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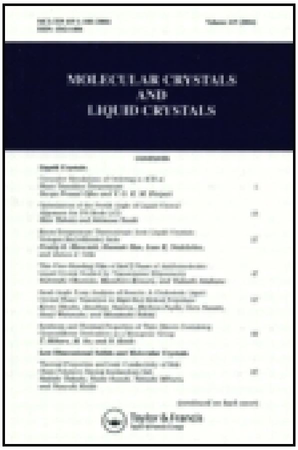

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Dielectric Behavior of Semifluorinated n-Alkane($F(CF_2)_n(CH_2)_mH$)

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Dielectric behavior of semifluorinated *n*-alkane $F(CF_2)_n(CH_2)_mH$, $(n, m) = (10, 10), (12, 8)$ has been observed over ranges of frequency and temperature. The distribution parameter of dielectric relaxation time obtained from the Cole-Cole plot is nearly equal to unity. The apparent activation energies for F10H10 and F12H8 are 134.6 kJ/mol and 65.8 kJ/mol, respectively. β-relaxation was observed which is associated with the rotation of the $(CF_2)_n$ group in semifluorinated *n*-alkane. The ratio of dipole moment, $\mu(\text{F12H8})/\mu(\text{F10H10})$ obtained from the Fröhlich modification of Onsager's equation is 2.29, even though these compounds have the same constitution except for two carbons linking to the fluorine or hydrogen atoms. In addition we discuss the time dependence of the dielectric loss factor in the vicinity of phase transition temperatures.

Keywords: Dielectric relaxation, semifluorinated n-alkane, β-relaxation.

1. INTRODUCTION

Aromatic or aliphatic rings are generally indispensable for the appearance of liquid crystalline phases. The materials of semifluorinated alkanes $F(CF_2)_n(CH_2)_mH$, in spite of their linear aliphatic structure, have been described to undergo mesophase-mesophase, mesophase-solid and/or solid-solid phase transitions.[1–4] Especially, the structure of F10H10 in the vicinity of the phase transition has been investigated in detail.[3] The compound has been found to present a liquid crystal-liquid crystal phase transition (between LC1 and LC2) above room temperatures. This structure transformation is caused by a change in tilt angles. Consequently, it is found that the layer spacings are different from each other in the liquid crystal phases.

The structures of F12H*m* ($m = 8, 10,$ and 12) in solid states have been investigated by Raman spectroscopy and X-ray,[2] and evidence for a tilted bilayered structure below a transition temperature was found. As the temperature is increased, the long period for $m = 8–12$ is seen to decrease to a value corresponding to the molecular length, and this decrease results from the translation of molecules along their axes to the antiparallel

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packing layered structure. The molecules in monolayered structures above the phase transition temperature are interdigitated by one-third of the length of the fluorinated segment. It is expected from these phenomena to change the molecular dynamics in the phase transition.

In general, dielectric relaxation behavior reflects the mobility of the constituent groups of materials. Therefore, dielectric relaxation studies provide us with new information on the relationship between molecular dynamics and molecular structure in these materials. The fluorinated polymers have been investigated for dielectric relaxations or thermal properties.[6–9] However, the dielectric behavior of the semifluorinated *n*-alkane has not yet been reported. In the present paper, we discuss the results obtained from dielectric relaxation spectra.

2. EXPERIMENTAL

Two materials were chosen for the semifluorinated *n*-alkane of semiflexible diblock molecules in the form $F(CF_2)_n(CH_2)_mH$ (referred to F*n*H*m* hereafter), i.e. F10H10 and F12H8. These were synthesized by a method similar to that of Twieg and Robolt.[4] Differential scanning calorimetric measurements were carried out for these compounds at heating and cooling rates of 1–3°C/min. Dielectric measurements were carried out over the frequency range 150 Hz to 1.5×10^7 Hz with a computer controlled YHP 4697 A Impedance Analyzer, and made in the temperature range from the solid (waxy state) to the isotropic state. The sample for dielectric measurements was prepared as a thin film of about 1.0 cm diameter and 100 μm thickness, sandwiched between two metal electrodes whose surfaces were not pre-treated in any way. Sample dimensions were kept constant by means of a Teflon ring spacer. The dielectric loss data are presented here as $G/\omega = \varepsilon'' C_0$, where G is the equivalent parallel conductance of the sample, $\omega = 2\pi f/\mathrm{Hz}$, ε'' is the dielectric loss factor and C_0 is the interelectrode capacitance. The samples for dielectric measurements were prepared by cooling to waxy state temperature at a rate of approximately $0.1\,\mathrm{K\,min^{-1}}$ from the isotropic state. The whole apparatus was immersed in an oil bath so that the temperature of the sample could be accurately controlled to equilibrate the system for 10 min each time the temperature was changed.

