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## The Study of Temperature Transitions in PVDF with Different Structure.

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### ABSTRACT

Studied the molecular mobility of PVDF by the method of dielectric spectroscopy. It is shown that during the crystallization of the film from acetone is not formed spherulites, which are usually characteristic of PVDF. In the glass transition region was two relaxation processes, one of which is above the glass transition, and the other below the glass transition, i.e. in the glassy state. Discovered that for the first process marked by high values of enthalpy and entropy of activation. At high temperatures it is noted that the relaxation process can be described by combined process of mobility. It is formed by the overlap of the cooperative mobility (above the glass transition) and local mobility (lower glass transition point). Discovered that the activation parameters affect the nature of the response field of high tension.

**Keywords:** Poly(vinylidene fluoride), dielectric loss, relaxation, X-ray diffraction, crystallinity

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## INTRODUCTION

Poly(vinylidene fluoride) is a convenient model material for studying molecular mobility in crystallizable polymers, having the additional advantage that the effects of polymorphism are highly pronounced in PVDF [1]. A specific feature of PVDF and its copolymers is that they show ferroelectricity [2, 3]. In these materials, some ferroelectric characteristics are determined not only by the parameters of the crystalline phase but also by the dynamics of cooperative motion forms of the disordered phase [2]. Such characteristics of the amorphous phase also manifest themselves in the mechanism of piezoelectricity that appears in these polymers [4]. In this connection, revealing the salient features of the cooperative mobility in these polymers seems to be a demanding problem.

Despite the fact that the dynamics of molecular motion in polymers have been studied in some works [5, 6], many details relevant to this problem remain unclear. In this work, we made emphasis on revealing the role played by the supermolecular organization type in the PVDF glass transition region. The relaxation processes in PVDF are usually studied on samples obtained through crystallization from solution in some solvent. In our case, the PVDF sample subjected to study was obtained by precipitation from acetone, which is an unconventional solvent for this purpose. The low affinity of the solvent to the polymer allowed films with a specific (nonspherulitic) morphology to be formed. Earlier, using the 94 : 6 vinylidene fluoride–tetrafluoroethylene copolymer with a similar morphology as an example, we observed an increase in the activation parameters of the combined  $\alpha_a$ - $\beta$  mobility process [9]. These activation characteristics seem to be important as they determine the parameters of forced elastic relaxation on the one hand and the characteristics of ferroelectric hysteresis on the other hand [9]. The investigation of these processes will allow us to substantiate the earlier advanced hypothesis that the amorphous phase in the materials of interest is primarily localized in an interphase layer with a mesomorphic ordering type [9].

## EXPERIMENTAL

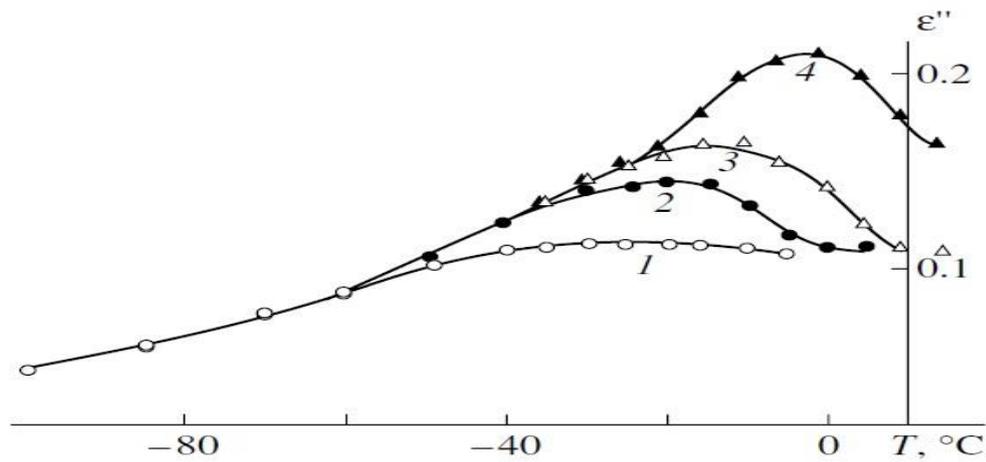
The subject of study was a PVDF homopolymer of the F2E brand (ONPO Plastpolimer, St. Petersburg) characterized earlier [10] and containing “wrong” linkages in an amount of 5 mol %. The films were prepared through crystallization from solution followed by vacuum drying. Structural studies were performed using the techniques of IR spectroscopy [11], X-ray diffraction, and small-angle scattering of polarized light. The dielectric properties were studied with a TR-9701 device over the frequency range of 30 Hz to 100 kHz. The measurements were made in the isothermal mode with temperature maintained with an accuracy of 0.5°C. Electric hysteresis was measured with a Sawyer–Tower circuit-based device powered by 50-Hz ac

