
OPTICAL
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Effective Refractive Index of a Quasi-Two-Dimensional Polydomain Film of a Conjugated Polymer

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Abstract—The relation between the effective ordinary refractive index $n^* = (n_o n_e)^{1/2}$ of a quasi-two-dimensional polydomain uniaxial film of a conjugated polymer F8BT in the visible transparency region and the refractive indices ($n_{o,e}$) of uniaxial domains with the optical axes randomly oriented in the plane of the film has been confirmed experimentally. The permissible interval of variations in n^* has been established and a strong spectral dispersion of this interval near the long-wavelength electronic absorption band of the film has been demonstrated.

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In optoelectronics, there have been widely used optically uniaxial thin films of conjugated polymers with planar (parallel to the plane of the film) and homeotropic (perpendicular to this plane) orientations of the optical axis of the film \mathbf{n} . Rigid-chain macromolecules of conjugated polymers consist of linear fragments, namely, conformational subunits [1, 2], which differ in the spatial orientation of the longitudinal axes \mathbf{l}_i and in the number of their constituent monomer units related by the π -electron conjugation. Single-domain films of conjugated polymers with the planar orientation \mathbf{n} and the axial (A) orientation of the \mathbf{l}_i axes of conformational subunits with respect to \mathbf{n} are obtained on orienting substrates in a high-temperature nematic phase, followed by the transition to a glassy state during a rapid cooling [3–5]. For light waves with polarizations $\mathbf{E} \perp \mathbf{n}$ and $\mathbf{E} \parallel \mathbf{n}$, this film is characterized by the ordinary (n_{oA}) and extraordinary (n_{eA}) refractive indices. Polydomain films of conjugated polymers on isotropic substrates with the homeotropic orientation \mathbf{n} and the planar (P) orientation of the \mathbf{l}_i axes of the conformational subunits are usually prepared by spin-coating [6–8]. These films consist of vitrified nematic domains [3, 9, 10] (crystallites [10–12]), with the optical axes \mathbf{n}_d randomly oriented in the film plane. Depending on the technology used for the preparation of films, the average domain size a varies from several tens of nanometers to several fractions of a micrometer [6, 9–12]. For light waves with a wavelength $\lambda \gg a$, this film with a thickness $d \ll \lambda$ is a quasi-two-dimensional composite medium with the uniaxial effective permittivity tensor ϵ^* , whose diagonal components correspond to the polarizations

of the electric vector of the light wave $\mathbf{E} \parallel \mathbf{n}$ and $\mathbf{E} \perp \mathbf{n}$. For the wave vector of the light wave $\mathbf{k}^* \perp \mathbf{n}$, in the transparency region the polydomain film is characterized by the effective values of the ordinary ($n_{oP} = (\epsilon_{\perp}^*)^{1/2} = n^*$) and extraordinary ($n_{eP} = (\epsilon_{\parallel}^*)^{1/2}$) refractive indices. For single-domain and polydomain films, the quantities $n_{j(A,P)}$ ($j = o, e$) are measured by the ellipsometric methods [4–8, 13].

The refractive indices n_{jP} and their relation to the quantities n_{jA} are important for controlling the morphology, local structure, and physical properties of the films [13], studying intermolecular interactions [14, 15], and understanding the microscopic nature of these objects. However, the question about the relation of $n^*(n_{jA})$ in the optical transparency region until recently remained open [4, 13]. In [16], it was shown that, for the dominant influence of intermolecular interactions on the local structure and optical properties of uniaxial domains as compared to the effect exerted by the orienting substrate, the refractive indices must satisfy the equality $n_{eP} = n_{oA}$ and the following relation:

$$n^* = (n_{oA} n_{eA})^{1/2} = n_{oP}. \quad (1)$$

The purpose of the present work is to verify this relation for single-domain and polydomain films of the polymer poly(9,9'-dioctylfluorene-co-benzothiadiazole) (F8BT) with the structural formula of the monomer shown in Fig. 1.

Macromolecules of F8BT with a persistence length $l_p \approx 10$ nm [1] are rigid-chain polymers of the polyfluorene class with side alkyl chains (the hairy-rods poly-

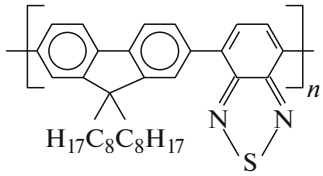


Fig. 1. Structural formula of the monomer unit of the F8BT polymer.

mers) [10]. The optical properties of F8BT films were thoroughly investigated using the ellipsometric methods [4–8], which is important for the objective verification of relation (1).

