Determination of Intrinsic Birefringence of Smectic Phase in Isotactic Polypropylene

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SYNOPSIS

When isotactic polypropylene is quenched at 0°C from the molten state, a biphasic material, amorphous-smectic, is obtained. The smectic phase has an intermediate order between the amorphous and the crystalline. In this study the intrinsic birefringence of the smectic phase was determined. Tapes with different draw ratio were prepared at room temperature, at which the smectic phase does not transform into the crystalline phase. The amount of the smectic phase was determined with measurements of density and sorption of vapors of dichloromethane. The value of the intrinsic birefringence for the smectic phase is: $\Delta°n_{sm} = 40 \cdot 10^{-3}$. This value is in good agreement with the values proposed by Samuels for the intrinsic birefringence of the amorphous and the crystalline phases. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Isotactic polypropylene (iPP) is one of the most investigated polymers because of its commercial and industrial importance. Depending on the thermal treatments, molecular mass, and the degree of tacticity, iPP can crystallize in three different polymorphic forms: α (monoclinic), β (hexagonal), and γ (triclinic).[1,2] Moreover, when iPP is rapidly quenched from the melt at low temperature (i.e., $-70°C$), a biphasic system is obtained: one phase is amorphous, the other has an order intermediate between the amorphous and the crystalline phase, described as the smectic,[3] paracrystal,[4] glass,[5] or mesomorphic phase.[6] The smectic phase is stable at room temperature for long periods of time, but it transforms into the monoclinic α form when heated above 60°C.[7,8]

The drawing at room temperature does not allow change of the smectic phase into the crystalline form.[9] Therefore, it is possible to obtain oriented smectic samples.

A complete characterization of the molecular orientation must take into account the orientation of

either the smectic phase or the amorphous phase. In this work we are interested in determining the intrinsic birefringence of the smectic phase that is a datum not available in the literature. For this reason the chain orientation, which is of primary importance for the improvement of physical properties and a better understanding of the processing–structure–property relationship,[10–18] must be measured. The molecular orientation was determined with the measurements of the total birefringence and FTIR spectroscopy.

Moreover, for the characterization of tapes one must know the amounts of the amorphous and smectic phases. The smectic volume fractions were determined from sorption of dichloromethane vapor at low activity.

EXPERIMENTAL

Materials

The iPP was a RAPRA product, M_w 307,000 and M_n 15,600. iPP films, 100-μm thick, were prepared by pressure molding pellets at 200°C followed by rapid quenching in a dry-ice acetone bath at $-70°C$. The films obtained were biphasic smectic-amorphous systems with a density of 0.8845 g/mL. The

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films were drawn at room temperature on an Instron tensile-testing machine at a crosshead speed of 10 mm min^{-1}. Tapes with the draw ratio ($\lambda = L/L_o$) 3, 4, 5, and 6 were prepared.

Density Measurements

Density measurements were performed by means of the floatation method, using a mixture of 1, 2 dimethoxy-ethane and 2 ethoxy-ethanol. The values used for the density of the amorphous and the smectic phase are $d_{am} = 0.856$ and $d_{sm} = 0.916$ g/mL.[19] From the density data, d, it is possible to determine the volume fraction of the smectic phase Φ_{sm} given by:

$$\Phi_{sm} = \frac{d - d_{am}}{d_{sm} - d_{am}}. \qquad (1)$$

Sorption Measurements

Sorption of dichloromethane vapor was measured by a microgravimetic method using a quartz spring balance with an extension of 15 mm/mg. Sorption was measured at 25°C as a function of vapor activity, $a = p/p_i$, where p is the actual pressure to which the sample was exposed and p_i is the saturation pressure at the temperature of the experiment.

Infrared Measurements

Infrared spectra were recorded using a Nicolet 5DXB FTIR spectrophotometer with a resolution of 4 cm^{-1} (50 scans collected). For the infrared dicroic measurements a Perkin–Elmer gold wire grid polarizer was used. To determine the orientation of either the smectic or the amorphous phase, the dicroic ratio for the bands at 998 and 973 cm^{-1} was detected for the tapes at different draw ratios.

