

# Research Journal of Pharmaceutical, Biological and Chemical Sciences

## The Influence on The Supramolecular Structure of Crystallizing Ferroelectric Polymers the Magnitude of Dipole Interactions.

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### ABSTRACT

Using low angle x-ray scattering we studied the formation of supramolecular structures of copolymers of vinylidene fluoride with non-polar comonomers. Checked the value of a big period in the studied polymers obtained in various ways. Found that with decreasing values vnutricerepnogo dipole interaction, the magnitude of a large period increases. At the same time increasing the value mailmessage gap between the neighboring crystals.

**Keywords:** supramolecular structure, ferroelectric polymers, crystallizing structure, dipole

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## INTRODUCTION

Crystallizing ferroelectric polymers based on poly(vinylidene fluoride) have attracted the particular attention of researchers, because these materials possess remarkable electrical properties. Owing to their ferroelectricity [1] and the large values of the piezoelectric and pyroelectric constants [2], these polymers have been used in fabricating various types of sensors [3]. The aforementioned constants are determined, to a considerable extent, by the morphology. Hence, investigation of the morphology with variations in the chemical structure is of special interest. In this study, our attention was focused on the change in the large spacing due to the controlled variation in the intrachain dipole interactions in crystallizing polymers.

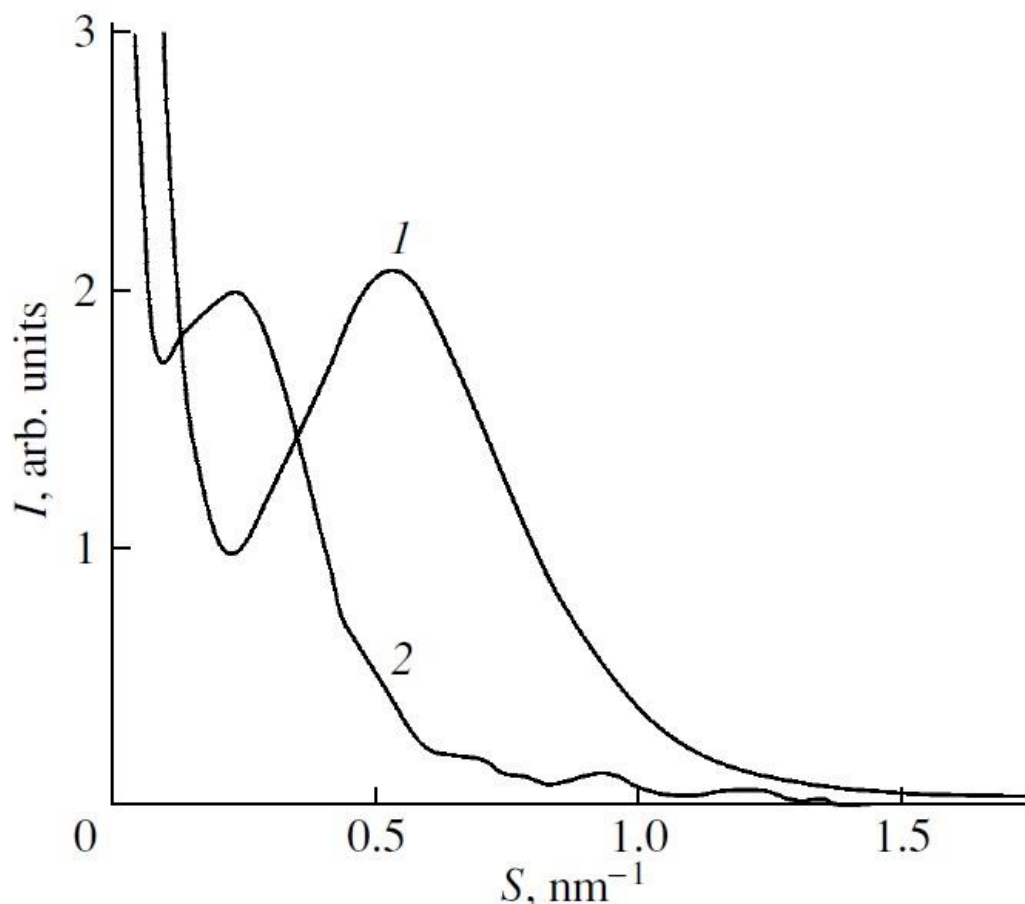
## SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

In the experiments, we used an F2Évinylidene fluoride homopolymer and its statistical copolymers with tetrafluoroethylene and hexafluoropropylene, which were previously characterized by  $^{19}\text{F}$  NMR spectroscopy [4–6]. We studied the vinylidene fluoride–tetrafluoroethylene copolymers with comonomer ratios equal to 94 : 6 and 71 : 29. Moreover, we examined the vinylidene fluoride–hexafluoropropylene copolymers with hexafluoropropylene contents of 7 and 14 mol %. The mean intrachain distances between strongly polarvinylidene fluoride units changed in both copolymers because of the nonpolarity of the tetrafluoroethylene and hexafluoropropylene groups. The measurements were performed with isotropic films of the vinylidene fluoride–tetrafluoroethylene (94 : 6) copolymer and also with extruded films of the vinylidene fluoride– hexafluoropropylene copolymer.

