On the α → β Transition of Carbon-Coated Highly Oriented PVDF Ultrathin Film Induced by Melt Recrystallization

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Poly(vinylidene fluoride) (PVDF) is one of the polymers which exhibit pronounced polymorphic crystalline forms, depending on crystallization conditions. At least four different crystalline modifications, designated as α, β, γ, and δ, have been reported thus far.[1] While the α-form is the most common one, the β-phase is the one that has attracted the widest interest due to its extensive piezo- and pyroelectric applications. It is well-known that melt crystallization of the PVDF at atmospheric pressure yields the α-form structure. The β-PVDF can be directly obtained by growth from solution,[2] molecular epitaxy on the surface of potassium bromide,[3] melt crystallization at high pressures, and application of a strong electric field.[4] Transformation from its α-phase to β-phase can be achieved by mechanical deformation, while its retransformation can be conducted through melt recrystallization.[5] The present communication deals with the α→β transition of carbon-coated highly oriented PVDF ultrathin films induced by melt recrystallization at atmospheric pressure.

The highly oriented ultrathin PVDF films were prepared by a special melt-draw technique.[6] The obtained PVDF thin films, about 30−50 nm in thickness, can be directly used for transmission electron microscopy observation. As an example, Figure 1 shows a defocused phase-contrast bright-field (BF) electron micrograph and an electron diffraction pattern of the melt-drawn PVDF thin films in the as-drawn state. In the phase-contrast BF images, the bright lines represent the lower mean inner potential amorphous regions, while the black areas between the bright lines are the high-density crystalline lamellar regions. It is clear that the melt-drawn PVDF thin films consist of highly oriented edge-on lamellae with average thickness of ∼10 nm. The electron diffraction result further confirms the high orientation of the melt-drawn PVDF thin films with the molecular chains aligned in the film plane along the drawing direction. As indicated in Figure 1b, all of the strong reflection spots on the electron diffraction pattern are accounted for by the monoclinic space group $P2_1/c$, C_{2h},[5] with unit cell parameters $a = 0.496$ nm, $b = 0.964$ nm, $c = 0.462$ nm, and $\beta = 90°$. This means that for the present sample preparation conditions the melt-drawn PVDF film consists mainly of the α-form crystalline lamellae. It should be pointed out that a very weak reflection spot close to the $(002)_\alpha$, which can be seen on the negative, can be indexed as the (001) reflection of the orthorhombic β-form with dimensions $a = 0.858$ nm, $b = 0.491$ nm, and $c = 0.256$ nm. This clearly indicates the existence of a very small amount of β-PVDF in the melt-drawn PVDF ultrathin films.

Figure 2 shows the defocused phase-contrast BF electron micrograph and its corresponding electron diffraction pattern of a vacuum carbon-coated melt-drawn PVDF thin film, which had been heat-treated at 200 °C for 10 min and subsequently quenched to room temperature. The BF electron micrograph, Figure 2a, illustrates again a highly oriented lamellar structure with the parallel PVDF lamellae aligned perpendicular to the drawing direction of
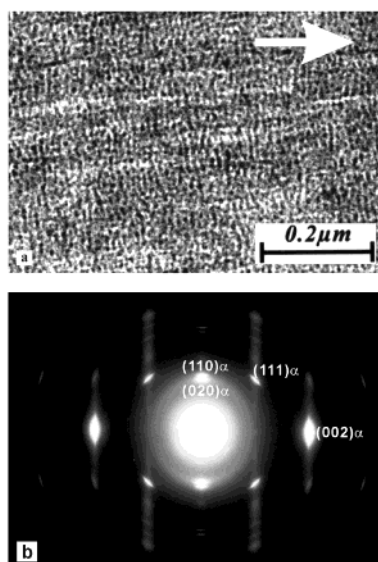

Figure 1. (a) BF electron micrograph and (b) its corresponding electron diffraction pattern of a melt-drawn PVDF thin film in the as drawn state. The arrow in the picture indicates the drawing direction of the film.
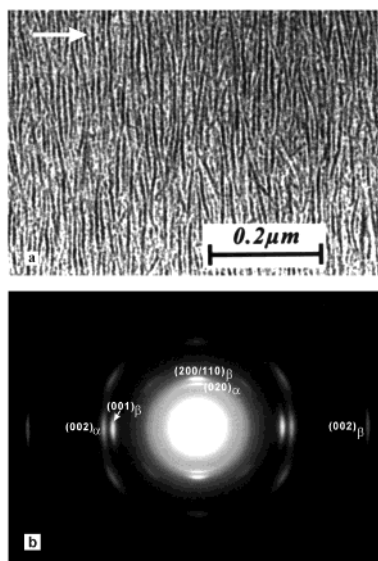

