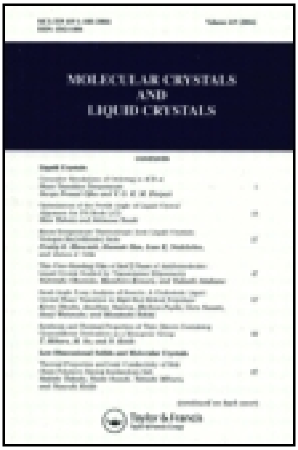

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Dielectric Relaxation and Order Parameters in Mixtures of 4-cyanobiphenyl and MBBA

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Dielectric Relaxation and Order Parameters in Mixtures of 4-cyanobiphenyl and MBBA[†]

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Dielectric studies on MBBA and its solutions doped with 4-cyanobiphenyl (CB) are reported at reduced temperatures of 0.996 over the frequency range of 0 to 200 MHz. The longitudinal and transverse dipole components are evaluated as well as the order parameter. The results are self consistent only after an additional relaxation process is presumed at frequencies greater than 200 MHz. This may arise from the internal rotation of the terminal methoxy group in MBBA.

INTRODUCTION

Dielectric relaxation studies provide information on the rate of dipolar reorientation, and in liquid crystals, the relaxation behavior in both the parallel and perpendicular alignments with respect to the director are amenable for study. Generally, four permittivity dispersion regions may be expected, two in each of the parallel and perpendicular alignments. The general situation is depicted in Figure 1, where the permittivity is schematically illustrated as a function of frequency for a nematogen with positive dielectric anisotropy. A reasonable, but simplistic, assignment for the reorientation processes is shown in Figure 2.[1] Dispersion A is envisaged as essentially an end over end tumbling motion and involves surmounting the "nematic potential barrier". It is therefore expected at low frequencies.

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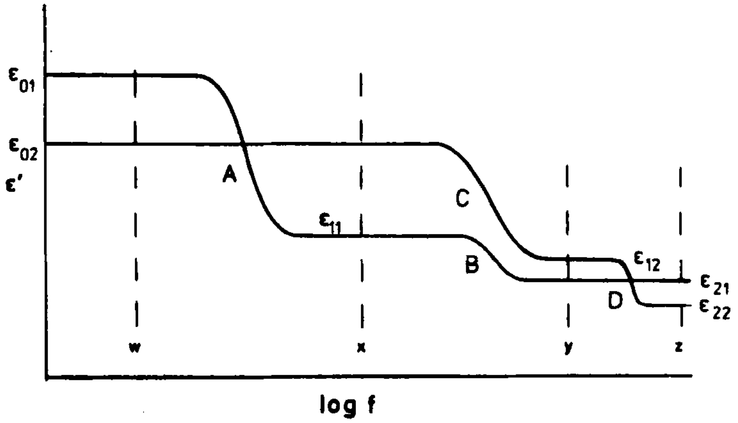

FIGURE 1 Schematic representation of dielectric dispersion in an aligned nematogen.

Dispersions B and C are depicted as having the same origin (essentially rotation about the long axis) and are expected at the same frequency, with dispersion B observed in the parallel alignment and C in the perpendicular alignment. There is some uncertainty about the location of dispersion D (the second dispersion in the perpendicular alignment) and the molecular mechanism is, therefore, uncertain. Its origin certainly lies in the motion of the longitudinal dipole component of the molecule, but further work at

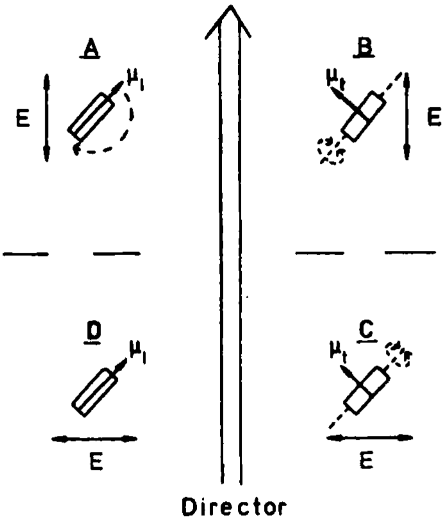

FIGURE 2 Possible pictorial representation for the mechanisms responsible for dielectric dispersion in aligned nematogens. (E represents the direction of the measuring electric field.)

higher frequencies than reported here is needed before it may be assigned to a particular rotational mode.

