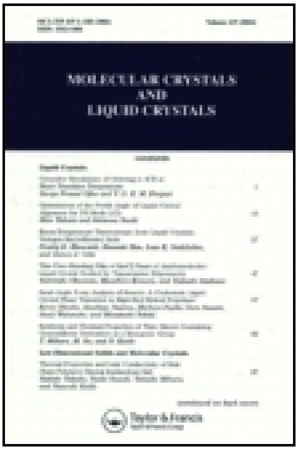

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A Pulsed NMR Study of Molecular Motions and Ordering in Ethyl-[*p*-(*p*-methoxybenzylidene)-amino]-cinnamate†‡

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Abstract—Pulsed nuclear magnetic resonance techniques were used to study the phase transitions in ethyl-[*p*-(*p*-methoxybenzylidene)-amino]-cinnamate from the room temperature solid phase through the isotropic liquid. Both the proton spin-lattice relaxation time and second moment were observed to change near each of the phase transitions. These quantities exhibited anisotropies in the smectic *B* phase similar to those observed for a typical nematic ordered in an electric field. The molecular order was stable in the smectic *B* phase, while molecular reordering was observed in the smectic *A* phase in the presence of moderate magnetic fields.

1. Introduction

Nuclear magnetic resonance has been widely employed in the study of liquid crystals, in particular, in the study of nematic liquid crystals.(1–11) Previous work has been especially concerned with the orientational dependence of the proton spin-lattice relaxation time and line shape of nematic liquid crystals ordered in electric fields and in other effects of electric fields upon these quantities.(10,11) Because of this interest in anisotropic relaxation mechanisms, a study of several *smectic* materials has been undertaken. Of particular interest here is the possibility of " freezing-in " order in a smectic phase by cooling from the nematic in the presence of a magnetic or electric field. It was hoped that a careful study of several properties

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of these materials would clarify the relationship between the various smectic modifications. In particular, we wished to see whether pulsed nuclear magnetic resonance would provide a useful tool for studying the phase transitions and pre-transitional phenomena; how well ordered the smectic phases are; the permanence of this order; and, of course, to investigate the general problem of nuclear spin-lattice relaxation in these phases.

The present work is a study of one material and touches upon several of these points. The material chosen for this study was ethyl-[*p*-(*p*-methoxybenzylidene)-amino]-cinnamate, abbreviated EMC. This material, whose structure is shown in Fig. 1, was selected because it exhibits several liquid crystal phases and because it has received some attention from other investigators using other techniques (cf. Ref. 12 and Refs. 1–11).

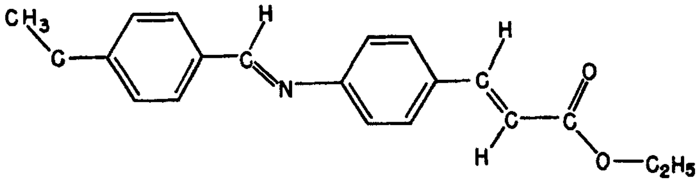

Figure 1. Molecular structure of EMC.

Figure 2 shows the various phase transitions that are possible for EMC. The temperatures shown for the phase transitions are taken from the data of Demus and Sackmann.(13) Note that EMC exhibits two distinct smectic modifications as well as a nematic phase and two solid phases and that several of these phases may coexist over certain temperature ranges.

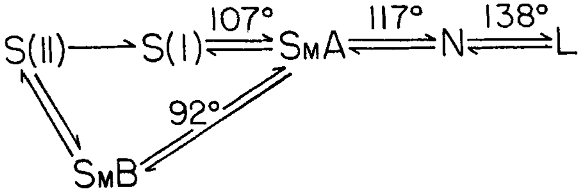

Figure 2. Phase transitions in EMC.

2. Experiment

The samples used for the present work were obtained commercially(14) and further purified by repeated recrystallization from ethynol. The purified samples were prepared as finely divided powder and sealed in evacuated 7 mm pyrex tubes. The samples were heated by forced convection in a closed probe. The probe heaters were electronically regulated giving temperature stability of better than ± 0.2 °C and thermal gradients of less than ± 0.1 °C over the sample volume.

The pulsed nuclear magnetic resonance spectrometer used was constructed in our laboratory following the general design discussed in Refs. 15–17. Because the transmitter section is untuned, the recovery time of the spectrometer is quite short, for example, less than 4 μsec at 30 MHz. This feature is especially useful in making measurements of the moments of the resonance lines.

The second moment data were extracted from the free induction decay using the method discussed in Sec. 3, below. The free induction decay signals were acquired on a Nicolet Instrument model 1070 signal averaging computer which provided a digital record of the data for computer analysis at 1 μsec intervals along the free induction decay.