## RESULTS AND DISCUSSION

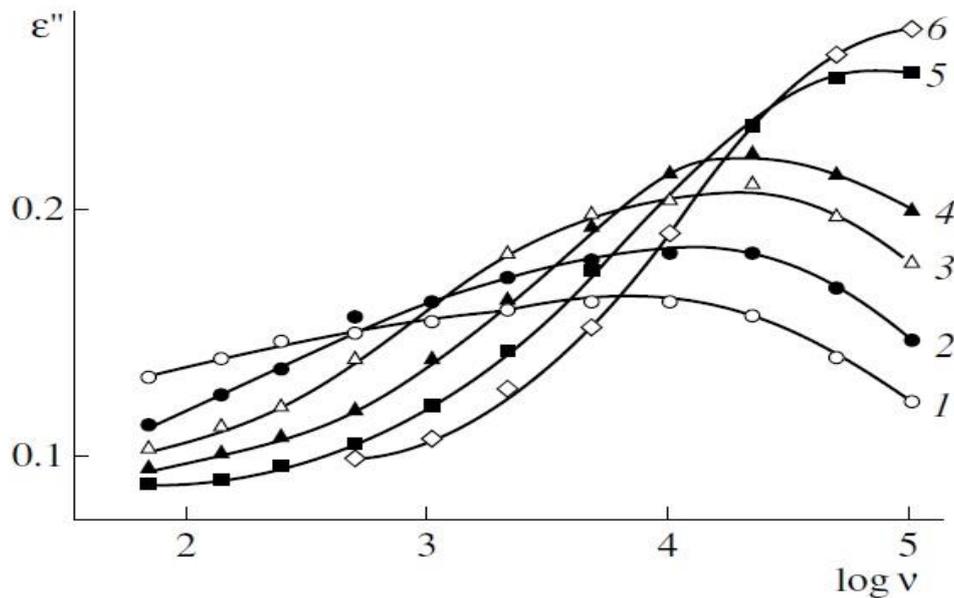
Figure 1 depicts isochronous curves for the dielectric loss  $\epsilon''$ . They show asymmetry and the coincidence of their low-temperature branches at different frequencies of the electric field. Such a coincidence for loss factor curves was also observed for the 94 : 6 VDF–TFE copolymer [9], although this effect is not characteristic of single relaxation processes. The line shape of the frequency dependence of  $\epsilon''$  is asymmetric in the low-frequency region at low temperatures (Fig. 2, curves 1–3). The analysis of the line shape for dielectric loss curves in both isochronous (Fig. 1) and frequency (Fig. 2) plots indicates the occurrence of two relaxation processes near the glass transition point. Their temperature–frequency position was determined by graphical separation of the experimental curves. The presence of two processes with close parameters was also indicated by the  $\epsilon''$ – $\epsilon'$  plots in the complex plane. In the vicinity of the glass transition temperature, the experimental data are described in the best manner by assuming the presence of two overlapping dispersion regions, each being characterized by a symmetric distribution of relaxation time.

From the parameters of arc segments formed by the data points in complex plots, the most probable relaxation times (reorientation frequencies) of these processes were determined. Their temperature dependences are shown in Arrhenius coordinates in Fig. 3b. It is seen that the two processes have different activation energies. The low-frequency motions (with the higher activation energy) were attributed to micro-Brownian motion in the disordered phase ( $\alpha_a$ -dispersion) since their freezing-in temperature lies in the glass transition region [1]. The Arrhenius plots for this process are known to be nonlinear [12]. However, as is seen from Fig 3b, this is not the case in our experiment.

There are several reasons for this disagreement [9]. One of them is that the observations were made at insufficiently high temperatures when the curve could be approximated by a straight line. Weak nonlinearity of this dependence is due to a special state of the amorphous phase in crystallizable polymers [13]. This circumstance also affects the characteristics of dielectric relaxation in crystallizable polymers in the glass transition region [14–16]. Crystallization results in a decrease in the free volume, with simultaneous broadening of its size distribution [17]. Since the value of the free volume affects the relaxation times of micro-Brownian motion, this leads to a shift of the  $\alpha$ -process to higher temperatures [14, 16]. It may be assumed that the crystal surface creates certain steric hindrances to the growth of the local free volume in the amorphous phase with increasing temperature [17].



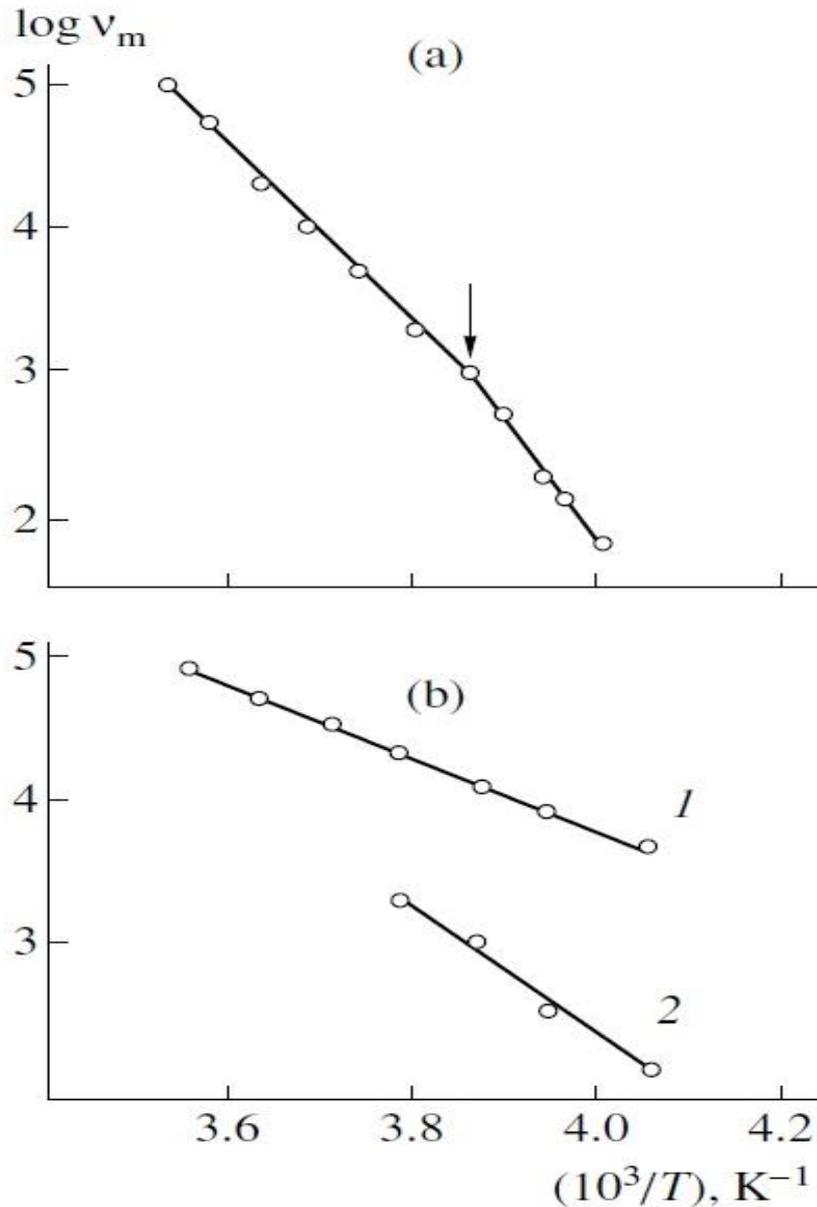
**Fig. 1.** Isochronous dielectric loss curves for an isotropic PVDF sample at frequencies of (1) 40 Hz, (2) 120 Hz, (3) 1 kHz, and (4) 10 kHz.