Analysis of these dispersions (or of the associated dielectric loss parameter) provides information about the dipole components μ_l and μ_t parallel and perpendicular to the long axis of rotation and of the order parameter. This paper describes a study of the changes in the dielectric properties of MBBA produced by the addition of a polar dopant [4-cyanobiphenyl (CB)]. The major component of the dipole moment of MBBA lies perpendicular to the "long axis" of the molecule, while the dipole moment of CB lies along the "long axis".

EXPERIMENTAL

MBBA was synthesized in the laboratory and showed a sharp clearing point at 316 K. CB was recrystallized from ethanol. Its melting point agreed with the literature value.

Dielectric measurements at frequencies up to 200 MHz were made as described in previous publications from this laboratory.[3] The dielectric absorptions were analyzed using the Fuoss-Kirkwood equation

$$\cosh^{-1}\frac{\varepsilon''_m}{\varepsilon''} = \beta \ln\frac{f_m}{f} \tag{1}$$

where ε'' is the dielectric absorption at frequency f, the subscript m refers to the properties at maximum absorption ($f_m = (2\pi\tau)^{-1}$, where τ is the dielectric relaxation time) and β is an empirical parameter used to describe the width of the absorption ($0 < \beta \leq 1$).

THEORY AND INTERPRETATION OF THE RESULTS

The mean field approach to the dielectric properties of aligned liquid crystals has been described by Maier and Meier[4] and after replacing the polarizability terms by the relevant refractive indices (using the Vuck's relations)[5] the individual dispersion regions indicated in Figure 1 may be related to the dipole components involved by the equations:

Dispersion A

$$(\varepsilon_{01} - \varepsilon_{11})\frac{\varepsilon}{N} = [hF)_w - (hF)_x]\frac{n_e^2 - 1}{\bar{n}^2 + 2}\frac{3\varepsilon}{N} + (hF^2)_w\frac{\mu_A^2}{3kT} + [(hF^2)_w - (hF^2)_x]\frac{\mu_B^2}{3kT} \tag{2}$$

Dispersion B

$$(\varepsilon_{11} - \varepsilon_\infty)\frac{\varepsilon}{N} = [(hF)_x - (hF)_y]\frac{n_e^2 - 1}{\bar{n}^2 + 2}\frac{3\varepsilon}{N} + (hF^2)_x\frac{\mu_B^2}{3kT} \tag{3}$$

with equivalent relations for dispersions C and D in the perpendicular alignment and involving μ_C^2 and μ_D^2. The significance of ε_{01}, ε_{11} etc. is appreciated after reference to Figure 1. Following the notation adopted by Maier and Meier

$$(hF)_i = \frac{\bar{\varepsilon}_i(\bar{n}^2 + 2)}{(2\bar{\varepsilon}_i + \bar{n}^2)} \quad : \quad (hF^2)_i = \frac{\bar{\varepsilon}_i(\bar{n}^2 + 2)^2(2\bar{\varepsilon}_i + 1)}{3(2\bar{\varepsilon}_i + \bar{n}^2)^2}$$

where $\bar{n}$ and $\bar{\varepsilon}_i$ are the mean values of the refractive index and permittivity respectively. The latter is calculated in the regions i = w, x, y, z as indicated in Figure 1. The dipole components μ_A, μ_B etc. are related to the molecular dipole components μ_l and μ_t by

$$\mu_A^2 = \mu_l^2(1 + 2S) \quad : \quad \mu_B^2 = \mu_t^2(1 - S)$$

$$\mu_C^2 = \mu_t^2\left(1 + \frac{S}{2}\right) \quad : \quad \mu_D^2 = \mu_l^2(1 - S) \tag{4}$$

Thus, the experimental dispersion curves allow of a determination of the dipole components parallel and perpendicular to the axis of rotation and of the order parameter. Their application to MBBA and to MBBA doped with CB is described in the next section.

EXPERIMENTAL RESULTS

A typical set of experimental results is shown in Figures 3 and 4, and the dielectric parameters of MBBA and its doped solutions are shown in Table I for both the parallel and perpendicular alignments. The results for pure MBBA agree with those previously reported.[3] Addition of CB increases the static permittivity in both alignments, and at concentrations around 0.04 mol fraction the dielectric anisotropy changes sign from negative to positive. This arises from the increased dipole moment component parallel to the director produced by the mutually parallel (or nearly parallel) alignment of the host and dopant molecules.

