Anisotropy of Dipole−Dipole Interactions in Ferroelectric Langmuir Films of Poly(Vinylidene Fluoride−Trifluoroethylene)

E. M. Aver'yanov

Kirensky Institute of Physics, Siberian Branch, Russian Academy of Sciences, Krasnoyarsk, 630036 Russia
e-mail: aver@iph.krasn.ru
Received March 28, 2014; in final form, April 8, 2014

The Lorentz tensor components L_j for poly(vinylidene fluoride−trifluoroethylene, 70/30) Langmuir−Blodgett films in the ferroelectric phase are determined experimentally. The results indicate that intralayer dipole−dipole interaction between the segments of the polymer is stronger than interlayer interaction. This conclusion agrees with the absence of the critical film thickness below which ferroelectricity would cease to exist.

1. In recent years, much interest has been attracted to the ferroelectric properties of low-dimensional films fabricated using the Langmuir−Blodgett technique from poly(vinylidene fluoride−trifluoroethylene) copolymers (P(VDF−TrFE, m/n)) with chain structure $(CH_2−CF_2)_m−(CHF−CF_2)_n$ [1]. A unique feature of these films is the persistence of ferroelectricity upon the reduction in the number of layers even to the point where the film consists of just one 0.5-nm-thick layer. The absence of a critical thickness below which ferroelectricity in such a film becomes impossible has remained an intriguing puzzle in the past decade [1−3]. The two-dimensional nature of monolayer films suggests that their ferroelectric properties originate from the interaction of polymer segments within the molecular monolayer, while the interaction between monolayers is weak [1]. However, direct information on the anisotropy of dipole−dipole interactions between polymer segments in ferroelectric Langmuir−Blodgett films has been lacking.

This information can be obtained by finding experimentally the components L_j of the Lorentz tensor that relates the macroscopic electric field E_j and the local electric field $E_j^{(loc)} = E_j + 4\pi L_j P_j$ in a medium with polarization P_j. The anisotropy of the tensor L characterizes the anisotropy of dipole−dipole interactions between the polymer segments and represents an indicator of the local anisotropy of the medium on a mesoscopic scale [4]. The known approaches used to determine the values of L_j [5] or $E_j^{(loc)}$ [6] in P(VDF−TrFE, m/n) films are based on the investigation of spectral features in the electroabsorption of probe impurity molecules, which are not isomorphic to the molecules of the matrix and distort its local structure. Obtaining correct values of L_j is also complicated owing to the

influence of the electrodes and the electric conduction on the properties of low-dimensional films [1] and the effect of anisotropic probe−matrix interactions on the spectral properties of the probe.

Contactless methods that make it possible to experimentally determine the values of L_j for films of arbitrary thickness and are sensitive to the chemical structure and polymer-chain conformation, morphology, and local structure of the film and to thermodynamic disturbances and fields applied to the film are required. The method to determine the components L_j in uniaxial molecular media [7] on the basis of the refractive indices $n_j(\lambda)$ in the transparency region satisfy these requirements, because the above-mentioned properties of the films are often monitored by measuring the components of the complex refractive index of the film $\hat{n}_j = n_j + ik_j$ for the polarizations of light parallel ($j = \parallel$) and perpendicular ($j = \perp$) to the optical axis **n**. This method was used in the studies of anisotropic polymer films of diverse origin [7, 8]. Here, it is used to determine the components L_j in the ferroelectric phase of uniaxial Langmuir−Blodgett films of the P(VDF−TrFE, 70/30) copolymer on the basis of the values of $n_j(\lambda)$ measured by ellipsometry and reflectometry techniques [9, 10].

