Fourier transform infra-red study of uniaxially-oriented isotactic polystyrene

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(*Received* 22 *September* 1980; *revised* 29 *December* 1980)

Fourier transform infra-red measurements have been made of the orientation in isotactic polystyrene as a function of draw ratio. Based on these results, new band assignments are made and orientation functions calculated.

INTRODUCTION

Processing of polymers usually introduces molecular orientation of the macromolecular chains which, in turn, strongly influences the mechanical properties. Thus, a great deal of interest exists in the measurement of the final orientation in order to correlate the processing conditions with the physical properties of the fabricated sample. Numerous methods have been proposed to measure this orientation: X-ray diffraction, birefringence, sonic modulus, polarized fluorescence, broad-line n.m.r., u.v. and infra-red dichroism and polarized Raman spectroscopy[1,2]. These methods give information on the overall orientation or are specific to crystalline or amorphous regions. Vibrational spectroscopy is particularly attractive since it allows the possibility of obtaining the orientation of both crystalline and amorphous regions using specific modes associated with these different structures.

The present experimental approach deals with the use of Fourier transform infra-red (*FT*i.r.) spectroscopy to evaluate the orientation of uniaxially-oriented isotactic polystyrene as a function of draw ratio.

THEORETICAL

Although the use of vibrational spectroscopy to measure orientation in polymers was recently reviewed[3], it is worthwhile to sum up briefly the information available from infra-red dichroism measurements. The orientation of a single unit of a polymer chain can be described by the three Eulerian angles, θ, φ and ψ, which define the three rotations required to bring into coincidence a set of Cartesian axes in the unit with a reference set of Cartesian axes in the oriented polymer. The orientation can be described by an orientation distribution function $f(\theta, \varphi, \psi)$. In the case of uniaxially-oriented systems, the orientation distribution of structural units is random with respect to φ and ψ.

Considering the spherical harmonic functions:

$$P_2(\cos\theta) = (3\cos^2\theta - 1)/2$$
$$P_4(\cos\theta) = (35\cos^4\theta - 3\cos^2\theta + 3)/8$$

the orientation distribution function can be expressed as:

$$f(\theta) = \sum_{n=0}^{\infty} (n + 1/2)\langle P_n(\cos\theta)\rangle_{\mathrm{av}} P_n(\cos\theta)$$

The dichroic ratio $R = A_{\parallel}/A_{\perp}$ ($A_{\parallel}$ and $A_{\perp}$ being the measured absorbance for electric vector parallel and perpendicular to the draw direction, respectively) is related to the harmonic orientation function $\langle P_2(\cos\theta)\rangle_{\mathrm{av}}$ by:

$$\langle P_2(\cos\theta)\rangle_{\mathrm{av}} = (3\langle\cos^2\theta\rangle_{\mathrm{av}} - 1)/2 = \frac{R-1}{R+2}\frac{R_0+2}{R_0-2}$$

with $R_0 = 2\cot^2\alpha$, where α is the angle between the dipole moment vector M and the chain axis, and θ is the angle between the chain axis and the draw direction (*Figure 1*). The angle α can usually be obtained from theoretical considerations[4] and dichroic ratio measurements allow the calculation of $\langle P_2(\cos\theta)\rangle_{\mathrm{av}}$. Alternatively, if the orientation function value is known using a well-defined absorption band, the orientation of the dipole moment vector relative to the chain axis can be determined for any other absorption band.

EXPERIMENTAL

The isotactic polystyrene used ($M_w \simeq 2\,000\,000$) was purified by precipitation into methane and was subsequently shown by infra-red spectroscopy to be ~100% isotactic.

