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The influence of the external electric field on the birefringence of nematic liquid crystal layers

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The main refractive indices and the birefringence of MBBA and PPMAEBOBA10^{-2} g/cm^3 in TCM nematic liquid crystals at room temperature were determined by interferometric means for some visible monochromatic radiations in the absence and in the presence of external electrostatic or alternate electric fields of different frequencies. This study revealed the increase in the degree of order with the magnitude of the electrostatic field acting on the MBBA thin layer at room temperature. The increase in the frequency of the external alternate electric field decreases the order degree of PPAMAECOBA in TCM lyotropic liquid crystal, showing that the dipolar collective interactions of the side chains of polymer are responsible for the liquid crystal nature of this mixture.

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1. Introduction

Liquid crystals are substances possessing one or more mesophases between their liquid and solid phases. Their sequence represents a step by step ordering of the substance. So, liquid crystals are considered intermediate phases between the isotropic liquids and the anisotropic crystals [1-6].

Liquid crystals are substances with captivating properties [7-10] and their study has made amazing progress in the past couple of years.

Nematics are thermotropic liquid crystals with long, rod-like molecules that are orientationally ordered relative to their neighbors, but whose centers of mass have no positional order [1-3]. The preferential direction (axis parallel to the average orientation) is given by a versor n, named nematic director.

In most experiments and applications, a nematic layer is sandwiched between two solid glass surfaces supporting transparent electrodes [11]. Special surface coatings and/or treatments allow controlling the director alignment at the bounding plates. There are two basic geometries: a planar one, where the director is parallel to the surfaces (n parallel to xoy plane) and a homeotropic one, where the director is perpendicular to the surfaces (n parallel to oz axis).

The surface treatments combined with the elastic torques ensure the initial homogeneous director alignment in liquid crystal cells. In most cases the interaction between the liquid crystal and the surface is strong enough to inhibit changes in the direction of n at the boundaries (strong anchoring), despite director gradients in the bulk.

Nematics exhibit inversion and cylindrical symmetry [7] around the preferential direction. In addition they are characterized by non-polar molecular packing, thus the nematic phase is invariant against the transformation n to –n. These properties of symmetry imply that the dielectric susceptibility (ε), electric conductivity (σ), and the magnetic susceptibility (χ) tensors have each only two different components in their principal axes system; ε_e , σ_e , χ_e and ε_o , σ_o , χ_o , respectively.

The differences:

$$\Delta\varepsilon = \varepsilon_e - \varepsilon_o ; \Delta\sigma = \sigma_e - \sigma_o ; \Delta\chi = \chi_e - \chi_o \qquad (1)$$

define the anisotropy of the corresponding physical properties.

Substances both with $\Delta\varepsilon > 0$ or $\Delta\varepsilon < 0$ can be found among nematics, moreover the sign may change with frequency or/and temperature in some compounds. Always $\Delta\varepsilon$ is positive at optical frequencies ($\Delta\varepsilon > 0$). In most of the cases the anisotropy of the nematic electrical conductivity $\Delta\sigma$ is positive, in other words the electric charges are more easily transported parallel to the preferential orientation (direction n) of the elongated nematic molecules than perpendicularly. The anisotropy of the magnetic susceptibility $\Delta\chi$ is positive for the majority of nematics, due to the saturated aromatic rings as main building blocks of the constituent molecules.

The sign of the anisotropies $\Delta\varepsilon$; $\Delta\sigma$; $\Delta\chi$ governs the behavior of the liquid crystal in an electric (E) or a magnetic (H) field via the electromagnetic contribution t_{em} to the orientational free energy density [7]:

$$t_{em} = -\frac{1}{2}\varepsilon_0 \Delta\varepsilon \left(\vec{n} \cdot \vec{E}\right)^2 - \frac{1}{2}\mu_0 \Delta\chi \left(\vec{n} \cdot \vec{H}\right)^2 \qquad (2)$$

Though equation (2) describes a similarity between the behavior in electric and magnetic fields, one crucial difference should be pointed out. As $\Delta\chi$ is of the order 10^{-6} in IS units, the distortions induced by the constant applied magnetic field when the director varies in space can safely be neglected. In the electric case, however $\Delta\varepsilon$ is usually of the order of unity, and then the distortions induced by the electric field have to be taken into account [7].

When $\Delta\varepsilon > 0$ and $\Delta\chi > 0$, electromagnetic torque tends to align the director along the field, while in the case $\Delta\varepsilon < 0$ and $\Delta\chi < 0$, an orientation perpendicular to the field direction is preferred [1,7]. This behavior establishes the basic principles of the most liquid crystalline electro-optic devices (displays).

