In-situ Synchrotron SAXS and WAXS Investigations on Deformation and α-β Transformation of Uniaxial Stretched Poly(vinylidene fluoride)

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ABSTRACT

The crystalline structure evolution of Poly(vinylidene fluoride) (PVDF) during tensile deformation at 60 °C, 140 °C and 160 °C, i.e. between the glass transition temperature (T_g) and the melting temperature (T_m), was investigated by in-situ synchrotron SAXS and WAXS techniques. The analysis of the obtained scattering results indicated either yielding or α-β transformation in PVDF occurred and initiated at almost the same strain level with different stretching temperatures. A deformation mechanism was proposed for PVDF to illustrate the structure evolution during uniaxial stretching at high temperature indicating that the initial crystallite and crystalline lamellae structures of stretched PVDF are destroyed and orientated not simultaneously, which is intimately related to the yield point and the initial of α-β transformation on a certain degree of orientation. The long period along tensile direction increases to maximum and then drops into a lower but stable value during this stage of deformation.

INTRODUCTION

Having extraordinary mechanical properties and complicated polymorphism, poly(vinylidene fluoride) (PVDF) has been well known since the 1960s, and has been extensively investigated and applied in many industrial fields, due to its excellent and versatile properties, such as chemical resistance, abrasion resistance, good biocompatibility, radiation resistance, mechanical strength, piezoelectric properties, and specifically excellent membrane forming capability. In the past decades PVDF and co-polymers have been increasingly used in devices such as sensors, transducers, solar energy devices and actuators for different applications. α-PVDF has been used in different structural applications and the properties of amorphous PVDF are also of great interest, as PVDF constitutes the major component in a variety of amorphous fluoroelastomers such as Viton.

PVDF is a crystalline polymer presenting pronounced polymorphic crystalline forms. There are five possible polymorphs phases α, β, γ, δ, and ε forms in PVDF, depending on the conditions of crystallization. Besides the most common α-PVDF with the TG−TG conformation, β-PVDF is responsible for the piezoelectric properties with a TTT planar zigzag conformation. The γ form has a GTTT conformation, while δ corresponds to the polar form of α. If the packed polymer chains in crystals have oriented dipoles, then the crystal should as well has a net dipole moment, as observed in polar form β, γ and δ phases. In such situation, both the molecular and crystal dipoles are perpendicular to the chain axis, whereas, in antiparallel chain dipoles, the net dipole moment vanishes as in non-polar α and ε phases. Once PVDF is slowly cooled and annealed from the melt, formation of the α-phase is favored. Another approach to form α-phase is using the direct immersion-precipitation method. Notwithstanding the crystal lattice energy of the β-phase unit cell is slightly lower than that of the α-phase cell, the barriers for
formation of the all trans phase prevent crystallization directly into the β-phase from the melt. A β film is usually prepared by the cold drawing of a melt-quenched film consisting of α crystals at a low temperature. Also electrospinning of PVDF from its N, N-dimethyl-formamide/acetone solutions results in higher fraction of β-phase.

The efforts have been made to transform the crystalline structure in PVDF by various methods. β phase can be obtained under different conditions, however, the most common and important one is the stretching of α phase. α-γ transition can be induced in couple of ways such as crystallization at a lower temperature under the influence of increasing electric field strength.

A crystalline polymer that can be schematically represented as crystalline lamellae embedded in amorphous phase; its mechanical behavior then becomes a combination of the deformation processes of each constituent and their interactions. Upon deformation, the isotropic structure of polymer materials can be transformed into anisotropic due to the orientation of polymer chains. The mechanical properties of semi-crystal heavily depend on the structural characteristics such as crystalline morphology, cavitation, spherulite breakdown, fiber bundle structure formation, phase transformation from lamellar (block) to fibril structure, which are influenced by strain rate and temperature. A typical stress-strain curve of polymer contains the stages of elastic deformation, plastic deformation, fragmentation of the lamellar structure, and formation of fibrillar structure at high strains. The corresponding deformation mechanisms in crystalline polymers usually include lamellae slipping, chain pulling-out from the lamellae, mechanically-induced melting recrystallization and formation of oriented crystals. Many measurements have been carried out to characterize the structure of PVDF, e.g. 2D IR, NMR and laser light scattering. Salimi and Yousefi used FTIR techniques to detect the variations of β-phase of PVDF and pointed out that chain ordering and disordering of crystallites during film stretching and the effect of chain mobility in disordered regions are the most probable reason of the maximum β-phase content under 90 °C and stretch ratio of about 4.5-5.