Preparation of samples

Films were obtained by casting a boiling 5% solution of polymer in decalin on a glass plate at room temperature. Samples of infra-red analysis were cut in the film (ASTM D1708-66 cutter), treated with hexane to extract residual

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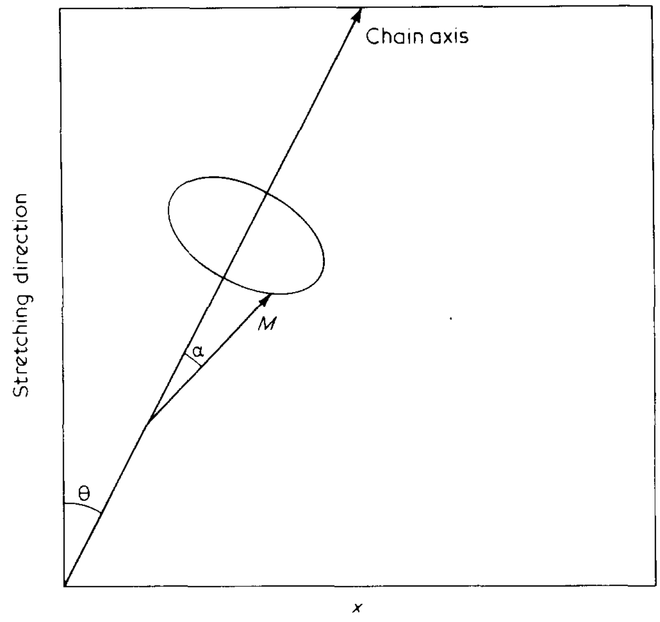

Figure 1 Partial axial orientation

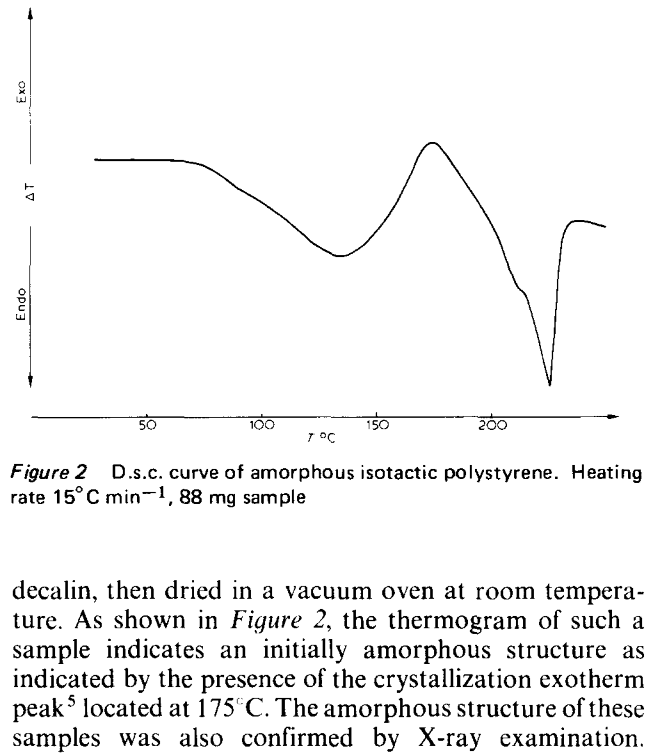

Figure 2 D.s.c. curve of amorphous isotactic polystyrene. Heating rate 15°C min^{-1}, 88 mg sample

decalin, then dried in a vacuum oven at room temperature. As shown in *Figure 2*, the thermogram of such a sample indicates an initially amorphous structure as indicated by the presence of the crystallization exotherm peak[5] located at 175°C. The amorphous structure of these samples was also confirmed by X-ray examination. Crystalline samples were obtained by annealing amorphous films for 12 h at 160°C. The thickness of all the samples before drawing varied between 0.06–0.07 mm. Drawing experiments were made in an air-heated oven (Messimer) using an Instron testing machine. Amorphous samples were drawn at 105°C up to a draw ratio of $\lambda = 2$ with a draw rate of 5 cm min^{-1}. Below 105°C the samples break quickly, and above 105°C some crystallization is induced under stress. Crystalline samples were drawn at 160°C at a draw rate of 0.5 cm min^{-1}. A necking process was observed under these conditions.

The draw ratio was defined as $\lambda = l/l_0$ (l_0, the initial length of the sample, was 1 cm; l = the length after drawing) and measured by two ink marks printed on the sample before stretching.