Birefringence

When a polymeric film is uniaxially deformed, molecules orient with respect to the deformation axis, manifesting anisotropic optical properties.[11] The total birefringence, Δn_T, defined as the difference between the refractive index in the stretch direction, $n_\parallel$, and the refractive index perpendicular to the stretch direction, $n_\perp$, was determined by using three wavelengths, 632.8, 514, and 457.9 nm. The radiation with wavelength 632.8 nm came from a Spectra Physics He–Ne laser, and radiations with wavelengths 457.9 and 514.5 nm were from a Spectra Physics Ar laser.

The method for determining the birefringence is based on the use of a compensator. In this study a tilting compensator with magnesium fluoride was used.

RESULTS AND DISCUSSION

Sorption

In Figure 1 the equilibrium concentration of dichloromethane is reported as a function of vapor activity for the completely amorphous atactic pp and for all the drawn samples.

The procedure to obtain the amorphous fraction in a biphasic amorphous-smectic system consists of determining the sorption of dichloromethane vapor in the deformed samples as a function of vapor activity. It was already shown that at low penetrant activity the smectic phase does not diffuse and sorb the vapor,[19,20] and the amorphous phase is the only permeable phase. Because the specific sorption is the same in all the samples,[19,20] the equilibrium concentration of vapor in each biphasic smectic-amorphous sample, C_{eq}, is related to the fraction of the amorphous phase X_a, by the relation:

$$C_{eq} = C_{sp}X_a \qquad (2)$$
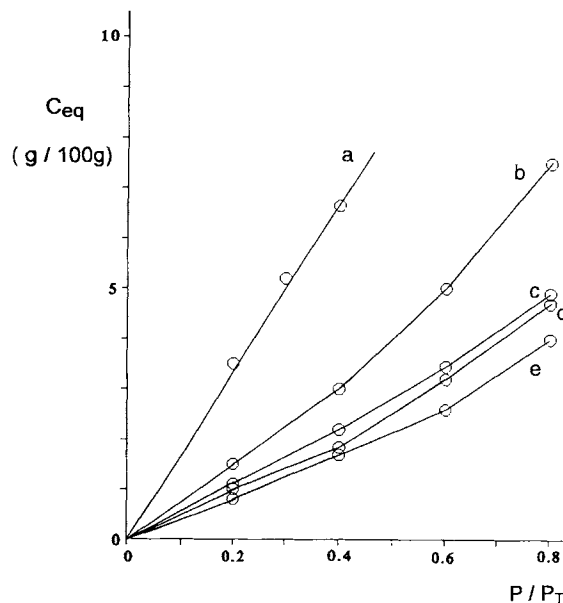
Figure 1 Equilibrium concentration of CH$_2$Cl$_2$ vapor as a function of activity $a = P/P_T$ for: (a) atactic polypropylene and for samples drawn at (b) $\lambda = 3$, (c) $\lambda = 4$, (d) $\lambda = 5$, and (e) $\lambda = 6$.

Table I   Smectic Fractions and Orientation Functions for Samples Drawn at Different Draw Ratio

λ	Density (g/mL)	Smectic Vol. Fraction from Density	Smectic Mass Fraction from Transport	Smectic Vol. Fraction from Transport	f_{sm} from 998 cm^{-1}	f_{av} from 973 cm^{-1}	f_{am} From Density	f_{am} From Transport	$\Delta n_T \cdot 10^3$
3	0.8907	0.58	0.64	0.62	0.68	0.54	0.35	0.31	22.4
4	0.8914	0.59	0.67	0.65	0.84	0.64	0.35	0.27	26.5
5	0.8923	0.61	0.70	0.68	0.93	0.72	0.39	0.28	29.2
6	0.8927	0.61	0.74	0.72	0.98	0.79	0.49	0.30	32.4

where the specific concentration C_{sp} can be assumed equal to C_{eq} of the completely amorphous atactic pp. Therefore, we derived at low activity the fraction of amorphous phase X_a by dividing the equilibrium concentration of vapor in each sample by the equilibrium concentration of the amorphous sample. The obtained values of X_a are reported in Table I.

