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A study of molecular dynamics and phase transitions in solid MBBA

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The solid state polymorphism of liquid crystalline MBBA was investigated by temperature dependent NMR spin–lattice relaxation time measurements. The sensitivity of the method could be utilized because the correlation time of the measurement is in the correlation time region of molecular motion. Motional correlation time and activation energy values were determined and the results show some interesting changes between the different solid phases. Non-trivial variation in the end-chain rotational motion in two crystalline phases has been observed. Conclusions were drawn on the relationship between rotational molecular dynamics, intermolecular order and phase transitions.

1. Introduction

Since the work of Mayer *et al.* [1], Janik *et al.* [2] and Andrews [3] substantial efforts have been devoted to structural transformations and dynamics of the solid phases of mesogenic substances. A liquid crystal substance (MBBA) served as a classical object in such studies. A non-trivial singularity was discovered [1] in the MBBA crystal phase heat capacity in the 200–220 K range. Andrews [3] interpreted the unusual heat capacity behaviour as the setting free of the rotational motion of molecular end-groups in the same temperature range (i.e. melting of the molecular tails). Later on, X-ray [4, 5] and neutron [6, 7] studies showed the singularity in heat capacity to be related to the phase transition between the metastable C_5 and C_6 structures ($T_{5-6} \approx 205$ K). If one analyses the spectral data, one may state that phonon type intermolecular dynamics practically does not change under phase transition. The relation between the phase transition mechanism and diffusion type rotation molecular dynamics has widely been discussed: no direct experimental data have been obtained so far, which would support or refute the original idea of Andrews. The molecular ordering of the nematic phase can be conserved at a quite high level by quenching in MBBA (glassy liquid crystal, or C_0 phase) [6, 8]. By heating this phase a series of irreversible phase transitions occurs (C_0–C_1–C_2–C_3–C_4), involving partially ordered and ordered crystal phases, besides a glassy liquid crystal.

The temperature of the initial transformation of intermolecular ordering C_0–C_1 (≈ 205 K) is practically equal to that of the C_5–C_6 transition (is the coincidence random or not?). The coherence length for a given region of the molecular short range order increases essentially on transition, though the variation of density of optical and

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acoustic vibrational states [7, 8] and dispersion of long-wave acoustic phonons [9] is negligible. The role of molecular dynamics (rotational or translational type) in the phase transition is still vague.

In the present paper, the NMR spin–lattice relaxation time T_1 has been measured for different solid phases of MBBA. On the basis of experimental data, the motional correlation time and activation energy of the end-group rotation were determined and conclusions drawn about the relationship between molecular dynamics and phase transitions.

2. Materials and methods

The spin–lattice relaxation time T_1 was measured for the C_4, C_5 and C_6 crystal phases, for glassy C_0 and for the partially ordered C_1 phase. Phases C_0 and C_6 were obtained by fast (100°C min^{-1}) and slow (1°C min^{-1}) cooling of the nematic phase down to $T \approx 80$ K and $T \approx 250$ K, respectively. The C_5 phase was obtained by cooling the C_6 phase below ≈ 205 K, phase C_1 by heating C_0 up to 205–215 K, phase C_4 by heating a fast frozen sample and storing it for an hour at 265–290 K. Phases C_1 and C_4 are stable: they can be cooled down to low temperatures without phase transitions. The measurements were carried out in the 130–320 K range at a frequency of 90 MHz using a Bruker SXP 100 NMR spectrometer, in the Central Research Institute for Physics, Budapest, Hungary.

3. Results and discussion

The temperature dependence of the measured spin–lattice relaxation time T_1 data is presented in figures 1 and 2. The C_0–C_1 transition is accompanied by some decrease in T_1 (see figure 2) and the C_5–C_6 transition occurs with hysteresis (see figure 1). For phases C_0, C_1, C_4 and C_5, minima are observed in the temperature dependence of the spin–lattice relaxation times.

