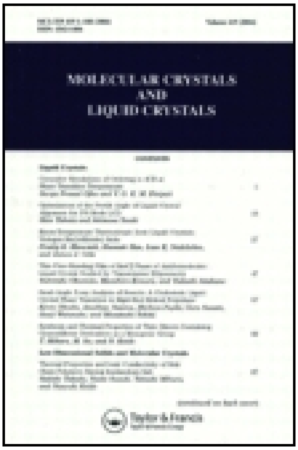


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Syntheses and Physical Properties of Ferrocene Derivatives (XIV) Dynamic Viscoelastic Property of Liquid Crystalline Ferrocene Derivatives Containing Cholesteryl Group as a Mesogenic One

Naotake Nakamura [a] , Hisashi Maekawahara [a] , Tomonori Hanasaki [b] & Takanari Yamaguchi [c]

[a] Department of Chemistry, Ritsumeikan University, 1-1-1, Nojihigashi, Kusatsu, Shiga, 525-8577, Japan

[b] Department of Materials Science, Shizuoka Institute of Science and Technology, 2200-2, Toyosawa, Fukuroi, Shizuoka, 437-8555, Japan

[c] Tsukuba Research Laboratory Sumitomo Chemical Co. Ltd., 6, Kitahara, Tsukuba, Ibaraki, 300-3266, Japan

Version of record first published: 24 Sep 2006

To cite this article: Naotake Nakamura, Hisashi Maekawahara, Tomonori Hanasaki & Takanari Yamaguchi (2000): Syntheses and Physical Properties of Ferrocene

Derivatives (XIV) Dynamic Viscoelastic Property of Liquid Crystalline Ferrocene Derivatives Containing Cholesteryl Group as a Mesogenic One, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 352:1, 125-132

To link to this article: http://dx.doi.org/10.1080/10587250008023169

Mol. Cryst. and Liq. Cryst., 2000, Vol. 352, pp. 125-132
Reprints available directly from the publisher
Photocopying permitted by license only

Syntheses and Physical Properties of Ferrocene Derivatives (XIV) Dynamic Viscoelastic Property of Liquid Crystalline Ferrocene Derivatives Containing Cholesteryl Group as a Mesogenic One

NAOTAKE NAKAMURA[a], HISASHI MAEKAWAHARA[a], TOMONORI HANASAKI[b] and TAKANARI YAMAGUCHI[c]

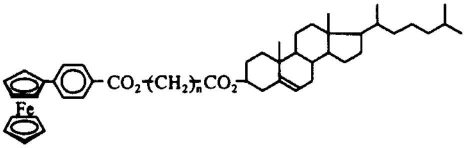
[a]*Department of Chemistry, Ritsumeikan University, 1–1–1, Nojihigashi, Kusatsu, Shiga 525–8577, Japan,* [b]*Department of Materials Science, Shizuoka Institute of Science and Technology, 2200–2, Toyosawa, Fukuroi, Shizuoka 437–8555, Japan and* [c]*Tsukuba Research Laboratory Sumitomo Chemical Co. Ltd. 6, Kitahara, Tsukuba, Ibaraki 300–3266, Japan*

The dynamic viscoelastic properties for [4-[ω-(cholesteryloxy carbonyl)alkoxycarbonyl]phenyl]ferrocenes with hexyloxy and octyloxy groups as an alkoxyl group were measured as functions of temperature and frequency. These samples showed liquid crystallinity. The results obtained here suggest that a kind of molecular order exists in the temperature range from the clearing point to about 20 degrees above it, in the liquid phase. Furthermore, the values of apparent activation energy in the liquid crystalline phase are as large as those of a primary dispersion of polymers, and its activation energy is not affected by the structural change at the clearing point.

Keywords: ferrocene derivative; liquid crystal; metallomesogen; dynamic viscoelastic property; phase transition

INTRODUCTION

A liquid crystalline ferrocene derivative is one of the typical metallomesogens, that is, the metal-containing liquid crystals. In our laboratory, a series of monosubstituted ferrocene derivatives, [4-[ω-(cholesteryloxycarbonyl)alkoxycarbonyl]phenyl]ferrocene (abbreviated to CAPF-*n*, where *n* is the number of carbon atoms in the methylene chain), had been synthesized[1,2]. The general structure of CAPF-*n* is shown below.



CAPF-*n* (*n*=1-11)

The series covers from CAPF-1 to 11. Phase transition phenomena of CAPF-*n* have been studied by differential scanning calorimetry, polarizing microscopic observation, X-ray diffraction methods, and so on[1-6]. Seven kinds of them (CAPF-2, 4, 6, 8, 9, 10 and 11) gave rise to a smectic C phase from a supercooled liquid.