The dielectric relaxation data do not show any indication of the reorientation of the CB molecule as a separate entity (calculations suggest that it is in sufficiently high concentration that such a process is detectable with the equipment used). It appears that the dielectric relaxation in these doped systems is a cooperative phenomenon involving the MBBA and CB reori-

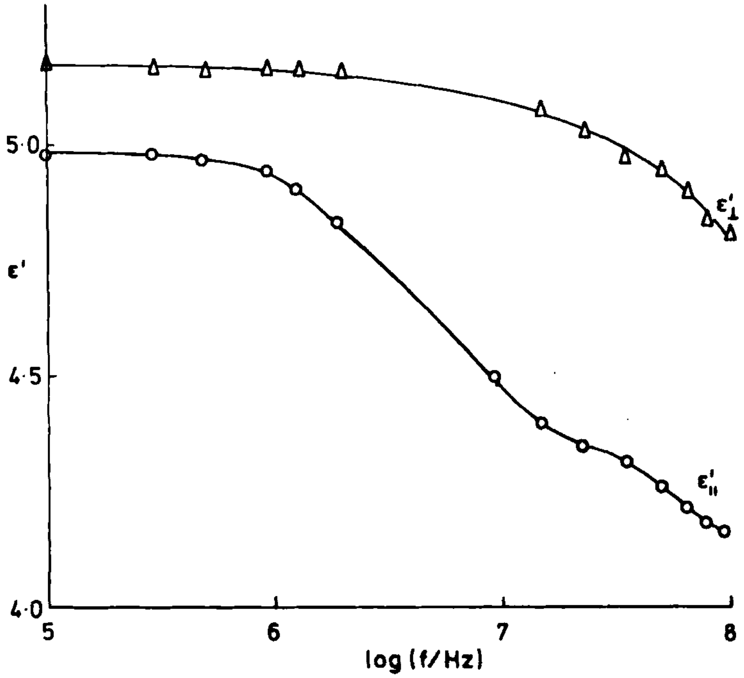

FIGURE 3 Dielectric dispersion in MBBA plus 0.018 mol fraction cyanobiphenyl at a reduced temperature of 0.966.

enting together. This suggestion is supported by the detailed analysis (see later) of the intensity of the absorptions.

One feature of the results is revealed by comparison of n_e^2 and ε_{2l} for the parallel alignment. The farily large difference ($\varepsilon_{2l} - n_e^2 = 0.66$ for MBBA) suggests the presence of another absorption at higher frequencies than those used in this study. The experimental results are only made self-consistent by assuming a dipole relaxation process (possibly due to internal rotation of the terminal methoxy group) at such higher frequencies. Hence, analysis of the experimental results according to equations 2,3 and 4 (and their perpendicular counterparts) is made from the intensity of dispersions A and B (both of which are amenable to direct measurement) and the *total* dispersion (i.e. from effectively zero frequency to the optical frequency and therefore includes any very high frequency dispersion and the far infra-red contribution) expected in the perpendicular alignment. The total dipole moment involved is expressed as

$$\mu^2 = \mu_C^2 + \mu_D^2 + \mu_R^2 = \mu_t^2\left(1 + \frac{S}{2}\right) + \mu_l^2(1 - S) + \mu_l^2\left(1 + \frac{S}{2}\right) \quad (5)$$