Small- and wide-angle X-ray scattering (SAXS and WAXS) measurements are powerful tools suited for probing subtle and complex changes in polymers including crystalline morphology, degree of crystallization, layer thickness and orientation. By means of X-ray experiments, Castagnet et al. precisely described the deformation and damage micromechanisms of a PVDF homopolymer at room temperature. They interpreted that the whitening phenomenon can be attributed to the induction and growth of micro-voids in the amorphous phase. Softening is related to the growth of micro-voids and the nucleation of cavities. The spherulites are responsible for the crystalline phase of the polymer remains unchanged for elongations whereas no crystalline phase transition was observed. Feng Zuo et al. concluded that the role of chain entanglement in the interlamellar amorphous region is important in affecting the
microstructure, from the deformation study of iPP by both WAXD and SAXS results. Zhigang Wang et al. lucubrated polymer field by synchrotron WAXD and SAXS techniques and described the crystallization\cite{45} and mesophase formation\cite{46-49} of polymer in details. They studied strain-induced crystallization in an amorphous poly(ethylene terephthalate) (PET) film and pointed out the mesophase developed immediately upon the neck formation and the strain-induced crystallization occurred mainly in the mesophase region.\cite{50} Wu et al.\cite{34} carried out in-situ simultaneous synchrotron WAXD and SAXS measurements to investigate PVDF fibers during stretch-hold deformation. Their results suggested that defects induced by yielding and plastic flow played an important role in α to β crystal transformation in PVDF and they also believed that crystallites are sheared apart at high strains. In addition in high strain, the crystallites (mixed α and β form) are linked by extended amorphous chains along the fiber axis and coexisting with the relatively strongly correlated microvoids.

The phase transformation and deformation mechanisms of PVDF have been reported in many previous works.\cite{23, 29, 37, 38, 43, 51, 52} However, our rather comprehensive study focuses more on these multiple micromechanisms during stretching deformation at 60 °C, 140 °C and 160 °C, i.e. between T_m. Synchrotron SAXS and WAXS techniques were used to quantify the crystalline structure of PVDF at different stretching temperatures conditions, in order to discuss the influence of the structure on the mechanical. On the basis of the results, a model was proposed to explain the observations during the small-strain process.

**EXPERIMENTAL SECTION**

**Materials and Sample Preparation**

Kynar PVDF HSV 900 resin (specific gravity: 1.76–1.79), was purchased from Arkema Inc. The T_g is around -39 °C and T_m is about 170 °C. The PVDF powder was prepared into sheets by melting in 230 °C and then tabletting. Dumbbell-shaped samples which were cut by a device with fixed razor blades had an overall length of 26 mm, a neck width of 1.5 mm and a length between the shoulders of 3 mm.

**Characterization measurements**

*In situ* X-ray scattering measurements were carried out at beamline 1W2A of Beijing Synchrotron Radiation Facility (Beijing, China). The wavelength of the radiation source was λ=0.154 nm. Mar165-CCD was set at 1606 mm and 168 mm sample-detector distance in the direction of the beam for SAXS and WAXS data collections, respectively.

Engineering stress-engineering strain curves were obtained at constant strain rate of 10μm/s with Linkam TST-350 tensile hot stage (Linkam Scientific Instruments, Ltd., U.K.), which stretched the sample bar symmetrically and heated the central part of the sample. The symmetric stretching ensured that the focused X-ray beam could illuminate the same sample position during deformation. Uniaxial tensile tests were carried out at 60 °C, 140 °C and 160 °C. The samples were kept at the fixed
temperatures until fracture and the WAXS and SAXS scattering data was recorded by Mar165-CCD detector. The tensile data was collected and analyzed by the Linksys 32 software.

