H), 7.51(d, 2H), 7.54(d, 2H), 7.60(d, 2H), 7.97(d, 2H), 8.26(d, 2H).

Thermal behavior was measured using Diamond DSC (Perkin Elmer) with heating and cooling rates of 5°C/min. The textures in the liquid crystalline phases were observed by a Nikon ECLIPSE E600 optical polarizing microscope equipped with a heating stage (Mettler Toledo FP90).

3. Results & Dicussion

The mesogenic group in MPAF-*n* has two phenyl rings, on the other hand, one phenyl group and one biphenyl one are included in MBPAF-*n*. Phase transition

Table 1. Phase transition behavior of MBPAF-6∼10



behavior of MBPAF-*n* ($n = 6\sim10$) is summarized in Table 1. Only MBPAF-6 showed enantiotropic liquid crystalline phase in accordance with our expectation, but disappointing results were obtained from all members of MBPAF-*n* except MBPAF-6. In addition, phase transition temperatures measured on 1st cooling of

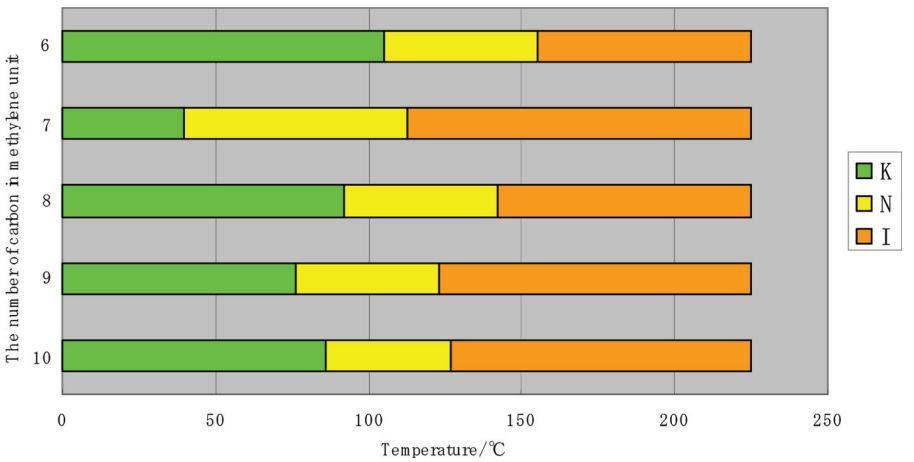


Figure 4. Phase transition diagram of MBPAF-*n* on 1st cooling.

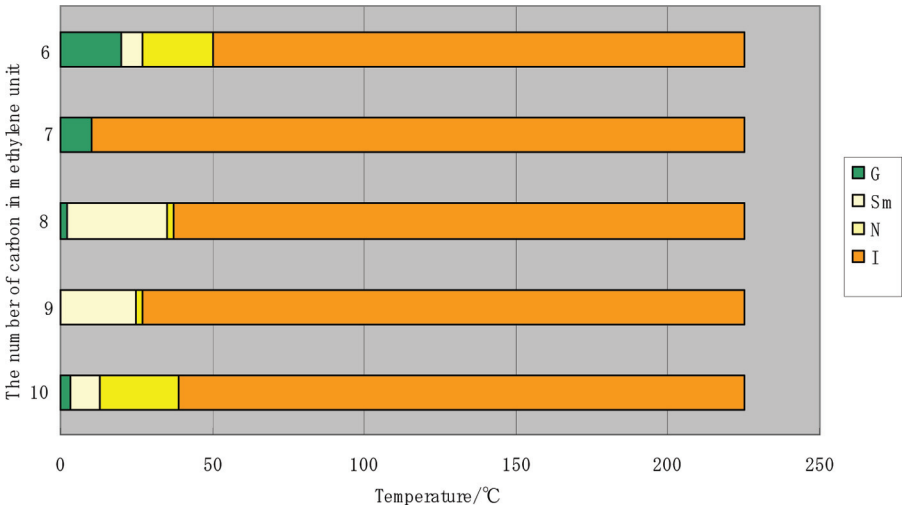


Figure 5. Phase transition diagram of MPAF-*n* on 1st cooling [3,4].

MBPAF-*n* ($n = 6 \sim 10$) and MPAF-*n*, ($n = 6 \sim 10$) are illustrated in Figures 4 and 5, respectively.

Figures show that melting and clearing temperatures of MBPAF-*n* are higher than those of MPAF-*n*. Moreover, temperature range of liquid crystal phase in MBPAF-*n* is wider than that of MPAF-*n*. As an example, characteristic Schlieren texture taken at 130°C in cooling of MBPAF-6 is shown in Figure 6. It suggests the phase is nematic one. Therefore, MBPAF-*n* exhibited stable nematic phase. It is considered that the fact is regarded as an existence of biphenyl group in the mesogen.

