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STRUCTURE AND PROPERTIES OF UNI- AND BIAXIALLY ORIENTED POLYPROPYLENE FILMS: PART I— STRUCTURAL CHARACTERIZATION

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STRUCTURE AND PROPERTIES OF UNI - AND BIAXIALLY ORIENTED POLYPROPYLENE FILMS

PART 1 : STRUCTURAL CHARACTERIZATION

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ABSTRACT : Six different laboratories have participated in a collaborative research programme on the characterization of five uniaxially and five biaxially drawn polypropylene films. The experimental results mainly concern the following characteristics : density, heat of fusion, principal refractive indices, surface and bulk birefringence, wide - and small angle X-ray diffraction, Infra-red dichroism. Crystallinity content and average molecular orientation in both crystalline and non-crystalline phases have been calculated from the experimental data. Substantial differences were found between the states of structural order in crystalline and non-crystalline phases, in particular with regard to : degree of molecular orientation, amount of planar orientation, and degree of unbalanced orientation in biaxially drawn films.

1 - INTRODUCTION

The present report is one of a series dealing with a collaborative study of the relationships between molecular orientation and end-use properties of polymers. Previous studies of the IUPAC Working Party were concerned with (i) uniaxially drawn sheets of atactic polystyrene, and (ii) uniaxially drawn sheets of rubber-modified atactic polystyrene. The results of both studies, reported by T.T. Jones (1) and W. Retting (2) respectively, have provided a wealth of information on the induction of essentially uniaxial molecular orientation in amorphous polymers and on the effect of degree of orientation on various mechanical properties.

An appropriate quantitative description of the degree of molecular orientation is a prerequisite for any further progress in our understanding of the complex relationships between polymer processing and molecular orientation, on the one hand, and between orientation and end-use properties, on the other hand. Although various experimental techniques designed to provide accurate information on the degree of molecular orientation in amorphous and/or semicrystalline polymers are available (Refs.3,4) their systematic use is still limited and mainly restricted to the particular case of uniaxial orientation. In industrial practice oriented polymer films or sheets are most often produced by means of simultaneous or sequential stretching in two orthogonal directions and the resulting anisotropic structure can only be described in terms of biaxial molecular orientation. For this reason the Working Party decided to include in its third collaborative programme devoted to the general theme of molecular orientation, an extensive study of biaxially oriented polymer films.

In addition, a semi-crystalline polymer containing a substantial amount of crystallinity, isotactic polypropylene, was chosen not only because of its industrial importance, but also because the presence of a voluminous crystalline phase would allow, with the aid of X-ray diffraction analysis, a reasonably complete description of the state of orientation in at least one important fraction of the material.

Uniaxially drawn fibers and films of isotactic polypropylene have been investigated in considerable detail by R.J. Samuels (4,5), who also developed a systematic analysis of the experimental data, based on a simple two-phase model (Ref. 6). One of the objectives of the present programme was to apply a similar analysis to both uni-and biaxially oriented polypropylene films and to examine its possible interest for developing unique structure-properties relationships.

Part 1 of the Report is mainly concerned with the structural characterization of the investigated polypropylene films prepared under conditions comparable to standard industrial practice. Subsequent Parts will be devoted to a discussion of mechanical and other end-use properties of the same films and to the results of laboratory experiments on uni-and biaxial stretching under well defined conditions.

2 - PARTICIPANTS

The following laboratories have participated in this part of the programme :

1.   BASF Aktiengesellschaft, Ludwigshafen am Rhein, F.R.G.

2. ▲,△ ICI   Plastics Division, Welwyn Garden City, U.K.

3.   SHELL Research B.V. Amsterdam, Netherlands

4.   SOLVAY & Cie Brussels, Belgium

5. ◇   T.N.O. Central Laboratory, Delft, Netherlands

6. ●,○ RHONE-POULENC INDUSTRIES, Aubervilliers and St-Fons, France.

Each participant will be referred to by the numbers or by the symbols given above.

3 - PREPARATION OF ORIENTED FILMS

The preparation of isotactic polypropylene films of varying nominal draw ratios was conducted on a continuous basis by means of extrusion of the polymer melt through a slit die, followed by cooling on a chill roll and stretching in the machine direction (MD) at a temperature of 120-140° C (uniaxially drawn films); in the case of biaxially drawn films stretching in the machine direction was immediately followed by stretching in the transverse direction (TD) by means of a tenterframe. TD-stretching was performed at a temperature at least 20° C higher than MD-stretching. Initial thickness of the extruded sheet was varied in order to attain a nearly constant film thickness, irrespective of draw ratio : for the uniaxially drawn films the average final thickness was 160 μm ($\pm$ 10 %), for the biaxially drawn films 21 μm ($\pm$ 10 %).

All films were prepared from the same commercial grade of isotactic polypropylene :

Napryl 63 200 (Naphtachimie) of the following characteristics :

Weight-average Molecular Weight, $\overline{M}_w$ = 350 000

Polydispersity, $\overline{M}_w / \overline{M}_n$ = 4.8

Soluble fraction in boiling n-heptane (low molecular weight isotactic polypropylene + atactic polypropylene) = 5 %

Melting point (DSC) = 161° C, Melt Index (ASTM 1238-65 T) = 3

The polymer contained small amounts of anti-oxydant and stabilizer. Each investigated film is referred to by a number : 1.01 for the isotropic film, 1.02 - 1.06 for the five uniaxially drawn films and 2.07 - 2.11 for the five biaxially drawn films, respectively. Nominal draw ratios in the machine direction (= final-to-initial length ratio) and in the transverse direction (= final-to-initial width ratio) are indicated in Table 1.

All films were prepared by Rhône-Poulenc in September 1976 and March 1977 and distributed to participating laboratories in July 1977 ; a major part of the measurements was performed at least six months after preparation of the films.

TABLE 1 : Density and crystallinity of polypropylene films

Sample Code	Nominal Draw Ratios M X T	Density, 23°C kg/m^3	v_x (Eq. 1)	w_x (= $v_x d_x$/d)	w_x (D.S.C.)	Participant
1.01	1 X 1	900.3 900.3 901.8 901.0	0.58	0.60	0.56	2 3 5 6
1.02	1.2 X 1	906.2 906.8 906.9 –	0.65	0.67	0.64	2 3 5 6
1.03	1.5 X 1	902.5 902.3 903.6 903.6	0.60	0.62	0.62	2 3 5 6
1.04	4 X 1	902.6 902.2 903.5 903.7	0.60	0.62	0.62	2 3 5 6
1.05	5 X 1	903.6 903.5 905.5 –	0.62	0.64	0.66	2 3 5 6
1.06	6 X 1	902.2 901.9 902.9 904.0	0.60	0.62	0.60	2 3 5 6
2.07	1.2 X 7	– 911.1 912.3 913.6	0.71	0.73	0.72	2 3 5 6
2.08	1.5 X 7	912.3 910.3 911.8 –	0.71	0.73	0.72	2 3 5 6
2.09	4 X 7	910.3 909.2 910.2 909.8	0.69	0.71	0.71	2 3 5 6
2.10	5 X 6	911.5 909.6 910.0 –	0.70	0.72	0.69	2 3 5 6
2.11	6 X 6	910.5 909.9 910.4 –	0.70	0.72	0.71	2 3 5 6

4 - DENSITY, CRYSTALLINITY AND AVERAGE REFRACTIVE INDEX

Density values determined by four participants with the aid of density gradient columns at 23° C are given in Table 1. Duplicate measurements carried out by Participant 5 show that results of successive measurements with the same column differ less than 0.5 kg/m^3. Differences between the results of different laboratories may amount to more than 1 kg/m^3 and do not seem to be related to the date of measurement. The effect of spontaneous volume relaxation or "physical ageing" (Ref. 7) was also investigated by Participant 5 who observed between September 1977 and January 1979 increases of density at 23° C which varied between 1.2 and 1.8 kg/m^3, apparently independent of the state and degree of orientation of the film considered. Volume changes in both amorphous and crystalline phases may be responsible for this ageing behaviour.

As to the absolute values of density no systematic effect of draw ratio can be detected from the data in Table 1 ; however the biaxially drawn films are much denser than the uniaxially drawn ones. The densities of the latter appear to be related to the date of manufacture, which may be explained by admitting that variations in processing conditions leading to differences in thermal history will have affected the final film densities.

