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Anisotropy of the Local Field in Anisotropic Films of Conjugated Polymers

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Abstract—Using the data on dispersion of refractive indices in the visible region, the experimental values of the components L_j of the Lorentz tensor have been obtained for uniaxial (crystalline, oriented on a substrate, and stretched) films of conjugated polymers from nanometer to micrometer thicknesses. The dependence of the components L_j on the axial and planar orientations of macromolecules with respect to the optical axis of the film, technology of fabricating the films, and chemical structure of macromolecules has been elucidated. The correlation between the components L_j and the measured parameter η has been determined and the analytical dependence $L_j(\eta)$ for films with both types of macromolecular orientation has been established. In the visible region ($0 \le \eta \le 0.5$), the presence of one point ($\eta = 1/3$) of isotropization of the tensor L and three points ($\eta = 0$, 1/3, and 0.5) of isotropization of the local field tensor f has been revealed. The point $\eta = 1/3$ of isotropization of the tensors L and f has been determined. A comparison has been made between the values of $L_j(\eta)$ with predictions of known models of the local field for conjugated polymers.

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1. INTRODUCTION

Anisotropic films of conjugated polymers (CP) are used in field diodes and transistors [1, 2], electroluminescent diodes [3], photovoltaic elements and solar batteries [4], polymer lasers [5, 6], and optical amplifiers [7]. The intensity of the processes lying in the basis of the optical properties of CP and their applications is determined by the local field of a light wave $E_j^{\text{loc}}(\omega) = f_j(\omega)E_j(\omega)$ acting on a molecule and coupled with the macroscopic field $E_j(\omega)$ of the light wave in a medium with the local field tensor $f_j(\omega) = 1 + L_j[\varepsilon_j(\omega) - 1]$. Here, $\varepsilon_j(\omega) = \hat{n}_j^2(\omega)$ are the components of the permittivity tensor of the film for the polarizations of the field $\mathbf{E}$ of the light wave parallel ($j = \parallel$) and perpendicular ($j = \perp$) to the optical axis of the film $\mathbf{n}$, $\hat{n}_j(\omega) = n_j(\omega) + ik_j(\omega)$ are complex refractive indices, and L_j are the Lorentz tensor components ($\mathrm{Sp}\,L = 1$) [8]. Experimental values of L_j and $f_j(\omega)$ are necessary for studying and modeling the properties of the [9–12] considered objects.

In the theory of optical properties of CP [9–11, 13, 14] developed for a system of densely packed macromolecules parallel to the optical axis $\mathbf{n}$, the model of the Lorentz cylindrical cavity [9] is used in which the component $L_\perp$ is given by the formula

$$L_\perp = \frac{l}{2(l^2 + d_c^2)^{1/2}}. \qquad (1)$$

Here, l and d_c are the length and diameter of the cylinder enclosing a macromolecule. The limiting values $L_\parallel = 0$ and $L_\perp = 0.5$ involved in the theory satisfy the condition $l \gg d_c$, which corresponds to an infinite chain of π-electron conjugation of monomers in a linear macromolecule, which is typical for crystalline polymers [15–17]. The same values of L_j are used for CP in the crystalline [9, 10] and amorphous states [11–14]. However, in the amorphous state, rigid-chain macromolecules of CP consist of relatively short linear fragments: conformational subunits (CS) [18], which differ in the length and spatial orientations. This circumstance poses a question on the possibility to use the limiting values of L_j of model (1) in the case of films with nonperfect axial orientation of macromolecules and their fragments. In the case of uniaxial crystals of CP with perfect axial orientation of macromolecules, a microscopic method for calculating the components L_j in the framework of the lattice model was proposed [19]. The applicability of models [9, 19] can be clarified in experimental determination of the components L_j.

A wide application in practice has been gained by films in which CS lie predominantly in the film plane (planar orientation) and the axis $\mathbf{n}$ is perpendicular to this plane. In this case, model (1) is inapplicable and other models for calculating L_j are absent. Therefore, approximations of noninteracting macromolecules with $L_j = 0$ [20–25] or isotropic Lorentz cavity with $L_j = 1/3$ [26–28] are used.

The aim of the present work is the experimental determination of the components L_j for uniaxial films of CP with the axial and planar orientations of macromolecules and revelation of the anisotropic properties of the tensors L and f with the orientation order and properties of macromolecules. The components L_j are determined by the method realized earlier for uniaxial media of different nature [29] and a number of anisotropic amorphous CP films [30]. In the present work, the majority of known crystalline and amorphous CP is studied. The method of determining the components L_j is presented in Section 2. The objects of investigation, results, and discussion are presented in Section 3. The conclusions drawn in this work are summarized in Section 4.

2. DETERMINATION OF THE COMPONENTS L_j FOR FILMS WITH DIFFERENT OPTICAL SIGNS

Let us consider a uniaxial homogeneous polymer film with the axis **n** lying in the film plane (planar orientation) or perpendicular to this plane (homeotropic orientation). Assume that the film consists of statistically identical macromolecules among which there are, in average, N_i uniaxial CS of the ith sort, differing in the orientation of the longitudinal axes $\mathbf{l}_i$ with respect to the axis **n**, the length ξ_i, the mean value $\bar{\gamma}_i(\xi_i) = (\gamma_{li} + 2\gamma_{ti})/3$, and the anisotropy $\Delta\gamma_i(\xi_i) = \gamma_{li} - \gamma_{ti}$ of the polarizability, where γ_{li} and γ_{ti} are the longitudinal and transverse components of the polarizability of CS of the ith sort. The mean polarizability of a macromolecule is $\bar{\gamma} = \Sigma_i N_i \bar{\gamma}_i = (\gamma_\parallel + 2\gamma_\perp)/3$, where γ_j is the ensemble-averaged components of the polarizability of macromolecules in the system of refraction ellipsoid. For isolated macromolecules, the quantities $\bar{\gamma}_i$ and $\Delta\gamma_i$ are independent of the position of CS in a molecule. In a film, the anisotropic interactions between CS cause variations in $\Delta\gamma_i$, $\bar{\gamma}_i$, and $\bar{\gamma}$ and their dependence on the character and degree of structural ordering of CS. The procedure of determining the components L_j depends on the sign of $\Delta n = n_\parallel - n_\perp$ or $\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp$ (the optical sign of the film), which coincides with the sign of $\Delta G = \gamma_\parallel - \gamma_\perp$. The expression for ΔG depends on the rigidity of macromolecules and their orientation (axial or planar) in the film. Let us consider two types of macromolecules.

