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Influense of the high-voltage conductivity on peculiarity of polarization ferroelectric polymer on based vinylidenefluoride

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Abstract. The phenomena of high-voltage polarization and conductivity in oriented vinylidenefluoride and tetrafluoroethylene copolymer films have been investigated. It was shown that under certain electric fields, injection of carriers from the material of electrodes appears

The barrier for holes injection in the copolymer was found to be lower than that for electrons. It results in more effective screening of the external field near the anode than near cathode. Electrones, ejected from cathode, creating negative charge by trapping on the surface.

It is shown that the electrons injected from cathodes create a negative homocharge on the copolymer surface and then become captured on the surface shallow traps. Their nature has been studied by the x-ray photoelectron spectroscopy. It was shown that these traps may consist of chemical defects in the form of new functional groups formed by reactions of surface macromolecules with sputtered atoms of aluminum. The asymmetric shape of hysteresis curves was explained by the difference in mobility of injected holes and electrons. These factors caused appearance of “non-closed” hysteresis curves for fluorine-containing polymer ferroelectrics. Hysteresis phenomena observed at low electric fields (below coercive ones) are to associate with the behavior of the domains localized in the ordered regions formed during secondary crystallization of copolymers.

Keywords: crystalline polymers; ferroelectricity; conductivity; injection of charges; dielectric hysteresis; *x*-ray photoelectron spectroscopy

1. Introduction

Polyvinylidenefluoride PVDF and its copolymers are crystalline flexible-chain ferroelectric polymers (Wang *et al.* 1988, Nalva *et al.* 1995). PVDF may form at least 4 polymorphic modifications Kochervinskii (1999). If the lattice formed does not have a center of inversion, after poling this polymer show high piezo- and pyroelectric properties. Because of the specific properties of such polymers, it is possible to use them as materials for various energy converters (Wang *et al.* 1988, Nalva *et al.* 1995, Kochervinskii 1994). Values of piezo- and pyroelectric

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*Corresponding Author, Ph.D., E-mail: kochval@mail.ru coefficients are determined to a considerable extent by the polarization process and so investigation of its mechanism seems to be very important.

While the dipole mechanism of ferroelectricity for polymers mentioned above is discussed by many researchers (Wang *et al.* 1988, Nalva *et al.* 1995, Kochervinskii 1999), the role of the space charge is touched upon much less (Ikeda *et al.* 1988). It is known that crystalline polymers have two-phase structure, the ratio of disordered (amorphous) phase being in many cases even greater than 50%. Moreover, these phases are not classical thermodynamic systems at any rate because of the absence of classical phase borders. That is why the role of the amorphous phase in mechanisms of the domain structure formation in the considered ferroelectric polymers may be non-trivial. It is most likely that due to these features, the presence of two types of ferroelectric phases in such objects (Wang *et al.* 1988, Nalva *et al.* 1995, Kochervinskii 1999) as well as unusual two-stage switching of spontaneous polarization (Furukawa *et al.* 1988, Koizumi *et al.* 1986, Tajitsu *et al.* 1987, Kochervinskii 1993, Kochervinskii *et al.* 1991, Kochervinskii *et al.* 2014) were often mentioned in the literature.

Earlier, polarization was studied at fairly high frequencies (60 Hz) of the high voltage field (Kochervinskii *et al.* 2014). On the other hand, formation of a space charge in dielectric materials is controlled by the low carrier's mobility. Therefore, to study the role of a space charge in the processes of spontaneous polarization switching with frequencies of electric field tens of mHz, should be used. Research was conducted with an emphasis on the mechanism of the space charge formation and its impact on switching of spontaneous polarization. The aim of this work is to trace features of high-voltage polarization by varying the strength of the electric field both below and above the coercive one.

It was shown, that contact high-voltage polarization is accompanied by phenomena of injection of carriers from the electrode material. Characteristics of carriers injection from the anode and cathode were found to be different. As these carriers are formed of the space charge, which affect the local field, the loop of dielectric hysteresis becomes unclosed and asymmetrical.

2. Experimental.

The copolymer of vinylidenefluoride and tetrafluoroethylene (VDF/TFE) (94/6) characterized by the high resolution NMR was the object of the study (Kochervinskii *et al.* 1988). Isotropic films were prepared by copolymer crystallization from its solution in acetone which, according to IR spectroscopy data, crystallized as the mixture of alpha-, beta-, and gamma- phases (Kochervinskii *et al.* 2014). Subsequent films orientation was carried out by uniaxial stretching at the temperature of 70℃ (7 times drawing) followed by isometric annealing that decreases internal stresses and improves their structure (Kochervinskii *et al.* 1989). Fig. 1 shows *x*-ray diffraction pattern of the copolymer oriented film. The angular position of the noted peaks indicates that in the drawing process the film crystallize in the polar β-phase with chain conformation in the form of a planar zigzag. The data of IR spectroscopy (Fig. 2) confirm this conclusion. Indeed, in the spectrum of the observed number of absorption bands (440, 470, 508 and 840 cm^{-1}), which are characteristic of observed polymorphic modifications (Wang *et al*. 1988, Nalva *et al*. 1995) From Fig. 2 is seen a strong IR dichroism observed bands, indicating good orientation of the chain segments in the planar zigzag conformation.

Aluminum electrodes 100 nm thick were produced by the vacuum deposition method. Measurements of high voltage electro-physical characteristics were performed at the room

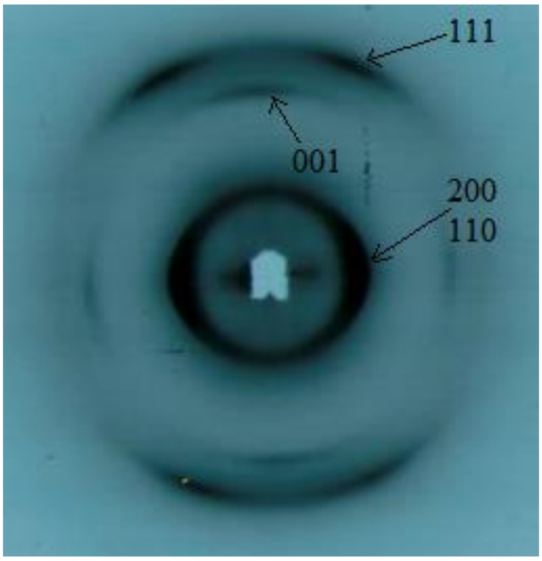


Fig. 1 *X*-ray pattern of the copolymer oriented film; drawing direction is vertical