The spin–lattice relaxation time T_1 in the solid state for MBBA-type molecules is dominated by the rotation of the end groups around the C–C bonds [10–12]. The expression for T_1, due to the rotational molecular dynamics, has the form [10]

$$\frac{1}{T_1} = B\left[\frac{\tau_c}{1+\omega_0^2\tau_c^2} + \frac{4\tau_c}{1+4\omega_0^2\tau_c^2}\right] \tag{1}$$

here τ_c is the correlation time for the rotational dynamics, ω_0 is the Larmor frequency of the protons at the magnetic field strength used, and B is a constant,

$$B = \frac{9}{40}\gamma^4\hbar^2\left(\frac{n_{\text{tail}}}{n_{\text{total}}}\right)^2 r^{-6}$$

characterizing the molecular structure and conformation; n_{tail} is the number of protons in the molecular tails, and n_{total} the total number of protons in the molecule. γ is the gyromagnetic ratio of the proton and r is the average inter-proton distance. The temperature dependence of the correlation time τ_c can be calculated from the Arrhenius equation

$$\tau_c(T) = \tau_\infty \exp\left(\frac{E_\alpha}{k_B T}\right), \tag{2}$$

where τ_∞ is the value of the correlation time in the $T = \infty$-limit, E_α is the activation energy, k_B the Boltzmann constant. The dominance of the end-chain rotation in the T_1

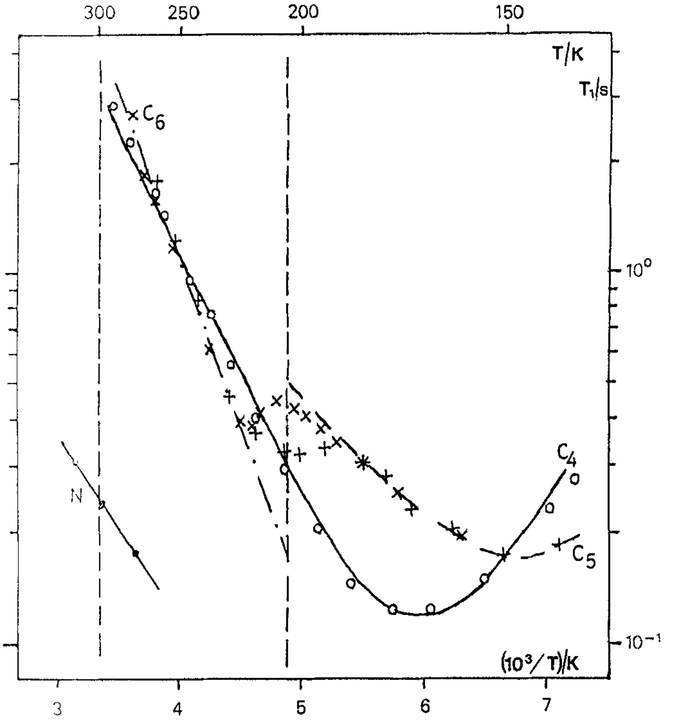

Figure 1. Temperature dependence of the spin–lattice relaxation time T_1 for phases C_4, C_5 and C_6 and the nematic and supercooled nematic states of MBBA. Vertical dashed lines indicate the transition temperatures of C_5–C_6 (at 210 K) and C_4–N (at 290 K) measured by structural and spectral methods [6, 8] (+-cooling, x-heating).

relaxation process at such temperatures was clearly proven in liquid crystalline systems, where the end-chains were in some cases replaced by chlorine [13].

The experimental data for phases C_0, C_1, C_4 and C_5 can be fitted by equation (1). The results of the fitting can be seen in figures 1 and 2. The τ_∞, E_α and B parameters of the best fitting lines are given in the table. The temperature dependence of T_1 does not reach the minimum in phase C_6 because of the phase transition. The activation energies in the C_6 and nematic phases were determined from the slope function of the T_1 $(1/T)$. Figure 3 shows the best fitting theoretical lines for the different phases. The table also shows that the values of parameter B do not change too much during the phase transitions; its values were kept in the range $(2{\cdot}3\text{–}4)10^{-9}\,\mathrm{s}^{-2}$, and therefore, the quantity τ_∞ in phase C_6 can be estimated by using the extreme values of B (see table). The corresponding region of τ_c values is presented in figure 3. To compare rotation dynamics in different MBBA phases, the $\tau_c(T)$ values for phases C_5 and C_6 were extended to the temperature region in which the corresponding structures are not realized because of phase transition.

Determination of activation energies and correlation times τ_c for different MBBA phases makes it possible to comment on the relationship of the rotational molecular dynamics and the intermolecular order, as well as the phase transitions:

(i) The E_α values differ noticeably for the different solid phases of MBBA; the value of τ_c involves a wide spectrum of times, i.e. the intermolecular ordering essentially affects the intramolecular dynamics of the molecular end-groups.