The optical properties of nematics correspond to those of uniaxial crystal [12]. The directory defines the local optical axis. The most obvious indication of the anisotropy of nematics is their birefringence. Composed of elongated molecules their extraordinary refractive index - n_e - is always bigger than the ordinary one - n_0 - i.e. nematics have a positive optical anisotropy [13,14].

$$\Delta n = n_e - n_o \qquad (3)$$

Like the refractive indices, the birefringence shows dispersion in the visible range.

When light is passing through a nematic layer, an optical path difference between the ordinary and extraordinary rays builds up. The optical path difference depends on the local directory orientation beside the light propagation direction.

If the nematic liquid layer is placed between the crossed polarizers, variation of the pathway results in changes of color and/or in the intensity of the transmitted light. This feature makes the polarizing microscope a standard tool for studying the textures of nematic liquid crystals [7,11].

All the physical parameters mentioned above are material specific and temperature dependent [3,4,7]. Nevertheless, some general trends are characteristic for most nematics. Increasing the temperature, the absolute value of the anisotropies usually decreases, until it drops to zero at the nematic – isotropic phase transitions. The electrical conductivity increases with increasing temperature, while the viscosity coefficients decrease. For these reasons, nematic liquid crystals are characterized by a parameter named degree of order [4,7], equal to the percent of the total ordered molecules in the sample. All anisotropies are dependent on the degree of order in the liquid crystalline layer.

2. Experimental

In this study we intend to determine the main refractive indices and the birefringence for some monochromatic radiations from the visible range for the following nematic liquid crystals:

• Pure N-(p-methoxy-benziliden)-p-n'-butylaniline (MBBA) purchased from Merck Company and used at 23 °C;

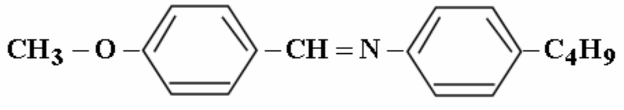


Fig. 1. MBBA structural formula.

• Mixture of poly-(phenyl-methacrylic) ester of cetyloxybenzoic acid (PPMAECOBA) $10^{-2}\ g/cm^3$ in tetrachloromethane (TCM), prepared at “Petru Poni” Institute of Macromolecular Chemistry of Iaşi and 296K as a lyotropic nematic liquid crystal. The molecular weight of the PPMAECOBA was determined by using the flow birefringence and optical anisotropy of the molecules, as it was described in [15]. To characterize the polymer, measurements of diffusion and sedimentation coefficients were performed and Svedberg equation was used to calculate the molecular weight of the polymer ($6.8 \cdot 10^6$).

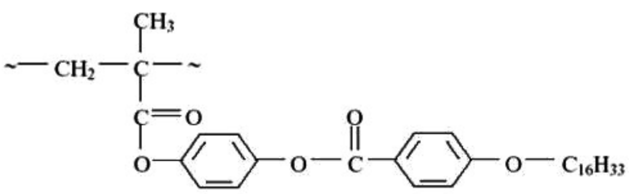


Fig. 2. PPMAECOBA structural formula.

Nematic liquid crystals were kept into a special cell (Fig. 3). This cell consists of two glass plates, provided with a transparent conducting thin layer of SnO_2 on its internal side and separated by four spacers with a calibrated thickness (determining the thickness of the nematic liquid crystal layer) [13,14].

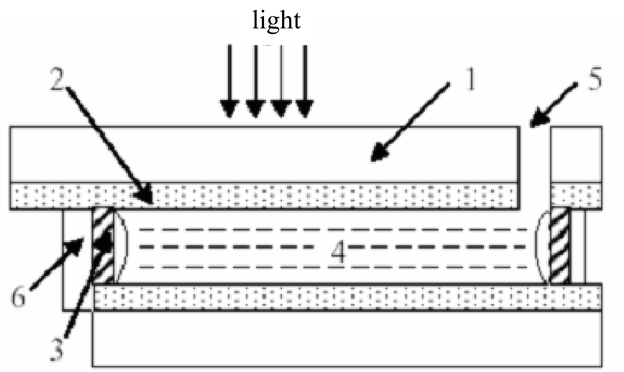


Fig. 3. The cell containing the NLC: 1 - glass plate; 2 – molecular orientation layer; 3 – spacers; 4 – NLC; 5 – filling aperture; 6 – epoxy resin.

Over the conducting layer there is a special layer of lecithin, named molecular orientation layer which improves the orientation of the liquid crystal coming in contact with it. The thin molecular orientation layer of lecithin was obtained by slowly moving the internal walls of the cell through a solution of 5% lecithin in water. In the upper glass plate a filling aperture is made, through which nematic liquid crystal can be introduced in the cell. The experiments were made with layers of a fixed thickness, $L = 14\mu m$, determined by the spacers. The cell was sealed on the outside, around the contour with epoxy resin.