Infra-red dichroism

The polarized spectra were recorded using a Digilab FTS-14 Fourier transform infra-red spectrometer. Because of the small width of the samples, (~ 2 mm), the sensitivity of the instrument was adjusted to obtain a similar energy output for all the samples under study. Single-beam spectra were run and the absorbance spectra were calculated using the computer facility and a stored polarizer spectrum as reference. The polarization of the infra-red beam was obtained by the use of a Perkin Elmer gold wire grid polarizer, the high efficiency of which makes polarization correction unnecessary. The polarizer was set at a maximum transmission and the samples rather than the polarizer were rotated 90° in order to obtain the two polarization measurements. An example of spectra and baseline determination is given in *Figure 3*. Infra-red dichroism was calculated as $R = A_{\parallel}/A_{\perp}$, with $A_{\parallel}$ and $A_{\perp}$ the optical densities at the absorption maximum.

Birefringence

Birefringence was measured at a wavelength of 486 nm, using an Olympus microscope fitted with a Berek compensator. The thickness of the samples was obtained with a micrometer comparator and averaged along the specimen.

Differential scanning calorimetry (d.s.c.)

Thermograms of amorphous samples were obtained using a Dupont 900 differential scanning calorimeter fitted with a d.s.c. cell at a heating rate of 15°C min^{-1}; sample weight ~ 80 mg.

RESULTS AND DISCUSSION

Besides the measurement of the orientation function, infra-red spectra of amorphous and crystalline oriented isotactic polystyrene samples revealed additional features as compared with the previous analysis of Painter and Koenig[6]. Two spectral regions are especially sensitive (850–950 cm^{-1} and 1000–1100 cm^{-1}) and we will first consider the new information on vibrational modes which can be deduced from these results.