The morphology of the copolymers under investigation was examined using small-angle x-ray scattering on a diffractometer designed at the Special Design Bureau of the Shubnikov Institute of Crystallography of the Russian Academy of Sciences (Moscow, Russia). Since we used the slit collimation, the results obtained were recalculated to the point collimation. The data were represented in the  $S$ – $I$  coordinates, where  $S = 4\pi\sin\theta/\lambda$  is the scattering vector and  $I$  is the intensity. The large spacing  $L$  was calculated from the relationship  $L = 2\pi/S_{\max}$ , where  $S_{\max}$  is the scattering vector corresponding to the intensity at the maximum.

## RESULTS AND DISCUSSION

The small-angle x-ray scattering curves for the vinylidene fluoride–tetrafluoroethylene copolymer films of compositions 94 : 6 and 71 : 29 are compared in Fig. 1. These films were prepared by crystallization under different conditions. Both copolymers are characterized by interference maxima, whose positions were used to estimate the large spacing  $L$ . For the copolymer with a higher tetrafluoroethylene content, this spacing appears to be larger by a factor of greater than 2. It is known that the thermal prehistory can significantly affect the large spacing for crystallizing polymers [7], specifically in chain molecules of the class under consideration [8, 9]. For the latter polymers, the large spacing depends substantially on the annealing in the paraelectric phase, which can lead to a more than twofold increase in the large spacing [9]. The crystallization under elevated pressures can result in an even more significant increase (by more than one order of magnitude) in the large spacing [8]. In this respect, we studied more than ten samples of vinylidene fluoride–tetrafluoroethylene (94 : 6) copolymers crystallized under different conditions. However, it turned out that the large spacings in these samples are virtually identical to within the limits of experimental error. The data obtained for one of the many samples are presented in Fig. 1 (curve 1). It should be emphasized that the origin of the observed behavior of the large spacing  $L$  differs from that proposed, for example, by Tasaka and Miyata [8] and Legrand [9], who explained the increase in this parameter as resulting from the increase in the degree of crystallinity. Indeed, the samples for which the small-angle x-ray scattering curves are compared in Fig. 1 have nearly identical degrees of crystallinity but considerably different large spacings. Thus, it is surprising that the large spacings  $L$  in all samples of the vinylidene fluoride–tetrafluoroethylene (94 : 6) copolymer are close to each other, even though their thermal prehistories are different.



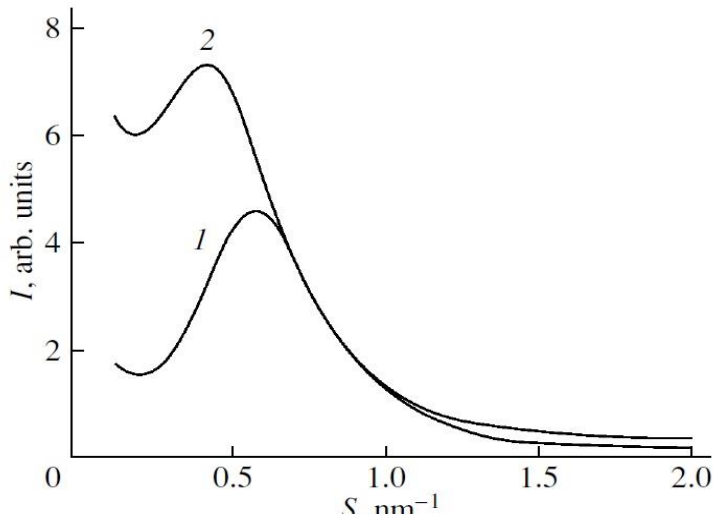
**Fig. 1.**

Comparison of the small-angle x-ray scattering curves for the isotropic vinylidene fluoride–tetrafluoroethylene copolymer films of compositions (1) 94 : 6 and (2) 71 : 29. The films were prepared by crystallization from dimethylformamide and acetone solutions, respectively.