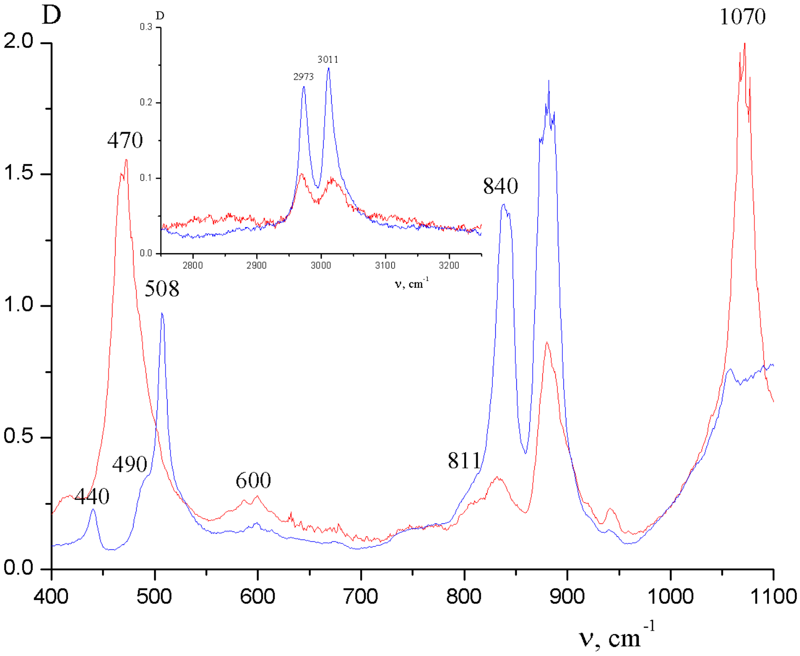
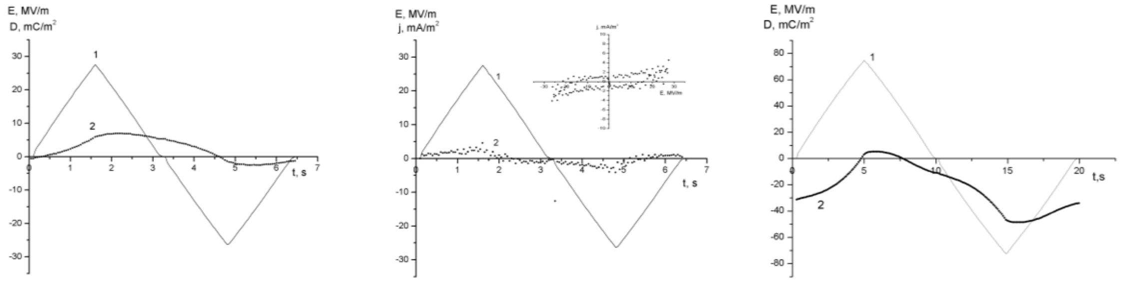


Fig. 2 IR spectra in polarized light for the copolymer film after the orientation process; red and blue- vector *E* of the radiation is respectively parallel and perpendicular to the direction of orientation

temperature according to the modified Sawyer-Touer scheme described earlier (Kochervinskii *et al.* 2011). Poling fields had the form of the bipolar triangle or rectangular wave. Frequencies used varied in the range of 1-100 mHz. Two series of films textured under different conditions were studied.



(a) (b) (c)

Fig. 3 The time dependences of the external field (1), electr4ic displacement and current density (2) in the samples of the I (a,b) and II (c) series of oriented films of the copolymer. *f*=160 (a,b) and 50 (c) mHz; insert on Fig. 1(b) - volt-ampere characteristic

3. Results

Fig. 3 shows the time dependence of the external field supplied on films of two series and their charge and current response. It can be seen that in the initial state, there is a charge on the surface of the films, as evidenced by a non-zero *D* electric displacement value. The comparison of curves 1a and 1c shows that for the film of series II, the *D* value is several times higher. It is not clear what causes such a difference. This can be explains by the fact that the film formation process conditions can affect surface charge density (Toureille *et al.* 1998). The initial point shifts to the negative *D*, indicating that before measurements the film is an electret's with a small negative surface potential. We believe that the surface potential is formed by free carriers located at deep traps. One of the causes of the noted potential appearance can be related to the contact phenomena on the metal-polymer boundary (Davies 1969, Fabish *et al.* 1976, Grzybowski *et al.* 2005), which is brought about on the polymer dielectric surface during the electrode metal sputtering. Really, appearance of the galvanic effect was noticed in M1-polymer-M2 systems (Ieda *et al.* 1975, Vijh 1978, Crine *et al.* 1979). In our case, symmetric electrodes were used, but occurrence of this effect is not excluded. In practice, polymer film surfaces are non-equivalent as to chemical defects and structural parameters (Kochervinskii *et al.* 2011). Then electronic state structures of the molecules near both surfaces are not the same, and their contact with the same metal can cause galvanic effect.

Insert on Fig. 4 confirms this. It can be seen that initial negative potential on two sides of the film are not the same. Besides, under uniaxial drawing and subsequent isometric annealing (Kochervinskii *et al.* 1989), the axial texture may not necessarily form. If the polar axis of the crystal has preferential direction normal to the surface of the film, it will form a remnant charge (potential) even in the absence of poling.

As follows from Fig. 4, hysteresis curves indicate the presence of two polarization components that was noted earlier (Furukawa *et al*. 1988, Koizumi *et al*. 1986, Tajitsu *et al*. 1987, Kochervinskii 1993, Kochervinskii *et al.* 1991, Kochervinskii *et al.* 2014). Another feature of hysteresis curves 1, and 2 (Fig. 4) is the fact, that they are not closed, i.e., the endpoint in the bipolar cycle of field changes is characterized by a negative potential (charge) increase. Such patterns are observed not only for the considered class of polymers (Guy and Unsworth 1988, Naber *et al.* 2004, Park *et al.* 2008, Kang 2009), but also in a number of inorganic ferroelectrics (Wurfel *et al.* 1973, Wurfel and Batra 1973). As follows from Fig. 4, the shape of the hysteresis

