Evaluation of the birefringence of uniaxially oriented poly(2,6-dimethyl 1,4-phenylene oxide)–atactic polystyrene blends

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The intrinsic birefringence of atactic polystyrene and poly(2,6-dimethyl 1,4-phenylene oxide) in their compatible blends are obtained from coupled birefringence and infra-red dichroism measurements. The experimental value obtained for poly(2-6-dimethyl 1,4-phenylene oxide) is in reasonable agreement with the value calculated from bond polarizabilities. These results allow evaluation of the angle between the normal to the benzene ring of polystyrene and the chain axis. This angle appears to be constant as a function of draw ratio and poly(2,6-dimethyl 1,4-phenylene oxide) percentage in the 0–35% studied range.

Keywords Polystyrene; poly(2,6-dimethyl 1,4-phenylene oxide); birefringence; oriented polymers; polymer blends; Fourier transform infra-red spectroscopy

INTRODUCTION

Birefringence is one of the easiest ways to measure overall orientation of uniaxially stretched polymers[1,2], and has been extensively used for this purpose. This method does not allow one to obtain directly the chain orientation relative to the different chemical units in a multicomponent system. However, the combination of birefringence with another method of measurement of orientation, specific to each component, makes this determination possible if one assumes birefringence additivity[1–3]. As an example, Hoshino *et al.* have calculated the orientation of amorphous regions of a low density polyethylene using birefringence and X-ray diffraction measurements[4].

As far as polymer blends are concerned, infra-red dichroism measurements on oriented samples allow determination of the second order moment of the orientation functions relative to the polymer chains using specific modes associated with the different chemical units. We recently used this method to evaluate the orientation of atactic polystyrene and poly(2,6-dimethyl 1,4-phenylene oxide) in their compatible blends[5].

The present experimental approach deals with the determination of intrinsic birefringence of atactic polystyrene (PS) and poly(2,6-dimethyl 1,4-phenylene oxide) (PDMPO) in their compatible blends using birefringence combined with infra-red dichroism measurement.

THEORETICAL BACKGROUND

Birefringence

The monomer unit orientation of a uniaxially stretched polymer can be described by an orientation distribution function $f(\theta)$ where θ is the angle between the chain axis and the stretching direction (*Figure 1*). Using spherical harmonic functions $P_n(\cos\theta)$, the orientation distribution function is expressed as[2]

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

where

$$P_2(\cos\theta)=(1/2)(3\cos^2\theta-1)$$
$$P_4(\cos\theta)=(35/8)\cos^4\theta-(15/4)\cos^2\theta+3/8$$

and

$$\langle P_n(\cos\theta)\rangle=\int_0^{\pi}f(\theta)P_n(\cos\theta)\sin\theta\,\mathrm{d}\theta$$

In the case of an oriented amorphous polymer, the relation between birefringence and second order spherical harmonic function is given by[1,2]:

$$\Delta=\Delta^0\langle P_2(\cos\theta)\rangle$$

where Δ^0 is the intrinsic birefringence characteristic of the polymer. If we consider a multicomponent system, the birefringence may be expressed as[1–3]:

$$\Delta=\sum_i f_i\Delta_i^0\langle P_{2i}(\cos\theta_i)\rangle+\Delta_F$$

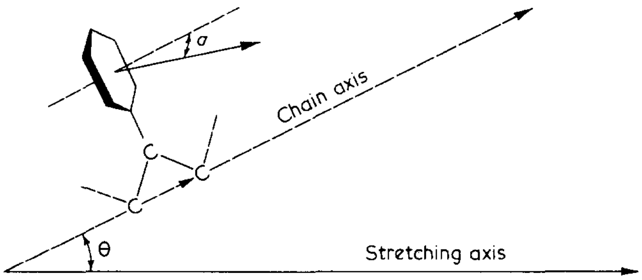

Figure 1 Orientation angles in polystyrene

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where f_i is the volume fraction of ith component, $\langle P_{2i}(\cos\theta_i)\rangle$ the orientation function, Δ_i^0 the intrinsic birefringence and Δ_F the form birefringence. Δ_F is related to the change of refractive index between the different phases. In the case of compatible blends, this term was shown to be negligible[3].

