Determination of the Chain Orientation in Liquid Crystalline Polymers by Means of Microfocus X-ray Scattering Measurements

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ABSTRACT: A microfocus camera with a focus of 7 μm fwhm and a flux of 10^{11} photons/s at the ESRF in Grenoble was used to investigate the microstructure of liquid crystalline polymer samples of 4-oxybenzoate-*co*-6-oxy-2-naphthoate (73:27) (Vectra A950 from Hoechst-Celanese). These samples show isotropic scattering when examined by means of a conventional X-ray camera with a large focus (2 mm). In melt-pressed thin films, we observed local variations of the direction of molecular orientation, which is due to the presence of disclinations. Except at the center of the disclinations, the order parameter is nearly constant within the scanned area. In samples cut out of the center part of an injection-molded bar, we detected a four-point scattering pattern due to a zigzag chain conformation.

A. Introduction

Nematic liquid crystalline polymers (LCP) show regions of different chain orientation separated by disclinations. The distances between the disclinations are strongly affected by the conditions of sample preparation and vary between 0.1 and 500 μm.[1] As there is no macroscopic preferential orientation direction, these polymers often appear to be isotropic in wide-angle X-ray scattering (WAXS) experiments using an X-ray beam with cross-section dimensions of a few mm, despite the chain alignment within small regions. This alignment, however, was revealed by means of small-angle light scattering measurements,[2] polarization microscopy,[3] electron diffraction,[4] and, recently, by electron microscopy investigations.[5,6]

If a nematic liquid crystalline polymer is extruded during fiber spinning or injection molding, an overall preferential orientation of the chains in the flow direction is obtained. Due to the shear gradient within the mold, the orientation, however, varies locally. While it is quite strong close to the surface of the mold, it almost disappears in the center of the sample.[7–9]

Quite recently, a microfocus X-ray scattering camera became available at the European Synchrotron Radiation Facility (ESRF) in Grenoble.[10] Using this camera with a focus of only 7 μm fwhm and films of suitable thickness, one can determine the scattering from very small regions within the sample. We have used this camera to investigate samples of the nematic liquid crystalline polymer 4-oxybenzoate-*co*-6-oxy-2-naphthoate (73:27) (Vectra A950 from Hoechst-Celanese), which appear to be isotropic when characterized by an ordinary X-ray camera. In particular, we have determined the orientation variation of the chains within a single domain in a thin melt-pressed film. Furthermore, we have examined the apparently unoriented center part of an injection-molded tensile bar.

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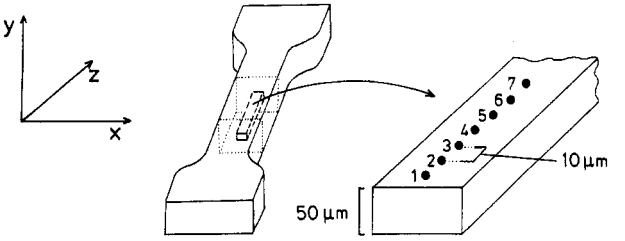

Figure 1. Schematic representation of the sample cut out of the center of the tensile bar (ASTM Type II). The sample (thickness 50 μm) was scanned with the microfocus camera in steps of 10 μm in the *z*-direction, with the primary beam being directed in the *y*-direction.

B. Experimental Section

A film of Vectra A950 with a thickness of 50 μm was obtained by melt-pressing at 320 °C and quenching in ice water. In the melt-pressing procedure, the material was first molten at a low pressure (3 bar) in order to prevent the material from flowing out of the sample frame. After 2 min, the pressure was increased to 50 bar for 10 s. Using the microfocus camera, the sample was scanned horizontally and vertically in steps of 10 μm.

A tensile bar (ASTM Type II, cross section 4 × 10 mm^2) of Vectra A950 was obtained by injection molding. The temperature of the melt was 290 °C and that of the mold was 100 °C. The time of injection was 5 s. For the X-ray scattering experiments, a sample (thickness 50 μm) was cut out of the center of the tensile bar, as indicated in Figure 1. For this procedure a milling machine was used to prevent orientation from being induced. The direction of the primary beam was the *y*-direction, and the sample was scanned in the *z*-direction in steps of 10 μm.