Adopting the usual two-phase model and assuming constant, orientation-independent densities for the crystalline and non-crystalline phases, d_x and d_{am}, respectively, the volume fraction of crystalline phase, v_x, is given by :

$$v_x = (d - d_{am}) \, / \, (d_x - d_{am}) \qquad\qquad (1)$$

if d is the film density. Estimated crystallinity values deduced from Eq. (1) by assuming $d_x = 936$, and $d_{am} = 853 \text{ kg/m}^3$, are given in Table 1.

Taking account of the spread in density values measured by different participants and of the error associated with the adopted value for d_{am} in particular, the estimated crystallinities indicated in Table 1 may possibly be wrong by at least 5 %.

Participants 3 and 6 measured the total heat of fusion by means of Differential Scanning Calorimetry and calculated the weight fraction of crystallinity, $w_x = v_x d_x / d$. The crystallinity values calculated from the D.S.C. results of Participant 3, by assuming a value of 35 cal/g (Ref. 8) for the heat of fusion of isotactic polypropylene crystals, are also given in Table 1 and appear to be in good agreement with those calculated from density.

Other methods liable to provide information on the amount of crystallinity, in particular Infra-red adsorption and X-ray diffraction, have been examined in some detail by several participants but the results obtained sofar did not lead to conclusive evidence concerning the general applicability of these methods in the case of oriented polypropylene films.

It is well-known that the general relationship between average refractive index and density, given by the Lorentz-Lorenz theory, is also valid in a first approximation for anisotropic polymers, irrespective of the degree of orientation. In the very limited range of densities usually encountered in the case of polymers, the Lorentz-Lorenz equation may be replaced by a simple linear relationship . Two slightly different empirical relationships of this kind have been reported for oriented polypropylene films (Refs.9,10) and are compared in Fig. 1 with the results obtained by Participants 2 and 6 who measured the principal refractive indices at the surface of the films. The average refractive index $\bar{n}$ is equal to :

$$\bar{n} = (n_M + n_T + n_N) \, / 3 \qquad\qquad (2)$$

where n_M is the refractive index in the machine direction, n_T the refractive index in the transverse direction, and n_N the refractive index in the direction normal to the film plane.

The experimental technique used was similar to the method described in Refs. 9 and 10 except for the fact that analysis of the refracted plane polarized light was based on a critical angle determination using an ABBE refractometer with a single prism. Since the light rays enter and leave the film at the same face the refractive indices measured are representative of a surface layer of undefined depth. As shown in Table 2 the corresponding refractive indices on both surfaces of the biaxially oriented films are identical, but in the case of the uniaxially oriented films a systematic difference exists, resulting in a lower average refractive index in the surface having been in contact with the chill-roll and, consequently, more rapidly cooled.

TABLE 2 : Surface refractive indices of polypropylene films

| Sample Code	n_M air cooled	n_M chill-roll	n_T air cooled	n_T chill-roll	n_N air cooled	n_N chill-roll	n average air cooled	n average chill-roll	Participant
1.01	1.5060	1.4940	1.5060	1.4940	1.5045	1.4940	1.5055	1.4940	6
1.02	1.5070	1.5075	1.5055	1.5045	1.5055	1.5035	1.5060	1.5052	6
1.03	1.5068	1.5082	1.5030	1.5036	1.5021	1.5020	1.5040	1.5046	2
1.03	1.5057	1.5088	1.5030	1.5018	1.5020	1.5000	1.5036	1.5035	6
1.04	1.5160	1.5166	1.4975	1.4949	1.4972	1.4948	1.5036	1.5021	2
1.04	1.5173	1.5187	1.4982	1.4952	1.4977	1.4946	1.5044	1.5028	6
1.05	1.5200	1.5195	1.4990	1.4940	1.4990	1.4940	1.5060	1.5025	6
1.06	1.5222	1.5205	1.4949	1.4914	1.4945	1.4911	1.5039	1.5010	2
1.06	1.5217	1.5210	1.4945	1.4926	1.4940	1.4926	1.5034	1.5020	6
2.07	1.5019		1.5236		1.5019		1.5091		6
2.08	1.5036		1.5261		1.5025		1.5108		2
2.08	1.5011		1.5224		1.5011		1.5082		6
2.09	1.5061		1.5216		1.5012		1.5097		2
2.09	1.5035		1.5202		1.4991		1.5076		6
2.10	1.5105		1.5155		1.5010		1.5090		6
2.11	1.5119		1.5154		1.5014		1.5096		2
2.11	1.5110		1.5135		1.5000		1.5081		6
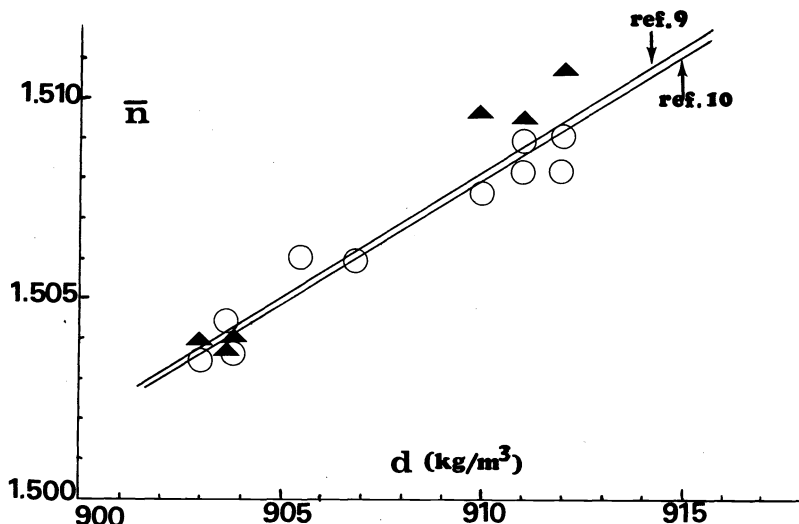
Fig. 1 : Average refractive index as a function of density (Participants 2 and 6)

The experimental scatter in the data of Fig. 1 does not allow us to distinguish between the two proposed empirical relationships (Refs. 9, 10) which both may be used for calculating density from measured average refractive index. Refractive index measurements by means of the method employed by Participants 2 and 6 also allow the calculation of surface birefringence values which may be compared with directly determined bulk birefringence as shown in the next section.

5 - SURFACE AND BULK BIREFRINGENCE

Bulk birefringence values in the plane of the film i.e. $n_M - n_T$, were determined with the aid of customary compensator methods by five participants. Moreover, Participants 1, 2 and 4 also determined the other components of the bulk birefringence, $n_M - n_N$ or $n_T - n_N$, carrying out measurements as a function of angle of inclination of the film with respect to the light beam, followed by an appropriate extrapolation (Ref.11). Finally, Participant 4 determined bulk refractive index values in the plane of the film, n_M and n_T, for some of the samples.

The bulk birefringence values obtained by these methods are compared in Table 3 with the surface birefringence calculated from the surface refractive indices measured by Participants 2 and 6.

In the uniaxially drawn films surface birefringence values are highest at the most rapidly cooled interface as expected but the absolute difference between two faces of the same film is relatively small and only slightly higher than the difference observed between values obtained in different laboratories. The largest difference observed is in the order of 5.10^{-3}. Bulk birefringence values are intermediate between the surface values in general and the results obtained in different laboratories are in fair agreement, the largest deviation observed being less than 4.10^{-3}.

In the biaxially drawn films surface birefringence is the same at both faces of a film and seems to be slightly lower than the bulk birefringence (although the differences are hardly significant with regard to the experimental error and the differences observed between different laboratories).

The deviation from "perfect transverse isotropy" ($n_T = n_N$) in the uniaxially drawn films is not negligible, but decreases with increasing draw ratio; in the case of low draw ratios (films 1.02 and 1.03) the fraction $(n_T - n_N)/(n_M - n_T)$ amounts to 0.2 - 0.25 but for the highest draw ratio (film 1.06) this fraction is smaller than 0.1. The strongly unbalanced biaxially drawn films 2.07 and 2.08 show only small deviations from isotropy perpendicular to the direction of highest draw (TD), similar in magnitude to the deviations found in the uniaxially drawn films of highest draw ratio.