Region 850–950 cm^{-1}

For atactic polystyrene, only one absorption band is

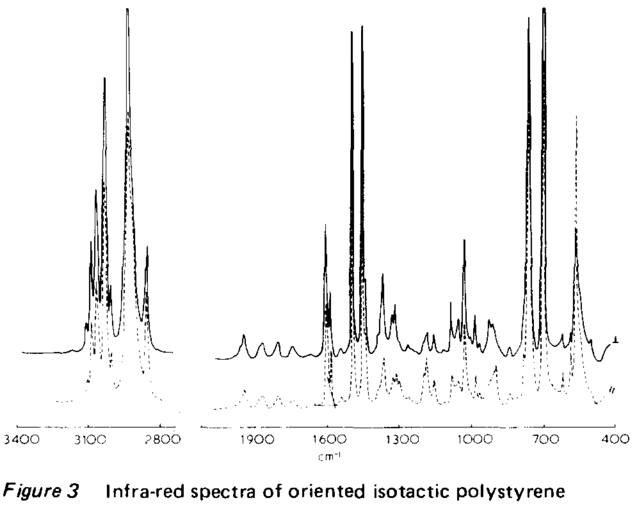

Figure 3 Infra-red spectra of oriented isotactic polystyrene

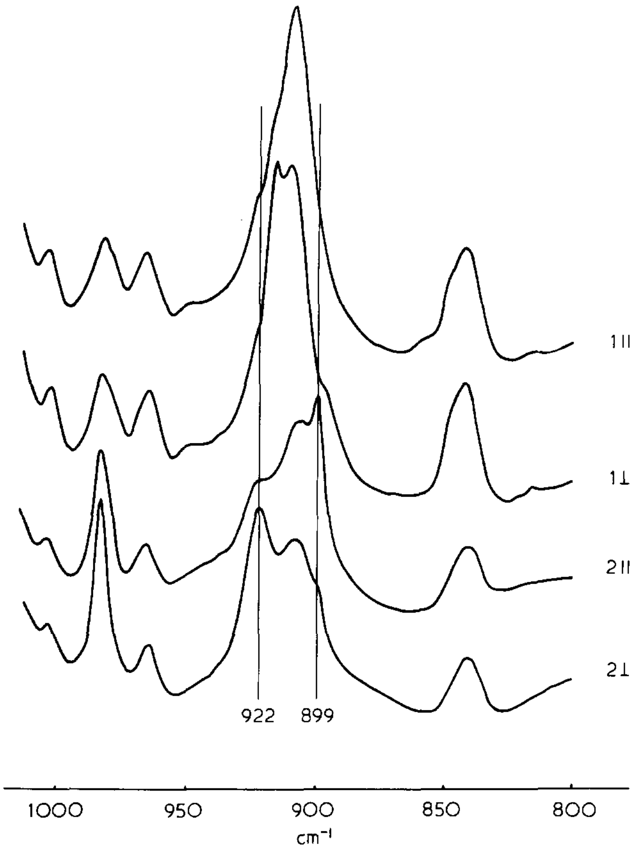

Figure 4 Infra-red spectra of oriented (1) amorphous and (2) crystalline isotactic polystyrene: frequency-expanded scale between 800 and 1000 cm^{-1}

observed in this region, at 906 cm^{-1}, corresponding to the ν_{17b} out-of-plane mode of the benzene ring. In the isotactic crystalline polymer, a splitting in two absorption bands at 898 cm^{-1} (parallel) and 920 (perpendicular) has been widely described in the literature[7]. Factor group analysis[8] predicts that a splitting into A and E modes, with the appropriate parallel and perpendicular dichroism, can occur when interaction between adjacent structural units is strong. The forces involved are presumably dipole–dipole coupling and/or short-range repulsive forces. However, the distance between adjacent rings in the same chain indicates that such essentially short-range intramolecular forces would be unlikely to produce the important observed splitting of 23 cm^{-1} [6]. Tadokoro *et al.*[8] suggested that the dichroism of these bands arose from interactions in the crystal lattice rather than the isolated chain. The normal vibrational analysis of isotactic polystyrene[6] agrees with this interpretation. Four absorption bands appear in the infra-red spectrum of isotactic polystyrene in the region 850–950 cm^{-1}. *Figure 4* illustrates a frequency-expanded scale between 800 and 1000 cm^{-1} of polarized infra-red spectra for oriented amorphous and crystalline isotactic polystyrene. In the amorphous polymer, a splitting of the 906 cm^{-1} absorption band into two components at 908 cm^{-1} (parallel) and 915 cm^{-1} (perpendicular) is observed. In crystalline samples two absorption bands are observed at 899 cm^{-1} (parallel) and 922 cm^{-1} (perpendicular) with a relatively important contribution at the 908 cm^{-1} amorphous absorbance band.

To assign these absorption bands, we will consider the conformational structures of isotactic polystyrene. *Trans–gauche* conformational sequences are the most likely to occur, corresponding to a 3_1 helix structure of the chain. An absorption band located around 560 cm^{-1} is characteristic of this structure[9]. Besides the helices, *gauche–trans–trans–gauche* conformational defects also exist as revealed by the 540 cm^{-1} absorption band[10]. In amorphous styrene samples, 3_1 helicial sequences are present although not organized in a crystal lattice, and the observed splitting arises from the coupling between adjacent units in the 3_1 helices. The presence of the 899 and 922 cm^{-1} absorption bands as shoulders in the amorphous polymer indicates the presence of these 3_1 helices in the material under study.

Region 1000–1100 cm^{-1}

In this region, the 1069 cm^{-1} absorption band in atactic polystyrene splits into two bands at 1083 and 1052 cm^{-1}. Some controversy concerning the assignments of these bands occurs. Normal vibrational analysis[6] indicates that these two bands consist of a mixture of ring and chain vibrations. However, the 1083 cm^{-1} band is mainly a ring mode with only a 5% contribution of the chain. However, the 1052 cm^{-1} absorption band is represented by 63% aliphatic and 37% aromatic vibrations. As shown in *Figure 5* not two but four absorption bands are present in this region, located at 1083 (per-

