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ADP011617

TITLE: Optical Dichroism of Homeotropically Oriented Films of Comb-Shaped Liquid Crystal Polymer

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TITLE: International Conference on Electromagnetics of Complex Media [8th], Held in Lisbon, Portugal on 27-29 September 2000. Bianisotropics 2000

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Optical Dichroism of Homeotropically Oriented Films of Comb-shaped Liquid Crystal Polymer

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Abstract

In this work the polarization absorption spectrum of homeotropically oriented comb-shaped liquid crystal polymer (LCP) film interposed in the electrooptical cell was investigated. The optical parameters of electrodes and polymer were estimated from the observed absorption spectra of the cell with and without polymer film using the method of interferometric extrema envelopes. This method enabled us to re-establish the true polarization absorption spectrum of the polymer. For this purpose the refractive index dispersion data of the substrates and the polymer obtained by independent investigations were used. From the dichroic ratio for the absorption band at $\lambda = 405$ nm the order parameter S was estimated taking into account the effects of local fields.

1. Introduction

Recently the oriented liquid crystal (LC) and liquid crystal polymer (LCP) films have occupied an important position in modern technologies and have been widely used as a material of integral optic elements, in optical recording and optical information systems including the polarization holography also [1–5].

The important characteristic of the oriented films is the orientation degree of the anisotropic molecules in LC films or mesogenic groups in LCP films. One of the methods of orientation degree estimation is the measurements of light absorption anisotropy (optical dichroism) of the polymer itself or dye absorption bands. The method is widely used for the films with planar orientation when the crystal optical axis is situated in the film's plane [6,7,8]. For such film orientation the dichroic ratio is easily obtained as the absorption coefficients ratio for the light polarization parallel and perpendicular to the crystal optical axis. However the producing of sufficiently large homogenous LCP films with planar orientation is connected with essential technical difficulties. Therefore for LCP films the homeotropical orientation is used when the crystal optical axis is directed perpendicular to the film plane. In this case for dichroic ratio estimation it is necessary to use the oblique polarized light incidence for the absorption coefficient measurements in the samples under study. To obtain the homeotropical orientation of the LCP sample the latter is placed in the electrooptical cell. The electrooptical cell is a multilayer system (sandwich) consisting of two substrates with thin electroconducting semiconductor films (electrodes) between which a thin layer of the polymer investigated is placed. When the oblique beam incidence is used the observed polarization absorption spectra are depending on Fresnel reflection losses at all layer boundaries of the cell and besides that on the absorption of these layers. The problem is reduced to LCP absorption coefficient estimation from the experimentally observed transmission spectra for the cell with and without the polymer film investigated using the light beam with different polarization.

2. The Theory of Method

Let us consider the case of isotropic absorbing film (electrode) placed between two isotropic transparent infinite dielectric layers (air – glass). If the refractive indices of dielectric, the complex refractive index of the electrode film and its thickness are known, the energetic transmission T and reflection R coefficients may be calculated from the expression, formulated in [9] both for the case of TE wave (s - polarization) and TM wave (p – polarization). In our case the thickness of the dielectrics is finite and the cell as a whole is a symmetrical system – air (1) – substrate (3) – electrode (2) – air (4) - electrode (2) – substrate (3) – air (1). In this case the transmission I_0 of the cell without polymer may be expressed by the following formula [10].

$$I_o = J_0^2 = (T_{34}T_{31})^2 / (1 - R_{34}R_{31})^2 , \tag{1}$$

where the transmission T_{31} and reflection R_{31} are calculated for the infinite layers [9] and T_{34} and R_{34} are the Fresnel energetic transmission and reflection coefficients on the boundary of the substrate material (glass (3) – air (4)). As the calculations show the denominator in formula (1) differs from the unity by $\approx 1\%$ and therefore later on we shall neglect this difference. Also we shall assume the absorption in the electrode to be sufficiently small to neglect the k^2 quantity compared with k in the expression of electrode complex refractive index $n_2^* = n_2(1-ik)$. In this case the quantity J_0 may be transformed to the following form:

$$J_0 = (64a^2b^2c^2exp(-\gamma_2)/[(a+c)^2(b+c)^2exp(\gamma_2)+(a-c)^2(b-c)^2exp(-\gamma_2)+2(a^2-c^2)(c^2-b^2)cos\varphi](a+b)^2 \tag{2}$$

where $a = cos\ i_0$ (i_0 – external angle of light incidence on the cell); $b_\perp^2 = n_3^2 - sin\ i_0$; $b_{//} = b_\perp / n_3^2$ (n_3 is the refractive index of substrate material (glass)); $c_\perp^2 = n_2^2 - sin\ i_0$; $c_{//} = c_\perp / n_2^2$ ($\perp$ is s - polarization and $||$ is p – polarization). The absorption in the electrode is defined by the expression $\gamma_2 = \varphi n_2^2 / c_\perp^2$, where $\varphi = 4\pi h c_\perp / \lambda$ (h is the electrode thickness, λ - light wavelength). So for any angle i_0 (if the parameters of substrate n_3, electrode n_2 and γ_2 and its thickness h are known) we can calculate the relative intensity of the polarized light transmitted though the cell. However the inverse problem solution – that is the estimation of the optical characteristics of substrate and electrode from the experimentally obtained transmission spectrum – is related to certain difficulties. In general case for the absorbing substrate and absorbing electrode this problem has not any analytical solution. For the approximate solution the most known method is the spectrophotometrical one of interferometric extrema envelops, which for the first time was suggested for transmission spectra by Valeev [11] and elaborated by Rakov [10]. The reflection spectra was worked out in detail by Filippov [12,13].

