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Organized Structures in Highly Oriented Poly(ethylene terephthalate) Revealed by X-ray Diffraction Study

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SUMMARY

The structure of poly(ethylene-terephtalate) deformed to draw ratio of about 3.2 in homogeneous (T = 80°C) and glassy (T = 20°C) state and subsequently crystallized at temperatures between 150 and 250°C has been studied by wide-angle X-ray scattering (WAXS) and small-angle X-ray scattering (SAXS). The results show, for annealing temperatures above 200°C, a stronger increase in long spacing values for cold drawn samples.

INTRODUCTION

The knowledge of the crystallization process of stretched oriented macromolecules is of great interest. In fact, this crystallization occurs very often during film or fiber processing and therefore influences considerably the mechanical properties of the polymeric material. Besides, it enables to enter upon extensive informations about structural changes during drawing process, like chain folding, extended-chain crystallization.

Keller and Machin (1) have proposed a model of macromolecular chain crystallization which can be obtained in three stages : - the twisting (molecular orientation along the fiber axis) - the increasing of the long spacing - the increasing of the supermolecular structure. Herein we tend to do a comparison between hot drawing (T = 80°C) and cold drawing (T = 20°C) results in order to understand the molecular process involved in the two

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types of drawing.

EXPERIMENTAL

X. Ray diffraction apparatus

Wide angle X Ray scattering was observed in transmission on flat films ($\lambda_{Cu}\ K_{\alpha_1} = 1.54$ Å). A Luzatti-Baro small angle camera (2), associated with a linear counter C.G.R., was used for small angle investigations. A sample-counter distance of 430 mm, coupled with a distance of 145 mm between collimation slits, were adopted for a good resolution, minimizing the zone perturbed by slit diffraction on both sides of the beam-stop.

Samples

Amorphous P.E.T. sheets were kindly supplied by Rhône-Poulenc-Industries. The intrinsic viscosity of the polymer is $[\eta] = 0.75$, i.e. $\bar{M}n = 25\ 000$ as calculated from the Mark-Houwink equation : $[\eta] = K\bar{M}n^{\alpha}$ where $K = 1.7 \times 10^{-4}$, $\alpha = 0.83$.

The initial piece was approximately 3 mm thick and was characterized by a low initial birefringence ($\Delta n < 0.3 \times 10^{-3}$). Samples were cut in the form of dumbbells with straight gauge length 50 x 10 mm. For cold drawn samples two symetrical notches initiated the neck propagation in the middle part of the sample. All samples were drawn in an Instron machine at a constant crosshead speed of 1 mm.mn^{-1} (a speed low enough to ensure isothermal conditions).

Isothermal crystallization

For the homogeneous deformation (T = 80°C) the molecular orientation along the drawing axis is preserved by cooling the stretched samples to room temperature. To avoid the samples to shrink during isothermal crystallization, with consequent disorientation of the amorphous regions, they were held under tension within two aluminium plates maintained by springs so that pression remains constant. The thermal treatment was carried

out in a silicone oil bath for one minute at the desired temperature. After cooling the samples were washed with alcohol and dried. The annealing temperatures T_a vary between 150°C and 250°C.

RESULTS

Extensive informations about structural changes during the drawing process can be obtained by both wide and small angle X Ray scattering investigations.

Wide-angle X Ray scattering (WAXS)

Figures 1 and 2 show the effect of shrinkage, which involves a disorientation in non-crystalline regions, on the subsequent annealing process efficiency.

The first sample (Fig. 1), which was held to constant length during crystallization so that shrinkage did not occur, presents diffraction photograph caracteristic of oriented fiber. The spots stretch in the deformation direction can be attributed to the non coincidence between the tension axis and the c axis of the crystalline network (3).

The second (Fig. 2), which was free annealed, exhibits no fiber structure (there exists no preferential orientation of the crystalline zones). The interplanar spacings, d_{100} = 3.09 Å, $d_{\bar{1}10}$ = 2.39 Å, d_{010} = 4.42 Å, $d_{0\bar{1}1}$ = 4.85 Å, which can be deduced, are not very sensitive to the thermomechanical treatment the sample has undergone.