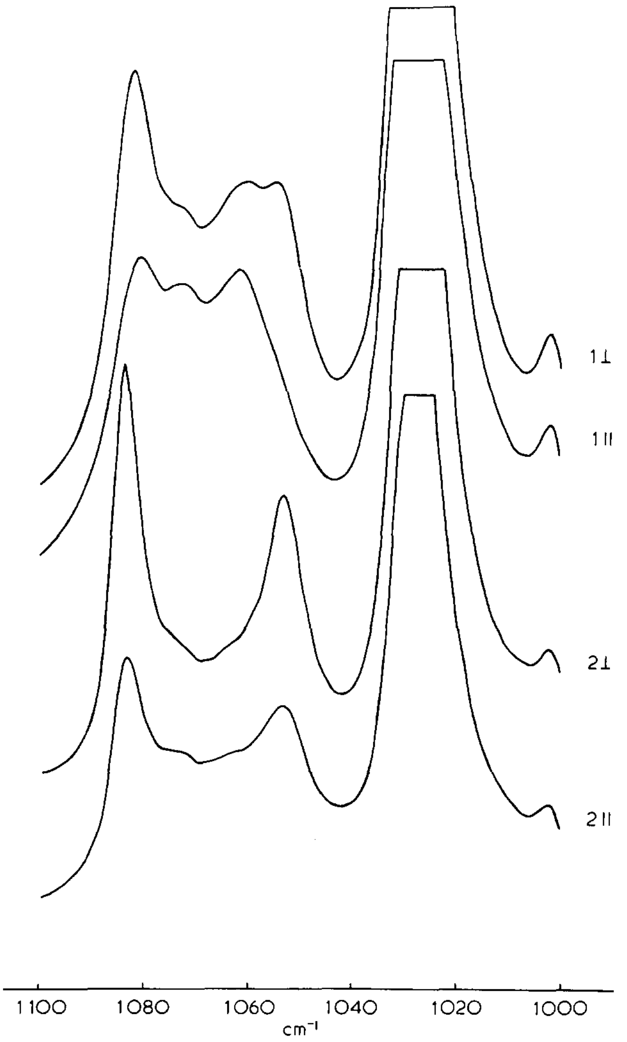

Figure 5 Infra-red spectra of oriented (1) amorphous and (2) crystalline isotactic polystyrene: frequency-expanded scale between 1000 and 1100 cm^{-1}

pendicular), 1075 (parallel), 1064 (parallel), and 1052 (perpendicular) cm^{-1}. Similar behaviour has been recently observed by Painter *et al.*[11] in an *FT*i.r. study of the gel form of isotactic polystyrene. The authors suggest that the conformation present in the gel is sufficiently different to enhance the intensity of the *A* modes and allow the splitting of these structurally sensitive bands to be observed. Unfortunately they did not obtain sufficiently well-oriented thin films for dichroism measurements.

Based on the dichroic character of the four observed absorption bands, it seems reasonable to assign these four bands to *A* and *E* modes of the corresponding vibrations in the 3_1 helices in the amorphous phase with splittings of 8 cm^{-1} and 12 cm^{-1}, respectively. Furthermore, a careful examination of the oriented crystalline polymeric spectra show that such a splitting also exists in these samples although with weak intensities at 1075 and 1064 cm^{-1}, confirming the amorphous phase origin of these bands. Notice, however, an inversion of the dichroic behaviour with respect to the calculated modes[6].

Orientation behaviour

The determination of the orientation function using dichroic ratio measurements requires the use of well-defined absorption bands. In polystyrene, the modes of the benzene ring can be satisfactorily analysed in terms of the C_{2v} local symmetry of the ring[7]. We chose four absorption bands (the numbering is according to Vaisanyi[12]): The carbon–carbon stretching modes $\nu_{8a}(A_1)$ at 1604 cm^{-1} and $\nu_{8b}(B_2)$ at 1584 cm^{-1}: the C–H in-plane bending mode $\nu_{18a}(A_1)$ at 1028 cm^{-1} and the out-of-plane mode ν_{16b} (B_1) at 566 cm^{-1}. For A_1 modes the dipole moment vector is along the C_1–C_4 axis of the ring. For the B_2 modes, the dipole moment vector is perpendicular to this direction and in the plane of the ring. For B_1 modes, the dipole moment vector is perpendicular to the plane of the ring. The ν_{8a}, ν_{8b} and ν_{18a} modes are not mixed and correspond to pure ring modes[6]: these are conformationally insensitive. As far as the ν_{16b} mode is concerned, experimental work on isotactic polystyrene[9] and on its model compounds[10] indicate that the out-of-plane mode of the benzene ring located around 566 cm^{-1} is directly related to the 3_1 helical structure.