TABLE 3 : Bulk and surface birefringence of polypropylene films

3 A - Uniaxially drawn films

Sample Code	$(n_M - n_T) \cdot 10^3$ bulk	surface air	surface chill-roll	$(n_M - n_N) \cdot 10^3$ bulk	surface air	surface chill-roll	$(n_T - n_N) \cdot 10^3$ bulk	surface air	surface chill-roll	Participant
1.01	0.6 0.5 0.5	0	0	1.2	1.5	0	0.7	1.5	0	1 3 6
1.02	2.2 2.1 2.2	1.5	3.0	2.9	1.5	4.0	0.7	0	1.0	1 3 6
1.03	4.0 3.9 4.2 5.0	3.7 2.7	4.6 7.0	5.0 5.2	4.6 3.7	6.2 8.8	0.9 1.3	0.9 1.0	1.6 1.8	1 2 3 6
1.04	18.8 18.6 20.5 21.5	18.5 19.1	21.7 23.5	19.5 20.6	18.8 19.6	21.8 24.1	0.8 2.0 1.9	0.3 0.5	0.1 0.6	1 2 3 4 6
1.05	20.9 23.7	21.0	25.5	20.3	21.0	25.5	- 0.6	0	0	1 3 6
1.06	25.6 24.6 27.3 27.0	27.3 27.2	29.0 28.4	26.5 26.8	27.7 27.7	29.3 28.4	0.9 2.2	0.4 0.5	0.3 0	1 2 3 4 6

TABLE 3 :   Bulk and surface birefringence of polypropylene films

3 B – Biaxially drawn films

Sample Code	$(n_M - n_T) \cdot 10^3$ bulk	surface air	surface chill-roll	$(n_M - n_N) \cdot 10^3$ bulk	surface air	surface chill-roll	$(n_T - n_N) \cdot 10^3$ bulk	surface air	surface chill-roll	Participant
2.07	- 21.9			1.4			23.4			1
	- 21.6			0.8			21.3			3
	- 19.2		- 21.7			0			21.7	4
	- 24.5									6
2.08	- 24.1			0.3			24.4			1
	- 23.5			2.9			26.4			2
	- 23.3		- 22.5			1.1			23.6	3
	- 22.0		- 21.3	1.2		0	22.4		21.3	4
	- 25.0									6
2.09	- 18.7			3.7			22.4			1
	- 15.6			7.1			22.7			2
	- 16.3		- 15.5			4.9			20.4	3
	- 17.2		- 16.7	4.9		4.4	21.8		21.1	4
	- 17.7									6
2.10	- 5.3			9.0			14.3			1
	- 4.5			11.4			15.4			3
	- 5.4		- 0.50			9.5			14.5	4
	- 4.3									6
2.11	- 1.7			12.4			14.1			1
	- 3.4			12.7			16.1			2
	- 3.1		- 3.5			10.5			14.0	3
	- 4.4		- 2.5	11.0		11.0	15.4		13.5	4
	- 2.5									6

Finally, the least unbalanced biaxially drawn film 2.11 is still significantly anisotropic in the film plane, the value of $n_T - n_M$ amounting to 20 % of the birefringence $n_T - n_N$.

6 – ORIENTATION AND BIREFRINGENCE IN THE CRYSTALLINE PHASE

The measured total bulk birefringence in an oriented semi-crystalline polymer film may be considered as the sum of various contributions as defined by the following well-known expression (Ref. 12).

$$\Delta n = v_x \cdot \Delta_x n + (1-v_x) \cdot \Delta_{am}n + \Delta_F \tag{2}$$

where the first two terms on the right-hand side represent the contributions of the crystalline and non-crystalline phases, respectively, and the last term the contribution of form birefringence Δ_F which is usually assumed to be negligibly small.

The crystalline phase birefringence $\Delta_x n$ is related to the principal refractive indices of the crystal as well as to the average crystal orientation, as follows :

$$\Delta_x n_{MT} = (n_M - n_T)_x = \frac{2}{3} \left[(n_c - n_a)(f_{cM} - f_{cT}) + (n_b - n_a)(f_{bM} - f_{bT}) \right]$$

$$\Delta_x n_{MN} = (n_M - n_N)_x = \frac{2}{3} \left[(n_c - n_a)(f_{cM} - f_{cN}) + (n_b - n_a)(f_{bM} - f_{bN}) \right] \tag{3}$$

$$\Delta_x n_{TN} = (n_T - n_N)_x = \frac{2}{3} \left[(n_c - n_a)(f_{cT} - f_{cN}) + (n_b - n_a)(f_{bT} - f_{bN}) \right]$$

n_a, n_b and n_c are the principal refractive indices along three orthogonal directions in the crystal and f stands for the so-called Hermans orientation function :

$$f_{cM} = \left(\overline{3\cos^2 \phi_{cM}} - 1 \right) / 2$$

$$f_{bM} = \left(\overline{3\cos^2 \phi_{bM}} - 1 \right) / 2$$

$$\text{etc...}$$

where ϕ_{cM} is the angle between the crystallographic c-axis and the M-direction, ϕ_{bM} the angle between the b-axis and the M-direction, etc. The orientation function is equal to 0 in the case of random orientation, equal to 1 for perfect axial orientation and equal to – 0.5 if the crystal axis is oriented perpendicular to the reference film coordinate.

Equations similar to Eq. (3) have already been published in 1958 by R.S. Stein (13), but since then apparently only applied to the particular case of uniaxial orientation. In order to calculate the crystalline phase contribution to the total birefringence by means of Eq. (3), Participant 6 has determined the various orientation functions for the crystallographic axes by Wide-Angle X-Ray Diffraction (Refs. 14, 15) and his results are given in Table 4.

Directly measured values for the principal refractive indices of the monoclinic polypropylene crystal do not exist but various estimates obtained by different methods have been published and discussed (Ref. 16). In general the crystal is assumed to exhibit uniaxial symmetry because of its helical structure, i.e. $n_a = n_b$ if the c-axis of the unit cell is taken parallel to the helical axis of the molecule. Eq. (3) may, consequently, be simplified as follows :

$$\Delta_x n_{MT} = (n_M - n_T)_x = \frac{2}{3} (n_c - n_b)(f_{cM} - f_{cT})_x$$

$$\Delta_x n_{MN} = (n_M - n_N)_x = \frac{2}{3} (n_c - n_b)(f_{cM} - f_{cN})_x \tag{4}$$

$$\Delta_x n_{TN} = (n_T - n_N)_x = \frac{2}{3} (n_c - n_b)(f_{cT} - f_{cN})_x$$

TABLE 4 : "HERMANS" - Orientation functions in crystalline phase derived from WAXD - Results by Participant 6

Sample Code	Nominal Draw-Ratios	f_{cM}	f_{cT}	f_{cN}	f_{bM}	f_{bT}	f_{bN}
1.02	1.2 X 1	0.105	0.018	- 0.122	- 0.07	- 0.007	0.076
1.03	1.5 X 1	0.175	- 0.05	- 0.125	- 0.11	0.03	0.08
1.04	4 X 1	0.745	- 0.32	- 0.425	- 0.41	0.115	0.295
1.05	5 X 1	0.865	- 0.44	- 0.425	- 0.47	0.16	0.31
1.06	6 X 1	0.92	- 0.47	- 0.45	- 0.46	0.18	0.29
2.07	1.2 X 7	- 0.33	0.83	- 0.50	0.06	- 0.45	0.39
2.08	1.5 X 7	- 0.35	0.85	- 0.50	- 0.04	- 0.47	0.51
2.09	4 X 7	- 0.23	0.73	- 0.50	- 0.14	- 0.43	0.57
2.10	5 X 6	0.16	0.31	- 0.47	- 0.20	- 0.245	0.445
2.11	6 X 6	0.20	0.28	- 0.48	- 0.26	- 0.26	0.52

In order to derive Equations (3) and (4) use has been made of the orthogonality relationships:

$$f_{aM} + f_{bM} + f_{cM} = 0 \; ; \; f_{aT} + f_{bT} + f_{cT} = 0 \text{ and } f_{aN} + f_{bN} + f_{cN} = 0$$

In the particular case of uniaxial orientation with respect to M, $f_{cT} = f_{cN} = -\frac{1}{2} f_{cM}$, since $f_{cM} + f_{cT} + f_{cN} = 0$, and Eq. (4) becomes :

$$\Delta_x n_{MT} = \Delta_x n_{MN} = (n_c - n_b) f_{cM} \equiv \Delta_x^\circ . f_x$$

$$\Delta_x n_{TN} = 0 \tag{5}$$

where Δ_x° is usually defined as the intrinsic crystalline birefringence and f_x as the crystalline orientation function. Eq. (4) shows that, in general, the crystalline contribution to the birefringence of oriented polypropylene films is proportional to the difference of two orientation functions defined with respect to the same pair of reference coordinate axes as used for defining birefringence.

