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Ferroelectric Polymers Based on Vinylidene Fluoride and The Processes of Structure Formation In Them.

Eugene V. Luchkin*, Anastasia S. Gadlevskaya, Sergey A. Bondarenko.

Joint Stock Company «Federal State Research and Design Institute of Rare Metal Industry» (Institute «GIREDMET»), 119017, Moscow, Russian Federation

ABSTRACT

The investigated copolymers of vinylidene fluoride with hexafluoropropylene in a variety of possible co-monomer. By x-ray diffraction at high angles is shown that the increase in the proportion of hexafluoropropylene is accompanied by a decrease of the crystal size in the direction of the reflex 002. By x-ray scattering at small angles it is shown that this long period increases. At the same time shows that the size of the amorphous gap between the neighboring crystals laminarnye more in the case of a copolymer with a high content of hexafluoropropylene.

Keywords: structure, ferroelectric polymers, relaxation, molecular mobility, fragility

**Corresponding author*

INTRODUCTION

The class of new crystallizing ferroelectric polymers based on poly(vinylidene fluoride) has been extensively investigated in recent years [1, 2]. These materials are convenient model objects for elucidating the mechanisms responsible for the manifestation of ferroelectricity in crystallizing polymers [3]. Owing to their high piezoelectric and pyroelectric activities, these polymers have been used in fabricating sensors with characteristics that cannot be obtained using classical materials [4]. As was shown earlier in [5, 6], the mechanism responsible for the manifestation of ferroelectricity in compounds of the given class is controlled primarily by the structural parameters. In this respect, investigation into the specific features in the formation of the crystal structure of these compounds is an important problem. It is known that, upon crystallization, the aforementioned polymer compounds exhibit polymorphism and that they can crystallize in at least four crystallographic modifications, namely, α , α_p , β , and γ . Polymer chains in the first two modifications are characterized by a TGTG⁻ conformation, whereas chains in the third and fourth modifications adopt the planar zigzag conformation and the T₃GT₃G⁻ conformation, respectively [7]. In the present work, we investigated how the introduction of hexafluoropropylene groups into the poly(vinylidene fluoride) chain affects the crystal structure.

SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

In the experiments, we used isotropic films prepared from poly(vinylidene fluoride) (F2É) and its copolymer with hexafluoropropylene. The microstructure of the chains in these polymers was previously characterized by ¹⁹F NMR spectroscopy [8]. Isotropic films of poly(vinylidene fluoride) were isothermally crystallized from a melt at a temperature of 150°C and a pressure of 150 atm. The vinylidene fluoride–hexafluoropropylene copolymer films of compositions 93 : 7 and 86 : 14 were prepared by extrusion and had virtually no texture. The structure of the films was determined using wide-angle x-ray diffraction on KARD-6 and KARD-7 diffractometers equipped with position-sensitive area detectors (CuK α radiation) [9]. The diffractometers were designed at the Shubnikov Institute of Crystallography of the Russian Academy of Sciences (Moscow, Russia). The size of coherent scattering regions in the direction normal to the *hkl* plane was determined from the Debye–Scherrer relationship 0.9 λ .

$$l_c = \frac{0.9k\lambda}{\cos\theta\sqrt{\beta^2 - \beta_e^2}}, \quad (1)$$

where k is the diffraction order; λ is the radiation wavelength; and β and β_e are the widths at half-maximum of the analyzed and reference lines, respectively.

RESULTS AND DISCUSSION

First and foremost, we discuss the data obtained for the homopolymer. Under the aforementioned crystallization conditions, we can expect the formation of the α polymorphic modification [7]. The x-ray diffraction patterns shown in Fig. 1 do in fact exhibit reflections characteristic of this phase. The separation of the overlapping reflections indicates amorphous halos of two types. One halo is observed in the range of reflections attributed to the interchain ordering, and the other halo is located in the range of reflections assigned to the intrachain ordering. According to the x-ray diffraction data, the degree of crystallinity is equal to 57%.