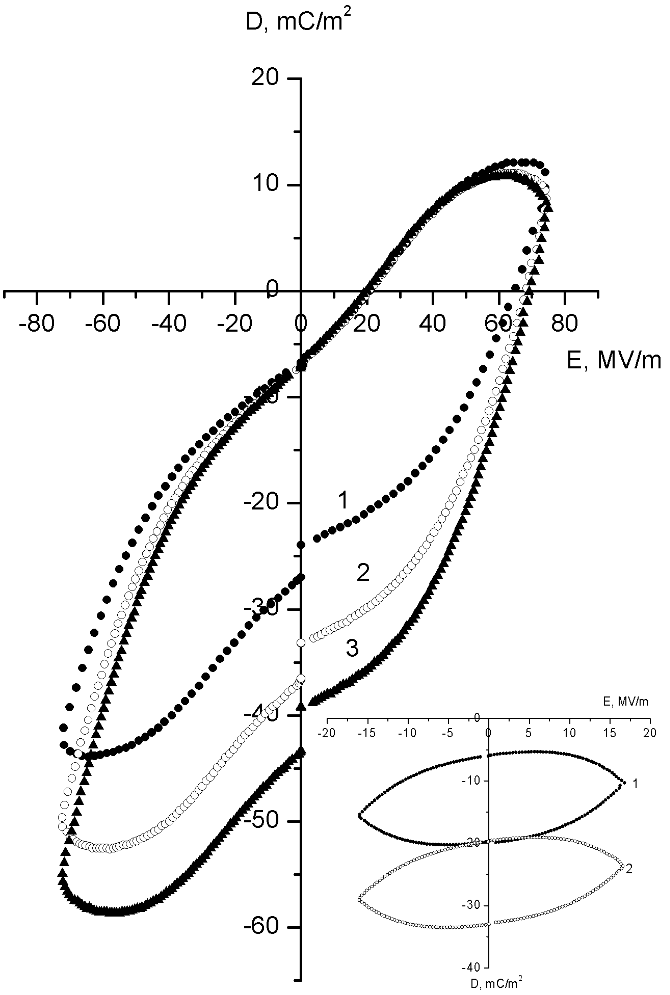


Fig. 4 Field dependence of electr4ic displacement for sample series II; 1-, 2-, 3 respectively 70, 40 and 30 mHz; insert - hysteresis curves on 1 and 2 initial film sides

loops and its parameters (in particular the “degree of unclosiness”) depend significantly on the frequency of the external field. The nature of this phenomenon will be considered below, but one cause may be connected with the fact thet along with ferroelectric phase in the original film there can be also the antiferroelectric one (Kochervinskii *et al.* 2010, Takahashi 1999). The current, passing through the capacitance depends also on the frequency of the field (Fig. 3). It is seen from Figs. 3(b) and (5), which strong current oscillations arise in the fields above the coercive ones, which usually amount to 40-50 MV/m (Wang *et al.* 1988, Nalva 1995).

Fig. 6 shows an influence of the number of polarization cycles on curves $D(E)$, when fields are below the coercive ones. It is seen that an increase in the number of polarization cycles without short circuit is accompanied by a significant increase in negative electret potential (hysteresis curves are shifted down along the y axis). Thus, an increase in the number of polarization cycles (in this case, and at the simultaneous growth of polarization fields) is accompanied by increasing

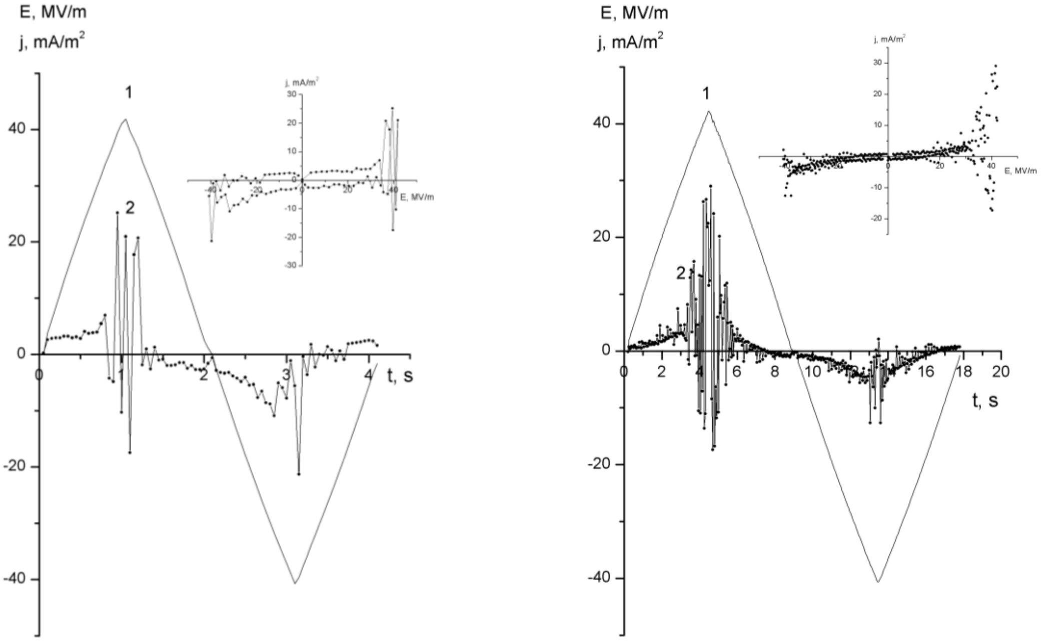


Fig. 5 Time dependences of the intensity of the external field (1) and current density (2) in the samples of series II; a and b respectively 240 and 55 mHz

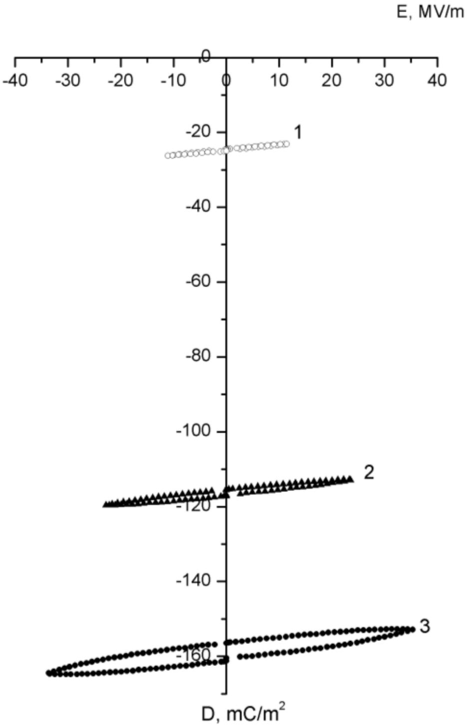


Fig. 6 The hysteresis curves obtained from three successive polarization cycles made without short circuit; 1,2, and 3, respectively 470, 230 and 160 mHz

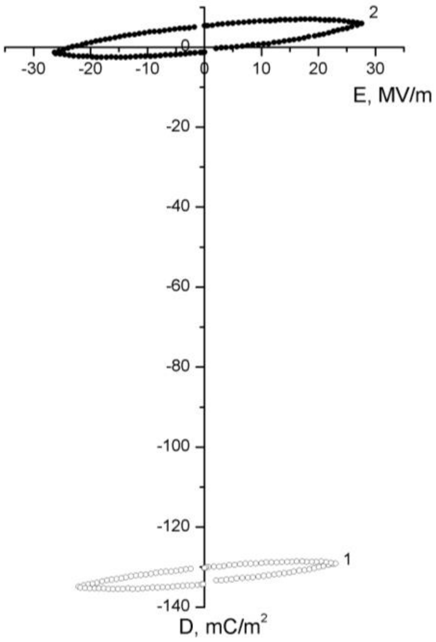


Fig. 7 The influence of the short circuit on the hysteresis curves; 1 - curve for the sample obtained after number of polarization cycles without short circuit, 2 - curve of the sample obtained from 1, after its short circuit; 1 and 2, respectively 190 and 160 mHz