All spin-lattice relaxation time, T_1, measurements were made using a saturation burst of 90° pulses followed by a single 90° pulse. All T_1 and second moment measurements were made at 30 MHz, corresponding to a magnetic field of approximately 7 kG.

3. Analyses and Results

In the temperature range where the two solid phases coexist (below ~80 °C), it was observed that the relaxation was non-exponential. A good fit to this non-exponential process was a sum of two single exponentials as shown in Eq. 1. If the amplitude of the free induction decay following the second pulse in a 90°–90° pulse T_1 measurement is denoted by $S(t)$, then the reduced signal $y(t)$ is given by:

$$y(t) = \frac{S(\infty) - S(t)}{S(\infty)} = A \exp(-t/T_1{}^A) + B \exp(-t/T_1{}^B) \qquad (1)$$

where $S(\infty)$ is the equilibrium signal observed for large pulse separation t, A and B are the relative abundances of the two solid species, and $T_1{}^A$ and $T_1{}^B$ are the respective relaxation times associated with these species.

The data were reduced by fitting several points $y(t)$ at large t to a single exponential. This fit provides trial values for the larger relaxation time and associated relative abundance. This trial fit was then subtracted from the original data, and the resulting values of $y(t)$ were fit to a single exponential. This fit yields trial values for the smaller relaxation time and associated relative abundance. The trial function thus obtained was then subtracted from the original data, yielding a better approximation to the longer relaxation data. This process was iterated, and provided a convergent fit to most of the data. This problem has been explored in some detail and is discussed elsewhere.⁽¹⁸⁾

Measurements of the second moment of the resonance line provide additional information about the molecular ordering of a liquid crystal. The formalism developed for solids by Van Vleck⁽¹⁹⁾ can be modified to an appropriate form. The elements B_{jk} in Van Vleck's expression for the second moment:

$$\langle M_2 \rangle \propto \sum_{j,k} B_{jk}^2, \tag{2}$$

have been transformed by Webber⁽²⁰⁾ to a coordinate system applicable to liquid crystals as follows:

$$B_{jk} \rightarrow \langle (\tfrac{3}{2}\cos^2\gamma_{jk} - \tfrac{1}{2})/r_{jk}^3 \rangle (\tfrac{3}{2}\cos^2\phi - \tfrac{1}{2}) \times (\tfrac{3}{2}\cos^2\zeta - \tfrac{1}{2})(3\cos^2\theta - 1), \tag{3}$$

where γ_{jk} is the angle between the para-axis and the vector r_{jk} connecting the j^{th} and k^{th} spins, ϕ is the angle between the para- and molecular axes, ζ is the angle between the molecular axis and the director, and θ is the angle between the director and the magnetic field. Thus, for example, the measurement of the orientational dependence of the second moment in the presence of an electric field, or some other non-magnetic ordering field, provides information about the orientation of the director with respect to the magnetic field.

Since the free induction decay and the absorption line shape are related by a Fourier transform, it can be shown⁽²¹⁾ that the moments, M_N, of the resonance line shape are related to the coefficients of an even power series expansion of the free induction decay, $G(t)$, by:

$$G(t) = \sum_{\substack{N \\ \text{even}}} \frac{M_N t^N}{N!}\,. \tag{4}$$

This power series fit was used to compute the second moments in the data that follow. The fit was carried to high order to minimize the influence of high frequency noise on the second moment. In most cases terms through t^{20} were retained where there were sufficient points to yield a non-singular fit. These data were acquired on a signal averaging computer, and high frequency noise was reduced using polynomial smoothing.

These techniques for the measurement and analysis of T_1 and the second moment were applied to EMC, and the results of the T_1 measurements are shown in Fig. 3. Note that T_1 changes near