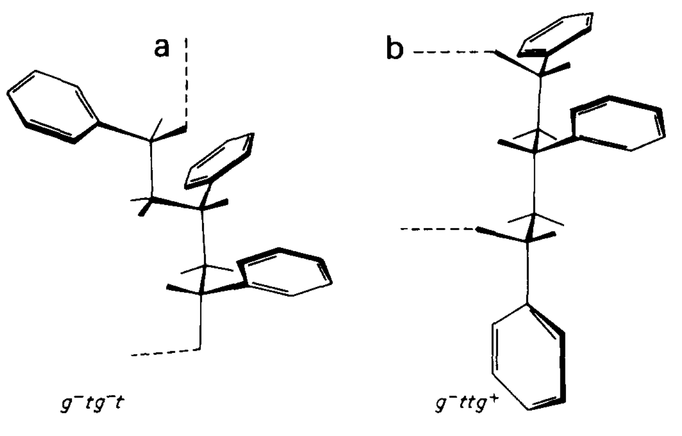

Figure 6 Conformational structures of isotactic polystyrene

A further point of discussion is the definition of a chain axis in isotactic polystyrene. The crystalline portion of the polymer chain has a *trans-gauche* (tg^+ or g^-t) conformation leading to a 3_1 helix structure (*Figure 6a*). The 566 cm^{-1} absorption band is indicative of this structure. However, in the amorphous regions *trans–trans* (*tt*) conformational defects occur, corresponding to a change of helix handedness (*Figure 6b*). The mixture of *trans–gauche* and *trans–trans* conformations does not allow the use of the helix axis as the chain axis. Thus, the overall orientation function will be defined with respect to a chain axis as in *Figure 7*. The experimental dichroic ratios as a function of draw ratio are given in *Table 1*.

Amorphous samples

The results obtained can be interpreted. First of all, the dichroic ratios of the 1028 and 1602 cm^{-1} absorption bands, both of A_1 symmetry, should be similar. The observed discrepancy could be assigned to the presence of a combination band overlapping the 1602 cm^{-1} band. However, the 1585 cm^{-1} absorption band exhibits a small or negligible dichroism throughout the range of draw ratios studied. For perfect uniaxial orientation such behaviour is observed when the transition moment vector makes an angle $\alpha = 56° 44'$ with respect to the orientation direction. This angle is considered to increase only a small amount when the orientation deviates from the perfect

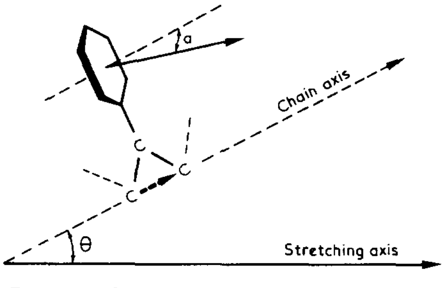

Figure 7 Orientation angles and chain axis in polystyrene structural unit

Table 1 Dichroic ratio as a function of draw ratio for different absorption bands

Isotactic polystyrene	Draw ratio	Dichroic Ratio 1602 cm^{-1}	1585 cm^{-1}	1028 cm^{-1}	565 cm^{-1}
Amorphous	1.20	0.97	1.0	0.90	1.08
	1.30	0.97	0.98	0.85	1.21
	1.43	0.97	0.96	0.81	1.24
	1.47	0.93	0.99	0.78	1.29
	1.60	0.93	0.98	0.77	1.32
	1.63	0.94	1.00	0.79	1.26
	1.80	0.91	0.96	0.77	1.37
	1.87	0.89	0.98	0.75	1.38
Crystalline	After necking	0.77	0.93	0.68	2.22

