

^1H Nuclear Magnetic Resonance of a Ferroelectric Liquid Crystalline System

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We used ^1H nuclear magnetic resonance (NMR) to study the phase transitions and molecular dynamics in a characteristic ferroelectric liquid crystal with a carbon number $n = 7$, S-2-methylbutyl 4-*n*-heptyloxybiphenyl-4'-carboxylate (C7). The results were compared with those of our recent work on S-2-methylbutyl 4-*n*-octanoyloxybiphenyl-4'-carboxylate (C8), with a carbon number $n = 8$. While the recrystallization and isotropic phase transitions exhibited a first-order nature in the ^1H NMR spin-lattice and spin-spin relaxation measurements, a second-order nature was shown at the Sm-*A* - Sm-*C*^{*} liquid crystalline phase transition. A soft-mode anomaly arising from the tilt angle amplitude fluctuation of the director, of which only a hint had been noticed in the C8 system, was manifested in the C7 system at this transition.

Keywords : nuclear magnetic resonance, ferroelectric liquid crystalline system, phase transitions

1. Introduction

Since the discovery of liquid crystals, numerous organic substances have been synthesized. In order to understand the phase transitions and molecular orientational order in liquid crystals, various types of study, including nuclear magnetic resonance (NMR) and electrical field effect, have been conducted. Thermotropic liquid crystals can have nematic, smectic and cholesteric phases at different temperatures [1-4]. In contrast to the nematic phase that possesses orientational order without any positional order, the smectic phase possesses both minimal and orientational orders. In the smectic *A* (Sm-*A*) phase, the preferred direction of the long molecule axis (director) is parallel to the planar normal, and is tilted with respect to the layer planes in the smectic *C* (Sm-*C*) phase. When the molecules possess chirality in a Sm-*C* phase, the phase is denoted as "Sm-*C*^{*}". Two distinct collective fluctuations of the tilt angle can take place. One of them, associated with the phase (azimuthal angle) of the tilt angle (the "Goldstone mode") is active in the Sm-*C*^{*} phase, and the other, associated with the tilt angle amplitude (the "soft mode"), appears around the Sm-*A* - Sm-*C*^{*} transition temperature.

Spontaneous polarization was first observed in the chiral smectic *C*^{*} (Sm-*C*^{*}) phase in *p*-(*n*-decyloxy) benzylidene-*p*-amino-(2-methylbutyl)cinnamate (DOMBC) liquid crystal [5, 6]. While the electric permittivity obeys Curie-Weiss law in this phase, the origin of its ferroelectricity is the molecular chiral asymmetry [1, 7]. There is no spontaneous polarization in Sm-*A*, but an electroclinic effect is shown under electric field [8]. Since molecular arrangement and the reflective index can easily be changed by applying either an electric field or a magnetic field, nematic liquid crystals are used as electro-optical devices such as displays and monitors [1, 9]. The ferroelectric liquid crystals show very fast operating time with low dielectric constants [1].

While the soft mode has been detected by means of dielectric [10] and optical measurements [11], anomalies associated with it have not been clearly observed by NMR [12], which is an effective means of investigation of the critical dynamics near the phase transitions and the behavior of particular nuclei in the structure [13]. In a recent work, we studied a ferroelectric liquid crystal, S-2-methylbutyl 4-*n*-octanoyloxybiphenyl-4'-carboxylate (C8) with a carbon number $n = 8$, in which a characteristic polarization inversion was sensitively reflected in the ^1H NMR measurements [12]. In the present work, we use NMR to investigate the phase transitions and molecular

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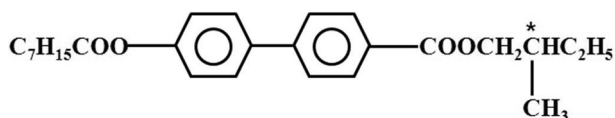


Fig. 1. Structure of the S-2-methylbutyl 4-*n*-heptyloxybiphenyl-4'-carboxylate (C7) ferroelectric liquid crystal.

dynamics in a ferroelectric liquid crystal with a carbon number $n = 7$, S-2-methylbutyl 4-*n*-heptyloxybiphenyl-4'-carboxylate (C7) (Fig. 1), showing an isotropic - Sm-*A* - Sm-*C** - recrystallization phase transition sequence. The isotropic phase transition, the Sm-*A* - Sm-*C** liquid crystalline phase transition, and the re-crystallization phase transition take place at temperatures of 62, 38, and 16 °C, respectively. The C7 and C8 compounds exhibit considerably different recrystallization temperatures.

2. Experiment

The S-2-methylbutyl 4-*n*-heptyloxybiphenyl-4'-carboxylate (C7) ferroelectric liquid crystal sample used in this work was synthesized and studied as reported in the literature [12, 14]. The ¹H NMR spin-lattice relaxation time (T_1) and spin-spin relaxation time (T_2) measurements were made on the ferroelectric liquid crystalline sample with decreasing temperature by using a pulsed spectrometer operating at 45 MHz [15].

