Liquid Crystalline Phase of Polymeric Esters of Alkoxybenzoic Acid in Tetrachloromethane

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The birefringence of some polymeric esters of alkoxy benzoic acid (PEABA) in tetra chloromethane (TCM) was determined by previously proposed interferometric methods in polarized light. An increase in PEABA birefringence when an external electric field acts on the liquid crystal layer was evidenced in this paper. The decrease of PEABA birefringence with the increase in the alternate electric field frequency was also evidenced. The dipolar nature of the collective interactions between the side-chains of PEABA in liquid crystalline phase and also the viscosity of the lyotropic liquid crystal obtained by mixing PEABA with TCM in concentrations of about 10^{-2} *g / cm*^{3}*, at room temperature are sustained by the results obtained in this paper.*

Keywords: PEABA birefringence, tetra chloromethane (TCM), polarized light

The polymeric esters of alkoxy benzoic acids (PEABA) [1-3] have the chemical structure shown in figure 1.

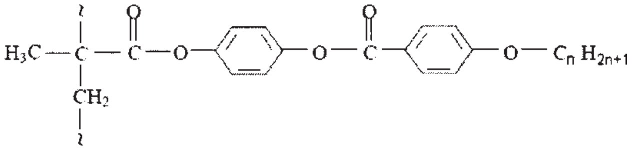

Fig. 1 PEABA chemical structure

The PEABA side-chains are dipolar substitutes of the bulk polymer showing a great rigidity responsible for the lyotropic liquid crystalline phase in the thermodynamically bad solvents.

The researches on the mechanical and optical properties of polymeric esters of alkoxy benzoic acids (PEABA) [1-5] emphasize that, in thermodynamically bad solvents for these polymers, the side chains are more ordered compared to the main chains. So, in tetra chloromethane (TCM), the PEABA main bulk polymeric chains can be disordered, but the side chains are ordered in parallel to one another by collective dipolar interactions. A preferential direction for the side chains alignment can be defined for PEABA in TCM liquid crystals. This direction determines the optical axis of the lyotropic liquid crystal. The PEABA anisotropy is very important in practical applications, due to the fact that the liquid crystalline phase of PEABA in TCM is realized at room temperature.

The optical birefringence of a liquid crystalline sample can be considered as an indicator of its degree of order [6-8]. An external electrostatic field can improve the degree of order in the liquid crystalline samples [9-14]. So, the degree of order of PEABA side-chains in TCM increases in the presence of an external electrostatic field oriented perpendicularly on the preferential direction of the side chains.

Such as N-(4-methoxybenzilidene)-4-butylaniline (MBBA) [15] and poly-(phenyl methacrylic) ester of cetyloxybenzoic acid (PPMAECOBA) [16, 17], PEABA in TCM may be used in different applications [18, 19] for changing the light spectral composition or its polarization state.

An optical device consisting from one liquid crystalline layer between two crossed polarizers has an emergent visible spectrum dependent on the liquid crystalline layer birefringence and on its thickness [16, 17]. This device can be used to separate some light components from the visible spectrum; its transmittance is directly dependent on the liquid crystal birefringence and it is electrically controlled.

From this point of view, the study of the birefringence of some polymeric esters of alkoxy benzoic acids (PEABA) in thermodynamically bad solvents becomes very important. The information about the values of birefringence is also important for the study of the degree of order in the liquid crystalline sample.

The birefringence in the absence or in the presence of an external electrostatic field is measured by a previously proposed method based on the channelled spectra obtained with an anisotropic layer (inorganic crystal or liquid crystal) [16-21]. The birefringence of the samples in the absence of the external electrostatic field is usually smaller than that measured in the presence of the field and increases with the intensity of the electrostatic field.

The high optical anisotropy of PEABA in TCM measured in [1-3] could be explained by the high degree of order in the side-chains of the polymer determined by collective dipolar interactions. The anisotropy of the electric polarizability was estimated by V. N. Tsvetkov as being of the order ~ - (3100 - 1700) x 10^{25} cm^3 for different molar weights of the polymer, while the monomer (corresponding to the lateral side-chains) anisotropy was estimated to be ~ -(130 - 70) x 10^{25} cm^3.

The electro-optical properties of the PEABA in bad thermodynamically solvents are practically unique [3-5]. These polymers have a negative Kerr constant:

$$k = \frac{\Delta n}{C \cdot E^2} \qquad (1)$$

where:

$$\Delta n = n_e - n_o \qquad (2)$$

Optical birefringence Δn from (2) is the difference between extraordinary (n_e) and ordinary (n_o) refractive indices (measured with linearly polarized light having its

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electric field intensity oriented in the plane determined by the optical axis and by the propagation direction and perpendicular to it, respectively). In relation (1), C is the polymer concentration in the solvent and E is the intensity of the external electric field.