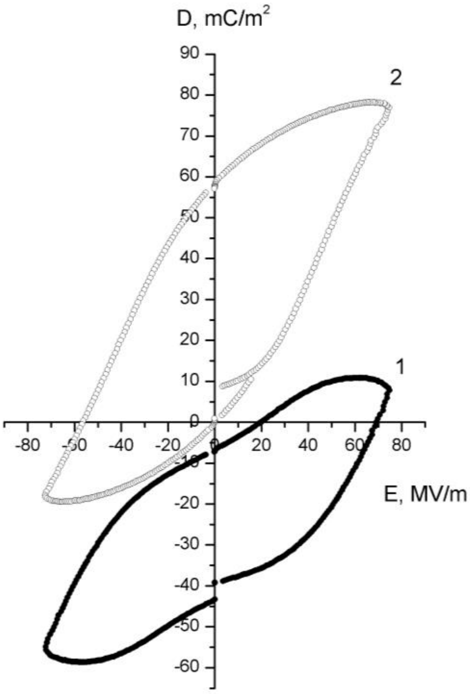


Fig. 8 Changes in the shape of the hysteresis curve on the original film series II (1) after 60 cycles of the bipolar polarization (2); *f*=30 mHz

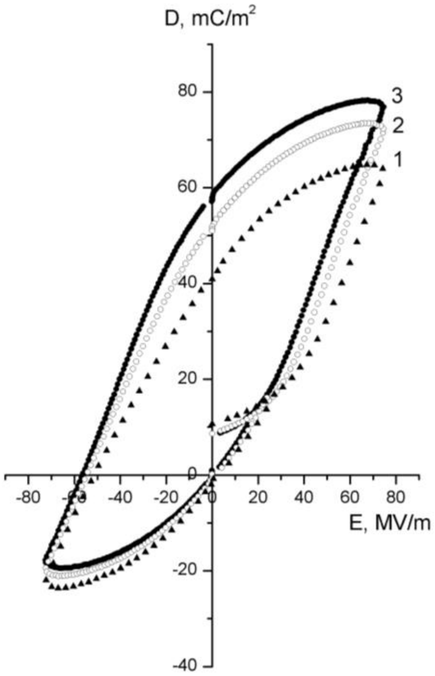


Fig. 9 The shape of the hysteresis curve in the film after 60 cycles of polarization, measured with different frequencies:1, 2 and 3 respectively 120, 50 and 30 mHz

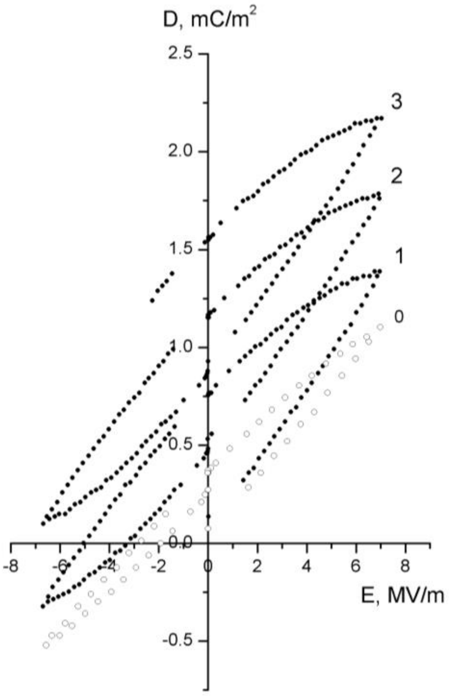


Fig. 10 Hysteresis loops obtained in the field below the coercive; *f*: 0 - 190 mHz, 1,2,3 three successive polarization cycles at 80 mHz

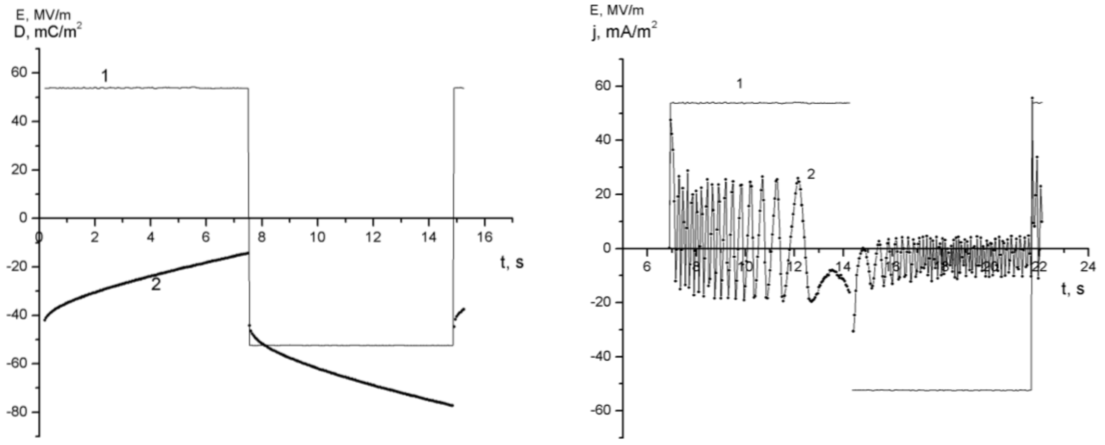
of negative potential on the surface of the poling film. This effect is observed only if the later is not subjected to short circuit. The data of Fig. 7 proof this statement. It is seen that the process of "short circuit" leads to sharp reduction of electret potential. As it is seen from Fig. 8, the number of polarization cycles (ceteris paribus) can greatly change the hysteresis curve if the external field is stronger than the coercive one. The form of the loop becomes closer to a common one with the asymmetry, which is opposite to the original curve (1). As it follows from Fig. 9, the loop, resulting from multicycle polarization, significantly depends on the frequency of the bipolar external field. Fig. 10 shows that the hysteresis phenomenon can occur when fields are substantially lower than coercive ones.

