



An effect of the film texture on high-voltage polarization and local piezoelectric properties of the ferroelectric copolymer of vinylidene fluoride

V. V. Kochervinskii¹ · D. A. Kiselev^{2,3} · M. D. Malinkovich² · N. A. Shmakova¹

Received: 20 December 2017 / Revised: 7 March 2018 / Accepted: 18 March 2018
© Springer-Verlag GmbH Germany, part of Springer Nature 2018

Abstract

Vinylidene fluoride and tetrafluoroethylene copolymer 94/6 texturing has been carried out by one-axis drawing at $T_d = 75$ °C up to the ratio of 6 with subsequent isometric tempering at 130 °C. Data of X-ray diffraction and IR-spectroscopy indicate partial polymorph transition from the metastable γ -phase to the polar β -modification with long segments in the conformation of the planar zigzag. The surface topography data show that the oriented film roughness turns out to be almost three times lower than that of the isotropic one. High-resolution vector piezoresponse force microscopy (PFM) has been used to investigate topography and ferroelectric domains in polymer films for visualization out-of-plane and in-plane polarization components. It is shown that, in the oriented sample, both crystallinity and the degree of polar β -phase crystal perfection are higher. It was found that conductivity “abnormal” dropping takes place at the stage of intensive P_r rising with the field growing. This fact is explained by quick trapping of charge carriers by polar planes of crystals with increasing the effective trap area.

Keywords Ferroelectric polymers · Structure · Polarization

Introduction

Ferroelectric polymers on the basis of polyvinylidene fluoride (PVDF) relate to the class of crystalline polymers. This respectively new class of materials is interesting in connection with its possible technical applications [1–3]. In comparison with inorganic ferroelectrics, these polymers have a number of specific qualities such as high shock viscosity, low dielectric permittivity, thermo-plasticity, the possibility of production of large active areas, high breakdown fields, etc. In a number of cases, it makes ferroelectric polymers competitive with

respect to classic inorganic materials. That is why the scientific world’s interest to these polymers does not subside. Nowadays, there is no strict theory of ferroelectricity. In complex morphology of crystallizing polymers, where along with the crystalline phase, there are regions without a long order that hinders such investigations. The situation is aggravated by the fact that at room and higher temperatures, the amorphous phase has liquid-like dynamics. Thus, polymers under consideration are systems which are characterized both by structural and by dynamic heterogeneity. All this creates complications for strict description both of ferroelectricity and of piezo- or pyroelectricity observed in such polymers. In this regard, accumulation of new data on the influence of structural particularities in polymers under consideration on their ferroelectric properties is required. Experimental works with such objects are carried out mainly on isotropic films which are characterized by polycrystal texture. Crystalline polymers may be textured, for example, by uniaxial drawing due to their high thermoplasticity. In such case, axes of c-crystals acquire the main direction in the film plane, and the symmetry type changes. In this work, comparison of ferroelectric characteristics of isotropic and textured films was carried out using as an example one of PVDF copolymers. Values of remnant

✉ V. V. Kochervinskii
kochval@mail.ru

¹ Karpov Institute of Physical Chemistry, Vorontsovo pole, 10, Moscow 105064, Russia

² National University of Science and Technology “MISiS”, Leninsky pr. 4, Moscow 119049, Russia

³ Kotel’nikov Institute of Radioengineering and Electronics of Russian Academy of Sciences, Vvedensky Square 1, Fryazino, Moscow Region 141190, Russia

polarization are shown to be higher in textured films. On the contrary, high-voltage conductivity falls.

Samples and investigation methods

Random PVDF and tetrafluoroethylene (TFE) copolymer 94-6 characterized earlier by ^{19}F NMR [4] was the object of our investigation. Isotropic films [1] have been prepared by the copolymer crystallization from its solution in acetone at the room temperature. Orientation of the film was carried out by uni-axial drawing at 75 °C up to the ratio value of 6 with subsequent isometric annealing at 130 °C. To measure electrical properties of the copolymer, 100-nm-thick Al electrodes were deposited on films via thermal vacuum evaporation. Low-voltage electrical characteristics were obtained with the use of the admittance-meter in the frequency range of 25–10⁶ Hz at the room temperature. Measuring of high-voltage polarization and conductivity was carried out on the modified setup combined according to the Sawyer–Tower scheme described earlier [5]. The external field amplitude being varied and short-circuit regime was applied to the sample before every experiment.

The surface morphology and the static domain structure of the polymer films were characterized by piezoresponse force microscopy using a commercial scanning probe microscopes MFP-3D (Asylum Research, USA) with Pt-coated conductive probes (CSG30/Pt, TipsNano). Vertical PFM (VPFM) and lateral (LPFM) images of the samples were recorded by applying an AC voltage of $V_{AC} = 2$ V with a frequency of 150 kHz to the cantilever.

Infrared spectra were obtained on Bruker Equinox 55 s (with Fourier transform) spectrometer. Shooting was performed in transmission and attenuated total reflection ATR (ZnSe crystal) regimes; the latter was used to probe 0.5–2 μm thick surface layer of polymer.

Results

Comparison of the electrical response of isotropic and oriented films at supplying them with the bipolar rectangular impulses with the same amplitude is shown in Fig. 1. It is seen that curves obtained differ significantly. As it follows from general relations in one-dimensional approximation for the ideal dielectric (with zero conductivity), changing of electrical induction D may be associated only with that of polarization value P :

$$D = \varepsilon_0 E + P_{\text{tot}} = \varepsilon_0 E + P_{\text{nf}} + P_{\text{f}}, \quad (1)$$

where E is the electrical field tension, and ε_0 is the electrical constant.

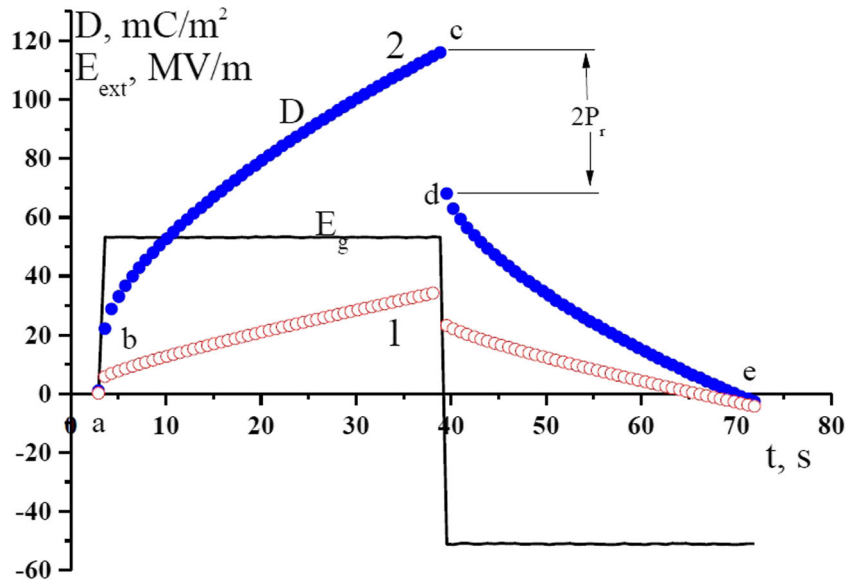
In Eq. 1, when applied to crystalline polymer, it is reasonable to divide the total polarization value P_{tot} in two parts: P_{nf} and P_{f} . As it is already noted, the material has a two-phase structure. Therefore, the second term must be associated with polarization of the amorphous phase which is not ferroelectric. Accordingly, the third term relates to the reaction in the field of polar crystals. Note that all said above relates to the case where only bound charges are considered. Real polymer ferroelectrics always have free carriers in the volume. They appear, for example, because of the presence of the catalyst remnants, introduction of additional ingredients, and so on. As far as the amorphous phase has an increased free volume, during the polymer crystallization, admixtures mentioned above will be displaced just here. As it is already noted, at the ambient temperature, chains of the amorphous phase are characterized by cooperative Brownian liquid-like dynamics. Since PVDF chains have high dipole moments (2.1 D), the amorphous phase may be considered a weak electrolyte. Therefore, molecules of the salt nature will partly dissociate with formation of additional free charges. For the polymer class under consideration, the presence of such free charges in a number of copolymers is confirmed by appearance of low-frequency relaxation of the space charge [6–9]. At high fields, appearance of additional carriers due to their injection from the electrode material is possible [10, 11]. As applied to polymer objects, special role of hole carriers injection was noted [12], which is shown experimentally with the use of PVF-TFE copolymers as an example [13].