(1) In rigid-chain macromolecules with a nearly rod-like shape, one can distinguish the longitudinal axis **l** that connected the ends of the molecule. The orientational ordering of CS of the ith sort in a macromolecule is characterized by the parameter $S_i = \overline{P_2(\cos\vartheta_i)}$ [31]. Here, ϑ_i is the angle between the axes $\mathbf{l}_i$ and **l**, $P_2(x)$ is the Legendre polynomial, and the overbar means the averaging over the orientations of CS of the ith sort with respect to the axis **l**. The anisotropy of the polarizability of the macromolecule is $\Delta\gamma = \gamma_l - \gamma_t = \Sigma_i N_i \Delta\gamma_i S_i > 0$. Here, $\gamma_{l,\,t}$ are the longitudinal and transverse components of the polarizability of a macromolecule. The degree of orientational order of macromolecules with respect to **n** gives the parameter $S = \langle P_2(\cos\theta) \rangle$, where θ is the angle between the axes **l** and **n** and the angular brackets $\langle \ldots \rangle$ mean the averaging over the ensemble of macromolecules. The sign of $\Delta G_r = S\Delta\gamma$ coincides with the sign of S. The values $0 < S < 1$ $(-0.5 < S < 0)$ correspond to the axial (planar) orientation O_A (O_P) of macromolecules in a film.

Films with the planar orientation of **n** and axial orientation of macromolecules are obtained on oriented substrates in the nematic phase (O_A) [25, 32, 33] or by uniaxial stretching in the amorphous state (O_{AS}) [12, 34, 35]. Films with the homeotropic orientation of **n** and macromolecular orientation O_P are obtained by centrifugal spreading of a drop of polymer solution over a rotating substrate surface [20, 25, 32] or by leveling gel polymer solution over a substrate surface by a special scratch blade [36].

(2) Nonrigid macromolecules are found in the solution in a state close to the state of a statistical coil [31]. Formation of films with the macromolecular orientation O_P and homeotropic orientation of **n** is accompanied by flattening of the coil in the film plane and condensation along the axis **n** after evaporation of solvent. In films with thicknesses comparable with or smaller than the diameter of the statistical coil, macromolecules may not be considered as uniaxial. The optical anisotropy of the film is determined by the orientational order of CS with respect to **n**. For a uniaxial film, we have $\Delta G_{nr} = \Sigma_i N_i \Delta\gamma_i R_i$, where $R_i = \langle P_2(\cos\phi_i) \rangle$, ϕ_i is the angle between the axes $\mathbf{l}_i$ and **n**, and angular brackets $\langle \ldots \rangle$ denote the averaging over all CS of the ith sort of all macromolecules. For uniaxial macromolecules in a uniaxial film with allowance for $R_i = S_i S$, the quantity ΔG_{nr} passes to ΔG_r. The axial (planar) orientation of macromolecules in a film corresponds to the values of $\Delta G_{nr} > 0$ $(\Delta G_{nr} < 0)$.

(3) Optically positive films. For such films with $\Delta\varepsilon > 0$ in the visible region, let us introduce the parameters $\bar{\varepsilon} = (\varepsilon_\parallel + 2\varepsilon_\perp)/3$ and $Q = \Delta\varepsilon/(\bar{\varepsilon} - 1)$ and the quantities

$$r_0 = 1 - \frac{2Q^2(\bar{\varepsilon} - 1)}{3(3 + Q)(\bar{\varepsilon} + 2)}, \quad b = \frac{3(\bar{\varepsilon} - 1)}{4\pi N \bar{\gamma}(\bar{\varepsilon} + 2)} - r_0,$$
$$b_1 = \frac{2r_0 Q^2}{(3 - Q)(3 + 2Q)}, \quad b_2 = b_1\left(\frac{6 + Q}{Q}\right)^2. \tag{2}$$

The sought quantity $L_\perp$ $(L_\parallel = 1 - 2L_\perp)$ is coupled with these quantities by the expression [29]

$$L_\perp = L_{\perp k} - \frac{(\bar{\varepsilon} + 2)}{12(\bar{\varepsilon} - 1)}$$
$$\times \left[(b_1 b_2)^{1/2} - b - [(b_1 - b)(b_2 - b)]^{1/2}\right]. \tag{3}$$

The signs of the values of $\Delta f = f_{\parallel} - f_{\perp}$ and b coincide. The quantity $L_{\perp k} = (3 + 2Q)/[3(3 + Q)]$ agrees with the conditions $\Delta f = b = 0$. At a given state of the film, which is characterized by the index T, expression (3) involves the unknown function $b(\lambda, T)$, depending of the unknown function $\bar{\gamma}(\lambda, T)$. The determination of $L_{\perp}(T)$ consists in the following. For known values of $n_j(\lambda, T)$, for a discrete set of quantities λ_q ($q = 1 - p$) in the visible region, the function $b(\lambda, T)$ in the interval $\lambda_1 - \lambda_p$ is approximated by the polynomial

$$b(\lambda, T) = a_0(T) + a_1(T)\lambda + \ldots + a_m(T)\lambda^m. \quad (4)$$

The quantity $L_{\perp}(T)$ is independent of λ and each state T is determined by $m + 2$ unknowns ($L_{\perp}^{(m)}$, $a_0 - a_m$). They are found from the system of $m + 2 = p$ equations (3), each of which corresponds to one of the quantities λ_q. An increase in the degree m in Eq. (4) requires to increase the accuracy of $n_j(\lambda, T)$, otherwise the system of equations with respect to ($L_{\perp}^{(m)}$, $a_0 - a_m$) cannot have physical solutions. The criterion for adequacy of the used approximation (4) is the agreement between the values of $L_{\perp}^{(m)}$ and the quantities $\langle L_{\perp}^{(m-1)} \rangle$, averaged over the values of $L_{\perp}^{(m-1)}$ corresponding to combinations of $p - 1$ frames of λ_q from the set of $\lambda_1 - \lambda_p$.

(4) Optically negative films. For such films in the visible region, $\Delta\varepsilon < 0$ and the following quantities are used: $Q_d = -Q$,

$$r_{0d} = 1 - \frac{2Q_d^2(\bar{\varepsilon} - 1)}{3(3 - Q_d)(\bar{\varepsilon} + 2)}, \quad d = \frac{3(\bar{\varepsilon} - 1)}{4\pi N\bar{\gamma}(\bar{\varepsilon} + 2)} - r_{0d},$$
$$d_1 = \frac{2r_{0d}Q_d^2}{(3 + Q_d)(3 - 2Q_d)}, \quad d_2 = d_1\left(\frac{6 - Q_d}{Q_d}\right)^2. \quad (5)$$

They are coupled with the component $L_{\perp}$ by the expression [29]

$$L_{\perp} = L_{\perp k} + \frac{(\bar{\varepsilon} + 2)}{12(\bar{\varepsilon} - 1)} \times [(d_1 d_2)^{1/2} + d - [(d_1 - d)(d_2 - d)]^{1/2}]. \quad (6)$$

The values of Δf and d have opposite signs. The quantity $L_{\perp k} = (3 - 2Q_d)/[3(3 - Q_d)]$ in Eq. (6) agrees with the conditions $\Delta f = d = 0$. For a function $d(\lambda, T)$, approximation (4) is used. The quantities ($L_{\perp}^{(m)}$, $a_0 - a_m$) are found by analogy with the aforesaid from the known values of $n_j(\lambda, T)$ for a set of quantities λ_q ($q = 1 - p$) from the system of equations (6), each of which corresponds to one of the quantities λ_q.