4. Discussion

Thus, the data show that the shape of the hysteresis curves greatly depends on the prehistory of the sample. Obviously, one should distinguish between two types of curves: two-stage hysteresis curves with constant negative potential (Fig. 4) and "classic" ones with positive potential (Fig. 9). Their transition from one to another can be realized through the stage of the multi-cycle polarization by the bipolar field (Fig. 8). We associate this with the high-voltage conductivity. The role of the latter can be seen at poling by the external field in the form of rectangular pulses (Fig. 11).

As can be seen, the process of polarization contains two components: fast and slow ones, as noted earlier (Seggern and Fedosov 2002, Seggern and Fedosov 2004). The time dependence (*D*) for imperfect ferroelectric materials (including polymers) with finite conductivity σ, can be described by equation (1) (Wang *et al*. 1988, Nalva 1995).

$$D = D_l + D_c + D_F = \varepsilon\varepsilon_0 E + \sigma t^m E + 2P_r\left[1 - \exp\left(-\left(\frac{t}{\tau}\right)^n\right)\right] \quad (1)$$

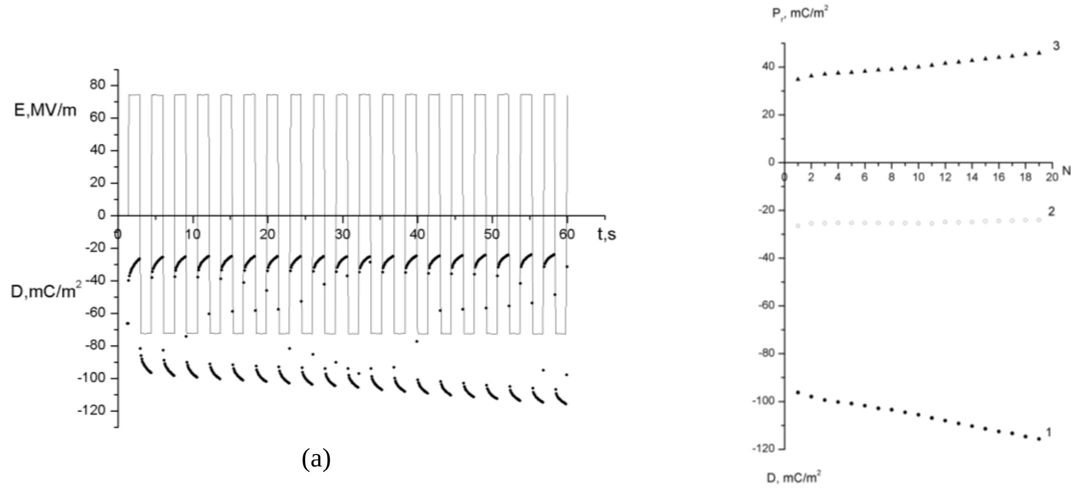


(a) (b)

Fig. 11 The time dependence of the charge (a) and current (b) response under applied bipolar field in the form of rectangular pulses with a frequency of 70 mHz on series II films where n and m are constants. The first and the second terms of the equation are related to the linear response and the contribution of the conductivity σ to the electric displacement D, respectively. The third one describes switching of remnant polarization P_r in ferroelectric domains with characteristic time τ (Wang *et al.* 1988, Nalva 1995, Kochervinskii 1999, Furukawa 1989). When polarization switching processes are studied, various methods are used to exclude the contribution of the first two terms to the D value (Seggern and Fedosov 2002, Seggern and Fedosov 2004, Dickens *et al.* 1992). In the present work such corrections are not introduced, because the aim was to determine the role of high-voltage conductivity on polarization processes. The analysis of curves $D(t)$ (Fig. 11) shows that the slow stage of polarization is well described by the second term of Eq. (1), where $m<1$ for all cases.

As for the mechanism of the copolymers conductivity, it should be taken into consideration that they belong to the class of crystalline polymers. So, at least amorphous and crystalline phases are present. The copolymers studied belong to the class of flexible-chain polymers with glass transition temperature of −40℃. Therefore, at the room temperature, the cooperative micro-Brownian segment mobility of the amorphous phase has the reorientation frequency of 10^6–10^7 Hz (Kochervinskii *et al.* 2007). As a consequence, the disordered phase has an increased free volume available where charge carriers are localized. In this regard, their migration over regions of the amorphous phase will be controlled by the cooperative mobility of surrounding macromolecules segments. The carriers accumulation process on the borders of amorphous phase with ferroelectric crystals will characterize formation of the space charge. The achievement of their equilibrium state requires time comparable with Maxwell relaxation time $\tau = \frac{\varepsilon_a \varepsilon_0}{A\sigma}$ (ε_a is permeability of the matrix and A is a form factor).

In the case of low carriers mobility $\tau \gg t_p$ (the duration of one pulse), an increase in the number of pulses (N) will lead the system to the equilibrium state. If this hypothesis is true, growth of N



(a)

(b)

Fig. 12 (a) The time dependence of the charge response in the film II under applied series of rectangular pulses with a frequency of 300 mHz (b) Effect of polarizing pulses number on electrical induction for negative (1) positive (2) polarity field and the remnant polarization (3) will change parameters of the slow poling stage. Fig. 12 confirms the above hypothesis. Indeed, the electric displacement magnitude decreases with increasing number of poling pulses (Fig. 10(a)). It is seen from Fig. 12(b), that while *D* changes only slightly during the positive half-cycle (curve 2), in negative half-cycle, its visible decrease is noticed (curve 1). As a result, growth in the number of poling pulses leads to a noticeable increase in the remnant P_r polarization (curve 3, Fig. 12(b)). The experiment has been carried out with the use of the film of series II with high initial negative potential (Fig. 12(a)). Therefore, these data can be compared with those shown in Fig. 4 related to the same films. It is seen that an increase in the period of bipolar triangle poling field (which is equivalent to increasing of the number of rectangular pulses) is accompanied by loop expansion through the shift of its borders to the negative *D* values.

When considering features of high-voltage conductivity, the geometry of the plane capacitor with the uniform electric field has been taken into consideration. In this case, one-dimensional current density with the vector directed along the perpendicular to the film surface (x-coordinate) can be taken into account. In the case of the time-depended field, the equation for the total current j in a ferroelectric polymer has the following form

$$j(t) = j_c(x,t) + j_p(x,t) + \varepsilon\varepsilon_0 \frac{\partial}{\partial t} E(x,t) \qquad (2)$$

where three terms characterize the “free” carriers current density, the polarization current of bound charges and the displacement one, respectively. The contribution of the latter part of the current can be observed in the explicit form at the low field when the polarization current contribution is small. Despite the spread in data, it can be seen from Fig. 3(b) that a change in the derivative sign is accompanied by the sign change of the current. It is proved by insert into this figure (see the insert in this figure).

From Figs. 5(a), 5(b) it can be seen that there is a critical field at which current oscillations appear which are higher at the anode side rather than at the cathode one.

