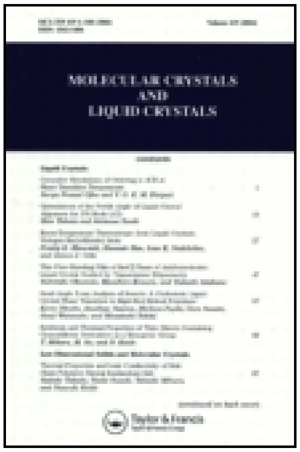

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K. S Krishnamurthy [a] & D. Krishnamurti [a]
[a] Department of Physics, University of Mysore, Mysore

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Proton Magnetic Resonance Absorption in n-Butyl Stearate

K. S KRISHNAMURTHY and D. KRISHNAMURTI

Department of Physics
University of Mysore
Mysore

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Abstract—The proton magnetic resonance absorption in *n*-butyl stearate has been investigated for the range −196° to 24 °C. The second moment data are discussed and the amplitudes of molecular rotations at different temperatures are calculated.

1. Introduction

The thermal, optical, X-ray, infrared and NMR behaviour of some stearates in their different condensed phases has been reported by us recently.[1] It was observed that liquid *n*-butyl stearate, on cooling, transforms into a translucent waxy mass at 26.1 °C, and this phase is referred to as the α_1-phase. At lower temperatures the substance exhibits two crystalline phases viz., α_2 and α_3, the transition points for $\alpha_1 \rightarrow \alpha_2$ and $\alpha_2 \rightarrow \alpha_3$ being respectively 14.8 °C and 11.1 °C. The studies revealed that the α_1-phase belongs to the category of ordered smectic mesophase in which there is hexagonal close packing of the long chain molecules in the smectic layers. The X-ray Debye-Scherrer patterns, infrared spectra and the preliminary studies on wide-line proton resonance enabled us to conclude also that in the α_1-phase the molecules execute rotational motions about their long axes. In the following we report the results of proton resonance studies undertaken to compare the second moment values in the α_1 and α_2 phases with the rigid-lattice value and estimate the extent of molecular rotation at different temperatures.

2. Experimental

The derivative curves of proton resonance were obtained using a Varian Associates Model 4200-B NMR spectrometer equipped with a variable temperature unit. The signals were recorded by a slow variation of the magnetic field, keeping the frequency of the R.F. oscillator constant at *ca.* 7.5 Mc/s. About 2 ml of the sample (of purity better than 99%) was degassed under vacuum for several hours before sealing the sample tube. In the solid state the material was polycrystalline. It was necessary to maintain the sample at the required temperature for at least an hour to obtain thermal equilibrium.

The second moments of the derivative curves were calculated using Simpson's method of numerical integration and the values were corrected for the effects of field modulation.[2] At least two sets of curves were obtained for each temperature to confirm their reproducibility and these were used to compute the second moments. The average values of the second moments at different temperatures are shown in Table 1.

TABLE 1

Temperature (°C)	24	23	16	12	10	0	−50	−195.8
Phase	α_1	α_1	α_1	α_2	α_3	α_3	α_3	α_3
Second moment (gauss^2)	5.0	5.4	9.0	15.1	16.0	20.1	22.5	27.0

3. Discussion

It is useful here to refer briefly to the texture of the material in the α_1 and α_2 phases, as observed under a polarizing microscope. Figures 1(a) and 2(a) reproduce the texture of the α_1-phase as seen between crossed polars. In Fig. 1(a) the dark area represents the homoeotropic region wherein the molecules are arranged with their long axes perpendicular to the supporting surface viz., the microscope slide and coverslip. The bright areas are the end-on