2. Multilayer films of P(VDF−TrFE, 70/30) [1, 9, 10] with the optical axis **n** oriented along the normal to the film surface represent mosaics of crystallites with area σ_c and thickness h_c, which depends on the thickness h_m of the nominal monolayer transferred onto the substrate and on the thermal treatment of the film. The value of h_m varies from the monomolecular layer thickness of 0.45 nm [1, 9] to 1.8 nm [3, 10]. The homogeneous axial orientation of the polymer chains within a crystallite is determined by the vector $\mathbf{l}_c \perp \mathbf{n}$. The misalignment of the $\mathbf{l}_c$ directions between neigh-

boring crystallites in adjacent monolayers and the random distribution of the $\mathbf{l}_c$ directions in the crystallites within each monolayer ensure the uniaxial symmetry of the optical characteristics of the film. The in-plane sizes of the crystallites lie in the submicron range [10], while the lengths of the light waves corresponding to the visible transparency region are $\lambda = 0.155-1.6$ μm; i.e., the condition $\lambda^2 \gg \sigma_c$ for the optical homogeneity of the film is not satisfied (especially for light polarization with $\mathbf{E} \perp \mathbf{n}$). For this reason, $k_\perp > k_\parallel$ in the absence of absorption bands and $k_j(\lambda)$ increases with decreasing λ [10]. As a result, the dependences $n_j(\lambda)$ in the visible range cannot be used in the method described in [7].

In the infrared transparency region, $\lambda = 12.5-35$ μm. Thus, $\lambda^2 \gg \sigma_c$, and the optical homogeneity of the films makes it possible to use the method described in [7]. Since an individual crystallite features preferred directions $\mathbf{n}$ and $\mathbf{l}_c$ and the plane $(\mathbf{n}, \mathbf{l}_c)$, one expects that, in the general case, the components ε_{ci} of its dielectric tensor corresponding to the light wave polarizations along the axes $i = x$, y, and z of the crystallite index ellipsoid (with $y \parallel \mathbf{n}$ and $z \parallel \mathbf{l}_c$) differ from each other. Taking into account that the films are fabricated by the Langmuir–Blodgett technique [1], we can, according to the results of [9, 10], disregard the dependence of ε_{ci} on σ_c and h_c. In the spectral region under consideration, $P_j = E_j(\varepsilon_j - 1)/4\pi$ and $P_i = E_{ci}(\varepsilon_{ci} - 1)/4\pi$; here, $\varepsilon_j = n_j^2$ and $\varepsilon_{ci} = n_{ci}^2$. The statistical distribution of CH_2-CF_2 and $CHF-CF_2$ fragments in the copolymer chain makes it possible to use spatially uniform values of L_j and L_{ci} for the film and an individual crystallite, respectively. As a consequence, $E_j^{(loc)} = f_j E_j$ and $E_{ci}^{(loc)} = f_{ci} E_{ci}$, where the components of the local-field tensor for the film and the crystallite are $f_j = 1 + L_j(\varepsilon_j - 1)$ and $f_{ci} = 1 + L_{ci}(\varepsilon_{ci} - 1)$, respectively. In copolymer films, there are several types α of polarizable fragments; their polarizability components averaged over the molecular ensemble in the system of the index ellipsoid of the film and the crystallite are $\gamma_{\alpha j}$ and $\gamma_{\alpha i}^{(c)}$, respectively. For the film, the components ε_j can be expressed as $\varepsilon_j = 1 + 4\pi N f_j \gamma_j$ [11], where $N = \Sigma_\alpha N_\alpha$, N_α is the number of fragments of type α per unit volume, $\gamma_j = \Sigma_\alpha x_\alpha \gamma_{\alpha j}$, and $x_\alpha = N_\alpha/N$. For a crystallite, $\varepsilon_{ci} = 1 + 4\pi N f_{ci} \gamma_{ci}$, where $\gamma_{ci} = \Sigma_\alpha x_\alpha \gamma_{\alpha i}^{(c)}$. Owing to the homogeneity of the dielectric and optical properties of the film along the $\mathbf{n}$ axis, which is the same for all crystallites, we have $E_\parallel = E_{cy}$ and $\varepsilon_\parallel = \varepsilon_{cy}$; this is equivalent to $\gamma_\parallel f_\parallel = \gamma_{cy} f_{cy}$. Then, taking into account that $\gamma_\parallel = \gamma_{cy}$, we find that $L_\parallel = L_{cy}$. It is sufficient to know this component in order to compare the intra- and interlayer dipole–dipole interactions between the polymer segments in a crystallite or in the film. The

values of L_{cx} and L_{cz} obey the relationship $L_{cx} + L_{cz} = 1 - L_{cy} = 2L_\perp$.