RESULTS AND DISCUSSION

Uniaxial Deformation and Formation of $\beta$ Crystals.

Uniaxial tensile deformation at 60 °C.

The engineering stress-strain curve of PVDF during uniaxial tensile deformation at 60 °C together with selected 2D SAXS and WAXS patterns collected at indicated strains are shown in Figure 1. The curve was terminated with a typical ductile fracture and displays a sharp yield with the yield stress of 29 MPa at a strain of 6%. After a small stress-strain ratio stage (10%-30%), the material showed typical strain hardening, which could be attributed to the dominant process of strain-induced crystallization and the orientation of crystallites as well as of macromolecules of amorphous phase down the drawing direction. Indeed the hardening mechanisms are coupled with void growth induced softening. From the WAXS and SAXS patterns, it can be seen that the initial sample is almost unoriented. In the initial 2D WAXS pattern, several nearly isotropic diffraction rings are detected, which could be indexed as (100), (020) and (110) diffraction of the $\alpha$-form crystal structure of PVDF. The corresponding SAXS pattern also exhibits a nearly isotropic ring, indicating the existence of a lamellar structure with a slight orientation, probably due to the spherulitic structure of the material. While WAXS probes the crystallographic composition and texture, SAXS is sensitive to the morphology, like lamellae distribution, microvoids, cracks, and fibrils.
As the strain increased, a second contribution in the SAXS patterns, a rising streak in the center can be detected, as shown in Figure 1 2S. The isotropic scatter from the lamellae is still visible, indicating that the overall lamellae morphology was unchanged. In addition, no changes in crystal structure are visible in the WAXS patterns at this stage of deformation as well. After the yield point, the SAXS patterns are dominated by a broad streak and the ring from lamellae scatter disappears. The orientation of the streak is orthogonal to the tensile direction. This kind of streak in the center of SAXS patterns is related with the cavities or microviods formed by stretching. At 60 °C, PVDF is subjected to a significant cavitation during deformation and after yield point the number of cavities increase, which plays a crucial role and induces a softening macroscopical behavior. The sample fractures as the large cavities orthogonal to the strain axis propagates. Meanwhile it is found that the corresponding WAXS patterns changed dramatically after yield point. The broadening of WAXS profiles is ascribed to the limited crystallite size and the existence of crystal disorder. However, at the strain of 18%-60%, an oriented signal is visible. There are still rings from the α-form, and additional diffractions from the β-form appeared. The specifics of α-β transformation will be discussed later.
strain (above 80%), the WAXS pattern exhibits two main peaks and no rings are visible, indicating highly anisotropic structure.

**Uniaxial tensile deformation at high temperatures (140 °C and 160 °C).**

The uniaxial tensile deformation of PVDF sample was also carried out at higher temperatures (140 °C and 160 °C). The engineering stress-strain curve and selected 2D WAXD and SAXS patterns obtained at 140 °C are illustrated in Figure 2. The observed engineering stress-strain curve at 140 °C is analogous to that obtained at 60 °C. An inconspicuous yield point can be seen and the yield stress is lower than that at 60 °C due to the increased molecular mobility at higher temperature. After that the stress drops and subsequently increases with strain. Distinct structure changes are also seen in the meantime, especially in the SAXS patterns. The 2D WAXS patterns show similar variation with 60 °C whereas the rings disappear at a lower strain value. The yield phenomenon is consistent with the corresponding SAXS pattern, in which the shape of ring transforms into four-point scattering, suggesting that the crystalline lamellae are oriented. However the angle between the oriented lamellae and tensile direction is enlarged by continuous stretching, meanwhile microfibrils are emerged which are responsible for the equatorial streak. Upon further deformation, the arcs observed along the meridian in the SAXS patterns instead of four-point scattering, implies orientation of samples. The lobes observed subsequently at the strain above 50% correlate well with the oriented lamellae and indicate a periodic system of alternating crystallites and noncrystalline regions. As the further strain increases, the SAXS patterns keep the blob-like feature. However, cavitations are not intimate with the deformation of PVDF at 140 °C. In that when amorphous flow is enhanced by arising temperature, the macroscopical deformation is better accommodated with stress. The cavitation onset is delayed and its importance to tensile deformation is decreased.
Figure 2. Engineering stress-strain curves and selected 2D SAXS and WAXS patterns acquired during uniaxial tensile deformation of PVDF at 140 °C (the sample was stretched in horizontal direction).

