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

Kazuo Araki [a], Katsuhiko Satoh [b] & Shoichi Kondo [b]
[a] Department of Materials Science and Engineering, Science University of Tokyo in Yamaguchi, Onodashi, Yamaguchi, 756, JAPAN
[b] Department of Chemistry, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo, 162, JAPAN

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DIELECTRIC BEHAVIOR OF SEMIFLUORINATED *n*-ALKANE ($F(CF_2)_n(CH_2)_mH$). II

KAZUO ARAKI
Department of Materials Science and Engineering, Science University of Tokyo in Yamaguchi, Onodashi, Yamaguchi 756, JAPAN

KATSUHIKO SATOH and SHOICHI KONDO
Department of Chemistry, Science University of Tokyo,
Kagurazaka, Shinjuku-ku, Tokyo 162, JAPAN

Abstract Dielectric measurements of diblock semiluorinated *n*-alkanes, ($F(CF_2)_n(CH_2)_mH$), n=10, m=6-14, were carried out in the frequency range 20Hz to 10^6 Hz and in the temperature range from the waxy solid to isotropic state. Dielectric loss curves were observed only in the mesophase/liquid crystal state. The activation energies for the materials of m=6-9 were smaller than those of m=11 and 12. Single relaxation process can explain the observations in liquid crystalline phase. An alternation in the total integrated intensity, $\Delta\varepsilon'$ in the vicinity of phase transition temperature was found against even/odd number of carbon in alkyl group.

INTRODUCTION

The compounds to form liquid crystalline phases have the mesogen of core ring and a flexible alkyl spacer. In spite of these conditions, the materials of semifluorinated *n*-alkanes $F(CH_2)_n(CH_2)_mH$ (referred to as FnHm in our notation) which have a linear aliphatic structure without a core ring have been known to undergo mesophase-mesophase, mesophase-solid and/or solid-solid phase transition1-5). The characterization of a series of FnHm has been studied by Raman spectroscopy, small-angle X-ray scattering (SAXS), wide-angle X-ray diffraction and Raman-active LAM1,2). The results of SAXS for the compounds of 2>n/m>1 reveal two different crystal packings, *i.e.* 1) two layers of interleaved molecules with overlapping hydrocarbon segments, 2) chain adjacently packed end-to-end in an antiparallel arrangement. For n/m<1, a crystal is composed of bilayered interleaved structure. The material of F10H10, *i.e.* n=m=10, has been found to present a liquid crystal-liquid crystal phase transition above room temperature. It is found that this transformation of structure is caused by a change in tilt angle, and that the spacing are different from each other in liquid crystal phases. Dielectric relaxation spectroscopy has been used for many years to study the molecular dynamics of the constituent chain to materials in liquid crystalline state⁶⁾. Nowadays, this method may be used as a powerful method for studying molecular dynamics. Consequently, the transformation as described above is expected to correlate with dielectric relaxation behavior. Recently, we have been reported the dielectric behavior of two semifluorinated *n*-alkanes, F10H10 and F12H8⁷⁾ . It was found that there was remarkable difference in the activation energy and dipole moment between two materials, even though these compounds have the same constitution except for two carbons linking to the fluorine or hydrogen atoms. The result of dielectric behavior lead to conclusion that there is a difference in the rotational motion of CF_2 group. In this work, we discuss the effect of the length of CH_2 in the materials, F10Hm (m=7 - 14) on dielectric relaxation behavior.

EXPERIMENTAL

Preparation of Materials

The synthesis and purification of 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-unhenicosafluoro-12-iodoeicosane (F10H10I) and 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7-8,8,9,10,10-unhenicosafluoroeicosane (F10H10) are given in detail and are generally representative of the preparations used for the semifluorinated *n*-alkanes employed in this study.

Perfluorodecyl iodide and 1-octene were placed in 100ml round-bottle flask equipped with stirbar, condenser, and nitrogen inlet. The mixture was warmed in a 90°C oil bath and AIBN of 10 g was added 5 times to the stirred solution at regular 10 minutes intervals. After the first few AIBN addition, a pink color due to free iodine persisted and the solution became homogeneous. After 30 minutes the bath temperature was raised to 100°C and additional AIBN was added, and then the product was cooled to room temperature. These materials obtained were purified by several recrystallizations from methanol/acetone and Kugelrohr distillations to give the product as a white powder.