3. OBJECTS OF INVESTIGATION, RESULTS, AND DISCUSSION

Figure 1 presents the structural formulas of monomer units of the polymers under study with generally accepted abbreviations. The formula of monomer RECP in [37] and in Fig. 1 is absent. The chosen polymers have macromolecules of three types: rigid linear molecules (P3OT, PPY, PFO, PF2/6, PE2/6am5, and F8BT); molecules with the fragments CH=CH (PPV, BuEH–PPV, MEH–PPV, OC1C10–PPV, DE15, and DE42), which provide the possibility of rotations about C=C-bonds with kinks of the polymer chain and facilitate division of a macromolecule into CS; and molecules with kinks of the polymer chain caused by the chemical structure of monomers (PPY.*Xm*, TFB, and PFB).

For uniaxial films of these CP with different types of macromolecular orientation, table mentions works containing tabulated (graphic) dependences $n_j(\lambda)$ or $\varepsilon_{1j}(\lambda)$ ($\varepsilon_j = \varepsilon_{1j} + i\varepsilon_{2j}$) in the transparency region. The film thickness varies from 50 nm to 5 (trans-PA, cis-PA [15], and PPV [34]) or 15 μm (PPV [12,35]). For single-crystal films of polyacetylenes (trans-PA, cis-PA) with linear macromolecules and the axis $\mathbf{n} \parallel \mathbf{l} \parallel Z$, the small difference between the refractive indices $n_{X, Y}$ is disregarded and the uniaxial approximation $n_{X, Y} = n_{\perp}$ [15] is used. In accordance with the results of [16, 17], the same approximation is used for bulk single crystals of PTS polymer.

For the majority of films, the values of $n_j(\lambda_q)$ for five frames λ_q made it possible to determine the quantities $L_{\perp}^{(3)}$ and $\langle L_{\perp}^{(2)} \rangle$. For films of PPV [34] and PTS crystal [17], the values of $L_{\perp}^{(1)}$ and $\langle L_{\perp}^{(0)} \rangle$ are presented. For films of PPV [36] and *m*-LPPP [24] and two films of DCHD–HS [49] obtained with the use of different solvents and differing in the quantities $n_j(\lambda_q)$, the values of $L_{\perp}^{(0)}$ are presented. Generally, the values of $L_{\perp}^{(3)}$ agree with $\langle L_{\perp}^{(2)} \rangle$ within the error of determining the latter. For films of trans-PA, PPV [12, 35], PFO, TFB, PFB, and PTS [16], the accuracy of $\langle L_{\perp}^{(2)} \rangle$ attains 10^{-3}–10^{-4}. For films of P3OT [38], PPY, PF2/6am5, and F8BT [33], the accuracy of $n_j(\lambda_q)$ is adequate to the degree $m \leq 2$ in Eq. (4).

The quantity $L_{\perp}^{(3)}$ is very sensitive to variations in $n_j(\lambda_q)$, which depend on the chemical and electronic structure of monomers. The transition from linear molecules of PPY to molecules of PPY.18*m* with step-like kinks of the polymer chain is accompanied by a significant increase in $\langle L_{\perp}^{(2)} \rangle$ and a decrease in the anisotropy of tensor L. In a less pronounced form, this phenomenon is observed in films of PPV [40], BuEH–PPV [41], and MEH–PPV [21] with a close thickness

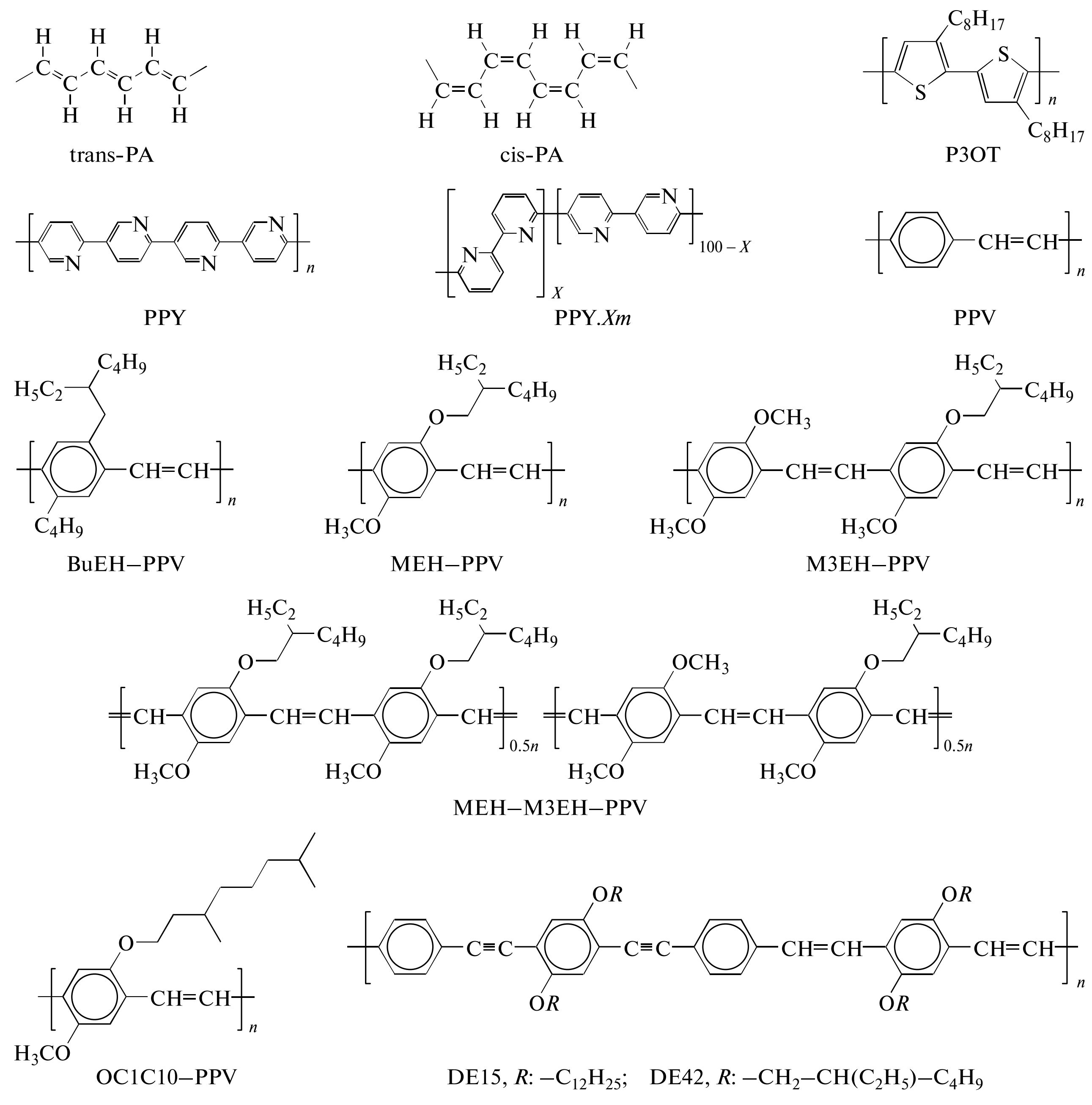

Fig. 1. Structural formulas of monomers for studied conjugated polymers.