In this study, dynamic viscoelastic properties of CAPF-6 and 8 were measured as functions of temperature and frequency in order to discuss the phase transition phenomena in further detail. The dynamic viscoelastic measurement can be utilized to the study on the phase transition phenomena of low molecular weight liquid crystals, because such method is very sensitive to the structural change.

EXPERIMENTAL

The samples, CAPF-6 and 8, were synthesized in our laboratory. The synthetic procedures were previously described in detail[1]. The samples synthesized here were confirmed thoroughly pure as they gave only one spot on a TLC analysis.

The dynamic viscoelastic measurement was made using a rheometer (Rheometrics RDS-2). The apparatus has a cone-plate rotating shear geometry. The cone angle was 0.1rad and its diameter was 25mm. The sample was heated up to 403K, and was maintained at the temperature for 5min. Then the measurement was started. A storage (*G'*) and a loss (*G"*) moduli were obtained in the temperature range of 303-373K and in the frequency range of 0.314-1000 rad/s (0.05-160Hz). The scanning rate of temperature was 2K/min. All measurements were carried out under an atmosphere of nitrogen.

RESULTS AND DISCUSSION

The meltings of as grown CAPF-6 and 8 were observed only on the 1st heating at 341 and 338 K, respectively. The phase transition behavior of these compounds after the 1st cooling is summarized in Figure 1 (scanning rate : 2K/min).

$$\text{CAPF-6} \quad \text{Glass} \underset{298\text{K}}{\overset{297\text{K}}{\rightleftarrows}} S_C \underset{322\text{K}}{\overset{324\text{K}}{\rightleftarrows}} \text{Liquid}$$

$$\text{CAPF-8} \quad \text{Glass} \underset{293\text{K}}{\overset{294\text{K}}{\rightleftarrows}} S_C \underset{325\text{K}}{\overset{326\text{K}}{\rightleftarrows}} \text{Liquid}$$

FIGURE 1 Phase transition behavior of CAPF-6 and 8.

The temperature and frequency dependence of dynamic moduli is explained mainly for the case of CAPF-8, because the results of dynamic viscoelastic measurements for CAPF-6 and 8 are very similar to each other.

Temperature Dependence of Dynamic Moduli

Figure 2 shows the temperature dependence of the storage modulus (*G'*), the loss modulus (*G"*) and a loss tangent (tanδ) at 62.8rad/s (10Hz) for CAPF-8 obtained in the heating process. The values of *G'* were smaller than those of *G"* in not only the liquid state but also the S_C phase. This fact suggests that the S_C phase shows a viscous character rather than an elastic one, whereas the smectic phase is generally regarded as showing the elastic character[7]. Such viscous character in the S_C phase indicates that the degree of the molecular order in the phase is relatively low. This result coincides with that from an X-ray

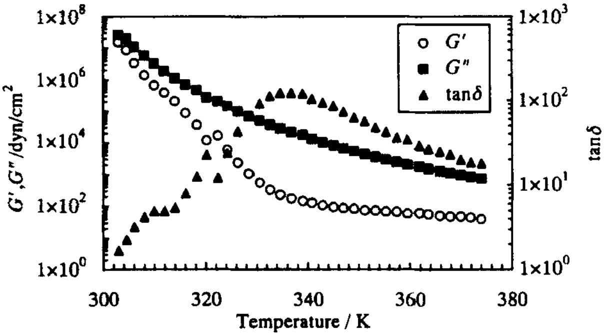


FIGURE 2 Temperature dependence of *G'*, *G"* and tanδ at 62.8rad/s (10Hz) for CAPF-8 on heating.

data. That is, reflections corresponding to long spacings were weak and broad compared with those of other smectic liquid crystals[3,4].

An abrupt drop of *G'* was not observed around the clearing point (326K), but a small anomalous change was observed. In the liquid phase, *G'* decreased gradually with increasing temperature, and it seems that *G'* converges to a constant value at about 20 degrees higher than the clearing point. Such behavior is different from that observed for other low molecular weight liquid crystals[8]. These results suggest that a kind of molecular order exists in this temperature range even in the liquid phase. This molecular order may be very short range one and/or locally existing one. It can be thought that an intermolecular week interaction exists between ferrocenyl moieties of the longitudinal neighboring molecules. This consideration is supported by the result of X-ray measurement, that is, the S_C phase has a double layer structure[3,4].

Frequency Dependence of Dynamic Moduli

The principle of time-temperature superposition is most useful in order to determine the frequency dependence of dynamic moduli. Figure 3 shows a *G'*-frequency master curve for CAPF-8 (reference temperature:303K).