In order to evaluate the degree of correspondence between formula (1) and the experimental data, we set the permissible intervals of variation in n^* for specified values of n_{jA} . From the constraints [16]

$$B_l = \frac{2n_{oA}^2 n_{eA}^2}{n_{oA}^2 + n_{eA}^2} \leq \varepsilon_{\perp}^* \leq \frac{n_{oA}^2 + n_{eA}^2}{2} = B_u, \quad (2)$$

it follows that the change in the value of $n^* = (\varepsilon_{\perp}^*)^{1/2}$ lies in the interval

$$b_l \leq n^* \leq b_u, \quad (3)$$

where $b_{l(u)} = (B_{l(u)})^{1/2}$ and $n^* = (b_l b_u)^{1/2}$. This is the maximum interval of variation in n^* . By applying the inequality $(a_1 a_2)^{1/2} \leq (a_1 + a_2)/2$ for $a_{1,2} > 0$ to the expression $n^* = (n_{oA} n_{eA})^{1/2}$, we obtain a narrower interval

$$\beta_l = \frac{2n_{oA} n_{eA}}{n_{oA} + n_{eA}} \leq n^* \leq \frac{n_{oA} + n_{eA}}{2} = \beta_u, \quad (4)$$

where $n^* = (\beta_l \beta_u)^{1/2}$. From the inequality $(n_{oA} + n_{eA})/2 \leq [(n_{oA}^2 + n_{eA}^2)/2]^{1/2}$, it follows that $\beta_u \leq b_u$. Hence, taking into account $\beta_l \beta_u = b_l b_u$, we obtain $\beta_l = b_l b_u / \beta_u \geq b_l$. The intervals $\Delta\beta = \beta_u - \beta_l$ and $\Delta b = b_u - b_l$ are related by the expression $\Delta\beta = \Delta b b_u / 2\beta_u \geq \Delta b / 2$. The dispersion $n_{jA}(\lambda)$ near the absorption bands of the film determines a strong spectral dispersion of the quantities

$$\Delta b = \frac{(n_{eA} - n_{oA})^2}{\sqrt{2(n_{eA}^2 + n_{oA}^2)}^{1/2}}, \quad (5)$$

$$\Delta\beta = \frac{(n_{eA} - n_{oA})^2}{2(n_{oA} + n_{eA})}.$$

If the dipole moment of the transition for the long-wavelength band of electronic absorption of the domain is oriented along one of the j axes of the ellipsoid of refraction of the domain, the approach of the wavelength λ to this absorption band with a maximum at the wavelength λ_j will be accompanied by a resonant increase in the difference $n_{eA} - n_{oA}$ and the quantities Δb and $\Delta\beta$.

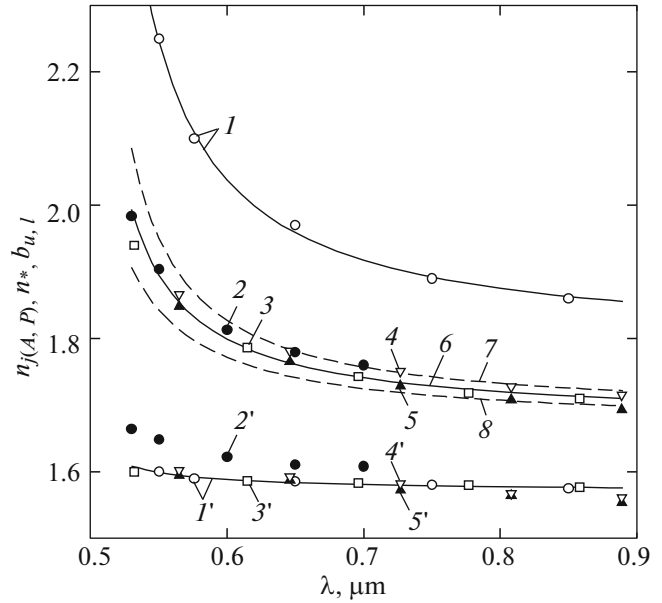


Fig. 2. Dispersion curves of (1) refractive index n_{eA} and (1') refractive index n_{oA} [4] for a single-domain uniaxial film of the F8BT polymer with the axial orientation of macromolecules; (2–5) n_{oP} and (2'–5') n_{eP} taken from (2, 2) [6], (3, 3') [7], and (4, 4', 5, 5') [8] for polydomain uniaxial F8BT films with the planar orientation of macromolecules; and (6) effective refractive index n^* , (7) boundary value b_u , and (8) boundary value b_l in formula (3). Symbols 2, 2', 5, 5' (3, 3', 4, 4') correspond to the unannealed (annealed) films. Solid lines 1, 1' show the approximations by function (6).