3.1. For uniaxial P(VDF–TrFE, 70/30) films with $\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp > 0$ in the range $\lambda = 12.5-35$ μm [9, 10], the components $L_\perp$ and $L_\parallel = 1 - 2L_\perp$ can be determined as follows [7]. We use the parameters $\bar{\varepsilon} = (\varepsilon_\parallel + 2\varepsilon_\perp)/3$ and $Q = \Delta\varepsilon/(\bar{\varepsilon} - 1)$ and the quantities

$$r_0 = 1 - \frac{2Q^2(\bar{\varepsilon} - 1)}{3(3 + Q)(\bar{\varepsilon} + 2)},$$

$$b = \frac{3(\bar{\varepsilon} - 1)}{4\pi N \bar{\gamma}(\bar{\varepsilon} + 2)} - r_0, \qquad (1)$$

$$b_1 = \frac{2r_0 Q^2}{(3 - Q)(3 + 2Q)}, \quad b_2 = b_1[(6 + Q)/Q]^2,$$

which depend on temperature T and λ. Here, $\bar{\gamma} = \Sigma_\alpha x_\alpha(T) \bar{\gamma}_\alpha(\lambda, T)$ and $\bar{\gamma}_\alpha = (\gamma_{\alpha\parallel} + 2\gamma_{\alpha\perp})/3$. The value of $L_\perp(T)$ that we seek is given by the expression [7]

$$L_\perp = L_{\perp k} - \frac{\bar{\varepsilon} + 2}{12(\bar{\varepsilon} - 1)} \qquad (2)$$

$$\times \{(b_1 b_2)^{1/2} - b - [(b_1 - b)(b_2 - b)]^{1/2}\},$$

where $L_{\perp k} = (3 + 2Q)/(3(3 + Q))$ and the function $b(\lambda, T)$ depends on the unknown function $\bar{\gamma}(\lambda, T)$. Using the known values of $n_j(\lambda, T)$ for a discrete set of wavelengths λ_i (where $i = 1 - p$) in the film transparency region, the function $b(\lambda, T)$ in the range $\lambda_1 - \lambda_p$ can be approximated by a polynomial:

$$b(\lambda, T) = a_0(T) + a_1(T)\lambda + \ldots + a_q(T)\lambda^q. \qquad (3)$$

The value of $L_\perp(T)$ is independent of λ. For a given temperature T, we have $q + 2$ unknown quantities ($L_\perp^{(q)}$ and $a_0 - a_q$). They can be found from a set of $q + 2 = p$ equations (2), each of them corresponding to one of the values λ_i. The adequacy of the approximation used in Eq. (3) is determined by the accuracy of the experimental values of $n_j(\lambda, T)$ and the width of the approximation wavelength range $\lambda_1 - \lambda_p$.

Plots of the dependences $n_j(\lambda)$ for ferroelectric P(VDF–TrFE, 70/30) films with spontaneous polarization $\mathbf{P} \parallel \mathbf{n}$ at room temperature are presented in [9, 10]. The values of $n_j(\lambda_i)$ are listed in the table. For the films described in [9], the above procedure performed for the interval $\lambda_1 - \lambda_3$ yields $L_\perp^{(1)} = 0.368$, and the average of three values of $L_\perp^{(0)}$ corresponding to the three pairs of reference wavelengths $\lambda_1 - \lambda_3$ is $\langle L_\perp^{(0)} \rangle = 0.360 \pm 0.006$. Performing the same procedure for the films described in [10] for the interval $\lambda_4 - \lambda_8$, we

Values of λ_i and $n_j(\lambda_i)$ for P(VDF−TrFE, 70/30) films according to [9] and [10] (for $i = 1-3$ and $i = 4-8$, respectively) and the values of $n_j^*(\lambda_i)$

i	λ_i, μm	$n_\parallel$	$n_\perp$	$n_\parallel^*$	$n_\perp^*$
1	12.5	1.5406	1.4679	1.5688	1.4529
2	14.286	1.4941	1.4553	1.5229	1.4403
3	16.667	1.4795	1.4504	1.5085	1.4354
4	12.5	1.5350	1.4630	1.5632	1.4480
5	15.0	1.4744	1.4480	1.5034	1.4330
6	17.5	1.4624	1.4432	1.4916	1.4282
7	20.0	1.4570	1.4408	1.4862	1.4258
8	25.0	1.4528	1.4402	1.4821	1.4252