**Fig. 2.** Dielectric loss vs. frequency plots for the isotropic PVDF sample:  $T =$  (1)  $-20$ , (2)  $-15$ , (3)  $-9$ , (4)  $-4$ , (5)  $8$ , and (6)  $12^\circ\text{C}$ .

Since the  $\alpha$ -process is characterized by cooperative rearrangements that require free volume [12, 18, 19], a decrease in the size of a cooperatively rearranged region with increasing temperature must be expressed to a less extent in crystallizable polymers. In addition, the amorphous phase in PDVF can reportedly [9, 20] be realized in the form of an interphase layer of mesomorphic ordering type. The dynamics of chains in

such regions have to resemble the dynamics in a polymer crystal. For crystallizable polymers, the relaxation motions in the crystalline phase are always described with the Arrhenius equation. Then, the mobility in the mesomorphic regions of the noncrystalline phase can be described by a similar equation (see Fig 3b and the experimental data from [21]).



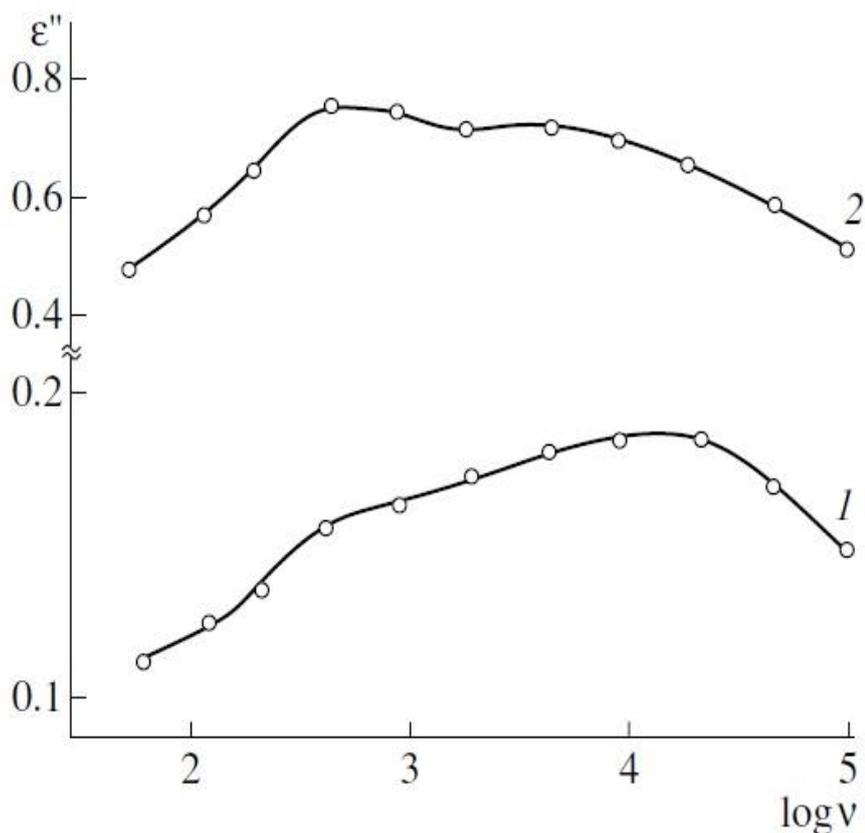
**Fig. 3.** Relaxation maps for the isotropic PVDF sample as obtained from (a) the isochronous and (b) the frequency dependence of dielectric loss: (1)  $\beta$ -process and (2)  $\alpha_a$ -process. For details, see the text.

The high-frequency  $\beta$ -process, as shown in Fig. 3b, also obeys the Arrhenius equation, although it is characterized by a lower activation energy. Earlier, it was noted that its intensity increased with an increasing degree of crystallinity [9, 22]. In this connection, the kinetic units responsible for  $\beta$ -relaxation are localized either in a crystal or in the region adjacent to the crystals. It seems that their occurrence in the latter region is more probable. The character of these regions should reflect the specific features of the amorphous phase in crystallizable polymers [13]. To date, numerous experiments, including those performed using the technique of dielectric spectroscopy [14, 16], have shown that there must be two types of the amorphous phase, isotropic and anisotropic. The latter is frequently called the rigid amorphous phase, and it resembles a crystal