The dominant orientation of the long molecular axes was mechanically ensured [11, 13].

The values of the ordinary and extraordinary refractive indices were interferometrically [14] estimated using a Rayleigh interferometer (Fig. 4).

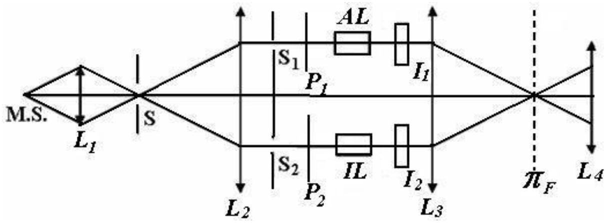


Fig. 4. Schematic representation of the Rayleigh interferometer: M.S. - monochromatic source; S- main slit; S_1 and S_2 - slits of diffraction grating; P_1 and P_2 polarizing filters; AL - anisotropic layer; IL - isotropic layer; I_1 and I_2 - compensatory system; L_1, L_2, L_3, and L_4 - lens.

Two identical polarizers (P_1 and P_2) are introduced in the two beams of the interferometer. The anisotropic NLC layer (contained in the special cell) has been introduced in the measure beam so that light propagates perpendicularly on the optical axis, while an identical cell filled with benzene ($n = 1.50$), or α -brome-naphthalene ($n = 1.65$) has been introduced in the comparison beam. So, the pathway differences in the two beams were small enough that the zero-fringe is moved in the visual field of the interferometer.

Refractive index n_i $(i = o, e)$ has been estimated with the formula:

$$n_i = n + \frac{k\lambda}{L}; i = o, e \qquad (2)$$

In (2) k is the order of the monochromatic fringe that coincides with the zero fringe from the fixed system of fringes [14].

The main values of the refractive index were determined when the polarizer from the measure beam had its transmission direction parallel (n_e) and perpendicular (n_o) to the optical axis.

3. Results and discussion

The results of the measurements, in the absence of the external electric field, for MBBA are contained in Table 1 and for PPMAECOBA in TCM in Table 2.

From Tables 1-2 it results an increase in the main refractive indices and in the birefringence with the increase of the wavenumber of the visible radiation.

Conventionally, the main axis Oc considered as being optical axis of nematic liquid crystal is parallel to the liquid crystal directory. In these conditions the ordinary value of the refractive index is determined for light propagating parallel to Oc axis, having its electric field intensity in the plane aOb.

MBBA nematic liquid crystal was studied in the presence and in absence of an electrostatic field, generated by differences of potential in the range [0.0, 2.0]V. Measurements were made for U=0.0; 0.75; 1.50 and 2.0 V. The results obtained for U=0.0V and U=2.0 V are illustrated in Figs. 5 and 6. From these figures it results that the main refractive indices increase with the radiation wavenumber increasing, showing a normal dispersion of MBBA.

Table 1. Interferometrically estimated main refractive indices of MBBA, ($L = 14 \mu m$, T=296 K).

No.	$\tilde{\nu}(\mathrm{cm}^{-1})$	n_o	n_e	Δn
1	20342	1.7005	1.8356	0.1351
2	19440	1.6490	1.7800	0.1310
3	18312	1.6029	1.7289	0.1259
4	17857	1.5895	1.7135	0.1239
5	17331	1.5774	1.6990	0.1216
6	17088	1.5729	1.6935	0.1205
7	16969	1.5710	1.6910	0.1200
8	15800	1.5600	1.6750	0.1150

Table 2. Interferometrically estimated main refractive indices for PPMAECOBA ($M = 6.8 \cdot 10^6$) in TCM ($C = 10^{-2}$ g/cm^3, $L = 14 \mu m$, T=296 K).

No.	$\tilde{\nu}(\mathrm{cm}^{-1})$	n_o	n_e	Δn
1	20342	1.5922	1.8056	0.2134
2	19440	1.5729	1.7773	0.2043
3	18312	1.5557	1.7472	0.1915
4	17857	1.5507	1.7367	0.1860
5	17331	1.5461	1.7255	0.1793
6	17088	1.5445	1.7206	0.1762
7	16969	1.5437	1.7184	0.1746
8	15800	1.5396	1.6986	0.1589

In Figs. 5b and 6b the birefringence of the MBBA layer in absence and in presence of an electrostatic field is plotted as function of radiation wave number. The MBBA birefringence also increases with the radiation wavenumber increasing.