Figures 3 and 4 refer to unannealed hot and cold drawn samples respectively. For homogeneous deformation, located diffraction spots are detectable revealing a certain degree of crystallinity. In the cold drawing process only two equatorial spots are visible caracterizing the existence of preferential orientation.

Small-angle X Ray scattering (SAXS)

Scattering spectra were taken from a C.G.R. com-

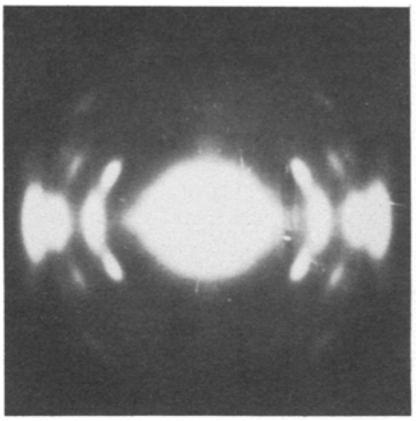

Fig. 1. WAXS pattern for hot drawn sample (T = 80°C, λ = 3.2) annealed at constant length.

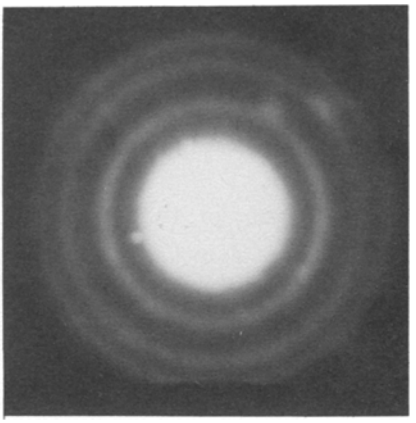

Fig. 2. Same as fig. 1 but with free annealing.

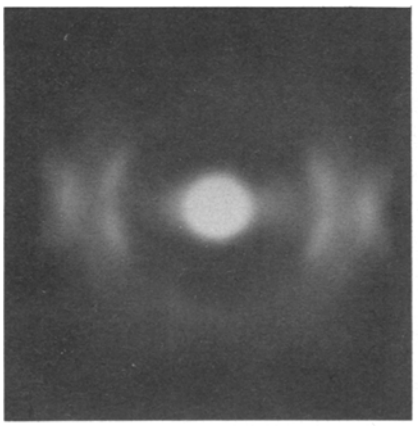

Fig. 3. WAXS pattern for unannealed hot drawn sample (T = 80°C, λ = 3.2).

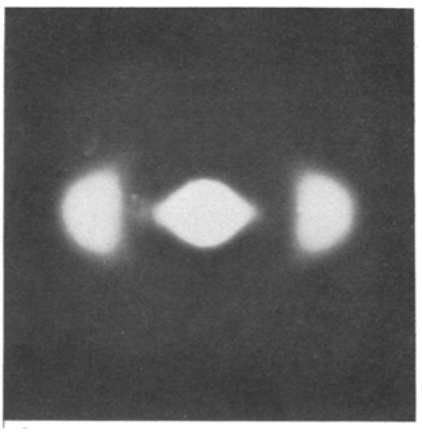

Fig. 4. WAXS pattern for unannealed cold drawn sample (T = 20°C, λ = 3.2).

puter with the deformation axis parellel as well as perpendicular to the slit direction. With unannealed samples, drawn at 20°C and 80°C no long period reflections are visible, i.e. there exists no two-phase structure (crystalline-amorphous superstructure).

Typical SAXS traces obtained from hot drawn, annealed samples are shown in figure 5. It can be noticed that the scattering behaviour depends strongly on the annealing conditions :

(i) When the tension axis is parallel to the camera slit, the scattering intensity $I_{//}$ increases with increasing temperature (Fig. 6). No long period reflection is observed.

(ii) For tension axis perpendicular to the slit direction, the intensity $I_{\perp}$ also increases with temperature. In addition above 180°C a long period reflection appears; the angle position of this maximum decreases with increasing temperature (Fig. 7). This indicates an increase in the long spacing L - calculated by means of the Bragg relation as shown in figure 8.

