Lyotropic liquid crystal in external electrostatic fields

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The birefringence of a sample consisting from 10^{-2} g/cm^3 PPMAECOBA in TCM was measured in an external electrostatic field with variable intensity. The birefringence of the PPMAECOBA in TCM increases with the electrostatic field intensity. The birefringence shows a normal dispersion, decreasing with the light wavenumber decreasing.

(Received January 09, 2010; accepted January 19, 2010)

Keywords: Polymer liquid crystal, Birefringence, Electrostatic field influence

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1. Introduction

Liquid crystals are substances possessing one or more mesophases between their liquid and solid phases. 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 [1-4]. The preferential direction (parallel to the direction of the average orientation) is given by a versor, named nematic director.

Lyotropic liquid crystals can appear in mixtures of mesogenes and thermodynamically bad solvents. Some polymers can form liquid crystalline layers in the thermodynamically bad solvents. Hydrodynamically and optically investigations [3,5,6] showed that the polyalchylmethacrylate mixtures, at determined concentrations in thermodynamically bad solvents possess a great ordering of their side-chains, while the main chains are usually disordered. So, poly-(-phenyl-methacrylic) ester of cetyloxybenzoic acid (PPMAECOBA) with molecular weights of $[20\text{-}0.1]10^6$ in tetrachloromethane (TCM) at a concentration of 10^{-2} g/cm^3 gives liquid crystalline phases by a pronounced collective dipolar ordering of the side-chains.

PPMAECOBA in TCM was characterized as a negative uniax liquid crystal, whose side-chains orient perpendicularly on the external electrostatic field [6,7]. A decrease in the anisotropy has been revealed by the molecular weight increasing. This anomaly of the PPMAECOBA in TCM has been explained by the decreasing of the mass density in the side-chains when the molecular weight increases. The anisotropy decreasing when the molar mass increases was correlated with the decrease in the ordered parameter [5].

The liquid crystalline mixtures of PPMAECOBA in TCM have a great negative flow birefringence [3,5], while the corresponding monomer has a positive one. The highest value of the monomer polarizability was measured along to its long axis.

The monomers are bonded chaotically around the main chains in PPMAECOBA, so, the components of the dipole moments acting perpendicularly on the main chains are reciprocally compensated. Only the components acting parallel to the main chains have an essential role in the polyester birefringence. Parts of the main chains become parallel to the external electrostatic field intensity and so, the side-chains orient perpendicularly on the external field, by the collective interactions.

The anisotropy of the polymer liquid crystals essentially depends on the solvent quality. In a bad solvent, the main chains are disordered, as bulk-chains. The degree of order in the lateral side-chains increases as orientation intermolecular forces increase and the interactions between the polymer and the thermodynamically bad solvent are lowered in competition with the side-chains collective interactions.

The optical properties of the nematics correspond to those of a uniax crystal. The birefringence of the nematics indicates, by its values, the degree of order in the liquid crystalline sample [2,3]. Like the ordinary (n_o) and extraordinary (n_e) refractive indices, the birefringence Δn is a dispersive parameter. It is defined by the relation:

$$\Delta n = n_e - n_o \qquad (1)$$

The degree of order in a liquid crystalline sample can be increased by using external mechanic, electric or magnetic fields. The birefringence can be measured by using linearly polarized light that propagates perpendicularly to the director, because in this situation a phase difference between the ordinary and extraordinary radiations appears and the polarization state is changed as function of the pathway introduced by the anisotropic layers. When an analyzer is introduced after the anisotropic layer, the emergent light can change its spectral composition [8,9].

The behavior of the liquid crystal in an external (electric, magnetic, mechanic) field depends on the field intensity and also on the electric, magnetic or mechanical anisotropy. The magnetic anisotropy $\Delta\chi = \chi_e - \chi_o$ is smaller than the electrical anisotropy, $\Delta\varepsilon = \varepsilon_e - \varepsilon_o$. So, in an external electrostatic field the induced distortions are bigger than those induced by a magnetic field [10,11].

2. Experimental

Poly(-phenyl-methacrylic) ester of cetyloxybenzoic acid (PPMAECOBA) in tetrachloromethane (TCM) in a concentration of $10^{-2}\,\mathrm{g/cm^3}$ is a bulk polymer whose side-chains exhibit an orientation order.

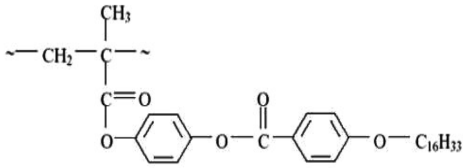

Fig. 1. ppmaecoba structural formula.

