
OPTICAL
PROPERTIES

Influence of the Dimension of a Polycrystalline Film and the Optical Anisotropy of Crystallites on the Effective Dielectric Constant of the Film

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Abstract—The dimension D of a polycrystalline film and the optical anisotropy $m = \epsilon_z/\epsilon_x$ of uniaxial crystallites with the principal components $\epsilon_x = \epsilon_y$ and ϵ_z of the tensor of the dielectric constant have been shown to produce a strong influence on the effective dielectric constant ϵ_D^* and the effective refractive index $n_D^* = (\epsilon_D^*)^{1/2}$ of the film in the optical transparency region, as well as on the boundaries of the intervals $B_{Dl} \leq \epsilon_D^* \leq B_{Du}$. The intervals $\Delta_2(m) = B_{2l} - B_{2u}$ and $\Delta_3(m) = B_{3l} - B_{3u}$ are separated by a gap for m in the range $1 < m < 2$, whereas the theoretical dependence $\epsilon_2^*(m)$ is separated by a gap from the interval $\Delta_3(m)$ for m in the range $1 < m < 4$. This is confirmed by a comparison of the experimental (n_{op}) and theoretical (n_2^*) ordinary refractive indices for uniaxial polycrystalline films of the conjugated polymer poly(*p*-phenylene vinylene) (PPV) with uniaxial crystallites and appropriate values of m . In the visible transparency region of the PPV films with a change in $m(\lambda)$ in the range $2 < m(\lambda) < 3$ due to the dependence of the components $\epsilon_{x,z}(\lambda)$ on the light wavelength λ , the refractive indices $n_{op}^2(\lambda) = \epsilon_{op}(\lambda)$ are consistent with the theoretical values of $\epsilon_2^*(\lambda)$ and lie outside the interval $\Delta_3(m)$. For $m(\lambda) > 3$ near the electronic absorption band of the crystallites, the values of $\epsilon_{op}(\lambda)$ lie in the region of the overlap of the intervals $\Delta_2(m)$ and $\Delta_3(m)$. The boundaries m_c of the range $1 < m < m_c$ are determined, for which the interval $\Delta_2(m)$ is separated by a gap from the dependences $\epsilon_3^*(m)$ corresponding to the effective medium theory with spherical crystallites and hierarchical models of a polycrystal, as well as from the proposed new dependence $\epsilon_3^*(m)$.

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1. INTRODUCTION

The optical properties of thin films of molecular organic semiconductors [1, 2], conjugated polymers [3–5], ferroelectric polymers [6], and other compounds on isotropic substrates have been widely used in modern optoelectronic devices. These films consist of crystallites (domains) with the average size a varying in the range from a few tens of nanometers [1–4] to a few hundred nanometers and a few fractions of a micrometer [5, 6], depending on the technology used for the preparation of the film. For a light wave with a wavelength $\lambda \gg a$, the film is a composite medium (D -dimensional polycrystal) with the effective dielectric constant tensor $\hat{\epsilon}_D^*$. The dimension D is equal to the number of identical principal components of the tensor $\hat{\epsilon}_D^*$ and depends on the character of the orientation distribution of the axes $i(x, y, z)$ of the refraction

ellipsoids of the crystallites with respect to the normal \mathbf{X} to the substrate. Since there is a physically defined axial symmetry axis \mathbf{X} , polycrystalline (polydomain) films with a thickness $d \ll \lambda$ on an isotropic substrate are usually uniaxial media with the optical axis \mathbf{X} [1–8] aligned parallel to the x axes of the crystallites (domains) with a random distribution of the y and z axes in the plane of the film. For light waves transmitted through a film with a wavelength $\lambda \gg a$ and a wave vector $\mathbf{k} \perp \mathbf{X}$, there is a uniaxial tensor $\hat{\epsilon}_2^*$ with the diagonal components ϵ_x^* and $\epsilon_y^* = \epsilon_z^* = \epsilon_2^*$ for the polarizations of the electric vector of the light wave $\mathbf{E} \parallel \mathbf{X}$ and $\mathbf{E} \perp \mathbf{X}$. In the transparency region, the film is characterized by the effective values of the ordinary ($n_{op} = (\epsilon_2^*)^{1/2} = n_2^*$) and extraordinary ($n_{ep} = (\epsilon_x^*)^{1/2}$) refractive indices. For a random orientation of the i axes of the crystallites with respect to the optical axis

X, the isotropic film is characterized by the effective dielectric constant ϵ_3^* and the refractive index n_3^* in the transparency region.

For both types of films, the refractive indices n_{jp} ($j = o, e$) and n_3^* measured by the methods of ellipsometry [1, 2, 6, 7] and integrated optics [8] are important for the control of the morphology, local structure, and physical properties of the films [1, 2, 6–8]; the optimization of technological parameters [7–9]; the investigation of the anisotropy of interparticle interactions [10–12]; and the understanding of the microscopic nature of the objects. For different materials, the quantity $\Delta n_p = n_{ep} - n_{op}$ varies over wide ranges. Therefore, in order to predict optical properties of the films [13], it is necessary to estimate the values of n_D^* with the use of the refractive indices n_i (components of the dielectric constant ϵ_i) of the crystallites. In this connection, we note the following important problems: the verification of the known dependences $n_D^*(n_i)$ and $\epsilon_D^*(\epsilon_i)$ in the visible transparency region with variations in the quantity Δn_p within the ranges corresponding to polycrystals of the known compounds [1–9, 13]; the investigation of the influence exerted by the anisotropy $m = \epsilon_z/\epsilon_x$ of uniaxial crystallites with the principal components of the dielectric constant $\epsilon_x = \epsilon_y$ and ϵ_z on both the effective dielectric constant ϵ_D^* and the boundaries of the intervals $B_{Dl} \leq \epsilon_D^* \leq B_{Du}$ [14–16]; and the determination of the regions of variations in the anisotropy m , which correspond to gaps between the intervals $\Delta_2(m) = B_{2l} - B_{2u}$ and $\Delta_3(m) = B_{3l} - B_{3u}$ and to gaps between the dependences $\epsilon_{2(3)}^*(m)$ and intervals $\Delta_{3(2)}(m)$.