Uniaxial tensile deformation was also carried out at 160 °C, near the melting point of PVDF, and the results are homologous with that at 140 °C. 

α-β transformation at both 60 °C and 140 °C.

Figure 3. 1D WAXS profiles along the meridional direction during stretching at 60 °C (A) and 140 °C (B).

The scattering intensity profiles along the meridional direction from 2D WAXS patterns dependent strain at both 60 °C and 140 °C are shown in Figure 3. The profiles
of PVDF before stretching at both temperatures show three characteristic peaks, which are assigned to the (100), (020) and (110) diffractions of α-form PVDF, corresponding with the reported results.\textsuperscript{1} It is inferred that the α-form crystalline is dominant in the PVDF sample without stretching at different temperatures. The results at the two temperatures indicate similar evolution of scattering curves during deformation.

Upon further stretching, the emergence of the new peak at $2\theta=20.8^\circ$, which is generally corresponded to β (110) (200) diffraction, instead of $20.2^\circ$ is observed. It is accompanied with the disappearance of the three α peaks and the decreasing content of α-form, which indicates the α to β form transformation induced by stretching as reported.\textsuperscript{9, 34} During the deformation at this stage, the spherulitic crystalline structures in PVDF are turned into microfibrils aligned in the tensile direction, which favors the α-β transformation.\textsuperscript{30, 54} Creation of defects and a heterogeneous stress distribution in the samples play critical roles in α-β transformation.\textsuperscript{34} Moreover, both crazing and shear yielding represent plastic deformation modes with high molecular orientations, which in the case of semicrystalline polymers may result in a phase transformation.\textsuperscript{23} Apparently α-peaks at 140 °C disappear during deformation at a remarkably higher strain, where the distinct diffraction of α form could be seen even at the strain of 53%. The reason is that the subsequent increase in chain mobility mainly results in relative lower stress at higher temperatures, which would result in lower α-β transformation efficiency. Meanwhile, the crystal orientation along the stretching direction without considerable conformational changes into the crystals due to high temperature, resulting in predominantly oriented α-form.\textsuperscript{31} Unlike Du et al’s study,\textsuperscript{1} we found that the α-β transformation happens even at 160 °C.

Superstructure Evolution and Crystal Orientation.

Long period evolution at 60 °C, 140 °C and 160 °C.

Information about superstructure evolution of polymer deformation can be extracted from the SAXS patterns. The long period of investigated samples was estimated from the position of the peak $q_{\text{max}}$ according to the Bragg’s law ($L=\lambda/2\sin\theta=2\pi/q_{\text{max}}$).\textsuperscript{55, 56} The strain related long period during stretching at different temperatures are showed in Figure 4. Considering cavitations effects during the stretching at 60 °C overlaid the SAXS patterns after the yield point, therefore only the long period propagation before the yield point was discussed. It can be seen from the curves obtained at 60 °C that the cavities are formed between the lamellae stacks in both directions. The estimated values of long period at 60 °C, 140 °C and 160 °C are 10 nm, 11.4 nm and 12 nm before deformation, respectively. The long period along the meridional direction decreases with strain increasing in all cases as shown in Figure 4A. It is visible that the deformation resulted in lower long period along the direction orthogonal to the tensile force.
Figure 4. The changes of the long period as a function of strain along the meridional direction (A) and the equational direction (B) during tensile deformation at different temperatures.