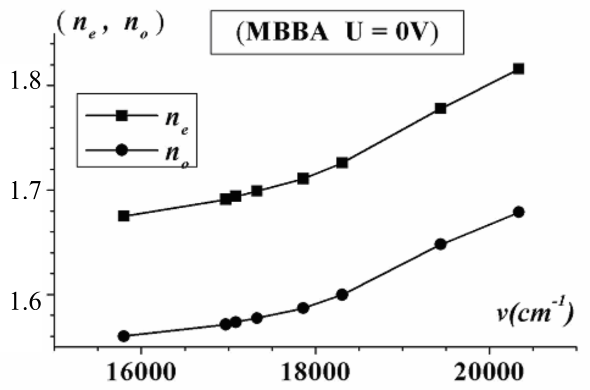


Fig. 5a. MBBA ordinary and extraordinary refractive indices in absence of the external electrostatic field (U=0 V, h=14 μm, T=296 K).

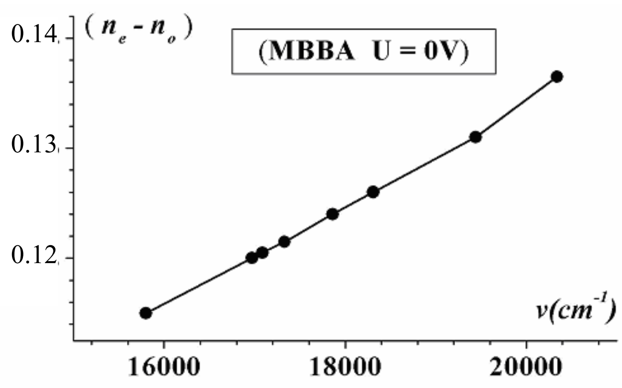


Fig 5b. MBBA birefringence in absence of the external electrostatic field (U=0V, h=14μm, T=296 K).

The ordinary refractive index is almost not dependent on the applied potential magnitude. The dependences of the extraordinary refractive index and of birefringence for the four values of the applied potential are given in Figs. 7 a and b. From these figures it results a saturation tendency for the extraordinary refractive index and for birefringence near the value of 2V of the applied potential.

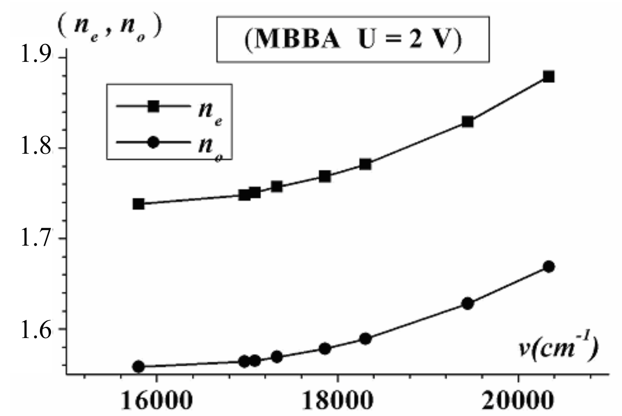


Fig. 6a. MBBA ordinary and extraordinary refractive indices in presence of the external electrostatic field (U=2V, h=14μm, T=296 K).

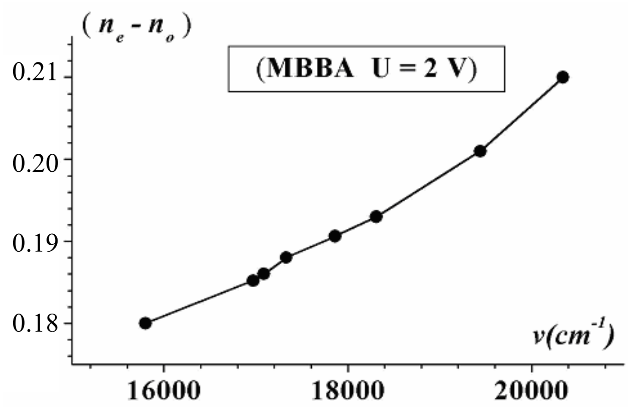


Fig. 6b. MBBA birefrinbence in presence of the external electrostatic field (U=2V, h=14μm, T=296 K).

The lyotropic liquid crystal obtained from PPMAECOBA (10^{-2} g/cm^3 in TCM) has the highest order symmetry axis parallel to the direction of the long side chains of the bulk polymer [14,15] which are oriented by dipolar interactions. The intrinsic anisotropy induced by the super-molecular aggregation of the side chains of PPMAECOBA in TCM is increased by the molecular orientation layer existent on the internal walls of the cell [13,14].