The solution of these problems is possible by using the exact expressions for $n_2^*(n_i)$ and $\epsilon_2^*(\epsilon_i)$ of crystallites with an arbitrary shape [16], the dependence $\epsilon_{3E}^*(\epsilon_i)$ in the effective medium theory for polycrystals with optically anisotropic spherical crystallites [17–20], and the relationship $\epsilon_{3S}^*(\epsilon_i)$ for model hierarchically organized isotropic polycrystals [21–23]. In order to verify the theoretical dependences $n_D^*(n_i)$, it is advisable to use the refractive indices n_{jp} for polycrystalline (polydomain) films of conjugated polymers and the refractive indices n_i for single-domain biaxial (uniaxial) films of the same conjugated polymers with the positions of the axes y and z (the optical axis z) of the domain in the plane of the film. The birefringence $\Delta n_A = n_z - n_{x(y)}$ and the anisotropy parameter m can be varied with a resonance change in the values of $n_i(\lambda)$ and $\epsilon_i(\lambda)$ in the vicinity of the absorption bands polarized along one of the i axes of the domain [16]. The relationship $n_2^*(n_i)$ was confirmed in the optical trans-

parency region of the films of the conjugated polymers poly(9,9'-dioctylfluorene) (PFO) [16] and poly(9,9'-dioctylfluorene-co-benzothiadiazole) (F8BT) [24] with vitrified nematic domains for small (PFO) and medium (F8BT) values of the birefringence $\Delta n_{A,p}$. This study is devoted to solving the aforementioned problems with invoking the dependences $n_{jp}(\lambda)$ for polycrystalline uniaxial films of the conjugated polymer poly(*p*-phenylene vinylene) (PPV) [8, 9] and the refractive indices $n_i(\lambda)$ [25–27] for the uniaxially stretched PPV films with different morphologies. These films have the maximum possible values of $\Delta n_{A,p}(\lambda)$ in the visible transparency region among the known conjugated polymers [8–11, 25–27], and their values of $m(\lambda)$ and $\epsilon_2^*(\lambda)$ vary within the ranges corresponding to the purposes of the present work.

2. DEPENDENCE $n_2^*(n_i)$ FOR PPV FILMS

Macromolecules of the conjugated polymers consist of linear fragments, namely, conformational subunits [28], which differ in the spatial orientation of the longitudinal \mathbf{l}_k axes and in the number of their constituent monomer units coupled by the π -electron conjugation. Let us consider the specific features of the polymers PFO, F8BT, and PPV (Fig. 1). For rigid-chain linear macromolecules of PFO and F8BT, the average length of the conformational subunit $\xi \approx 10$ nm [29] is close to the persistence lengths $l_p = 8.6$ nm for PFO [29] and 10 nm for F8BT [30]. In polydomain films of these polymers on isotropic substrates with the average domain sizes $a \approx 30$ nm for PFO [4] and 100–150 nm for F8BT [5], inside the domain the \mathbf{l}_k axes of the conformational subunits have an axial (nematic) order with respect to the optical domain axis \mathbf{n}_d , whereas the directions of the \mathbf{n}_d axis are randomly oriented in the plane of the film.

In the PPV macromolecules, the CH=CH fragments allow for rotations around the C=C bonds, as well as for bends of the polymer chain with the separation of the macromolecule into conformational sub-

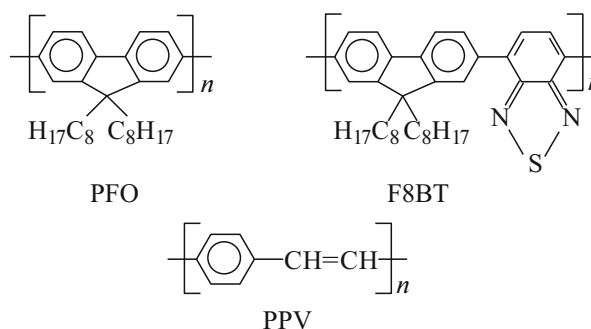


Fig. 1. Structural formulas of monomeric units for the polymers under investigation.

