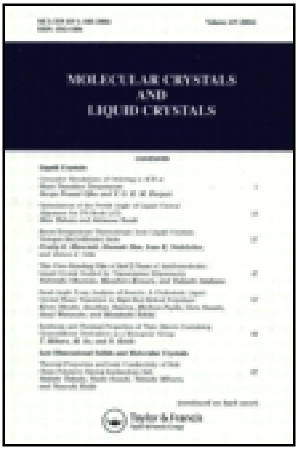

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Syntheses and Physical Properties of Ferrocene Derivatives (*X*) Dielectric Study of Liquid Crystalline Ferrocene Derivatives Containing Cholesteryl Group as a Mesogen

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Dielectric constant and loss measurements were made using a LCR meter at different frequencies from 100 Hz to 100 kHz with the aid of a personal computer. The samples used were ferrocene derivatives containing the mesogenic group, [4-[ω-(cholesteryloxycarbonyl)alkoxycarbonyl]phenyl]ferrocene of which carbon atoms number in the alkyl chain as a flexible spacer are 2, 4, 6, 8, 10, 11 and 15. These samples showed liquid crystallinity. The phase transition points were clearly observed in the curves of the temperature dependence of the dielectric constant. Activation energy was estimated from the Williams–Landel–Ferry (WLF) equation. The result obtained suggests that the molecular motion in the liquid crystalline phase is nearly the same as that of main chain segments of the polymers.

Keywords: Dielectric constant; dielectric dispersion; ferrocene derivative; metallomesogen; liquid crystal

INTRODUCTION

As is well known, ferrocene has an iron atom, which is one of the typical transition metal elements, between two cyclopentadienyl (abbreviated hereafter Cp) rings. Therefore, it is expected that ferrocene derivatives

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including the mesogenic group will exhibit not only liquid crystallinity but also many interesting physical properties such as electric, magnetic and chromatic ones. In our laboratory, many different kinds of ferrocene derivatives, including a flexible spacer between the ferrocenyl group and the mesogenic one, have been synthesized and investigated by DSC measurements, polarizing microscopic observations, the X-ray diffraction method, Mössbauer spectroscopic measurements and so on [1 – 12].

The ferrocene derivatives containing the cholesteryl group as a mesogenic one, [4-[ω-(cholesteryloxycarbonyl)alkoxycarbonyl]phenyl]ferrocene (abbreviated hereafter CAPF-*n*, where *n* is the number of carbon atoms in an alkyl chain as the flexible spacer), were already synthesized up to $n = 15$ except $n = 12$, 13 and 14 and studied in regard to the liquid crystalline phase transition phenomenon in our laboratory. The results obtained showed that CAPF-2, 4, 6, 8, 9, 10, 11 and 15 indicated liquid crystallinity [1, 2, 7]. Structural studies on the liquid crystalline phase have been done using the X-ray diffraction method [5] and the X-ray PSPC system [8]. Quite recently, the crystal structure of one of the CAPF-*n*, that is CAPF-6, was analyzed by X-ray single crystal structural analysis and discussed in regard to the mechanism of liquid crystalline phase transition also [8].

Dielectric constant and loss measurements are one of the most useful techniques in order to understand the molecular motion in the liquid crystalline phase [13]. Although many studies of the CAPF-*n* have been carried out using many different kinds of experimental methods mentioned above, few reports on the dielectric behavior of the compounds have been published.

In this paper, dielectric experimental results of liquid crystalline CAPF-*n* will be presented and the molecular motion in the liquid crystalline phase will be discussed.

EXPERIMENTAL

The liquid crystalline CAPF-*n* was prepared and purified in our laboratory. The synthetic method was described in our previous paper in detail [1]. The structures of the objective compounds were confirmed by ^{1}H-NMR spectra. Dielectric constant and loss were measured on the liquid crystalline CAPF-*n* at different frequencies from 100 Hz to 100 kHz using a Hewlett-Packard 4274A Multi Frequency LCR meter. The dielectric cell was a three-terminal type and thin gold electrodes were formed by the vacuum evaporation process [14]. The cell mounted on the sample was inserted into the measurement jacket in which the inside air was replaced by dried nitrogen gas in order to prevent the harmful effect of the moisture. The temperature range of the measurement depended on the samples, usually from about 25°C higher than its melting point to the solid state temperature. The temperature of dielectric cell assembly was controlled by the aid of a personal computer, and the rate of varying temperature was 2.5°C/min., which was the same as that of DSC measurements. The values of capacitance and conductance were measured as a function of temperature. These measurements and calculations of the dielectric constant and loss were made by the personal computer.