In Figure 2 the volume fraction of the smectic phase obtained with transport and density measurements is reported as a function of the draw ratio λ. The data obtained with the density measurements are lower than those obtained with transport measurements. This could be explained by the presence of microcrazes formed during the deformation process, and their concentration lightly increases with the draw ratio.

Infrared Dicroism

The orientation of the smectic and amorphous phase is defined by the Hermans orientation function[21]:

$$f = \frac{3 \cos 2\theta - 1}{2} \tag{3}$$

in which θ represents the average angle between the chain axis in a particular phase and a reference axis that usually is the drawn direction.

The average orientation function, which takes into account the overall orientation of the smectic and amorphous phases, is defined as[11,22]

$$f_{av} = \Phi_{sm}f_{sm} + (1 - \Phi_{sm})f_{am} \tag{4}$$

in which Φ_{sm} has already been defined, f_{am} and f_{sm} are the orientation functions for the amorphous and the smectic phase, respectively, and f_{av} refers to the total state of orientation of the system.

Infrared dicroism is widely used to determine molecular orientation. The intensity of an infrared absorption band depends upon the angle between the transition moment, M, of the specific vibration
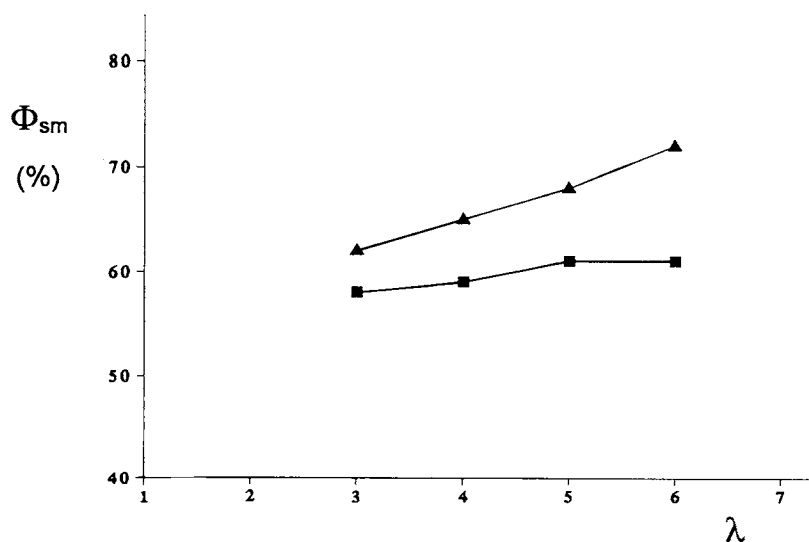
Figure 2   Volume fraction of the smectic phase as a function of the draw ratio λ: ($\triangle$) from transport and ($\square$) from density.
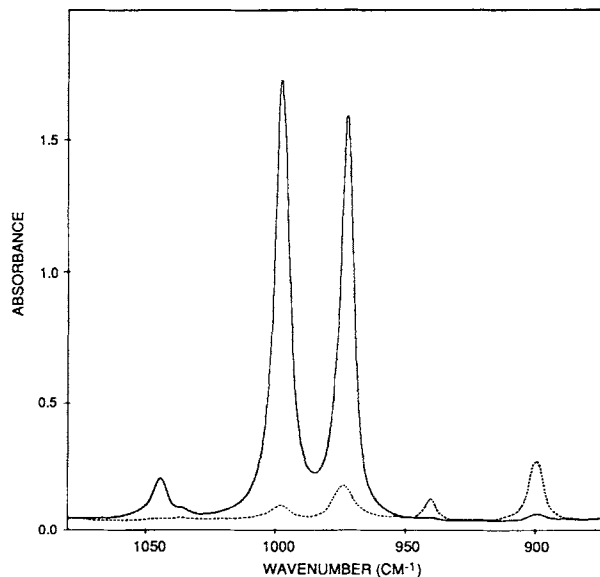
Figure 3 Infrared spectrum of a drawn sample: (- - -) polarization vector parallel to draw direction and (· · ·) polarization vector perpendicular to draw direction.