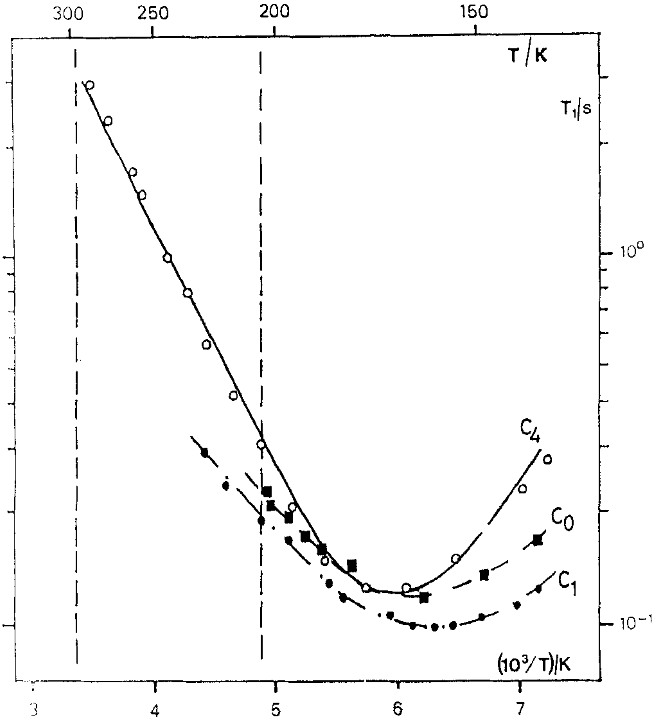

Figure 2. Temperature dependence of the spin–lattice relaxation time T_1 for C_0 (■), C_1 (●) and C_4 (○) of MBBA. Dashed lines indicate the transition temperatures between the C_0–C_1 and C_4–N phases on the basis of structural and spectral measurements [6, 8].

(ii) In the glassy liquid crystal phase (C_0), the magnitude of the barrier for reorientation is low, E_α being close to the magnitude of E_α in nematics. This means that the orientational order and the short range order are identical in the nematic liquid crystal and in the frozen liquid crystal phases [6, 8, 14].

(iii) Transition of glassy nematic to a partially ordered C_1 phase does not cause important changes in E_α and τ_c. The transition is related to an increase of the correlation length of the short range order [4–6, 8], and practically does not affect either the density of intermolecular phonon states [7], or the non-phonon-type rotational molecular dynamics. The local arrangement and the magnitude of the energy barrier for reorientations are retained during the transitions.

(iv) In phases C_5 and C_6, both E_α and τ_c are distinguished, which confirms the Andrews hypothesis [3] on the relationship between the singularity in thermal capacity in the 200–220 K range, and the variation in the rotation dynamics of end groups. But at the same time, there is the unexpected result that the end-group behaviour turned out to be opposite to Andrews' suggestion. The potential barrier for reorientations in the C_6 phase is higher (see table). Extension of the Arrhenius dependence (see equation (2)) of τ_c for phase C_5 to the temperature range where phase C_6 is stable (dashed line in figure 3) corresponds to a shorter reorientation time of the end groups, as compared to phase C_6. By increasing the temperature the structure of the C_5 phase, characterized by a low barrier, E_α, becomes unstable relative to the rotation of