RESULTS AND DISCUSSION

The dielectric constant and loss measurements of the liquid crystalline CAPF-2, 4, 6, 8, 10, 11 and 15 were made in this study. Phase transition temperatures of CAPF-*n* obtained from DSC measurements are summarized in Table I. The liquid crystalline CAPF-9 was excluded from the samples of the measurements performed here, because the temperature range of the liquid crystalline phase was very narrow, only 19°C, in which it was quite difficult to obtain the linear relation in the WLF plots described

TABLE I Phase transition temperatures of CAPF-*n*. The temperatures were obtained from DSC measurement in which scanning rate is 2.5°C/min.

	Phase transition temperatures/°C	
n	*Cooling process*	*Heating process*
2	$L \xrightarrow{70} L.C. \xrightarrow{40} G$	$G \xrightarrow{41} L.C \xrightarrow{69} L \xrightarrow{74} K1' \xrightarrow{124} L \xrightarrow{137} K2 \xrightarrow{140} L$ $L \xrightarrow{74} K1'' \xrightarrow{127} L$ $L \xrightarrow{74} K1 \xrightarrow{133} L$
4	$L \xrightarrow{51} L.C. \xrightarrow{26} G$	$G \xrightarrow{27} L.C \xrightarrow{51} L \xrightarrow{66} K2 \xrightarrow{117} L$
6	$L \xrightarrow{48} L.C. \xrightarrow{23} G$	$G \xrightarrow{23} L.C \xrightarrow{48} L$
8	$L \xrightarrow{51} L.C. \xrightarrow{19} G$	$G \xrightarrow{21} L.C \xrightarrow{52} L$
10	$L \xrightarrow{49} L.C. \xrightarrow{14} G$	$G \xrightarrow{14} L.C \xrightarrow{48} L \xrightarrow{50} K1' \xrightarrow{63} K1 \xrightarrow{70} L \xrightarrow{75} K2 \xrightarrow{93} L$
11	$L \xrightarrow{37} L.C. \xrightarrow{7} G$	$G \xrightarrow{7} L.C \xrightarrow{39} L \xrightarrow{42} K2' \xrightarrow{64} L$ $L \xrightarrow{47} K2 \xrightarrow{64} L$
15	$L \xrightarrow{46} L.C. \xrightarrow{8} G$	$G \xrightarrow{6} L.C \xrightarrow{47} L \xrightarrow{48} K2' \xrightarrow{64} L$ $L \xrightarrow{50} K2 \xrightarrow{64} L$

n **: the carbon atoms in the methylene chain L : liquid K1 : metastable crystal K2 : stable crystal L.C : liquid crystal K1′ : metastable crystal K2′ : metastable crystal G : glass state K1″ : metastable crystal.**

later. CAPF-6 and 8 indicated the most simple phase transition sequence in the series of CAPF-*n* studied here. DSC thermograms on 1st cooling and 2nd heating scans of CAPF-8 are shown in Figure 1. Clearing point and glass transition one were clearly observed at 51 and 19°C on cooling, respectively. And these phase transition phenomena were reversibly observed on heating.

Temperature dependencies of dielectric constant ε' and loss ε'' on cooling of CAPF-8 are shown in Figure 2. A typical dielectric relaxation phenomenon was observed. The dielectric constant at the lower frequencies increases gradually *via* a small anomalous change at the clearing point, and quickly decreases at about 45°C with decreasing temperature. At the higher frequencies, the dielectric constant starts to decrease gradually from a temperature a few degrees higher than the clearing point, and continuously decreases *via* a small change at the clearing point with decreasing temperature. The dielectric constant converges to a constant value near the glass transition point. The increment of dielectric constant observed at the low frequencies from liquid phase to about 45°C will be considered as follows. The molecular reorientation by an outer applied field will not be affected with thermal motion because it will be weakened with decreasing temperature. Namely, the molecular reorientation is more easy at low temperature region because an effect of thermal agitation in low

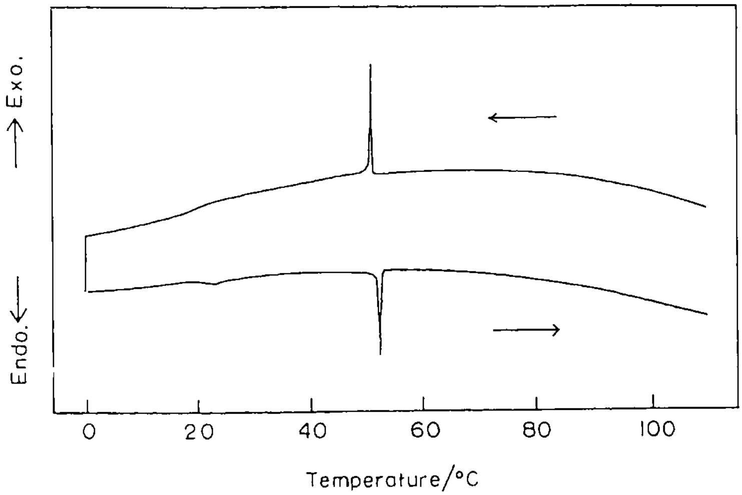

FIGURE 1 DSC curves of CAPF-8 on cooling and heating. Scanning rate is 2.5°C/min. Arrows indicate the direction of temperature change.