mode and the electric vector, E, of the incident radiation. The dicroic ratio, D, is defined as:

$$D = \frac{A_{\parallel}}{A_{\perp}} \qquad (5)$$

where $A_{\parallel}$ and $A_{\perp}$ are the absorbances in which the incident radiation is parallel and perpendicular to the draw direction, respectively. The dicroic ratio is related to the orientation function by[22,23]:

$$f = \frac{(D - 1)(D_o + 2)}{(D + 2)(D_o - 1)} \qquad (6)$$

where $D_o = 2 \cot^2\alpha$, α being the angle between the chain axis and the transition moment M of the specific absorption band. Therefore, if the angle α is known, the average orientation of the chain segments can be determined from the measured dicroic ratios of each specific band.

In this work 973 and 998 cm^{-1} bands were studied. They can be described as being very strong in intensity and showing parallel polarization characteristics (Fig. 3).

The 998 cm^{-1} band was assigned to crystalline or highly ordered material with $\alpha = 18°$.[22] This band is used here to determine the orientation function of the smectic phase. This is reasonable because in the smectic phase the chains in the helix conformations are arranged parallel but with little or no lateral register.[3,24] Moreover, this peak remains even when the regular sequence length is reduced below 10 units.[25] A weak band at this frequency in the spectrum of the melt was explained by Zerbi et al.[26] as being due to segments of at least five monomer units in the helical conformation.

Also for this band $\alpha = 18°$.[22] In a recent paper Karacan et al.[18] found for this band an angle of 23°, but in this study $\alpha = 18°$ was considered. In Table I and Figure 4 the average orientation function and the smectic orientation function are obtained from the two dicroic bands at 973 and 998 cm^{-1}, respectively. From eq. (4) it is possible to determine the orientation function for the amorphous phase:
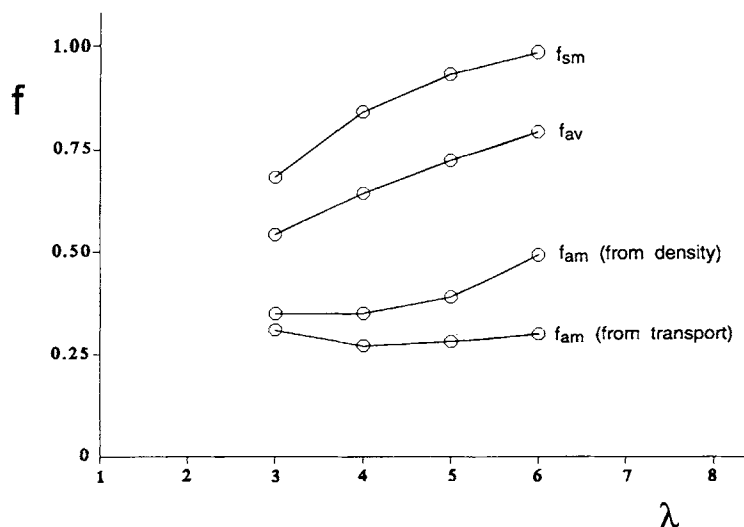
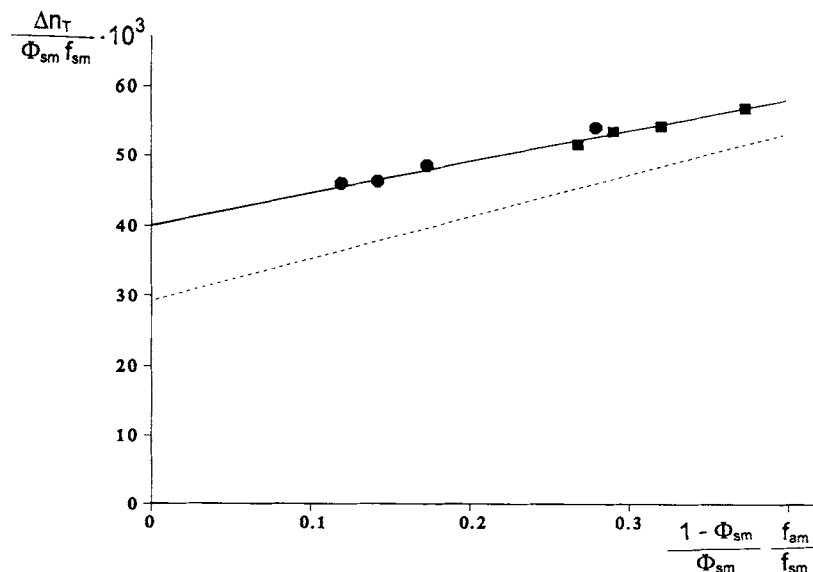**Figure 4** Orientation functions as a function of the draw ratio.