and the orientation O_P. The emergence of side bulk substituents in phenyl rings as a result of transition from PPV to BuEH–PPV and MEH–PPV leads to an increase in $L_\perp^{(3)}$. On transition from MEH–PPV to M3EH–PPV with a close molecular weight [44], the disappearance of the side alkyl chain in each second phenyl ring of the polymer molecule is accompanied by a decrease in $L_\perp^{(3)}$ and $\langle L_\perp^{(2)} \rangle$ and increase in the anisotropy of tensor L. As expected, for polymer MEH–M3EH–PPV, in which each fourth phenyl ring is devoid of a branched side alkyl chain, the values of $L_\perp^{(3)}$ and $\langle L_\perp^{(2)} \rangle$ are intermediate between those of polymers MEH–PPV and M3EH–PPV. For films of PFO and PF2/6 with the macromolecular orientations O_A and O_P, the small distinction in the side substituents of the monomer unit manifests itself in a difference between the values of $L_\perp^{(3)}$. The proximity of the quantities $\langle L_\perp^{(2)} \rangle$ for films of PF2/6 and PF2/6am5 shows a small influence of terminal substituents in macromol-

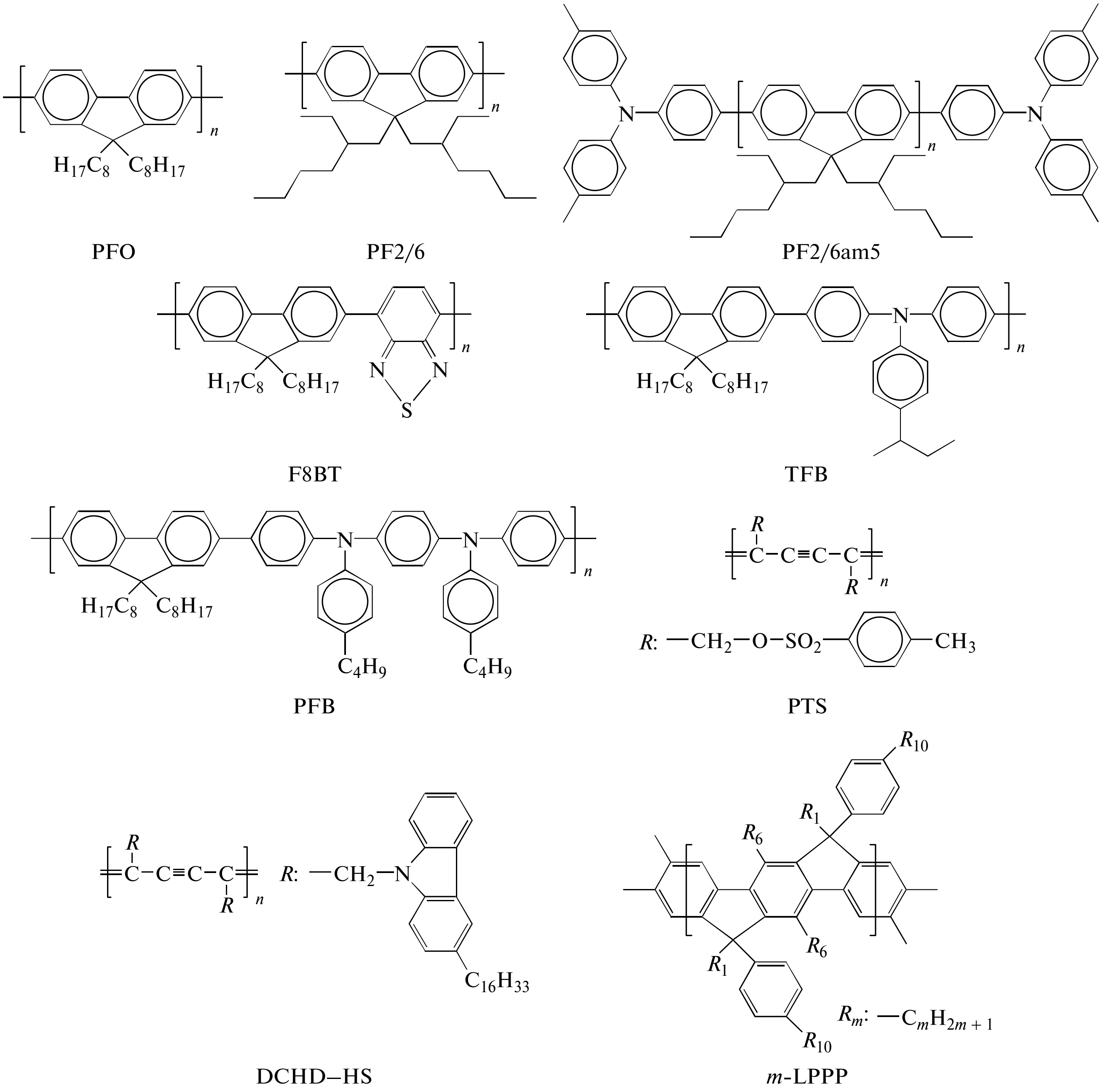

Fig. 1. (Contd.)

ecules of PF2/6am5 on $\langle L_\perp^{(2)} \rangle$. The difference in the chemical structure of monomers TFB and PFB does not influence $L_\perp^{(3)}$.

For films of one polymer with the same type of orientation of macromolecules, the quantities $n_j(\lambda_q)$ [25] and $L_\perp^{(m)}$ can be noticeably different, depending on the molecular weight M_W of the polymer and the technology of producing and thermal treatment of the films. For polymer MEH–PPV, the successive reduction of M_W from 1.6×10^6 g/mol [21, 43] to 4.2×10^5 ($L_\perp^{(3)} = 0.186$) [42], 2.76×10^5 [43], 2.65×10^5 ($L_\perp^{(3)} = 0.222$) [42], and 4.03×10^4 g/mol [44] is accompanied by a monotonic increase in $L_\perp^{(3)}$ and $\langle L_\perp^{(2)} \rangle$. For F8BT film [47], the quantities $L_\perp^{(3)}$ are sensitive to variations in $n_j(\lambda_q)$ on thermal annealing of film.