Thus, the time dependence of electrical induction (Fig. 1) must show the contribution both from bound and free charges. For this purpose, it is possible to use the half-empirical relation which gives free carriers contribution to D through the value of conductivity σ :

$$D = \varepsilon_0 E + \sigma t^m E + 2P_r \left[1 - \exp\left(-\left(\frac{t}{\tau_s}\right)^n\right) \right]. \quad (2)$$

The contribution of bound charges is shown by the third term through the domain switching time τ_s that provides appearance of remnant polarization P_r . Conductivity values were calculated by the method of quasi-stationary currents, which were registered at supply the film with the bipolar rectangular impulse (Fig. 2). It was presumed that σ and the quasi-stationary current j obey the Ohm law: $j = \sigma E$. Apparently, empirical parameters m and n in Eq. 2 are connected with peculiarities of local fields at motion of free and bound charges, respectively. For free carriers, parameter m , changing with the field for the oriented sample, is presented in Fig. 3. It is seen that there are two regions of this parameter behavior. Its growing is observed up to the field ~ 40 MV/m, which approximately corresponds to the Ohm law. At higher fields, substantial parameter m reduction is noted, which corresponds

Fig. 1 Time dependencies of the external electric field and electrical induction in the isotropic (1) and oriented (2) film at supplying it with bipolar pulses with the amplitude of 53 MV/m



to changing of the mechanism of high-voltage conductivity. This may be associated with the fact that apparently, the local field will be formed out of the field of the external source E_{ext} , those of the ferroelectric domain E_f , and the space charge E_{sc} . Let us consider which component of the local field may lead to curves $D(t)$ observed experimentally (Fig. 1). It is seen from this picture that field E_{ext} rises during millisecond range ab, which corresponds to appearance of remnant polarization due to reaction of domains on the external source, and shows that the field of the ferroelectric E_f rises approximately during the same time. Thus, the character of the time dependence $D(t)$ in

the range of tens of seconds must be associated only with the component of the space charge field:

$$E_{sc}(x, t) = \int_0^d \frac{\rho(x, t)}{\epsilon_0 \epsilon} dx \int_0^\infty dt, \quad 0 \leq x \leq d \quad (3)$$

here, $\rho(x, t)$ is a volume density of the charge formed by quasi-free carriers. This characteristic for the one-dimensional case is the function both of coordinate x and time t . Since materials studied are dielectrics, impurity carriers must be localized on

Fig. 2 Current response in the isotropic copolymer film at supplying it with the bipolar pulses of the external electric field with the amplitude of 50 MV/m

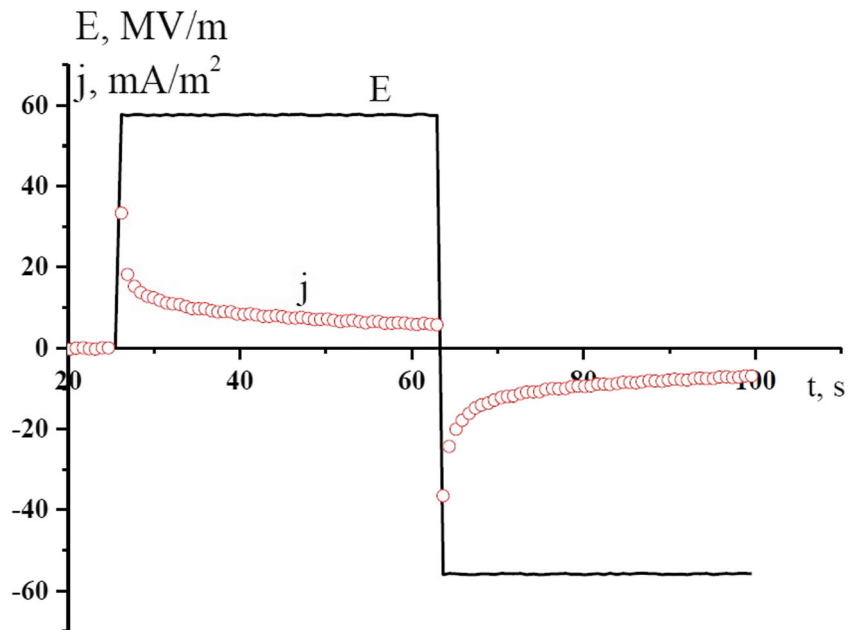
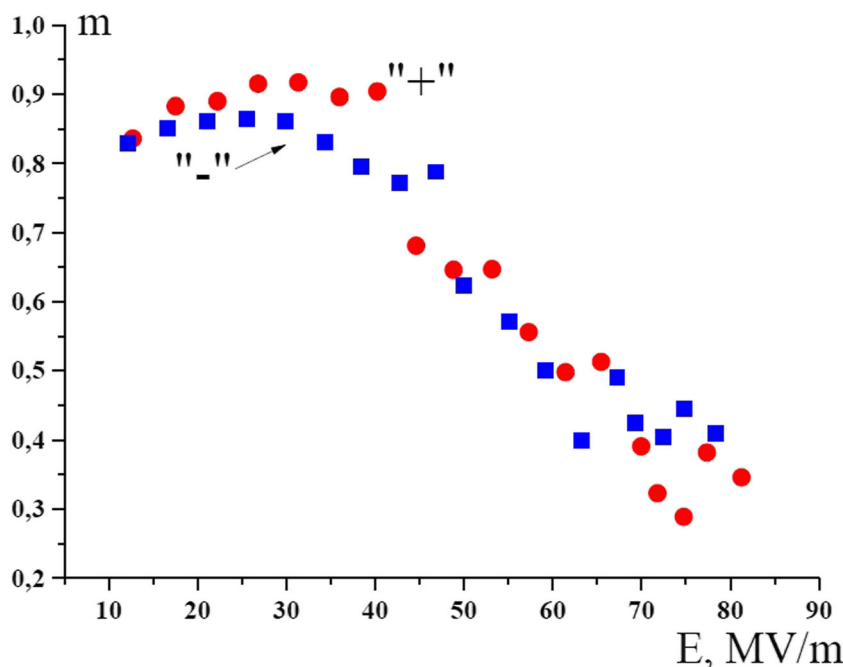


Fig. 3 Field dependencies of the empiric parameter m at different sign of the field for the oriented sample



traps of various kinds such as defects of chemical joining of PVDF chains, crystal imperfections, and boundaries between crystal and amorphous phases. In the electric field, drift of such carriers is slow, which explains low conductivity of polymers studied. Formation of the equilibrium state of space charges in heterogeneous systems is usually characterized by Maxwell–Wagner relaxation time τ_M which, for a medium with dielectric permittivity ε_a , may be written as follows:

$$\tau_m = \frac{\varepsilon_a \varepsilon_0}{A\sigma} \quad (4)$$

At low conductivity σ , this relaxation time may reach units and tens of seconds. Thus, region “b–c” in (Fig. 1) reflects the contribution of the space charge field formation into D value measured.

The task of the further analysis was to estimate high-voltage conductivities on the basis of field dependencies of current densities (Fig. 2) and compare them for isotropic and oriented samples. Such data are presented in (Fig. 4). It is seen that for both samples the field conductivity dependencies have forms of curves with maxima. At some field, σ starts to “abnormally” go down. There are some differences between these films. In the isotropic sample, the conductivity maximum is shifted a little to higher fields, but σ values at identical fields turn out to be two to three times as high (Fig. 4). As it follows from (Fig. 5), for the same samples, field dependencies of remnant polarization P_r determined according to the scheme in (Fig. 1) also differ. It can be seen that here there are two regions of the P_r behavior as well. At fields lower than 40 MV/m, weakly expressed non-linearity is observed for

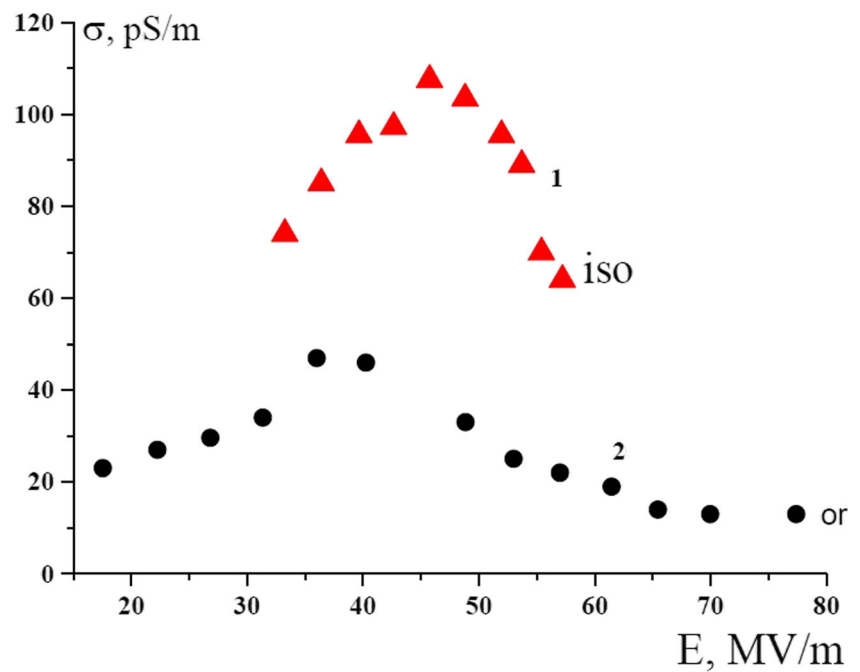
both samples. We associate the existence of this region with contribution of its component from disorderly P_{nf} regions into full polarization (Eq. 1). Apparently, at higher fields, more intensive growing of P_r takes place. We associate this with contribution of the ferroelectric phase P_f into full polarization of domains. It is seen that if the field is the same, remnant polarization in isotropic samples turns out to be lower. Coercive fields we register are in good agreement with those for this class of compounds [1, 2]. As it also follows from (Fig. 5) data, isotropic films have lower breakdown fields than those of oriented samples.