Figure 5 Samuels plot: (O) from density, (□) from transport, and (- - -) after Samuels.[11]

$$f_{am} = \frac{f_{av} - \Phi_{sm}f_{sm}}{1 - \Phi_{sm}}. \qquad (7)$$

Because the volume fraction for the smectic phase is obtained with the transport and density measurements, and the data are not coincident, we deduce for each draw ratio two values for f_{am}.

Birefringence

In an oriented polymeric system the birefringence can be considered, assuming the additivity of contributions of different phases, as[10]

$$\Delta n_T = \Delta n_f + \sum \Phi_i \Delta n_i \qquad (8)$$

where i refers to the ith phase, Φ_i its volume fraction, and Δn_f is the part of the total birefringence, Δn_T, that arises from form or deformation effects rather than orientation.

In our case, because the system is biphasic smectic and amorphous, and considering the contribution of the form birefringence negligible, the equation for the total birefringence can be written in the form

$$\Delta n_T = \Phi_{sm}f_{sm}\Delta^\circ n_{sm} + (1 - \Phi_{sm})f_{am}\Delta^\circ n_{am} \qquad (9)$$

in which $\Delta^\circ n_{sm}$ and $\Delta^\circ n_{am}$ are the intrinsic birefringences of the smectic and the amorphous phases, respectively. The data of the total birefringence are reported in Table I.

In eq. (9) the total birefringence is measured for the samples with draw ratio 3, 4, 5, and 6; Φ_{sm} can

be obtained from the density and from the transport data; and f_{sm} and f_{am} are determined with the infrared dicroism.

If we divide all the terms of eq. (9) by $\Phi_{sm}f_{sm}$, we obtain

$$\frac{\Delta n_T}{\Phi_{sm}f_{sm}} = \Delta^\circ n_{sm} + \Delta^\circ n_{am} \frac{1 - \Phi_{sm}}{\Phi_{sm}} \frac{f_{am}}{f_{sm}}. \qquad (10)$$

If $\Delta n_T/\Phi_{sm}f_{sm}$ values are reported versus $(1 - \Phi_{sm})f_{am}/\Phi_{sm}f_{sm}$, it is possible to determine $\Delta^\circ n_{sm}$ and $\Delta^\circ n_{am}$ graphically.