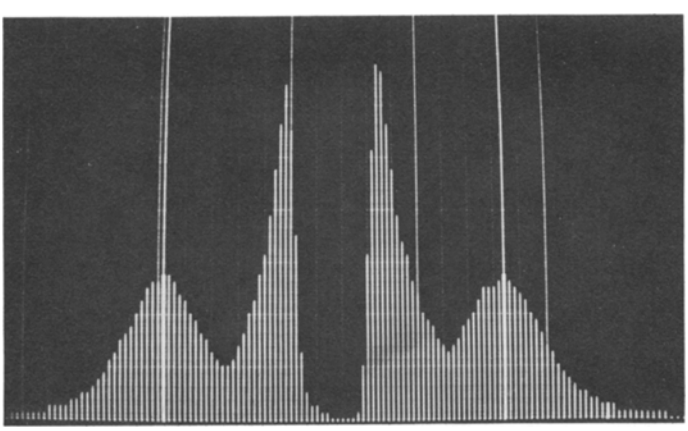

Fig. 5. Typical SAXS spectrum from C.G.R. computer-divisions on intensity and diffraction angle axis are in arbitrary units.

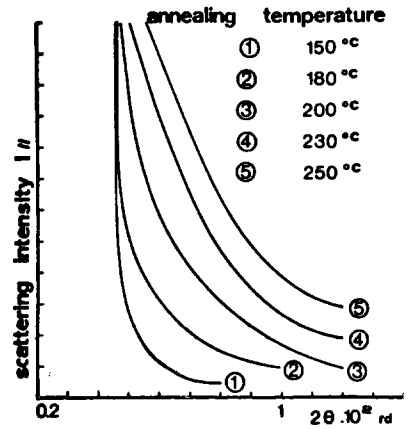

Fig. 6. SAXS patterns of hot drawn samples annealed at constant length for different temperatures ; the drawing axis is parallel to the slit.

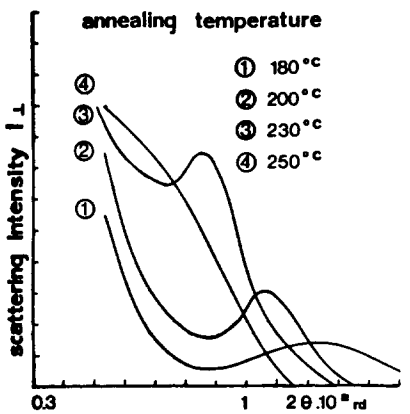

Fig. 7. Same as fig. 6, but with drawing axis perpendicular to the slit.

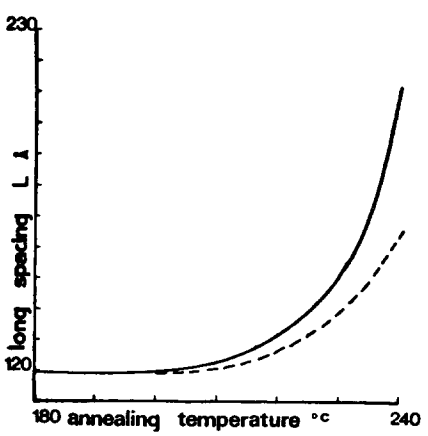

Fig. 8. Dependence of the long-spacing L on the annealing temperature at constant length for the two deformation processes: cold drawing at 20°C (continuous line), hot drawing at 80°C (dotted line).

The same procedure was applied to the diffraction spectra of cold drawn samples in order to compare the scattering power and long spacing values of homogeneous and cold drawn samples with the same draw ratio (λ=3.2). As previously mentioned by Fisher and Fakirov (4) similar effects on intensity and long spacing values are observed up to 200°C. After that the L distance increases more rapidly for cold drawn than hot drawn material.

REFERENCES

1. KELLER A., MACHIN M.J., J. Macromol. Sci. Phys., B1 261 (1967).
2. ALEXANDER L.E., in X ray diffraction methods in polymer science, p. 111, Wiley-Interscience editions (1969).
3. DAUBERY P., BUNN C.W., Proc.Roy. Soc. London, 1167 (1964).
4. FISCHER E.W., FAKIROV C., J. Mat. Sci., 11 1041 (1976).

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