The obtained data reflect the correlation of $L_\perp$ with the values of $\eta = \langle L_{\perp k}(\lambda_q) \rangle$ presented in table, where angular brackets denote the averaging over the interval $\lambda_1 - \lambda_p$ [30]. In order to reveal the physical meaning of

The values of λ_q(μm), $L_\perp^{(m)}$, $\langle L_\perp^{(m-1)}\rangle$, and η for films of the studied polymers with the axial orientation of macromolecules on orienting substrates (O_A), in the uniaxially stretched state (O_{AS}), and in the crystalline state (O_{AC}) and for unannealed (O_P) and annealed (O_P^*) samples with planar orientation of macromolecules

Polymer	Orientation	λ_1	λ_2	λ_3	λ_4	λ_5	$L_\perp^{(m)}$	$\langle L_\perp^{(m-1)}\rangle$	η
trans-PA	O_{AC} [15]	1.000	1.143	1.333	2.000	4.000	0.5224	0.5220 ± 0.0004	0.462
cis-PA	O_{AC} [15]	0.827	1.000	1.333	2.000	4.000	0.492	0.520 ± 0.023	0.467
P3OT	O_P [38]	0.653	0.689	0.729	0.775	0.827	–	0.231 ± 0.009	0.298
P3OT	O_P [39]	0.653	0.689	0.729	0.827	1.033	0.100	0.141 ± 0.022	0.276
PPY	O_P [23]	0.496	0.551	0.620	0.709	1.240	–	0.100 ± 0.032	0.265
PPY.18*m*	O_P [23]	0.451	0.496	0.551	0.709	1.240	0.156	0.159 ± 0.003	0.273
PPV	O_{AS} [12]	0.540	0.580	0.620	0.700	0.800	0.5178	0.5164 ± 0.0005	0.460
PPV	O_{AS} [35]	0.588	0.625	0.714	0.833	1.053	0.513	0.510 ± 0.002	0.454
PPV	O_{AS} [34]	0.589	0.602	0.609	–	–	0.479	0.494 ± 0.001	0.450
PPV	O_P [36]	0.633	1.064	–	–	–	0.163	–	0.250
PPV	O_P [40]	0.550	0.600	0.700	0.800	0.900	0.116	0.179 ± 0.027	0.242
BuEH–PPV	O_P [41]	0.525	0.535	0.545	0.560	0.590	0.136	0.136 ± 0.037	0.270
MEH–PPV	O_P^* [21]	0.590	0.620	0.663	0.775	1.000	0.120	0.106 ± 0.011	0.262
MEH–PPV	O_P [42]	0.633	0.700	0.800	0.900	1.000	0.186	0.196 ± 0.003	0.282
MEH–PPV	O_P [43]	0.633	0.700	0.800	0.900	1.000	0.203	0.229 ± 0.011	0.296
MEH–PPV	O_P [42]	0.633	0.700	0.800	0.900	1.000	0.222	0.246 ± 0.012	0.300
MEH–PPV	O_P [44]	0.633	0.700	0.800	0.900	1.000	0.280	0.301 ± 0.003	0.322
M3EH–PPV	O_P [44]	0.633	0.700	0.800	0.900	1.000	0.196	0.221 ± 0.011	0.296
MEH–M3EH–PPV	O_P [44]	0.633	0.700	0.800	0.900	1.000	0.258	0.252 ± 0.005	0.306
OC1C10–PPV	O_P^* [22]	0.600	0.650	0.696	0.777	0.858	0.090	0.102 ± 0.011	0.250
DE15	O_P [45]	0.539	0.590	0.653	0.775	1.033	0.217	0.242 ± 0.022	0.303
DE42	O_P [45]	0.539	0.590	0.653	0.775	1.033	0.164	0.194 ± 0.018	0.290
PFO	O_A [25]	0.466	0.500	0.600	0.700	0.850	0.4527	0.4530 ± 0.0002	0.394
PFO	O_P [25]	0.466	0.500	0.600	0.700	0.850	0.267	0.274 ± 0.007	0.319
PF2/6	O_A [32]	0.425	0.450	0.500	0.600	0.750	0.475	0.468 ± 0.006	0.397
PF2/6	O_P [32]	0.450	0.475	0.500	0.600	0.750	0.231	0.210 ± 0.019	0.309
PF2/6am5	O_P [46]	0.450	0.475	0.500	0.600	0.750	–	0.219 ± 0.020	0.299
F8BT	O_A [25]	0.550	0.576	0.650	0.750	0.850	0.470	0.452 ± 0.018	0.399
F8BT	O_A [33]	0.550	0.600	0.650	0.700	0.780	–	0.475 ± 0.023	0.398
F8BT	O_P [47]	0.565	0.646	0.727	0.808	0.889	0.183	0.200 ± 0.008	0.295
F8BT	O_P^* [47]	0.565	0.646	0.727	0.808	0.889	0.214	0.200 ± 0.007	0.293
F8BT	O_P^* [22]	0.532	0.615	0.696	0.777	0.858	0.186	0.171 ± 0.010	0.292
F8BT	O_P [48]	0.530	0.550	0.600	0.650	0.700	0.130	0.187 ± 0.023	0.290
TFB	O_P [47]	0.484	0.565	0.646	0.727	0.808	0.2969	0.2969 ± 0.0001	0.321
PFB	O_P [47]	0.484	0.565	0.646	0.727	0.808	0.299	0.300 ± 0.001	0.320
RECP	O_P [37]	0.638	0.675	0.750	0.825	0.900	0.2682	0.2681 ± 0.0076	0.311
PTS	O_{AC} [16]	0.642	0.653	0.670	0.689	0.729	0.5243	0.5239 ± 0.0003	0.456
PTS	O_{AC} [17]	0.650	0.675	0.700	–	–	0.521	0.502 ± 0.006	0.447
DCHD–HS	O_P [49]	0.849	1.321	–	–	–	0.328	–	0.331
DCHD–HS	O_P [49]	0.849	1.321	–	–	–	0.323	–	0.328
m-LPPP	O_P^* [24]	0.632	0.800	–	–	–	0.319	–	0.326

the parameter η, it should be noted that, e.g., for films with the macromolecular orientation O_A, it follows from the expressions $L_{\perp k} - 1/3 = Q/[3(3+Q)]$ and $Q \propto \Delta\gamma S/\bar{\gamma}$ [29] that the difference $L_{\perp k} - 1/3$ is an indicator of variations in the quantities $\Delta\gamma$ and/or S. With allowance for a weak dependence $L_{\perp k}(\lambda)$ in the region of $\lambda_1 - \lambda_p$, the dynamics of the difference $\eta - 1/3$ can reflect the dependence of S at a fixed $\Delta\gamma$ on the technology of production or thermal treatment of the film or variation in ΔG with variation in the chemical structure of macromolecules and M_W.