The components of the electric dipole oriented perpendicularly on the main chains direction are reciprocally compensated, and only the components parallel to this direction have an important role in the electrically induced birefringence of PEABA. For this reason, Kerr constant takes negative values. In the external electrostatic field, the polymeric side-chains are oriented parallel to each other and perpendicularly to the electric field intensity. The macromolecules show important dipolar moments along the main chain direction. The normal components to the polymer main chain are reciprocally compensated, due to the parallel directions of the side chains. It becomes possible that the side chains of the polymer (strongly interacting by dipolar forces) become more close to one another, causing a relative high flexibility of the main polymeric chain [1-4].

The birefringence of the PEABA in thermodynamically bad solvents shows an important dispersion in external sinusoidal electric fields, as has been shown [1-3]. This fact demonstrates a high rigidity of the side chains in the bad solvent determining big values of its viscosity. The birefringence of PEABA in TCM can be modified in an electrostatic field in which the side-chains of the polymer become aligned perpendicularly on the field direction.

The liquid crystalline layer between two electrically charged transparent walls becomes anisotropic with the director perpendicular to the field direction. This kind of layer can change the light polarization state.

An optical device consisting from a liquid crystalline layer between two crossed polarizers does not transmit the monochromatic radiations which keep their polarization state, while the radiations with changed polarization state can cross this device.

The PEABA in TCM have potential practical applications in changing the radiation spectral composition. One optical system consisting from an anisotropic layer between two crossed polarizers induces changes in the spectral composition of radiations. The wavenumber of the radiations which pass from this system depends both on the birefringence and on the thickness of the anisotropic layer.

The aim of this paper is to show the possibility to control electrically the birefringence of PEABA in TCM lyotropic liquid crystal.

Materials and methods

The polymeric esters of alkoxy benzoic acids (PEABA) were achieved from Sigma-Aldrich Company.

Liquid crystals are kept in special cells described below [9-12]. The cell (fig.2a) is made of two glass plates with a transparent conducting layer deposed on their internal walls. An orientation layer was deposed over the conducting layer, by slowly moving the internal walls of the plate in a diluted solution of lecithin in water. Four identical spacers of a constant thickness (14 μm) were used in order to obtain a plan parallel liquid crystalline layer. The cell was tightened with an epoxy resin, in order to avoid the liquid crystal contact with the atmosphere.

The special cell can be connected to an electric source by a variable resistor. So, the electric field intensity acting on the liquid crystalline layer can be slowly modified. The electrostatic field acts parallel to the light direction. Being a negative anisotropic sample, the side chains of PEABA are supplementary oriented perpendicularly on the electric field direction. In this case light propagates perpendicularly on the preferential direction of the nematic liquid crystal (it coincides with the optical axis).

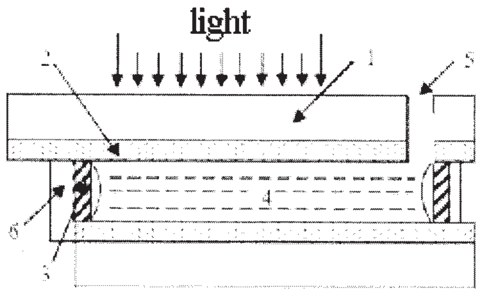

Fig. 2a Special cell for liquid crystal: 1. glass plate; 2. conducting transparent layer and lecithin orientation layer; 3. spacers; 4. liquid crystal; 5. orifice for empting; 6. epoxy resin

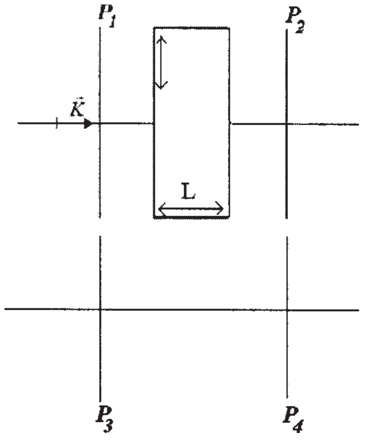

Fig. 2b Optical device for channelled spectra recording

The device used for obtaining the channelled spectra [16] is drawn in figure 2b. Placed between two identical crossed polarizers, P_1 and P_2, the cell (of thickness L) with liquid crystal is introduced in the measure beam of the spectrophotometer. Two polarizers P_3 and P_4 having their transmission directions parallel are concomitantly introduced in the comparison beam. The components of the device from figure 2b can be rotated around the light propagation direction, $\vec{k}$.