In contrast, the values of long period in the equational direction at high temperatures (140 °C and 160 °C) increase gradually with strain until reach the max of 14.2 nm and 15.8 nm at the strain of 11.3% and 11.8% following the yield points. Then they drop to 12 nm or 13 nm at the strain of about 30% and again increase slightly but slowly. The increase of long period is ascribed to the extension of the chains in the amorphous layers between crystalline lamellae, which indicates that the crystalline lamellae along the tensile direction fall apart during stretching and contribute to the larger spacing of lamellar planes. The behavior after the strain of about 30% is analogous with the results by Castagnet et al., which can be interpreted as the fragmentation and the strain-induced crystallization coupled with slippage process between fragmented crystal and strain-induced melting. The oriented chains makes part of lamellae along the equatorial direction turn into fragments and the long period drops rapidly from the max to low ones for nearly complete extension of less entangled.

Orientation of PVDF with deformation.

Figure 5. Orientation of PVDF during tensile deformation obtained from WAXS and SAXS at different temperatures.

The orientation (f) of the crystal structure can be calculated from the corrected 2D X-ray scattering intensity distribution.
\[ f = \frac{(3 <\cos^2 \varphi> - 1)}{2} \quad (1) \]

where \( \varphi \) is the angle between the chain axis and the reference axis (stretching direction); \( <\cos^2 \varphi> \) is defined as:

\[
\cos^2 \varphi = \frac{\int_0^{\pi/2} I(\varphi) \sin \varphi \cos^2 \varphi d\varphi}{\int_0^{\pi/2} I(\varphi) \sin \varphi d\varphi} \quad (2)
\]

where \( I(\varphi) \) is the scattered intensity along the angle \( \varphi \).

The orientation factor of the a- and b-axes for the \( \alpha \) form PVDF were obtained from the intensity distribution of the (100) and (020) diffractions, and the \( f_c \) which is the orientation function of the c-axis was obtained from the relationship that holds for the orientation functions of pseudo-orthorhombic crystal lattice.

\[ f_a + f_b + f_c = 0.0 \quad (3) \]

On the other hand, the orientation parameters from SAXS patterns were obtained by the formula (1) and (2) as well.

The calculated orientation obtained from WAXS and SAXS patterns are shown in Figure 5. The initial orientation value of about zero as shown in Figure 5A which is also shown in Zuo’s results, corresponding to a random orientation of polymer crystals. The crystal alignment increases asymptotically toward a stable value at the strain of about 30% with tensile deformation, indicating the alignment of chains within lamellar crystals along the stretching force. Contrary to the reported result, the rate of crystal alignment during stretching at low temperature (60 °C) is found to be slower than that at low temperature, and when the orientation during stretching at high temperatures reaches the max value at the strain of 30%, which shows a slight decrease. The inconsistency in the change of orientation during stretch in different works are probably due to the distinction of material type between iPP and PVDF or experiment conditions. However, the final constant value is much higher than that at 60 °C to be ascribed to the chains mobility at higher temperature and the applied strain.

The lamellar orientation of PVDF at high temperature during deformation obtained from SAXS patterns are illustrated in Figure 5B, which shows particular variation in the same trend as aforementioned. It increases and reverses into positive at the strain of about 19% after the yield point. It is worth noting that the \( \alpha-\beta \) transformation initiates just at this degree of lamellar orientation. We concluded that the initial isotropous lamellae of PVDF orientates more tend to the equational direction after yield, then the angle between lamellae and tensile direction continues to be larger. A certain angle is related to \( \alpha-\beta \) transformation intimately. The values of orientation function increase with stretching up to 0.5 at the strain of about 35%, suggesting the alignment of lamellae.

From the results in Figure 5 we found that the orientation of crystallite and crystalline lamellae are not simultaneous. Once elongation, the crystallites orientate
rapidly and the orientated ratio changes at a strain of about 20%, where the lamellae orientation still increases and α-β transformation occurs. The stretching leads to lamellar deformation which stimulates melting and recrystallization, and then affects phase transformation.