3. RESULTS AND DISCUSSION

3.1 Relaxation Behavior

The thermal properties of F10H10 and F12H8 obtained with DSC are summarized in Table I. These results agree very closely with the published data.[3,4] Figures 1 and 2 show the dielectric loss curves as a function of temperature for F10H10 and F12H8, respectively. Dielectric loss curves for both samples are fairly sharp and remain relatively invariant in the temperature range of the liquid crystal state except that the peak is shifted to higher frequencies with increasing temperature. The peak height in dielectric loss curves for F12H8 is greater than that for F10H10. However, the widths of the overall loss curves are quite the same for F10H10 and F12H8. Figures 3 and 4 show

TABLE I

Phase transition temperatures (°C)

Materials	K[a]		M[b]		I[c]
F10H10	●	35.5	●	61.2	●
			●	(58.4)[d]	●
F12H8	●	45.7	●	84.2	●
	●	(33.9)	●	(82.4)	●

[a] Crystal state, [b] Mesophase/liquid crystal phase, [c] Isotropic phase, [d] On cooling.

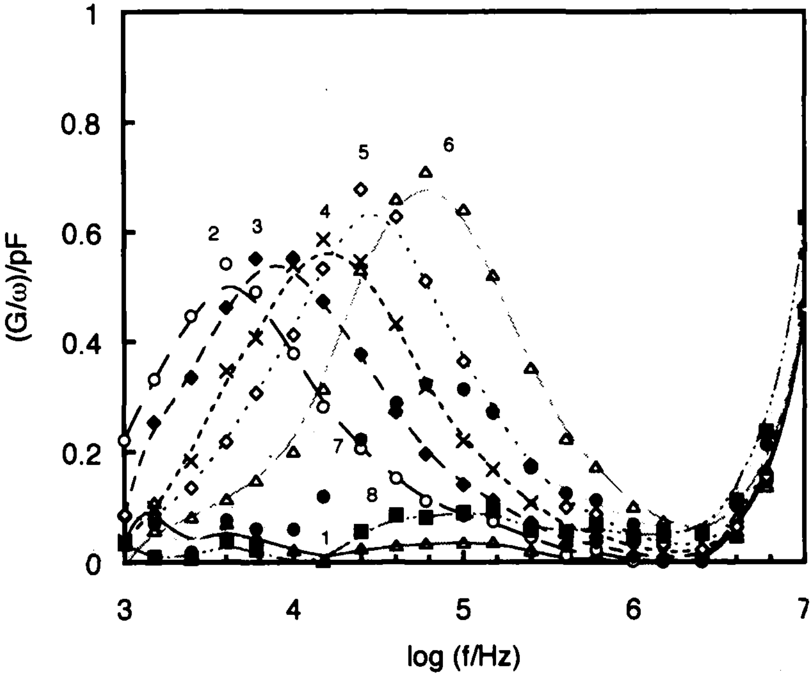

FIGURE 1 Frequency dependence of the dielectric loss factor, G/ω for F10H10 in the temperature range 40.2 to 64.0°C. Curves 1–8 correspond to 40.2, 44.4, 45.6, 52.4, 56.3, 62.3, 63.3 and 64.0°C.

the peak height of the dielectric loss curves as a function of temperature, either on the heating or on the cooling process for F10H10 and F12H8, respectively. The peak height of dielectric loss curves becomes drastically greater at the temperature from waxy solid to the liquid crystal phase. The peak height of the dielectric loss factor, $(G/\omega)_m$ in the liquid crystal phase increases gradually with an increase in temperature, as is seen in Figure 3. From this figure, $d(G/\omega)_m/dT$ is found to be 1.24×10^{-2}(pF/°C). On the other hand, the height of $(G/\omega)_m$ for F12H8 does not change with temperature in the liquid crystal phase. This dielectric behavior explains distinct formations of the liquid crystal phase for F10H10 and F12H8, as described in Ref. 2 and Ref. 5. On heating the peak height of dielectric loss curves disappears in the isotropic phase. It is apparent that