To our opinion, it is useful to compare field dependencies of high-voltage conductivity and P_r that is done in (Fig. 6) for the oriented sample. It is seen that the region of weak P_r rising coincides with the “normal” conductivity behavior, where intensive rising of remnant polarization is observed in the “abnormal” region of the field dependency σ . Thus, it is possible to ascertain that appearance of abnormal lowering of conductivity with the field should be explained by intensive switching of domains in fields which are higher than coercive ones.

Discussion

It has been shown that there are a number of differences in the behavior of isotropic and oriented samples in the high field. We associate it with changes in structural characteristics during the process of films texturing. Earlier [14], it was shown that isotropic films of the polymer class studied after crystallization from low-boiling solvents at the room

Fig. 4 Field dependencies of high-voltage conductivity in the isotropic (1) and oriented (2) film



temperature, along with the ferroelectric phase, have metastable paraelectric one. It is also possible to see some indication to this from IR-spectroscopy data (Fig. 7). In the isotropic film, it was found the presence of a noticeable number of polymer segments of the $T_3GT_3G^-$ conformation since characteristic lines 813 and 1235 cm^{-1} were found. These peaks are characteristic of the chain conformation in γ -phase crystals. The latter is present in the composition of the paraelectric phase [1, 2]. So, this fact also confirms the

presence of the metastable paraelectric phase in the isotropic film. During the process of texturing at transition of lamellar crystals to fibril ones, it is possible to see the process of conformational transition in polymer chains. Changing intensity ratios in pairs of peaks 813, 840, and $1235, 1275\text{ cm}^{-1}$ indicates that orientation process is accompanied by polymorph transition $\gamma \rightarrow \beta$. It is known that for chains in the last phase with conformation chain of a planar zigzag, the dipole moment of the monomer unit was being oriented perpendicularly

Fig. 5 Field dependencies of remnant polarization in the isotropic (1) and oriented (2) film

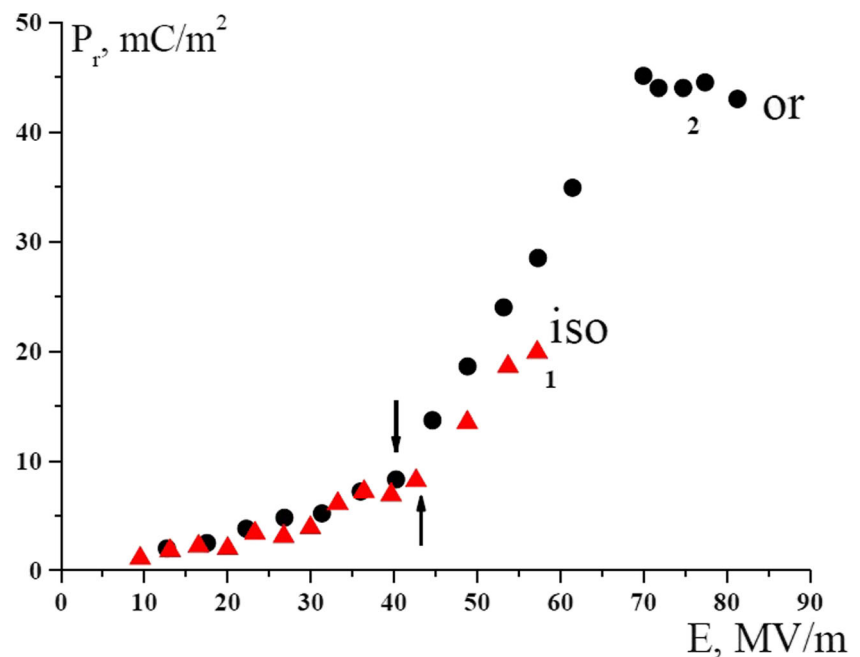
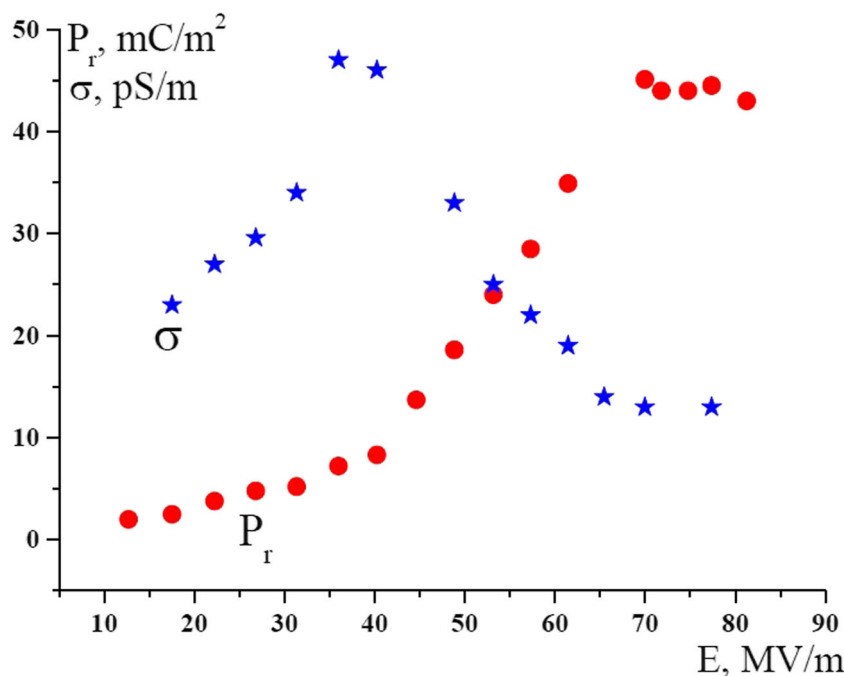


Fig. 6 Field dependencies of high-voltage conductivity (σ) and remnant polarization (P_r) for the oriented copolymer film



to the chain axis. An increase in the intensity of peaks 840 and 1275 cm^{-1} at the film orientation indicates an increase in the proportion of chains with conformation of a planar zigzag since they are associated with the presence of sequences $(-TT-)_{n \geq 3}$ and $(-TT-)_{n \geq 4}$ [1, 2]. Intensity lowering of the amorphousness peak 905 cm^{-1} in case of oriented sample indicates also rising of its crystallinity. Besides, it is seen from Fig. 7 that peaks sensitive to the chain conformation have lesser width. It means that more perfect crystals of the ferroelectric phase, polar planes of which will have higher surface density, are present in the oriented sample. Then, one can say that the oriented film obtains a “monocrystal texture” [15, 16]. Because of such structure changes, it is possible to formulate the rising cause of remnant polarization at texturing of the isotropic sample (Fig. 5). Texture analysis of the oriented sample by the method of X-ray diffraction [13] indicates that c-crystal axes are oriented along the drawing direction, e.g., in the plane of the film where electrodes are deposited. It means that polar planes a–b of ferroelectric crystals will be parallel to the plane of the film measured. Accordingly, dipole moment (b-axis of the lattice) will be line up along lines of the field. To the contrary, in the isotropic film, random location of crystals as well as all three axes of the lattice a, b, and c will take place on the film plane. Accordingly, probability of the polar axis of the b-lattice to be normal to the film surface goes down. Such conceptions give qualitative explanations for differences in $P_r(E)$ dependences for both films (Fig. 5). Ideas about changing of the texture character with the film orientation may be also used at analysis of field dependencies of high-voltage conductivity (Fig. 4). As it is noted above, the field rising at its low values is accompanied by an increase in σ for both

samples. Such behavior may be predicted quantitatively on the basis of the Poole–Frenkel effect:

$$j_{\text{PF}} = n_T \mu q E \exp \left[-\frac{E_{T_0} - \beta_{\text{PF}}(E)^{\frac{1}{2}}}{kT} \right]. \quad (5)$$

It is associated with lowering of the activation barrier E_{T_0} for carriers drift due to the field energy E . It is possible to connect the fact that σ values in the isotropic sample are higher than those in the oriented film (Fig. 6) with higher mobility of carriers in the first case (assuming that their type and concentration are constant). Charges under consideration are in the amorphous phase. Therefore, their mobility will be determined by the character of liquid-like dynamics. Since in the oriented sample, the proportion of the metastable paraelectric phase of the γ -polymorphous modification falls down, the character of dynamics in the amorphous phase may change. Such suggestion is confirmed by last data on the copolymer of VDF with trifluoroethylene (TrFE) [17]. It has been shown that a decrease in the proportion of the metastable paraelectric phase in the sample leads to an increase in the activation parameter for cooperation mobility in the amorphous phase by 40%. Carrier motion over the amorphous phase will proceed via the “trap–detrap” mechanism. Therefore, more hindered dynamics in the matrix where charge transition goes on must result in lowering of its drift rate.