units with shorter average lengths ξ as compared to PFO and F8BT. Films of the insoluble PPV polymer on isotropic substrates are prepared by deposition of a solution of the polymer precursor (PPC) onto a substrate (solvent-coating, drop-casting), blade-coating [8] or spin-coating [9], followed by evaporation of the solvent and thermal conversion of PPC into PPV. In all the cases under consideration, the PPV macromolecules in the film have an in-plane orientation of the \mathbf{l}_k axes of the conformational subunits aligned parallel to the substrate, as in the near-surface layers of amorphous nonconjugated polymers [31, 32]. After thermal annealing, amorphous films of PPV become polycrystalline with crystallite sizes $a \approx 10\text{--}20$ nm [33–35]. These values are less than the sizes of nematic domain films in the PFO and F8BT films. In PPV crystallites with the tensor principal components $\varepsilon_x \approx \varepsilon_y < \varepsilon_z$, the z axes are parallel to the longitudinal axes of the macromolecules and are randomly oriented in the plane of the film [33–35], which provides the uniaxiality of the polycrystalline film with the optical axis \mathbf{X} . Despite the anisotropic distribution of the crystallographic axes of the crystallites x' ($x' \perp z$) with respect to the \mathbf{X} axis [33, 34], the approximate equality $\varepsilon_x \approx \varepsilon_y$ suggests that the x axes of the refraction ellipsoids of all the crystallites under consideration are parallel to the \mathbf{X} axis. In the case where the intercrystallite amorphous regions weakly affect the refractive indices n_{jP} , such a film should correspond to the equality $n_{eP} = n_x$ and the following relationship [16]:

$$n_2^* = (n_y n_z)^{1/2} = n_{oP}. \quad (1)$$

The refractive indices n_i of crystallites can be determined from the optical properties of the films with optical anisotropy in the plane of the film. Such PPV films of two types with different morphologies are prepared by different methods. We consider separately the relationships $n_2^*(n_i)$ with the refractive indices n_{jP} for each type of PPV films.

The PPV films of the first type are prepared by uniaxial stretching of PPC amorphous films followed by the conversion of PPC into PPV. These processes result in the formation of optically biaxial polycrystalline PPV films [25] with the orientation of the z axes of the crystallites in the direction of the stretching axis \mathbf{Z} and with the same distribution of the x' axes of the crystallites with respect to the surface normal \mathbf{X} of the film [33, 34], as is the case with unstretched polycrystalline PPV films. However, approximate equality $\varepsilon_x \approx \varepsilon_y$ leads to a negligibly small difference in the refractive indices of the film $n_x < n_y$ [25]. For a high draw ratio R and close thicknesses d of the uniaxial and biaxial polycrystalline films, the refractive indices $n_{Y(Z)}$ of the biaxial film can be used instead of the quantities $n_{y(z)}$ in formula (1).

Figure 2 shows the dispersion curves of the refractive indices $n_{jP}(\lambda_k)$ for polycrystalline PPV films with

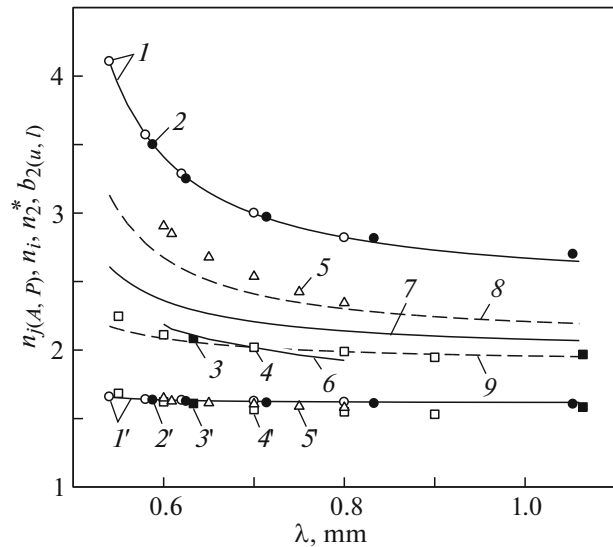


Fig. 2. Dispersion curves of (1, 2) refractive index n_{eA} and (1', 2') refractive index n_{oA} according to the data taken from (1, 1') [26] and (2, 2') [27] for uniaxial stretched films of the PPV polymer; (3, 4) refractive index n_{oP} and (3', 4') refractive index n_{eP} taken from (3, 3') [8] and (4, 4') [9] for uniaxial polycrystalline PPV films; (5) n_Z and (5') n_Y for biaxial stretched PPV films [25]; and (6) effective refractive index $n_2^* = (n_y n_z)^{1/2}$, (7) effective refractive index $(n_{oA} n_{eA})^{1/2}$, (8) boundary value b_{2u} , and (9) boundary value b_{2l} in formula (5). Solid lines 1 and 1' show the approximations of the dispersion curves $n_{jA}(\lambda_k)$ [26] by function (2).

the optical axis \mathbf{X} , which were prepared by the blade-coating [8] and spin-coating [9] methods. For substantially different thicknesses of the PPV films ($d = 1.5\text{--}2.8$ μm [8] and 0.16 μm [9]), the refractive indices n_{jP} coincide with each other at the same values of λ . This indicates large thicknesses ($H_0 \gg 1$ μm) of the near-surface anisotropic layers of PPC and PPV polymers with the orientation of the \mathbf{l}_k axes of their conformational subunits (and the z axes of PPV crystallites [33–35]) in the plane of the film, as well as for other polymers [31, 32].