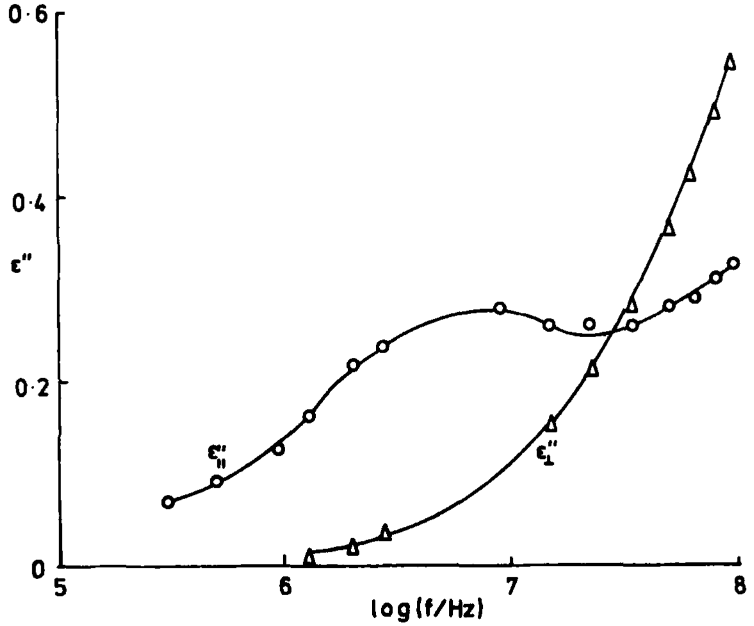

FIGURE 4 Dielectric absorption in MBBA plus 0.018 mol fraction cyanobiphenyl at a reduced temperature of 0.966.

where μ_l is the dipole component due to dispersion contributions at frequencies beyond 200 MHz (the upper limit of our measurements). The results of such an analysis are shown in Table II. The dipole component (μ_l) calculated for the solutions studied agrees reasonably well with the value of 3.9×10^{-30} Cm expected for the methoxy group rotation about the O—C (aromatic) bond,[6] and the resultant dipole moment for MBBA is in good agreement with the measured value[6] of 7.3×10^{-30} Cm. Reference to Table II shows that the dipole components μ_t and μ_l are reasonably constant over the whole concentration range studied while the square of the longitudinal dipole component increases linearly with the concentration. The slope of this graph yields a value of 11.2×10^{-30} Cm for the dipole moment of the CB dopant in fair agreement with the literature value of 14.4×10^{-30} Cm (in benzene solution).[7] This and the inability to resolve a separate relaxation process for the CB strongly supports the suggestion that the dielectric relaxation in these mixtures is a cooperative phenomenon involving both components. They also show the absence of molecular association involving the CB component in the concentration range studied.

The calculated order parameter (0.48) in pure MBBA is lower than the 0.56 expected from the mean field theory. The magnitude of the order parameter calculated from dielectric data is subject to considerations

TABLE I

Dielectric parameters in MBBA and its solutions containing 4-cyanobiphenyl (CB) at a reduced temperature of 0.96 (see Figure 1 for the significance of ε_{01}, ε_{11} etc).

Parallel Alignment

Mole Fraction	Low Frequency Dispersion				High Frequency Dispersion				
CB	ε_{01}	ε_{11}	$10^9\tau/s$	β	ε_{11}	ε_{21}	$10^9\tau/s$	β	n_e
0	4.65	4.31	49.7	0.96	4.31	3.65	0.96	0.97	1.730
0.0181	4.98	4.28	28.9	0.76	4.28	3.62	0.88	1	1.729
0.0317	5.24	4.26	22.4	0.75	4.26	3.57	0.91	1	1.730
0.0474	5.43	4.23	22.1	0.82	4.23	3.56	0.91	1	1.731
0.0609	5.74	4.19	20.9	0.75	4.19	3.50	0.82	1	1.733

Perpendicular Alignment

Mole Fraction CB	ε_{02}	ε_{12}	$10^9\tau/s$	β	n_0
0	5.07	3.91	0.90	0.95	1.551
0.0181	5.19	3.92	1.06	0.93	1.554
0.0317	5.31	3.80	1.06	0.88	1.555
0.0474	5.36	3.88	1.18	0.91	1.555
0.0609	5.49	3.78	1.22	0.85	1.557

TABLE II

Dipole components in MBBA and its solutions doped with CB

Dopant mol fraction	$10^{30}\mu_l/Cm$	$10^{30}\mu_t/Cm$	$10^{30}\mu_l/Cm$	S
0	1.82	4.51	4.06	0.48
0.0181	2.62	4.27	4.30	0.44
0.0317	2.91	4.49	3.87	0.51
0.0474	3.21	4.54	3.94	0.52
0.0609	3.50	4.70	3.68	0.57

such as the internal field corrections which are not at all well defined. The order parameter in solution appears to increase with increasing dopant concentration.

CONCLUSIONS

Dielectric studies on mixtures of MBBA and CB show no evidence for separate relaxations from the two components. The relaxation seems to be a cooperative phenomenon. Order parameters calculated from the dielectric spectrum are in reasonable agreement with those expected from the mean field theory. Evidence is also presented for the possible presence of a contribution to the relaxation process from the internal rotation of the terminal methoxy group in MBBA.

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