In Figure 5 the experimental data are reported. For each draw ratio, the quantities $\Delta n_T/\Phi_{sm}f_{sm}$ and $(1 - \Phi_{sm})f_{am}/\Phi_{sm}f_{sm}$ were calculated either with the density data or with the transport data. In the same figure the line obtained by Samuels is also reported.[11] He worked on biphasic iPP samples, amorphous-monoclinic, and he found that the intrinsic birefringence of the crystalline regions, $\Delta^\circ n_c = 29.1 \cdot 10^{-3}$, and that for the amorphous regions, $\Delta^\circ n_{am} = 60.0 \cdot 10^{-3}$. The fact that the intrinsic birefringence for the amorphous phase is greater than that of the crystalline phase was explained by Samuels as due to the internal field that is more anisotropic in the ordered lattice of the crystal than in the disordered amorphous phase.[11] This means that there are different effective polarizabilities in the two phases. Stein derived a theory to account for internal field effects in the polyethylene crystal.[27] He found that, due to internal field effect, the intrinsic birefringence of the crystal will be lower than that of the amorphous material.
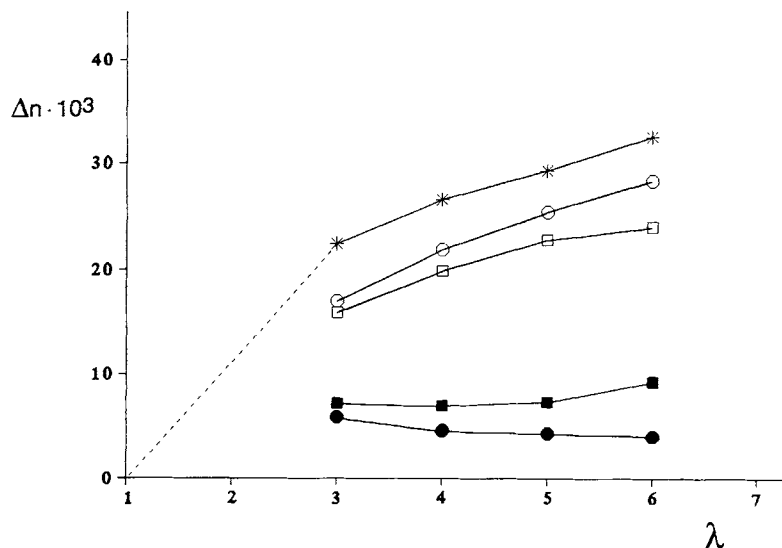
Figure 6 Total birefringence and amorphous and smectic contributions as a function of the draw ratio λ. ($*$) Total birefringence; (○) smectic contribution calculated with transport data, (□) and with the density data; (●) amorphous contribution calculated with transport data, and (■) with the density data.

For iPP other values for the intrinsic birefringence of the crystalline and the amorphous phase are available in the literature. Matsuko et al. found the values $41.6 \cdot 10^{-3}$ and $37.9 \cdot 10^{-3}$, respectively, for the crystalline and the amorphous phase.[28] These data are not in good agreement with those found by Samuels.[11]

From Figure 5 we can deduce $\Delta^\circ n_{sm} = 40 \cdot 10^{-3}$ and $\Delta^\circ n_{am} = 48 \cdot 10^{-3}$. The datum of the intrinsic birefringence of the smectic phase has a value intermediate between the intrinsic birefringence of the crystalline and the amorphous phase found by Samuels.[11] This is reasonable if we consider that the smectic phase can also be considered a phase of intermediate order between the crystalline and the amorphous. The value of the intrinsic birefringence of the amorphous phase, lower than that found by Samuels,[11] can be explained in terms of modification of the internal field due to the presence of the smectic phase instead of the crystalline phase.

Once the intrinsic birefringence for the amorphous and the smectic phases are known, it is possible to calculate the contribution of the two phases to the total birefringence according to

$$\Delta n_{sm} = \Phi_{sm} f_{sm} \Delta^\circ n_{sm}, \qquad (11)$$

$$\Delta n_{am} = (1 - \Phi_{sm}) f_{am} \Delta^\circ n_{am}. \qquad (12)$$

In Fig. 6 the amorphous and the smectic contributions calculated with the data of density and

transport are reported. The trends of the curves for the smectic and amorphous contributions are quite reasonable. However, the smectic and the amorphous contribution obtained with different techniques do not overlap. This discrepancy can be due to the presence of microcrazes in the samples due to the deformation process; and, because the difference is more evident at higher draw ratios, their concentration increases with the draw ratio.

CONCLUSIONS

In the present study the intrinsic birefringence of the smectic phase of iPP was determined. Its value $\Delta^\circ n_{sm} = 40 \cdot 10^{-3}$ is intermediate between the intrinsic birefringence of the crystalline and amorphous phases proposed by Samuels.[11] The smectic fraction was determined with measurements of density and sorption of methylene chloride. The results are not coincident, probably because of the presence of microcrazes in the oriented samples. In the oriented samples, moreover, the amorphous phase remains significantly less oriented than the smectic phase. This result has already been observed in biphasic crystalline-amorphous PP.

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