obtain $L_\perp^{(3)} = 0.367$, while the average of five values of $L_\perp^{(2)}$ corresponding to the five quadruples of reference wavelengths $\lambda_4-\lambda_8$ is $\langle L_\perp^{(2)} \rangle = 0.362 \pm 0.006$. The agreement between the values of $L_\perp^{(3)}$ and $L_\perp^{(1)}$ obtained for different films and the values of $L_\perp^{(q)}$ and $\langle L_\perp^{(q-1)} \rangle$ for the same film gives evidence of the adequacy of the approximations underlying Eq. (3). The relationship $L_\perp = 0.367 > 1/3 > L_\parallel = 0.266$, which is valid for the films under discussion, indicates that intralayer dipole−dipole interaction between polymer segments is stronger than interlayer interaction. This result supports the suggestion put forward in [1].

Approximation of the values $n_j(\lambda_{4-8})$ by the function [11]

$$n_j(\lambda) = n_{bj} + A\lambda^2\lambda_j^2/(\lambda^2 - \lambda_j^2) \qquad (4)$$

yields equal values for $n_{b\parallel} = 1.426 \pm 0.001$ and $n_{b\perp} = 1.427 \pm 0.003$ and the values of $\lambda_\parallel$ and $\lambda_\perp$ determined by the absorption bands with $\lambda_{max} = 11.287$ and 11.765 μm [9, 10], responsible for the dispersion of $n_j(\lambda_{4-8})$. This fact indicates that electronic transitions and the dispersion of $n_j(\lambda)$ in the visible range has no effect on the dependences $n_j(\lambda_{1-8})$ and, thus, on the obtained values of L_j. At the same time, the behavior of $n_j(\lambda)$ in the wavelength range of 12.5−35 μm [10] and the fact that this range is far away from the absorption bands related to the low-frequency dispersion of the components $\varepsilon_j(\omega)$ in the region of tens of kilohertz [1] imply that the low-frequency dispersion does not affect the dependences $n_j(\lambda_{1-8})$ or the values of L_j either.

For $k_j(\omega) = 0$, Eqs. (1) and (2) are valid for any spectral range (visible, infrared, or microwave) and hold also for $\omega = 0$ if the medium is not electrically conductive. In the case where the values of L_j and L_{ci} are real and are the same for all regions of the spec-

trum, the values of $f_j(\omega)$ and $f_{ci}(\omega)$ and the ratios of their components may vary considerably between the spectral ranges. For $k_j(\omega) \neq 0$, the values of $f_j(\omega)$ and $f_{ci}(\omega)$ are complex because $\varepsilon_j(\omega)$ and $\varepsilon_{ci}(\omega)$ are complex.

3.2. Using the known values of L_j and the dependences $n_j(\lambda)$ and $k_j(\lambda)$ in the range $\lambda = 6.5-12.5$ μm [9] for the absorption bands polarized along **n**, one can estimate the maximum (minimum) value $L_\perp^*$ ($L_\parallel^*$) for a film with the most ordered state of transition dipole moments $\mathbf{d}_\mu$ corresponding to these bands. The degree of ordering in the orientations of vectors $\mathbf{d}_\mu$ with respect to **n** is characterized by the parameter $S_\mu = (3\overline{\cos^2\theta_\mu} - 1)/2$, where θ_μ is the angle between $\mathbf{d}_\mu$ and **n** and the bar indicates averaging over the orientations of molecular fragments corresponding to the transition moments $\mathbf{d}_\mu$. The relationship between S_μ and the dichroism $D_\mu = k_\parallel(\lambda_\mu/k_\perp(\lambda_\mu)$ of the absorption band with the maximum at λ_μ is expressed as follows [11]:

$$S_\mu = \frac{D_\mu g_\mu - 1}{D_\mu g_\mu + 2}, \quad g_\mu = \frac{n_{b\parallel}f_{b\perp}^2}{b_{b\perp}f_{b\parallel}^2}. \qquad (5)$$