3. Results and Discussion

Fig. 2 shows the temperature dependence of the ¹H NMR spin-lattice relaxation time, in which distinct changes are noticed at the transition temperatures. In particular, discontinuous changes characteristic of a first-order transition occurred at the recrystallization and isotropic phase transition temperatures. On the other hand, the Sm-*A* - Sm-*C** phase transition showed a second-order nature. At this phase transition temperature, T_1 showed a weak divergent behavior in the critical, which was attributed to critical slowing down associated with the soft mode. The soft mode, which is the collective mode at the Sm-*A* - Sm-*C** phase transition, was attributed to fluctuations of the tilt angle (electroclinic effect). Detection of the soft mode may be difficult when the Goldstone mode, occurring only in the Sm-*C** phase, is dominant [10] and is possible only when the detection frequency is within the observable frequency region of the soft mode [11]. The change in T_1 according to temperature may arise from the rotational motion of methyl groups, which is related to the increase in the Sm-*A* orientational order on cooling.

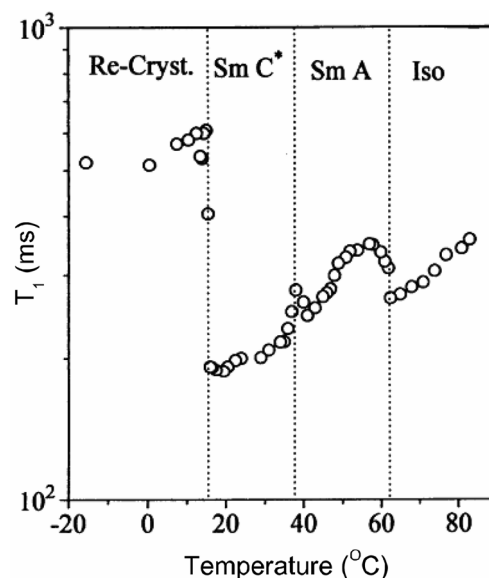


Fig. 2. Spin-lattice relaxation time (T_1) of the C7 ferroelectric liquid crystal as a function of temperature.

An abrupt increase in T_1 at the recrystallization phase transition temperature could arise from the reduction of the amplitude fluctuations due to the increased tilting angle on cooling. The orientational and positional orders both exist in the Sm-*C** but the orientational order disappears with recrystallization on cooling. In the (isotropic) liquid phase, the activation energy was measured as 3.0 meV from the temperature-dependent T_1 in the fast-motion limit [12, 16].

It is interesting to compare the results on the C7 ferroelectric liquid crystal in this work with those on the C8 system in our previous work [12]. In contrast to the C8 sample that exhibited a characteristic polarization inversion, the C7 sample displayed no polarization inversion associated with the conformational change, indicating a chain-length effect. On the other hand, an anomaly attributed to the soft mode, of which only a hint had been noticed in the C8 sample, was manifested in the C7 system, as was a peculiar chain-length effect associated with the conformation of the hydrocarbon chains [14]. Fig. 3, showing the spin-spin relaxation time as a function of temperature, provides information on the slow dynamics which may be difficult to detect by the T_1 measurements alone [17]. As in the case of the temperature-dependent T_1 , the recrystallization and isotropic phase transitions exhibited a discontinuity indicative of a first-order nature. On the other hand, a continuous change, with an anomaly ascribed to the soft mode, was noticed at the Sm-*A* - Sm-*C** liquid crystalline phase transition temperature. The decrease in T_2 (increase in the spin-spin

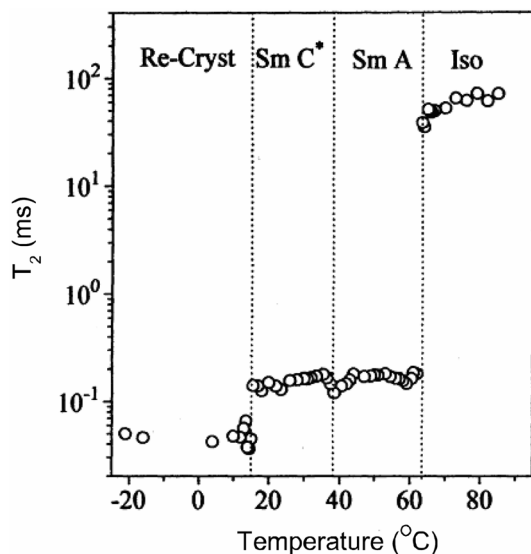


Fig. 3. Spin-spin relaxation time (T_2) of the C7 ferroelectric liquid crystal as a function of temperature.

interaction) at the recrystallization phase transition was attributed to the disappearance of the orientational order.

In summary, S-2-methylbutyl 4-*n*-heptyloxybiphenyl-4'-carboxylate (C7) ferroelectric liquid crystal with a carbon number $n = 7$ was studied by ^1H nuclear magnetic relaxation time measurements. The results were compared in terms of the chain-length effects with those of our recent work on S-2-methylbutyl 4-*n*-octanoyloxybiphenyl-4'-carboxylate (C8) with a carbon number $n = 8$. Discontinuities characteristic of first-order phase transitions were observed at the isotropic and recrystallization transitions, similar to those of the C8 system. However, a peculiar, second-order anomaly attributed to the soft mode, of which only a hint had been noticed in the C8 system, was manifested at the Sm-A - Sm-C* liquid crystalline transition of the C7 system. In further contrast to the C8 system, no polarization inversion was observed.

Acknowledgements

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