The dispersion curves of the refractive indices $n_{j(A, P)}(\lambda_k)$ for single-domain and polydomain glassy F8BT films with close thicknesses are shown in Fig. 2. The refractive indices $n_{j(A, P)}(\lambda_k)$ for five values of the wavelength λ_k [14, 15] in the visible transparency region were obtained from the dependences $n_{j(A, P)}(\lambda)$ [4, 6–8] measured by the ellipsometric method at room temperature. Single-domain uniaxial F8BT film with a thickness $d = 100$ nm [4] on a rubbed polyimide substrate with a planar orientation of the optical axis \mathbf{n} , which is aligned parallel to the rubbing direction of the substrate, and with the axial (nematic) orientational order of the \mathbf{l}_i axes of the conformational subunits with respect to \mathbf{n} were obtained by a rapid cooling of the high-temperature nematic phase. For a single-domain F8BT film on a rubbed substrate of the polymer poly(3,4-ethylene dioxythiophene) : poly(styrenesulphonate) (PEDOT : PSS), the values of $n_{jA}(\lambda_k)$ in the wavelength range $\lambda = 0.55$ – 0.78 μm [5, 15] almost completely coincide with the dependences $n_{jA}(\lambda)$ shown in Fig. 2. This indicates the decisive influence of intermolecular interactions on the orientational order of the \mathbf{l}_i axes of the conformational subunits of the polymer with respect to local directions $\mathbf{n}(\mathbf{r})$ in the single-domain sample. The role of the anisotropic substrate is reduced to the formation of single domain

in the film due to the orientation of the axes $\mathbf{n}(\mathbf{r})$ along the rubbing axis of the substrate \mathbf{n} .

Polydomain uniaxial F8BT films with thicknesses of 90 [6], 150 [7], and 133 nm [8] were prepared by spin-coating on isotropic quartz (spectrosil B) substrates [6–8]. Some samples were subjected either to a fifteen-hour annealing in a vacuum at a temperature of 115°C [7] below the glass transition temperature $T_g \approx 140^\circ\text{C}$ or a two-hour annealing in a nitrogen atmosphere at a temperature of 150°C [8], followed by a rapid cooling to room temperature in both cases. The first and second procedures correspond to the average sizes of nematic domains $a < 100$ nm and ~ 100 –150 nm [12], which satisfies the requirement $a \ll \lambda$ in the visible region.

The dependences $n_{j(A, P)}(\lambda_k)$ are approximated with a high accuracy by the function [17]

$$n_j(\lambda) = n_{bj} + G_j \lambda^2 \lambda_j^2 / (\lambda^2 - \lambda_j^2), \quad (6)$$

where λ_j corresponds to the maximum of the isolated long-wavelength electronic absorption band of the F8BT film, G_j is proportional to the integrated absorption coefficient of the film $\alpha_j = \int \alpha_j(\omega) d\omega$ within this band, and the background contribution n_{bj} is determined by shorter-wavelength transitions. Using the limiting value $n_{jl} = n_j(\lambda \rightarrow \infty)$, we have $G_j \lambda_j^2 = n_{jl} - n_{bj}$ and $R_j = G_j \lambda_j^2 / n_{bj} \ll 1$. For a single-domain F8BT film [4], the values of $\lambda_{eA} = 0.488 \pm 0.010$ μm and $\lambda_{oA} = 0.468 \pm 0.005$ μm obtained from approximation (6) are in agreement with the experimental value $\lambda_{eA} \approx 0.470 \pm 0.005$ μm [4], and the dichroic ratio $D_A = G_{eA}/G_{oA} = 10.5$ coincides with the experimental ratio $D_A(\lambda_{eA}) = k_{eA}/k_{oA} = 10.8$ [4] of the imaginary parts $k_j = \lambda \alpha_j / 4\pi$ of the complex refractive index $N_j = n_j + ik_j$. The high value of D_A provides a strong dispersion $n_{eA}(\lambda)$ and a weak dispersion $n_{oA}(\lambda)$ in the visible transparency region. The relationship $n_{be} = 1.686 > n_{bo} = 1.562$ is consistent with the dichroic ratio $D_A \approx 3$ for the shorter-wavelength insulated electronic absorption band of the F8BT film with a maximum at the wavelength $\lambda_{eA} \approx 0.310$ μm [4].

Functions (6) for the refractive indices $n_{jA}(\lambda_k)$ were used to calculate the dependences $n^*(\lambda)$ and $b_{u,i}(\lambda)$ shown in Fig. 2. For the unannealed F8BT films [6], the values of $n_{eP}(\lambda_k)$ lie above the dependence $n_{oA}(\lambda)$, but the values of $n_{oP}(\lambda_k)$ lie within the interval $\Delta b(\lambda)$. For the annealed F8BT films [7], the values of $n_{eP}(\lambda_k)$ coincide with the dependence $n_{oA}(\lambda)$, whereas the values of $n_{oP}(\lambda_k)$ coincide with the dependence $n^*(\lambda)$ or lie within the interval $\Delta b(\lambda)$. The annealing of the F8BT films [8] almost does not affect the values of $n_{eP}(\lambda_k)$, which coincide with the dependence $n_{oA}(\lambda)$, and is accompanied by a weak increase in the values of $n_{oP}(\lambda_k)$, which lie within the interval $\Delta b(\lambda)$. It can be

seen from Fig. 2 that there is a six-fold resonant increase of the interval $\Delta b(\lambda)$ as the long-wavelength absorption band is approached. Thus, the polydomain F8BT films on isotropic substrates [6–8] with a high accuracy satisfy the relations $n_{eP} = n_{oA}$ and (1).