The refractive indices $n_{jP}(\lambda_k)$ are approximated with a high accuracy by the function [36]

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

where the effective wavelength λ_j (here, the subscript P is omitted) corresponds to the multiplet of overlapped absorption bands due to the long-wavelength 0–0 electronic transition in PPV, as well as to its vibronic satellites. All the multiplet bands are polarized along the \mathbf{l}_k axes of the conformational subunits of the macromolecules and along the z axes of the PPV crystallites [25, 26, 37]. The background contribution n_{bj} is caused by the short-wavelength electronic transitions

in PPV. The approximation of the refractive indices $n_{jP}(\lambda_k)$ [9] by formula (2) (see Fig. 2) gives the values of $\lambda_{oP} = 0.456 \pm 0.023 \mu\text{m}$ and $\lambda_{eP} = 0.437 \pm 0.013 \mu\text{m}$, which are close to the maxima of the structureless envelope of the multiplet bands in the spectra $k_{jP}(\lambda)$ of the imaginary part of the complex refractive index $N_{jP} = n_{jP} + ik_{jP}$ [9]. The value of λ_{oP} coincides with the wavelength $\lambda_{\text{exc}} = 0.458 \mu\text{m}$ of the laser radiation used for the efficient luminescence excitation of PPV films in optoelectronic devices [9, 37, 38]. In the limit $\lambda \rightarrow \infty$, we have $n_{oP}^{(\infty)} = 1.903$ and $n_{eP}^{(\infty)} = 1.5$.

For stretched PPV films of the first type ($R = 6$, $d = 5 \mu\text{m}$) [25], the refractive indices $n_Y(\lambda_k)$ shown in Fig. 2 coincide with the values of n_{eP} [8, 9] with only small differences in the refractive indices n_X and n_Y [25]. This suggests that the intercrystallite amorphous regions weakly affect the values of n_{jP} [8, 9] and $n_{X, Y, Z}$ [25]. The approximation of the dispersion curve of the refractive index $n_Y(\lambda_k)$ by function (2) gives the wavelength $\lambda_Y = 0.456 \pm 0.077 \mu\text{m}$, which coincides with the value of λ_{oP} , and the refractive index $n_Y^{(\infty)} = 1.545$ close to $n_{eP}^{(\infty)}$. By substituting the values of $n_{Y(Z)}$ instead of the refractive indices $n_{Y(Z)}$ into formula (1), we obtain the dispersion curve $n_2^*(\lambda_k)$ shown in Fig. 2, which coincides with the dependence $n_{oP}(\lambda_k)$ [8, 9].

The PPV films of the second type are prepared by uniaxial stretching of the polycrystalline PPV film, which is accompanied by the axial order of the z axes of the crystallites and the \mathbf{I}_k axes of the conformational subunits of macromolecules in intercrystallite amorphous regions with respect to the stretching axis \mathbf{Z} [35, 37]. Depending on the draw ratio R , the uniaxial symmetry of the distribution of the x axes of the crystallites in the XY plane can be cylindrical or hexagonal [34, 35]. This determines the uniaxiality of the stretched films with the optical axis \mathbf{Z} [26, 27, 37] and the refractive indices $n_X = n_Y = n_{oA}$ and $n_Z = n_{eA}$. In the case where the intercrystallite regions weakly affect the values of $n_{jA(P)}$, the initial and stretched films should correspond to the equality $n_{eP} = n_{oA}$ and the following relationship [16]:

$$n_2^* = (n_{oA}n_{eA})^{1/2} = n_{oP}. \quad (3)$$

The effective dielectric constants ε_2^* lie in the interval [16]

$$B_{2l} = \frac{2\varepsilon_{oA}\varepsilon_{eA}}{\varepsilon_{oA} + \varepsilon_{eA}} \leq \varepsilon_2^* \leq \frac{\varepsilon_{oA} + \varepsilon_{eA}}{2} = B_{2u}, \quad (4)$$

where $\varepsilon_{jA} = n_{jA}^2$. The effective refractive indices $n_2^* = (\varepsilon_2^*)^{1/2}$ are limited by the interval

$$b_{2l} \leq n_2^* \leq b_{2u}, \quad (5)$$

where $b_{2l(u)} = (B_{2l(u)})^{1/2}$, and in formula (3), we have $n_2^* = (b_{2l}b_{2u})^{1/2}$.

For stretched PPV films of the second type ($R = 5$, $d = 15 \mu\text{m}$) [26, 27], the refractive indices n_{oA} (Fig. 2) almost completely coincide with the values of n_{eP} [8, 9] and n_Y [25], whereas the refractive indices n_{eA} are significantly higher than the values of n_Z [25]. This indicates a weak (significant) influence of the anisotropic intercrystallite amorphous regions [34, 35] on the refractive indices n_{eP} and n_{oA} (n_{eA}), which is possible only with the in-plane orientation of the \mathbf{I}_k axes of the conformational subunits of macromolecules in the intercrystallite regions of the initial polycrystalline film. In this case, the refractive indices n_{eP} and n_{oA} are determined primarily by the contribution from the transverse components γ_i of the polarizability tensor $\hat{\gamma}$ of the macromolecules in crystallites and the components $\gamma_i^{(k)}$ of the polarizability tensor $\hat{\gamma}_k$ of the conformational subunits in the intercrystallite regions. The polarizability tensor components γ_i and $\gamma_i^{(k)}$ depend weakly on the degree of longitudinal conjugation of polymer chain units and are close to each other, which determines the closeness of the refractive indices n_{eP} and n_{oA} . In the uniaxial stretching of the polycrystalline film, the orientational ordering of the z axes of the crystallites and the \mathbf{I}_k axes of the conformational subunits in the intercrystallite regions along the optical axis \mathbf{Z} of the film is accompanied by an increase in the lengths ξ_k of the conformational subunits [34, 35] and an enhancement of the π -conjugation of the polymer chain units involved in a conformational subunit. The latter fact is responsible for the increase in the longitudinal components $\gamma_i^{(k)}$ of the polarizability tensor $\hat{\gamma}_k$. For a stretched PPV film, the refractive indices n_{eA} are determined primarily by the longitudinal components of the polarizability tensor γ_i and $\gamma_i^{(k)}$. The contribution from the components $\gamma_i^{(k)}$ to the refractive index n_{eA} can be responsible for the differences in the refractive indices $n_{eA} > n_Z$.