in its dynamic behavior. A certain indicator of its presence in crystallizable polymers is an increased value of the acoustic modulus  $E_s$  above the glass transition temperature [13]. It is in the samples of the 94 : 6 VDF–TFE copolymer with an increased  $E_s$  value (3.6 GPa at  $T = 20^\circ\text{C}$ ) that the maximum intensity of the  $\beta$ -process was observed. In the homopolymer examined,  $E_s$  turned out to be even higher, 5 GPa, at the same temperature [11]. If we assume that the degree of crystallinity and elastic properties are identical in the copolymer and homopolymer, the fraction of the rigid phase in the homopolymer must be higher. Figure 4 collates frequency dependence curves for  $\epsilon''$  of both samples at the coexistence temperatures of the  $\alpha$ - and  $\beta$ -dispersion regions. Despite the strongly differing values of  $\epsilon''$  in the two films, the transition from the copolymer to homopolymer is accompanied by redistribution of the shape of the curves in a consistent manner. The  $\epsilon''$  value in the copolymer appears to be higher for the low-frequency  $\alpha$ -process than for the high-frequency  $\beta$ -transition, whereas the converse is observed in the homopolymer.

Thus, two relaxation processes occur in the glass transition region, one associated with the isotropic (mobile) amorphous phase and the other (high-frequency) related to anisotropic (rigid) disordered regions. The latter regions, most probably, occur along the boundaries with crystals whose surfaces create steric hindrances [13].

A decrease in the conformational entropy of chains in these regions does not necessarily lead to cooperative rearrangements, and motions become more localized and require a lower activation energy (Fig. 3b).

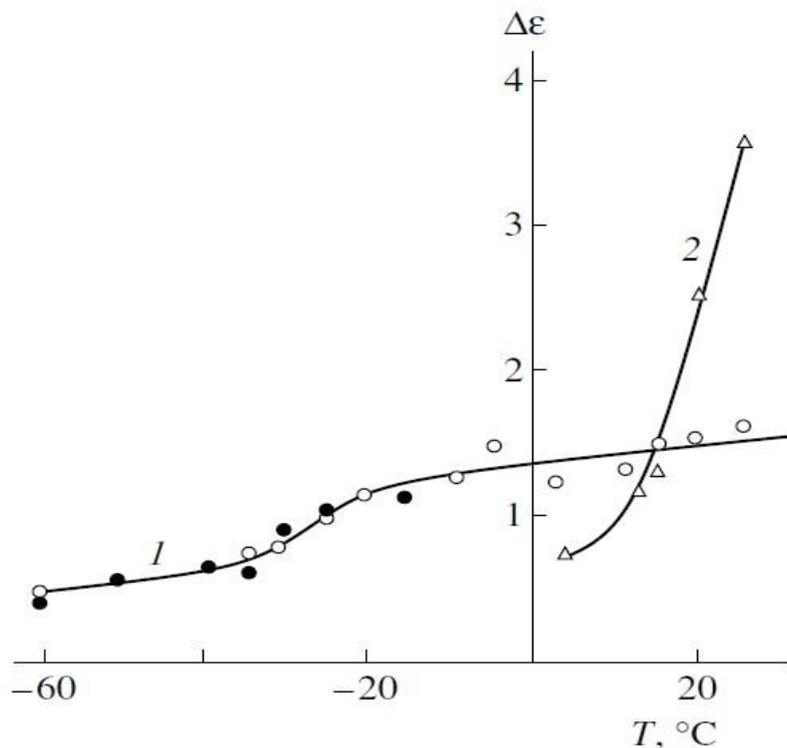


**Fig. 4.** Comparative dielectric loss–frequency curves in the temperature region of coexistence of the  $\alpha$ - and  $\beta$ -transitions for the (1) homopolymer ( $-15^\circ\text{C}$ ) and (2) 94 : 6 VDF–TFE copolymer ( $35^\circ\text{C}$ ).

Since the temperature dependence of  $\alpha$ -dispersion relaxation times has a finite curvature over a wide temperature range, the relaxation times of both motional processes will become equal and experimentally indistinguishable at a certain temperature [18, 19, 23]. For cooperative  $\alpha$ -transition, elevation of the temperature is accompanied by a decrease in the magnitude of cooperativity because of the weakening

of intermolecular interactions [12, 19] and, in the region above the glass transition temperature when its activation parameters become comparable with those for the localized mobility, we may talk about a certain joint (combined)  $\alpha_a$ – $\beta$ -process [18]. It is impossible to determine the characteristics of this process from the frequency dependences of  $\epsilon''$  because of the limited frequency–temperature interval. However, certain information on this process can be obtained from the isochronous dependence of the loss factor (Fig. 1). Due to the closeness in the relaxation times of the two processes, their presence is detected only in the abnormal merging of low-temperatures wings of the  $\epsilon''(T)$  curves for different electric-field frequencies. Such merging is untypical of single relaxation processes [24] and indirectly points to the presence of two inseparable processes. From the isochronous plots, it is possible to construct relaxation maps, which are represented in Fig. 3a. As is seen from Fig. 3a, there is a kink in the linear dependence at a certain temperature (marked by the arrow), which corresponds to a change in the activation energy. This is due to the fact that the low-temperature (high-frequency)  $\beta$ -process becomes comparable with the  $\alpha_a$ -transition in relaxation time. Above this temperature, the joint  $\alpha_a$ - $\beta$ -process will exist, which can be characterized by the activation parameters as given in Table 1.