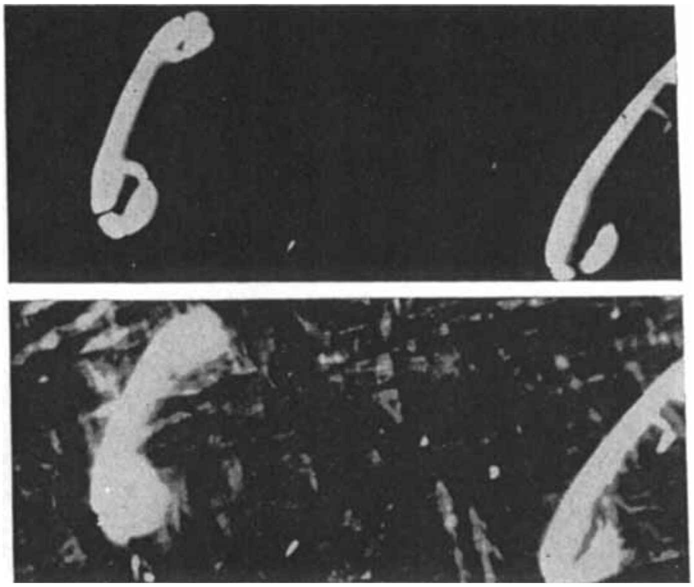

Figure 1. (a) Birefringent tapes in the α_1-phase (16 °C). Crossed polarizers. 450 ×. (b) Crystalline texture in the α_2-phase (13 °C). Crossed polarizers. 450 ×.

view of the homoeotropic plates and they appear as tapes. In Fig. 2(a), the tape has formed around an air bubble and outside the tape the dark homoeotropic region is seen. By the use of a full wave retardation plate as also a quartz wedge, it has been confirmed that the molecules are arranged with their long axes perpendicular to the length of the tapes. In other words, where the tape is circular, the molecules lie transverse to the circumference.

On transformation to the α_2-phase there is no change in the texture of the tapes. However, as may be seen from Figs. 1(b) and 2(b), at the originally homoeotropic areas, there appears a microcrystalline texture showing birefringence. The origin of this birefringence is explainable as follows. The structure of the uniaxial homoeotropic plates consists of a hexagonal cylindrical packing of the molecules which are executing rotational motions

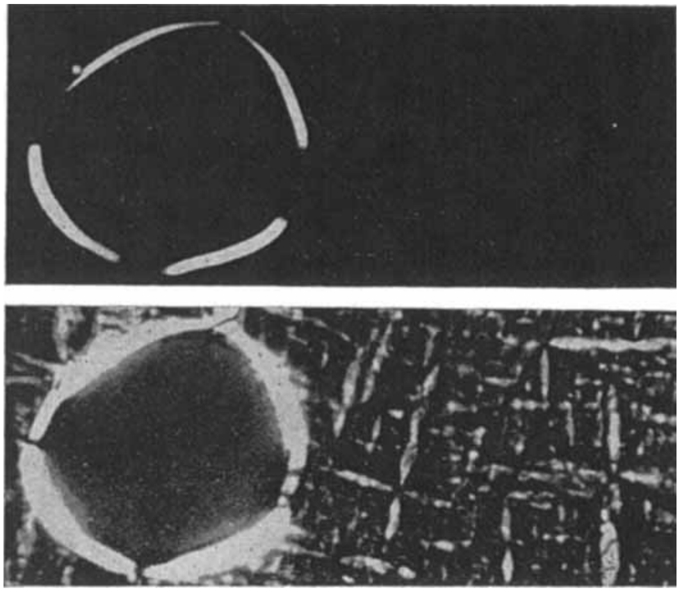

Figure 2. (a) A birefringent tape formed around an air bubble, in the α_1-phase (15.5 °C). Crossed polarizers. 450 ×. (b) Crystalline texture in the α_2-phase (13 °C). Crossed polarizers. 450 ×.