It is known little about the nature of intrinsic carriers, though they are usually considered to be the remnants of the catalyst, etc. At high fields some other factors may lead to an additional effect. In polymers, chemical changes in their chains induced by the field may take place (Robejko *et al.* 1981, Zakrevskiy and Sudar 1990, Zakrevskiy and Sudar 1998, Zakrevskiy and Sudar 2013, Kao and Tu 2003, Li *et al.* 2003, Averkiev *et al.* 2009, Vettegren *et al.* 2010). In the polymers studied, additional carriers, containing fluorine atoms, can appear, too (Felix-Vandorpe *et al.* 1985). Their concentration is supposed to be high, since at elevated temperatures giant low frequency dielectric dispersion is found to appear due to relaxation of the space charge formed by such carriers (Kochervinskii *et al.* 2007, Kochervinskii *et al.* 2010, Kochervinskii *et al.* 2010). Another source of additional carriers is connected with phenomena of carriers injection from the electrode material to polymers (Lachinov *et al.* 2004, Ionov *et al.* 2007, Zakrevskiy and Sudar 1992, Zakrevskiy and Sudar 2005, Zakrevskiy and Slutsker 2009, Chen *et al.* 2001), in particular, into fluorine-containing polymer ferroelectrics (Hofman and Fuhrmann 1981, Hofman and Fuhrmann 1986). Appearance of current oscillations (Fig. 3(a), (b), 9(b)) is explained by injection of additional carriers from the electrode material. Similar oscillations were previously observed in the copolymer of VDF with hexafluoropropylene (Kochervinskii 2011) and in other polymers (Kochervinskii *et al.* 2011, Swan 1967, Toureille 1978). All phenomena observed can be associated with those with the negative field coefficient of conductivity (Toureille 1976, Swaroop *et al.* 1971, Zhao *et al.* 2012, Levis and Llewellyn 2013, Wintle 1986). As noted below, current oscillations at the positive field are higher than those at the negative one (Fig. 3(a), 3(b), 9(b)) which is in good agreement with earlier data (Mizutani 1984). Besides, this work shows that the thermodepolarization current at positive polarization potential is always higher than that at negative one.

It is known that the character of the surface topography can significantly affect the probability of injection processes. Fig. 13 shows the surface AFM images of the investigated samples which is rough. Appearance of roughness in the film surface may result in local field concentrating in some parts of the film, and therefore serves as an additional factor, facilitating carriers injection. From our data (Figs. 5(a), 5(b), 11(a)), large time intervals between neighboring points of the curves did not allow to characterize the full curve form of the signal in the digital form. Therefore, it was analyzed by a signal in the analog form. The current is shown to be of the form of a distorted sinusoid with the frequency of several kHz where the signal amplitude at the positive polarity is always higher than that at the negative one. This is confirmed by the value of the signal in the digital form (Fig. 11(b)). It is noteworthy, that the current oscillations are observed in the fields close to the coercive ones. It is not excluded that ion gas emission products are also registered, because their appearance is noticed at the same fields (Bihler *et al.* 1987). From inserts to Figs. 3(a), 3(b), it can be seen that the holes injection arises at lower fields than that of electron ones. In our opinion this is a feature of organic polymers, where there is a high probability of ionization of macromolecules, being in contact with the metal (Zakrevskiy and Sudar 1992, Zakrevskiy and Sudar 2005, Zakrevskiy and Slustker 2009, Zhao *et al.* 2012, Levis and Llewellyn 2013).

Thus, the carrier injection from electrodes and gaseous emission of charged fragments of polymer chains at high fields can change the concentration of carriers. Therefore, the standard

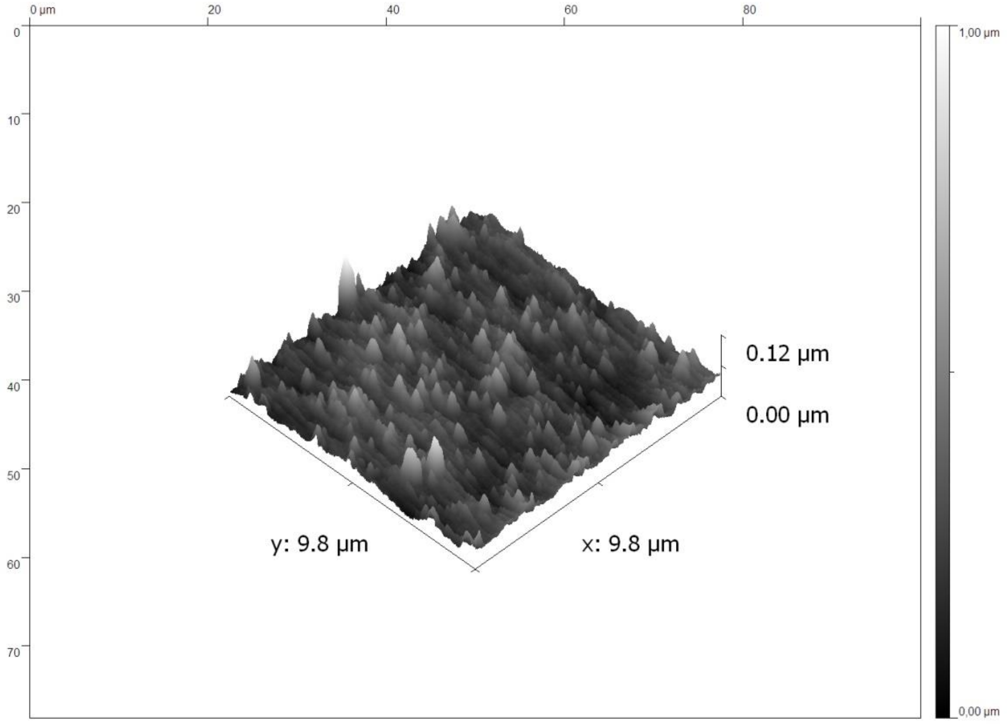


Fig. 13 Topography of the copolymer oriented film surface topography

expression for the current j_c with one type of a carrier must have the following form

$$j_c(x,t) = en(F,x,t)\mu(x,t)F(x,t) - eD\frac{\partial}{\partial x}n(F,x,t), \tag{3}$$

where e is a carrier charge, n and μ are their concentration and mobility; F, x, and t are field strength, coordinate and time, respectively. As it follows from Eq. (3), carrier concentration is a function of the field strength, coordinate and time. D is a parameter (usually the diffusion coefficient), which describes the probability of ejected carriers back to the electrode. In these terms, the above-mentioned current oscillations can be attributed to injection of carriers into the polymer (positive current values) and their ejection to the metal (a negative current value).