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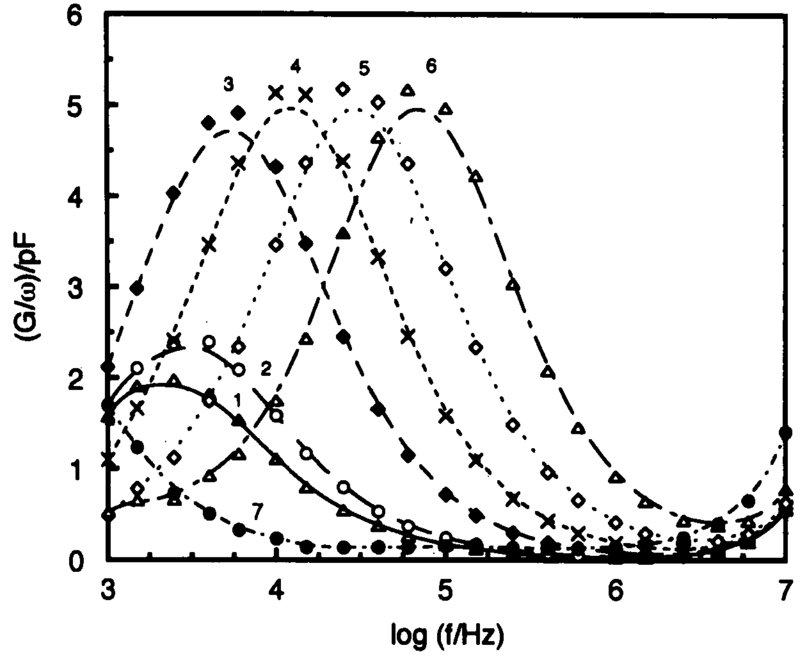

FIGURE 2 Frequency dependence of the dielectric loss factor, G/ω for F12H8 in the temperature range 41.3 to 85.8°C. Curves 1–7 correspond to 41.3, 44.8, 50.2, 61.2, 74.6, 84.4 and 85.8°C.

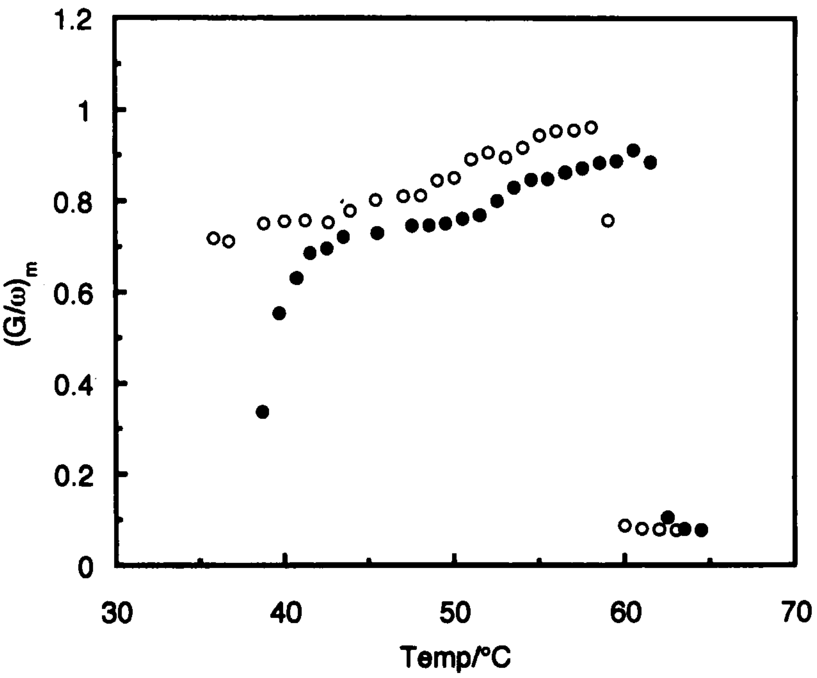

FIGURE 3 Temperature dependence of maximum dielectric loss factor, $(G/\omega)_m$ for F10H10. (●): on heating, (○): on cooling.