Intrinsic birefringence

Intrinsic birefringence is given by the Lorentz–Lorentz equation[6]:

$$\Delta_x = n_z - n_y = \frac{2(n^2+2)^2}{9\,n}(P_z - P_y)$$

where Δ_x is the birefringence in the direction perpendicular to the plane of the film, n_z and n_y the refractive indices along two orthogonal axes in the plane of the film, z being the stretching axis; n is the average refractive index of the polymer, P_y and P_z the polarizability for light polarized in the y and z directions respectively. In the case of a uniaxial symmetry P_y and P_z can be evaluated from the monomer unit polarizability according to the relation:

$$P_z - P_y = N_m\langle P_2(\cos\theta)\rangle\left(P_a - \frac{P_b + P_c}{2}\right)$$

where N_m is the number of monomers per unit volume, $\langle P_2(\cos\theta)\rangle$ the second spherical harmonic function and P_a, P_b, P_c the molecular polarizabilities along three arbitrary orthogonal directions, a being chosen as the chain axis.

These three values can be calculated using the b_1, b_2, b_3 principal aces of the polarizability ellipsoid of the monomer unit:

$$P_i = b_1\cos^2\theta_{1i} + b_2\cos^2\theta_{2i} + b_3\cos^2\theta_{3i}$$

$$i = a, b, c$$

where θ_i are the angles between the direction vector i and the principal axes b_1, b_2, b_3.

Infra-red dichroism

The second moment of the orientation function $\langle P_2(\cos\theta)\rangle$ can be evaluated using the dichroic ratio $R = A_\parallel/A_\perp$ ($A_\parallel$ and $A_\perp$ being the absorbance parallel and perpendicular to the stretching axis) of any absorption band[7] as:

$$\langle P_2(\cos\theta)\rangle = \frac{R-1}{R+2}\,\frac{2\cot^2\alpha + 2}{2\cot^2\alpha - 1}$$

where α is the angle between the dipole moment vector of the vibration and the chain axis.

EXPERIMENTAL

The polymers used were atactic polystyrene ($\bar{M}_n = 149\,000$, $\bar{M}_w = 254\,000$) from CdF chimie Co. and poly(2,6-dimethyl 1,4-phenylene oxide) ($\bar{M}_n = 15\,000$, $\bar{M}_w = 35\,000$) kindly provided to us by R. P. Kambour (General Electric Co., Schenectady).

Preparation of samples

The sample preparation has been described previously[5]. Stretching experiments were performed at a strain rate of 0.026 s^{-1} and a temperature of $T = T_g + 11.5°C$ on an apparatus developed in our laboratory. In the present work, 27 samples have been studied within a draw ratio range of 1.5 to 4.5 and a PDMPO amount varying between 0 and 35%.

Infra-red measurements

The polarized spectra were recorded using a Nicolet 7199 Fourier transform infra-red spectrometer. The polarization of the infra-red beam was obtained by the use of a Perkin–Elmer gold wire-grid polarizer. The polarizer was set at a maximum transmission position and the samples, rather than the polarizer, were rotated 90° in order to obtain the two polarization measurements. Infra-red dichroism was calculated as $R = A_\parallel/A_\perp$ with $A_\parallel$ and $A_\perp$ optical densities at the absorption maximum. Dichroic ratios were calculated using non-overlapping absorption bands of polystyrene and PDMPO.

As far as polystyrene is concerned, we chose the 906 cm^{-1} absorption band which is assigned as the $\nu_{17b}(B_1)$ out-of-plane mode of the benzene ring in the C_{2v} local symmetry[8]. In uniaxially oriented atactic polystyrene the dipole moment vector of this vibration, which is perpendicular to the plane of the ring, was shown to make an angle ~35° with respect to the chain axis defined in *Figure 1*[9].

In order to perform the calculation in absorbance unit ranges for which Beer's law still holds we used three different absorption bands in PDMPO as a function of the amount of this polymer in the blends. The asymmetric ether stretching vibration at 1190 cm^{-1} was used up to 6% of PDMPO. We then used the ν_2 (A_1) mode of the ring at 1305 cm^{-1} between 6 and 20% of PDMPO, and the ν_{11} out-of-plane mode of the ring at 865 cm^{-1} for blends containing more than 20% of PDMPO. The orientation function was calculated with respect to a chain axis as in *Figure 2*, the choice of which is justified elsewhere[5].