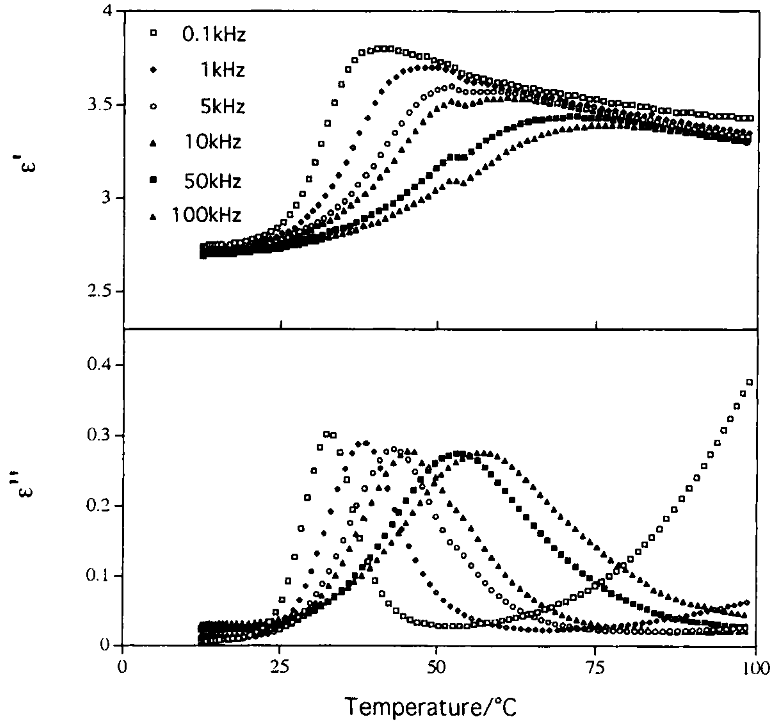

FIGURE 2 Temperature dependence of dielectric constant and loss for CAPF-8 on cooling.

temperature region is considered to be smaller than that in higher temperature one. The convergence in dielectric constant at higher frequencies at the glass transition temperature indicates that all the thermal motions are frozen at this point. The small anomalous change of the dielectric constant observed at the clearing point may be attributed to the density change at that temperature. In the temperature dependence of the dielectric loss, peak position of the dielectric loss curves shifts to the higher temperature side with increasing frequency. Temperature dependence of dielectric constant and loss of CAPF-8 on heating is shown in Figure 3. The behavior is quite similar to that of CAPF-8 on cooling. Feature of the dielectric dispersion observed here is summarized in following two points. First, at the clearing point which is observed at about 50°C by DSC measurement, anomalous small change is observed at the same temperature. Second, the dielectric dispersion is observed at higher temperature region than the glass transition point. These facts suggest that the dispersion may