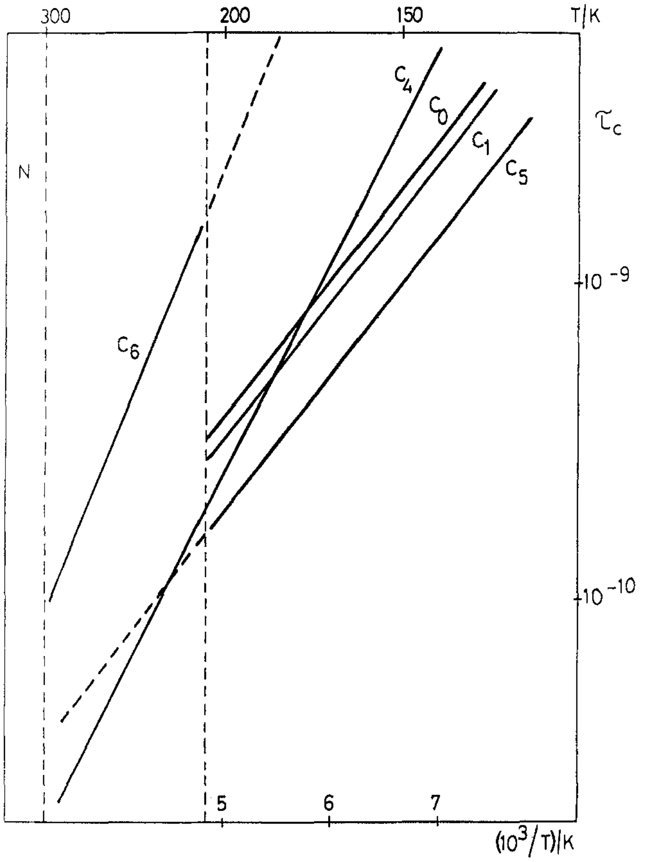

Figure 3. Temperature dependence of motional correlation times τ_c for the different phases of MBBA.

Parameters of the best fitting lines in figures 1 and 2.

Phase	C_0	C_1	C_4	C_5	C_6		N
E_α/kcal mol^{-1}	2	2	3	2	4		2·2
$B/10^{-9}\,s^{-2}$	3·3	4	3·3	2·3	4	2·3	
$\tau_\infty \times 10^{12}$ s	2·3	2·3	0·13	1·3	0·76	0·14	

the end groups, which results in the transition to the C_6 structure with a higher barrier and less rotational mobility of molecular end groups.

In the C_6 phase E_α is above the barrier in C_4, therefore the C_4–C_6 transition near the melting temperature [7] can be assumed to be related to the intermolecular packing of the central part of the molecules and not because the peripheral groups are advantageous in energy.

4. Conclusion

With regard to the density data in the different phases, we lack information about the changes in average molecular packing in the different phases. A phase transition with decreasing temperature usually leads to increasing order, which might change the rotational freedom in a complicated way. The more and more uniform neighbourhood increases the motional freedom for some molecules, but decreases it for others, simply by decreasing the standard deviation of molecular site distribution. There is also a general tendency for increasing density by increased ordering, which means a general decrease in the space available for the end chain motion.

Systematic studies are needed for the various phases, investigating the rotational motion of the end chains and the central body of the molecule, and the relationship between the rotational dynamics and the various phase transitions.

References

[1] MAYER, J., WALUGA, T., and JANIK, J. A., 1972, *Physics Lett.* A, **41,** 102.
[2] JANIK, J. A., JANIK, J. M., MAYER, J., SCIESINKA, E., SCIESINKI, J., TWARDOWSKI, J., WALUGA, T., and WITKOV, W., 1975, *J. Phys., Paris,* **36,** C1, 159.
[3] ANDREWS, I. T. S., 1974, *Phys. Lett.* A, **46,** 377.
[4] DOLGANOV, V. K., NOVOMLINSKII, L. A., and SHMITKO, I. M., 1982, *Sov. Solid St. Phys.*, **24,** 2605.
[5] PEPY, G., FURET, R., MORE, M., and ROSTA, L., 1989, *Phys. scripta,* **39,** 485.
[6] DOLGANOV, V. K., GAL, M., KROO, N., ROSTA, L., and SHEKA, E. F., 1984, *Molec. Crystals liq. Crystals Lett.*, **92,** 281.
[7] BELUSHKIN, A. V., DOLGANOV, V. K., NATKANIEC, I., and SIMKIN, V. G., 1987, *Molec. Crystals liq. Crystals,* **150b,** 187.
[8] GAL, M., DOLGANOV, V. K., KROO, N., ROSTA, L., and SHEKA, E. F., 1985, *Sov. Solid St. Phys.*, **27,** 3084.
[9] DOLGANOV, V. K., CSILLAG, L., KROO, N., and ROSTA, L., 1983, *Liq. Crystals,* **4,** 693.
[10] BLOMBERGEN, N., PURCELL, E. M., and POUND, R. V., 1948, *Phys. Rev.*, **73,** 679.
[11] ABRAGAM, A., 1961, *The Principles of Nuclear Magnetism* (Clarendon Press).
[12] THOMSPON, R. T., KYDON, D. W., and PINTAR, M. M., 1974, *J. chem. Phys.*, **61,** 4646.
[13] PÓCSIK, I., and TOMPA, K., 1979, *Magnetic Resonance and Related Phenomena*, edited by E. Kundla, E. Lippmaa and T. Saluvere (Springer), p. 450.
[14] DOLGANOV, V. K., 1979, *Sov. Solid St. Phys.*, **21,** 2629.