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Dielectric and Resistivity Measurements on Room Temperature Nematic MBBA†

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Abstract—Measurements are presented on the dielectric relaxation versus temperature [0–10 MHz] and resistivity anisotropy of a room temperature nematic, the *p*-methoxy benzylidene *p*-*n*-butylaniline, (MBBA), pure or doped with organic ions.

Recent synthesis of room-temperature nematics connected with potential applications for display systems has stimulated the study of the electrical properties of nematic liquid crystals. One of these is MBBA (*p*-methoxybenzylidene-*p*-*n*-butylaniline). We have already presented[1] dielectric and resistivity anisotropy measurements on this material. We publish here complementary results: mainly a study of dielectric relaxation versus the temperature T, in the range 0–10 MHz and the measurement of conductivity anisotropy in MBBA doped with organic ions.

The experimental apparatus has already been described.[2] It consists of a plane-parallel, copper electrode capacitor filled with the nematic liquid crystal. The electrodes are spaced apart by mylar films with a thickness of 50μ . We measured both parallel resistance and capacitance, R_p and C_p, with an A.C. bridge. For low frequency measurements we used the Wayne-Kerr bridge B 641, with the 1592 Hz internal frequency; for frequency, f, from 100 KHz to 10 MHz, we used the Wayne-Kerr B 602. Between 2 and 10 MHz, we had to make line propagation corrections. The accuracy of the measurements of the electrical constants of MBBA is one per cent at 1592 Hz and decreases up to ten per cent at 10 MHz.

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The alignment of the molecules by a magnetic field of about 10 KG enables us to define two geometries, parallel and perpendicular, depending on whether the long axis of the molecules is parallel or perpendicular to the electric field. In the first case we obtain $\rho_{\parallel}$ and $\epsilon_{\parallel}$, in the other $\rho_{\perp}$ and $\epsilon_{\perp}$. Our sample was prepared by Mme Hochapfel in the laboratory of the Ecole Normale Supérieure de St Cloud, from a condensation between butylaniline (K and K product) and anis-aldehyde. The clearing temperature T_c of a fresh sample is 44–45 °C, relatively sensitive to air exposure.

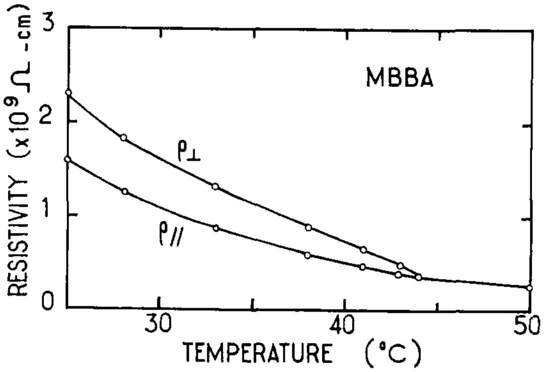

Figure 1. Values of the two resistivities, $\rho_{\perp}$ and $\rho_{\parallel}$, versus temperature—(T_c = 44.7 °C).

In Fig. 1, we plot values of resistivities for a typical specimen of " pure " MBBA. Above T_c, $\rho_{\perp}$ and $\rho_{\parallel}$ are equal and decrease linearly with temperature. Under T_c, the anisotropy of resistivity, that we define by the ratio $\rho_{\perp}/\rho_{\parallel}$ is more or less constant (1.5 at 25 °C). This value is to be compared with the measurements of Svedberg[3] in PAA (para-azoxyanisole). For MBBA doped with tetramethyl ammonium bromide (TMAB), Fig. 2 shows that the anisotropy of conductivity decreases from 1.5 to 1.2 when the concentration of TMAB increases up to saturation, at 25 °C. This suggests that both the nature of the charge carriers and the nematic matrix play a role in the overall conductivity anisotropy.

To study the dielectric relaxation versus T, we vary f from 0 to 10 MHz. We observe one dielectric relaxation for $\epsilon_{\parallel}$ and no relaxation for $\epsilon_{\perp}$. This is very similar to the observation of W. Maier and

G. Meier[4] in PAA. Figure 3 shows a typical curve of relaxation for $\epsilon_{\parallel}$, using now the generalized dielectric constant $\epsilon_{\parallel} = \epsilon'_{\parallel} + i\epsilon''_{\parallel}$. At 25 °C, $\epsilon'_{\parallel}$ goes from 4.72 at 1592 Hz to 4.46 above 3 MHz. Simultaneously, we observe a peak in the dielectric absorption $\epsilon''_{\parallel}$. Using

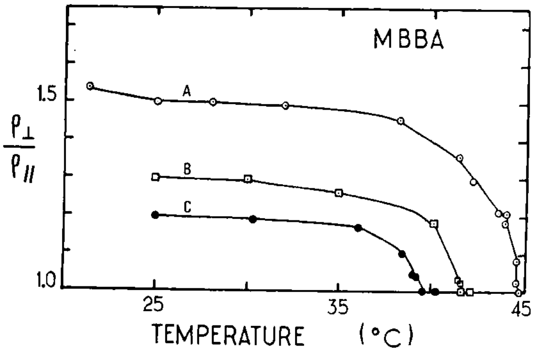

Figure 2. Ratio $\rho_{\perp}/\rho_{\parallel}$ versus temperature for MBBA doped with TMAB. The three curves correspond to different doped concentration of TMAB.