For CP films with the macromolecular orientation O_P, the inequalities $L_\perp < \eta < 1/3$ are satisfied and an increase in η corresponds to a reduction in $|\Delta n|$ and $\Delta\gamma|S|$ ($|\Delta G_{nr}|$). In particular, on transition from linear molecules of PPY to molecules of PPY.18m with kinks in the polymer chain, the increase in η and $L_\perp$ correlates with the reduction in $|\Delta n|(\lambda_{1-5})$ and is caused by the reduction in $\Delta\gamma|S|$. This fact is confirmed by a reduction in the quantity $|S|$ [23], short-wave shift in the band of the long-wave electron $\pi-\pi^*$-transition, polarized along the axes $\mathbf{l}_i$ of CS and the reduction in the oscillator strength of this transition [23], which corresponds to a reduction in the quantity $\Delta\gamma(\lambda_{1-5})$. The gradual increase in η and $L_\perp$ on transition from M3EH–PPV to MEH–M3EH–PPV and MEH–PPV with an increase in the number of phenyl rings of the polymer chain with side bulk substituents correlates with a gradual reduction in $|\Delta n|(\lambda_{1-5})$ and $|S|$ [44]. For polymer MEH–PPV, the monotonic increase in η and $L_\perp$ with a monotonic decrease in $|\Delta n|(\lambda_{1-5})$ is explained by such a reduction in $|S|$ [42, 43]. For films of DCHD–HS and m-LPPP, the quantities η and $L_\perp$ show a transition to isotropic tensors $L = 1/3$ and $f = (n^2+2)/3$ as $\Delta\gamma$, $|\Delta n| \longrightarrow 0$.

The character of the correlation $L_\perp(\eta)$ is evident from Fig. 2, where the quantities $L_\perp^{(3)}$, $\langle L_\perp^{(2)}\rangle$, and η for CP are presented. Vertical dashes give the standard deviation of $L_\perp^{(2)}$ from $\langle L_\perp^{(2)}\rangle$ and horizontal one, that of $L_{\perp k}(\lambda_q)$ from η. The quantities $\langle L_\perp^{(2)}\rangle$ are presented for films in which the values of $L_\perp^{(3)}$ either are absent or differ from $\langle L_\perp^{(2)}\rangle$ by more than the standard deviation. Figure 2 also presents the quantities $L_\perp^{(3)}(\eta)$ for discotic liquid crystals (LC) of derivatives of pyrene (Py) and benzoperylene (Bp), polyvynil alcohol (PVA) films, multilayer Langmuir–Blodgett cadmium arachidate (Cd-A) films, freely suspended smectic A films for MHPOBC LC [29], and the smectic phase A of cholesteric ECh8 LC [50]. For PVA film with the macromolecular orientation O_P and optically negative discotic LC, the relationship $L_\perp < \eta < 1/3$ takes place. It is worth noting the proximity between the values of η and $L_\perp$ for films of conjugated polymer m-LPPP and nonconjugated polymer PVA. For optically positive smectics A, Langmuir–Blodgett films, and CP films with the macromolecular orientation O_A, we have $L_\perp > \eta > 1/3$.

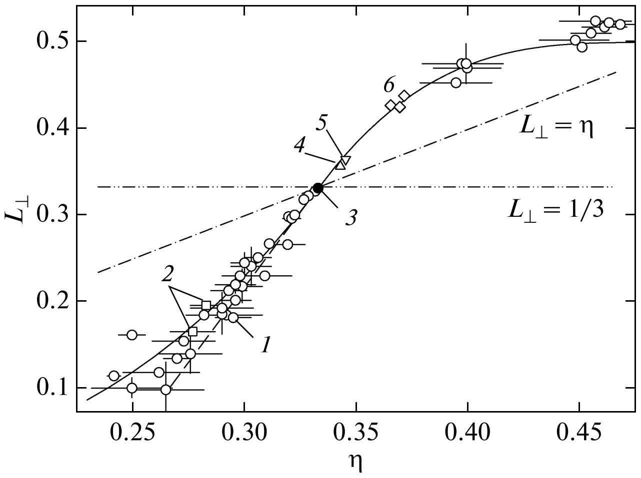

Fig. 2. Correlation of the quantities $L_\perp = L_\perp^{(3)}$ (circles with horizontal dashes) and $\langle L_\perp^{(2)}\rangle$ (circles with horizontal and vertical dashes) with the values of η for (*1*) conjugated polymers and the same data for $L_\perp^{(3)}$ of (*2*) discotic Py and Bp LC, (*3*) PVA film, (*4*) Langmuir Cd–A film [29], and smectic A phase for (*5*) ECh8 [50] and (*6*) MHPOBC LC [29]. The solid line corresponds to dependence (9) for $\eta \le 1/3$ and to dependence (10) for $\eta \ge 1/3$, and the dashed line corresponds to dependence (7).

An increase in η corresponds to an increase in $L_\perp$, and, in the vicinity of $\eta = 1/3$, the linear correlation

$$L_\perp = A_p\eta + B_p \qquad (7)$$

takes place. In the interval $0.28 < \eta < 1/3$, the coefficients $A_p = 3.473$ and $B_p = -0.826$ are coupled by the relationship $(1 - A_p)/3 = -0.824 \approx B_p$, which implies the condition

$$A(\eta) = (L_\perp - 1/3)/(\eta - 1/3) = \text{const} = A_p. \qquad (8)$$

We may expect that dependences (7) and (8) take place for CP films for $\eta > 1/3$, as for optically positive low-molecular compounds. Then, we have $L_\perp \longrightarrow 1/3$ as Q, $Q_d \longrightarrow 0$ and $\eta \longrightarrow 1/3$. For $\eta < 0.28$, the dependence $L_\perp(\eta)$ is nonlinear and a decrease in η corresponds to a decrease in $A(\eta)$ and the quantities $L_\perp(\eta)$ for CP films agree with those for discotic Py and Bp LC. If $(\varepsilon_\perp - 1) \gg (\varepsilon_\parallel - 1)$, the quantity Q_d is close to $Q_d^{\max} = 1.5$, which corresponds to the values $L_{\perp k} = \eta = 0$. Under the restrictions $0 < L_\perp < \eta$ and $\eta \longrightarrow 0$, we have $L_\perp(\eta) \longrightarrow 0$. The value $\eta = 0$ ($\varepsilon_\parallel = 1$) corresponds to polarization of all molecular transitions along the CS axes $\mathbf{l}_i$ and their perfect planar ordering with $\mathbf{l}_i \perp \mathbf{n}$ ($R_i = -0.5$). This is possible for nonrigid macromolecules (see Section 2), but the limit at $\eta = 0$ is unattainable because of the requirement to polarization of all molecular transitions.