By using the above described device, the channelled spectra were recorded at a spectrophotometer Specord UV VIS Carl Zeiss Jena. The positions of the maxima and minima were precisely determined from the channelled spectra achieved in the presence and the absence of an external electrostatic field.

The channelled spectra from the spectral range [14000 - 23000] cm^{-1} of PEABA in TCM liquid crystalline layers, in the absence and in the presence of an electrostatic field are given in figures 3 a and b. In the studied spectral range the birefringence dispersion is very small. The number of the channels increases in the presence of an external electrostatic field, as it results from figures 3a and 3b.

Results and discussions

The birefringence was estimated by the wavenumbers maxima and minima from the channelled spectra and formula (3) [16].

$$\Delta n = \frac{1}{2L}\frac{\nu_{2(k+1)} - \nu_{2k}}{\nu_{2(k+1)}\nu_{2k+1} + \nu_{2k}\nu_{2k+1} - 2\nu_{2(k+1)}\nu_{2k}} \quad (3)$$

In relation (3), ν_{2k} and $\nu_{2(k+1)}$ are the wavenumbers corresponding to the consecutive two minima, and ν_{2k+1} corresponds to the maximum between them.

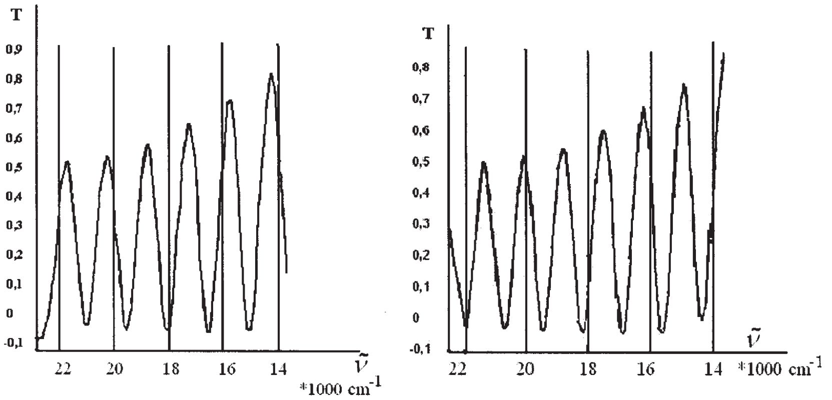

Fig. 3 Channelled spectra in 22000-14000 cm^{-1} range of PEABA in TCM
a)in the absence and b) in the presence of the external electric field

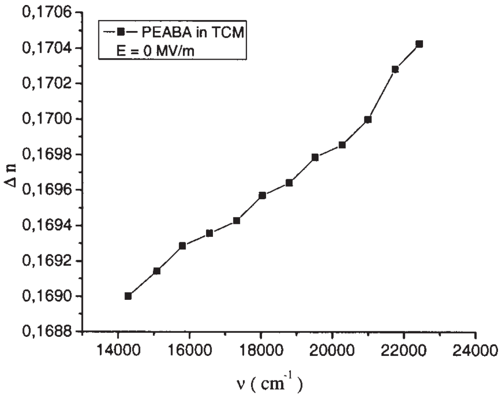

Fig. 4a) PEABA in TCM birefringence in the absence of the electrostatic field

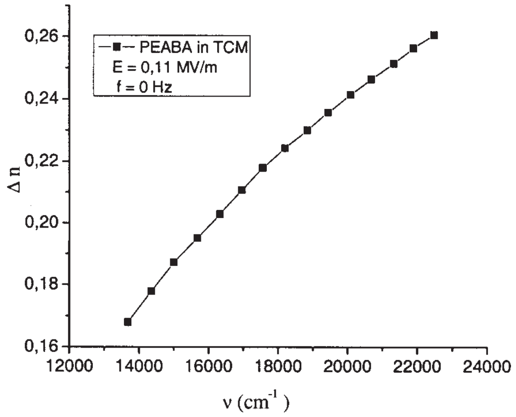

Fig. 4b) PEABA in TCM birefringence in external electrostatic field

The birefringence dispersion in the analysed spectral range [14000 - 23000] cm^{-1} results from figures 4 a and b, obtained in the absence and in the presence of the external electrostatic field.

The increase in the channels number in the presence of the external electrostatic field proves an increase in birefringence in the external electrostatic field. The maxim value of the birefringence in the absence of the electrostatic field is of about 0.170, while the maxim value in the presence of the external field is of about 0.265.

