

Effects of Stretching on Crystalline Phase Structure and Morphology of Hard Elastic PVDF Fibers

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ABSTRACT: The phase characteristics and morphology of stretched hard elastic poly(vinylidene fluoride) (PVDF) fibers were investigated by X-ray diffraction (XRD) and wide-angle and small-angle X-ray scattering (WAXS and SAXS). It was indicated that α and β phases coexisted in stretched PVDF fibers, stretching assisted in α to β phase transformation. The β/α ratios of stretched PVDF fibers were affected by stretching temperature, rate, and ratio. The β phase content of stretched PVDF fibers had an abrupt increase when stretched near 70°C, and then it decreased with increasing stretching temperature. Besides, the β/α ratio of PVDF fibers increased with stretching rate and ratio. The total crystallinity of PVDF fibers did not change much even on different stretching conditions. WAXS

results indicated that the unstretched and stretched PVDF fibers all exhibited three strong equatorial streaks, with d -spacing (0.964, 0.488, and 0.439 nm) and (0.946, 0.494, and 0.480 nm), which suggested that PVDF fibers still remained the crystalline reflections of c -axis orientation even after being stretched. The long periods of stretched PVDF fibers, calculated from SAXS curves, increased from 19.04 to 39.75 nm. On the basis of these results, the β transformation mechanism of stretched PVDF fibers was also discussed. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2254–2259, 2007

Key words: PVDF; fibers; crystal structures; morphology; stretching

INTRODUCTION

Having extraordinary mechanical properties and complicated polymorphism, poly(vinylidene fluoride) (PVDF) has been well known since the 1960s. There were at least four different crystallines including α , β , γ , and δ form in PVDF, which could transform from one to the other under certain conditions.^{1,2} Among the four crystalline forms, the most common polymorph was α form, which could be produced during crystallization from the melt. β form was the most important polymorph with outstanding piezoelectric and pyroelectric properties. The β crystal in PVDF could be obtained from nonpolar α modification by various processes such as mechanical deformation,^{3,4} poling under large electric fields,^{5,6} crystallization from the melt under high pressure,^{7–9} or very high cooling rates.^{10–12}

The β crystal phase also appeared in melt-spun PVDF fibers. Cakmak et al.¹³ found that the melt-spun PVDF fibers were polymorphic possessing both α and

β crystalline forms, with the β phase first occurring at spinning stresses of 3 MPa, and then the β phase increased in quantity with increasing spinning stress. It was suggested that the β phase was derived by a stress-induced phase transition from the melt. The crystal structure of PVDF fibers under deformation was also studied by Wu et al.,¹⁴ and it was found that the alternating necked and unnecked regions were aligned along the fibers and the α to β phase transformation were found during the deformation, in necked regions more α to β phase transformation took place than in unnecked regions. It was also suggested that the mechanism of α to β phase transformation might be due to the creation of defects during the crystallite breakage. In their studies, hard elasticity was not observed in PVDF fibers.

The mechanism of α to β phase transformation of PVDF materials during deformation was also discussed by several authors.^{3,4,15,16} Matsushige et al.⁴ studied the α to β phase transformation of PVDF with a tensile experiment found that PVDF sample necked upon stretching at room temperature and that the α to β phase transformation was observed by WAXD at the necked region. Thus, they pointed out that a heterogeneous stress distribution in the sample played a critically important role during α to β phase transition. Moreover, this transition occurred only in the region with the local stress higher than some critical stress. Another point¹⁵ suggested that the existing

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of defects in α phase may be the reason of α to β phase transition. A developed viewpoint^{3,16} indicated that this transformation was due to α_c transition/relaxation in PVDF, while the α_c transition/relaxation was related with molecular motions in the crystalline/amorphous interphase. Until now, the mechanism of the transition is still an open question.

Hard elastic PVDF fibers as a new material has been studied by our research group recently.^{17,18} In the fibers, stacked crystalline lamellae aligned in the direction normal to the fiber axis existed, which made the fibers have distinguished morphological and mechanical properties from other ordinary PVDF material. When the fibers were stretched, no necked and unnecked regions appeared along the fibers, which was different from ordinary PVDF fibers. Moreover, in hard elastic PVDF fibers, only α phase existed and it was essential to the formation of hard elasticity of the fibers. Hard elastic PVDF fibers can be used to prepare microporous membranes by further stretching, which will be reported in our following study. During stretching, the crystalline forms and morphology of hard elastic PVDF fibers would have great influences on the microporous structure and properties of PVDF membranes.