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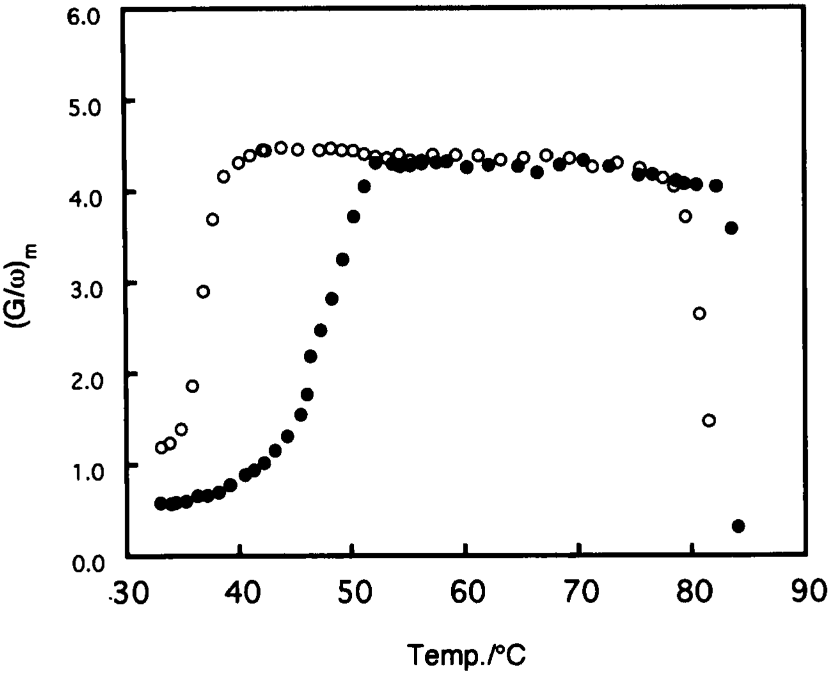

FIGURE 4 Temperature dependence of maximum dielectric loss factor, $(G/\omega)_m$ for F12H8. (●): on heating, (○): on cooling.

these variations in the peak heights of dielectric loss curve change reversibly in both processes. For both samples the change of their peak heights on cooling occurs at lower temperatures in comparison with that on the heating process. The molecular structure in the liquid crystal phase is not understood, but it might be of highly ordered smectic phases.

Figure 5 shows Arrhenius plots for both samples on heating and on cooling. The apparent activation energies for F10H10 were 134.6 on heating and 124.6 kJ/mol on cooling, respectively. On the other hand, these values for F12H8 were 65.8 on heating and 68.3 kJ/mol on cooling, respectively.

Generally, dielectric relaxation studies of materials exhibit the α, β, and γ relaxation at decreasing temperature. α- and β-relaxations are assigned respectively to a reorientational whole molecule and a hindered rotational motion of the short range in the molecule, and then lay at high temperature. γ-relaxation is assigned to a local motion, and observed at low temperature. As a result in this work, there are observed β-relaxation in the liquid crystalline state, which is associated with the rotation of the $(CF_2)_n$ group in semifluorinated *n*-alkane. The difference in the activation energy of F10H10 and F12H8 seems to be caused by the formation of different layer structures in the mesophase, i.e. packing mode and tilt angle.[2,3] The results of semiempirical energy calculations for evaluating possible packing modes in Ref. 2 provide no remarkable difference in energies for various packing modes in the case of $n/m = 1$, i.e. F12H12. For $n/m > 1$, i.e. F12H6, a parallel packing mode has, on the other hand, much lower energy

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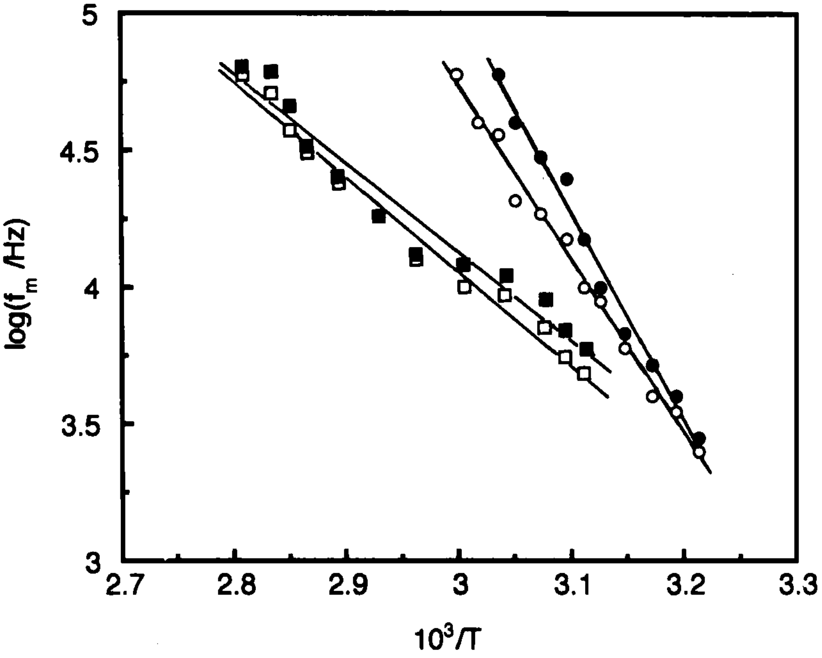

FIGURE 5 Temperature dependence of the frequency of β-relaxation for F10H10 and F12H8, respectively. F10H10; (●): on heating and (○): on cooling, F12H8; (■): on heating and (□): on cooling.

in comparison with several antiparallel packing modes. Parallel packing analogous to the structure with the lowest energy is generally suggested to be acceptable in the case of $n > m$.