The X-ray scattering measurements were performed at the microfocus beamline at the ESRF in Grenoble at a wavelength of 0.9 Å. The beam was focused by means of an ellipsoidal mirror. Postcollimation resulted in a beam with a diameter of 7 μm fwhm. Monochromatization was performed by a channel-cut Si(111) monochromator, and the flux at the sample was 10^{11} photons/s. Molecular dynamics image plates were used to detect the scattering (pixel size: 176 × 176 $μm^2$).

C. Results and Discussion

Figure 2 shows the scattering pattern of the melt-pressed film obtained by a conventional focus with a

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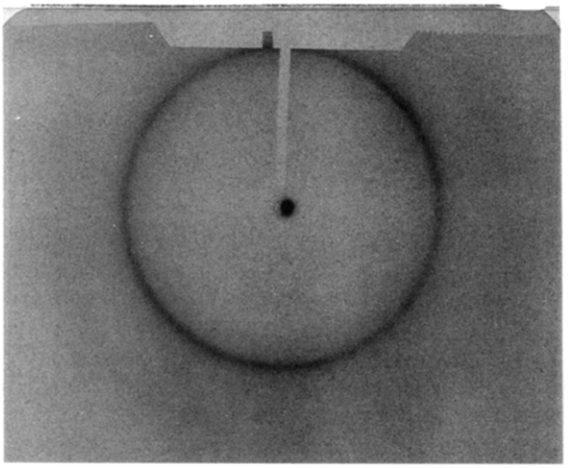

Figure 2. Isotropic scattering pattern of the melt-pressed film obtained by a conventional X-ray camera with a large focus (diameter 2 mm).

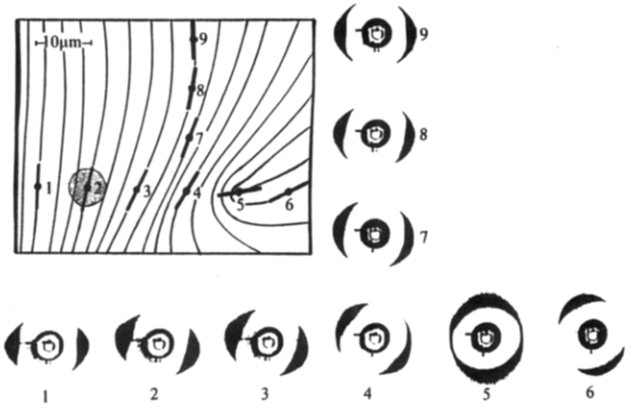

Figure 3. Scattering patterns of the melt-pressed film obtained by means of the microfocus camera at different locations indicated by the numbers 1–9, main orientation of the chains according to these scattering patterns (thick lines), and director map constructed with respect to these orientations (thin lines). The approximate beam size is indicated by the circle at point 2 in the director map.

diameter of 2 mm. It can be recognized that the scattering is isotropic, which was confirmed by a quantitative investigation of the azimuthal intensity distribution.

Figure 3 shows the scattering patterns obtained by means of the microfocus camera at different positions in the film labeled by the numbers 1–9. One clearly recognizes that the scattering is anisotropic. As it is known that the strong 110 reflection of Vectra polymers appears at the equator, one has to conclude that the direction of the chain orientation in the liquid crystalline structure is identical with the meridian in the scattering patterns. The direction of chain orientation at the corresponding points of the sample is indicated by thick straight lines in Figure 3. According to the orientation variations within the scanned area, a complete director map of the investigated sample area was constructed as also shown in this figure by means of thin lines.