The point of the method consists in employing the interferometric extrema envelops for obtaining the wavelengths and light intensity for the maxima J_+ and minima J_- of the experimental quasi-periodic spectrum. The extremum arises at the condition (see (2)) $cos\ \varphi = (-1)^m$ (m – being an integer). In this case the expression (2) may be essentially simplified. Multiplying the numerator and the denominator by $exp(-\gamma_2)$ and extracting the square root we see that the denominator is a product of two perfect squares. Further introducing the denomination

$$A' = (I_+(a+b))^{0.25} / 8ab \tag{3a}$$

$$A'' = (I_-(a+b))^{0.25} / 8ab \tag{3b}$$

$$F = (a+b)+(A'-A'')/2A'A'', \tag{3c}$$

we obtain:

$$c = 0,5(F) + (0,25F^2 - ab)^{0,5} \tag{4a}$$

$$exp(\gamma_2) = [c - A'(a-c)(c-b)] / A'(a+c)(c+b),\qquad(4b)$$

where the values c and $exp(\gamma_2)$ are defined only for the extrema wavelengths. The thickness of the electrodes h may be calculated from the condition $4h = m_i\lambda_i / c_i$. To obtain the values $c(\lambda)$ and $\gamma_2(\lambda)$ for all wavelengths it is possible to use the dispersion dependence model of Chandrasekhar-Drude:

$$n_2^2 - 1 = A\lambda^2 / (\lambda^2 - \lambda_0^2)\qquad(5a)$$

$$n_2^2 k = \lambda c\gamma_2 / 4\pi h = B\lambda^3 / (\lambda^2 - \lambda_0^2)^2.\qquad(5b)$$

Having the values of h and $n_2^2 k$ for the extrema, A, B, and λ_0 parameters may be obtained and functions $c(\lambda)$ and $\gamma_2(\lambda)$ accordingly.

Let us consider the second part of the problem – that is the absorption indicatrix components estimation for the LCP investigated. For this purpose we shall transform the expression (2) for the case of the cell filled with LCP

$$J_{LCP}=[64adb^2c^2exp(-\gamma_2)exp(-\gamma_{LCP})^{0,5}] / [exp(\gamma_2)(d+c)^2(b+c)^2+exp(-\gamma_2)(d-c)^2(b-c)^2 +$$

$$+2(d^2-c^2)(c^2-b^2)cos\varphi](a+b)^2\qquad(6)$$

where the d parameter was obtained from the independent measurement N_o, N_e [14,15]. This parameter is characterizing LCP as an uniaxial crystal and its value depends on incident light polarization [9,16]: $d_\perp = (N_o^2 - sin^2 i_0)^{0,5}$ (for s – polarization) and $d_{//} = (n_e^2 - sin^2 i_0)^{0,5} / n_e^2$ (for p – polarization), where N_o, N_e are the principle refractive indices of LCP, and

$$n_e^2 = N_o^2 + [(N_e^2 - N_o^2)sin^2 i_o] / N_e^2.\qquad(7)$$

Dividing the equation (6) on (2) we solve the resulting equation relatively γ_2 for both types of incident light polarization. Further, using the relation $\gamma_{LCP} = \alpha_{LCP} h_{LCP}$ we obtain the values $\alpha_\perp^{angl}$ and $\alpha_{//}^{angl}$. Extracting the imaginary part from the Fresnel equation [9,16] for the uniaxial absorbing crystals we obtain absorption ellipsoid principal values $\alpha_\perp^0$ and $\alpha_{//}^0$. The ratio of absorption indicatrix principal values (for maximum of absorption band) $N = \alpha_{//}^0 / \alpha_\perp^0$ is termed the dichroic ratio.

3. Experimental Results and Discussion

The object of investigation in our work was the acryl copolymer containing easily oriented in the external electric field cyanbiphenil mesogenic groups. The structural formula and some optical properties of this LCP are presented in [14,15].

After the statistical processing of the quasi-periodical transmission spectra of the empty cell recorded for TE and TM waves at $i_0 = 0$ and $i_0=45^0$ the following electrode parameters were evaluated by the above mentioned technique:
$A = 1,79\pm0,01$; $B = 0,0008\pm0,0005$; $\lambda_o = 0,219\pm0,003$ µm and $h = 0,45$ µm.. From the transmission spectra of the cell with the polymer, using the data of the refractive index dispersion obtained in [14,15], the true polymer absorption spectra $\alpha_{//}^0(\lambda)$ and $\alpha_\perp^0(\lambda)$ were re–established. The both spectra have shown a pronounced maximum in the vicinity of $\lambda \approx 0,405$ nm. For this maximum the dichroic ratio $N = 2,67$ was obtained. As it is known [6,7,8] the orientational order parameter S is related to the effective dichroic ratio value N^* by the following expression $S = (N^* - 1) / (N^*+2)$. The dichroic effective value differs from the true one by the correction factor g, define by the local field model chosen [17]. For the simplest Vuks-Chandrasekhar-Madhusudana model [6] $g = N_e/N_o$. In this case $N^*=gN = 3,32$ and hence $S = 0,44$. This value of parameter S essentially differs from the value S obtained by us formerly [15] for the same polymer from the refractometrical data. This unexpected

result has motivated us to reconsider the method of refractive index temperature dependence approximation used in [15]. These new researches carried out have led to the new value of $S = 0,42$ [18] which is satisfactory coinciding with the value obtained from the dichroic ratio in the present investigation.

Acknowledgment

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