The birefringence of PPMAECOBA in TCM depends on the frequency of the electric field as it is shown in Fig. 8 for five values of natural monochromatic radiations.

Analyzing the data from Fig. 8, the following results are evidenced:

In the visible range the PPMAECOBA birefringence increases with the increasing of the light wave number.

The highest value for the birefringence of PPMAECOBA in TCM is obtained for electrostatic field acting perpendicularly to the direction of light propagation and on the nematic director (in the plane perpendicular to the light propagation direction, the nematic director and the external electric field are perpendicular each other).

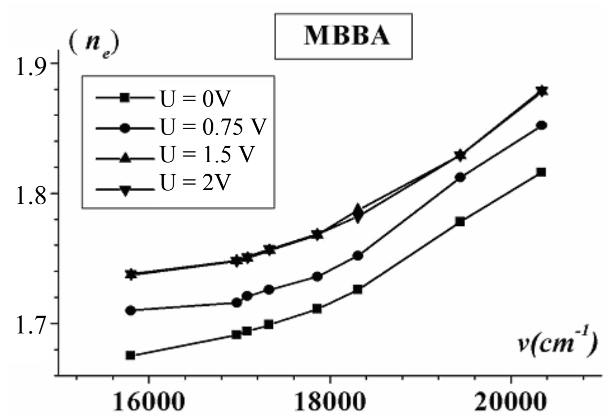


Fig. 7a. Extraordinary refractive index of MBBA at different values of the applied potential (h = 14 μm, T=296 K).

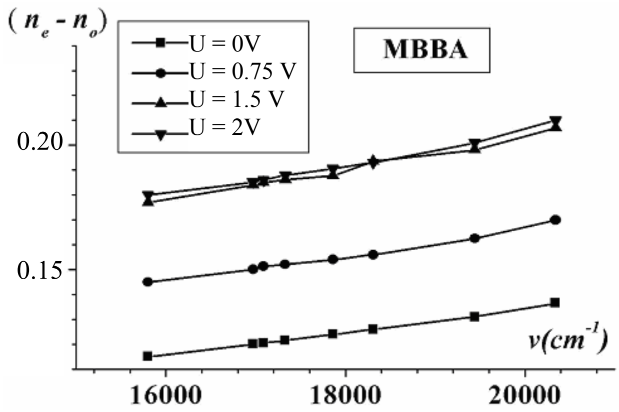
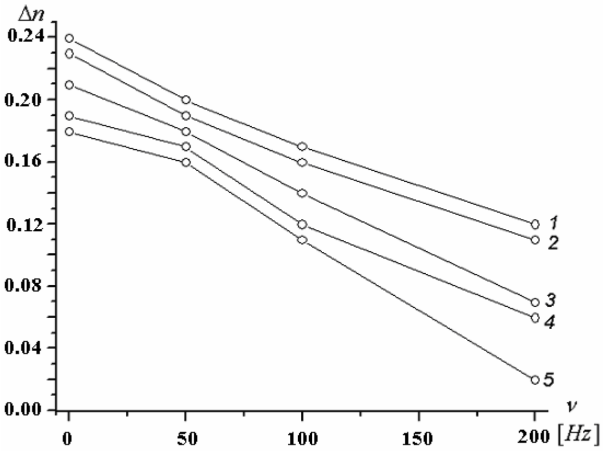


Fig. 7b. Birefringence of MBBA at different values of the applied potential (h=14μm, T=296 K).



$\tilde{\nu}(\mathrm{cm}^{-1})$ 1) 24000; 2) 22950; 3) 19440; 4) 16960; 5)15800

Fig. 7. The PPMAECOBA birefringence Δn *vs. frequency of the external alternate electric field (magnitude of the applied potential U = 1.5 V, h=14* μm *, T=296K)).*

When an alternating electric field acts perpendicularly to the light propagation direction, a decrease in the birefringence occurs with the increase in the alternating electric field frequency for all monochromatic visible radiations used in this study.

The decrease in the birefringence with increasing the frequency of the alternating electric field emphasizes a high viscosity of the solved polymer side chains.

4. Conclusions

At room temperature, the mesogenic molecules of MBBA and the side chains of PPMAECOBA in TCM are enough oriented that their birefringence has measurable values.

A decrease in the main refractive indices as well as of birefringence with the wavelength increasing has been evidenced, both for MBBA and PPMAECOBA in TCM.

The increase in the anisotropy of the PPMAECOBA in TCM, produced by the electrostatic field emphasizes the fact that the polymer side chains are oriented by dipolar interactions.

The birefringence of PPMAECOBA in TCM decreases with the increase in the frequency of the external alternating electric field.

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