The approximation of the dependences $n_{jA}(\lambda_k)$ [26] by function (2) gives $\lambda_{eA} = 0.448 \pm 0.002 \mu\text{m}$ and $\lambda_{oA} = 0.476 \pm 0.018 \mu\text{m}$ with the limiting values $n_{eA}^{(\infty)} = 2.488$ and $n_{oA}^{(\infty)} = 1.65 > n_{eP}^{(\infty)}$. Functions (2) for the refractive indices $n_{jA}(\lambda_k)$ were used in formulas (3)–(5) for the calculation of the dependences $n_2^*(\lambda)$ and $b_{2l,u}(\lambda)$. It can be seen from Fig. 2 that, in the entire transparency region of PPV, the effective refractive indices $n_2^*(\lambda)$ are higher than the values of $n_{oP}(\lambda)$ [8, 9], which lie near the lower boundary of the interval $\Delta b = b_{2u} - b_{2l}$. The

spectral dependences of the effective refractive index n_2^* and the interval

$$\Delta b = \frac{(n_{eA} - n_{oA})^2}{\sqrt{2}(n_{eA}^2 + n_{oA}^2)^{1/2}} \quad (6)$$

are determined by the resonance dispersion $n_{eA}(\lambda)$ in the vicinity of the multiplet of long-wavelength absorption bands polarized along the optical axis \mathbf{Z} of the film. For PPV films [8, 9, 26, 27], an increase in the wavelength λ leads to a decrease in the difference $n_2^* - n_{oP}$, and we have $(n_{eA}^{(\infty)} n_{oA}^{(\infty)})^{1/2} \approx n_{oP}^{(\infty)}$. Therefore, for a D -dimensional polycrystal, the closeness of the theoretical and experimental static dielectric constants $\epsilon_{D,st}^*$ (in the limit $\lambda \rightarrow \infty$) does not ensure the closeness of the corresponding values of ϵ_D^* in the optical transparency region near the absorption bands polarized along one of the i axes of the refraction ellipsoid of the crystallite.

Large values of $\Delta b \sim (\Delta n_A)^2$ in the nonresonance transparency region can also be determined by the high optical anisotropy Δn_A of the crystallites due to the specific features of the chemical structure and conformation of the molecules. This is the case for PPV molecules with a strong π -conjugation of the phenyl rings and CH=CH bridges, which are coplanar with each other in the PPV crystallites [33, 34], in contrast to the PFO molecules with non-coplanar planes of the adjacent fluorene fragments [4, 29, 30], as well as the F8BT molecules with non-coplanar planes of fluorene and benzothiadiazole [5]. As a result, in the entire visible transparency region for PPV films, the values of $\Delta b(\lambda)$ are significantly higher than those for PFO [16] and F8BT [24] films.

3. DEPENDENCE OF ϵ_D^* ON THE OPTICAL ANISOTROPY OF THE CRYSTALLITES

In contrast to the exact expression for the effective dielectric constant ϵ_2^* [16] of crystallites with an arbitrary shape, a similar expression for ϵ_3^* is unknown. The expressions for ϵ_3^* [39, 40] in the optical transparency region were obtained in the approximation $(m - 1) \ll 1$, which is not applicable for polycrystals of conjugated polymers. For crystallites with the principal components ϵ_i ($i = x, y, z$) of the dielectric constant tensor $\hat{\epsilon}$, the function $\epsilon_3^*(\epsilon_i)$ must satisfy the requirements of the first-order homogeneity: $\epsilon_3^*(a\epsilon_x, a\epsilon_y, a\epsilon_z) = a\epsilon_3^*(\epsilon_x, \epsilon_y, \epsilon_z)$; the invariance with respect to the permutations of the components ϵ_x, ϵ_y , and ϵ_z ; and the compatibility $\epsilon_3^*(a, a, a) = a$. Thus, the function $\epsilon_3^*(\epsilon_i)$ is a symmetric function of the components ϵ_i or the

function $\epsilon_3^*(I_p)$ of the symmetric polynomials $I_1 = \epsilon_x + \epsilon_y + \epsilon_z$, $I_2 = \epsilon_x\epsilon_y + \epsilon_x\epsilon_z + \epsilon_y\epsilon_z$, and $I_3 = \epsilon_x\epsilon_y\epsilon_z$. By using the functions I_p , the standard restrictions on ϵ_3^* [15] can be conveniently represented in the form

$$B_{3l} = \frac{3I_3}{I_2} \leq \epsilon_3^* \leq \frac{I_1}{3} = B_{3u}. \quad (7)$$