Concerning the control of the crystalline phase structure of hard elastic PVDF fibers during stretching is essential for preparing them into specific material, and the crystalline phase structure and morphology of the stretched fibers will be studied in the present article.

EXPERIMENTAL

Preparation of hard elastic PVDF fibers

SOLEF 1010 PVDF pellets, supplied by Solvay Solaxis Company (Brussels, Belgium), has a melt flow index of 6 (230°C, 5 kg), only α conformation is present. PVDF fibers were melt-spun from a melting extruder at 230°C. The diameter of the spinneret die was 2.5 mm. The melt-draw ratio was defined as the ratio of take-up speed to the extrusion rate; the fibers used in the stretching experiment have a melt-draw ratio of 200. The extruded fibers were taken up on a homemade roller and then annealed at 140°C; thus, the hard elastic PVDF fibers were obtained.¹⁷ The fibers with a length of 200 mm were mounted in the stretching equipment made by Zheda Hyflux Company (Hangzhou, China). Different stretching temperature and rate were applied. If no special explanation, the stretching temperature and rate were chosen as 90°C and 30 mm/min, respectively. After reaching final deformation, a homemade device with the taut samples was removed from the equipment and then heat set at 140°C for 30 min.

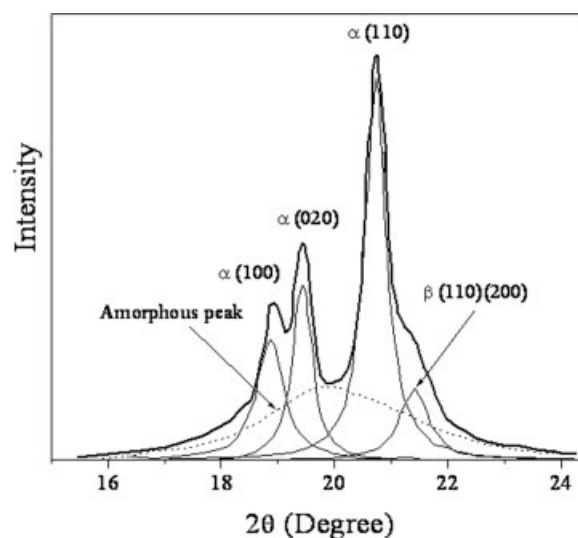


Figure 1 XRD pattern of PVDF fibers.

Characterization

XRD curves were performed on an X-ray Diffractometer (Rigaku D/max-rA, Tokyo, Japan) with CuK α radiation ($\lambda = 0.154$ nm). Wide-angle and small-angle X-ray scattering (WAXS and SAXS) were carried out at a 2D diffraction system (D8 Discover GADDS, Bruker AXS, Germany) with Cr radiation ($\lambda = 0.229$ nm). The direction of X-ray was perpendicular to the fiber axis.

The crystallinity of PVDF fibers was calculated by the following formula:

$$\text{Degree of crystallinity} = \frac{S_c}{S_c + S_a} \times 100\% \quad (1)$$

where S_c and S_a are the sum of areas of the crystalline parts and amorphous parts. A PSET (Peaks separation) program was used for XRD curve separation as shown in Figure 1. The β/α value could be obtained by calculating the ratio of the crystallinity of α to β phase.

RESULTS AND DISCUSSION

Effect of stretching temperature

XRD patterns of hard elastic PVDF fibers at different stretching temperatures are shown in Figure 2. In hard elastic PVDF fibers, only α phase existed, and it was essential to the formation of hard elastic fibers. Compared to XRD curve of the unstretched sample presented in Figure 2(a), a new peak appeared at $2\theta = 20.6^\circ$ in stretched fibers, which corresponded to $\beta(110)(200)$ peak.⁵ The total crystallinity did not change obviously with increasing stretching temperature presented in Figure 3. It was indicated that the main transformation in the fibers was α to β phase transformation, while the amorphous phase has little