Published estimates of the intrinsic crystalline birefringence

$$\Delta_x^\circ = n_c - n_b \text{ , vary between 23 and } 41.10^{-3} \text{ (Ref. 16)}$$

A maximum value may be estimated from measured total birefringence and by taking account of Eqs .(2-4) which can be combined to give :

$$\Delta n / v_x . f_x = \Delta_x^\circ + (1 - v_x) . \Delta_{am} n / v_x . f_x \tag{6}$$

where $f_x = \frac{2}{3} (f_{cM} - f_{cT})_x$ if $\Delta n = n_M - n_T$,

$$= \frac{2}{3} (f_{cM} - f_{cN})_x \text{ if } \Delta n = n_M - n_N , \quad \text{or}$$

$$= \frac{2}{3} (f_{cT} - f_{cN})_x \text{ if } \Delta n = n_T - n_N . \tag{7}$$

Since $\Delta_{am} n$ may be considered equal to $f_{am} . \Delta_{am}^\circ$, where f_{am} is the orientation function of the non-crystalline phase and Δ_{am}° the intrinsic birefringence of the completely oriented non-crystalline phase, the second term on the right-hand side of Eq. (6) will be positive for sufficiently high degrees of total orientation. In that case, it follows from Eq. (6) that : $\Delta_x^\circ < \Delta n / v_x . f_x$. Participant 6 performed uniaxial drawing experiments at different temperatures, the results of which (to be reported in detail in Part 3) show that at high draw-ratios leading to a high degree of crystalline orientation ($f_x = 0.94$), the value of $\Delta n / v_x . f_x$ may be as low as 35.10^{-3} which may reasonably be considered as a maximum value for Δ_x°. The non-crystalline orientation functions (f_{am}) for these uniaxially drawn films have been calculated from sonic modulus measurements as suggested by R. Samuels (4) and the results obtained have been used for constructing a plot of $\Delta n / v_x . f_x$ versus $(1 - v_x) . f_{am} / v_x . f_x$. The results obtained, shown in Fig. 2, are in fair agreement with the linear relationship of Samuels, leading to the following values for intrinsic birefringence :

$$\Delta_x^\circ = 29.10^{-3} \text{ and } \Delta_{am}^\circ = 60.10^{-3} \tag{8}$$

It should be kept in mind, however, that the accuracy of the method is not very high, because of experimental scatter and the limited range of f_{am} - values which varied between 0.30 and 0.70 for the films in this series. Moreover, the intrinsic sonic compliances for crystalline and amorphous polypropylene, determined by Samuels, on which the calculated f_{am} - values are based, have been assumed to be equally valid for the films investigated here.

Adopting $\Delta_x^\circ = 29.10^{-3}$, the crystalline contribution to the total birefringence can be calculated from :

Crystalline birefringence $= v_x . \Delta_x n = v_x . f_x . 29.10^{-3}$.

The values of f_x , defined by Eq. (7), have been deduced from Table 4 and are given in Table 5 together with the calculated crystalline contribution to the birefringence.

TABLE 5 : Birefringence and orientation in crystalline and non-crystalline phases of polypropylene films

5 A – Uniaxially drawn films

Sample Code	Total Δn $\times 10^3$		f_x (Eq. 7)	$v_x \Delta_x n$ $\times 10^3$	$(1-v_x) \Delta_{am} n$ $\times 10^3$	f_{am}	f_{av} (Eq. 14)	v_x
1.02	Δn_{MN}	2.9	0.15	2.8	0.1	0.005	0.10	0.65
	Δn_{MT}	2.2	0.06	1.1	1.1	0.05	0.06	
1.03	Δn_{MN}	5.1	0.20	3.5	1.6	0.06	0.14	0.60
	Δn_{MT}	4.0	0.15	2.6	1.4	0.06	0.11	
1.04	Δn_{MN}	20	0.78	13.6	6.4	0.27	0.58	0.60
	Δn_{MT}	19	0.71	12.4	6.6	0.27	0.53	
1.05	Δn_{MN}	22	0.86	15.4	6.6	0.29	0.64	0.62
	Δn_{MT}	22	0.87	15.6	6.4	0.28	0.64	
1.06	Δn_{MN}	27	0.92	16	11	0.46	0.74	0.60
	Δn_{MT}	27	0.92	16	11	0.46	0.74	

TABLE 5 :   Birefringence and orientation in crystalline and non crystalline phases of polypropylene films

5 B - Biaxially drawn films

Sample Code	Total Δn X 10^3	f_x (Eq. 7)	$v_x \Delta_x n$ X 10^3	$(1-v_x) \Delta_{am} n$ X 10^3	f_{am}	f_{av} (Eq. 14)	v_x
2.07 Δn_{MN}	1.0	0.11	2.3	- 1.3	- 0.075	0.056	0.71
Δn_{TN}	23	0.88	18	5.0	0.29	0.71	
Δn_{TM}	22	0.77	15.8	6.2	0.36	0.65	
2.08 Δn_{MN}	1.0	0.10	2.0	- 1.0	- 0.06	0.054	0.71
Δn_{TN}	25	0.90	18.5	6.5	0.37	0.75	
Δn_{TM}	24	0.80	16.5	7.5	0.43	0.69	
2.09 Δn_{MN}	5.0	0.18	3.6	1.4	0.075	0.15	0.69
Δn_{TN}	22	0.82	16.4	5.6	0.30	0.66	
Δn_{TM}	17	0.64	12.8	4.2	0.225	0.51	

../..

5 B – Biaxially drawn films (contd.)

Sample Code	Total Δn X 10^3		f_x (Eq. 7)	$v_x \Delta_x n$ X 10^3	$(1-v_x) \Delta_{am} n$ X 10^3	f_{am}	f_{av} (Eq. 14)	v_x
2.10	9.5	Δn_{MN}	0.42	8.5	1.0	0.055	0.31	0.70
	14.5	Δn_{TN}	0.52	10.5	4.0	0.22	0.43	
	5.0	Δn_{TM}	0.10	2.0	3.0	0.17	0.12	
2.11	12	Δn_{MN}	0.45	9.0	3.0	0.17	0.36	0.70
	15	Δn_{TN}	0.50	10.0	5.0	0.28	0.43	
	3.0	Δn_{TM}	0.05	1.0	2.0	0.11	0.07	

Fig.2 : Determination of intrinsic birefringences by means of Samuels' method
(Ref. 4) based on birefringence, WAXD and modulus measurements by Participant 6, on films uniaxially drawn at temperatures between 100° and 160° C.

It is obvious from the data in Table 5 that the calculated crystalline contribution to the total birefringence is very important and amounts in most cases, in particular for the biaxially drawn films, to more than 70 %. It is rather improbable, therefore, that the exact value of the intrinsic crystalline birefringence, Δ°_x, would be substantially higher than about 30.10^{-3}; a value of 41.10^{-3} e.g. as proposed in Ref. (17) would inevitably lead to negative values for the non-crystalline birefringence in many of the films investigated. Although negative values for the non-crystalline orientation function are not impossible their occurrence would be difficult to explain in uni-and biaxially drawn films with relatively high crystalline orientation.

The orientation functions derived from X-ray analysis, given in Table 4, clearly illustrate the tendency of the crystallographic c-axis to align parallel to the M-direction in the uniaxially drawn films. Perfect uniaxial orientation i.e. $f_{cT} = f_{cN} = -\frac{1}{2} f_{cM}$, is only obtained in a good approximation for the higher draw-ratios, corresponding to f_{cM} - values larger than 0.7. Even in the latter case, however, the b-axis which is perpendicular to both c-and a-axes in the monoclinic polypropylene crystal, remains still preferentially oriented normal to the plane of the film ($f_{bN} > f_{bT}$) which means that the crystallographic (040)-planes have a tendency to be oriented parallel to the film plane. The amount of planar orientation becomes very important in the biaxially drawn films in particular in the case of nearly balanced biaxial orientation. This conclusion is quite evident from the data in Table 6, which represent the relative amounts of axial, planar and random orientation with regard to the c-axis and the (040)-planes, respectively.