The calculated order parameter (see below) is nearly constant all over the scanned area ($\Delta S = 0.04$). Despite the constant order parameter, the direction of molecular alignment bears continuous variations. Moreover, one particular scattering pattern (no. 5) shows a significant low orientation. Due to this particular scattering pattern and its surrounding orientation arrangement, a disclination with a strength of $s = +1/2$ has been

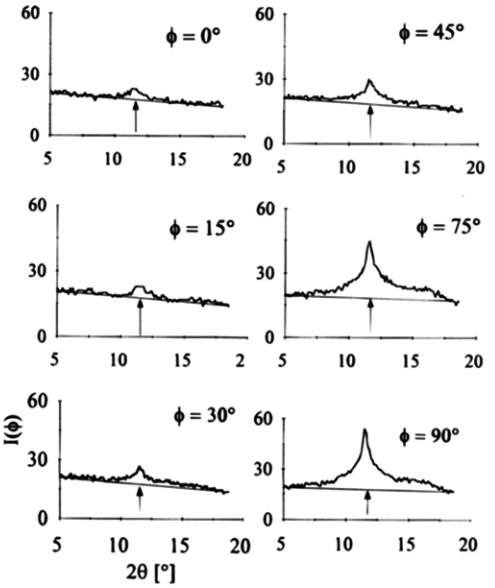

Figure 4. Scattered intensity obtained from the melt-pressed film as a function of the scattering angle 2θ at different azimuthal angles ϕ. The subtracted background for calculating the order parameter is indicated by the straight lines.

determined in the vicinity of this point, as indicated in the director map.

The scattering curves were corrected with respect to the air scattering. Next, radial scans at different azimuthal angles ϕ were formed as shown in Figure 4. $\phi = 0$ corresponds to the meridian, which is assumed to be parallel to the director. These scans show a peak which, in case of the wavelength of 0.9 Å used in this work, is located at $2\theta = 11.5°$. This peak corresponds to the 110 reflection at $2\theta = 19.7°$ found with Cu Kα radiation usually employed.[11] As proposed by Blundell et al.,[7] a background scattering was subtracted by drawing a straight line between the intensities at $2\theta = 5°$ and $2\theta = 18°$ (corresponding to $2\theta = 8.5°$ and $2\theta = 30°$ when Cu Kα radiation is used).

From the corrected azimuthal intensity distribution the order parameter S was calculated by using the equation

$$S = 1 - 3\langle\cos^2\phi\rangle$$

with

$$\langle\cos^2\phi\rangle = \frac{\int_0^{90°} I(\phi)\sin\phi\cos^2\phi\ \mathrm{d}\phi}{\int_0^{90°} I(\phi)\sin\phi\ \mathrm{d}\phi} \qquad (1)$$

which was derived by Lovell and Mitchell[12] for the evaluation of reflections which have their maximum on the equator and thus represent the orientation distribution of a vector which is arranged perpendicular to the chains. Using this procedure, we determined the order parameter $S = 0.52$.

Alternatively, we have also used another procedure. As suggested by Mitchell et al.,[13] a constant background, not depending on 2θ, was subtracted resulting in a zero intensity for the scattering at the meridian, indicated by the straight dashed line in Figure 5. This kind of background subtraction results in an order parameter of $S = 0.65$.

The value found for S is considerably low in both procedures of evaluation. At highly oriented fibers of the same material we have measured a value of $S =$

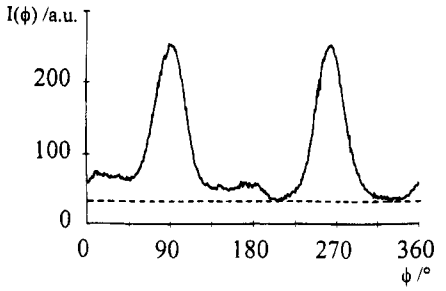

Figure 5. Azimuthal intensity distribution $I(\phi)$ of the scattered radiation obtained from the melt-pressed film at a scattering angle of $2\theta = 11.5°$, the maximum of the 110 reflection. The subtracted background to calculate the order parameter according to the second procedure is indicated by the dashed line.

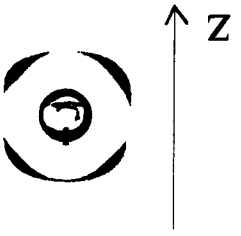

Figure 6. Four-point scattering pattern of the sample cut out the tensile bar obtained by means of the microfocus camera. The z-direction represents the direction of injection.