For CP films with the macromolecular orientation O_A and low-molecular compounds Cd-A, ECh8, and MHPOBC for $\eta > 0.35$, the dependence $L_\perp(\eta)$ is nonlinear and, with an increase in η, the quantity $A(\eta)$ decreases. If $(\varepsilon_\parallel - 1) \gg (\varepsilon_\perp - 1)$, the quantity Q is close to $Q_{\max} = 3$, which corresponds to the values $L_{\perp k} = \eta = 0.5$. Under the restrictions $0.5 > L_\perp > \eta$ and $\eta \longrightarrow 0.5$, we have $L_\perp(\eta) \longrightarrow 0.5$. The value $\eta = 0.5$ $(\varepsilon_\perp = 1)$ is unattainable due to the above-mentioned requirements to the polarization of molecular transitions, coaxiality $\mathbf{l}_i \parallel \mathbf{l}$ of all CS and their perfect ordering with $\mathbf{l} \parallel \mathbf{n}$.

Taking into account the determined values of $L_\perp(\eta)$ at $\eta = 0$, 1/3, and 0.5, the relationships between $L_\perp$ and η, the value of $dL_\perp/d\eta = A_p$ at $\eta = 1/3$, and requirement of monotonic increase of $L_\perp(\eta)$, we can approximate the dependence $L_\perp(\eta)$ by polynomials $P_1(\eta)$ $(0 \le \eta \le 1/3)$ and $P_2(\eta)$ $(1/3 \le \eta \le 0.5)$ that have the form [30]

$$P_1(\eta) = \eta + \eta(\eta - 1/3)(2.724 + 14.085\eta), \tag{9}$$

$$P_2(\eta) = \eta + (\eta - 1/3)(0.5 - \eta) \times (33.617 - 56.337\eta). \tag{10}$$

As is evident from Fig. 2, they approximate well the dependence $L_\perp(\eta)$ for amorphous CP films and low-molecular compounds with a smectic structure. The rigidity of macromolecules manifests itself for $\eta < 0.3$, where the difference between functions (7) and (9) becomes noticeable. For films of linear macromolecules without fragments CH=CH (P3OT, PPY, PFO, PF2/6, PE2/6am5, and F8BT) and for polymer DE42 film with long rigid monomer sections without these fragments, the values of $L_\perp(\eta)$ lie on line (7). For films of macromolecules with fragments CH=CH (PPV, BuEH–PPV, MEH–PPV, and OC1C10–PPV) the values of $L_\perp(\eta)$ are close to dependence (9). On transition from PPY films with linear molecules to PPY.18*m* film with kinks of the polymer chain, the point $L_\perp(\eta)$ is displaced from line (7) to curve (9).

For CP films with the axial orientation of macromolecules in the liquid crystal state on orienting substrates (PFO, PF2/6, and F8BT [25,33]), the values of $L_\perp$ coincide, lie on the curve $P_2(\eta)$ (10), and are close to the limiting value 0.5 in model (1) for $l \gg d_c$. However, model (1) disregards the correlations $L_\perp(\eta)$ and the fact that the equality $L_\perp = \eta = 0.5$ is practically unattainable. Let us compare the values of $L_\perp$ for crystalline samples of trans-PA, cis-PA, and PTS with the results of microscopic calculation of the components L_j in the model of monomers as point dipoles [19]. For a uniaxial CP crystal with one monomer in the cubic unit cell and the monomer conjugation axis $\mathbf{l} \parallel \mathbf{n}$, the quantity $L_\parallel$ is given by the expression [19]

$$L_\parallel = 1/3 - \zeta(3)/\pi, \tag{11}$$

where $\zeta(3)$ is the Riemann zeta function. Since $\zeta(3)/\pi \approx 0.3826$, we obtain from it the values $L_\parallel \approx -0.0493$ and $L_\perp \approx 0.5246$, which agree with those obtained for crystalline films of trans-PA and cis-PA and bulk PTS crystals. However, the given and other CP in the crystalline state have low-symmetric unit cells with several nonequivalent monomer units. The obtained values of $L_\perp > 0.5$ can reflect the difference of the real optical biaxiality of these crystals from their uniaxial model accepted by the authors of [15–17] in determination of the dependences $n_j(\lambda)$ and used in the present publication. They can also reflect the difference of the crystal structure of these objects from the model of uniaxial ensemble of statistically ordered macromolecules for which formulas (3) and (6) are valid.

For PPV films [12, 35] with the degree of stretching $r = 5$ and thickness $h = 15$ μm, the values $L_\perp = 0.510$–0.516 are overestimated with respect to $P_2(\eta) < 0.5$ at $\eta \approx 0.46$, whereas, for a PPV film [34] with $r = 6$ and $h = 5$ μm, the value $\langle L_\perp^{(0)} \rangle < 0.5$ coincides with $P_2(\eta)$. A probable reason of the overestimation of $L_\perp$ for PPV films [12, 35] may be their known heterogeneity with a large volume fraction of crystallites [51].

For the analysis of the variation $\Delta f(\eta)$, we will take into account that the dependence $\Delta f(\lambda)$ in the region $\lambda_1 - \lambda_q$ is weak and use the representation

$$\Delta f = (L_{\perp k} - L_\perp)(\bar{\varepsilon} - 1)(3 + Q). \tag{12}$$

For each polymer film, we will introduce its own value λ_η at which the equality $L_{\perp k}(\lambda_\eta) = \eta$ in formulas (3) and (12) is fulfilled and use the notations $\bar{\varepsilon}(\lambda_\eta) = \bar{\varepsilon}(\eta)$, $Q(\lambda_\eta) = Q(\eta)$, and $\Delta f(\lambda_\eta) = \Delta f[\eta, L_\perp(\eta)]$. The expression for $L_{\perp k}(Q)$ in formula (3) at $\lambda = \lambda_\eta$ implies that $Q(\eta) = 3(3\eta - 1)/(2 - 3\eta)$, substitution of which into (12) yields

$$\Delta f[\eta, L_\perp(\eta)] = \frac{3[\bar{\varepsilon}(\eta) - 1]}{2 - 3\eta}[\eta - L_\perp(\eta)]. \tag{13}$$

The form of this dependence is the same for optically positive and optically negative films. For most of the studied films, an increase in $\bar{\varepsilon}(\eta)$ with increasing difference $|\eta - 1/3|$ is typical. For films with the orientation O_P in the series DCHD–HS – RECP – MEH–PPV [42] – OC1C10–PPV, the reduction in η corresponds to the series 2.449–2.622–2.877–3.020 of increasing values of $\bar{\varepsilon}(\eta)$. For films with the orientation O_A, the increase in η in the series Cd-*A* [29]–PF2/6–PPV [34]–PPV [35]–PPV [12] corresponds to an increase in $\bar{\varepsilon}(\eta)$ in the series 2.389–2.665–4.561–4.679–5.377. However, a number of films exhibit deviations from this tendency. For example, for the PPY film with η higher than that for the OC1C10–PPV film, the quantity $\bar{\varepsilon}(\eta) = 3.685$ is greater than