The F10H10I intermediate and absolute ethanol (200 ml) were placed in a 1000ml three-neck round-bottle flask equipped with stirbar, condenser, bubbler, and gas-dispersion inlet. The stirred solution was brought to a gentle boil, hydrogen chloride gas was admitted in a slow stream, and zinc powder was added in small portions over the next 30 minutes. After all the zinc was consumed, the solution was cooled to room temperature and transferred to a separator funnel with the aid of hexane (250 ml). The phases were separated, and the organic phase was washed with water (250 ml) and saturated sodium hydrogen carbonate solution (50 ml) and then dried over magnesium sulfate, filtered, and concentrated to a white solid by rotary evaporation. This material was purified by recrystallizations from methanol/acetone and Kugelrohr distillation (25-130°C) to give the product as a white powder. The final products were identified with ^{1}H-NMR, FT-IR, mass spectroscopy, elemental analysis.

Dielectric measurements

The dielectric measurements were made in the range 20 to 1×10^6 Hz with a computer controlled HP4284A Precision LCR meter. The sample for dielectric measurements of F10Hm was prepared as a thin film of about 1.0 cm diameter and 100μm thickness, sandwiched between two metal electrodes whose were not pre-treated in any way. The spacing of cell was kept constant by means of a Teflon ring spacer. The equivalent parallel conductance G/ω was measured at each frequency and these are related to the dielectric loss factor ε'' , *i.e.* $G/\omega = \varepsilon'' C_0$, where C_0 is the interelectrode capacitance and ω is the angular frequency, *i.e.*, $2\pi f$/Hz. The whole apparatus was immersed in an oil bath so that the temperature of the sample could be accurately controlled to equilibrate the system every 10 minutes when temperature was changed.

RESULTS AND DISCUSSION

The thermal properties obtained by DSC are summarized for F10Hm in Table 1. These values agree very closely with the published data. Figures 1 and 2 show the dielectric loss curves as a function of frequency for F10H6 and F10H7, respectively. As shown in figures, maxima in dielectric loss curves for both samples appear except at the temperature near the transition, and they remain relatively invariant in the temperature range of the liquid crystalline state except that the peak is shifted to higher frequencies with increasing temperature. No maxima in the loss curves appeared in the isotropic state. Similar temperature dependency of loss curves was obtained for other materials in the mesophase. The loss curves of the F10H13 and F10H14 could not be obtained because the both samples do not exhibit a mesophase as shown in Table I. Figure 3 shows the variation of the peak height in loss curves for the materials from m=6 to 12. The peak height in loss curves decreases with an increase in the methylene length. It should be noted that the peak height of loss curves for F10H6 and F10H8 is larger than that of F10H7. This result would be interpreted by the slight

TABLE I Phase transition temperatures (°C)

Materials	K[a]	M[b]	I[c]
F10H6	33.0	47	
F10H7	36.6	53.9	
F10H8	36.3	59.5	
F10H9	38.7	63.2	
F10H10	48.5	65.7	
F10H11	56.3	67.6	
F10H12	66.2	68.6	
F10H13		67.0	
F10H14		69.0	

a: Crystal state, b: Mesophase/Liquid crystalline state, c: Isotropic state.