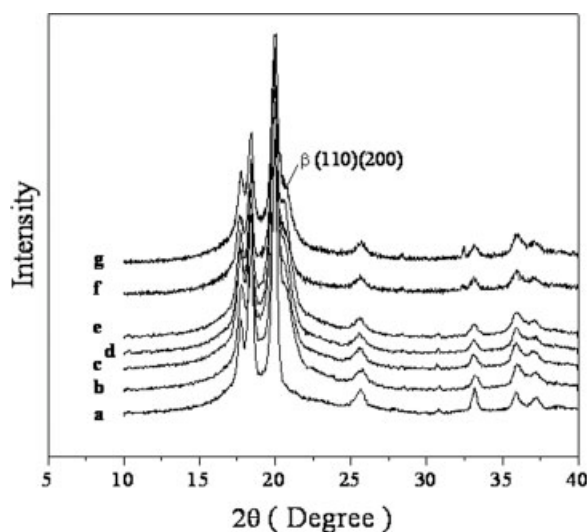


Figure 2 XRD patterns of unstretched (a) and stretched PVDF fibers at different stretching temperatures: (b) 25°C; (c) 50°C; (d) 70°C; (e) 90°C; (f) 115°C; (g) 140°C, at 60% deformation.

contribution to it. The β/α ratio of stretched PVDF fibers changed distinctly with stretching temperature, and approached a maximum value near 70°C, then decreased with the increase of stretching temperature presented in Figure 3. The abrupt increase in orientation of β phase in ordinary PVDF fibers and films had also been explained by various authors.^{3,5,19} Gregorio and Cestari²⁰ considered that the high viscosity of the material and the stress introduced by deformation was sufficiently high to destroy a crystalline order near 80°C. When stretching ceased, the crystals reorganized in the phase that was most stable at the process temperature. Sajkiewicz et al.³ suggested that the maximum of α to β phase transformation was due to the α_c transition/relaxation, which was associated with the molecular motions in the crystalline/amorphous interphase, and suggested that the abrupt change of orientation of β crystallites occurred in the range between 70 and 87°C. These explanations about α to β phase transformation were all based on the ordinary PVDF films and fibers.

In our opinion, the phase transformation in hard elastic PVDF fibers was related with the reorganization of some imperfect crystals (e.g., microcrystallites and paracrystals) existed among the lamellae (α phase), and they were mainly formed during the spinning process as reported by Wu et al.¹⁴ Xu et al.²¹ also reported that there were two kinds of crystals in hard elastic polypropylene fibers, one was the stacked lamellar crystals (I) and the other was small imperfect crystals (II). As for hard elastic PVDF fibers, the stacked lamellar crystals were aligned in the direction normal to the fiber axis. When stretched, the stacked lamellae would be sepa-

rated, which caused the fibers stress whitening without necked and unnecked phenomenon. This was different from ordinary PVDF fibers.¹⁴ In our viewpoints, during the stretching process, the stacked crystalline lamellae of hard elastic PVDF fibers would be separated, slipped, and deformed, but not be reorganized. However, the imperfect crystals existed among the lamellae could be easily reorganized and transformed into a new phase (β phase) by stress. This transformation was relatively weak at lower stretching temperature. When stretched near 70°C, the stress introduced by stretching was sufficiently high to induce a higher efficiency of α to β phase transformation. When stretched above 80°C, the stress introduced by the stretching became relative lower due to the higher chain mobility, which would result in a lower α to β phase transformation. When stretched above 140°C, the chain mobility of the fibers became even higher, resulting in recrystallization to form the kinetically favored α form.¹⁴ Thus, no α to β transformation occurred above 140°C.

Effect of stretching rate and ratio

XRD patterns of hard elastic PVDF fibers at different stretching rates are shown in Figure 4, a distinct β diffraction peak also appeared at $2\theta = 20.6^\circ$ in stretched fibers. The total crystallinity and β/α ratio at different stretching rates are shown in Figure 5. It was found that the total crystallinity did not change obviously, while the β/α ratio increased with the stretching rate. These results could be explained by the fact that at a faster stretching rate, the degree of deformation and reorganization of the imperfect crystals induced by stress was large enough to cause a higher β phase transformation.

