

# Swelling of slightly annealed doubly oriented samples of nylon-11

## Part 1 *Modification of macroscopic dimensions and long spacing*

M. DOSIERE

*Université de l'Etat a Mons, Service de Chimie-Physique et Thermodynamique,  
Avenue Maistriau 21, B-7000 Mons, Belgium*

Doubly oriented samples of nylon-11 obtained by unidirectional rolling and annealed in formic acid in the temperature range 25 to 76° C have been swollen in allylic alcohol at room temperature. Reversible modifications of the macroscopic length  $Y$  and of the long spacing  $d_y$  have been observed although the X-ray and the macroscopic swelling ratios differ significantly. A schematic model with lamellar regions arranged "in series" with "non-lamellar regions" allows one to explain the discrepancy between both the swelling ratios.

### 1. Introduction

Swelling of semicrystalline polymers has been extensively used as a method of morphological investigation [1, 2, 20–23, 25]. The long spacing of single crystal mats of polyethylene was found to increase reversibly around 15 to 20% on the addition of liquids which normally act as swelling agents [3, 24]. A complete correspondence between mechanically induced macroscopic extension and change in SAXS (small angle X-ray scattering) maxima was found on double textured low density polyethylene (LDPE) samples [4]. In the same samples, there is an analogous correspondence between these quantities on swelling [5]. This implies that a model consisting exclusively of stacked layers should hold for these samples. This model breaks down for the rather special single textured samples [6]. Indeed, swelling experiments on doubly oriented LDPE with a single texture lead one to assume that these specimens are not fully lamellar [7].

Swelling experiments have been carried out on representative nylon-11 samples of the annealing series to obtain additional information about their structure.

In doubly oriented nylon-11, annealed in formic acid near its dissolution temperature (80° C), the basal planes of the lamellae are

parallel to (001) planes [8] as in filter mats of single crystals [9–11]; the lamellar surface normals are along the rolling direction OY. In a preceding paper [2], we have reported that the long spacing  $d_y$  and the macroscopic dimension along OY changed reversibly during swelling for doubly oriented samples of nylon-11 annealed in formic acid at 80° C.

This paper is devoted to swelling results obtained on doubly oriented nylon-11 annealed in formic acid in the temperature range 25 to 76° C. Changes of intensity in the small angle X-ray (SAXS) pattern, when such samples are wetted with liquids having different electronic densities, shall be reported elsewhere on the basis of results computed from two extreme models: the lamellar and the switchboard models.

### 2. Experimental details

Doubly oriented samples of nylon-11 are prepared by unidirectional rolling following a technique detailed elsewhere [8]. Adopting the previously used notation [8], we define the macroscopic rolled film by the orthogonal directions OX, OY and OZ: OY is the rolling direction and OX is normal to the rolling plane YOZ. The dimensions of the parallelepiped samples cut in the rolled sheet are denoted  $X_0$ ,  $Y_0$ ,  $Z_0$ .

Two series of specimens have been investigated: (a) specimens 1 to 13 annealed in formic acid (90%) in the temperature range 25 to 76° C for one hour; (b) specimens A and B, respectively, annealed at 47 and 37° C. The annealed samples are dried under vacuum until a constant weight is reached: then the macroscopic dimensions are labelled by  $X$ ,  $Y$  and  $Z$ . The annealed samples are afterwards immersed in allylic alcohol at room temperature (25° C) until their dimensions ( $X_s$ ,  $Y_s$ ,  $Z_s$ ) no longer change.

SAXS and WAXS (wide angle X-ray scattering)

patterns are recorded on film in a Kiessig camera. X-rays are provided by a copper rotating anode powdered by a GX6 Elliott generator. The height between the SAXS layer lines gives the long spacing  $d_y$ ; this long spacing is also obtained from the SAXS curve recorded with a Kratky camera fitted with a linear position – sensitive proportional detector [12].

### 3. Results

The crystal structure of rolled nylon-11 annealed in formic acid has been reported elsewhere [1, 3,