As it is seen from Fig. 4, at higher fields, lowering of σ is observed that contradicts to the Poole–Frenkel relation. Analysis shows that “anomaly” noted above should be associated with decreasing in free carrier’s concentration. An

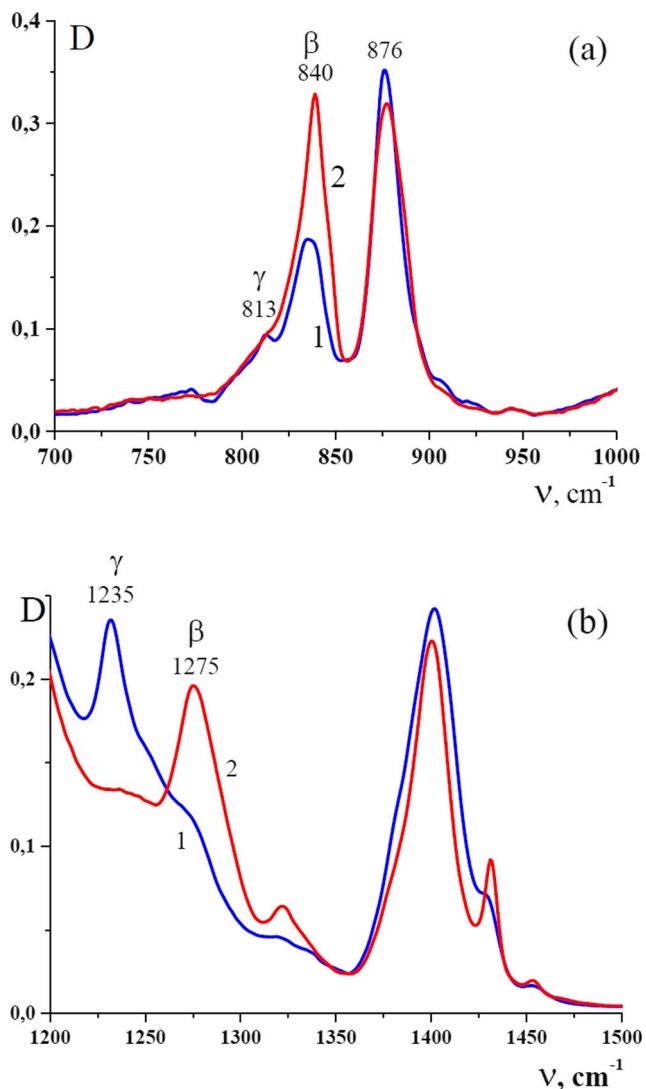


Fig. 7 ATR IR spectra of the isotropic (1) and oriented (2) film for spectral interval 700–1000 cm^{-1} (a) and 1200–1500 cm^{-1} (b)

indirect evidence of this can be found in Fig. 6 where field dependences P_r and σ are compared. The region of sharp rising of remnant polarization corresponds to the turning of the normal to crystal polar planes in the direction of the field. We see a decrease in conductivity in the region where P_r starts to grow rapidly. If it is considered that polar planes of crystalline domains are deep traps for free carriers, this corresponds to rising of their effective cross section of trapping. These carriers, being on the polar plane, become quasi-bound ones, which corresponds to a decrease in n_T in Eq. 5.

As it is mentioned above, breakdown voltage in the isotropic state turns out to be notably lower (Fig. 5) than that in textured film. It may be caused by the fact, that high-voltage conductivity is lower in the isotropic film (Fig. 4). Another cause may be associated with the character of the surface topography, which is represented in Fig. 8a, b for both films. Data processing shows that roughness of isotropic and

oriented film surfaces R_{ms} is equal to 12.3 and 4.5 nm, respectively. So, the former is three times greater. When electrodes are deposited, their inner layers will repeat the relief of the film surface. In case of high roughness of the latter, the probability of metal formation in the form of “spikes” increases. Such regions may be sources of “overvoltage” that must increase the possibility of breakdown. The topography of the oriented film indicates texturing of the surface. That is why it seems reasonable to estimate correlation parameters in two directions, which are perpendicular to each other (Fig. 9a, b). Analysis of results obtained show that the correlation length in direction X_2 (the direction of drawing) turns out to be several times greater than in direction X_1 . Similar analysis for the piezoelectric response (Fig. 9c) indicates that its anisotropy in two directions is expressed weaker.

It seems interesting to consider domains statistic of polymer films studied (Fig. 10). Two distinctions can be seen. First, the sample orientation results in the maximum shift to lower voltage values for a vertical piezo-response, which may be considered as lowering of the coercive field. It means that definite correlation with data on macroscopic polarization arises. In this case for the isotropic sample, intensive growing of remnant polarization takes place at higher fields. Another distinction, which is seen from Fig. 10, consists in the fact that after orientation, distribution curves turn out to be narrower. This is an evidence of higher homogeneity of structural parameters of domains in the process of drawing and subsequent isometric thermal treatment. An increase in the proportion of long sequences of chains in conformation of a planar zigzag (Fig. 7) may cause domain equilibrium structure formation. Most likely that the latter determines stability of the polarized condition which is demonstrated in the inset to Fig. 11. It is seen that 2-h exposure of the sample at the room temperature does not practically change intensity lowering of polarized condition. Our earlier data on the isotropic sample show that entire relaxation of the polarized state is observed as soon as in 20 min [14]. Data shown in Fig. 11 are obtained at polarization time of 10 min. Note that this period of time is much greater than that at macroscopic polarization (see Fig. 1). We consider the field influence time to be the important characteristic for the final polarized state. It can be seen in Fig. 12 where comparison of $D(t)$ curves for the first and second polarization series has been carried out for the same external field. Let us recall that each polarization series was carried out by input of bipolar voltage impulses with the changing amplitude at preliminary electrodes shorting. As it can be seen from Fig. 12a, $D(t)$ curves for both polarization series differ notably. In particular, after the first series, remnant polarization rises by 40% and parameter m in Eq. (2) becomes several times less. Qualitatively, the similar result is fixed at supplying the film with bipolar triangular voltage (Fig. 12b). The shape of the D – E curves in the last figure indicates the contribution to them from conductivity. Indeed, according to Figs. 4 and 6 at the