A complex dielectric constant ε^* is defined as

$$\varepsilon^* = \varepsilon' - i\varepsilon'' \tag{1}$$

where ε' is the measured dielectric constant of the dielectric material in the condenser and ε'' its loss factor. The simple relaxation theory to express the frequency dependence of ε' and ε'' is represented by the single relaxation time, τ

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + i\omega\tau} \tag{2}$$

where ε_∞ is the limiting dielectric constant on the high-frequency, ε_0 the static premittivity and $\omega = 2\pi f$ the angular frequency. Substitution of Equation (1) in and separation of real and imaginary pats give,

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (\omega\tau)^2} \tag{3}$$

$$\varepsilon'' = \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (\omega\tau)^2} \tag{4}$$

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when $\omega\tau = 1$, i.e. $2\pi f_m \tau = 1$, $\varepsilon'' = \varepsilon_0''$ where f_m is the frequency of maximum loss, also $\varepsilon_m'' = (\varepsilon_0 - \varepsilon_m)/2$. Consequently, the total width at half height for a single relaxation time for F10H10 is readily shown to be $\Delta \log_{10} f = 1.14$ *from Equation (4)*. It means for $\Delta\log_{10} f = 1.22$ for F12H8 that the distribution of relaxation times for F12H8 is broader than that for F10H10. Figure 6 shows the Cole-Cole diagrams for the β-relaxation of F10H10 and F12H8, respectively. The Cole-Cole plots of the β-relaxation are fairly well fitted to the Cole-Cole equation and the β value of the distribution parameter close to unity for F10H10 and 0.85 for F12H8. These results suggest that the molecular motion of F10H10 has a single relaxation time and that of F12H8 is slightly broader than that for a single relaxation process. These results are consistent with those of the total width at half height, as described above.

The configuration of F12H8 is different from that of F10H10. We are interested in the estimation of dipole moment to establish the arrangement of the compounds. If two compounds with similar configurations have different dipole moments, these compounds are expected to have different arrangements. The dipole moment in β-relaxation can be calculated using the Fröhlich modification of Onsager's equatio,[10]

$$\mu^2 = \frac{3kT}{4\pi N g}(\varepsilon_r - \varepsilon_u)\frac{3\varepsilon_r + \varepsilon_u}{3\varepsilon_r}\left(\frac{3}{3\varepsilon_u + 2}\right)^2 \tag{5}$$

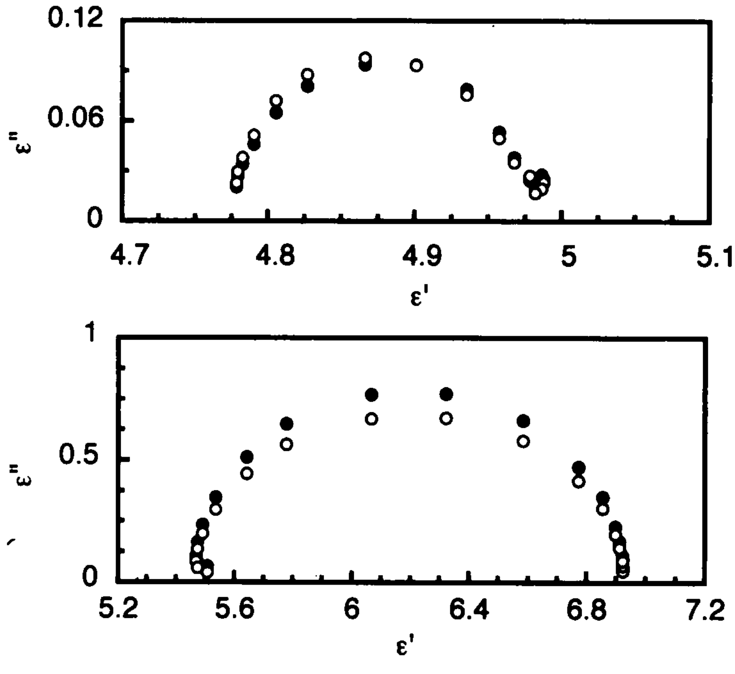

FIGURE 6 Cole-Cole diagram for β-relaxation in F10H10 (a) on heating (60.8°C: ●) and on cooling (60.5°C: ○), and F12H8 (b) on heating (79.4°C: ●) and on cooling (80.2°C: ○).