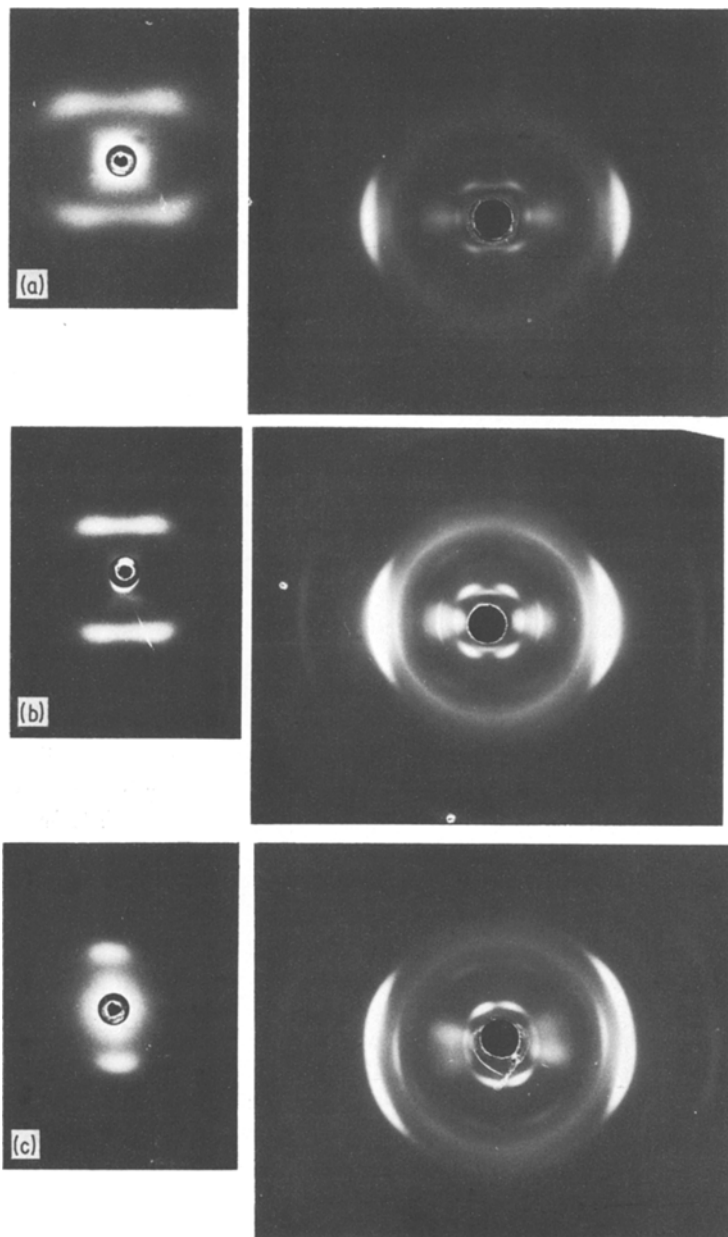


Figure 1 SAXS (left-hand side) and WAXS (right-hand side) patterns of doubly oriented samples of nylon-11 annealed in formic acid (90%) at (a) 25° C; (b) 53° C; (c) 73° C. The X-ray incident beam is along OZ; the rolling direction OY is vertical and the normal OX to the rolling plane is horizontal. The most prominent reflections in the WAXS patterns in order of decreasing spacing are indexed (001), (002), (010)–(210). (00l) reflections are nearly polar; (010)–(210) are on or near the OX axis.

TABLE I Swelling data on oriented nylon 11 annealed in formic acid at temperature  $T_a$  (swelling agent is allylic alcohol)\*

Specimen number	Annealing temperature $T_a$ ( $^{\circ}\text{C}$ )	$d_y$ (nm)	$\Phi$ ( $^{\circ}$ )	$\psi$ ( $^{\circ}$ )	$X_0/X$	$Y_{(s)}/Y = g_m$	$d_y^{(s)}/d_y = g_{XR}$	$Y\Delta d_y/d_y\Delta Y$
13	25	11.5	(40)	34.0	0.763	1.088	1.18	$2.23 \pm 0.13$
5	53	12.5	31	34.0	0.641	1.124	1.20	$1.69 \pm 0.08$
7	61	11.2	15	28	0.574	1.188	1.24	—
8	65	11.2	< 10	26	0.552	1.173	1.22	—
4	66	11.2	< 10	25.5	0.543	1.184	1.21	—
1	67	11.2	< 10	24	0.532	1.189	1.23	—
2	69	—	< 10	24.5	0.526	1.197	1.23	—
12	70.8	11.2	< 5	21.5	0.515	1.181	1.16	—
3	73	11.0	0	18.5	0.483	1.187	1.22	$1.22 \pm 0.08$
9	74.7	11.2	0	15	0.472	1.186	1.15	—
10	76	11.2	0	—	0.412	1.191	1.17	$0.89 \pm 0.09$

\* $T_a$  is the annealing temperature;  $d_y$  is the long spacing along OY. The lamellar normal  $n_L$  makes an angle  $\Phi$  with OY.  $\psi$  is the angle between the normal to (00*l*) planes and OY.  $X_0/X$  is the ratio of the sample thickness before and after annealing in formic acid.  $g_m$  is the macroscopic swelling ratio along OY. The subscript (s) refers to swelling data.  $g_{XR}$  is the X-ray swelling ratio computed from long spacings  $d_y$ .  $\Delta d_y$  is the increase of long spacing  $d_y$  resulting from swelling.  $\Delta Y$  is the increase of the length of the sample due to swelling. Swelling has been carried out at  $25^{\circ}\text{C}$  in allylic alcohol.