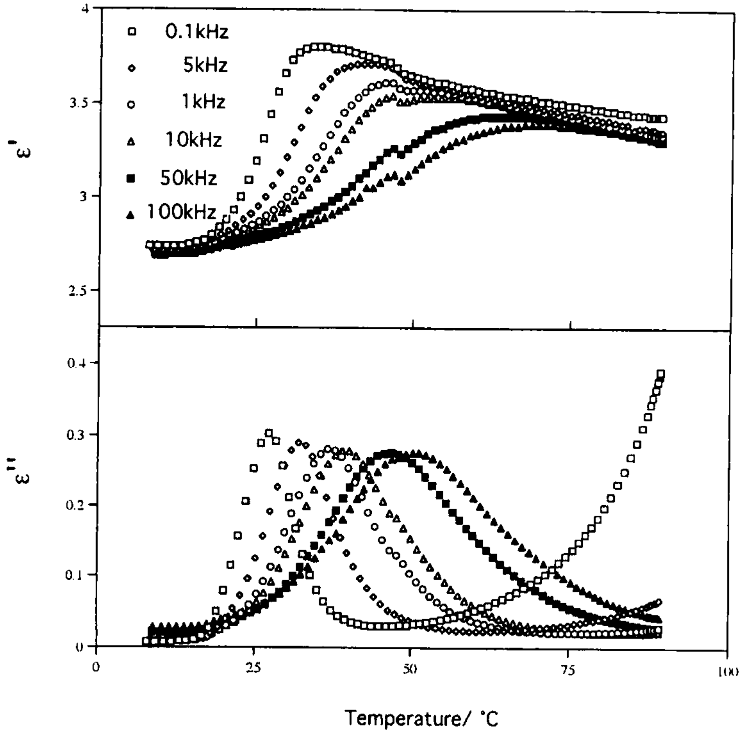

FIGURE 3 Temperature dependence of dielectric constant and loss for CAPF-8 on heating.

be main-chain type one, which is caused by micro-Brown motion of the polymer, usually observed in the polymers.

The results of dielectric constant and loss for CAPF-2, 4, 6, 10, 11 and 15 on cooling were quite similar to those of CAPF-8. A small anomalous change at the clearing point and a convergence to a constant value at about glass transition temperature were observed. The results obtained on heating are divided into two groups. One includes CAPF-6 and 8 (shown in Fig. 3). Another group includes CAPF-2, 4, 10, 11 and 15. These samples crystallize again at a temperature higher than the clearing temperature as was indicated in Table I. Although the results obtained from these samples were a little different from sample to sample, anomalous changes of dielectric constant and loss were clearly observed at the clearing, the crystallization and the melting points. As an example, the temperature dependence of CAPF-4 on heating is shown in Figure 4. The change at about 55°C corresponds to the clearing point, the change at about 70°C corresponds to crystallization

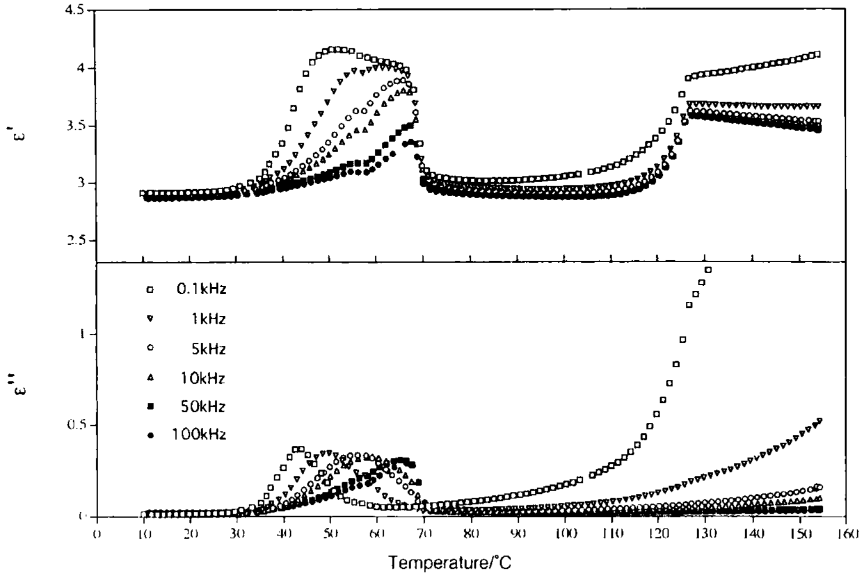

FIGURE 4 Temperature dependence of dielectric constant and loss for CAPF-4 on heating.

point, and the change at about 122°C corresponds to the melting point of the crystal grown at about 70°C. The dielectric constant observed in the crystalline phase is a little smaller than those both in the liquid crystalline phase and the liquid one. A small discrepancies in the phase transition temperatures obtained by DSC and dielectric measurements are understood as follows. As shown in Table I, CAPF-2,11 and 15 show the coexistence of plural crystalline phases. However, the results obtained from these samples show that no clear changes in the phase transition of each crystalline phase are observed at corresponding transition points. Phase transition between the crystalline phases was also not observed in the dielectric constant measurements.