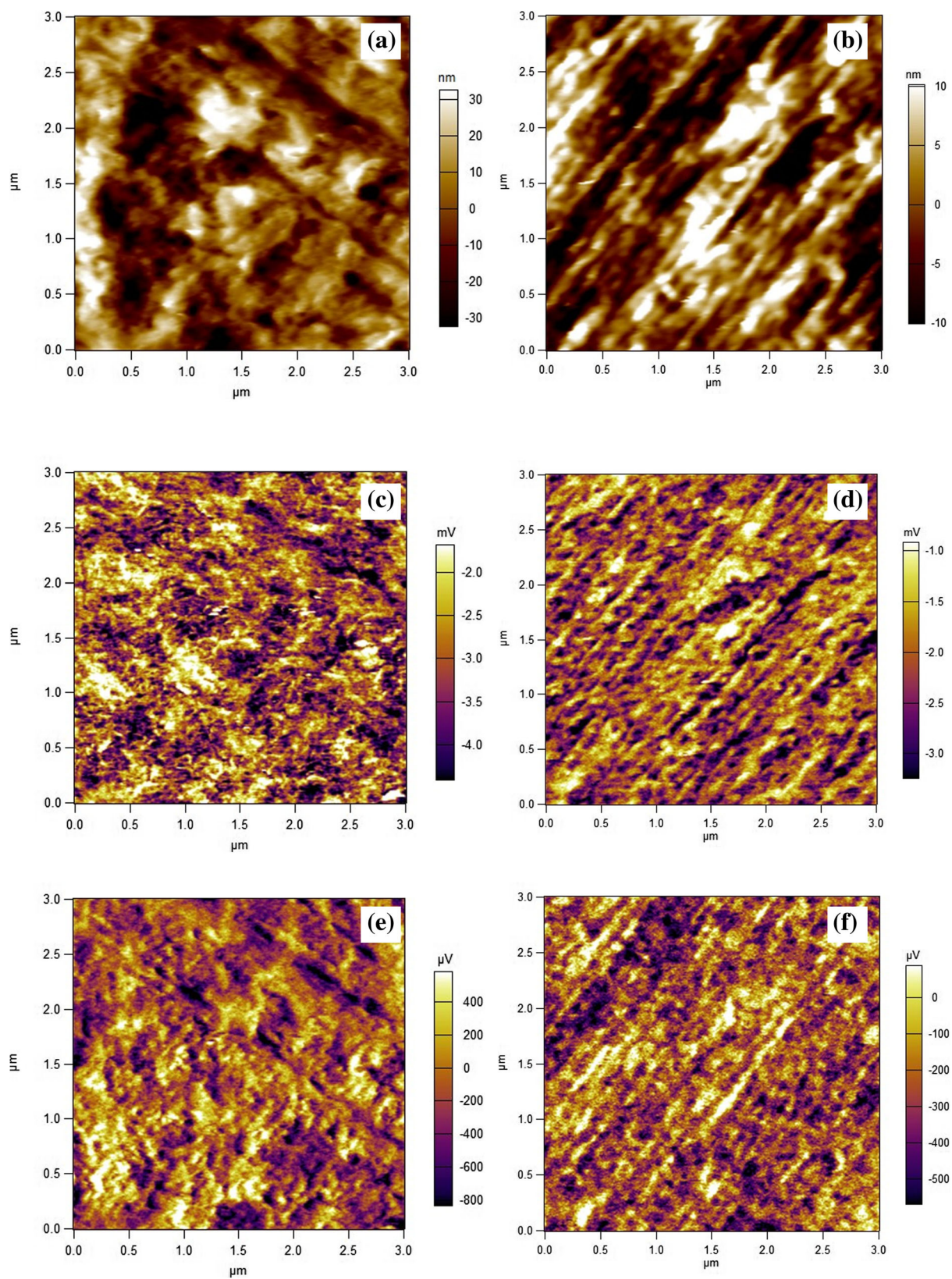


Fig. 8 Comparison of topography (a, b), vertical (c, d), and lateral (e, f) local piezoresponse for the isotropic (a, c, e) and oriented (b, d, f) films

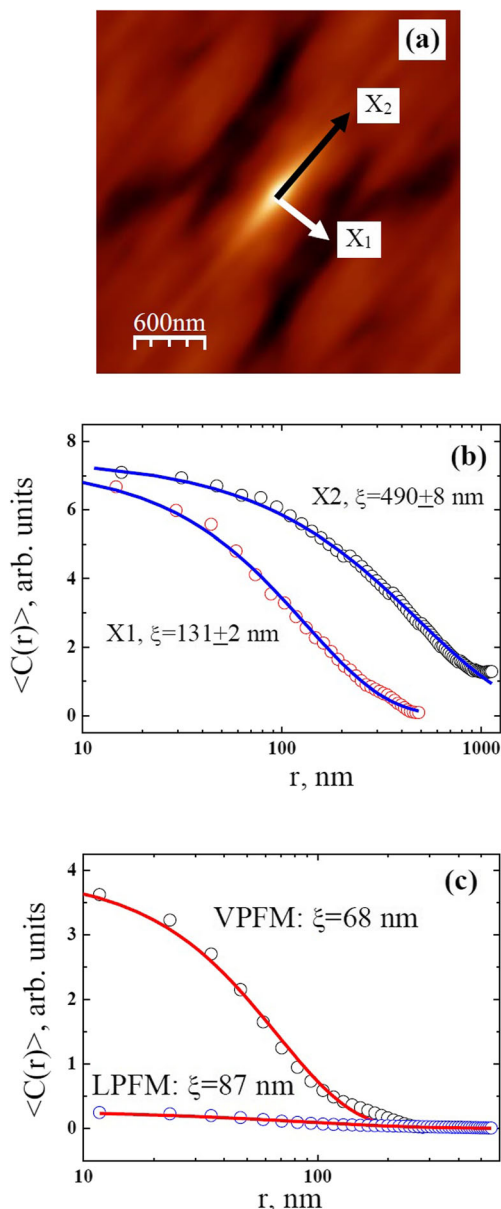


Fig. 9 Autocorrelation image (a) for orient polymer film obtained from Fig. 8b, the corresponding autocorrelation functions for topography in X_1 and X_2 directions (b), and ferroelectric domains (c) calculated from Fig. 8d, f

selected fields in Fig. 12b, high voltage conductivity has the maximum value. As can be seen in higher fields (Figs. 4 and 6), conductivity of in several times decreases. Therefore, the D – E curves obtained in such fields have a smaller contribution from the marked conductivity (Figs. 13b and 14).

One more demonstration of the polarization time role on peculiarities of domains formed is presented in Fig. 13. It is seen that an increase in the number of cycles results in regular change of $D(t)$ curves. This phenomenon manifests itself in lowering of maximal electrical induction values, being even more substantial for the field positive half-period. At such high fields, the switching time of spontaneous polarization t_s will have values of milliseconds and even lower [1, 2]. So

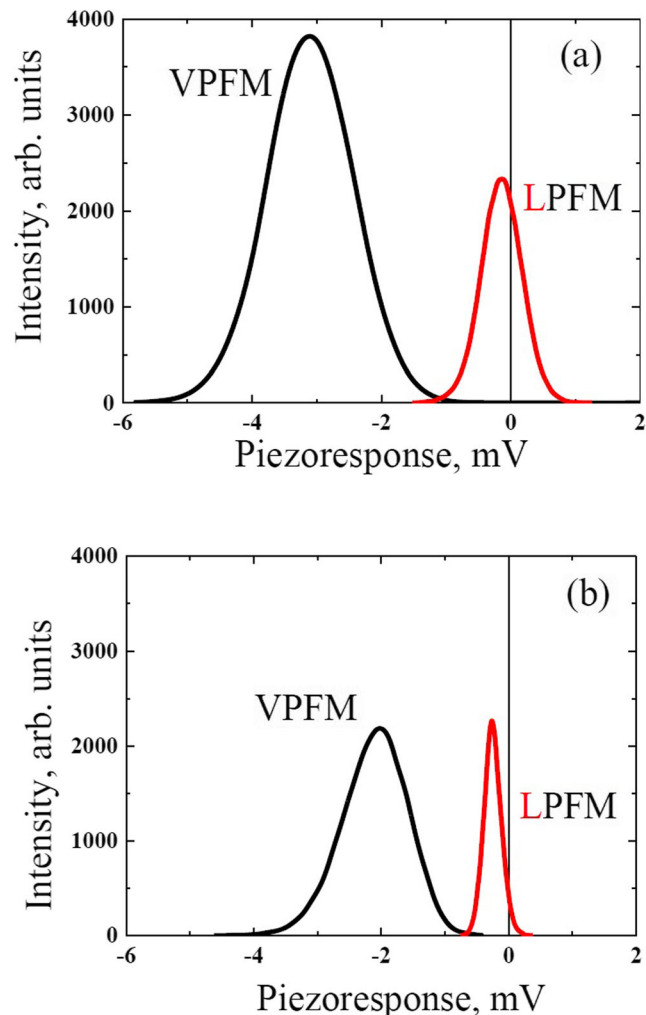


Fig. 10 Characteristics of domains in the isotropic (a) and oriented (b) films for vertical and lateral piezoresponse

times in seconds and above should only be associated with the process of forming a space charge. At the bipolar field, charges of different sign, which are present in the polymer at the initial state, should be taken into consideration. Besides, they can additionally be injected from the electrode material as well. In this case, effectiveness of different signs charges injection and their drift mobility may differ [13]. In particular, injected electrons must be effectively trapped by polymer chains, since there are fluorine atoms in their composition which are strong electron acceptors. In this connection, mobility of charges of different sign in the polymer studied must differ, and the space charge formed may have asymmetry with respect to its sign. Therefore, asymmetric change of $D(t)$ curves with an increasing number of polarization cycles may reflect this process. It is seen from the inset to Fig. 13a that an increase in the number of polarization cycles is accompanied by some decreasing of P_r , which has a tendency to stabilization. We associate this fact with the equilibrium space charge formation mentioned above when some part of carriers is