The total crystallinity and β/α ratio at different stretching ratio are shown in Figure 6. It was indi-

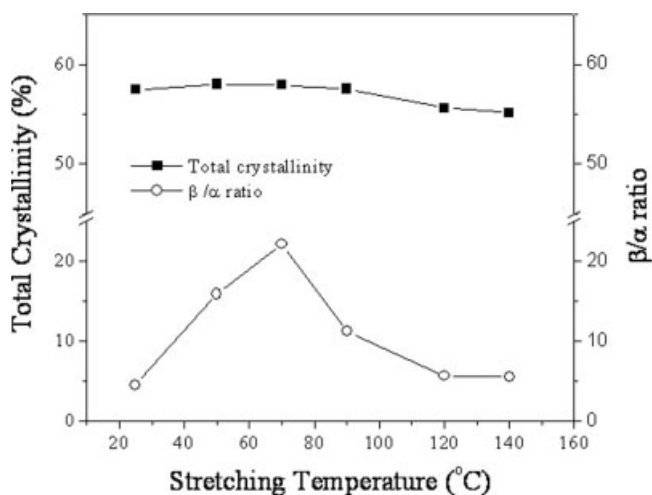


Figure 3 Total crystallinity and β/α ratio at different stretching temperatures.

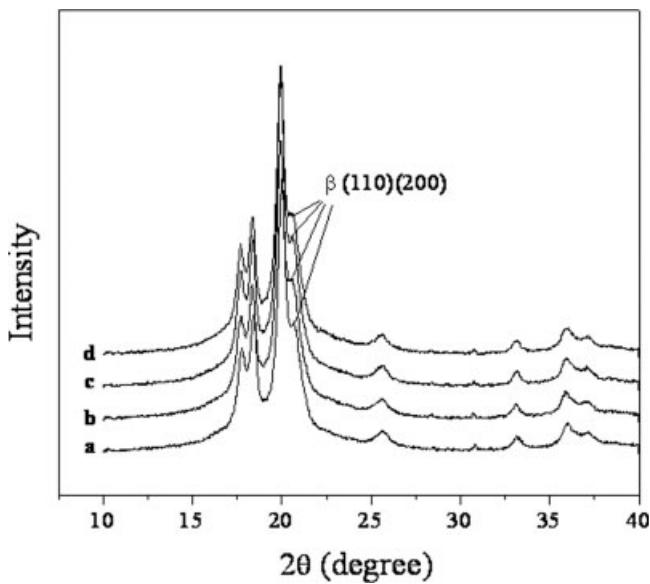


Figure 4 XRD patterns of PVDF fibers at different stretching rates: (a) 10 mm/min; (b) 30 mm/min; (c) 60 mm/min; (d) 120 mm/min, at 60% deformation.

cated the β/α ratio increased with stretching ratio, while the total crystallinity did not change greatly. These can be explained that at a low stretching ratio, the stress was not high enough to make the imperfect crystals among the lamellae reorganize into a new phase, so the β phase transformation was lower. When the stretching ratio was above 40%, the stress was large enough to induce the imperfect crystals to reorganize into a more stable β crystalline form. Further deformation would result in the slippage and breakage of the stacked lamellar structures, and finally led to the rupture of the fibers.

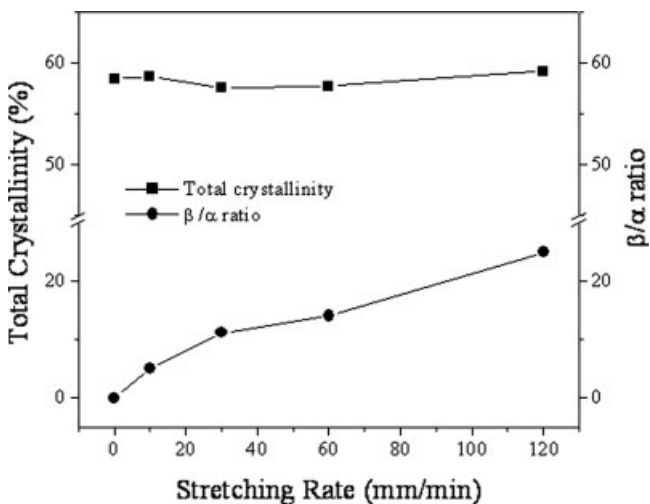


Figure 5 Total crystallinity and β/α ratio of PVDF fibers at different stretching rates.

Morphology of PVDF fibers

To further explain the phase transformation mechanism and investigate the morphology of stretched PVDF fibers, WAXS and SAXS measurements were carried out, and the results are presented in Figures 7 and 8. WAXS patterns of unstretched [Fig. 7(a)] and stretched [Fig. 7(b)] PVDF fibers all exhibited three strong equatorial streaks, with d -spacing (0.964, 0.488, and 0.439 nm) and (0.946, 0.494, and 0.480 nm). It was indicated that the fibers still remained the crystalline reflections of c -axis orientation even after being stretched, which meant that during the stretching process, the crystalline lamellae would not be reorganized, while the imperfect crystals existed among the crystalline lamellae would be easily reorganized and transformed into β phase.