Next, we consider the formation of the structure upon introduction of bulky hexafluoropropylene substituents into the poly(vinylidene fluoride) chain. The x-ray diffraction pattern of the copolymer film containing 7 mol % hexafluoropropylene is shown in Fig. 2. A comparison of this x-ray diffraction pattern with the diffraction pattern of the homopolymer (Fig. 1) shows that the copolymer also crystallizes in the α phase. The analysis of the x-ray diffraction pattern separated into components demonstrates that, upon introduction of 7 mol % hexafluoropropylene into the poly(vinylidene fluoride) chain, the crystallization of the copolymer in the same phase is characterized by two features. First, the number of reflections attributed to the α phase decreases. Second, the sizes of coherent scattering regions along different directions in the crystal lattice are significantly reduced. These features become more pronounced as the hexafluoropropylene content in the copolymer increases. This is clearly seen from the data presented in the table 1. In particular, the longitudinal

size of the crystals, which is determined from relationship (1) for the 002 reflection, decreases by a factor of more than 2 when the hexafluoropropylene content 150 increases from 7 to 14 mol %.

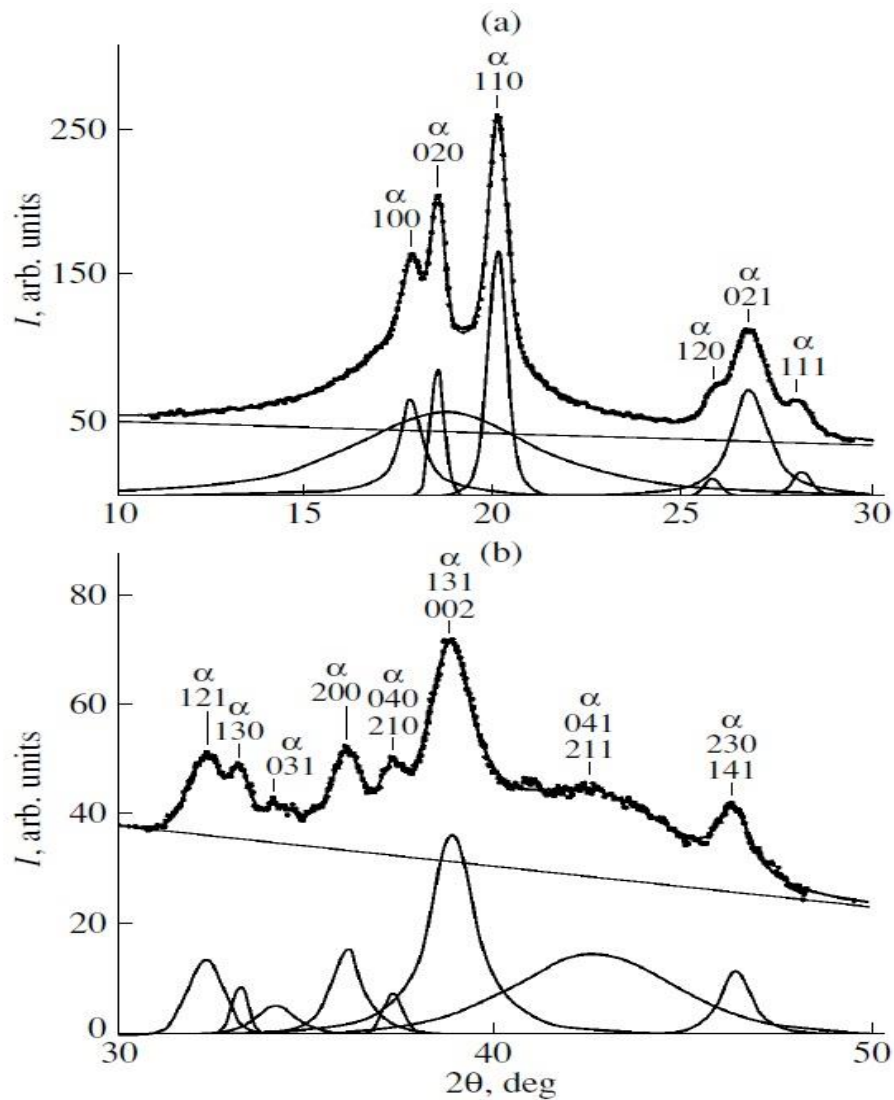


Fig. 1.

X-ray diffraction patterns measured in the ranges $2\theta =$ (a) 10° – 30° and (b) 30° – 50° for the isotropic poly(vinylidene fluoride) sample (F2É) prepared by isothermal crystallization from a melt at $T_{cr} = 150^\circ\text{C}$.