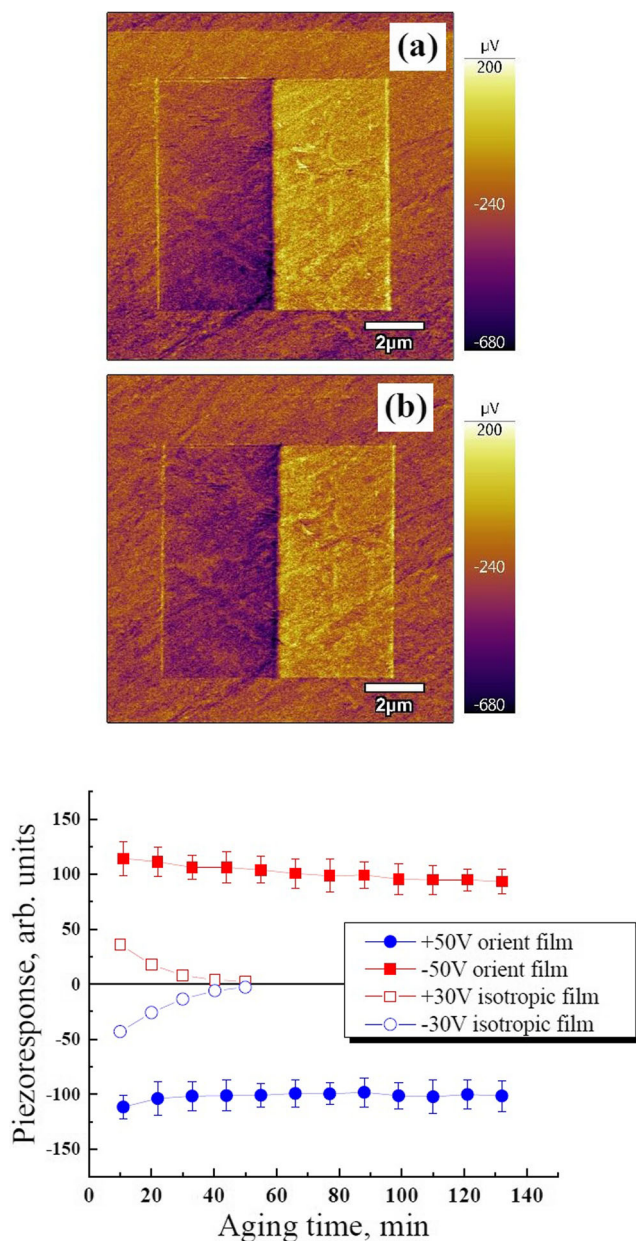


Fig. 11 The polarization picture of the oriented sample just after polarization in the bipolar field (a) and after its exposure during 2 h (b); inset—kinetics of polarization decrease in the isotropic (1) and oriented (2) film

captured by deep traps of polar crystal planes. It is evident that such process must result in decreasing of the domain spontaneous polarization and P_r , respectively. Kinetics of this process changing is seen in the inset to Fig. 13a.

At supplying the sample with the “triangular” low frequency bipolar external field, these effects must be reflected on curves of the electrical response. Indeed, as it can be seen from Fig. 13b, for the third cycle of the external field scanning, the hysteresis curve is characterized by lower D values mainly in the region of positive fields, too. At the same time, it may be

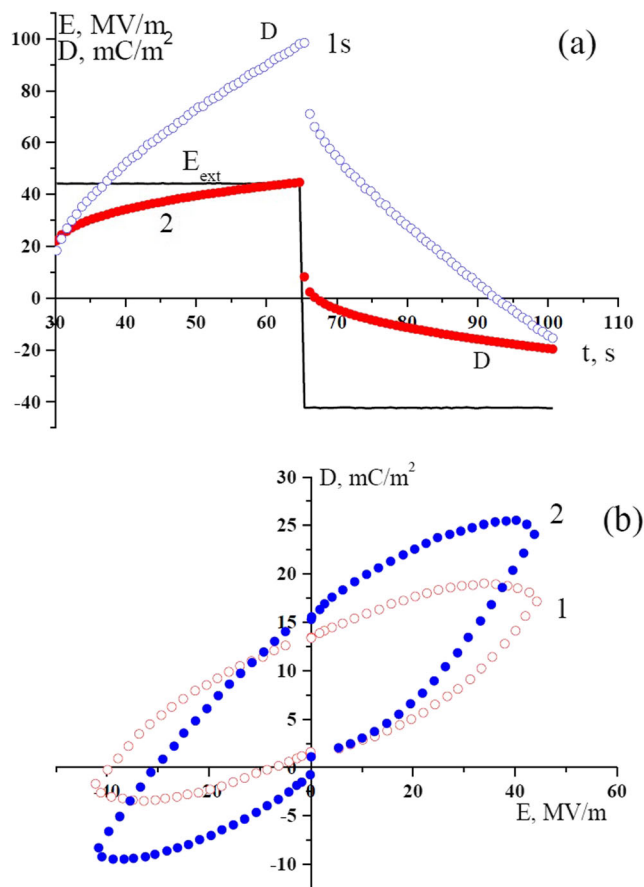
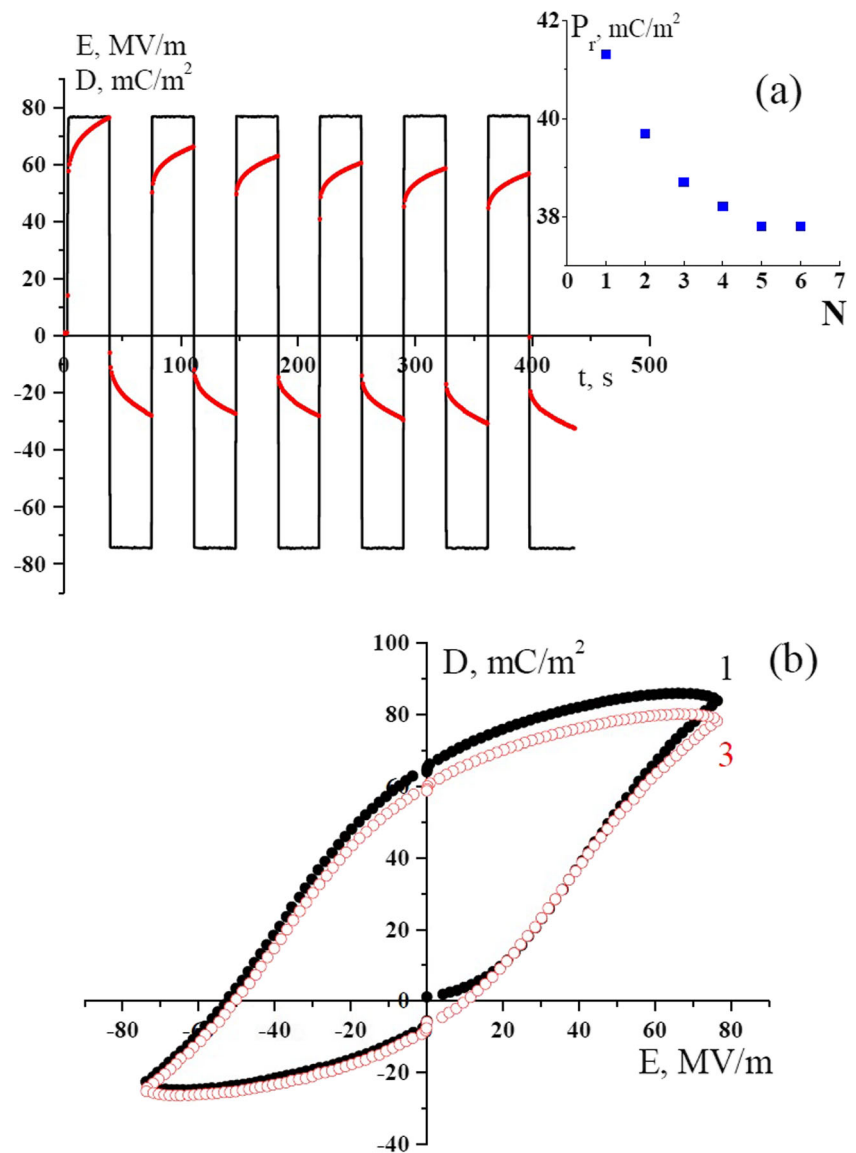


Fig. 12 Time (a) and field (b) dependencies of electrical induction n the oriented sample for the first (1) and second (2) series of polarization at supplying rectangular (a) and triangular (83 mHz) (b) bipolar voltage

noted that an increase in the number of polarization cycles is also accompanied by some P_r lowering.

As it is seen from Figs. 12b, 13b, and 14, hysteresis curves obtained by supplying the sample with bipolar triangle voltage have two particular features. As a rule, curves are not closed, indicating that the system is not at equilibrium with respect to the number of the external field impulses supplied. This effect is observed not only in polymers studied but also in ferroelectrics of the inorganic nature [18–20]. From the point of view of the general analysis of ferroelectrics, the asymmetry of the hysteresis curve is characterized by the term of “non-complete” polarization [21]. One of causes of this phenomenon may be associated with the material of electrodes, which compensated the depolarization field [22–28]. However, in our case, the same electrodes were used in both samples. So, there must be another factor. Polymers studied have the two-phase structure; at the polarization temperature $T_p = +20$ °C, both phases being different with respect to the dynamics character. Namely, liquid-like mobility in the amorphous phase and high impurity conductivity in it may cause non-uniformity of the space charge distribution at the anode or cathode side.