Comparison with clearing points of MBPAF-*n* and MPAF-*n* series is summarized in Figure 7. It is easily understand that clearing point of even members of

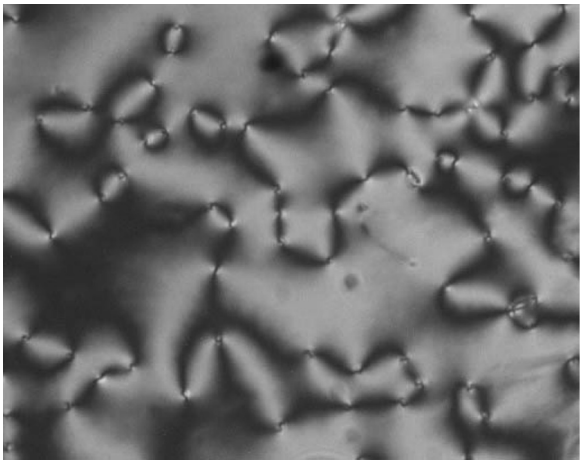


Figure 6. Optical texture of the liquid crystalline phase of MBPAF-6 taken at 130°C on cooling.

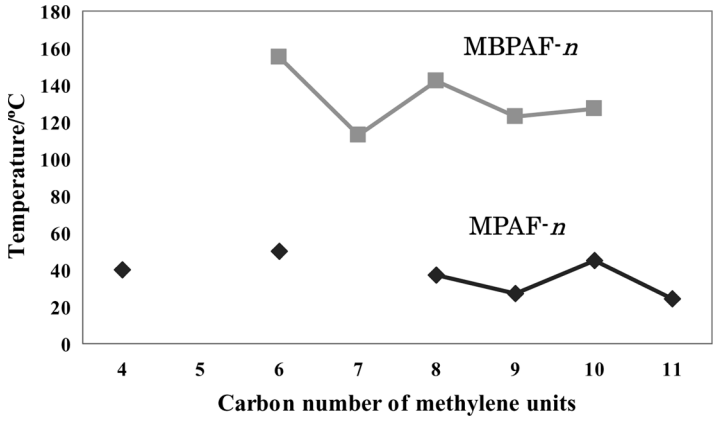


Figure 7. Clearing point of MBPAF-*n* and MPAF-*n* [3,4] against the carbon number of methylene units on 1st cooling. No clearing points of MPAF-5 & 7 were observed [3].

MBPAF-*n* series is higher than those of odd members. In the odd member series, the ferrocenyl moiety and the mesogenic group are located in the same side about the molecular axis. On the other hand, the moiety and the group stand in the opposite side about the axis in the even members. Therefore, even members regarded as more linear molecular shape than that of odd ones. This means that more rigid alignment could be possible in even members. From the point, the odd even effect is explained in monomer and dimmer liquid crystals in general. As a result, MBPAF-*n* exhibits odd even effect on the phase transition temperature.

In addition, phase transition temperatures such as clearing points and melting one of MBPAF-*n* are higher than those of MPAF-*n* as mentioned above. This phenomenon is ordinary one, because introduction of the biphenyl group in a molecule leads to increase of phase transition point [5].

In the case of MBPAF-6, the length of the flexible spacer containing 6 carbon atoms regarded as nearly equal to that of mesogenic moiety. It suggests that the stable molecular arrangement is easily possible in this case, compared with the cases of MBPAF-7 $\sim$ 10. Therefore, it is considered that MBPAF-6 exhibited enantiotropic liquid crystalline phase. If the value of the flexible spacer decreases in MBPAF-*n* series, the compounds have a liquid crystal phase in the wider temperature range. This is may be caused by an increment in the liquid crystallinity by short flexible spacer. Therefore, MBPAF-6 has most stable liquid crystalline phase in the homologues.

The advantage of the liquid crystalline phase of MPAF-*n* series is observed in longer spacer members, such as MPAF-4, 6, 8, 9, 10, and 11 [3,4]. This fact was explained from a point of an aspect ratio. If it increases, the possibility to appear liquid crystalline phase also increases. In the case of MBPAF-*n*, lower members become more stable. Probably, this fact is explained that an occupancy ratio of biphenyl group to total molecular eight increases with decreasing the length of the flexible spacer.

4. Conclusion

We synthesized monosubstituted ferrocene derivatives with type 2 which contained biphenyl group in the mesogenic group, because the compounds were expected to

exhibit enantiotropic liquid crystalline phase. The name of the compounds is MBPAF-6∼9. All compounds except MBPAF-6 exhibited monotropic nematic phase with characteristic Schlieren textures. Only, MBPAF-6 showed enantiotropic nematic phase. The length of flexible spacer and mesogenic group of MBPAF-6 could be regarded as nearly equal each other. It may be effective to promote a close attractive interaction between the molecules. As a result, it is considered that MBPAF-6 exhibited enantiotropic smectic liquid crystalline phase.

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