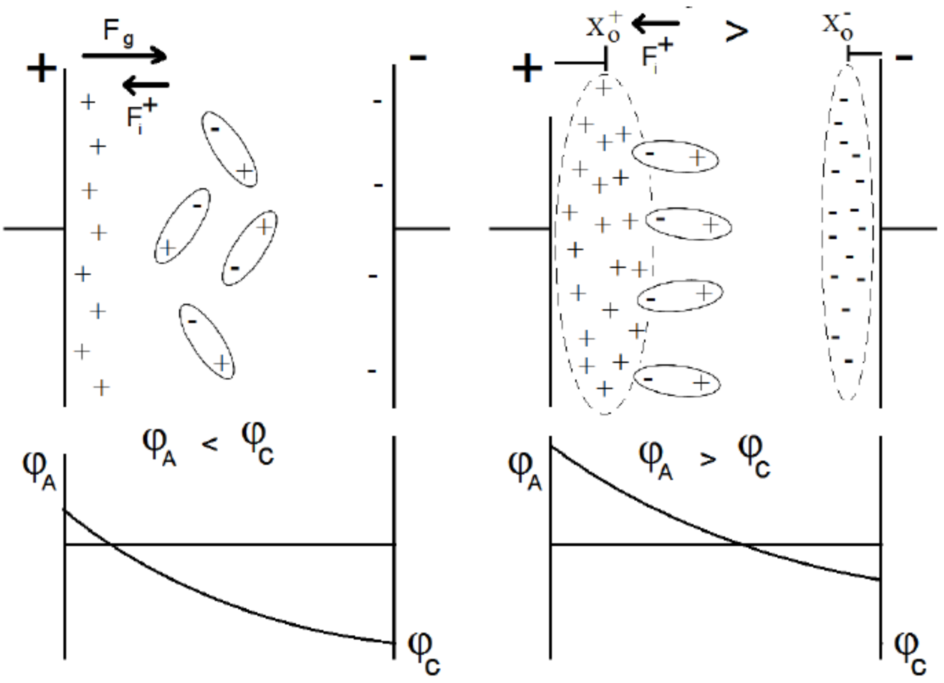
Since the carriers in the polymers have low mobility (Gross *et al.* 1985), one should expect a local increase in the concentration of carriers at the boundary with the electrode. If this non-uniform charge distribution is characterized by the volume density $\rho(x)$, then in the dielectric with thickness of d and ε permittivity of amorphous phase, the strength of the field created by these charges has the following form

$$F_i(x) = \int_0^d \frac{\rho(x)}{\varepsilon\varepsilon_0}dx \tag{4}$$

It should be remembered that the field of injected carriers near the electrode F_i will be directed against the external one. This means that the effective field $F(x,t)$ will be lower than the source field $F_g(t)$.

If it is accepted that hole injection is preferable with respect to electron one (Figs. 5, 11(b)), then at the first stage of poling, $F_i(x,t)$ value near the anode would be lower than that near the cathode. In accordance with Eq. (5), the local field $F(x,t)$ from the cathode side will be higher than that from the anode one. In other words, in this case, the external field near the anode will be screened more effectively. It is shown schematically in Fig. 14(a). The space charge generated on the anode side will not be in equilibrium, as holes should move to the cathode. Because of the low mobility of carriers, it requires much time which exceeds the period of the external field. Therefore, the package of hole carriers formed will be for some time in a quasi-equilibrium state. In this situation, at relatively low fields, the higher potential near the cathode will lead to electron injection in the polymer. These electrons are captured in traps, and surface gains negative electret potential (Fig. 6, curve 2). In the next poling cycle, this negative potential increases (Fig. 6, curve 3) due to an increase in injected electrons concentration. The same conclusion follows from the data of Fig. 12(b), where an increase in negative potential with increasing a number of poling pulses is observed.

Traps for such electrons must be shallow, about ~0.025 eV deep (kT at room temperature). As it follows from Fig. 7, the negative potential on sample 1 (which was poled by a number of cycles without short circuit) become practically zero after short circuit. Apparently, disappearance of negative potential is caused by the current, arising due to release of electrons from shallow traps (thermodepolarization of homocharge). Our data allow understanding the nature of shallow traps. Data of *x*-ray photoelectron spectroscopy XPS for the copolymer studied are shown in Fig. 15. It is seen that sputtering of the Al electrode material on the polymer is accompanied by appearance of new surface functional groups in the form of Al-C bounds and Al_2O_3. Similar changes have been previously found in the copolymer of VDF with HFP (Kochervinskii 2011) and also in polyethylene (Kochervinskii *et al.* 2011). Marked new functional groups are chemical defects for



(a) (b)

Fig. 14 The distribution scheme of the injected carriers and the potential across the thickness of the polarizable film at low (a) and high (b) voltage

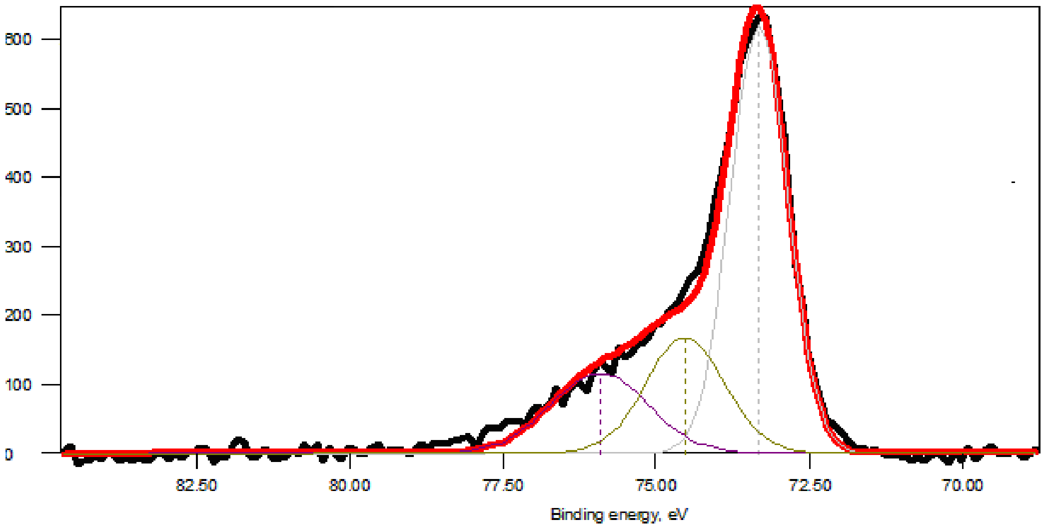


Fig. 15 Al 2p line of aluminum layer with a thickness of 2 nm deposited on the copolymer film surface

main bonds of the copolymer and therefore can be considered as traps for electrons (Meunier *et al.* 2001, Tu and Kao 1999). Such chemical defects must be locate near surface, due to they are registered by the XPS method (Fig. 15) where the signal in the surface layer is limited by the depth of 2-4 nm. Taking in to account surface roughness, package density of noted defects will be low. As a consequence, the electron traps depth is low.