about their long axes. On transforming to the α_2-phase the rotational motions of the lath-shaped molecules decrease in amplitude and the order deviates from the ideal hexagonal packing. In fact, the α_2-phase has been observed to show two X-ray diffraction rings corresponding to two different side spacings, indicating that the α_2 structure probably corresponds to orthorhombic symmetry.[1] In such a case, the long axes of the molecules would correspond to the acute bisectrix of the refractive index ellipsoid and hence the birefringence is observable at the originally homoeotropic areas. The texture of the tapes shows no change on passing to the α_2-phase, because here the direction of observation is perpendicular to the long axes of molecules and also because in this projection the molecular rearrangement is not expected to give rise to significantly altered optical properties. It may also be mentioned that there is no change in the optical texture or

X-ray Debye-Scherrer pattern on passing from α_2 to α_3-phase, indicating that here the molecular reorientation is not considerable. The above facts are in agreement with the features observed in proton magnetic resonance, as shall be seen in the following.

For polycrystalline materials in which protons are the only species of magnetic nuclei, Van Vleck's formula for the rigid-lattice second moment, S, simplifies to:

$$S = \frac{716}{N} \sum_{j>k} r_{jk}^{-6},$$

where N is the number of protons in the interaction cell considered and r_{jk} is the distance (in A.U.) between the jth and kth protons.[3] We may suppose that (i) the skeleton (including the ether linkage) of the n-butyl stearate molecule is zig-zag throughout, with tetrahedral interbond angle, (ii) the CH and CC bonds are arranged in the all-trans configuration and (iii) the CH and CC bond lengths are 1.094 and 1.54 Å respectively.[4] With these assumptions, the calculated intramolecular contribution to the second moment is 19.1 gauss^2. In the absence of detailed information concerning the crystal structure of n-butyl stearate, we assume that the intermolecular contribution to S is 7.8 gauss^2, as in the case of n-paraffins.[4] The total second moment is therefore, 26.9 gauss^2. For the curve recorded at liquid nitrogen temperature, the calculated experimental second moment of 27 gauss^2 is hence in close agreement with the theoretical rigid-lattice value.

It is well-known that the width of the resonance line and also the second moment value are reduced as a consequence of molecular motion in solids.[2,4] Andrew[4] has discussed theoretically the reduction in the rigid-lattice second moment arising from the rotational oscillations of long chain molecules and shown that for a complete rotation of the molecules about their long axes, the rigid-lattice second moment value is reduced by a factor of three. As may be seen from Table 1 the value of S progressively decreases with increasing temperature, indicating rotational motions at the higher temperatures. Following Andrew's procedure, the angular amplitudes of rotational oscillations at $-50°$, $0°$, $10°$ and $12\ °C$ are calculated to be about $23°$, $28°$, $40°$ and $43°$, respectively. The onset of free rotation may be expected to occur near 16 °C where the experimental second moment is one third of the rigid-lattice value. At higher temperatures, the further reduction in second moment may be explained as due to molecular vibrations including the flexing of the chain, the rotation of the CH_3 group independently of the rest of the chain and motion of the molecules in lattice defects.[4,5]

The variation in the value of S for a change in temperature of 8 °C on cooling the sample from 24 °C to 16 °C is 4 gauss^2. On the other hand, for a change in temperature of 4 °C on cooling from 16 °C to 12 °C, the variation is 6.1 gauss^2. This increase in the rate of change of second moment is in agreement with the fact that the $\alpha_1 \rightarrow \alpha_2$ transition occurs at 14.8 °C. On heating the sample from 12 °C to 16 °C the value of S is found to be 9.9 gauss^2, which is nearly the same as that observed at 16 °C from cooling experiment, showing that the $\alpha_1 \rightarrow \alpha_2$ transition is reversible, in agreement with our observations from optical and X-ray studies made earlier.[1] The small difference of 0.9 gauss^2 may be due to thermal hysteresis. The $\alpha_2 \rightarrow \alpha_3$ transition does not give rise to any pronounced increase in the second moment because (i) the contribution to S is mainly from intra-molecular interactions and (ii) the molecular rearrangement on passing to α_3 is probably not considerable, as mentioned earlier.

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