Table 1. Structural parameters for vinylidene fluoride–hexafluoropropylene copolymer films of different compositions

| Composition of the vinylidene fluoride–hexafluoropropylene copolymer | 93 : 7 | 86 : 14 |
|--|--------|---------|
| L, nm | 10.5 | 16.0 |
| l^{002}_α , nm | 2.9 | 1.4 |
| l_α , nm | 7.6 | 14.6 |
| φ_l | 0.28 | 0.09 |
| φ | 0.41 | 0.24 |

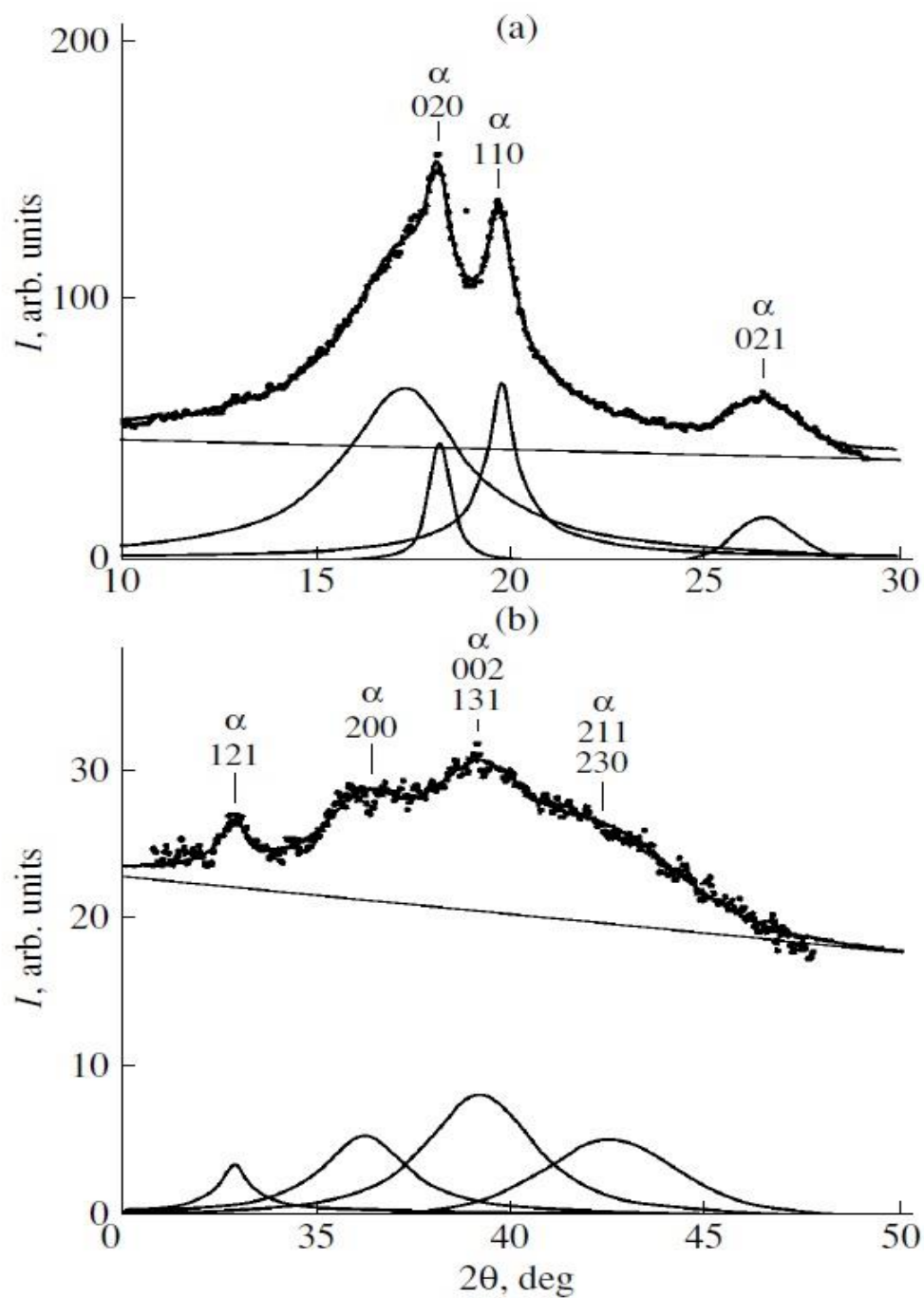


Fig. 2.