As follows from Fig. 8, the kinetic factor in formation of the equilibrium space charge plays a significant role. It is seen that after 60 poling cycles (sample 2), the hysteresis curve changes cardinally in comparison with that of sample 1. The curve becomes more “classic”, but shifted along the *y* axis upwards. It is seen from Fig. 5(a), that at such fields injection of electrons also takes place. Thus, a space charge will form from the cathode side also. A great number of poling cycles at relatively high external field leads to shifting of the space charge packet near the anode in the direction of the cathode. Accordingly, the packet near the cathode must move to the anode. In other words, the configuration of the resulting field will be determined both by the number of carriers in the packet, and the drift mobility of electrons and holes. We believe that electron mobility is lower than hole one. This is connected with the presence in chains of the copolymer fluorine atoms, which are strong electron acceptors. All this fact must result in reduction of the effective mobility of electrons in the matrix of the copolymer. It should be remembered that a negative charge in these polymers can be transported not only by electrons, but also by F^- ions (Felix-Vandorpe *et al.* 1985). According to work by Bihler *et al.* (1987), the latter appear in the volume of the film due to destruction of PVDF molecules induced by the field. The resulting drift mobility of negative charges in this case will diminish at least due to the large size of fluoride ions.

Thus, during the long poling process in strong fields, centroids of space charges near the anode and cathode will be displaced to the center of the sample. Accordingly, fields changes (ΔF) near the anode (+) and cathode (−) can be expressed as follows (Tu and Kao 1999)

$$F_i^+ = \frac{Q_{tr}^+}{\varepsilon}\left(1-\frac{x_0^+}{d}\right) \qquad\qquad F_i^- = \frac{Q_{tr}^-}{\varepsilon}\left(1-\frac{x_0^-}{d}\right) \qquad (6),$$

x_0^+, x_0^- - coordinates of the centroids of space charge Q_{tr}^+ Q_{tr}^- captured on traps from respectively the anode and cathode.

Since the carriers forming the space charge will be replaced in the field with increased free volume. i.e., in the amorphous phase, the ε_{am} - its dielectric constant.

As follows from Eq. (5), the space charge field will determine the degree of screening of the external field. If hole carriers have higher mobility than electrons, at high fields and long poling times, x_0^+ coordinate will be higher than x_0^- one (Fig. 14(b)). As follows from Eqs. (5) and (6), this means that the potential at the anode will be higher than that at the cathode (Fig. 14(b)). As a consequence, remnant polarization in the sample on the anode side will be higher than that on the cathode one (Fig. 9). For the polymers studied, it is shown that values of piezo - and pyroelectric coefficients are proportional to the magnitude of the remnant polarization (Furukawa 1989). According to our data, one should expect non-equivalence of noted signals from different sides of polarized films. The validity of such conclusion is confirmed by works where for polarized PVDF film, both the signal of pyroresponse (Tahakashi *et al.* (1977)) and piezo-resonance phenomena (Sussner and Dransfeld (1978)) are higher from the anode side.

At high electric fields and a great number of poling cycles, structure improvements must take place, which is realized by a gradual orientation of polar lattice planes in the direction of the normal to the film surface (Kochvervinskii 2006). In other words, it corresponds to formation of heterocharge formed by bound charges of polar crystals. In our opinion, traps for “free” carriers become more “effective” because the perpendicular to polar surfaces of the crystals will coincide with the direction of the current density vector of these carriers. Taking into account the above consideration, let us refer to Fig. 9. It is seen that a reduction in the frequency of the bipolar poling field leads to expanding the hysteresis curve from the side of its positive values. Thus, even if the sample is in the "stabilized" polarization state, there is a contribution of space charge fields in the shape of the hysteresis curve. It was announced almost 40 years ago about the decisive role of the surface charge in phenomena of piezoelectricity (Murayama 1975, Murayama *et al.* 1975). Our data show that injected carriers manifest themselves in ferroelectricity phenomena in more complex way.

There are several articles (Wang *et al.* (1988), Nalva *et al.* (1995), Kochervinskii (1999)) where detection of the second ferroelectric phase is mentioned. It is believed that this phase is less perfect, and therefore it has a lower Curie point. Consequently, the lower coercive field can be expected for this structure. Hysteresis curves presented in Fig. 10 are obtained at fields, approximately an order of magnitude lower than it is usual for PVDF (about 50 MV/m). It can be seen, that even in such fields, hysteresis phenomena are clearly pronounced, although the remnant polarization is much less than it is usually observed in PVDF (Wang *et al.* 1988, Nalva *et al.* 1995, Kochervinskii 1999). In our opinion, the cause of these phenomena lies in peculiarities of crystalline polymer morphology. It is known th*et al*ong with large crystals, an ordered region can form between them due to secondary crystallization (Neidhofer *et al.* 2004). For the fluorine-containing ferroelectric polymers, such secondary crystals are also found (Kochervinskii *et al.* 2007, Neidhofer *et al.* 2004, Kochervinskii *et al.* 2013). These crystals are of small size and low perfection, which is proved by small values of fusion enthalpy (Kochervinskii *et al*. 2007, Neidhofer *et al*. 2004, Kochervinskii *et al*. 2013). This circumstance and data of Fig. 8 indicate that domains of the second (weakly-perfect) ferroelectric phase should be localized in ordered fields generated by secondary nucleation. It can be noted that the second (weak) pyroelectric response found in PVDF earlier Rollik *et al.* (1999) was connected with the amorphous phase. We think that these phenomena should be explained by the response of the weakly-perfect regions formed during secondary crystallization to the thermal pulse.

5. Conclusions

Formation mechanisms of non-usual curves of dielectric hysteresis in ferroelectric polymers such as vinylidenefluoride and tetrafluoroethylene copolymers have been considered, taking into account the contribution of high-voltage conductivity to processes of polarization. The analysis showed that at fields near the coercive ones, there are current oscillations in the films studied. We connect these phenomena with injection of carriers from the electrode to the polymer. It was found that tunneling barriers for hole carriers turned out to be lower than those for electrons. It resulted in hysteresis curves to be observed against the background of the negative electret potential of the film surface. By short circuit experiments with polarized films, it was found that traps for injected electrons were less than 0.02 eV deep. To explain the nature of such traps, the data of the x-ray photoelectron spectroscopy were used. Chemical changes in the surface of the copolymer during the deposition of Al electrode material were observed.

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