5, 13–17] and found to exist in a planar zig-zag conformation. The triclinic unit cell contains two monomer units with the following parameters [8]:  $a = 0.98$  mm,  $b = 0.525$  mm,  $c$  (chain axis) = 1.49 mm;  $\alpha = 50.5^{\circ}$ ,  $\beta = 90^{\circ}$ ,  $\gamma = 72^{\circ}$ .

Generally the SAXS patterns contain four spots (Fig. 1). As usual  $d$  is the long spacing;  $d_y$  is the long spacing along OY. In the SAXS pattern, the lamellar surface normals  $n_L$  make an angle  $\Phi$  with the rolling direction OY. In the WAXS pattern obtained with the X-ray incident beam along OZ,  $\psi$  is the angle between the normal to (00*l*) planes and OY. The magnitude of the tilt of the chain axes with respect to OY in the YOX plane is given by  $\theta$ , the angle between the normal to (010) planes and OX.

Swelling data on doubly oriented samples of series 1 and 2 are given in Table I and II. The SAXS patterns of samples 8, 4, 1, 2 and 12 contain two polar reflections slightly spread along the layer line: the values of  $\Phi$  given in Table I are the maximum values obtained by assuming that each spread spot results from the superposition of two separate spots.  $X_0/X$  is the ratio of the sample thickness measured, respectively, before and after

annealing in formic acid. The linear swelling ratio  $g_m = Y_{(s)}/Y$  and  $g_{XR} = d_y^{(s)}/d_y$  are also given. Results relative to successive swelling and drying experiments on samples 13, 5 and 3 and 10 are given in Table III.

#### 4. Discussion

The SAXS patterns of the samples used in swelling experiments are not generally "two point patterns", i.e. the basal plane of lamellae are not necessary perpendicular to OY. However, one must always have the following relation between the relative changes of the long spacing  $d_y$  and the macroscopic dimension  $Y$ :

$$\frac{d_y^{(s)} - d_y}{d_y} = \frac{Y^{(s)} - Y}{Y} \quad \text{or} \quad \frac{\Delta d_y}{d_y} = \frac{\Delta Y}{Y} \quad (1)$$

The subscript (s) is relative to the swollen rate. The results given in Table I show that this relation is not verified, the discrepancy being more important for samples annealed in the range 25 to  $53^{\circ}\text{C}$ . Nevertheless, the accuracy in  $\Delta d_y$ , difference between the long spacings of swollen and dried samples, is difficult to estimate. Therefore, long spacing and macroscopic length measurements

TABLE II Swelling of samples A and B in allylic alcohol

Specimen number	$T_a$ ( $^{\circ}\text{C}$ )	$X_0/X$	$\Phi$ ( $^{\circ}$ )	$d_y$ (nm)	$d_y^{(s)}$ (nm)	$g_m$	$g_{XR}$
B	37	0.637	30.5	11.3	13.9	1.11	1.23
A	47	0.533	< 7	11.2	13.7	1.19	1.22

TABLE III Experimental values of  $Y$ ,  $d_y$  for samples 13, 5, 3 and 10 relative to successive swelling experiments in allylic alcohol

Sample 13		Sample 5		Sample 3		Sample 10	
$Y$ (nm)	$d_y$ (nm)	$Y$ (nm)	$d_y$ (nm)	$Y$ (nm)	$d_y$ (nm)	$Y$ (nm)	$d_y$ (nm)
6.32 <sub>s</sub>	11.47	10.71	11.83	5.87	11.05	4.91	10.91
6.88	13.57	12.04	14.18	6.97	13.43	5.85	12.74
6.32 <sub>s</sub>	11.51	10.94	11.96	6.11	11.20	5.01	11.05
6.72	13.25	10.87 <sub>s</sub>	11.87	6.98	13.4	5.83	12.94
6.79	13.51	11.87	13.79	5.90	10.95	4.98	11.35
6.38	11.71	12.17	14.32				
		11	12.27				

have been performed on successively swollen and dried samples. As reversible variations of long spacing  $d_y$  and macroscopic length  $Y$  are noted for samples 13, 5, 3 and 10, a least square regression about all measurements have been performed, Equation 1 being used in the slightly modified following form:

$$Y\Delta d_y = \Delta Y d_y. \quad (2)$$

Results are given in the last column of Table I. In Fig. 2 the ratio  $(Y\Delta d_y/\Delta Y d_y)$  is plotted against the ratio  $X_0/X^*$  ( $X_0$  and  $X$  being, respectively, the