From figures 4 a and b, an increase of the birefringence with the wavenumber increasing is evidenced. In the considered spectral range, the dependence of Δn vs. ν(cm^{-1}) is expressed by a line in the presence of the electrostatic field.

The total dispersion of PEABA in TCM in the spectral range [14000 - 23000] cm^{-1} is of about 0.001 in the absence of the external electrostatic field, while in the presence of the electrostatic field it becomes 0.097.

When an alternate electric field is applied between the walls of the cell containing liquid crystalline sample, important modifications of birefringence are induced by the variation of the electric field frequency.

In order to compare more easily the values of the birefringence determined in the electrostatic and alternate electric fields, one defines the relative birefringence as follows:

$$\Delta n_r = \frac{\Delta n_f}{\Delta n_0} \qquad (4)$$

In relation (4), Δn_f is the birefringence in an alternate electric field of frequency *f* and Δn_0 is the birefringence in the electrostatic field (f=0).

From figure 5 it results a decrease in the relative birefringence with the increase in the electric field frequency. This proves the high viscosity of PEABA lyotropic liquid crystal. Concomitantly, a decrease in the relative birefringence with increasing wavelength was evidenced.

The PEABA birefringence in the absence and in the presence of electrostatic and alternate fields is plotted in figure 6. From this figure it results that the birefringence increases when an electrostatic field is applied. If an alternate electric field acts on the lyotropic liquid crystalline layer (samples 3-5), the birefringence decreases with the increase in the electric field frequency.

In figures 5 and 6, the birefringence values were determined interferometrically [15] for the wavelengths corresponding to a LED (λ=432nm), a Natrium lamp (λ=589nm) and Hydrogen lamp (λ=632nm). These monochromatic radiations belong to the studied spectral range. These determinations are in a good accordance with the data obtained by spectral means on the basis of channeled spectra.

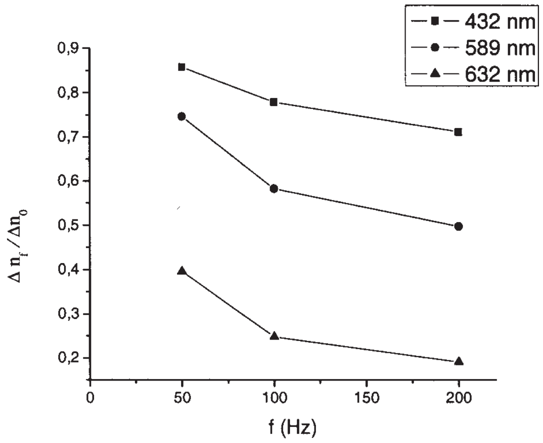

Fig. 5 Relative birefringence vs. alternate electric field frequency

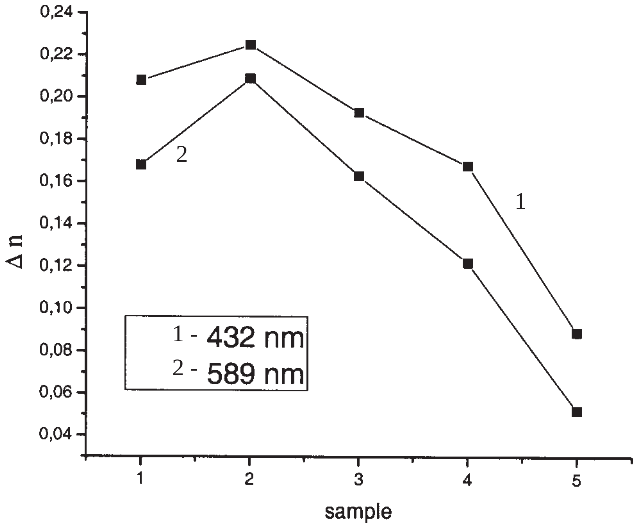

Fig. 6 PEABA birefringence for monochromatic radiations 432 nm and 589 nm

The degree of order in the liquid crystalline layers determines the values of the refractive indices of the studied samples. An electrostatic electric field can increase the degree of order in the liquid crystalline sample, since an alternate electric field decreases the degree of order, decreasing the liquid crystal birefringence. The degree of order and the stability of the liquid crystalline layers can be also analyzed by other methods [22-24].

Conclusions

The birefringence increasing with the light wavenumber can be influenced in the presence of an external electrostatic field.

The dipolar nature of the collective interactions responsible for the liquid crystalline phase appearance is evidenced by the birefringence dependence on the alternate electric field frequency.

Some applications in various fields of optoelectronics can be obtained due to the capacity of the electrostatic field to increase the degree of orientation of the polymeric side-chains and consequently to improve the anisotropy of the liquid crystals.

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