For the c-axis orientations, the fraction of axial orientation with respect to the M-axis, $\varphi_{ax}(M)$, in the uniaxially drawn films is given by :

$$\varphi_{ax}(M) = \frac{2}{3} (f_{cM} - f_{cT}) = f_x^{MT} ,$$

The fraction of planar orientation $\varphi_{pl} = \frac{4}{3} (f_{cT} - f_{cN}) = 2 f_x^{TN}$, and the fraction of random orientation $\varphi_r = 2 f_{cN} + 1$

In the biaxially drawn films, axial orientation has been defined with respect to the T-axis and the corresponding expressions are :

$$\varphi_{ax}(T) = \frac{2}{3} (f_{cT} - f_{cM}) = f_x^{TM}$$

$$\varphi_{pl} = \frac{4}{3} (f_{cM} - f_{cN}) = 2 f_x^{MN}$$

$$\varphi_r = 2 f_{cN} + 1 \tag{9}$$

TABLE 6 : Axial, planar and random crystal orientation in polypropylene films

Sample Code	c-axis orientation (Eq. 9)			(040)-planes orientation (Eq.10)		
	φ_{axial}	φ_{planar}	φ_{random}	$\varphi_{planaxial}$	$\varphi_{uniplanar}$	φ_{random}
1.02	0.06	0.19	0.75	0.08	0.06	0.86
1.03	0.15	0.10	0.75	0.19	0.03	0.78
1.04	0.71	0.14	0.15	0.70	0.12	0.18
1.05	0.85	0	0.15	0.84	0.10	0.06
1.06	0.90	0	0.10	0.85	0.07	0.08
2.07	0.77	0.23	0	0.68	0.22	0.10
2.08	0.80	0.20	0	0.57	0.37	0.06
2.09	0.64	0.36	0	0.39	0.47	0.14
2.10	0.10	0.84	0.06	0.06	0.43	0.51
2.11	0.05	0.91	0.04	0	0.52	0.48

Similar expressions can be easily derived for the orientation of the (040)-planes which in the terminology of Heffelfinger and Burton (18) may be divided in plan-axial, uniplanar and random orientation :

$$\varphi_{\text{plan-axial}}{}^{(M)} = \frac{4}{3} \, (f_{bT} - f_{bM})$$

$$\varphi_{\text{uniplanar}} = \frac{2}{3} \, (f_{bN} - f_{bT})$$

$$\varphi_{\text{random}} = 2 \, f_{bM} + 1$$

for the uniaxially drawn films, and

$$\varphi_{\text{planaxial}}{}^{(T)} = \frac{4}{3} \, (f_{bM} - f_{bT})$$

$$\varphi_{\text{uniplanar}} = \frac{2}{3} \, (f_{bN} - f_{bM})$$

$$\varphi_{\text{random}} = 2 \, f_{bT} + 1 \qquad\qquad\qquad\qquad\qquad (10)$$

for the biaxially drawn films.

Equivalent expressions have been derived earlier for the description of crystalline orientation in polyethylene (Ref. 19) and polyethylene terephthalate (Ref. 20).

The data of Table 6 confirm the predominance of uniaxial c-axis orientation in the uniaxially drawn films of relatively high draw-ratio and the persistence of a small amount (< 10 %) of uniplanar orientation of (040) planes.

Although uniaxial c-axis orientation is still predominant in the highly unbalanced biaxially drawn films 2.07 and 2.08, the amount of planar orientation is already quite substantial; in the nearly balanced biaxially drawn film 2.11, about 90 % of the c-axis orientation is planar whereas uniaxial orientation has practically disappeared. Uniplanar orientation of (040) planes also, is already important in the unbalanced biaxially drawn films and becomes the unique mode of orientation in the nearly balanced film 2.11. An important fraction of the planes remains randomly oriented in the nearly balanced films, reflecting the smaller preference of the a-axis (compared to the c-axis) to lie in the plane of the film.

The rapid change from axial to planar c-axis orientation when biaxial draw approaches perfect balance is further illustrated by the curves in Fig. 3, which represent the fractions of axial and planar orientation as a function of the degree of unbalanced draw characterized by the ratio λ_T / λ_M.

Further information on the two-phase morphology was obtained by Participants 2 and 5 by means of Small Angle X-ray Diffraction. A long period of 14 nm was calculated by Participant 5 from the SAXD-pattern of the unoriented film 1.01. The diffraction patterns of the uniaxially drawn films show pronounced meridional maxima for suffiently large draw-ratios ($\lambda_M \geq 4$), corresponding to a long period spacing of about 17 nm in the draw direction (Fig. 4). Only in films 1.02 and 1.05 which have a higher density (due probably to a somewhat higher draw temperature), the long period is also significantly higher and equal to 20 nm. These values are in good agreement with those reported by Baltá-Calleja and Peterlin (21) for draw and annealing temperatures between 120 and 140° C. It is remarkable that the long period spacing is practically independent of the crystalline c-axis orientation as determined by WAXD, down to very low values of f_{cM} (~ 0.1) as shown in Fig. 4.

The SAXD pattern of the highly unbalanced biaxially drawn films 2.07 and 2.08 is similar to that of the uniaxially drawn films but the asymmetry is much weaker, and disappears completely when the state of biaxial orientation becomes more balanced. In the latter case the determination of the long period is rather inaccurate, although there seems to be no doubt that its value (~ 40 nm) is larger than in the unbalanced films (~ 30 nm), from which it might be deduced that with increasing orientation in the M-direction, the average distance between the crystalline regions, measured in the T-direction, becomes greater (Fig. 4). The much larger values of the long period spacings in the biaxially drawn films, relative to the uniaxially drawn ones, may be compared to the higher densities and are most probably related to higher draw temperatures in the case of the biaxially drawn films resulting in larger values for the crystallinity and for the average size of the crystalline regions. Participant 5 also observed that the width of the intensity peaks in general decreases with increasing orientation in the corresponding direction.
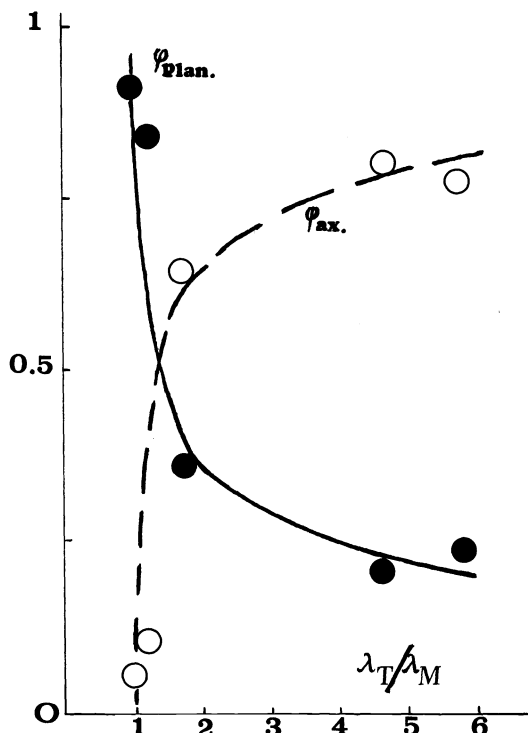
Fig. 3 : Axial and planar c-axis orientation in crystalline phase of biaxially
drawn polypropylene films as a function of degree of unbalanced draw;
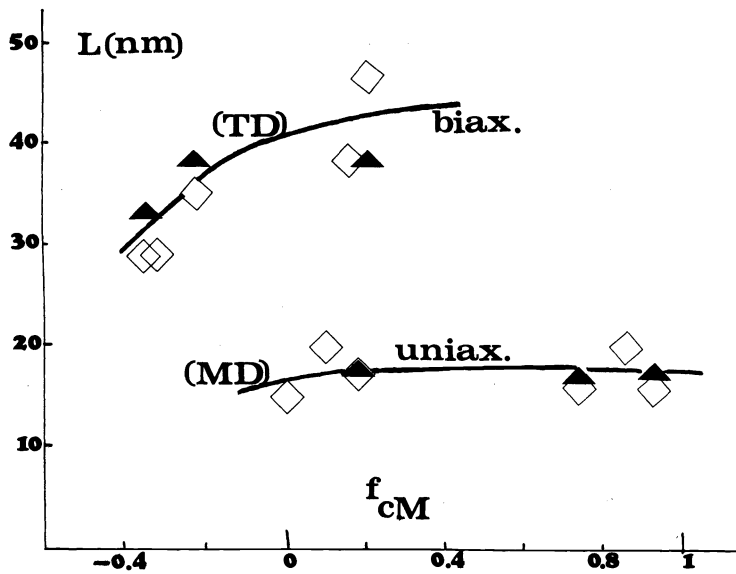λ_T and λ_M are nominal draw-ratios in T- and M - direction respectively.