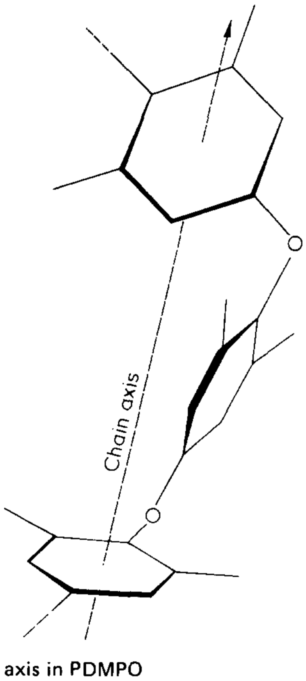

Figure 2 Chain axis in PDMPO

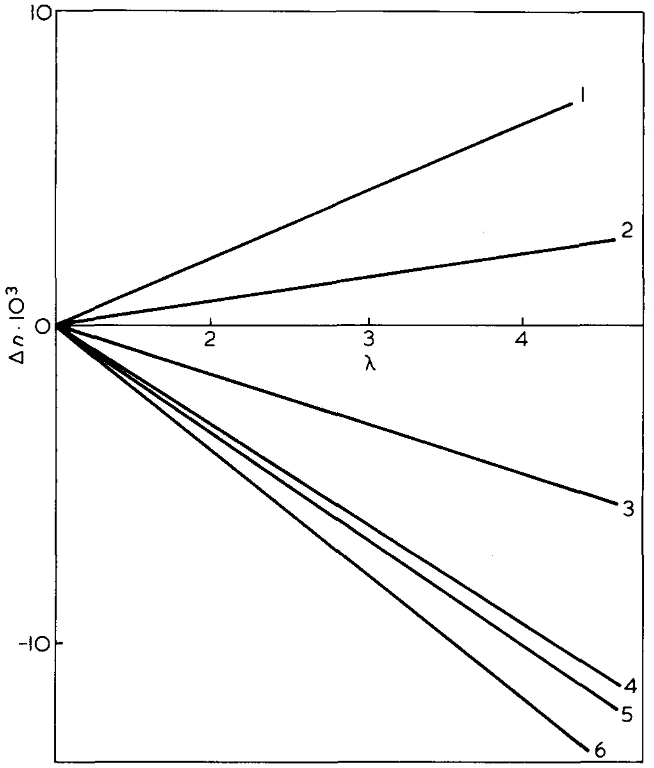

Figure 3 Birefringence of PDMPO–PS blends as a function of draw ratio. Temperature of stretching $T = T_g + 11°C$: (1) blend 35% PDMPO; (2) blend 30% PDMPO; (3) blend 20% PDMPO; (4) blend 10% PDMPO; (5) blend 6% PDMPO; (6) blend 0% PDMPO

Birefringence

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

RESULTS AND DISCUSSION

Figure 3 illustrates the change in birefringence of the blends as a function of draw ratio. A linear relationship is observed in agreement with the birefringence additivity assumption already considered.

For any blend the relation between birefringence and second order moments of the orientation function of the two polymers is given by:

$$\Delta n = \Delta n_F + f\Delta^0{}_{PS}\langle P_2(\cos\theta)_{PS}\rangle + (1-f)\Delta^0{}_{PDMPO}\langle P_2(\cos\theta)_{PDMPO}\rangle$$

where: Δn_F = form birefringence; f = volume fraction of polystyrene in the blend; Δ^0_{PS}, Δ^0_{PDMPO} = intrinsic birefringence of PS and PDMPO, respectively; $\langle P_2(\cos\theta)_{PS}\rangle$, $\langle P_2(\cos\theta)_{PDMPO}\rangle$ = second moment of the orientation function of PS and PDMPO, respectively.

The determination of Δ^0_{PS} is difficult on account of the dependence of $\langle P_2(\cos\theta)_{PS}\rangle$ on the angle α between the dipole moment vector of the ν_{17b} vibration and the chain axis according to:

$$\langle P_2(\cos\theta_{PS})\rangle = \frac{R-1}{R+2}\,\frac{R_0+2}{R_0-1}$$

with $R_0 = 2\cot^2\alpha$.

This angle α could change as a function of draw ratio or PDMPO amount. We then solved the 27 subsequent equations

$$\Delta_n = \Delta n_F + f\Delta^0_{PS}\frac{R-1}{R+2}\,\frac{R_0+2}{R_0-1} + (1-f)\Delta^0_{PDMPO}\langle P_2(\cos\theta)_{PDMPO}\rangle$$

obtained from birefringence measurements on samples stretched at different draw ratios and PDMPO amounts. Infra-res data were taken from ref. 5. A least squares resolution of these equations gave the values of

$$\Delta^0_{PS}\frac{R_0+2}{R_0-1},\ \Delta^0_{PDMPO} \text{ and } \Delta n_F$$

(see *Table 1*).