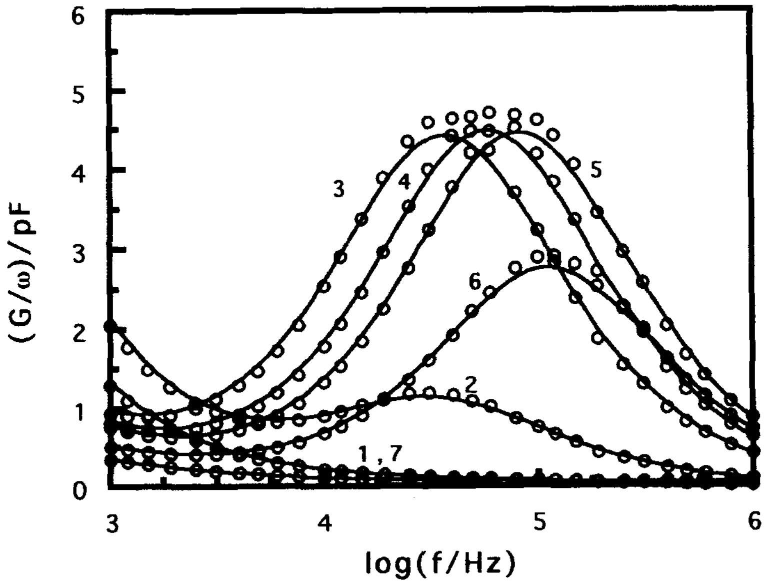

FIGURE 1 Frequency dependence of loss factor,G/ω for F10H6 in the temperature range 25.0 to 44.8°C. Curves 1-7 correspond to 25.0, 29.0,31.1,37.1, 41.6,43.6 and 44.8°C.

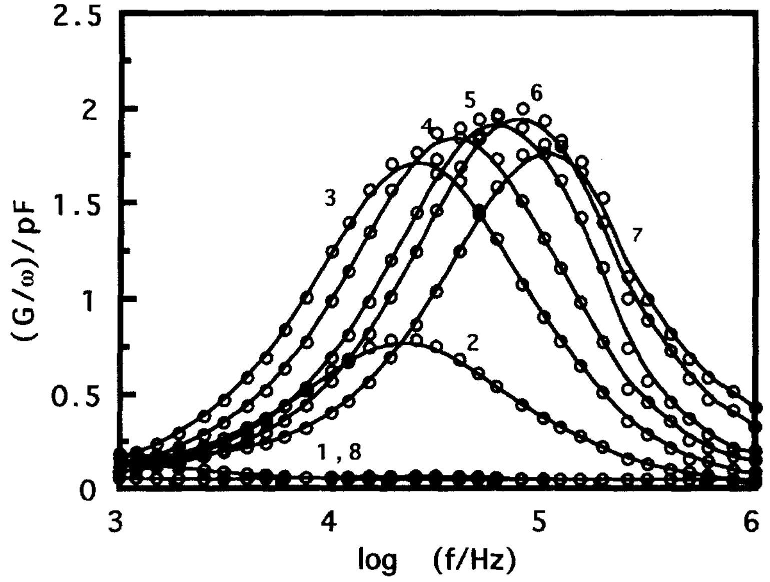

FIGURE 2 Frequency dependence of loss factor, G/ω for F10H7 in the temperature range 30.6 to 52.3°C. Curves 1-8 correpond to 30.6, 31.6,33.6,39.0,47.6,44.3,50.1,52.3°C.

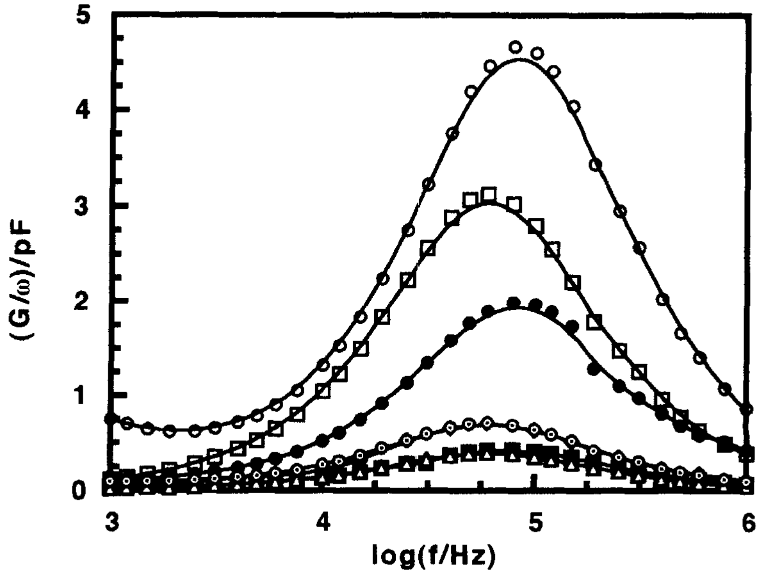

FIGURE 3 Frequency dependence of loss factor,G/ω in the vicinity of phase transition temperatures for F10Hm. (○):6;41.6°C,(●):7;49.0°C,(□):8;52.2°C,(■):9;55.8°C, (◇):10;62.3°C,(△):11;60.6°C,(⊙):12;60.9°C.