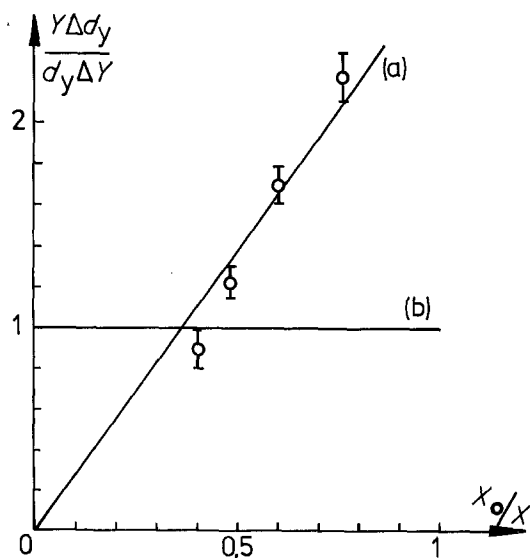


Figure 2 Plot of the ratio  $(Y\Delta d_y/\Delta Y d_y)$  against  $(X_0/X)$ .  $X_0$  and  $X$  are, respectively, the thickness of the sample before and after annealing.  $Y$  and  $d_y$  are the macroscopic dimension and the long spacing measured on the dried sample along the rolling direction OY.  $\Delta Y = Y^{(s)} - Y$ ;  $\Delta d_y = d_y^{(s)} - d_y$ . Curves (b) and (a) are, respectively, relative to the lamellar model and a model with lamellar and extralamellar material.

thickness of the sample before and after annealing). For these doubly oriented samples annealed in formic acid, the long spacing  $d_y$  increases more significantly than the macroscopic length  $Y$ .

The following elementary model can explain this discrepancy. Let us assume that the sample is not completely lamellar. More precisely it contains regions with lamellar crystals disposed in alternate way "in series" with regions without lamellar structure. The lamellar regions swell by insertion of solvent in the amorphous interfaces between the crystalline cores; the regions without lamellar structure do not deform during swelling (Fig. 3). A similar proposition has been made from studies on doubly oriented LDPE with a single texture [6, 7, 18, 19]: swelling, thermal expansion and annealing anisotropies in oriented LDPE are indeed inconsistent with a simple model of oriented lamellae. It was concluded that the oriented samples contained another phase which was relatively disordered and arranged in layers parallel to the rolling plane YOZ.

Let us examine the results which can be deduced from the model shown in Fig. 3.  $X$ ,  $Y$  and  $Z$  are the macroscopic dimensions of the annealed sample along the three orthogonal axes OX, OY and OZ;  $Y$  is the sum of the thickness of the lamellar ( $Y_l$ ) and non-lamellar regions ( $Y_{nl}$ ) along OY:

$$Y = Y_l + Y_{nl}. \quad (3)$$

During the annealing process, the sample shrinks along OY and thickens along OX, the width of the sample (OZ) remaining constant [8]. The volume  $V$  of the sample keeps, of course, a constant value during annealing ( $V = XYZ = X_0 Y_0 Z_0$ ).

\*The ratio  $(X_0/X)$  has more physical meaning than the annealing temperature  $T_a$  for a given annealed sample [8].