Taking into account the polarizability of the bonds and the valence angles, Stein[10] obtained the relation:

$$\Delta^0{}_{PS} = 0.194 - 0.51\,\langle\cos^2\alpha'\rangle$$

where α' represents the angle between the perpendicular to the plane of the benzene ring and the chain axis (see *Figure 1*).

We thus deal with two angles: the angle α related to the direction of the dipole moment vector of the vibration used, and the angle α' involved in birefringence measurements, related to the axis perpendicular to the plane of the benzene ring. It comes out from a previous study on uniaxially oriented atactic polystyrene[9] that these two angles are not equal and that the dipole moment vector of the ν_{17b} vibration makes an angle $\simeq 4°$ with respect to the perpendicular to the plane of the benzene ring: $\alpha' = \alpha + 4°$.

Combining the various previous equations and experimental values we get $\alpha' = 40° \pm 6°$, and $\Delta^0_{PS} = -0.10 \pm 0.05$, in good agreement with former work performed on polystyrene[9,11]. This result shows that no significant change of benzene ring orientation with respect to the chain axis occurs during the orientation process in the blends under study, whatever the orientational behaviour of PS may be.

Intrinsic birefringence of PDMPO has not yet been calculated and it is interesting to compare the calculated value obtained from bond polarizability with the experimental one.

We used the principal polarizabilities b_1, b_2, b_3 of 1,3-dimethylbenzene[12,13] and ether bond polarizability in paraldehyde[14] to calculate the polarizability ellipsoid of PDMPO monomer unit (see *Table 2* and *Figure 4*). We

Table 1 Form and intrinsic birefringence of PS and PDMPO in their compatible blends

Birefringence	Calculated value	Variance	Value with a 10% confidence level
Δn_F	-4×10^{-4}	5×10^{-4}	–
$\Delta^0_{PS}\cdot\frac{R_0+2}{R_0-1}$	−0.22	2×10^{-2}	−0.22 ± 0.04
Δ^0_{PS}	−0.10	–	−0.10 ± 0.05
Δ^0_{PDMPO}	0.21	2.4×10^{-2}	0.21 ± 0.04

Table 2 Polarizabilities of chemical units

Chemical unit (see *Figure 4*)	b_1	b_2	b_3	Ref.
a	161	178	85	12, 13
b	8.1	3.9	3.9	14
c	6.4	6.4	6.4	16
d	164.4	173	80	

thus obtained a value $\Delta^0_{\mathrm{PDMPO}} = 0.14$. As discussed by Le Fevre *et al.* in a diphenyl ether study[15] the calculated value has only to be considered as an order of magnitude on account of the uncertainty of ether linkage polarizabilities, and the result is in reasonable agreement with the observed value $\Delta^0_{\mathrm{PDMPO}} = 0.21 \pm 0.04$.

At least a very low form birefringence ($\Delta n_F = 4 \times 10^{-4}$) is obtained. This term is negligible, in agreement with the compatible nature of the blends under study where no phase separation occurs.

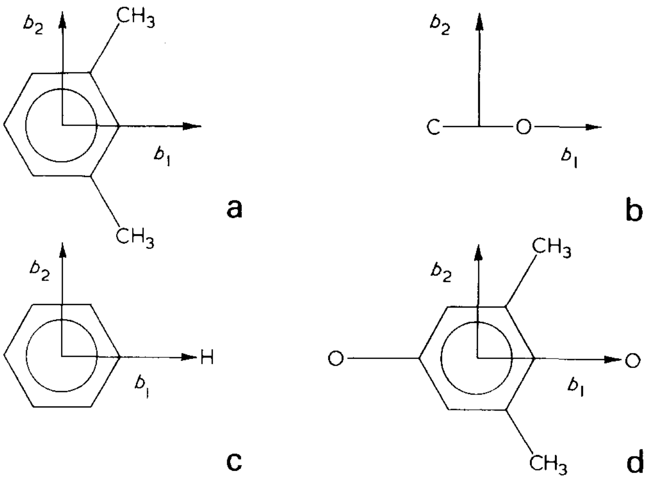

Figure 4 Principal polarizabilities of PDMPO chemical units; b_3 axis is perpendicular to the plane b_1, b_2

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