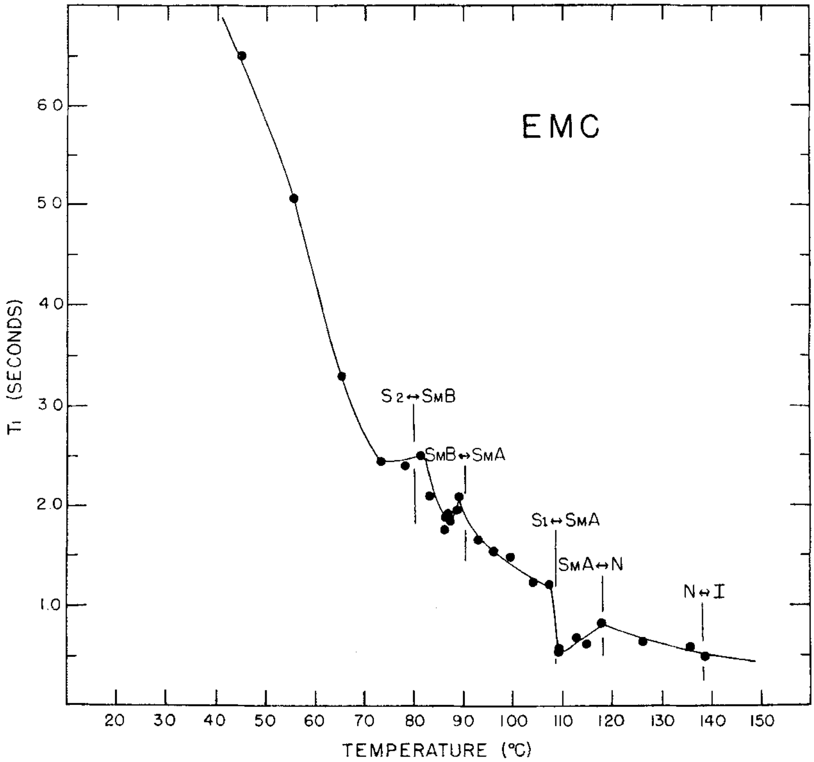

Figure 3. Proton spin-lattice relaxation time at 30 MHz vs. temperature. Data taken with temperature increasing monotonically.

each of the phase transitions. In most cases T_1 shows an increase indicating either a reduction in motional narrowing in the sample or an orientational averaging of the internuclear vectors near these transitions.

Figure 4 shows the second moment of the proton resonance absorption in EMC as a function of temperature. Here, the phase transitions are clearly evidenced by rather large changes in the second moment near the transitions, supporting the conclusions drawn from the T_1 data.

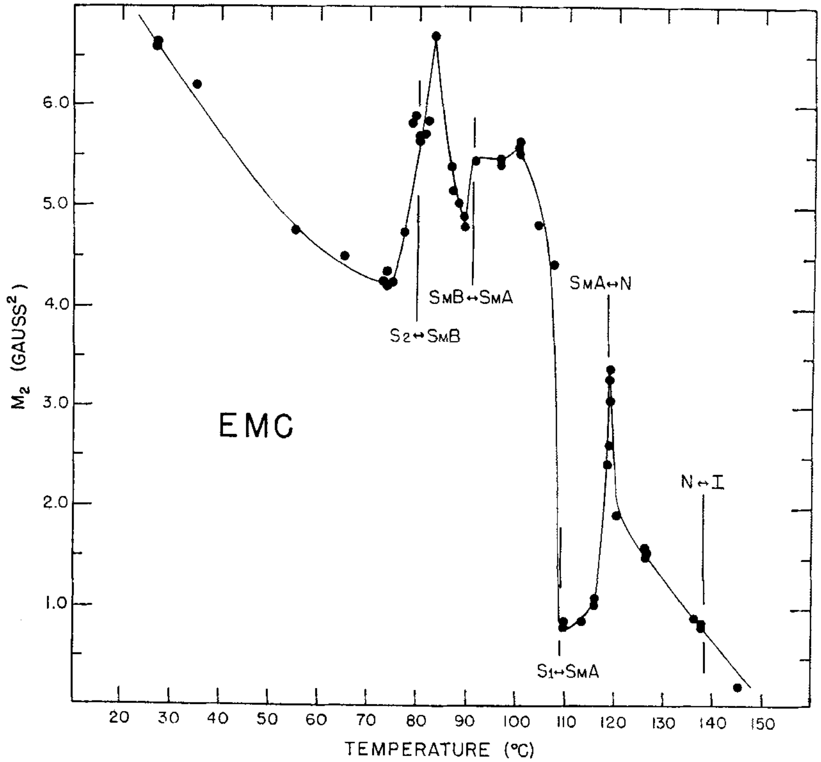

Figure 4. Proton second moment vs. temperature. Data taken with temperature increasing monotonically.

Since both T_1 and the second moment depend to some degree on the sample history, the data in Figs. 3 and 4 were taken on a single sample. This sample was prepared as a finely ground powder from freshly recrystallized material, and the temperature was increased monotonically, the temperature was varied slowly, and the temperature was allowed to stabilize for approximately ½ h at each point before a measurement was attempted. The data in Figs. 3 and 4 were acquired in a single series of measurements of approximately 52 h duration.

Measurements of T_1 and the second moment in a sample of EMC ordered in the nematic phase and cooled to the smectic *B* in the presence of a magnetic field showed an orientational dependence as the magnetic field was rotated with respect to the original ordering direction. This anisotropic behavior was similar to that observed for nematic materials ordered in electric fields.(10,11) The order in the smectic *B* phase was stable for the several hour duration of these experiments.