conformational difference in $(CH_2)_m$ segment. It is generally well known that the thermal behavior shows a pronounced alternation as the number of carbon atom in the chain end increases. It is also expected in a dielectric relaxation behavior similar to the thermal behavior. Figure 4 shows Arrhenius plots for all materials exhibiting the mesophase. The apparent activation energies were found to be 57.4, 67.9, 74.8, 98.3, 141.3 and 133.8 kJ/mol for m=6 to 11, respectively. Consequently the activation energies increased with increasing the length of methylene group. The values of activation energy in the case of n/m>1 are smaller than those for n/m<1. Robolt *et al.*[1)] have shown that there are two different structures depending on the ratio of segment length for fluorocarbon and hydrocarbon in the case of n=12. The difference in the activation energy seems to be arised from different crystal packings between n/m<1 and n/m>1.

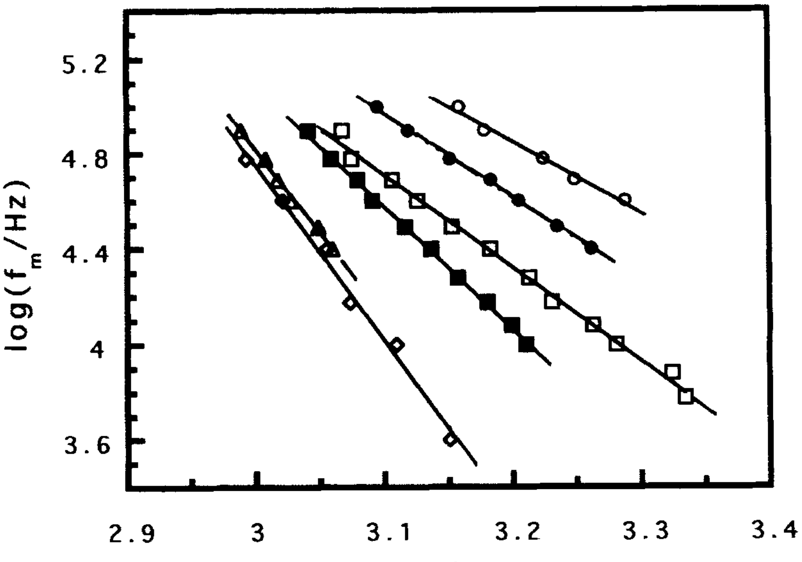

FIGURE 4 Plots of log f against 1/T for F10Hm. (○): m=6, (●): m=7, (□): m=8, (■): m=9, (◇): m=10, (▲): m=11

To evaluate dipole moment for materials in this work, the total integrated intensity, $\Delta\varepsilon'$ ($=\varepsilon'_r - \varepsilon'_u$) is employed in the evaluation of dipole moment as a matter of convenience. Consequently, we tried the Cole-Cole plots to obtain

ε'_r and ε'_u , respectively, where ε'_r is dielectric constant at low frequency, and ε'_u is dielectric constant at high frequency. Figure 5 shows Cole-Cole diagrams for m=6,7,8 and 9, respectively. From Figure 5, the values of $\Delta\varepsilon'$ decrease with increasing the length of alkyl group, and the molecular motion of these materials is explained to be a single relaxation process.

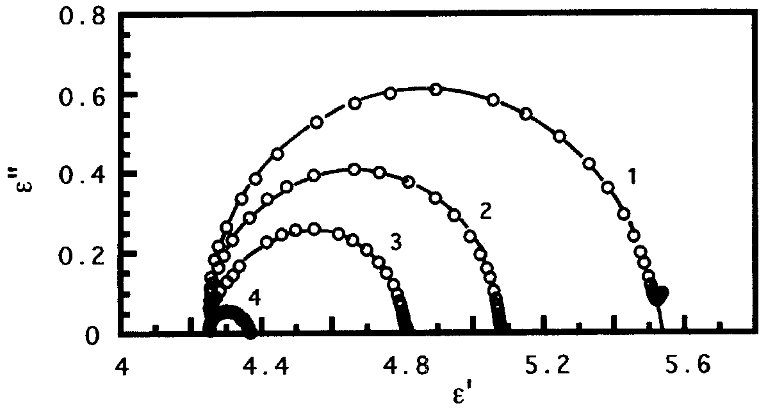

FIGURE 5 Cole-Cole diagram for F10Hm. Curves 1-4 correspond to m=6, 7, 8, and 9.