From the aforementioned  $\epsilon''$ – $\epsilon'$  plots in the complex plane, values for the relaxation intensity  $\Delta\epsilon = \epsilon_0 - \epsilon_\infty$ , where  $\epsilon_0$  and  $\epsilon_\infty$  are the static and high-frequency dielectric permittivities, respectively, were determined. Figure 5 shows the temperature dependence of  $\Delta\epsilon$  for both of the processes. The values of  $\Delta\epsilon$  for another, high-temperature or  $\alpha_c$  process, which will be discussed below, are also given there. From the data presented in Fig. 5, we see that  $\Delta\epsilon$  values for the  $\alpha_a$ -process are very low (a few times lower than, e.g., in the VDF–TFE copolymer [9]) and comparable with those for the  $\beta$ -process. As a consequence, the data points, although with some scatter, fit to the same curve. The curve resembles in its pattern the one obtained for the 94 : 6 VDF–TFE copolymer [9]. Nearly linear dependences show two kinks each. One occurs at the glass transition temperature and the other appears in the temperature region of overlapping  $\alpha_a$  and  $\beta$ -processes.



**Fig. 5.** Relaxation intensity as a function of temperature for the isotropic PVDF sample: (1)  $\alpha_a$ -process (open circles) and  $\beta$ -process (closed circles) and (2)  $\alpha_c$ -process.

The change in the slope of the  $\Delta\epsilon(T)$  curve in the glass transition region corresponds to the freezing-out of qualitatively new degrees of freedom with high cooperativity of the kinetic unit [12, 18, 19]. The appearance of the characteristic point in this curve at a higher temperature can indicate the occurrence of a certain transition. Taking into account that the joint (indistinguishable in the relaxation time)  $\alpha_a$ - $\beta$ -process appears in this temperature region, this transition can be dynamic in character [18]. Two characteristic points in the  $\Delta\epsilon(T)$  plot are qualitatively consistent with the data reported in [25], which shows that the slope of the temperature dependence for the specific volume of PVDF changes approximately in the same temperature regions. As in our case, one of these points occurred at the glass transition and the other was associated with the appearance of a new type of motion in the crystalline regions ( $\alpha_c$ -dispersion). Thus, the high-temperature transition in the cited work can also be considered to be dynamic.

It may be assumed that the characteristics of the combined  $\alpha_a$ - $\beta$ -transition and the freezing-out temperature of the  $\alpha_c$ -dispersion are related to one another. Localized motions ( $\beta$ -process) occur in the anisotropic regions of the amorphous phase at the boundary to the crystals. Therefore, the attaining of a certain intensity of the  $\alpha_a$ - $\beta$ -process can induce excitation of qualitatively new modes of motion in the crystal ( $\alpha_c$ -dispersion). As is shown in the preliminary data, certain dielectric abnormalities in the high-temperature transition region are also observed in Langmuir–Blodgett ultrathin PVDF films. It cannot be ruled out that these anomalies are also due to the aforementioned dynamic transition.

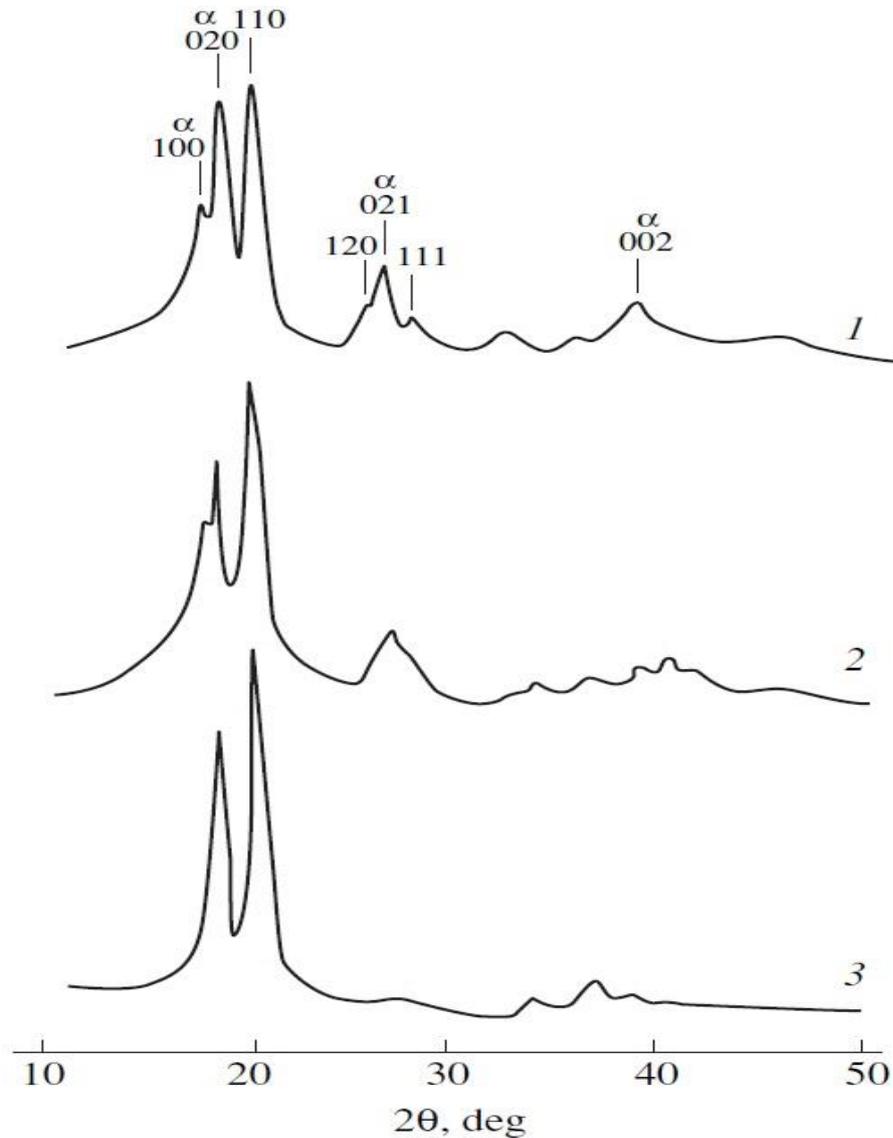
Below, we will consider how the specific features of the morphology formed in the film influence the characteristics of the observed relaxation processes. The low value of  $\Delta\epsilon$  for the  $\alpha_a$ -transition in the PVDF sample can be understood from Fig. 6, which represents X-ray diffraction curves for samples obtained through different techniques. For the films crystallized from melt, all characteristic reflections of the  $\alpha$ -phase are observed. For the sample obtained through quenching of the melt, the proportion of the amorphous phase has to increase. As has been noted above, the portion of the amorphous phase in PVDF (as the interphase layer) is mesomorphic in nature and has a lattice corresponding to paraelectric crystals [2]. Since the intermolecular reflection characteristic of these crystals occurs about the reflection 100 of the  $\alpha$ -phase crystals per se, an increase in the proportion of the amorphous phase in the quenched sample leads to an increase in the intensity and some broadening of this reflection (curve 2 in Fig. 6). As we can see in Fig. 6 (curve 3), the sample examined is characterized by an almost complete absence of the maximum in the region of the halo reflection 100. This means that the fraction of the amorphous phase in this sample must be smaller than in the samples obtained by crystallization from melt. The difference may be due to the low affinity of the solvent to the polymer when an increased concentration of nucleation sites is formed upon crystallization from solution. Due to steric hindrances by the neighbors, the crystals of the  $\alpha$ -phase do not necessarily reach a large size when the formation of fold surfaces becomes thermodynamically favorable (Table 1).