The thicknesses of polydomain F8BT films [6–8] are significantly less than typical thicknesses of near-surface layers of amorphous polymers with a planar orientation of macromolecules [18, 19]. Therefore, the equality $n_{eP} = n_{oA}$ indicates a decisive influence of intermolecular interactions on the intradomain orientational order of the \mathbf{l}_i axes of the conformational subunits of the polymer with respect to the optical axis of the domain \mathbf{n}_d . The isotropy of the substrate is responsible for the absence of long-range orientational order of the directions \mathbf{n}_d in the film plane. Moreover, the equality $n_{eP} = n_{oA}$ is possible only in the case of a weak influence of domain walls and interdomain regions with a broken orientational order of the conformational subunits on the optical properties of the film. This is a specific feature of the morphology of polydomain F8BT films [6–8] as compared to films of the polymers poly(9,9'-dioctyl fluorene) (PFO) [4] and poly(9,9'-diethylhexyl fluorene) (PF2/6) [20], which are characterized by the inequality $n_{eP} > n_{oA}$ [16].

The confirmation of formula (1) in the entire visible transparency region and the use of function (6) allow us to draw certain conclusions about the relationship between the quantities $G_{jA} \propto \alpha_{jA} \propto k_{jA}$ for a single-domain film and the effective values of $G^* = G_{oP} \propto k^* = k_{oP}$ for the refractive index $N_{oP}(\lambda) = n_{oP}(\lambda) + ik_{oP}(\lambda)$ for a polydomain film. The approximation of the dependence $n^*(\lambda)$ shown in Fig. 2 by function (6) gives the value of $n_b^* = 1.623$, which coincides with the value of $(n_{bo}n_{be})^{1/2}$. On this basis, in the limit $\lambda \rightarrow \infty$, from formulas (1) and (6) we obtain the following relation between the quantities R_{jA} and $R^* = G^*(\lambda^*)^2/n_b^*$:

$$R^* = [(1 + R_{oA})(1 + R_{eA})]^{1/2} - 1. \quad (7)$$

Using the inequality $(a_o a_e)^{1/2} \leq (a_o + a_e)/2$ with $a_j = 1 + R_{jA}$, we obtain $R^* \leq (R_{oA} + R_{eA})/2$. Taking into account the smallness of quantities $R_{jA} \ll 1$, in the approximation quadratic in these quantities, we have $R^* = (R_{oA} + R_{eA})/2 - (R_{eA} - R_{oA})^2/8$. As a result, at $R_{eA} \gg R_{oA}$, the value of R^* is noticeably less than the average value of $(R_{oA} + R_{eA})/2$. Considering the proximity of the values of $\lambda_{jA} \approx \lambda^*$ and $n_{bj} \approx n_b^*$, as well as the relationship $G_{jA} \propto k_{jA}$, we find that, for a large difference $G_{eA} \gg G_{oA}$, the value of $k^* = k_{oP}(\lambda_{oP})$ at the maximum of the absorption band $k_{oP}(\lambda)$ for the polydomain film is noticeably less than the average value of $[k_{oA}(\lambda_{oA}) + k_{eA}(\lambda_{eA})]/2$ of the quantities k_{jA} at the maxima of the absorption bands $k_{jA}(\lambda)$ for the single-domain film. This was observed previously when com-

paring the single-domain and polydomain films of PFO [4] and PF2/6 [20].

The results of this work have solved the problem of relation between the refractive indices n_{jA} and n_{jP} for single-domain and polydomain films of conjugated polymers [4, 13]. Equation (1) here is confirmed over the entire visible transparency region of the F8BT polymer for an array of independent data obtained by different authors [4–8]. The values of n^* for the unannealed and annealed polydomain films lie within intervals (3) and (4), the widths of which are characterized by a strong spectral dispersion near the long-wavelength electronic absorption band of the film. The experimental dependences $n_{j(A, P)}(\lambda)$ in the entire visible region with a high accuracy are approximated by dispersion relation (6), the coefficients of which are consistent with independent data of the polarized absorption spectra. This demonstrates the advantages of relation (6) over the widely used Cauchy formula $n_j(\lambda) = A_j + B_j/\lambda^2 + C_j/\lambda^4$ [4–8, 13, 20], which follows from relation (6) and holds true at the long-wavelength edge of the visible region.

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