Fig. 4 : Long period spacings in uni-and biaxially drawn films as a function of
crystal c-axis orientation ; SAXD-measurements by Participants 2 and 5,
orientation calculated from WAXD by Participant 6.

The contribution of the non-crystalline phase to the total birefringence, $(1 - v_x) \Delta_{am} n$, has been calculated from Eq. (2), neglecting the form birefringence and by adopting the calculated values for the crystalline contribution based on $\Delta^\circ_x = 29.10^{-3}$ (see Table 5). Comparing the crystalline and non-crystalline contributions to the birefringence in the case of biaxially drawn films, the following differences may be noted :

- in the unbalanced films 2.07 and 2.08, the non-crystalline contributions $\Delta_{am} n_{MN}$ are slightly negative, reflecting the predominant influence of the second draw (TD) which seems to have completely eliminated the effect of the first draw (MD) on the molecular orientation in the non-crystalline phase,

- in the nearly balanced films 2.10 and 2.11 the remaining degree of unbalance as expressed e.g. by the ratio $\Delta n_{TN}/ \Delta n_{MN}$ is much more important in the non-crystalline than in the crystalline phase. The final state of orientation in the crystalline phase is still strongly dependent on the degree of orientation induced during the first draw in the M-direction; the higher segmental mobility of the molecules in the non-crystalline regions, however, will favour a relatively rapid destruction of the initial MD-orientation, and the final state of non-crystalline orientation, therefore, mainly depends on the last draw in the T-direction.

Orientation in the non-crystalline phase may also be described in terms of orientation functions f_{am} derived from the non-crystalline contribution to the birefringence :

$$f_{am} = \Delta_{am} n/ \Delta^\circ_{am} = (\Delta n - v_x f_x \Delta^\circ_x) \Big/ (1 - v_x) \Delta^\circ_{am} \qquad (11)$$

No general agreement exists as to the exact value to be adopted for Δ°_{am}, the intrinsic birefringence of perfectly oriented non-crystalline polypropylene. If Samuels' method based on f_{am} determinations from sonic modulus measurements, is applied to the data of Participant 6, a value of about 60.10^{-3} is found as shown in Fig. 2, in good agreement with the results reported by Samuels (4). Recently still higher values for Δ°_{am} have been reported by Seferis and Samuels (16), derived from a large number of measurements of the angular distribution of refractive index in uniaxially oriented films for which the crystalline and non-crystalline orientation functions had been determined by means of WAXD and sonic modulus measurements.

In spite of the uncertainty concerning the absolute values of Δ°_x and Δ°_{am}, most of the evidence available at present seems to indicate that Δ°_{am} is significantly larger than Δ°_x; the f_{am}-values given in Table 5 have been calculated from Eq.(11) adopting $\Delta^\circ_{am} = 60.10^{-3}$. It is obvious from these data that the average molecular orientation in the non-crystalline regions is substantially lower than in the crystalline phase. The importance of this difference in average orientation will of course depend on the adopted values for the intrinsic birefringences but it is highly improbable that any reasonable modification of the latter parameters would seriously affect the general conclusion about the differences in molecular orientation between the two phases. These differences which are of particular interest in the biaxially drawn films as already discussed above, may be further analyzed by trying to distinguish between axial and planar c-axis orientation in both phases. The non-crystalline orientation functions in Table 5 are defined by Eq. (7) where "X" has to be replaced by "am". The relative amounts of axial, planar and random orientation are given by Eq. (9) which may be applied to both crystalline and non-crystalline phases. For the nearly balanced films 2.10 and 2.11 this analysis leads to the following results :

Film n° 2.10 :

crystalline phase : $\varphi_{ax} = 0.10$; $\varphi_{pl} = 0.84$; $\varphi_r = 0.06$

non-crystalline phase : $\varphi_{ax} = 0.17$; $\varphi_{pl} = 0.11$; $\varphi_r = 0.72$

Film n° 2.11 :

crystalline phase : $\varphi_{ax} = 0.05$; $\varphi_{pl} = 0.90$; $\varphi_r = 0.05$

non-crystalline phase : $\varphi_{ax} = 0.11$; $\varphi_{pl} = 0.34$; $\varphi_r = 0.55$

The data obtained clearly bring out the importance of randomly oriented molecules in the non-crystalline regions, in contrast with the crystalline phase where the amount of random orientation is negligible. The absolutes values concerning the non-crystalline phase depend of course ont he absolute value adopted for Δ°_{am} , but the latter parameter does not affect, as easily shown, the calculated ratio of planar-to-axial orientation in the non-crystalline regions. This ratio, φ_{pl} / φ_{ax}, is much smaller than the corresponding ratio for the crystalline phase and even smaller than one in the case of film 2.10. A preference for planar orientation in the non-crystalline regions exists, however, in film 2.11 (φ_{pl}/ $\varphi_{ax} \simeq 3$) in spite of the still important difference in f_{am}-values with respect to the M - and T directions (see Table 5)

Although a still larger preference for planar orientation may be anticipated in perfectly balanced biaxially drawn films, it is not expected that planar orientation in the non-crystalline regions will ever attain the same importance as in the crystalline phase.

8 - MOLECULAR ORIENTATION AND INFRA-RED DICHROISM

Infra-red dichroic ratios for different absorption bands were determined by four participants. Although, in general, two independent dichroic ratios have to be known for a full description of the dichroic behaviour of an absorption band, only one ratio as been measured in this study, D_{MT} for uniaxially drawn films or its inverse, D_{TM} in the case of biaxially drawn films :

$$D_{MT} = A_M / A_T = D_{TM}^{-1}$$

if A_M is the absorbance of radiation polarized parallel to the M-direction and A_T the absorbance of radiation with its plane of polarization parallel to the T-direction.

All four participants explored several absorption bands, the maximum number being eleven. In general the results obtained with different spectrometers were in fair agreement ; one participant who found systematically weaker dichroism than the other participants, using a convential instrument, obtained better agreement by performing measurements with a Fourier Transform I-R spectrometer which seems to indicate that the results may be affected by the instrument's resolving power.
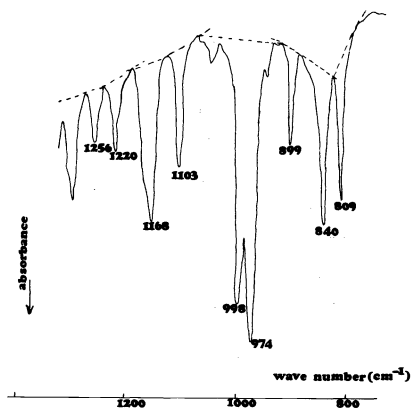

Fig. 5 : Typical I-R absorption spectrum between 800 and 1400 cm^{-1}.(Participant 6)

Differences in base line definition may also be responsible for part of the disagreement observed. A typical example of a spectrum with its base line definition is shown in Fig.5. Some absorption bands proved to be unsuitable for accurate dichroism measurements, because their absorbance was either too weak or too strong and for this reason most participants were unable to explore all absorption bands for both uni-and biaxially drawn films, due to the large difference in thickness between these two types of film. An interesting example of this particular problem is provided by the 1220 cm^{-1} band, generally considered to be one of the specific absorption bands which reflect chain ordering of helical isotactic structures (Refs. 5, 22, 23) only existing in the crystalline regions of the polymer.

The absorbance of the 1220 cm^{-1} band was considered strong enough by several participants for dichroism measurements on the uniaxially drawn films, but in the case of the much thinner biaxially drawn films only participant 2 was able to obtain significant results. On the contrary the absorbance of other bands, e.g. at 840 and 998 cm^{-1}, was considered too strong by most participants for obtaining significant results in the case of the relatively thick uniaxially drawn films.