SAXS patterns of unstretched and stretched PVDF fibers are shown in Figure 8. The unstretched PVDF fibers [Fig. 8(a)] showed two-point pattern, and it was indicated that the crystals existed in the form of crystalline lamellae and the lamellar planes were perpendicular to the fiber axis.^{17,18} As for the pattern of stretched PVDF fibers [Fig. 8(b)], the two-point pattern could not be distinguished clearly, which indicated the lamellar structure was deformed after the fibers were stretched. The scattering curves for unstretched and stretched PVDF fibers are presented in Figure 8(c) (curves a and b). The unstretched fibers showed a primary scattering peak at $2\theta = 0.69^\circ$, which corresponded to a long period of 19.04 nm [curve a in Fig. 8(c)], while the stretched fibers show a primary scattering peak at $2\theta = 0.33^\circ$, which corresponded to a long period of 39.75 nm [curve b in Fig. 8(c)]. The long periods of the fibers increased from 19.04 to 39.75 nm after being stretched. It was indicated that the crystalline lamel-

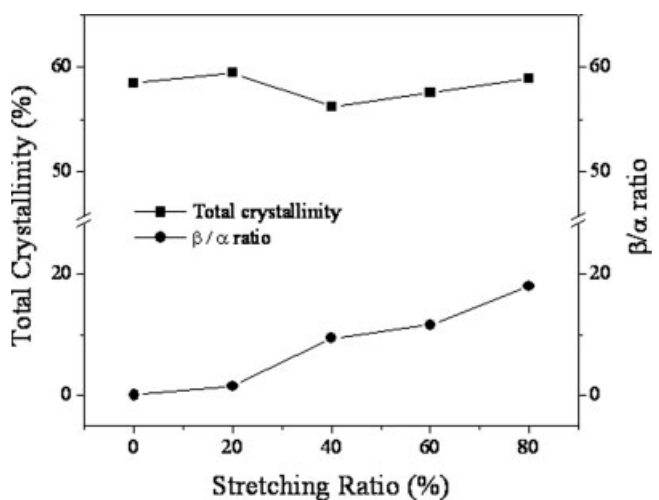


Figure 6 Total crystallinity and β/α ratio of PVDF fibers at different stretching ratio.

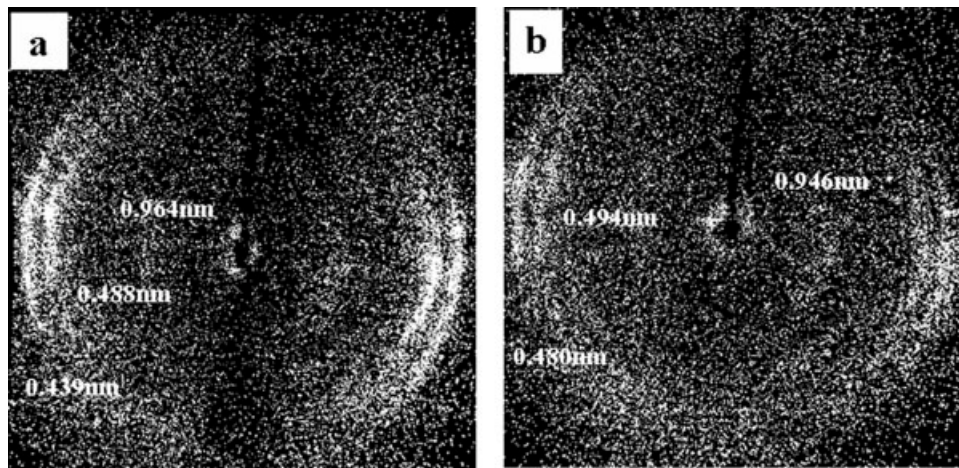


Figure 7 WAXS patterns for hard elastic PVDF fibers: (a) unstretched fibers and (b) stretched fibers with 60% deformation.

lae fell apart during stretching, which resulted in the increase of the spacing of lamellar planes. The results obtained from WAXS and SAXS analysis also supported our viewpoints mentioned above.