The experimental values of ϵ_{oP} for PPV (PFO [16], F8BT [24]) films with optically uniaxial crystallites (nematic domains) are distributed over the entire interval $\Delta_2 = B_{2l} - B_{2u}$. This correlates with the fact that, for polycrystals with the uniaxial tensor $\hat{\epsilon}_{st}$ of the crystallites, the experimental values of $\epsilon_{3,st}^*$ fill the entire interval $\Delta_3 = B_{3l} - B_{3u}$ [21]. Then, by analogy with the exact value of $\epsilon_2^* = (B_{2l}B_{2u})^{1/2}$ in interval (4), it is natural to assume that the exact value of ϵ_3^* in interval (7) is well approximated by the function

$$\epsilon_{3A}^* = (B_{3l}B_{3u})^{1/2} = \left(\frac{I_1 I_3}{I_2} \right)^{1/2}, \quad (8)$$

which satisfies the above requirements and restrictions (7). Let us determine narrower boundaries for ϵ_{3A}^* taking into account the conditions $\epsilon_i > 0$ and $I_p > 0$, as well as the known inequalities [41] for the functions of I_p . Using the inequalities $I_1 \geq 3I_3^{1/3}$ and $3I_1 I_3 \ll I_2^2$ in expression (8), we obtain the relationships

$$B_{3l}^{(A)} = \left(\frac{3I_3^{4/3}}{I_2} \right)^{1/2} \leq \epsilon_{3A}^* \leq \left(\frac{I_2}{3} \right)^{1/2} = B_{3u}^{(A)}. \quad (9)$$

From the inequality $3I_3^{2/3} \leq I_2$ ($3I_2 \leq I_1^2$), it follows that $B_{3l} \leq B_{3l}^{(A)}$ ($B_{3u}^{(A)} \leq B_{3u}$) and interval (9) is narrower than interval (7). For model hierarchically organized isotropic polycrystals with optically anisotropic crystallites, the effective dielectric constant $\epsilon_{3S}^* = I_3^{1/3}$ [21–23] is expressed in the form $\epsilon_{3S}^* = (B_{3l}^{(A)} B_{3u}^{(A)})^{1/2}$ and is limited by interval (9). The ratio $\epsilon_{3A}^*/\epsilon_{3S}^* = (I_1 I_3^{1/3}/I_2)^{1/2}$ is determined by the ratio of the components ϵ_i .

In the framework of the effective medium theory for a polycrystal with spherical crystallites, the effective dielectric constant ϵ_3^* is a solution of the equation [17–20]

$$\sum_i \frac{\epsilon_i - \epsilon_3^*}{\epsilon_i + 2\epsilon_3^*} = 0, \quad (10)$$

which is reduced to the following equation:

$$(\epsilon_3^*)^3 - \epsilon_3^* I_2/4 - I_3/4 = 0. \quad (11)$$

Relation of the functions $F_q(m)$ to the specified quantities for polycrystals with optically uniaxial crystallites at dielectric constants $\epsilon_x = \epsilon_y$ and optical anisotropy parameter $m = \epsilon_z/\epsilon_x$

	$q = 1$	$q = 2$	$q = 3$	$q = 4$	$q = 5$	$q = 6$	$q = 7$	$q = 8$	$q = 9$	$q = 10$	$q = 11$	$q = 12$
$F_q \epsilon_x$	B_{2u}	ϵ_2^*	B_{2l}	B_{3u}	$B_{3u}^{(HS)}$	$B_{3u}^{(A)}$	ϵ_{3E}^*	ϵ_{3A}^*	ϵ_{3S}^*	$B_{3l}^{(HS)}$	$B_{3l}^{(A)}$	B_{3l}
F_q	$\frac{m+1}{2}$	$m^{1/2}$	$\frac{2m}{m+1}$	$\frac{m+2}{3}$	$\frac{2m^2+7m}{8m+1}$	$\left(\frac{1+2m}{3}\right)^{1/2}$	$\frac{1+(1+8m)^{1/2}}{4}$	$\left(\frac{m^2+2m}{2m+1}\right)^{1/2}$	$m^{1/3}$	$\frac{5m+4}{2m+7}$	$\left(\frac{3m^{4/3}}{2m+1}\right)^{1/2}$	$\frac{3m}{2m+1}$

By virtue of the inequality $I_2^3 \geq 27I_3^2$, the discriminant of this equation is negative, and it has three real roots, from which the desired positive root is given by the expression

$$\epsilon_{3E}^* = \left(\frac{I_2}{3}\right)^{1/2} \cos \left[\frac{1}{3} \arccos \left(\frac{I_3 \sqrt{27}}{I_2^{3/2}} \right) \right]. \quad (12)$$

By setting $\arccos(\dots) = A$ and taking into account the inequalities $\cos[A] \leq \cos[A/3] \leq 1$, we obtain the restrictions $B_{3l} \leq \epsilon_{3E}^* \leq B_{3u}^{(A)}$. From equation (11), we derive the identity $4(\epsilon_{3E}^*)^3 = \epsilon_{3E}^* I_2 + I_3$. Let us replace the parameter ϵ_{3E}^* on the right-hand side of this identity by the smaller quantity B_{3l} . As a result, the identity is transformed into the inequality $(\epsilon_{3E}^*)^3 \geq I_3$ or $\epsilon_{3E}^* \geq \epsilon_{3S}^*$.

Let us consider the case of uniaxial crystallites. The table presents the functions $F_q(m)$ for the quantities appearing in formulas (4), (7)–(9), and (12) and normalized to the value of ϵ_x and the formulas for the upper ($B_{3u}^{(HS)}$) and lower ($B_{3l}^{(HS)}$) boundaries of the interval for the effective dielectric constant ϵ_3^* [14, 15] at $m > 1$. The functions $F_q(m)$ together with the dependences $F_{oP}(\lambda_k) = (n_{oP}/n_Y)^2$ for PPV films [9, 25] with the corresponding values of $m(\lambda_k) = (n_Z/n_Y)^2$ are shown in Fig. 3. For $m \rightarrow 1$, the functions $F_{2,3}(m)$ and $F_{5-12}(m)$ asymptotically approach the functions $F_1(m)$ and $F_4(m)$, and for $m = 1$, they have the derivatives $F'_{1-3} = 1/2$ and $F'_{4-12} = 1/3$. When $(m - 1) \ll 1$, the function $F_7(m) = F_4(m) - 2(m - 1)^2/27$ corresponds to the standard expressions for ϵ_3^* [39, 40].