X-ray diffraction patterns measured in the ranges $2\theta =$ (a) $10^\circ - 30^\circ$ and (b) $30^\circ - 50^\circ$ for the extruded vinylidene fluoride-hexafluoropropylene (93 : 7) copolymer film.

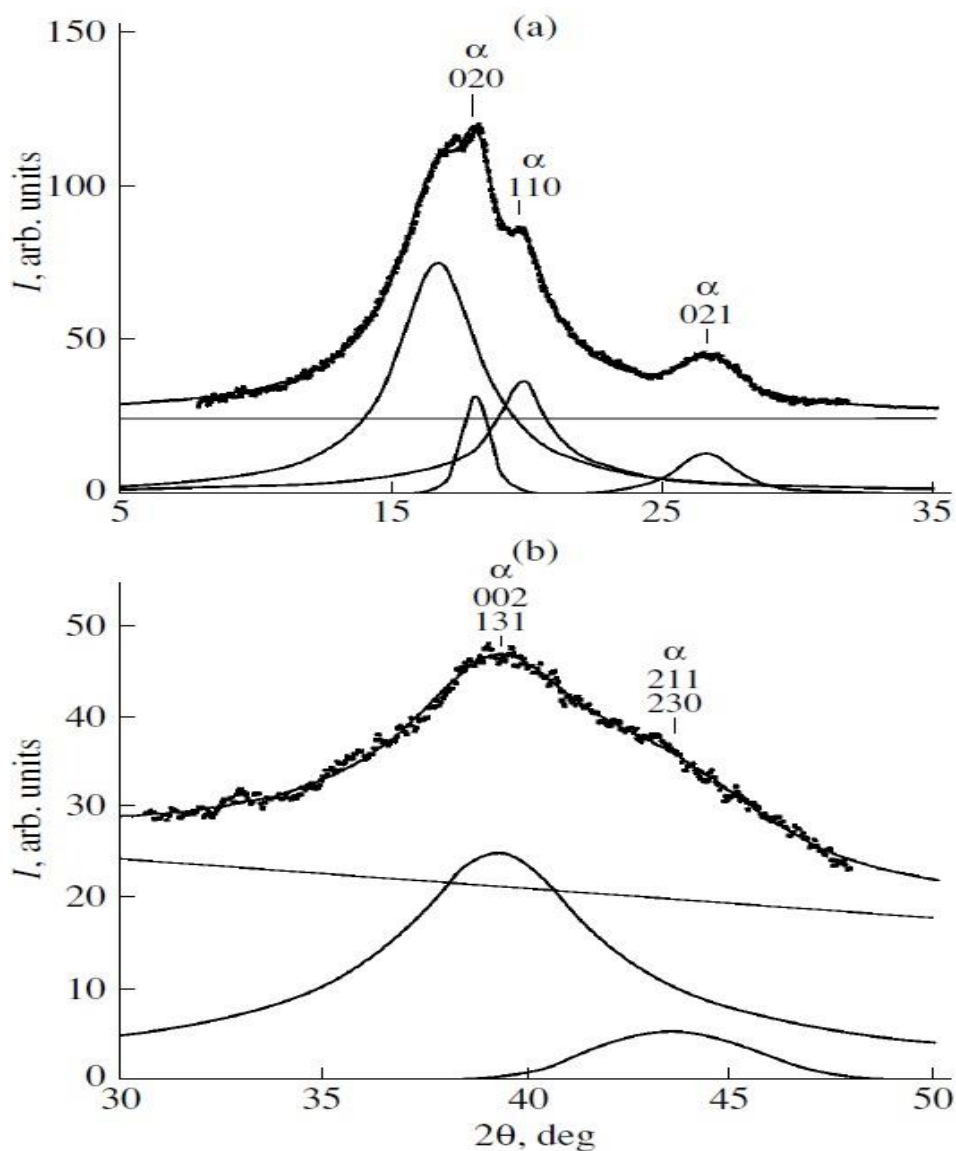


Fig. 3. X-ray diffraction patterns measured in the ranges $2\theta =$ (a) 5° – 35° and (b) 30° – 50° for the extruded vinylidene fluoride–hexafluoropropylene (86 : 14) copolymer film.