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where μ is the dipole moment (Debye unit), k Boltzmann constant, T absolute temperature, N the concentration of dipole (mol/cm^3), and g the Kirkwood factor. The g factor is taken to be unity in this work. The value of μ is computed by dividing the density by the molecular weight of the repeating unit. The densities are measured to be 1.28 and 1.47 for F10H10 and F12H8 at the isotropic phase just above the transition temperatures. The values of the relaxed low frequency dielectric constant, ε_r and unrelaxed high frequency dielectric constant, ε_u in Equation (5) are found from Cole-Cole plots. These values are shown in Table 2. The ratio of the dipole moment, $M = \mu(\mathrm{F12H8})/\mu(\mathrm{F10H10})$ is 2.29 using the data shown in Table II. This result would support the difference in the packing mode for F10H10 and F12H8. As mentioned above, the activation energy difference could also be explained by considering the parallel or antiparallel packing.

3.2 Kinetics

As shown in Figures 3 and 4, dielectric loss heights change considerably in the vicinity of phase transition temperatures, i.e. from T_K to T_{lc}, and/or T_{lc} to T_i. Dielectric relaxation spectroscopy provides a simple and direct method for monitoring the stability of the phase. Therefore, considerable attention has been focused on the kinetics of the growing and disappearance of the liquid crystal phase. For F10H10, Figure 7 shows the maximum dielectric loss factor as a function of time at 60.1, 59.3 and 32.5°C on cooling, respectively. For F12H8, Figure 8 shows the maximum dielectric loss factor as a function of time at 45.1, 46.2, 81.1, 82.3 and 82.6°C on heating, respectively. The growing of the liquid crystalline phase of these samples arises from the phase transition between the solid and liquid crystal(lc), at low temperature on heating, and/or at high temperature from the isotropic phase to lc on cooling. On the other hand, the reverse would be true for the disappearance of the liquid crystalline phase of these samples.

As shown in Figures 7 and 8, the time dependence of the maximum dielectric loss factor $(G/\omega)_m$ means the growing or disappearance rate of the liquid crystalline phase in the vicinity of the phase transition temperatures on heating or on cooling. In each experiment, we estimate the $(G/\omega)_m$ defined by the following equation,

$$(G/\omega)_m(t) = (G/\omega)_m(0)\exp(-t/\tau) \tag{6}$$

where $(G/\omega)_m(0)$ and $(G/\omega)_m(t)$ are the values of $(G/\omega)_m$ at the time $t = 0$ and t, and τ is the relaxation time.

TABLE II

Dielectric constants, ε_r and ε_u of β-relaxation in F10H10 and F12H8

Materials	T/°C	ε_r	ε_u
F10H10	60.8	4.980	4.776
F12H8	79.4	6.940	5.420

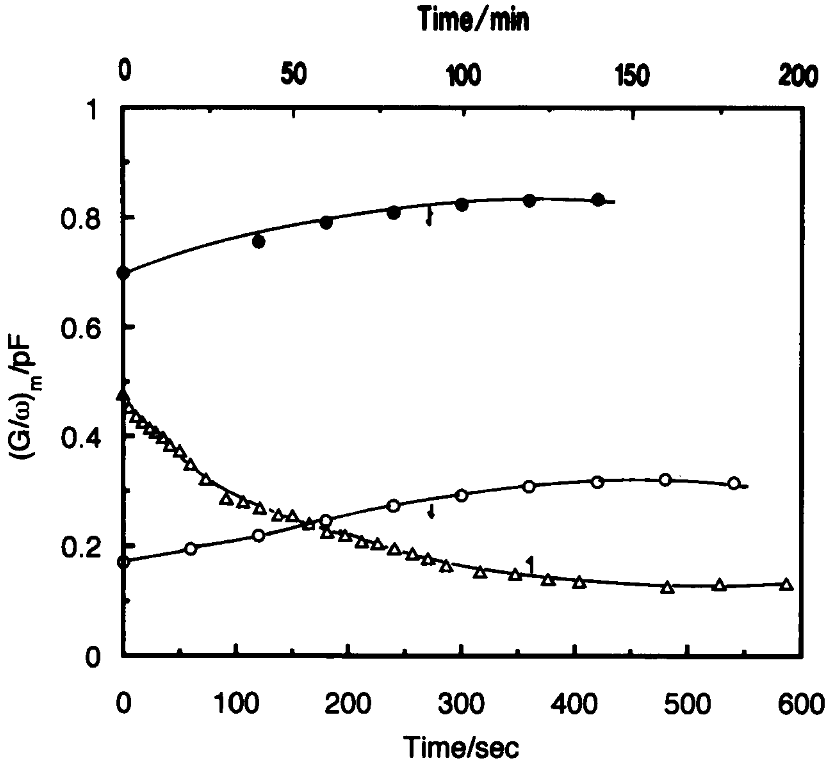

FIGURE 7 Time dependence of maximum dielectric loss factor, $(G/\omega)_m$ on cooling for F10H10. (●): 60.1°C, (○): 59.3°C and (△): 32.5°C.