CONCLUSIONS

In the present work, the phase transformation and morphology of stretched hard elastic PVDF fibers were dis-

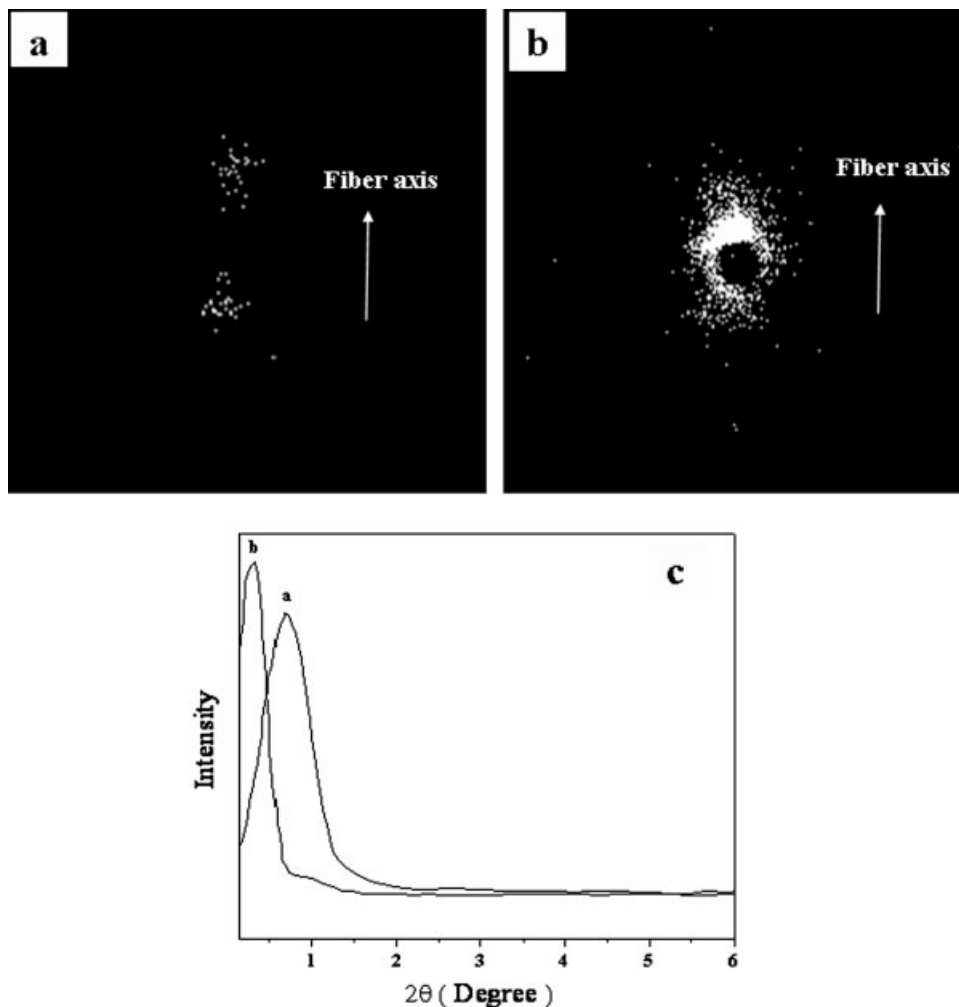


Figure 8 SAXS patterns and curves for hard elastic PVDF fibers: (a) unstretched fibers; (b) stretched fibers with 60% deformation; and (c) intensity curves for unstretched and stretched PVDF fibers.

cussed. The following conclusions were reached in examination of the present data.

Mixed α and β phase were found to coexist in stretched PVDF fibers, and stretching assisted in the transformation from α phase to β phase. The β/α ratios of stretched PVDF fibers were affected by stretching temperature, rate, and ratio. The β/α ratio had an abrupt increase when stretched near 70°C, and then it decreased with the increasing stretching temperature. Besides, the β/α ratio of PVDF fibers increased with stretching rate and ratio. The total crystallinity of PVDF fibers did not change much even on different stretching conditions. WAXS results indicated that stretched PVDF fibers still remained the crystalline reflections of *c*-axis orientation compared to unstretched fibers, while SAXS results showed that the long periods of PVDF fibers increased about two times after being stretched, which indicated the increase of the spacing of lamellar planes in stretched PVDF fibers. Based on these results, it can be concluded that the β phase transformation in hard elastic PVDF fibers was due to the reorganization of the imperfect crystals existed among crystalline lamellae, while not the stacked crystalline lamellae. When stretched, the stacked crystalline lamellae in PVDF fibers would be separated, slipped, and deformed, but not be reorganized.

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