Moreover, the lamellar orientation increases persistently at yield point, however the crystallites just initiate to align along the tensile direction. Figure 5 shows that the crystallites are orientated at once and the lamellae maintain their position during stretching. Critical strain results in the instability of crystallites which may be tensile to be fragments. The yielding is induced by the irreversible structure destruction which changes the stress-strain ratios distinctly as shown in stress-strain curves.

**Evolution of the Crystalline and Amorphous Phases during Tensile Deformation. Initial of α-β transformation and yield point.**

![Figure 6. The typical engineering stress-strain curves of PVDF during uniaxial tensile deformation at different temperatures (red arrows indicate the yield point, green arrows indicate the max value of long period, blue arrows indicate initial of α-β transformation and cyan arrows indicate the point whose long period gets low and stable after maximum).](attachment:image)

The temperature depended initiation of α-β transformation, yield point, and long period along the equator together with the related stress-strain curves are showed in Figure 6. We considered that the point where the stress-strain ratio changes distinctly in the curves as the yield point and the point where β peak could be detected in the 1D WAXS profiles as the onset of α-β transformation. The yield stresses decrease with temperature due to the molecular mobility. The temperature related yield phenomenon occurs at almost the same strain as shown in Figure 6, suggesting that strain induced structure changes are crucial element for the yielding of crystalline polymers. The yield stress and yield strain at different temperatures are shown in Figure 7. The SAXS patterns show four-point scatterings at yield point, which indicate slightly orientated lamellae structure corresponding to the orientation function of PVDF at 140 °C and 160 °C as shown in Figure 5. As mentioned above, when the crystallites have been elongated and orientated primarily, the lamellae along the equator keep parallel to tensile direction even they are taut as shown in Figure 8(b). During the deformation, due to the inhomogeneity between crystallites and lamellae, the concentration of
stress breaks the lamellae abruptly at certain strain, resulting in the beginning of the lamellar orientation. The stability of crystallite is broken at higher temperature, which reduces the difficulty to orientate lamellae in PVDF. Therefore, the synthetic action results in that the critical strain to destroy the lamellar stacks and orientate it keeps almost constant at different temperatures. The structure of amorphous polymers is in disorder state comparing to the crystalline polymers. It is possible for the strain to induce irreversible change of random coil and display a variation tendency at different temperatures.

![Graph showing temperature dependent yield stress and yield strain.](image)

**Figure 7.** Temperature dependents yield stress and yield strain.

As shown in Figure 6, another remarkable phenomenon is that the phase transformation also initiates nearly with the same value of strain at different temperatures. It is possibly that the initiation of the $\alpha$-$\beta$ transformation take places at the turning point of orientation of PVDF obtained from WAXD, which is almost at the same strain in present measurements, whereas the lamellae is still wringed (Figure 8b and e), and Figure 8 is the schematic drawing that shows the revolution of a lamella during stretching. The time of out-sync at certain angle between lamellae and tensile direction may alter the phase type. The microstructure oriented by stretching makes the chains packed more closely to increase the content of $\beta$-phase which is more compact. Besides, relatively high temperatures and external force accelerate the progress.
Figure 8. The evolution of lamella along tensile direction and chains within it (the sample was deformed in horizontal direction).

In addition, we considered that the orientation and breaking of lamellae along tensile direction accompanied by melting and recrystallization result in the variation tendency of long period along equator. Comparing to 160°C, the breaking of lamellae occurred a little earlier that the long period reaches the max value with relatively lower strain at 140°C. The fragments of crystallites initiate to orient to vertical along the tensile direction with the tensile deformation. The growth of perpendicular lamellae with stretching increases the long period. The increasing of fragment mobility with temperature leads the decreasing long period to reach a stable value at lower strain level, as shown in Figure 6. The relatively stable value could be higher or lower than the initial one and it slightly increases or maintains constant due to experiment conditions and the kind of materials.