Figure 6 shows the total integrated intensity, $\Delta\varepsilon'$ obtained from Cole-Cole plots against the number of carbon of methylene group in materials. It was found that the value of $\Delta\varepsilon'$ changes either rise or fall with alternation like a temperature behavior of phase transition. This result suggests that there is appreciable interaction between the hydrocarbon group for m=6-8 and $(CF_2)_{10}$ group. A plot of transition temperatures for the number of carbon atoms in hydrocarbon group from data in Table I is shown in Figure 7. However, a clear odd-even phenomenon do not appear in the transition temperature.

The total integral intensity correlated to the dipole moment suggests that the different molecular packings in the mesophase are formed for the materials with the odd or even carbon number in the hydrocarbon segment.

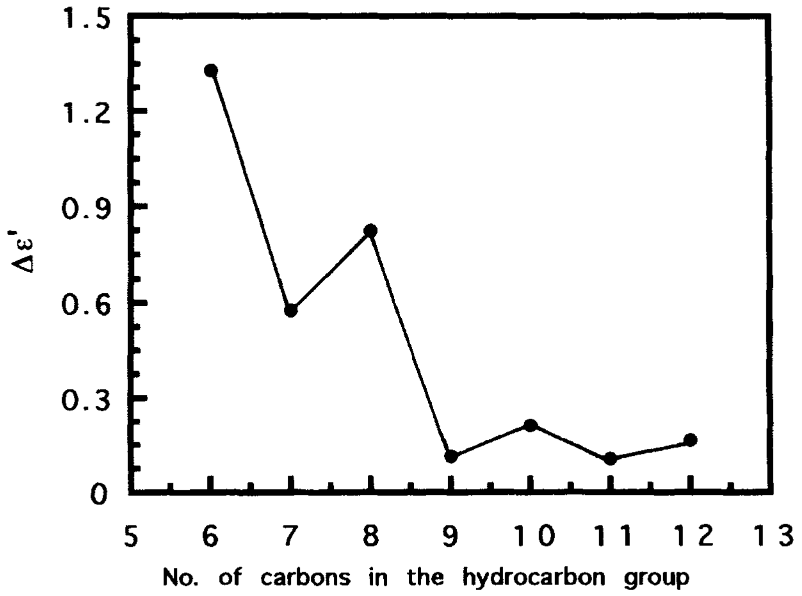

FIGURE 6 The total integrated intensity, Δε' (=ε'_r - ε'_u) for F10Hm.

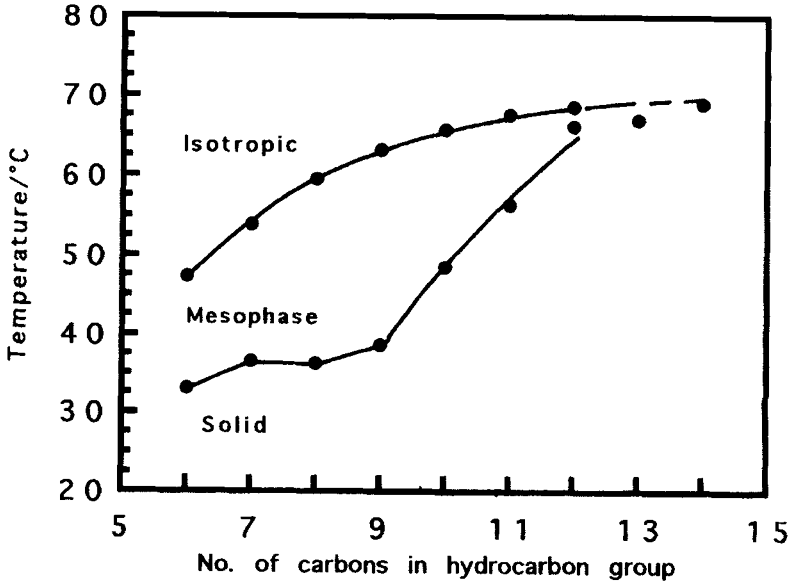

FIGURE 7 Transition temperatures for F10Hm.

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