**Table.1. Activation parameters of low-temperature relaxation process in isotropic PVDF films**

| Process           | T <sub>g</sub> , °C | ΔE     | ΔH  | ΔS, e.u. |
|-------------------|---------------------|--------|-----|----------|
|                   |                     | kJ/mol |     |          |
| α <sub>a</sub>    | -37                 | 146    | 144 | 383      |
| α <sub>a</sub> -β | -44                 | 115    | 113 | 267      |

This is indicated by the data obtained in the measurements of small-angle polarized light scattering. For the films crystallized from melt, the depolarized scattering characteristic of spherulites are always observed [10]. For the films studied in this work, the H<sub>v</sub> and V<sub>v</sub> indicatrices suggest a fundamentally different type of morphology. An increased number of small crystals can lead to a specific state of chains in the noncrystalline regions. In particular, the number of taut tie molecules that form the aforementioned regions of the anisotropic amorphous phase is expected to increase in these noncrystalline regions. The high acoustic modulus mentioned above, which is very sensitive to the presence of taut tie molecules in the film, supports this assumption. Since these regions occur in the area of an increased mechanical stress, this may lead to a change in the conformational state in them as applied to PVDF. As the mechanical stress in PVDF chains

increases, the alltrans conformation becomes preferable [1]. According to the spectroscopic data [11, 26], the films examined indeed display bands at 510 and 840  $\text{cm}^{-1}$  characteristic of this conformation [1], the crystalline phase occurring in the  $\alpha$ -polymorph ( $\alpha_p$ ) with the TGTG<sup>-</sup> conformation of the chain (Fig. 5 in [26]). In addition, an increased number of chains in the T<sub>3</sub>GT<sub>3</sub>G<sup>-</sup> conformation, which is intermediate between the all-trans and TGTG<sup>-</sup> conformations, can be immobilized at a temperature above  $T_g$  and be disengaged from the relaxation process for the above reason. This means that the concentration  $N$  of mobile kinetic units is low and, in accordance with Eq. (1), leads to low values of  $\Delta\varepsilon$ :



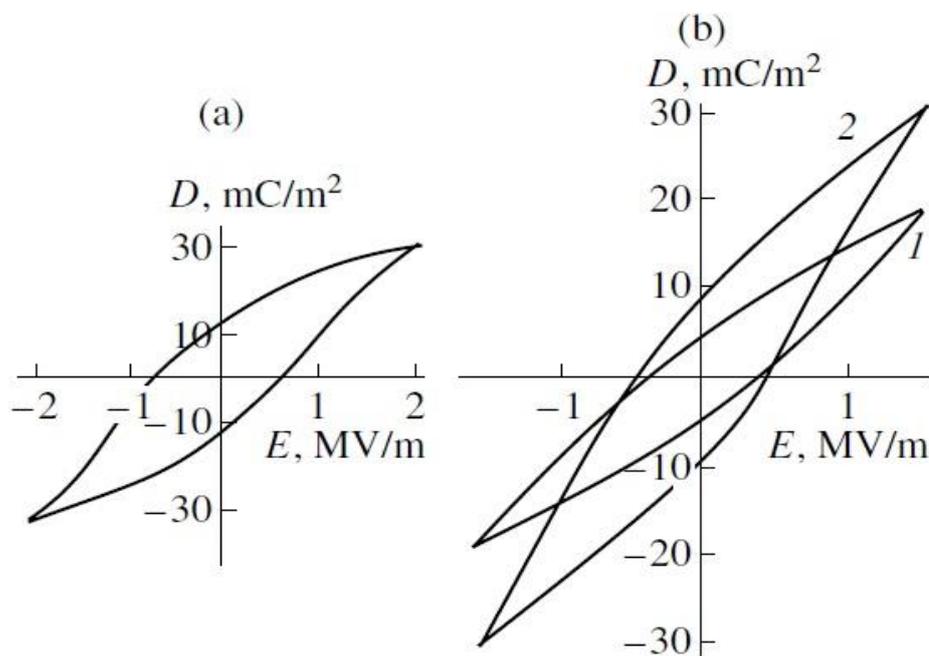
**Fig. 6.** X-ray diffraction curves for isotropic PVDF samples obtained through (1) slow crystallization, (2) quenching from the melt, and (3) precipitation from acetone solution.