### CONCLUSION

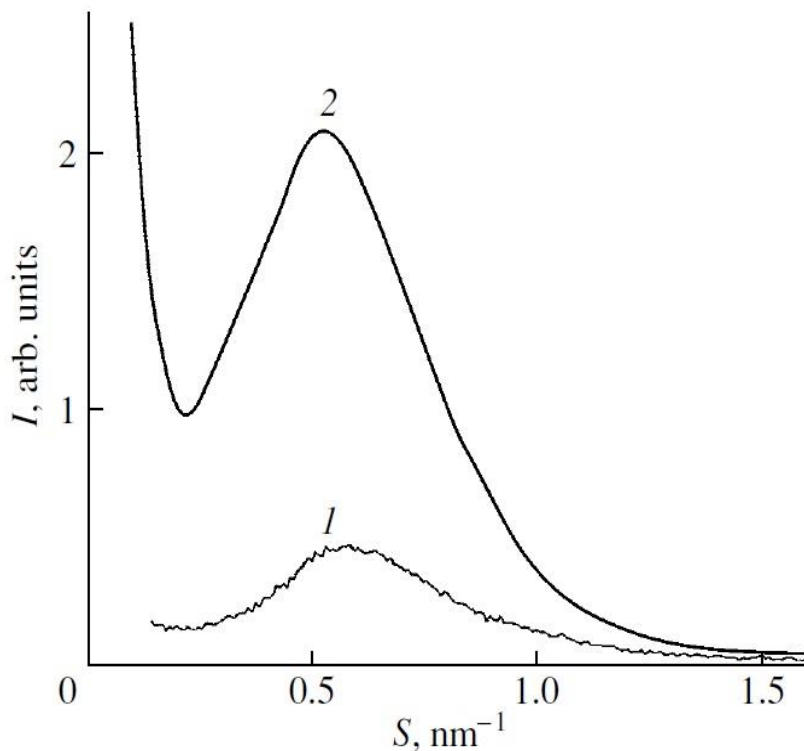
If the increase in the large spacing  $L$  with an increase in the tetrafluoroethylene content in the copolymer under investigation is caused primarily by the weakening of the intrachain dipole interactions, the corresponding dependence should be observed for copolymers with an intermediate component composition. Unfortunately, we had no such copolymers. However, we can invoke the small-angle x-ray scattering data obtained in [8] for a copolymer of similar composition, namely, the vinylidene fluoride–tetrafluoroethylene (80 : 20) copolymer. For the sample with a close degree of crystallinity ( $\varphi = 0.6$ ), the large spacing is equal to 20 nm, which is consistent with the proposed approach. Indeed, the large spacings  $L$  for the vinylidene fluoride–tetrafluoroethylene copolymers of compositions 94 : 6 and 71 : 29 are equal to 12 and 30 nm, respectively. The validity of our hypothesis can be independently verified using another homologous series, for example, vinylidene fluoride–hexafluoropropylene copolymers of different compositions. Figure 2 depicts the small-angle x-ray scattering curves for the vinylidene fluoride–hexafluoropropylene copolymer films. It can be seen from Fig. 2 that an increase in the hexafluoropropylene content in the copolymer leads to a shift of the diffraction maximum toward the small angle range. Therefore, as in the case with the vinylidene fluoride–tetrafluoroethylene copolymer (Fig. 1), an increase in the content of the nonpolar comonomer in the poly(vinylidene fluoride) chain results in an increase in the large spacing. Finally, we can analyze the small-angle x-ray scattering curves depicted in Fig. 3 for films of two different vinylidene fluoride copolymers. These copolymers contain different nonpolar comonomers (tetrafluoroethylene and hexafluoropropylene) in

approximately equal amounts (6 and 7 mol %, respectively). As can be seen from Fig. 3, the angular positions of the diffraction maxima (and, consequently, the large spacings  $L$ ) appear to be close to each other. This once again confirms the hypothesis that the intrachain dipole–dipole interactions play an important role in the structure formation during the crystallization of ferroelectric polymers.



**Fig. 2.**

Comparison of the small-angle x-ray scattering curves for the extruded vinylidene fluoride–hexafluoropropylene copolymer films of compositions (1) 93 : 7 and (2) 86 : 14.



**Fig. 3.** Comparison of the small-angle x-ray scattering curves for (1) the vinylidene fluoride–hexafluoropropylene (93 : 7) copolymer film and (2) the vinylidene fluoride–tetrafluoroethylene (94 : 6) copolymer film.

One more parameter characterizing the morphology formed upon crystallization is the interlamellar spacing  $l_a$ , i.e., the spacing between the neighboring lamellar crystals (arranged in stacks) in the direction normal to their end surfaces. To a first approximation, the interlamellar spacing  $l_a$  can be calculated from the formula  $l_a = L - l_{001}$ , where  $l_{001}$  is the longitudinal size of the crystal along the axis of the macromolecule. The corresponding crystal sizes upon crystallization of the film in the  $\beta$  and  $\alpha$  phases were determined from the broadening of the 001 and 002 reflections, respectively [10]. According to the estimates, the weakening of the intrachain dipole interactions always leads to an increase in the interlamellar spacing  $l_a$ .

#### ACKNOWLEDGMENTS

The article was prepared within the framework of the Federal Target Program (FTP) «Research and development on priority directions of development of scientific-technological complex of Russia for 2014-2020». The number of Agreements for the provision of grants: 14.576.21.0029, the unique project code: RFMEFI57614X0029.

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