Approximate crystalline orientation functions f_{IR} calculated from D_{MT} mesured for different "crystallinity bands" in uniaxially drawn films have been plotted versus f_{cM}-values obtained from WAXD in Fig. 6. Some additional data on other films with intermediate f_{cM}-values, obtained by Participant 6, were also plotted in the same figure. The following expressions have been used :

$$f_{IR} = 2 \ (1 - D_{MT}) \ / \ (D_{MT} + 2) \qquad \text{for } D_{MT} < 1$$

$$= (D_{MT} - 1) \ (D_{MT} + 2) \qquad \text{for } D_{MT} > 1 \qquad (12)$$

It is well-known (Refs. 24,25) that Eqs. (12) are only valid for uniaxial orientation if the transition moment **M** of the absorbing vibration is either perpendicular or parallel to the polymer chain axis. For a transition moment angle smaller than $90°$ ($D_{MT} < 1$) or larger than $0°$ ($D_{MT} > 1$), use of Eq. (12) should lead to underestimated values for the orientation function. If transition moment vectors form an angle α with the chain axis and are randomly distributed with respect to other axes, Eq. (12) should be replaced by a more general relationship :

$$f_{IR} = \left[(D_{MT} - 1) \ / \ (D_{MT} + 2) \right] \cdot \left[(D_o + 2) \ / \ (D_o - 1) \right] \qquad (13)$$
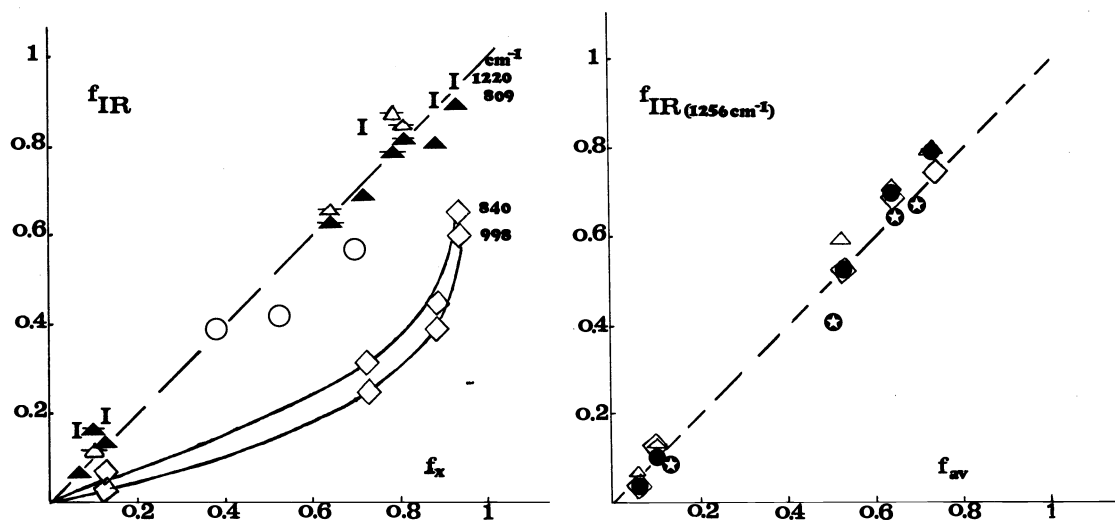
where $\qquad D_o = 2 \cot^2 \alpha$

Fig. 6 : Crystalline phase orientation calculated from IR-dichroism (Eq. 12)
versus crystal orientation deduced from WAXD.

I range of values obtained by Participant 2,5 and 6 on uniaxially
drawn films at 1220 cm^{-1},

◯ measurements by Participant 6 on films of intermediate orientation
(1220 cm^{-1})

▲ measurements by Participant 2 at 809 cm^{-1}

◇ measurements by Participant 5 at 840 and 998 cm^{-1}

△ ▲ measurements by Participant 2 (1220 and 809 cm^{-1}) on biaxially drawn
films

‒ ‒ ‒ ‒ ‒ ‒ ‒ ‒ ‒ $f_{IR} = f_X$

Fig. 7 : Average orientation calculated from IR-dichroism at 1256 cm^{-1} (Eq. 12)
versus average orientation deduced from WAXD and birefringence (Eq. 14).
Measurements by Participants 2,5 and 6 on uniaxially drawn films (△ ,
◇ , ●) and on biaxially drawn films (✪)

‒ ‒ ‒ ‒ ‒ ‒ ‒ ‒ ‒ $f_{IR} = f_{av}$

Results of dichroism measurements published by Samuels (5) show that orientation functions calculated from Eq. (13) in the case of the 1220 cm^{-1} band are in reasonable agreement with WAXD - data if α is taken equal to 72°. The results of the present study, plotted in figure 6 are in fair agreement with Eq. (12) which means that α would be equal to 90°. In view of the rather good accordance of results obtained in three laboratories it is improbable that systematic or other experimental errors in the present study be responsible for the significant difference in angle compared to the results of Ref. (5).

As to the other absorption bands considered to be specific of the crystalline regions only, the 941 cm^{-1} and 809 cm^{-1} bands also seem associated with a vibration mode whose transition moment is practically perpendicular to the chain axis. Unfortunately the absorbance at 941cm^{-1} was found to be still weaker than at 1220 cm^{-1} and too weak for investigating the biaxially drawn films in this study with the aid of conventional spectrometers. For most other "crystallinity bands" the transition moment angle should be somewhere between 0 and 90° , because the orientation functions calculated from Eq. (12) are more or less significantly smaller than the real ones. This conclusion is not in agreement with various results reported in the litterature, in particular with regard to the 840 and 998 cm^{-1} bands (Refs. 26, 27). If IR-absorption is not limited to the crystalline regions, application of Eq. (12) or (13) will lead to orientation function values which are in disagreement with those calculated from WAXD but which may be expected to correlate with some average orientation function. Samuels (5) has shown, e. g. that the dichroism of the 1256 cm^{-1} band correlates well with average orientation defined by :

$$f_{av} = v_x \cdot f_x + (1 - v_x) \cdot f_{am} \tag{14}$$

The orientation function calculated by means of Eq. (12) from the observed dichroism at 1256 cm^{-1} for uniaxially drawn films is compared with f_{av} calculated from combined WAXD and birefringence measurements in Fig. 7. It is obvious that both sets of values are practically identical which means that the transition moment vectors associated with the 1256 cm^{-1} vibration would be parallel to the polymer chain axis. This conclusion does not apply to the data published by Samuels (5) that seem to indicate an average transition moment angle significantly different from zero.

Another band which has been sometimes used (Ref. 26) for the determination of an average orientation function, is the 974 cm^{-1} band. The absorbance of this band was considered too strong by most participants for yielding accurate values in the case of the uniaxially drawn films ; in the biaxially drawn films its dichroism was found to be smaller than for the 1256 cm^{-1} band although the importance of this difference varied somewhat from one laboratory to another. It follows that application of Eq. (12) to dichroism data at 974 cm^{-1} may be expected to yield underestimated values for the average orientation in uniaxially drawn films too.

If Eq. (12) is applied to the dichroic ratios D_{TM} measured on the biaxially drawn films (which means that one ignores the absence of transverse isotropy with respect to the T-direction) "apparent" values for the orientation function are obtained that may be compared to the values of f_x and f_{av}, determined by WAXD and birefringence, as defined by :

$$f_x = \frac{2}{3} \quad (f_{cT} - f_{cM})_x \tag{7'}$$

$$f_{am} = (n_T - n_M)_{am} / (1 - v_x) \Delta_{am}^{\circ} \tag{11'}$$

and Eq. (14).

Values for f_{IR} obtained in this way from observed ratios D_{TM} at 809, 1220 and 1256 cm^{-1}, respectively, are also plotted in Figs .6 and 7 and appear to be in rather good agreement with the f_x - and f_{av} - values derived from WAXD and birefringence. This unexpected agreement may be fortuitous and needs further confirmation. A general description of Infra-red Dichroism in biaxially oriented films has been proposed by several authors (Refs. 13, 24, 25, 28); in the particular case of the 809, 1220 and 1256 cm^{-1} absorption bands of isotactic polypropylene we have tempted the following simplified analysis :

If the transition moment vector is parallel to the molecular c-axis,

$$D_{TM} = A_T/A_M = k \, \overline{cos^2 \, \phi_{cT}} \, / \, k \, \overline{cos^2 \, \phi_{cM}} \quad \text{where k is a proportionality constant.}$$