$$\Delta\varepsilon = \frac{4\pi\xi N\mu_e^2}{3kT}, \quad (1)$$

where  $\xi$  is the factor of the local field and  $\mu_e$  is the effective dipole moment per monomeric unit. Thus, the situation in the homopolymer turns out to be similar to that observed in the 94 : 6 VDF–TFE copolymer [9]; in both cases, an increase in temperature facilitates an increase in  $\Delta\varepsilon$ , which may be attributed to an increase in the active concentration of dipoles according to Eq. (1).

The task of further analysis is to verify the earlier advanced conclusion on the influence of the type of supramolecular structure on the activation parameters of the  $\alpha_a$ - $\beta$ -process. Earlier, it was shown that the enthalpy  $\Delta H$  and the entropy  $\Delta S$  of activation of this process significantly increased in the case of nonspherulitic morphology obtained through crystallization from solution in a solvent with low affinity to the polymer [9]. In the same manner, these parameters were also calculated for the homopolymer. They are presented in the table. It is seen that the  $\Delta H$  and  $\Delta S$  values for the joint  $\alpha_a$ - $\beta$ -process turn out to be quite high, so that they approach those for the cooperative  $\alpha_a$ -process. It is of special importance that these parameters are almost identical to those of the 94:6 VDF-TFE copolymer of similar morphology. Thus, the formation of crystals with nonspherulitic morphology from a solution with a low solvent affinity to the polymer is accompanied by a considerable increase in the activation parameters of the combined  $\alpha_a$ - $\beta$ -process.

For the copolymer in question, it was shown that it is the high values of the activation enthalpy and entropy of the process under consideration that can limit some ferroelectric properties, in particular, the value of remanent polarization  $P_r$  [9]; this was examined for a sample of the homopolymer. For this purpose, a polarizing field was applied to a film at 20°C when the mobility was characterized by the joint  $\alpha_a$ - $\beta$ -process, whose activation parameters are given in the table. Figure 7a depicts a dielectric hysteresis curve for this film. First, it may be noticed that breakdown voltages for this film are almost twice as high as those for conventional (extruded and oriented) films [27]. This difference is another piece of evidence for there being a large proportion of chains with highly impeded motion at the polarization temperature. As follows from the data presented in Fig. 7a, despite the high polarizing field (2.1 MV/m), the values of the remanent and maximum polarization  $P_s$  is lower here than in samples with another morphology [27]. Thus, as in the VDF-TFE copolymer, the increase in activation parameters of the mobility process realized at the temperature of exposure to a high-strength field leads to a decrease in the ultimate values of induced polarization.



**Fig. 7.** (a) Electric hysteresis curves for an isotropic PVDF sample and (b) comparative electric hysteresis curves for an isotropic (1) homopolymer and (2) 94 : 6 VDF-TFE copolymer films as measured under identical polarizing-field conditions.

It is of interest to compare the structural characteristics of the homopolymer and copolymer. In the latter, crystallization occurs in the ferroelectric  $\beta$ -phase [1] with the all-trans conformation. As follows from the spectroscopic data [11, 26], the chains in the homopolymer films have predominantly the TGTG<sup>-</sup> conformation. This conformation is characteristic of the lattice of both its nonpolar ( $\alpha$ -) and polar ( $\alpha_p$ -) modifications; therefore, they are spectroscopically indistinguishable. The X-ray technique is more appropriate

for this purpose. Although the lattice parameters of these two phases are identical, the  $\alpha_p$ -form reveal the extinction of some reflections, in particular, the reflection 100 as one of the most intense reflections [1]. As seen from the data presented in Fig. 6 (curve 3), it is this reflection that is absent from the X-ray diffraction curve of the sample under study. Thus, the crystallization of the homopolymer under the conditions described above is accompanied by the formation of a polar ( $\alpha_p$ ) modification. Indirectly, this is also confirmed by the hysteresis curves (Fig. 7) as the appearance of hysteresis being due to the presence of spontaneous-polarization regions which are absent in the case of crystallization in the  $\alpha$ -modification with the nonpolar cell [1].