For EMC ordered in the nematic phase and cooled to the smectic *A* phase in the presence of a magnetic field, however, it was noted that T_1 and the shape of the free induction decay varied with time. Figure 5 shows the free induction decays for several orientations of the magnetic field with respect to the original ordering direction. These data were taken over a very short period of time to minimize any variations. Note that the free induction decays are quite similar to those observed for a typical nematic liquid crystal and exhibit a similar orientational dependence. This indicates that the original degree of ordering obtained in cooling through the nematic–smectic *A* transition was reasonably complete.

Since it was clear that reordering was taking place, an experiment was performed to measure the time required for this reorientation to occur. A sample was ordered in the nematic phase and cooled to the smectic *A* in a magnetic field of approximately 7 kG. The magnet was then turned through an angle of 55°, corresponding to the direction of maximum width of the free induction decay, and the free induction decay was recorded as a function of time. Since there was insufficient time to acquire statistically significant data for moment calculations, some other measure of the orientation was needed. The time required for the free induction decay to fall to 1 e^{th} of its original amplitude was measured, and the results are shown in Fig. 6. This rough measure of the spin–spin relaxation time T_2 shows a relatively rapid return of the direction of molecular alignment to the direction of the magnetic field. This unexpected result

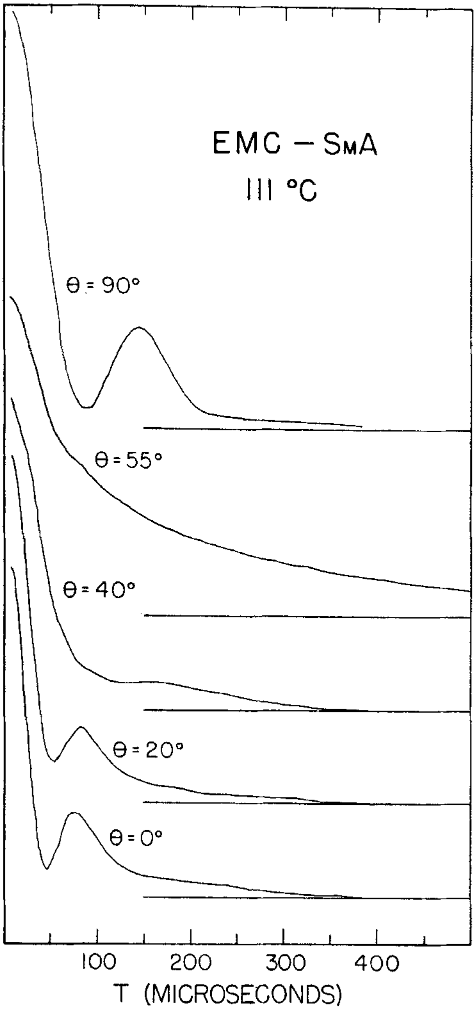

Figure 5. Free induction decays for several orientations of the magnetic field with respect to the original ordering direction in the smectic *A* phase.

indicates that molecular ordering in the smectic *A* modification is not stable in EMC, in marked contrast to that in the smectic *B*. Experiments are currently under way in our laboratory to determine the mechanism for reordering and to determine the dependence of the reordering time on impurities and on such parameters as the rate of cooling through the phase transition.

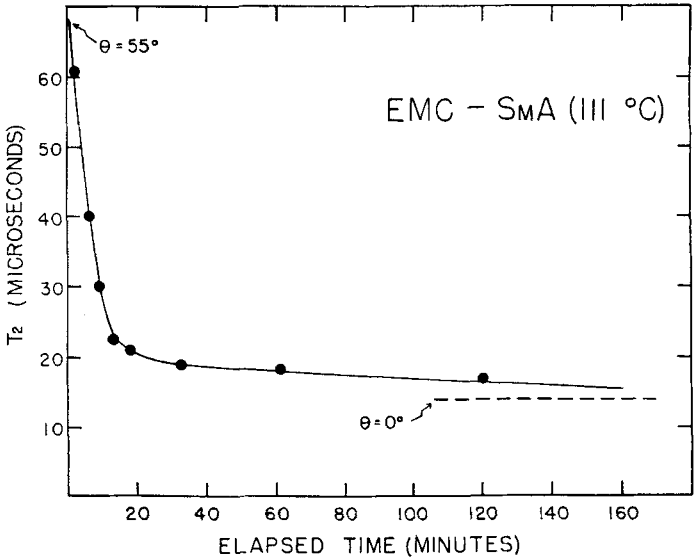

Figure 6. T_2 (see text) vs. reordering time in the smectic *A* phase.

4. Conclusions

The data show that both the proton spin-lattice relaxation time and the second moment show significant changes near the various phase transitions in EMC. These parameters clearly mark the phase transitions including those below the visual melting point. The orientational dependences of both T_1 and the second moment in the smectic *B* modification are similar to those observed in nematic liquid crystals ordered in electric fields. The order in the smectic *B* is found to be stable, while that in the smectic *A* is observed to be relatively unstable.

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