Orientation analysis for single electrospun PE nanofibers by transmission electron microscopy

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Keywords: electrospinning, nanofiber, molecular orientation, polyethylene, SAED

The electrospinning technique, which is based on the action of an electrostatic force field, involves many physical instabilities [1]. Well known phenomena resulting from the spinning instabilities are a broad distribution of diameter, non-uniformity of fiber morphology, and random jet passes. Actually, while the diameter and morphology of electrospun fibers have always been carefully analyzed and also controlled based on the consideration of this point not so the fiber structure (degree of orientation of the molecular chains, of the crystallites and of the ordered superstructures). Taking into consideration that electrospun fibers generally are in the diameter range of several tens of nanometers up to several microns, transmission electron microscopy (TEM) is the appropriate technique for analyzing the fiber structure by simultaneously deducing morphological as well as crystallographic information. However, due to the problem of electron beam damage there are a few reports only on studies of single electrospun organic nanofibers.

Polyethylene (PE), due to its simple backbone structure, is considered a model polymer in various fields of polymer research including studies of orientation-induced crystallization processes. Electrospinning of PE, however, provides serious experimental difficulties in terms of an appropriate solvent at room temperature, and of PE's poor electrical conductivity. Recently, Rein et al. [2] have successfully electrospun PE nanofibers from high-temperature solution in a mixture of *p*-xylene and cyclohexanone, and have shown the presence of oriented and non-oriented crystal parts by X-ray diffraction (XRD). However, XRD could not distinguish between the single fiber structure and the superposition of structures of different kinds of fibers in the bundle. In this study, we performed electrospinning of PE from high-temperature solution and investigated the structure of individual nanofibers by TEM.

For the purpose of high-temperature solution spinning of PE an infrared heating system was installed in a conventional electrospinning setup. Spinning experiments were performed at a mean temperature of 112°C, and *p*-xylene was used as a solvent. In order to enhance the electrical conductivity of the solution, a small amount (0.2wt%) of tetrabutylammonium hydrogen sulfate (t-BAHS) was added. Electropinning was performed at different applied voltages from 10 to 30 kV and at different distances from 10 to 35 cm between the tip of the spinneret and the collector. The fibers were collected directly on copper grids covered with a thin carbon film. Crystallographic analysis of single nanofibers was done by selected-area electron diffraction (SAED) in a JEM-3010 (JEOL Ltd., Japan) at an accelerating voltage of 300kV using a slow scan CCD camera (Gatan Inc., USA) for image recording.

The electrospun PE fibers showed a broad diameter distribution from 30 nm to several micrometers including a small amount of beaded-fibers. The SAED patterns of fibers having different diameter are shown in Figure 1. All patterns reveal sharp crystalline reflections from

W. Grogger, F. Hofer, P. Pölt (Eds.): MC2009, Vol. 3: Materials Science,
DOI: 10.3217/978-3-85125-062-6-569 , © Verlag der TU Graz 2009

orthorhombic PE crystals, however, the crystal orientation varies remarkably. While the SAED pattern (a) obtained from the fiber having a diameter of 1.38μm showed random orientation, the SAED patterns (b) and (c) obtained from the fibers having diameters of 620 and 350 nm, respectively, showed uniaxial orientation with the *c*-axis being oriented parallel to the fiber axis (110 and 200 reflections on the equator). The SAED pattern (c') from the thinnest fiber showed more developed orientation than the thicker one (b'), and many high-order reflections including the 002 reflections on the meridian. This tendency of the thinner diameter fibers possessing the higher degree of orientation was highly reproducible. The crystalline orientation in electrospun PE fibers can be roughly divided into three different types: i) non-orientation, ii) low orientation showing only the 110 and 200 equatorial arc reflections, and iii) high orientation showing high order reflections including nearly spot like 110 and 200 reflections. The corresponding diameter ranges are: i) thicker than 1μm, ii) 500nm to 1μm, and iii) thinner than 500nm, respectively. It is reasonable to consider that the thinner fibers were subjected to the stronger bending instability and experienced the longer jet path, which leads to a stronger and longer time action of the elongational force forming a more developed fiber structure. These observations indicate that the XRD result reported by Rein et al. [2] was a superposition of oriented and unoriented crystalline fibers.

On the other hand, Figure 2 shows an orientational analysis by a sequence of SAED patterns for successive parts of a single beaded-fiber. The SAED patterns were obtained from (b') a straight part and (c') a bead part. The straight part showed an oriented crystalline pattern, while an unoriented sharp ring pattern are revealed in the bead part. This result indicates also that the XRD result by Rein et al. [2] included different orientational degrees of crystalline structures from the single beaded-fibers.

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3. We thank Prof. J.H. Wendorff for provision of research facilities. T.Y. is grateful to Alexander von Humboldt Foundation (Germany) for a fellowship.

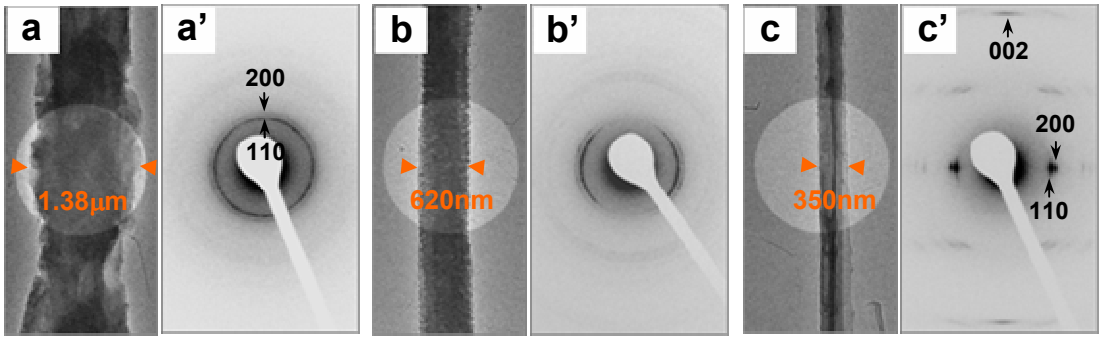

Figure 1. TEM images of electrospun PE fibers having different diameters (a-c), and the corresponding SAED patterns obtained from each single fiber (a'-c').

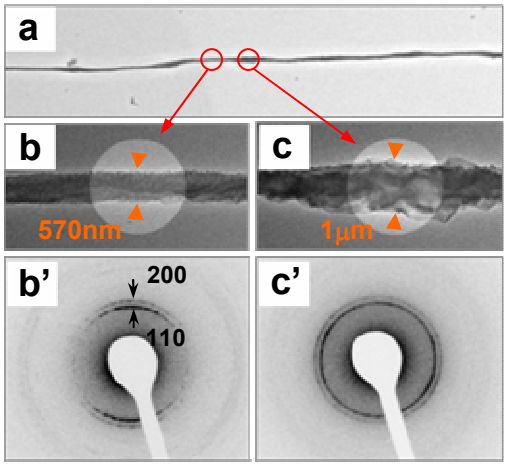

Figure 2. Sequence SAED analysis for a single beaded-fiber. The SAED pattern (b') was obtained from the straight part (b), and the pattern (c') from the bead part (c).

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