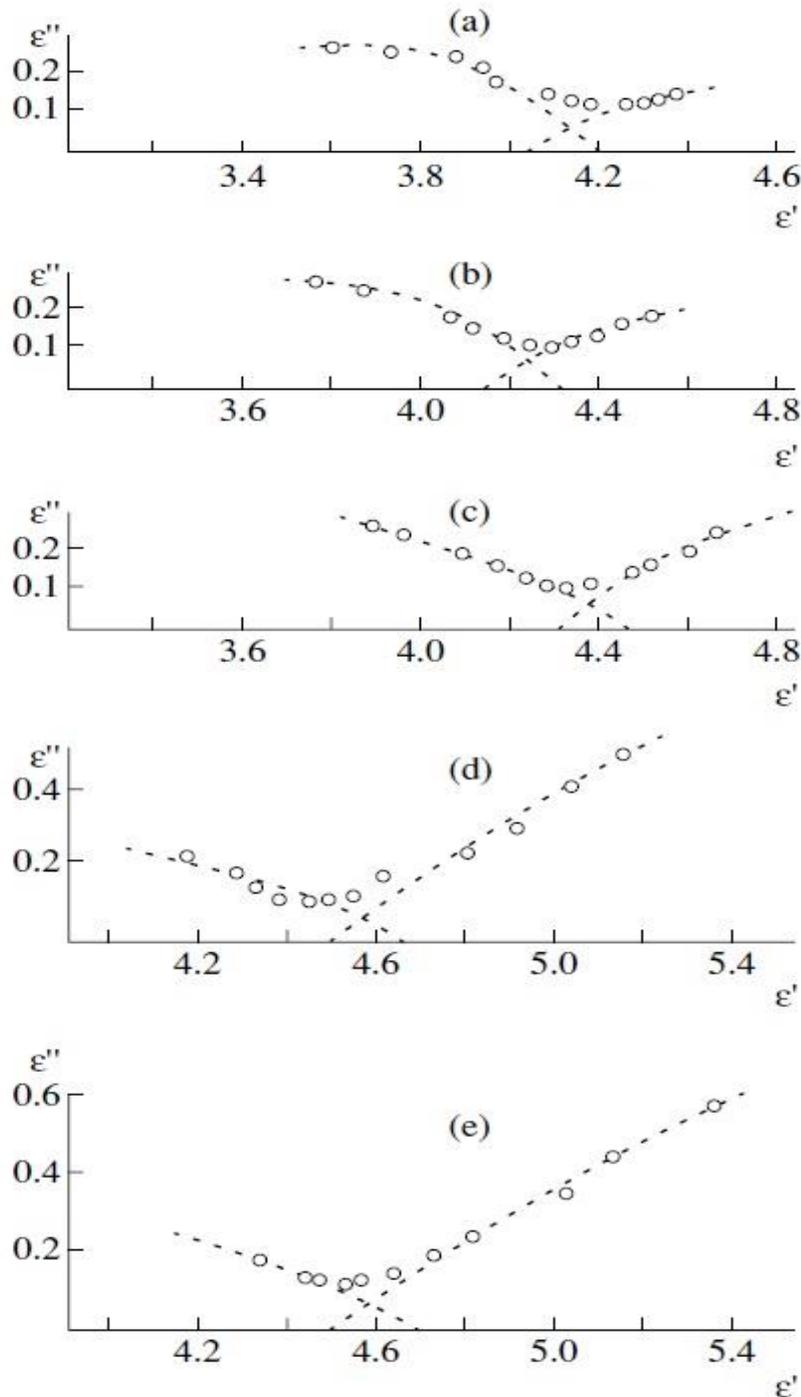


Fig. 8. Cole-Cole plots in the complex plane for  $\alpha_c$ -dispersion at (a) 8, (b) 12, (c) 15, (d) 20, and (e) 26°C.

Another indication of crystallization in the  $\alpha_p$ -modification can be the relaxation parameters measured. Figure 8 shows complex diagrams for the corresponding temperature region. It is seen that the  $\epsilon_0$  value for the low-frequency  $\alpha_c$ -dispersion increases with increasing temperature. Correspondingly, a rise in the relaxation intensity is observed for this process (Fig. 5). The analysis of the published data [1, 5] shows that this mobility region is associated with the crystalline phase. If crystallization occurs in the nonpolar  $\alpha$ -phase,  $\Delta\epsilon$  does not vary with increasing temperature in this dispersion region [5]. As is seen, another situation is observed in our case. The unusual growth in  $\Delta\epsilon$  with temperature can also be due to crystallization of PVDF chains in the polar  $\alpha_p$  phase.

## CONCLUSION

More proof of the presence of the latter in the initial state can be obtained from a comparison of the electric hysteresis parameters for a homopolymer film and the 94 : 6 VDF–TFE copolymer film studied earlier [9]. Figure 7b depicts comparative hysteresis curves for both films in a permanent polarizing field. The hysteresis curves greatly differ from classical curves as they do not reach the spontaneous polarization frequently met in this class of polymers [2]. It is seen that, despite the lower coercive field, the  $P_r$  and  $P_s$  values turn out to be lower for the homopolymer than for the copolymer. As shown earlier [9], the mobility parameters of the  $\alpha_a$ – $\beta$ -transition (realized at a sample polarization temperature) affect the generation and growth of domains of a new type. The comparison of the activation parameters for this transition in the copolymer [9] and the homopolymer (table) shows their resemblance.

Thus, this factor cannot explain the aforementioned difference between the ferroelectric characteristics of the samples compared. However, it should be taken into account that crystallization in both samples is accompanied by the formation of different lattices. The polar  $\beta$ -modification is formed in the copolymer, whereas the polar  $\alpha_p$ -form is predominantly formed in the homopolymer, as mentioned above. The  $\alpha_p$ -form is characterized by less dense packing, and its characteristic chain conformation TGTG<sup>-</sup> has a smaller dipole moment than the all-trans conformation of the  $\beta$ -phase [1]. All of this explains the lower values of  $P_r$  and  $P_s$  in the examined homopolymer films as compared to the copolymer.

The possibility of formation of isotropic PVDF in the  $\alpha_p$ -modification remains an open question. It is known that, for films obtained through crystallization from melt, such a structure is produced only via multistage thermal-field treatment. Analysis of the published data shows that, in the film formation from solution, the crystallization of PVDF in the  $\alpha_p$ -form is feasible. For example, when crystallization occurs in a mixture of the nonpolar  $\alpha$ - and polar  $\gamma$ -phase, the ratio between these phases in the film formed can depend on the conductivity of the solvent used [1, 28]. This finding was also independently confirmed in [29] for a copolymer which crystallizes from solution in a good solvent (DMSO). In that case, even within one forming film, regions that crystallize in both ferroelectric  $\beta$ -phase and nonpolar  $\alpha$ - or polar  $\alpha_p$ -phase [29] can be formed.

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