The background values n_{bj} and $f_{bj} = 1 + L_j(\varepsilon_{bj} - 1)$ in the region of the λ_μ absorption band originate from all other bands. For an isolated band characterized by a known dependence $n_j(\lambda)$, we have $n_{bj} \approx (n_j(\lambda') + n_j(\lambda''))/2$ [11], where λ' and λ'' correspond to the maximum and the minimum of $n_j(\lambda)$ within the given band. For the absorption band with the largest value of D_μ in a uniaxial film, it can be assumed that $S_\mu = SS_{\beta\mu}$. Here, $S = (3\overline{\cos^2\theta_\mu} - 1)/2$ is the parameter of orientational ordering of the fragments corresponding to the transition moments $\mathbf{d}_\mu$, θ_μ is the angle between the longitudinal axis of the fragment $\mathbf{l}_\mu$ and **n**, $S_{\beta\mu} = (3\cos^2\beta_\mu - 1)/2$, and β_μ is the angle between $\mathbf{d}_\mu$ and $\mathbf{l}_\mu$. Taking into account the proportionality $L_\perp(S) - 1/3 \propto S$, valid for low-molecular and polymer media [7, 8], we can write the relation

$$L_\perp^* = 1/3 + [L_\perp(S) - 1/3]/S. \qquad (6)$$

For P(VDF−TrFE, 70/30) films in the range $\lambda = 6.5-12.5$ μm, the largest value $D_\mu = 5.227$ is attained for the most intense band with $\lambda_\mu = 8.46$ μm, for which the dependence $n_j(\lambda)$ is known [9]. Using these data, we find the values of $n_{b\parallel} = 1.470$ and $n_{b\perp} = 1.443$. For this band, formula (5) yields $S_\mu = 0.628$. For $S_{\beta\mu} = 1$, it follows from Eq. (6) that $L_\perp^* = 0.387$ and $L_\parallel^* = 0.226$.

Another way to estimate L_j^* is based on the dependence of the refractive indices $n_j(E)$ of the film on the field $\mathbf{E} \parallel \mathbf{n}$, which is caused by the orientational order-

ing of the polymer chain fragments with respect to **n**. The variation $\delta = n_\perp - n_\perp^* = 0.015$ in the range $\lambda = 0.3$–0.8 μm was found in P(VDF–TrFE, 70/30) films for the largest values of E and lowest $n_\perp^*(E)$ values [12]. The approximation of the dependence $n_\perp(\lambda)$ [10] in the range $\lambda = 0.155$–0.8 μm by function (4) yields the extrapolated value $n_\perp^{(ext)}(\lambda_{1-8}) = 1.424$, which coincides with $n_{b\perp}$ obtained upon approximating the values of $n_\perp(\lambda_{4-8})$ by function (4). The same procedure for the dependence $n_\perp^*(\lambda) = n_\perp(\lambda) - \delta$ yields $n_\perp^{*(ext)}(\lambda_{1-8}) = n_\perp^{(ext)} - \delta$. As a result, it can be assumed that $n_\perp^*(\lambda_i) = n_\perp(\lambda_i) - \delta$. The values of $n_\parallel^*(\lambda_i)$ in this region are determined by the condition $\varepsilon_\parallel^* + 2\varepsilon_\perp^* = \varepsilon_\parallel + 2\varepsilon_\perp$ for each λ_i and are given by the expression

$$n_\parallel^* = [\varepsilon_\parallel + 2(\varepsilon_\perp - \varepsilon_\perp^*)]^{1/2}. \tag{7}$$

The values of $n_j^*(\lambda_{1-8})$ are listed in the table. Using the values of $n_j^*(\lambda_{1-3})$ yields $L_\perp^{*(1)} = 0.386$ and $\langle L_\perp^{*(0)} \rangle = 0.380 \pm 0.005$. For the interval λ_4–λ_8, we obtain $L_\perp^{*(3)} = 0.386$ and $\langle L_\perp^{*(2)} \rangle = 0.382 \pm 0.005$. Thus, the values of $L_\perp^* = 0.386$ and $L_\parallel^* = 0.228$ agree with those given above and demonstrate that, in extremely high fields $\mathbf{E} \parallel \mathbf{P} \parallel \mathbf{n}$, intralayer dipole–dipole interaction between the fragments of the polymer in ferroelectric films of P(VDF–TrFE, 70/30) is enhanced.