For curve A, $\rho_{\perp} = 2.3 \quad 10^9 \Omega \times cm \quad (25\,°C)$
B, $\rho_{\perp} = 1.0 \quad 10^9 \Omega \times cm \quad (25\,°C)$
C, $\rho_{\perp} = 1.1 \quad 10^8 \Omega \times cm \quad (25\,°C)$.

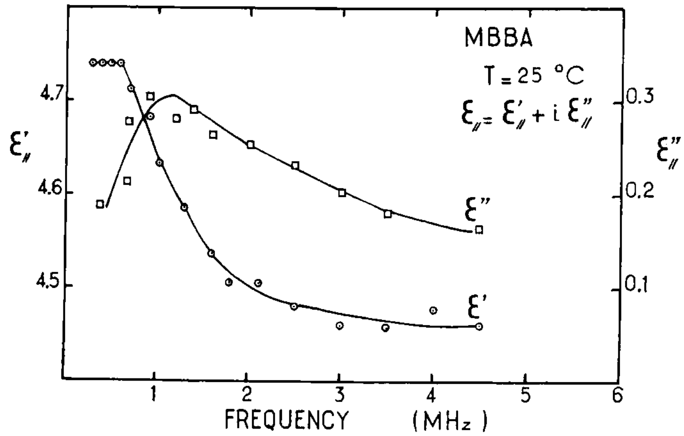

Figure 3. Generalized dielectric constant $\epsilon_{\parallel} = \epsilon'_{\parallel} + i\epsilon''_{\parallel}$ versus frequency.

the Debye formula[5] with a single relaxation time, a least square fit gives $f_c = 1.1 \pm 0.1$ MHz for the relaxation frequency.

f_c is lower in MBBA than it is for PAA. This can be expected because its viscosity is an order of magnitude higher. As in PAA,

f_c increases with T, at least for temperatures not too close to the transition point. The results are shown on Fig. 4 and Table 1.

TABLE 1 Relaxation Frequency Versus Temperature

T, °C	25	27	29	33	37	44
f_c, MHz	1.1	1.0	1.4	2.7	6	> 10

From Table 1, we can compute the retardation factor g of Ref. 6, defined by

$$f_c = g f_{\text{Debye}}$$

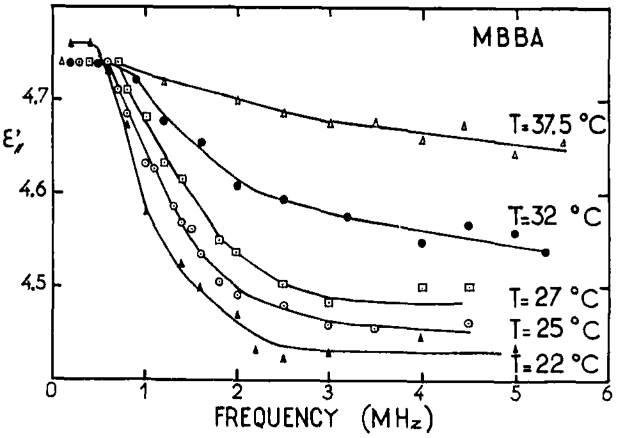

Figure 4. Real part of the dielectric constant $\epsilon_\parallel$ as a function of frequency for different temperatures.

and the activation energy,[6] W, for rotational diffusion around an axis perpendicular to the long axis of the molecule, by taking, $g \approx (kT/W \exp W/kT)$ and f_{Debye} to be:

$$f_{\text{Debye}} = \frac{kT}{4\pi\eta a^3}$$

a is a molecular dimension. Using for the viscosity η (T) a recent measurement,[7] we can estimate W from our data:

$$W \simeq 0.1 \text{ eV}$$

which is to be compared with 0.18 eV in PAA.[6]

To conclude, we would underline some experimental difficulties. The nematic → isotropic transition point of our samples is higher than other values reported in the literature.[8,9] As all Schiff bases, MBBA is very sensitive to hydrolysis. Moreover, in our cell, there is probably a chemical reaction with the copper of the electrodes; we notice, indeed, a surface oxydation after 18 hours. Figure 5 shows

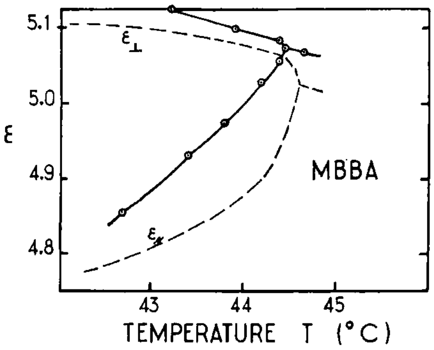

Figure 5. Dielectric constants, $\epsilon_\parallel$ and $\epsilon_\perp$, versus temperature. The dotted lines correspond to fresh samples, the full lines to the same sample in contact with copper electrodes, 18 hours later.

values of ϵ on a sample which has remained in contact with electrodes for 18 hours. We do not observe a significant variation of T_c ($\Delta T_c \simeq 0.2$ °C); however, the dielectric anisotropy is reduced by a factor of 2. To avoid these effects in our measurements, we always dealt with fresh samples. Nevertheless, results above 44 °C cannot be taken as definitive; if one keeps MBBA under vacuum for a few days, the transition point raises to 47 °C.[10] At T lower then 44 °C, the results are independent of T_c on fresh samples. We are resuming these measurements with a sealed cell and highly pure MBBA to improve accuracy close to T_c.

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