The average angle between the c-axis and any coordinate axis, Z, is related to the orientation function by :

$$f_{cZ} = (3 \overline{\cos^2 \phi_{cZ}} - 1) /2 \qquad\qquad , \text{ or}$$

$$\overline{\cos^2 \phi_{cZ}} = (2 f_{cZ} + 1) /3 \qquad\qquad (15)$$

It follows that the dichroic ratio in this case is given by :

$$D_{TM} = (2 f_{cT} + 1) / (2 f_{cM} + 1) \qquad\qquad (16)$$

In the case of a transition moment vector **M** which on the average is randomly oriented in a plane perpendicular to the molecular c-axis (a reasonable approximation for the crystallinity bands at 809 and 1220 cm^{-1}), the angle Θ_Z formed between this vector **M** and any coordinate axis Z is given by :

$$\overline{2 \cos^2 \Theta_Z} = 1 - \overline{\cos^2 \phi_{cZ}} \qquad\qquad (17)$$

The dichroic ratio in this case is, therefore, equal to :

$$D_{TM} = k \overline{\cos^2 \Theta_T} / k \overline{\cos^2 \Theta_M} = (1 - \overline{\cos^2 \phi_{cT}}) / (1 - \overline{\cos^2 \phi_{cM}}) \qquad (18)$$

which after substitution of Eq. (15), leads to :

$$D_{TM} = (1 - f_{cT}) / (1 - f_{cM}) \qquad\qquad (19)$$

It can be easily verified that in the particular case of uniaxial orientation, either with respect to the M-axis ($f_{cM} = - 2 f_{cT}$) or the T-axis ($f_{cT} = - 2 f_{cM}$), Eqs. (16) and (19) will reduce to one of the forms of Eq. (12).
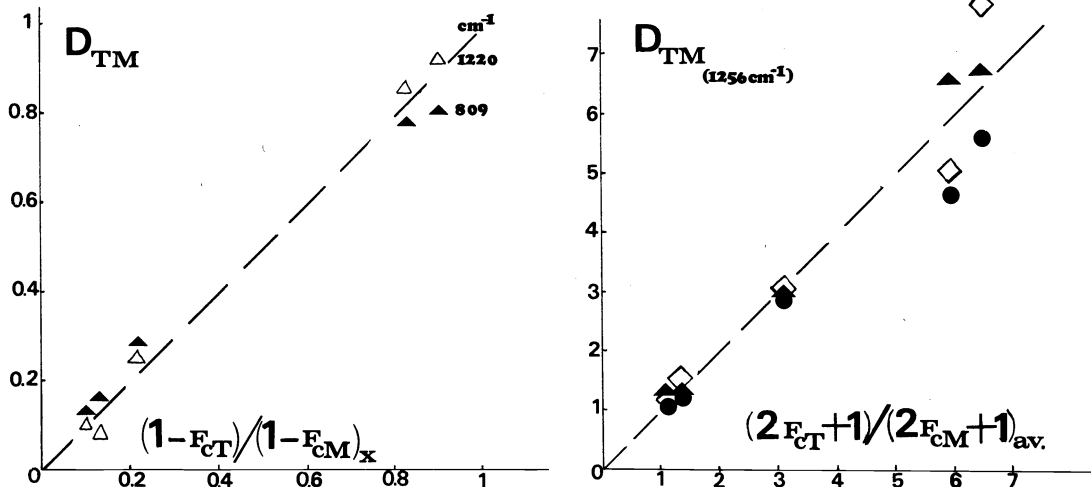

Fig. 8 : Observed versus calculated dichroic ratios for biaxially drawn polypropylene films (Eq. 19). Measurements by Participant 2 at 809 (▲) and 1220 cm^{-1} (△)

Fig. 9 : Observed versus calculated dichroic ratios for biaxially drawn polypropylene films (Eq. 16). Measurements at 1256 cm^{-1} by Participants 2,5 and 6.

In Fig. 8 we have plotted the observed dichroic ratios at 809 and 1220 cm^{-1} reported by Participant 2 versus D_{TM} - values calculated with the aid of Eq. (19) from the crystalline orientation functions f_{cM} and f_{cT} given in Table 4. The agreement is very good except for film 2.07 whose measured dichroic ratio at 1220 cm^{-1} is about 35 % lower than the calculated one.

A similar plot for the 1256 cm^{-1} band is shown in Fig. 9, which compares the dichroic ratios reported by three participants with values calculated by means of Eq. (16) from the average orientation functions f_{cT} and f_{cM}, as defined by Eq. (14). The discrepancies between the experimental results of the three participants are relatively important, in particular for films 2.07 and 2.08, but the mean observed values, even in this case, are less than 10 % different from the calculated ones.

We conclude that Eqs. (16) and (19) may be simultaneously used for the determination of two independent orientation functions associated with a particular phase , if the dichroic ratios for at least one parallel and one perpendicular absorption band are measurable.

9 - DISCUSSION AND CONCLUSIONS :

The results obtained in this collaborative study show that the combination of various experimental techniques may provide quantitative information on the state of molecular orientation in both crystalline and non-crystalline phases of uni-and biaxially drawn polypropylene films. Wide Angle X-ray Diffraction is undoubtedly the most appropriate characterization method if one wants an unambiguous description of average orientation in the crystalline regions of the polymer. WAXD - analysis proved to be particularly useful in the case of biaxially drawn films as it allowed us to distinguish between axial and planar orientation as well as to determine the degree of unbalanced orientation in the plane of the film.

Birefringence data either directly measured or calculated from the measured principal refractive indices provide complementary information required for a more general description of molecular orientation in both crystalline and non-crystalline phases. Because of the relatively high degree of crystallinity, birefringence in the films investigated here, is mainly determined by orientation in the crystalline phase ; nevertheless the contribution of the non-crystalline regions cannot be neglected. The importance of the latter contribution and the degree of molecular orientation in the non-crystalline regions which is proportional to this contribution depend critically on the assumed values for the intrinsic birefringence of both phases. The results obtained in the present investigation do not allow any definite conclusion about the exact values for these intrinsic parameters, but it may be concluded that they are not incompatible with the values proposed by Samuels (4). In particular our results seem to indicate that the most probable value for Δ°_{x} should not be very different from 30 ($\pm$ 5). 10^{-3} and that the value of Δ°_{am} must be substantially higher than Δ°_{x}.

Irrespective of the exact values adopted for the intrinsic birefringences, the conclusion that average molecular orientation in the non-crystalline regions is lower than in the crystalline phase for both uni-and biaxially drawn films, appears inevitable. This difference between the two phases is particularly important in the biaxially drawn films and can be further qualified in terms of degree of unbalanced orientation, on the one hand and ratio of planar-to-axial c-axis orientation, on the other hand.

The observed differences are not unexpected if one takes account of the higher segmental mobility in the non-crystalline regions and if one remembers that the biaxially oriented films have been obtained by means of a sequential stretching process.

Measurement of principal refractive indices does not only allow a complete description of birefringence but may also be used for a rapid determination of density and crystallinity (by adopting the usual two-phase model).

Small Angle X-ray Diffraction yields values for long period spacings which appear to be strongly dependent on fabrication conditions (draw and annealing temperatures), but which do not seem to be related in a straight forward way to molecular orientation in the crystalline phase. In biaxially drawn films the long period spacing in the T-direction was even shown to increase with decreasing molecular orientation with respect to the same direction.

However, the width of the SAXD-intensity peaks also decreased, in general, with increasing orientation (in the M-direction for uniaxially and in the T-direction for biaxially drawn films), which tends to indicate that supermolecular structural units (crystal lamellae, microfibrils) align themselves in the direction of highest draw-ratio. The orientation of these structural entities may be more or less closely coupled to the orientation of molecular chain axes in the crystalline phase (Refs. 4,29) but the quantitative aspects of such a relationship have not been further examined in the present investigation.

Finally our study has confirmed that Infra-red Dichroism measurements may provide valuable information on molecular orientation in both crystalline and amorphous phases by means of an appropriate choice of absorption bands. In biaxially oriented films the knowledge of two independent dichroic ratios would be required for a complete description of each absorption band. Two particular examples, corresponding to the limiting case of a perfectly parallel and a perfectly perpendicular absorption band, respectively, have been analyzed showing that the dichroic ratio will be determined, in general, by two independent orientation functions of the molecular chain axis. The agreement between calculated and observed dichroic ratios for the 809, 1220 and 1256 cm^{-1} bands in the case of biaxially drawn films is rather satisfactory and serves to illustrate the potential possibilities of this experimental technique for quantitative characterization of any state of molecular orientation.

As to other methods proposed in the literature for the characterization of molecular orientation in semi-crystalline polymers, two participants in this programme have performed sonic modulus measurements at room temperature. Their results will be discussed together with the results of relaxation and dynamic modulus measurements in Part 2 of the present report.

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