The values of $\ln\{(G/\omega)_m(t)/(G/\omega)_m(0)\}$ are derived from the curves of Figure 7 using Equation (6) are plotted as a function of time, t/sec on cooling in the vicinity of two transition temperatures for F10H10 as shown in Figure 9. This relation gives a qualitative picture of the kinetics of the growing phase. The experimental points lie on a straight line at each temperature in the liquid crystalline phase and the relaxation time τ is given by the slope of the line using Equation (6). Figure 10 shows the same relationship for F12H8 on heating. Since plots in Figure 10 show some scatter from the solid straight line, the data seem to be followed by two straight lines rather than one line. The Transition is accomplished in two stages to the liquid crystalline phase for F10H10. The transition is achieved by a change in molecular tilt, together with a relative longitudinal displacement in adjacent molecules.[3] The transformation for F12H8 at lower temperatures on heating may be interpreted in the same manner as mentioned above. As shown by the dashed line, there is an intersection in the dashed lines at 700 sec as shown in Figure 10. The τ values obtained from the slope of these lines are summarized in Table III. Furthermore, it is obvious from the large value at 32.4°C for F10H10 and 41.6°C for F12H8 that the kinetics at low temperatures are different from those at high temperature on cooling.

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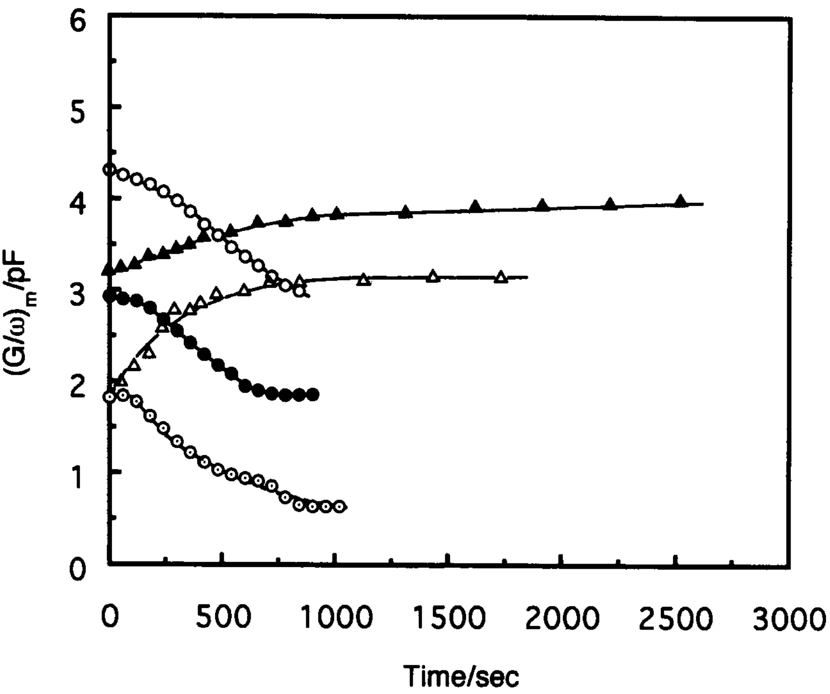

FIGURE 8 Time dependence of maximum dielectric loss factor, $(G/\omega)_m$ on heating for F12H8. (△): 45.1°C, (▲): 46.2°C, (○): 81.1°C, (●): 82.3°C and (⊙): 82.6°C.