Fig. 13 **a** Changing of the character of electrical response in the second polarization series at supply the oriented film with six successive bipolar pulses of the electrical field with the amplitude of 75 MV/m. Inset— P_r against polarization cycles number N . **b** Changing of the hysteresis curve at transition from the first to the second cycle of polarization with the use of bipolar triangular voltage with the same amplitude and frequency equal to 8 mHz



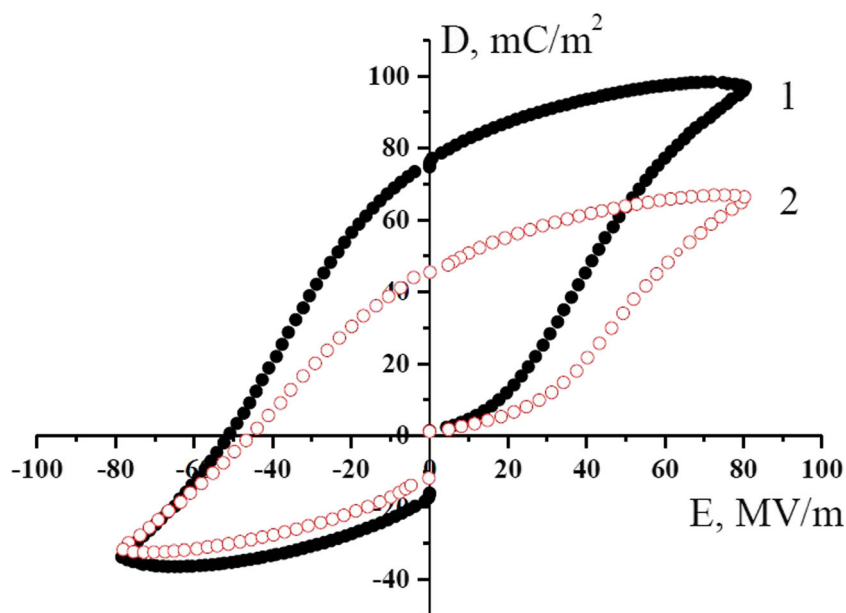
Since the field of the space charge takes part in formation of the local field, this may result in the asymmetry in hysteresis curves observed experimentally. Under conditions of carrier low mobility, formation of the equilibrium space charge demands much time. It means that the hysteresis curve form must substantially depend on the period of the outer bipolar triangular voltage. Data of Fig. 14 confirm such a hypothesis. Changing of the external field frequency leads to notable changing of the hysteresis curve form. In case of the Maxwell mechanism of the space charge formation, lowering of the field frequency from 190 to 7 mHz creates conditions for its approaching the equilibrium state. It follows from this figure that at the low frequency of the field, the hysteresis curve changes more if the field sign is positive. This fact indicates once more the special role of hole current carriers which are injected from the electrode and take part in the space charge formation.

Earlier, it was shown that the size of domains in polymers studied turned out to be much higher than the average size of the polar crystal [14]. It means that chains of the amorphous phase are present in domains. In this connection, it is interesting to study the high-voltage polarization of the latter. It can be done using dielectric data presented in Fig. 15. As it is seen, the dispersion region, in which cooperative mobility of amorphous phase chains [1, 2], exists in the frequency region of 10^6 – 10^7 Hz. It means that low-frequency values of ϵ' characterize static dielectric permittivity ϵ_0 .

The uni-axially drawn film is an unisotropic body where dielectric permittivity has a view of the following matrix:

$$\begin{bmatrix} \epsilon_{11} & 0 & 0 \\ 0 & \epsilon_{22} & 0 \\ 0 & 0 & \epsilon_{33} \end{bmatrix}, \quad (6)$$

Fig. 14 Curves of electrical hysteresis of the oriented sample at supply it with triangular voltage of the amplitude of 80 MV/m and frequency of 7 mHz (1) and 190 mHz (2)



where direction 1 coincides with the axis of drawing, and directions 2 and 3 coincide perpendicular to it. In this case, it is possible to write the following equation [29, 30]:

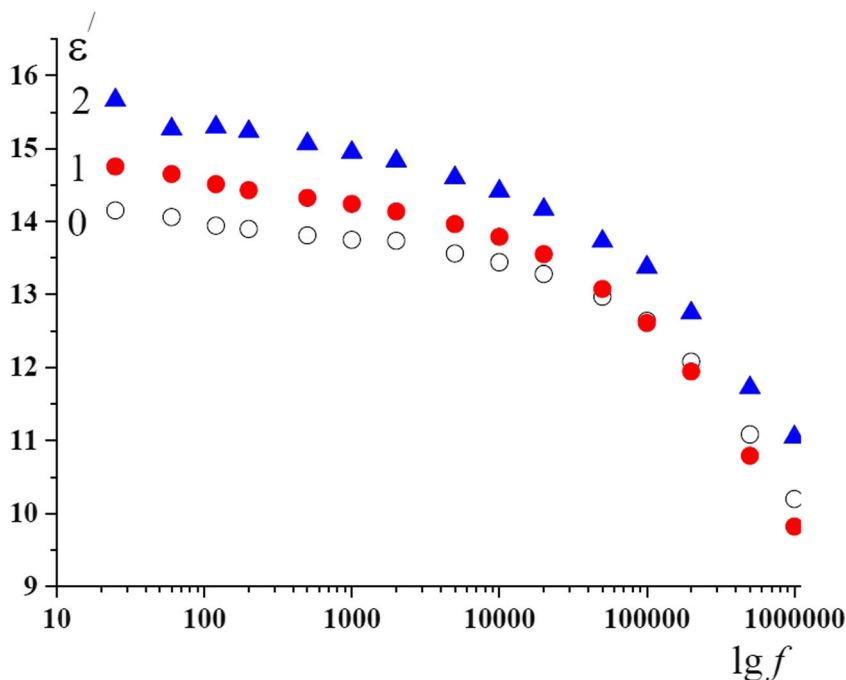
$$\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty = \Delta\varepsilon_{33} = \zeta \frac{4\pi n}{3kT} \mu_e^2 \cos^2 \gamma, \quad (7)$$

where ζ is a factor of the local field, n is concentration of kinetic units (polymer segments) with the effective dipole moment μ_e , and γ is an angle between of the dipole moment with respect to the vector of the electrical field.

As noted above, the increase in the number of cycles of polarization is accompanied by increase ε_0 . On the other hand, the high-frequency permittivity ε_∞ does not change.

Thus, as it follows from Fig. 15, an increase in the number of cycles of the oriented film polarization is accompanied by rising of the dielectric increment of the amorphous absorption ($\Delta\varepsilon_{33}$). An increase in the amorphous phase proportion (n) is excluded since usually just an opposite phenomenon is observed [31]. According to Eq. 7, either an increase in μ_e or a decrease in γ may happen. Indeed, in high voltage fields in polymer segments of the amorphous

Fig. 15 Frequency dependencies of dielectric permittivity of the oriented film in the initial state (0) and after the first (1) and second (2) series of polarization cycles at the room temperature



phase, conformational transitions of the type $(T_3GT_3G^{-1}) \rightarrow (-TT)_n$ and $(TGTG^{-}) \rightarrow (-TT)_n$ are possible. This is profitable from the point of view of the energetic since ranges of chains in the conformation of the planar zigzag $(-TT)_n$ have the higher dipole moment. Such conformational transformations may be accompanied by decreasing in the disorientation angle γ , too. Thus, structural conversions under influence of the field in amorphous phase regions will assist in formation of the irreversible “monocrystal texture.”

As it is noted above, investigations of ferroelectricity in textured films have been carried out extremely rarely. That is why it is interesting to confront results of this work with similar data, concerning oriented films of VDF and hexafluoropropylene (HFP) copolymer [32]. In particular, it is interesting to compare the coercive field E_c , which is one of the fundamental characteristics of ferroelectrics. As it follows from Fig. 5, for our oriented polymer, it has the value of 40 MV/m, for the oriented copolymer VDF/HFP $E_c = 100$ MV/m [32]. Such substantial difference shows that the VDF copolymer composition may strongly influence final ferroelectric characteristics. The character of molecular dynamics in the amorphous phase of VDF/HFP will depend on the proportion of the latter comonomer, which has great steric hindrances. Earlier, we showed that in the copolymer studied, an increase in HFP proportion from 7 to 14% is accompanied by growing of a number of parameters such as glass transition temperature, equilibrium temperature of transition to glass, enthalpy of micro-Brownian motion, and so on [7]. It indicates more hindered dynamics in the copolymer amorphous phase if the copolymer contains much HFP. In case of ferroelectricity, the character of such dynamics may affect acts of generation of domains of new direction during polarization process. It may be associated with the fact that in crystalline polymers, the same chain (with covalent bonds) can be either in the crystal or adjacent amorphous phase with intensive Brownian dynamics. Since the copolymer with high HFP content (15%) was used in work [32], facts on change of dynamics character in the copolymer amorphous phase noted there could lead to high values of the coercive field.

It makes sense to compare presented data on Fig. 1 with similar results in the work [33]. Here the authors on the example of VDF copolymer with TFE followed the charge response when applying to the sample, as in our case of a rectangular voltage pulse. The difference was that the authors had a time of 100 ms, whereas in our case, the times were two orders of magnitude longer. However, the curves are in Fig. 1 and in [33] are qualitatively the same. In [33], an analytical method for estimating the contribution of conductivity to the measured curve $D(t)$ was proposed. In our case, the empirical Eq. (2) was used for this purpose. The authors of the cited paper found the relaxation of a part of the polarization after a field shutdown. Similar preliminary experiments on our samples show that they also observed a qualitatively similar relaxation of polarization.

We believe that the marked fast relaxation proves the validity of the previously obtained conclusion [14] that domains in ferroelectric polymers in addition to polar crystals include sections of amorphous phase chains. The fluid-like dynamics in the latter at room temperature may be responsible for the rapid relaxation of the polarization part after field removal.