From analyzing the above results, we cannot answer reliably the question as to whether the copolymers under investigation can crystallize in the polar α_p modification. It is known that the unit cell and the chain conformation of the polar α_p modification are identical to those of the nonpolar α phase [7]. The differences are reduced to the changes in the intensity ratio of some reflections. Therefore, this analysis becomes impossible in the case when the perfection of the lattice formed in the structure of the copolymers is deteriorated as compared to that of the homopolymer.

The specific features of the formation of the amorphous phase in the copolymers are as follows. The halo reflection in the range of angles approximately equal to 18° can be assigned to the amorphous phase, as is the case with vinylidene fluoride–trifluoroethylene copolymers [10–13]. It can be seen from Fig. 1a that, in this range of scattering angle, the x-ray diffraction pattern of the homopolymer contains the 100 reflection and the amorphous halo is shifted toward larger angles. The characteristic feature of the halo for the copolymers is that it appears to be narrower than the halo for the poly(vinylidene fluoride) polymer. One more difference lies in the fact that the halo for the copolymers is considerably shifted toward smaller angles ($2\theta_M = 17.4^\circ$) as compared to the halo for the homopolymer ($2\theta_M = 18.7^\circ$). Under the assumption that there are amorphous halos of two types (as for the homopolymer), the calculated degree of crystallinity is equal to 0.41. When the mole fraction of the hexafluoropropylene comonomer in the copolymer increases by a factor of 2, the

reflections of the α phase become poorly distinguishable from the background of the intense amorphous halo (Fig. 3a). The reflections attributed to the intrachain ordering (Fig. 3b) are strongly broadened. This indicates that the above tendency toward a decrease in the size of coherent scattering regions becomes more pronounced. For the vinylidene fluoride–hexafluoropropylene (86 : 14) copolymer, the degree of crystallinity obtained only from the data on the scattering angles in the range 5° – 30° (Fig. 3a) is equal to 0.24. It should be noted that an increase in the hexafluoropropylene content in the copolymer from 7 to 14 mol % is accompanied by a further shift of the angular position of the amorphous halo toward the small-angle range ($2\theta_M = 17.0^\circ$). This implies that the introduction of bulky hexafluoropropylene substituents into the poly(vinylidene fluoride) chain leads to a change not only in the parameters of the crystal lattice but also in the packing of chains in the disordered phase. Formally, we can state that, upon introduction of the substituents, the higher the hexafluoropropylene content, the lower the packing density of chains in the amorphous phase. This inference is important for the understanding of the mechanisms responsible for the manifestation of the ferroelectricity revealed earlier in the films under investigation [8]. It was concluded that, in the structure of these copolymers, there should exist domains of spontaneous polarization, as could be judged from the appearance of an anomaly in the permittivity at a temperature of $\sim 50^\circ\text{C}$ for the vinylidene fluoride–hexafluoropropylene (86 : 14) copolymer. In the vinylidene fluoride–hexafluoropropylene (93 : 7) copolymer, this transition is shifted toward the high-temperature range [14]. Thus, there is a correlation between the packing density in the amorphous phase and the ferroelectric transition temperature.

CONCLUSION

As follows from the data presented in the table 1, an increase in the hexafluoropropylene content in the copolymer leads to a change in the morphology of the crystals. In [15], the interlamellarspacings l_a , i.e., the spacings between the neighboring lamellar crystals arranged in stacks, were calculated from the data on the large spacing L . It can be seen from the table that the interlamellarspacings are considerably larger in the copolymer with the higher hexafluoropropylene content. Let us also consider the difference in the degrees of crystallinity determined from the x-ray diffraction data in the wide-angle (φ) and small-angle (φ_L) ranges. It follows from the table that, for both copolymers, $\varphi > \varphi_L$. In the latter case, the fraction of the amorphous phase was estimated only from the contribution of onedimensional diffraction in the direction normal to the end surfaces. Therefore, we can draw the conclusion that part of lamellar crystals does not form stacks. It should be noted that the fraction of these crystals is higher in the vinylidene fluoride–hexafluoropropylene (86 : 14) copolymer.

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