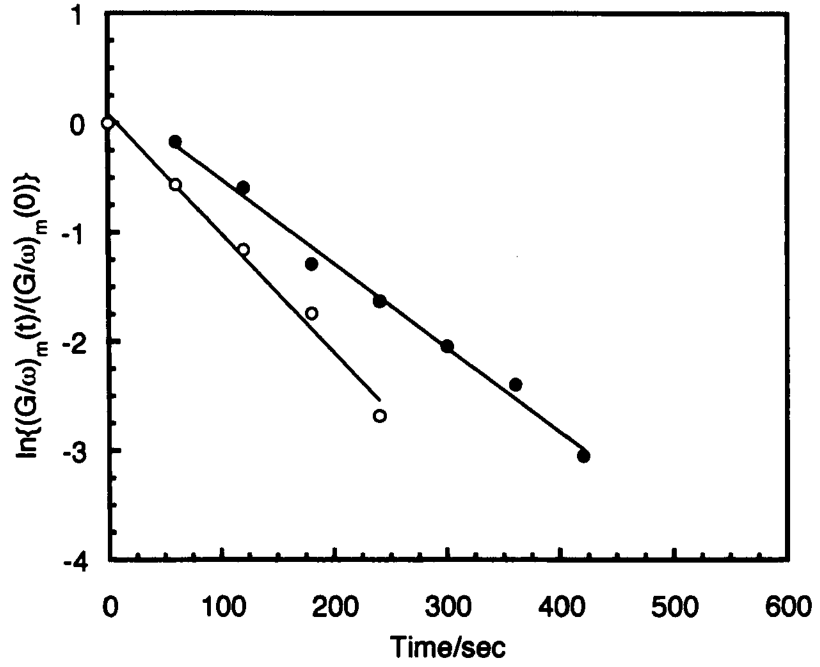

FIGURE 9 Plots of $\ln\{(G/\omega)_m(t)/(G/\omega)_m(0)\}$ against time. (●): 60.1°C and (○): 59.3°C.

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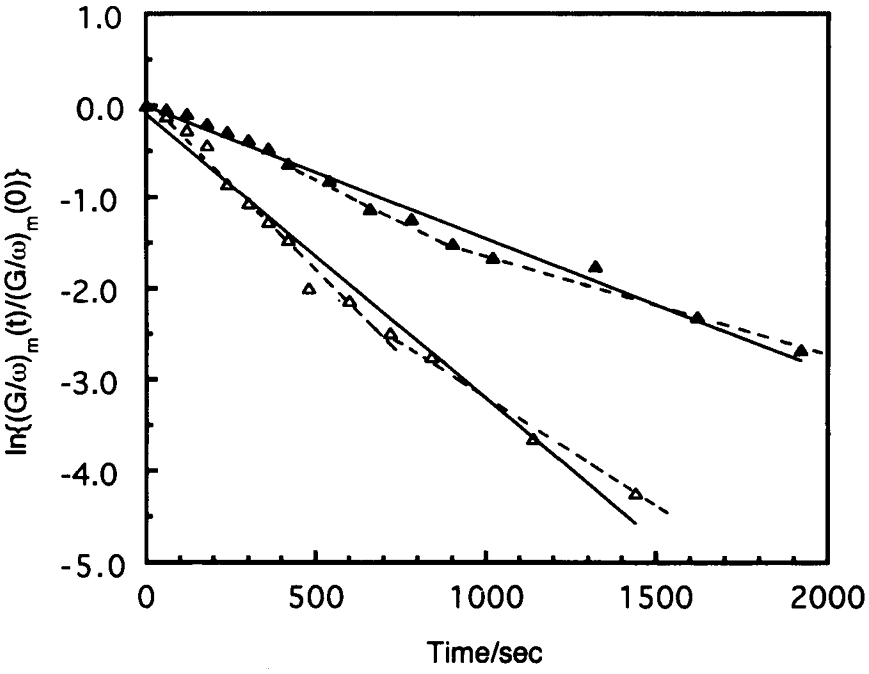

FIGURE 10 Plots of $\ln\{(G/\omega)_m(t)/(G/\omega)_m(0)\}$ against time. (▲): 45.1°C and (△): 46.2°C.

TABLE III

Kinetics of the height of maximum dielectric loss factor, $(G/\omega)_m$ in liquid crystal phase

Materials	T/°C	τ/sec[a]	T/°C	τ/sec[b]
F10H10	39.1	1.19×10^2	60.1	1.29×10^2
	60.0	1.18×10^2	59.3	9.71×10
	60.5	9.80×10	32.4	4.44×10*
F12H8	45.1	1.72×10^3	82.0	1.15×10^2
		1.40×10^3	81.1	8.77×10
	46.2	1.73×10^3	41.6	3.88×10*
		1.40×10^3		
	81.2	2.03×10^3		
	82.6	8.06×10^2		

[a] On heating, [b] On cooling, * Relaxation time in minutes.

These results lead to the conclusion that there is a difference in the rotational motion of the (CF_2) group based on the apparent activation energy for F10H10 and F12H8, and the growing and the disappearance of the liquid crystalline phase on cooling can be expected to display different kinetics.

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