Conclusions

Comparison of hysteresis curves for isotropic and oriented films shows that in the last case under equal conditions, polarization is higher. IR-spectroscopy data indicate that it should be attributed to the fact that at orientation the proportion of regions with conformation of a flat zigzag increases. Such conformation is characterized by the higher value of the dipole moment transverse component. Data of the atomic force microscopy show that the film orientation with its subsequent isometric tempering results in substantial decrease in the surface roughness. According AFM data, appearance of fibrils with average thickness of 132 nm has been fixed. Calculation of the correlation length along and across fibrils shows that in the last case, it turns out to be four times lower. Such structural transformation at orientation results in the narrower size distributions of ferroelectric domains and to smaller relaxation of the local piezoelectric response after polarization. Hysteresis curve asymmetry noted in the experiment is also attributed to the spatial charge field contribution to the local field. Comparison of hysteresis curves obtained at different frequencies of the external field indicates an important role of the hole carriers injected from the electrode material in formation of the space charge.

Funding information The reported study was funded by the RFBR according to the research project no. 18-03-00493. The PFM studies were performed at the Center of Collective Use “Material Science and Metallurgy” of the National University of Science and Technology “MISIS” and were supported by the Ministry of Education and Science of the Russian Federation (Grants 11.9706.2017/7.8 and 16.2811.2017/4.6).

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

1. Wang TT, Herbert JM, Glass AM (1988) The applications of ferroelectric polymers. Blackie and Son, Glasgow
2. Nalwa HS (ed) (1995) Ferroelectric polymers: chemistry, physics, and applications. CRC Press
3. Kochervinskii VV (1994) The properties of fluoride-containing polymer films with piezoactivity and pyroactivity. Russ Chem Rev 63(4):367–371

4. Kochervinskii VV, Glukhov VA, Sokolov VG, Romadin VF, Murasheva EM, Ovchinnikov YuK, Trofimov NA, Lokshin BV (1988) Microstructure and crystallization of isotropic films of a copolymer of vinylidene fluoride and tetrafluoroethylene. *Vysokomolekulyarnie Soedineniya Seria A* 30(9): 1969–1976 in Russian
5. Kochervinskii VV, Chubunova EV, Lebedinskii YY, Shmakova NA, Khnykov AY (2011) The role of new functional groups in the surface layer of LDPE during its high-voltage contact polarization. *Polym Sci Ser A* 53(10):929–946
6. Malyshkina IA, Markin GV, Kochervinskii VV (2006) Investigation into the dielectric relaxation of vinylidene fluoride copolymers with hexafluoropropylene. *Phys Solid State* 48(6): 1197–1199
7. Kochervinskii VV, Malyshkina IA, Markin GV, GavriloVA ND, Bessonova NP (2007) Dielectric relaxation in vinylidene fluoride–hexafluoropropylene copolymers. *J Appl Polym Sci* 105(3): 1101–1117
8. Kochervinskii V, Malyshkina I (2010) Peculiarities of high-temperature dielectric relaxation in vinylidene fluoride–hexafluoropropylene copolymers. *J Non-Cryst Solids* 356(11): 564–567
9. Kochervinskii V, Malyshkina I, Pavlov A, Pakuro N, Bessonova N, Shmakova N, Bedin S, Chubunova E, Lebedinskii Y (2015) An effect of the electrode material on space charge relaxation in ferroelectric copolymers of vinylidene fluoride. *J Appl Phys* 118(24): 244102 (9pp)
10. Wolf U, Arkhipov VI, BäSSLer H (1999) Current injection from a metal to a disordered hopping system. I. Monte Carlo simulation. *Phys Rev B* 59(11):7507–7513
11. Ishii H, Sugiyama K, Ito E, Seki K (1999) Energy level alignment and interfacial electronic structures at organic/metal and organic/organic interfaces. *Adv Mater* 11(8):605–625
12. Zakreevskii VA, Sudar NT (1992) Injection of holes into polymers from metal electrodes in strong electric fields. *Fizika Tverdogo Tela* 34 (10): 3228–3232 in Russian
13. Kochervinskii VV, Chubunova EV, Lebedinskii YY, Pavlov AS, Pakuro NI (2015) Influence of the high-voltage conductivity on peculiarity of polarization ferroelectric polymer on based vinylidene fluoride. *Adv Mater Res* 4(2):113–132
14. Kochervinskii VV, Kiselev DA, Malinkovich MD, Pavlov AS, Kozlova NV, Shmakova NA (2014) Effect of the structure of a ferroelectric vinylidene fluoride-tetrafluoroethylene copolymer on the characteristics of a local piezoelectric response. *Polym Sci Ser A* 56(1):48–62
15. Ohigashi H, Omote K, Gomyo T (1995) Formation of “single crystalline films” of ferroelectric copolymers of vinylidene fluoride and trifluoroethylene. *Appl Phys Lett* 66(24):3281–3283
16. Ohigashi H (1988) In: Wang TT, Herbert JM, Glass AM (eds) *The application of ferroelectric polymers*. Black, Glasgow, pp 237–273
17. Kochervinskii VV, Malyshkina IA, Korlyukov AA, Shakhirzyanov RI, Shoranova LO (2016) On the influence of metastable paraelectric phase on the characteristics of low-temperature cooperative and local molecular mobility in a ferroelectric copolymer of vinylidene fluoride and trifluoroethylene. *Intern J Pharm Technol* 8(4):27225–27237
18. Pike GE, Warren WL, Dimos D, Tuttle BA, Ramesh R, Lee J, Keramidias VG, Evans JT (1995) Voltage offsets in (Pb, La)(Zr, Ti)O₃ thin films. *Appl Phys Lett* 66(4):484–486
19. Lee J, Choi CH, Park BH, Noh TW, Lee JK (1998) Built-in voltages and asymmetric polarization switching in Pb(Zr,Ti)O₃ thin film capacitors. *Appl Phys Lett* 72(25):3380–3382
20. Lee HJ, Kim IW, Kim JS, Ahn CW, Park BH (2009) Ferroelectric and piezoelectric properties of Na_{0.52}K_{0.48}NbO₃ thin films prepared by radio frequency magnetron sputtering. *Applied Physics Letters* 94(9) 092902 (3 pp)
21. Miller SL, Schwank JR, Nasby RD, Rodgers MS (1991) Modeling ferroelectric capacitor switching with asymmetric nonperiodic input signals and arbitrary initial conditions. *J Appl Phys* 70(5):2849–2860
22. Mehta RR, Silverman BD, Jacobs JT (1973) Depolarization fields in thin ferroelectric films. *J Appl Phys* 44(8):3379–3385
23. Wurfel P, Batra IP (1976) Depolarization effects in thin ferroelectric films. *Ferroelectrics* 12(1):55–61
24. Tagantsev AK, Pawlaczyk C, Brooks K, Landivar M, Colla E, Setter N (1995) Depletion and depolarizing effects in ferroelectric thin films and their manifestations in switching and fatigue. *Integr Ferroelectr* 6(1–4):309–320
25. Dawber M, Chandra P, Littlewood PB, Scott JF (2003) Depolarization corrections to the coercive field in thin-film ferroelectrics. *J Phys Condens Matter* 15(24):L393–L398
26. Black CT, Farrell C, Licata TJ (1997) Suppression of ferroelectric polarization by an adjustable depolarization field. *Appl Phys Lett* 71(14):2041–2043
27. Baudry L, Tournier J (2001) Lattice model for ferroelectric thin film materials including surface effects: investigation on the “depolarizing” field properties. *J Appl Phys* 90(3):1442–1454
28. Bratkovsky AM, Levanyuk AP (2006) Depolarizing field and “real” hysteresis loops in nanometer-scale ferroelectric films. *Appl Phys Lett* 89(25):253108 (3pp)
29. Hsu BS, Kwan SH, Wong LW (1975) Dipole moments in oriented poly (ethylene terephthalate). *J Polym Sci B Polym Phys* 13(11): 2079–2090
30. Phillips PJ, Kleinheins G, Stein RS (1972) Anisotropy of the dielectric relaxation of a crystalline polymer. *J Polym Sci B Polym Phys* 10(8):1593–1607
31. Kochervinskii VV (2006) Structural changes in ferroelectric polymers under the action of strong electric fields by the example of polyvinylidene fluoride. *Crystallogr Rep* 51:S88–S107
32. Wegener M, Künstler W, Richter K, Gerhard-Multhaupt R (2002) Ferroelectric polarization in stretched piezo- and pyroelectric poly (vinylidene fluoride-hexafluoropropylene) copolymer films. *J Appl Phys* 92(12):7442–7447
33. Liu J, Zhao Y, Chen CH, Wei X, Zhang ZH (2017) Study on the polarization and relaxation processes of ferroelectric polymer films using sawyer-tower circuit with square voltage waveform. *J Phys Chem C* 121(23):12531–12539