**Structure changes during deformation.**

Crystalline polymers have complex hierarchical structure composite of the crystalline and amorphous layers in turn. In the crystalline phase, molecular chains are oriented in a specific direction along with an enforced inextensibility. Spherulite is formed with a radial arrangement of broad thin lamellae. The mechanical behavior of crystalline polymers far above the glass transition temperature particularly points out the role of the confined amorphous phase which is in a rubbery state, as reported.
The structure changes of PVDF during uniaxial tensile deformation at small strain attracted interests of researchers. A model can be proposed from analysis based on the mechanical and structural characterizations of PVDF deformation. The evolution of the crystalline and amorphous during stretching at high temperature is shown in Figure 9 that we accentuated the lamellae along the horizontal and vertical direction and the sample was stretched in horizontal direction. The deformation at high temperature with a negligible or no role of cavitation is mostly related with crystalline lamellae, amorphous phase and tie chains between them. The initial structure is isotropic and the scheme of the crystalline and amorphous phase is shown in Figure 10. The tie molecules relaxed prior to the application of stress, a fraction of the amorphous phase is inter-lamellae and some chains are involved in the crystallization of several adjacent crystallites.

As shown in Figure 9b, the molecules have been pulled taut accompanied with that the crystalline lamellae vertical to the stretching direction has moved and the
spacing between adjacent lamellae gets larger after elongation. On the contrary, the lamellae which are along the tensile force has been impacted corresponding with the decreasing long period and minus degree of orientation. In this stage, the “rubbery” amorphous phase and tie chains between crystals are important parts to undertake the stress with the oriented crystallites. Meanwhile crystallographic slip occurs along this direction as shown in Figure 9b and above Tg the elastic part of the deformation can be entirely accounted for by reversible interlamellar slip. However, the stage of elastic deformation in crystalline polymers is not real Hookean deformation for the out-of-sync of orientation function and the complex hierarchical microstructure consisting a two-phase morphology with crystalline lamellae and amorphous layers. As the elongation of the PVDF, the force generates from the entangled amorphous phase may reach a critical value under which the crystalline blocks are no longer stable. The original lamellar stacks were broken and became fragmented, and the lamellar structure is destroyed, as the crystals shear apart and the amorphous chains become stretched and closely packed. The critical stress for destruction of crystal blocks must be related to the intrinsic stability of the crystal blocks. This kind of “broken” structure, which is slightly orientated, correspond with the four-point SAXS patterns. And the fracture of the crystals leads to polymer yielding phenomenon, which is irreversible. The yielding resistance includes the dislocating forces and the internal friction force. Beyond the yield point the stress increases again, while the long period along the equational direction reaches the max, which is shown in Figure 9d. However, at high temperature the max value of long period is always followed the yield point in our experiments, indicating a broken-adjusted lamellar structure evolution after elastic deformation. Generally at this stage the spherulitic form changed into a fibrillar microstructure. Deformation occurs by destruction of the lamellar morphology. Meanwhile the corresponding SAXS patterns obtained during this stage also show a tiny streak in the center, which is attributed to microfibrils. Due to further stretching of the phase, a fraction of the lamellar fragments are oriented perpendicular to the stretching direction, accompanying with the melting and recrystallization. PVDF lamellae gets oriented well at this stage meanwhile the long period along the equational direction decreases rapidly as shown in Figure 5B and 4B. Due to the out-of-sync of orientation accompanying melting and recrystallization, the α-β transformation occurs by stretching (Figure 9e).

CONCLUSIONS

From the study of PVDF deformation stretched at different temperatures(60 °C 140 °C and 160 °C), we concluded that PVDF shows α-β transformation in the entire Tg to Tm range and high temperature lowers the efficiency of transformation during uniaxial stretching. The cavitation plays an important role during tensile deformation at 60 °C, which can be ignored at higher temperatures. The initial lamellar structure along tensile direction of PVDF can be destroyed and oriented with elongation,
resulting in yielding. The strain induced lamellar changes under stretching after yielding lead to α-β transformation, which occurs with constant strain at different temperatures. The associated factor of α-β transformation is the out-of-sync of orientation between crystallites and crystalline lamellae of PVDF at certain degree. In addition, the long period along tensile direction shows increase-decrease-stable variation tendency at higher temperatures, which is related with the extension of lamellae by stretching and orientation of lamellae fragments.

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References