Figure 2. (a) BF electron micrograph and (b) its corresponding electron diffraction pattern of a carbon-coated melt-drawn PVDF thin film, which has been heat-treated at 200 °C for 10 min and subsequently quenched to room temperature. The arrow in the picture indicates the molecular chain direction of PVDF.

the sample. The average thickness of the lamellae (ca. 8 nm) is slightly thinner than that of the original sample. The lateral width of the lamellae is, however, much larger than that of the melt-
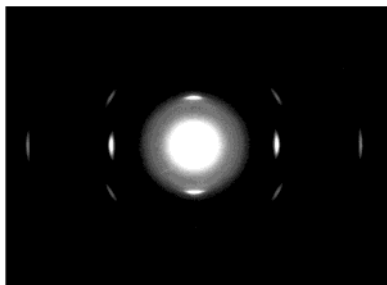
Figure 3. Electron diffraction pattern of a carbon-coated melt-drawn PVDF thin film, which has been heat-treated at 200 °C for 10 min and subsequently cooled with a rate of 2 °C/min to room temperature.

drawn sample. This clearly indicates the occurrence of a melt-recrystallization process. The corresponding electron diffraction pattern, Figure 2b, shows slightly arced sharp reflection spots. This implies that the melt-recrystallized carbon-coated melt-drawn PVDF thin film exhibits still a high degree of orientation. From these results, we are compelled to conclude that the vacuum-evaporated thin carbon layer has preserved the high orientation of the preoriented PVDF thin film. The oriented regrowth of the carbon-coated preoriented polymer thin films is explained by their surface-confined recrystallization.[7] Moreover, on the electron diffraction pattern, except for the reflection spots corresponding to the highly oriented α-form PVDF, as already observed in Figure 1b, those associated with its β-modification can now clearly be identified. Namely, a mixture of PVDF with α- and β-modifications has been obtained by melt-recrystallizing the carbon-coated melt-drawn α-form PVDF thin films. It was further found that the content of the β-PVDF increases with the reduction of the cooling rate. By cooling the melts to room temperature with a rate slower than 5 °C/min, highly oriented PVDF thin film with complete β-modification can be obtained, see Figure 3.

The above obtained results are quite different from the bulk recrystallization of the PVDF, where no β-PVDF could be created at atmospheric pressure. For the formation mechanism of the β-PVDF under the present procedure, one may suggest that the aforementioned very small amount of β-PVDF in the melt-drawn PVDF thin film is finely dispersed in the surface layer, i.e., forms a so-called skin-core morphology with the β-phase produced in the skin layer.[8] Taking into account that the vacuum-evaporated thin carbon layer has prevented the surface monolayer molecules from relaxation during the melting process, it is reasonable to imagine that the β-PVDF resulted from these extended all-trans molecular chains. According to the above consideration, the increase of β-PVDF content with the reduction of the cooling rate can be explained as follow: Through surface carbon evaporation, the nucleation of the PVDF in the surface layer has been improved significantly. During the cooling of the carbon-coated PVDF from 200 °C to room temperature with slower cooling rates, the nucleation and crystal growth of the PVDF are triggered by the modified surface layer. As a result, pure β-PVDF was induced. The coexistence of the α- and β-PVDF at fast cooling conditions may be associated with (i) a growth transition from β- to α-phase in the film during the fast cooling process or (ii) the competition of the β- and α-nucleation process with the enhancement of the bulk nucleation at high supercoolings, i.e., the nucleation and crystal growth of PVDF in the surface layer with carbon coating and those away from the carbon-coated surface started simultaneously. While the highly oriented β-PVDF is generated by the carbon-coated surface layer, the highly oriented α-PVDF resulted from its bulk crystallization in the areas away from the surface due to the well-known memory effect. A more detailed study on the origin of the above-mentioned phenomenon is still under way.

The reported phenomenon may of great importance in many applications. First of all, as mentioned in the first paragraph, β-PVDF exhibits exceptional piezo- and pyroelectric properties, and this has led to numerous applications such as in the fields electromechanical and electroacoustic transducers.[9] The α → β transition can be successfully used for preparing the β-PVDF in a highly oriented ultrathin film. Moreover, it is useful to compare the present technique with the traditionally used method for generating β-PVDF. The polar β-PVDF films have been commonly produced through tensile deformation of its nonpolar α-phase, which yields relative thick films of homogeneous β-modification. In contrast, the present procedure possesses an important advantage of being able to produce patterned microstructures of PVDF with well-oriented polar β-phase and nonoriented nonpolar α-phase by selective carbon coating, with the help of a mask, and subsequent melt recrystallization.[10] Such prepared microstructured thin PVDF films may find potential applications in many fields.

Supporting Information Available: Sample preparation and structure characterization (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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