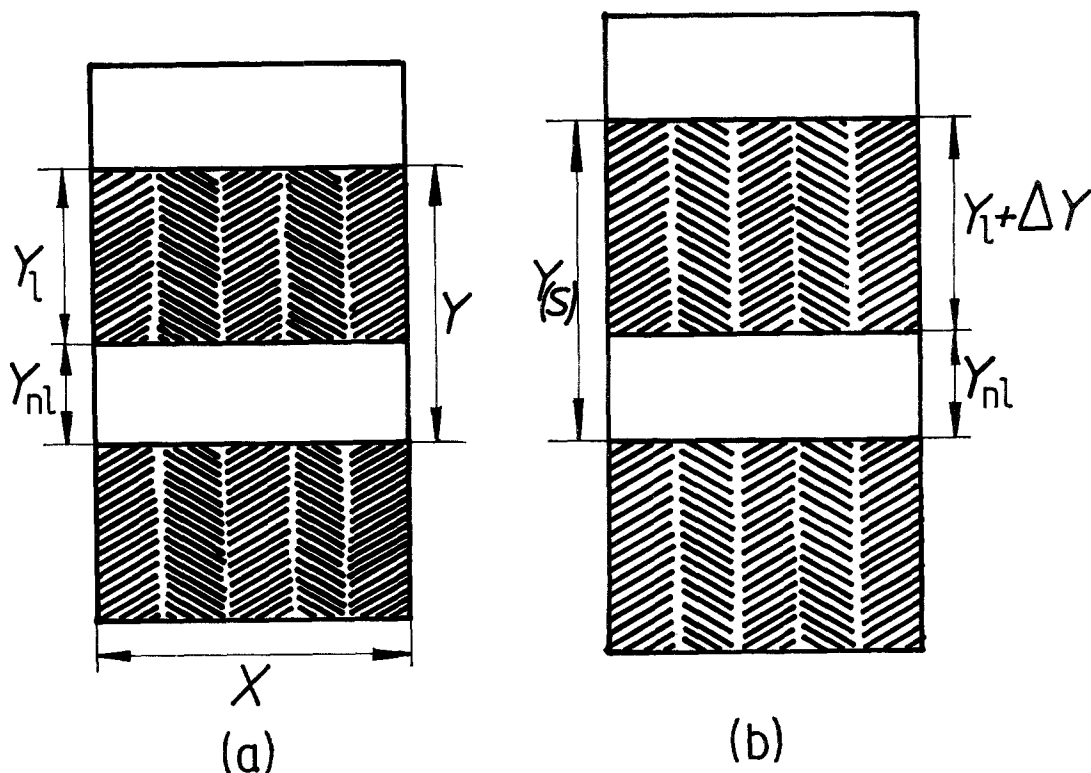


Figure 3 Schematic model showing in the YOX plane lamellar crystals arranged in alternate way "in series" with regions without lamellar structure in the unswollen (a) and swollen (b) states.

From these results, it follows that:

$$XY = V/Z = \text{constant.} \quad (4)$$

The long spacing  $d_y$  of doubly oriented samples of nylon-11 annealed in formic acid remains constant in the annealing temperature range 50 to 80°C [8]. Therefore one has:

$$Y_1 = \text{constant.} \quad (5)$$

The macroscopic dimensions of the sample are modified as follows after swelling (Table I):

$$X_{(s)} = X \quad (6)$$

$$Y_{(s)} = Y + \Delta Y = Y_1 \frac{d_y + \Delta d_y}{d_y} + Y_{nl} \quad (7)$$

$$Z_{(s)} = Z \quad (8)$$

$$\begin{aligned} \frac{\Delta Y}{Y} &= \frac{Y_1}{Y} \frac{\Delta d_y}{d_y} = Y_1 \frac{ZX}{V} \frac{\Delta d_y}{d_y} \\ &= Y_1 \frac{X_0 Z}{V} \frac{X}{X_0} \frac{\Delta d_y}{d_y}. \end{aligned} \quad (9)$$

$X_0$  being the thickness of the sample before thermal annealing in formic acid.

Finally, the Equation 9 gives

$$\frac{Y \Delta d_y}{d_y \Delta Y} = \frac{1}{x_L} \frac{X_0}{X} \quad (10)$$

$x_L$  being the fraction of the unannealed sample having a lamellar structure. The curve labelled (b) in Fig. 2 represents the expectation in the case of a lamellar model; the curve (a) is obtained by putting the experimental data given in Table III in the Equation 10. As a qualitative agreement is observed, the model given in Fig. 3 seems satisfactory, taking into account the measurement accuracy and the common use of the Bragg's relation in order to obtain the spacing of the lamellae. The fraction of unannealed sample having a lamellar structure is around 0.4.

Other models, for example with lamellar and extralamellar regions irregularly disposed, can also explain the observed differences between the macroscopic and lamellar crystals stacks dilatation. It seems very unlikely that doubly oriented samples of nylon-11 are uniformly made of lamellar crystals.

## 5. Conclusion

Reversible modifications of the macroscopic

length  $Y$  and of the long spacing  $d_y$  are observed during swelling experiments at room temperature on doubly oriented samples of nylon-11 annealed in formic acid in the temperature range 25 to 76°C. However, the X-ray swelling ratio  $\xi_{RX}$  differs from the macroscopic swelling ratio along the OY axis by a factor which can reach 2. These swelling results suggest again that slightly annealed samples are not completely lamellar. A schematic model with lamellar regions arranged "in series" with extralamellar regions allows to explain the presently reported swelling results.

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Received 19 July  
and accepted 4 October 1982