Liquid crystalline layer made from PPMAECOBA in TCM is kept in a special cell having interior conducting layers of SnO_2 deposed on the glass plates in order to permit the application of an external electrostatic field, perpendicularly oriented on the plate's surfaces. An orientation layer facilitates the initial orientation of the side chains polymers parallel to the plate surface. The field improves the degree of orientation and increases the birefringence of the sample [6,10,11].

The values of the main refractive indices were interferometrically determined as described previously [12].

A Rayleigh interferometer was used for this kind of measurements. Two polarizers were used to obtain linearly polarized light in both beams of the interferometer. The supplementary pathway introduced by the liquid crystalline layer compared with those introduced in the comparison beam by an isotropic layer, has been estimated by the order of the monochromatic fringe that coincides with the zero fringe from the fixed system of fringes [8,12]. The main refractive indices were determined when the transmission directions of the polarizer from the measure beam were parallel and perpendicular, to the optical axis of the liquid crystalline layer, respectively.

3. Results

The measurements were made in the absence and in the presence of the external electrostatic field applied between the opposite wells of the cell and having a variable intensity.

The main refractive indices were interferometrically determined, and the birefringence estimated by using formula (1).

The results obtained are given in Fig. 2. PPMAECOBA in TCM shows a normal dispersion [13] as Cauchy formula predicts. Both the principal refractive indices and the birefringence of the studied samples decrease with the light wavelength increasing.

This dependence is most evident in the absence of the electrostatic field and also for the smallest values of the electrostatic field. For electric field intensities higher than 0,07MV/m, the velocity of the birefringence variation is indeed small.

Experimental data revealed an increase in the birefringence with the increasing in the electrostatic field intensity. A saturation of this phenomenon appeared for the electrostatic field intensities (E) higher than 0.11MV/m.

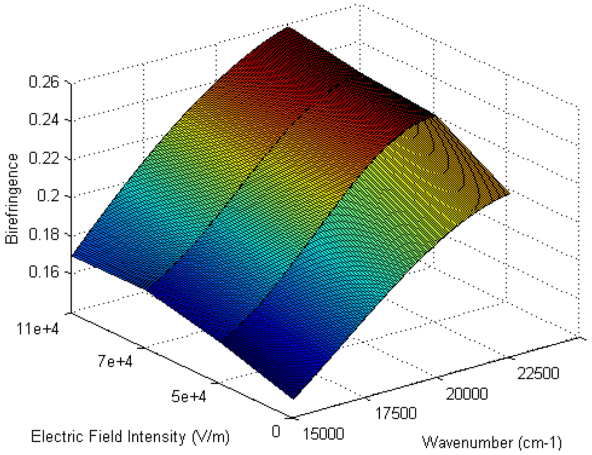

Fig. 2. The dependence of the birefringence on the wavenumber and on the appplied electrostatic field.

The increase of the birefringence was explained by the increase of the degree of order in the side chains of the bulk polymer PPMAECOBA, by dipolar interactions with the electrostatic field intensity increasing.

By modifying the birefringence of the sample, the external electrostatic field can act indirectly on the spectral composition of the emergent light from a system consisting of two crossed (or parallel) polarizers having a thin layer of liquid crystal between them. So, the spectral composition of the emergent light from such system can be precisely controlled by an external electrostatic field [14-16].