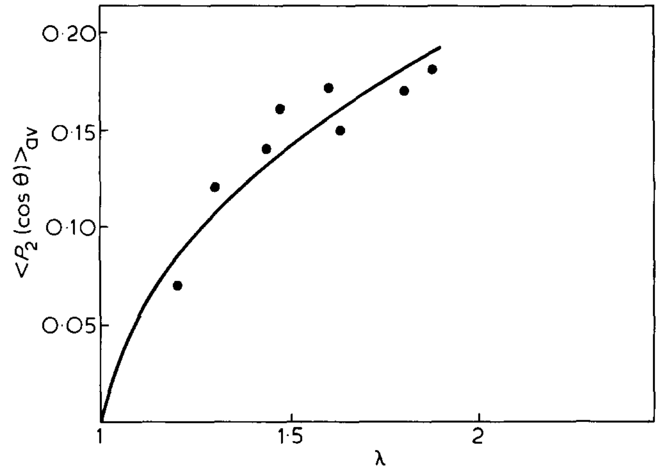

Figure 8 Orientation function as a function of draw ratio for amorphous isotactic polystyrene stretched at 105°C for the 1028 cm^{-1} absorption band

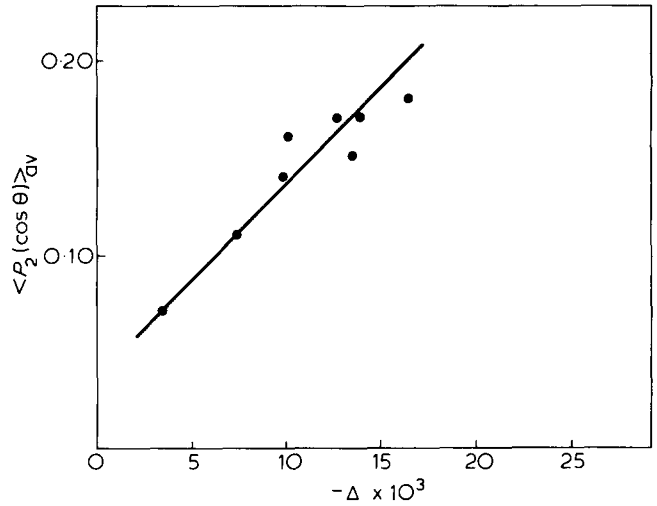

Figure 9 Orientation function as a function of birefringence for amorphous isotactic polystyrene stretched at 105°C for the 1028 cm^{-1} absorption band

one[8]. This result suggests that an angle of ~55° exists between the transition moment of this vibration and the chain axis, corresponding to a tilted angle of 35° for the benzene ring. This value is similar to the value previously observed in uniaxially-oriented atactic polystyrene[12]; it corresponds to a 20° tilt angle between the benzene ring and the helix axis, a value in reasonable agreement with the 26°–25° previously assumed[7,8]. The evolution of the orientation function as a function of draw ratio for the 1028 cm^{-1} absorption band is represented in *Figure 8*. Similarly to atactic polystyrene[12], a linear relationship is observed between birefringence and the second order orientation function as shown in *Figure 9*. Using the relation between birefringence and orientation function, taking into account the polarizability of the bands and the valence angles, as calculated by Stein[14] (the corresponding equation in Stein's paper contains a misprint) with a refractive index $n = 1.584$ and a density of 1.06 g cm^{-3} for amorphous isotactic polystyrene, we obtained:

$$\Delta = (0.194 - 0.51\langle\cos^2\alpha\rangle_{av})\langle P_2(\cos\theta)\rangle_{av}$$

where α represents the angle between the normal to the benzene ring and the chain axis. Experimental data lead to a value of ~40°, in reasonable agreement with the infrared value of ~35°.

Crystalline samples

No orientation was detectable in crystalline samples before necking. In the necked region, a higher degree of orientation is obtained with $\langle P_2(\cos\theta)\rangle_{av} = 0.24$ using the relation:

$$\langle P_2(\cos\theta)\rangle_{1028} = \left(\frac{R-1}{R+2}\,\frac{R_0+2}{R_0-1}\right)$$

a value of ~59° is obtained for the angle between the dipole moment vector of the 1585 cm^{-1} absorption band and the chain axis. This result is in good agreement with the dichrosim behaviour of this absorption band in amorphous samples. It corresponds to a 31° tilt angle of the benzene ring.

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