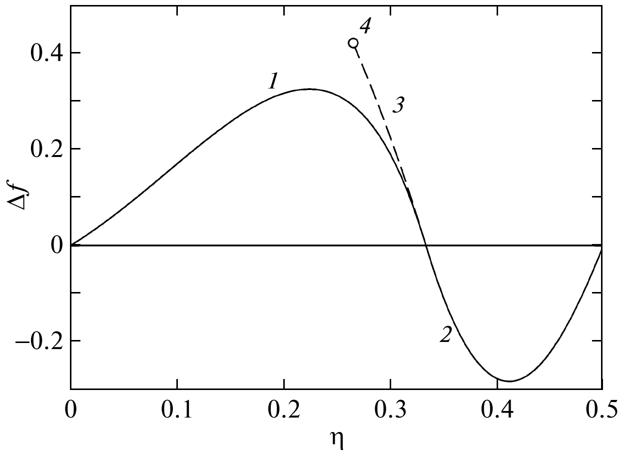

Fig. 3. Dependences (*1*) $\Delta f_1(\eta)$ for $\eta \le 1/3$, (*2*) $\Delta f_2(\eta)$ for $\eta \ge 1/3$, and (*3*) $\Delta f_3(\eta)$ calculated from formulas (15)–(17) and (*4*) the experimental value of Δf_3 for the PPY film.

that for OC1C10–PPV and, for films of PF2/6 and F8BT [33] with equal values of η, the values $\bar{\varepsilon}(\eta) = 2.665$ and 3.082 are noticeably different. In order to exclude such anomalies, we will use the functions

$$\begin{aligned} \Delta f_1(\eta) &= \frac{\Delta f[\eta, P_1(\eta)]}{\bar{\varepsilon}(\eta)-1}, \\ \Delta f_2(\eta) &= \frac{\Delta f[\eta, P_2(\eta)]}{\bar{\varepsilon}(\eta)-1}. \end{aligned} \tag{14}$$

Substitution of Eqs. (9), (10), and (13) into Eq. (14) yields

$$\Delta f_1(\eta) = \frac{\eta(1-3\eta)}{2-3\eta}(2.724 + 14.085\eta), \tag{15}$$

$$\Delta f_2(\eta) = \frac{(1-3\eta)(1-2\eta)}{2(2-3\eta)}(33.617 - 56.337\eta). \tag{16}$$

Linear correlation (7) with allowance for Eq. (8) corresponds to the function

$$\Delta f_3(\eta) = \frac{2.473(1-3\eta)}{2-3\eta}. \tag{17}$$

Figure 3 shows the dependences $\Delta f_r(\eta)$ calculated by formulas (15)–(17). The function $\Delta f_1(\eta)$ has the maximum $\Delta f_1^{\max} \approx 0.325$ at $\eta_1 \approx 0.224$. The maximum of the function $\Delta f[\eta, P_1(\eta)]$ is displaced to the region $\eta < \eta_1$ due to the dependence $\bar{\varepsilon}(\eta)$. The asymptotic limit $\Delta f_1(\eta = 0) = 0$ corresponds to the values $f_j = 1$. For CP films with the orientation O_P, the narrow interval $\eta_1 < \eta < 1/3$ corresponds to a wide range of functions $\Delta f_1(\eta)$ and $\Delta f_3(\eta)$. For the PPY film with the value $L_\perp(\eta) = 0.1$, which lies on line (7), the value $\Delta f_3 = 0.421$ significantly exceeds $\Delta f_1 = 0.291$.

The function $\Delta f_2(\eta)$ has the minimum $\Delta f_2^{\min} \approx -0.283$ at $\eta_2 \approx 0.412$. The minimum of the function $\Delta f[\eta, P_2(\eta)]$ is displaced to the region $\eta > \eta_2$ due to the dependence $\bar{\varepsilon}(\eta)$. For films of amorphous and crystalline CP with the orientation O_A, the values of $\Delta f_2(\eta)$ are localized in the vicinity of the minimum of the functions $\Delta f_2(\eta)$ and $\Delta f[\eta, P_2(\eta)]$. In this case, a small difference of $P_2(\eta_2)$ from 0.5, corresponds to a large difference $\Delta f_2^{\min}$ from the asymptotic value $\Delta f_2(\eta = 0.5) = 0$, at which $f_j = 1$. The values $L_\| = 0$ and $L_\perp = 0.5$ [9, 10, 14] for real films with $\varepsilon_\perp > 1$ and $\eta < 0.5$ correspond to the components $f_\| = 1$ and $f_\perp \neq 1$.

4. CONCLUSIONS

The aforesaid shows the possibility of determining the components L_j with a high accuracy for CP films of nanometer to micrometer thickness with planar or homeotropic orientation of the optical axis. The accuracy of modern methods of measuring $n_j(\lambda)$ is sufficient for revealing fine details of variation in L_j as a function of the chemical structure of monomers, the molecular weigh of the polymer, rigidity of macromolecules, and the technology of producing and thermal treatment of films. Dependences (9) and (10) enable one to determine the quantity $L_\perp(\eta)$ from the values of $n_j(\lambda)$ in the visible transparency region. The correlation $L_\perp(\eta)$ has a universal character for uniaxial statistically ordered molecular media of different nature (conjugated and nonconjugated polymers, layered smectic LC, Langmuir–Blodgett films, and columnar discotic LC), consisting of structural units of different nature (rigid- and flexible-chain macromolecules and rod and disk shaped molecules). The relationship of the parameter η with the polarizability anisotropy of molecules $\Delta\gamma$, π-electron conjugation of molecular fragments, and delocalization of the electron density shows the necessity to take into account these factors in the theory of local fields in addition to nonlocality of molecular polarizability.

In contrast to the monotonically increasing dependence $L_\perp(\eta)$, the dependence $\Delta f(\eta)$ is nonmonotonic and alternating and the most ordered state of known CP films with a planar (axial) orientation of macromolecules corresponds to the maximum positive (negative) values of $\Delta f(\eta)$. This circumstance shows the inapplicability to CP of the model with $L_j = 1/3$, which corresponds to negative (positive) values of $\Delta f = \Delta\varepsilon/3$ for CP films with a planar (axial) orientation of macromolecules. The function $\Delta f(\eta)$ vanishes at the points $\eta = 0$, 1/3, and 0.5, of which the point $\eta = 1/3$ is experimentally attainable and is determined as a point of joint anisotropization of tensors L and f. Dependences (15)–(17) solve the problem of determining the quantities $\Delta f(\eta)$ from the values of $n_j(\lambda)$ in the visible region of transparency.

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