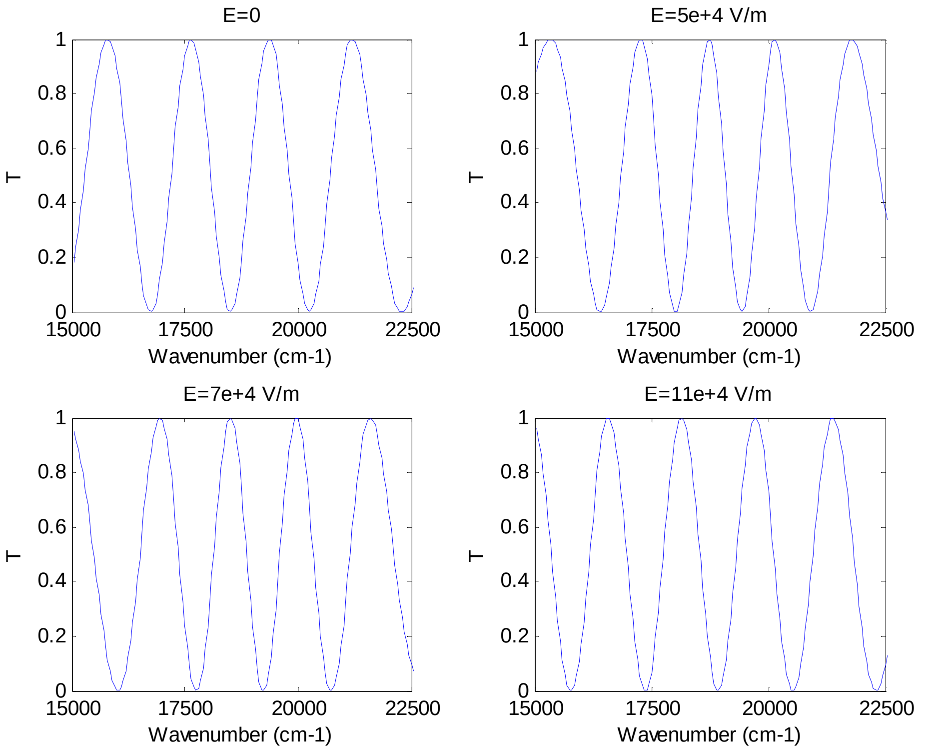

Fig. 3. Transmission factor of PPMAECOBA between two crossed polarizers vs light wavenumber for different values of the external electrostatic field intensity (L=14μm).

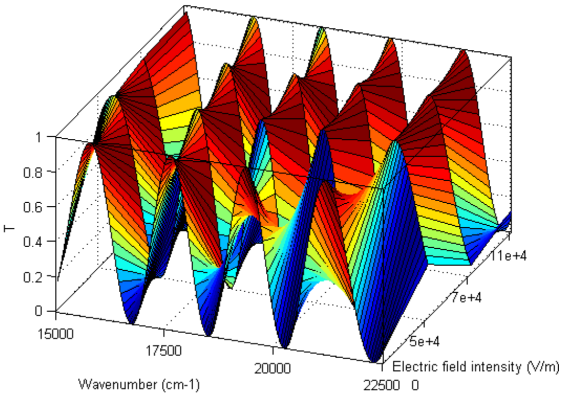

Fig. 4. Transmission factor of PPMAECOBA between two crossed polarizers vs light wavenumberand the intensity of the external electrostatic field (L=14μm).

The dependence of the birefringence on the light wavenumber and on the applied electrostatic field is illustrated in Fig. 2. In order to obtain this dependence, interferometric measurements of the main refractive indices were made in the absence and in the presence of an electrostatic field acting perpendicularly on the glass plates of the cell. The light propagation direction was parallel to the electrostatic field intensity.

From Fig. 2 it results a normal dispersion of the liquid crystal birefringence and a decrease of the birefringence when the electrostatic field intensity decreases to zero.

The transmission factor of PPMAECOBA vs. wavenumber when the electrostatic field intensity is modified between 0 and $11\cdot 10^4\,\mathrm{V/m}$ is plotted in Figures 3 and 4. These figures suggest that the spectral composition of light emerging from a device consisting by two crossed polarizers having between them the liquid crystalline layer with a constant tickness (L=14μm) and its optical axis bisecting the angle between the transmission directions of the polarizers. This fact has important optical applications.

4. Discussion

Hydrodynamical and optical studies show that the mixtures of polyalchylmethacrylates in bad solvents have a great orientation order of their side chains. The optical properties of the polymer essentially depend on the solvent nature.

PPMAECOBA with molecular weight between $(20\text{-}0.2)\times 10^6$, in concentrations of $10^{-2}\,\mathrm{g/cm^3}$ in CCl_4, is an anisotropic mixture with negative Kerr constants [5]. This fact proves that the side-chains of the polymer orient perpendicular to the main chains. The side chains of this polymer have mesomeric structures with a high polarizability. The dipol moment of the side chains can be decomposed into two components, one perpendicular and one parallel to the main chain. The side-chains are randoomly bond to the main chain, so the components of the dipole moment acting parallel to the side-chains are reciprocally compensated and the component parallel to the main chain have esential role in the birefringence of the polymer.

The side chains bond to a bulk main chain are oriented parallel one to another in the bad solvent by cooperative interactions.

In an external electric field, the main chains, possessing a great dipole moment, have parts parallel to the field and the side-chains orient perpendicular to the field. This effect determines the negative value of the polymer birefringence.

5. Conclusions

The spectral composition of the emergent light from a device made by two crossed polarizers and the anisotropic layer between them can be easily modified in the presence of an electrostatic field, by the variation of the liquid crystalline layer birefringence.

The side-chains of the bulk polymer PPMAECOBA in TCM form an oriented system with uniaxial properties, showing a normal dispersion. The higher the birefringence the higher the parameter of order is. This study is important for producing devices for the modification of the spectral composition of the emergent light.

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