With respect to the values of $L_\perp$ and $L_\perp^*$, it is interesting to compare the films under consideration with nonpolar molecular media [8] using the parameter $\eta = \langle L_{\perp k}(\lambda_i) \rangle$ averaged in the interval λ_4–λ_8. The quantity η characterizes the anisotropy of the structural order in the medium. The correlation $L_\perp(\eta)$ for diverse uniaxial low-molecular and polymer media is described by the function [8]

$$P_2(\eta) = \eta$$
$$+ (\eta - 1/3)(0.5 - \eta)(33.617 - 56.337\eta). \tag{8}$$

For P(VDF–TrFE, 70/30) films in zero field and in the highest fields, we have $\eta = 0.342$ and $\eta^* = 0.353$, respectively, and Eq. (8) yields values of 0.361 and 0.393, respectively, which are close to the respective experimental values $L_\perp = 0.367$ and 0.386. Thus, with respect to the dependence of the L_j components on the structural ordering of the medium, the films under consideration are similar to other media [8].

4. Using the above relationship between the components L_j of the Lorentz tensor of a uniaxial Langmuir–Blodgett film and the components L_{ci} of this tensor characterizing biaxial crystallites constituting the film and the method described in [7], we determine the value $L_\parallel = L_{cy} = 0.266$ for P(VDF–TrFE, 70/30) films at room temperature and estimate the value of $L_\parallel^* = L_{cy}^* = 0.226$ corresponding to the maximum orientational ordering of the film fragments. The above value of $L_\parallel^*$ agrees with the value $L_\parallel^* = 0.228$ obtained using the data on the variation of the optical properties of the film in the highest electric field $\mathbf{E} \parallel \mathbf{n}$ reported in [12]. The relationship $1/3 > L_\parallel > L_\parallel^*$ indicates that intralayer dipole–dipole interaction between the polymer segments in P(VDF–TrFE, 70/30) films is stronger than interlayer dipole–dipole interaction and this difference is enhanced in high fields $\mathbf{E} \parallel \mathbf{n}$. This result supports the suggestions put forward in [1].

REFERENCES

1. L. M. Blinov, V. M. Fridkin, S. P. Palto, A. V. Bune, P. A. Dauben, and S. Ducharme, Phys. Usp. **43**, 243 (2000).
2. V. M. Fridkin, Phys. Usp. **49**, 193 (2006).
3. V. M. Fridkin, R. V. Gaynutdinov, and S. Ducharme, Phys. Usp. **53**, 199 (2010).
4. E. M. Aver'yanov, J. Exp. Theor. Phys. **108**, 176 (2009).
5. K. Hasegawa, A. Tomioka, and K. Miyano, Appl. Phys. Lett. **66**, 775 (1995).
6. L. M. Blinov, K. A. Verkhovskaya, S. P. Palto, and A. V. Sorokin, Appl. Phys. Lett. **68**, 2369 (1996).
7. E. M. Aver'yanov, J. Exp. Theor. Phys. **110**, 622 (2010).
8. E. M. Aver'yanov, Phys. Solid State **53**, 1933 (2011).
9. M. Bai, M. Poulsen, A. V. Sorokin, S. Ducharme, C. M. Herzinger, and V. M. Fridkin, J. Appl. Phys. **94**, 195 (2003).
10. M. Bai, A. V. Sorokin, D. W. Tompson, M. Poulsen, S. Ducharme, C. M. Herzinger, S. Palto, V. M. Fridkin, S. G. Yudin, V. E. Savchenko, and L. K. Gribova, J. Appl. Phys. **95**, 3372 (2004).
11. E. M. Aver'yanov, *Effects of Local Field in Optics of Liquid Crystals* (Nauka, Novosibirsk, 1999) [in Russian].
12. L. M. Blinov, V. V. Lazarev, S. P. Palto, and S. G. Yudin, J. Exp. Theor. Phys. **114**, 691 (2012).

Translated by M. Skorikov