Estimation of activation energy in the liquid crystalline phase on the cooling process of CAPF-*n* was made using the Eyring absolute rate process theory, that is, Ahrrenius plots, which was one of the most useful and convenient methods [15, 16]. Specifically, log $\omega_{\max}$ is plotted *versus* reciprocal values of absolute temperature, where $\omega_{\max} = 2\pi f_{\max}$, $f_{\max}$ is the frequency at which dielectric loss exhibited maximum values. However, the plot showed no linear relation as is shown in Figure 5. In such a case, the Williams–Landel–Ferry (WLF) free volume theory is effective in order to estimate the activation energy, as is generally well known [17]. The WLF

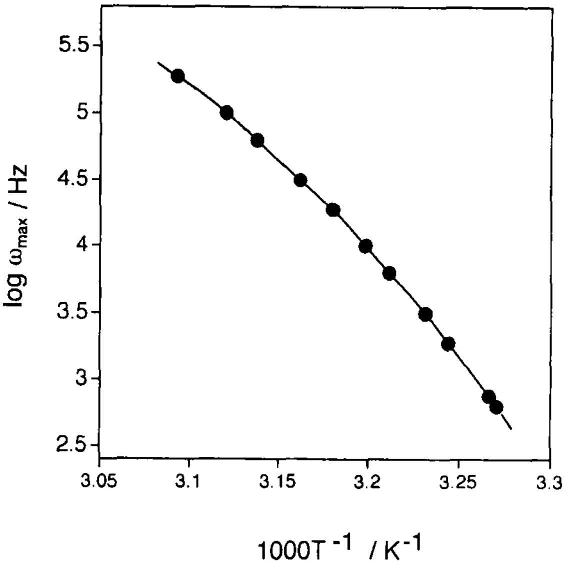

FIGURE 5 Ahrrenius plots for CAPF-8.

equation is expressed as follows;

$$\log b_T = \log\frac{f_{\max}(T_s)}{f_{\max}(T)} = \frac{c_1(T - T_s)}{c_2 + T - T_s}$$

where $\log b_T$ is a shift factor, $f_{\max}$ is a frequency corresponding to the dielectric loss maximum, T is an absolute temperature and T_s, c_1 and c_2 are constants.

Figure 6 shows a plot using the WLF equation for CAPF-8 on cooling, where the temperature at a maximum point of dielectric loss measured at 100 Hz was used as a T_s. Sufficiently linear relation is obtained. In the cases of CAPF-2, 4, 6, 10, 11 and 15, similar linear relation in the test plots was also confirmed. Therefore, the use of the WLF theory is reasonable for the estimation of the activation energy in this study. In Table II, the activation energies obtained here are listed. Roughly speaking, the values were of the order of 250 to 350 kJ/mol. The activation energies for various compounds, including typical polymers, were cited from the papers [16, 18 – 20] and listed in Table III. The values of CAPF-*n* estimated here are rather close to those of α relaxation of the polymers rather than those of other low molecular weight molecules. Therefore, it is considered that the relaxation of CAPF-*n*

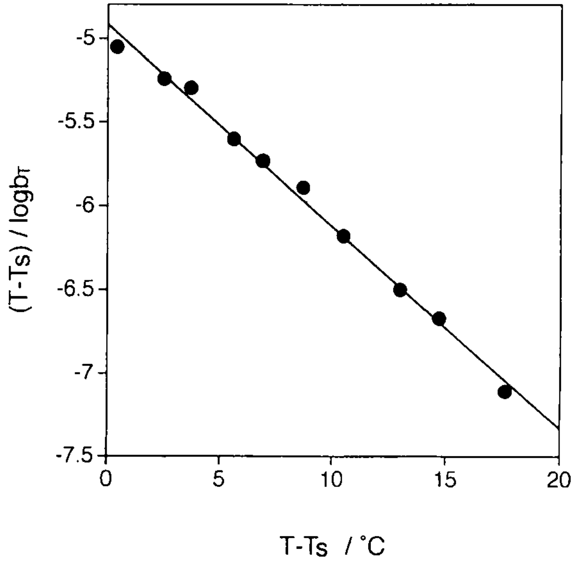

FIGURE 6 WLF plots of CAPF-8. T_s = 305.75.

TABLE II Activation energies for dielectric relaxation of CAPF-*n*

n	*Activation energy/kJ mol^{-1}*	*Temperature/K*
2	408	333
4	326	319
6	321	316
8	287	312
10	270	307
11	268	300
15	236	301

TABLE III Activation energies of various reference compounds

Sample	*Activation energy/kJ mol^{-1}*
Chloropentamethylbenzene	32.2 [18]
d,l-camphor	41.8 [18]
Methylpentachlorobenzene	46.4 [18]
Polyvinylacetate (α relaxation)	240 [16]
Polyvinylacetate (β relaxation)	35.9 [19]
Polymethacrylate (α relaxation)	222 [20]
Polymethacrylate (β relaxation)	30.9 [20]
Polyethacrylate (α relaxation)	188 [20]
Polyethacrylate (β relaxation)	30.1 [20]
Polymethylmethacrylate (α relaxation)	460 [20]
Polymethylmethacrylate (β relaxation)	79.4 [20]

is understood as that of a motional mode of main chain segments of the polymers.

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