0.88. It is not possible to explain the low value found for S by the finite cross section of the beam. The cross section, actually, is small compared to the region in the sample in which the orientation is changing (see Figure 3). Furthermore, a smearing effect can be excluded if one considers the geometry of the instrument, namely a diameter of 7 μm and a distance between sample and detector of 20 cm. Thus, other reasons must be responsible for the small value of S, as for example the following ones:

(i) The orientation within each plane parallel to the film surface may be high, whereas the direction of the director is slightly varying with changing distance from the surface. This would include that the disclination considered is not situated on a straight line perpendicular to the film surface.

(ii) There might occur some small local fluctuations of the orientations on a scale which is small compared to the diameter of the beam (7 μm). Such fluctuations have never been found in melt-pressed films but cannot be excluded.

The sample cut out of the injection-molded bar was also investigated by means of a large focus and a microfocus camera, respectively. Using a large focus, we obtained an isotropic scattering pattern similar to the one presented in Figure 2. In contrast, with the microfocus we found a four-point pattern (Figure 6), indicating that two preferential orientation directions exist within small regions. The reflections appear at an angle of about 45° with respect to the direction z, the direction of injection. This angle and the degree of orientation slightly vary locally, as can be seen in Figure 7, where the azimuthal intensity distributions of the scattering at a radial angle of $2\theta = 11.5°$ are shown. The number at each curve is related to the numbers in Figure 1. Averaging these curves, however, one does not obtain an isotropic scattering. Obviously, in larger regions there occur larger variations in the azimuthal intensity distribution of the scattered radiation. It is a known fact that the direction of the chain orientation

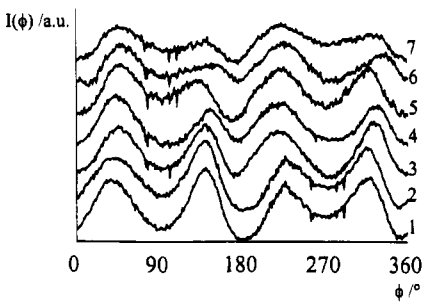

Figure 7. Azimuthal intensity distribution $I(\phi)$ of the scattered radiation at a scattering angle of $2\theta = 11.5°$ obtained by means of the microfocus camera from the sample cut out of the tensile bar. The curves are related to different positions of the sample as indicated in Figure 1.

in injection-molded bars sometimes deviates from the injection direction,[7] especially in the center area, due to a fountain flow profile during injection.[8]

The measured chain distribution is consistent with previous observations of a "banded texture" consisting of chains with a zigzag conformation. From the diameter of the X-ray beam it can be concluded that the band spacing is considerably smaller than 7 μm. Similar morphologies have already been found in fibers, moldings, and sheared thin films of liquid crystalline polymers by means of polarization microscopy,[14] microarea electron diffraction (MAED),[15] and electron microscopy.[16] According to these investigations, the molecules with their zigzag molecular trajectory lie in layers perpendicular to the shear plane.

The formation of this particular microstructure is assumed to be caused by an appropriate shear rate[16] together with partial thermal relaxation of the chain orientation. For example, the angular spread of the molecular trajectory in banded textures is found to be reduced by decreasing shearing temperature,[15] which demonstrates the influence of relaxation on the formation of banded structures. The shear rate strongly decreases from the edge to the center of the mold. Furthermore, after injection into the mold, the melt cools from the surface to the center and interior chains have more time to relax. Therefore a fibrillar microstructure with mostly extended chains is found close to the surface of the mold, whereas the central layers contain chains with a zigzag conformation.

D. Conclusion

By using a microfocus X-ray camera with a focal spot of 7 μm, it becomes possible to investigate the local variation of molecular orientation in liquid crystalline polymers. Thus one can determine the kind and separation of disclinations in a macroscopically isotropic sample. Furthermore, it was shown that from the center part of an injection-molded tensile bar a four-point scattering pattern is obtained that is consistent with a zigzag chain conformation. The formation of such a microstructure can be explained by partial thermal relaxation due to slower cooling and a lower shear rate during injection molding compared to the layers near the mold surface which consist of mostly extended chains and therefore have a fibrillar microstructure.

A further decrease of the focus to the μm or sub-μm range without lowering the flux can be reached by using Bragg–Fresnel[17] or glass-capillary optics.[18] Such optics would result in even more detailed information on local

orientation, which is to be proved in forthcoming investigations.

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