The *G'* values in a lower frequency range at higher temperature region deviate from a single master curve, in contrast with those in a higher frequency range at lower temperature region, where the *G'* values are well superposed on to the master curve. Furthermore, this tendency becomes greater above the clearing point(326K). It is considered that the smectic structure changes gradually into less order over several tens of degrees across the clearing point. This result is in

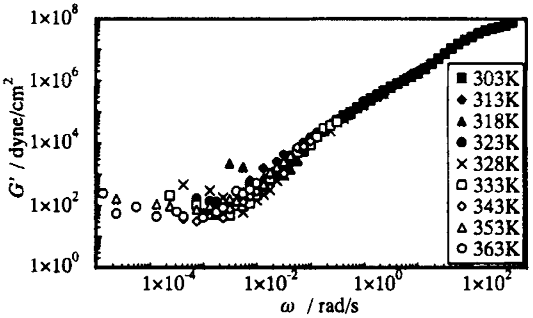


FIGURE 3 *G'*-frequency master curve for CAPF-8.

good agreement with the results of the temperature dependence of *G'* mentioned above.

In general, apparent activation energy is estimated from a shift factor a_T . This a_T is defined as an amount of horizontal shift of *G'* to the master curve along the frequency axis. It is assumed that a_T follows the equation,

$$\log a_T = \frac{\Delta H_a}{2.303R}\left(\frac{1}{T}-\frac{1}{T_r}\right)$$

, where ΔH_a is the apparent activation energy, R is the gas constant, T is the absolute temperature, and T_r is an arbitrary reference temperature. In this case, ΔH_a can be estimated from the plot of log a_T against $1/T$. However, no linear relationship was recognized in the data obtained here. On the other hand, if log a_T conforms to the WLF equation,

$$\log a_T = -\frac{c_1(T-T_r)}{c_2+T-T_r}$$

, where c_1 and c_2 are constant, ΔH_a is calculated from next equation.

$$\Delta H_a = 2.303R\frac{d\log a_T}{d(1/T)} = 2.303R\frac{c_1c_2T^2}{(c_2+T-T_r)^2}$$

In Figure 4, $-(T-T_r)/\log a_T$ is plotted against $T-T_r$. As is evident from Figure 4, the data give good linear relation in spite of spreading over two phases across the clearing point. The apparent activation energies

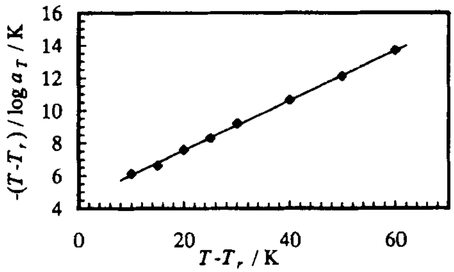


FIGURE 4 Plots of $-(T-T_r)/\log a_T$ against $T-T_r$ for CAPF-8.

TABLE 1 ΔH_a of CAPF-6 and 8.

Temperature / K	ΔH_a / kJ/mol	
	CAPF-6	CAPF-8
303	652	388
308	441	
313	321	232
318	247	188
323	196	157
328	161	134
333	135	116
338	116	
343		90
353		73
363		61

ΔH_a for CAPF-6 and 8 estimated from the WLF equation are listed in Table 1. The values of ΔH_a in the liquid crystalline phases are very large as those of a primary dispersion of polymers. In our previous study, similar results were obtained by dielectric dispersion measurements for the compounds[6]. From these results, it is considered that the apparent activation energy ΔH_a is not affected by the structural change at the clearing point. The large values of ΔH_a may be due to an intermolecular friction from the peculiar shape of the molecule. This consideration is supported by the large values of dynamic moduli in the liquid crystalline phase, as those of polymers, which is more than two orders of magnitude lager than those of other low molecular weight liquid crystals. In addition, these facts may be correlated to the molecular order remaining in the liquid phase.

Acknowledgments

KAWASAKI STEEL 21st Century Foundation is gratefully acknowledged for its partial support of the present work.

References

[1] N. Nakamura, T. Hanasaki, and H. Onoi, *Mol. Cryst. Liq. Cryst.*, **225**, 269 (1993).
[2] N. Nakamura, T. Hanasaki, H. Onoi, and T. Oida, *Chem. Express*, **8**, 467 (1993).
[3] N. Nakamura, H. Onoi, T. Oida, and T. Hanasaki, *Mol. Cryst. Liq. Cryst.*, **257**, 43 (1994).
[4] N. Nakamura, T. Oida, M. Shonago, H. Onoi, and T. Hanasaki, *Mol. Cryst. Liq. Cryst.*, **265**, 1 (1995).
[5] N. Nakamura and T. Takayama, *Mol. Cryst. Liq. Cryst.*, **307**, 145 (1997).
[6] N. Nakamura and T. Oida, *Mol. Cryst. Liq. Cryst.*, **326**, 55 (1999).
[7] T. Asada, Y. Murahashi, and S. Onogi, *J. Phys. (Paris)*, **36**, 299 (1975).
[8] For example, T. Yamaguchi, M. Yamada, S. Kutsumizu, and S. Yano, *Chem. Phys. Lett.*, **240**, 105 (1995).