For $m > 1$, we have $\epsilon_2^* > \epsilon_3^*$, regardless of the method used for the calculation of ϵ_3^* . When $m \neq 1$, the inequality $\epsilon_{3E}^* > \epsilon_{3A}^*$ is satisfied, but these quantities differ slightly from each other and, with an increase in m , tend to the limit $\epsilon_x(m/2)^{1/2}$. The values of $m > 1$ ($m < 1$) correspond to the relationship $\epsilon_{3A}^* > \epsilon_{3S}^*$ ($\epsilon_{3A}^* < \epsilon_{3S}^*$). The intervals $\Delta_2(m)$ and $\Delta_3(m)$ are separated by a gap, and the experimental values of ϵ_2^* and ϵ_3^* are clearly distinguishable in the range $1 < m < 2$. This is

consistent with the visible transparency region for polydomain films of PFO ($m = 1.3-1.9$) [16] and F8BT ($m = 1.4-2.0$) [24]. The values of $\epsilon_2^*(m)$ are separated by a gap from the interval $\Delta_3(m)$ in the range $1 < m < 4$. This corresponds to polycrystalline PPV films in the range $2 < m < 3$ when the values of $\epsilon_{oP}(m)$ close to $\epsilon_2^*(m)$ lie outside the interval $\Delta_3(m)$. As the wavelength decreases below $\lambda < 0.6 \mu\text{m}$ and the long-wavelength electronic absorption band of the crystallite is approached, the resonance increase in $m(\lambda) > 3$ is accompanied by the shift of $\epsilon_{oP}(m)$ toward the region of the overlap of the intervals $\Delta_2(m)$ and $\Delta_3(m)$. For the PPV film, the shift of $\epsilon_{oP}(m)$ from the upper to lower boundary of the interval $\Delta_2(m)$ with an increase in $m(\lambda)$ is similar to that for the PFO [16] and F8BT [24] films.

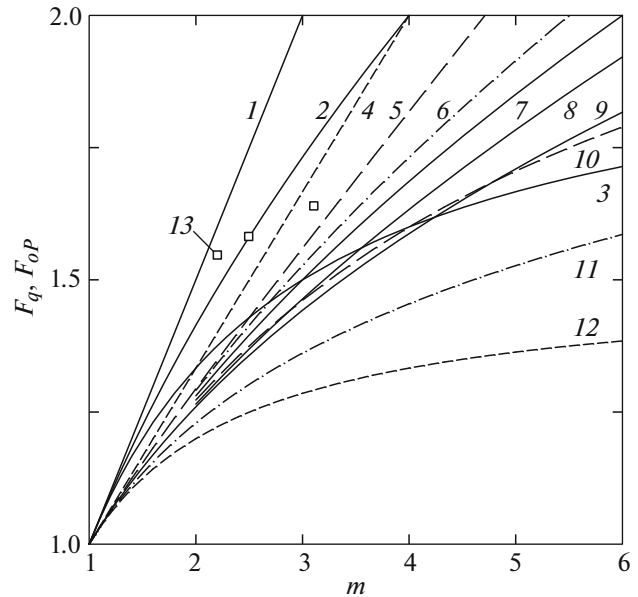


Fig. 3. (1–12) Tabulated functions $F_q(m)$ with numbers $q = 1-12$, respectively, and (13) correlation of the experimental values of $F_{oP}(\lambda_k) = (n_{oP}/n_Y)^2$ with the quantities $m(\lambda_k) = (n_Z/n_Y)^2$ of the PPV films with the refractive indices n_{oP} [9] and $n_{Y, Z}$ [25] at wavelengths $\lambda_k = 0.6, 0.7$, and $0.8 \mu\text{m}$.

We note other points m_{k-q} of intersection of the curves $F_k(m)$ and $F_q(m)$. The values of m_{3-q} correspond to the upper boundaries of the gaps between the minimum values of ε_2^* in the interval $\Delta_2(m)$ and the maximum theoretical values of $\varepsilon_3^*(m) = \varepsilon_x F_q(m)$ for the given parameter m . Using the tabulated functions, we obtain $m_{3-5} = 2.5$, $m_{3-6} \approx 2.686$, $m_{3-7} = 3$, $m_{3-8} \approx 3.562$, $m_{3-10} = 4$, and $m_{3-9} \approx 4.236$. The inequality $F_5(m) < F_6(m)$ is satisfied in the range $1 < m < m_{5-6} \approx 1.715$ for the maximum difference $F_6 - F_5 \approx 0.0009$; i.e., for ε_{3E}^* , the upper boundary $B_{3u}^{(A)}$ is better than $B_{3u}^{(HS)}$, whereas for $\varepsilon_{3(A,S)}^*$, the upper boundary ε_{3E}^* is better than $B_{3u}^{(A)}$. The relationship $F_8(m) < F_{10}(m)$ is valid in the range $1 < m < m_{8-10} \approx 2.886$ for the maximum difference $F_{10} - F_8 \approx 0.007$. When $m > m_{8-10}$, for ε_{3E}^* , the lower boundary ε_{3A}^* is better than $B_{3u}^{(HS)}$. The relationship $F_{10}(m) > F_9(m)$ holds true in the range $1 < m < m_{9-10} \approx 4.794$. The inequality $F_{10}(m) > F_{11}(m)$ is valid in the range $1 < m < m_{10-11} \approx 56.3$, and for $m \approx 11.9$, we have the maximum difference $F_{10} - F_{11} \approx 0.249$. Thus, in the ranges $1 < m < m_{8-10}$ and $m > m_{9-10}$ ($m_{8-10} < m < m_{9-10}$) for the effective dielectric constant ε_{3A}^* , the best lower boundary is ε_{3S}^* ($B_{3l}^{(HS)}$).

4. CONCLUSIONS

The results of the present and recent studies [16, 24] demonstrated the importance of the systematic experimental verification of the known relations $n_D^*(n_i)$, $\varepsilon_D^*(\varepsilon_i)$ in the visible transparency region of polycrystalline conjugated polymers on the background of a large number of theoretical calculations of the static dielectric constant $\varepsilon_{3,st}^*$ [14, 15, 17–23] with a lack of experimental data [21]. For optically uniaxial polycrystalline films of the conjugated polymer PPV with biaxial crystallites, the dispersion curves of the experimental (n_{oP} [8, 9]) and theoretical (n_2^*) effective refractive indices agree with each other in the visible transparency region, regardless of the method used for the preparation of the films (the blade-coating [8] or spin-coating [9] method) and their thicknesses varying in the range from 0.16 μm [9] to 5 μm [8, 23]. The equality $n_{eP} = n_{oA}$ and increased values of $n_2^* > n_{oP}$, which are calculated using the refractive indices n_{jA} [26, 27] for uniaxially stretched PPV films with uniaxial crystallites, correspond to the in-plane orientation of the longitudinal \mathbf{l}_k axes of the conformational subunits of the polymer chain in intercrystallite regions of the unstretched polycrystalline film. This difference in the morphologies and optical properties of uniaxial PPV films prepared by the stretching of the polymer

precursor, followed by its thermal conversion into PPV [25], or by the stretching of polycrystalline PPV films [26, 27, 34, 35, 37] is important for the technology of the fabrication of optoelectronic devices based on conjugated polymers.

The variation used in this study for the optical anisotropy parameter $m(\lambda) = \varepsilon_z/\varepsilon_x$ of the PPV crystallites in the transparency region due to the resonance change in the components $\varepsilon_{x,z}(\lambda)$ of the dielectric constant near the polarized electronic absorption band of the crystallites revealed that the optical methods have an advantage in the investigation of the effective dielectric constant $\varepsilon_D^*(m)$ as compared to measurements of the static values of $\varepsilon_{3,st}^*(m)$ [21] with a fixed value of m for a particular material. Furthermore, as was shown above, the closeness of the theoretical and experimental values of the effective dielectric constant $\varepsilon_{D,st}^*$ for a particular polycrystal does not ensure the closeness of the corresponding values of $\varepsilon_D^*(\lambda)$ in the optical transparency region in the vicinity of the polarized absorption bands of the crystallites.

For the PPV films with uniaxial crystallites, as well as for PFO [16] and F8BT [24] films with uniaxial domains and lower values of m , the experimental effective dielectric constants $\varepsilon_{oP}^*(m)$ fill the interval $\Delta_2(m)$ of the permissible values of $\varepsilon_2^*(m)$ with variations in the parameter $m(\lambda)$ in the visible transparency region of the films. This demonstrates the importance of the dependences of the parameters ε_D^* and Δ_D on the dimension D and the optical anisotropy parameter m . With an increase in m , the rapid increase of the intervals $\Delta_2(m)$ and $\Delta_3(m)$ is accompanied by their overlap for $m > 2$. The experimental values of $\varepsilon_2^*(m)$ and $\varepsilon_3^*(m)$ are reliably distinguishable for $m < 2$ in PFO [16] and F8BT [24] polydomain films. The theoretical dependence $\varepsilon_2^*(m)$ is separated by a gap from the interval $\Delta_3(m)$ in the range $1 < m < 4$. This is true in the visible transparency region of the PPV films, for which the dielectric constants $\varepsilon_{oP}(m)$ in the range $2 < m(\lambda) < 3$ are close to the theoretical values of $\varepsilon_2^*(m)$ and lie outside the interval $\Delta_3(m)$, whereas in the range $m(\lambda) > 3$ near the electronic absorption band of the crystallites, the quantities $\varepsilon_{oP}(m)$ lie in the region of the overlap of the intervals $\Delta_2(m)$ and $\Delta_3(m)$.

For three-dimensional polycrystals with optically biaxial and uniaxial crystallites, we obtained the relationship $\varepsilon_{3A}^*(\varepsilon_i)$, which does not depend on the shape of the crystallites. We also established the relations between the function $\varepsilon_{3A}^*(\varepsilon_i)$, the function $\varepsilon_{3E}^*(\varepsilon_i)$ in the effective medium theory with spherical crystallites

[17–20], and the function $\varepsilon_{3S}^*(\varepsilon_i)$ for hierarchical models of the polycrystal [21–23], as well as determined the restrictions on the quantities $\varepsilon_{3(A,E,S)}^*$. In the case of uniaxial crystallites, we determined the boundaries m_c of the range $1 < m < m_c$, which correspond to the gaps between the dependences $\varepsilon_{3(A,E,S)}^*(m)$ and the lower boundary of the interval $\Delta_2(m)$.

The results of this study extend the possibilities for the prediction and optimization of the technological parameters of polycrystalline films in optoelectronics without restrictions on the anisotropy parameter m of crystallites.

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