Fourier transform infra-red and birefringence studies of orientation in uniaxially-stretched poly(2,6-dimethyl 1,4-phenylene oxide) – atactic polystyrene blends

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Infra-red measurements of the dichroic ratio of polystyrene and poly(2,6-dimethyl 1,4-phenylene oxide) absorption bands provide a valuable method for the determination of orientation of chains of both polymers during stretching of their compatible blends. Influence of blend composition on orientation of both polymer chains has been studied in the overall range of concentration. A similar behaviour is observed for both polymers. Orientation is concentration-dependent when the corresponding component is present in a large amount up to a limit concentration C_l. In the present case $C_l \simeq 20\%$ of PPO for PS orientation and $C_l \simeq 25\%$ of PS for PPO orientation. Between these two values, orientation of both components is insensitive to the composition of the blend. The increase in orientation observed for both polymers in the blends when compared with the pure components is in good agreement with an increase in friction coefficient.

(Keywords: PS; PPO; polymer blends; orientation; friction coefficient)

INTRODUCTION

In two previous papers[1,2] we described the behaviour of poly(2,6-dimethyl 1,4-phenylene oxide) (PPO)–atactic polystyrene (PS) blends. It was pointed out that PPO and PS chains orient in a different way when subjected to a uniaxial strain in spite of the compatible nature of the blend. PPO chains acquire a strong orientation independent of the composition while PS chain orientation strongly increases with PPO concentration and then levels off. Unfortunately, due to experimental limitations, these studies were restricted to blends containing up to 35% of PPO. Also, the oven of the stretching machine used was limited in temperature and did not allow the stretching of blends containing more than 35% of PPO above the glass transition temperature.

However, it was of interest to study the whole range of PPO–PS blends. For this purpose, we built a new oven allowing samples to be heated up to 300°C, i.e. well above the glass transition temperature of PPO.

In this paper we present the results obtained for the orientation behaviour of PS–PPO blends in the whole concentration range using infra-red dichroism and birefringence measurements.

THEORY

Uniaxial stretching of polymer materials induces anisotropy in the orientation of the molecular segments. This orientation can be described by an orientation distribution function $f(\theta)$ where θ is the angle between the chain axis and the stretching direction.

Then $f(\theta)$ is expressed as[3]:

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

where $Pn\ (\cos\theta)$ are the Legendre polynomials:

$$P_2(\cos\theta)=(3\cos^2\theta-1)/2$$

$$P_4(\cos\theta)=(35\cos^4\theta-30\cos^2\theta+3)/8 \qquad \text{etc...}$$

Different techniques have been proposed for the measurement of the different moments $\langle Pn(\cos\theta)\rangle$ of the orientation function[4,5]. Among these techniques, infra-red spectroscopy allows one to determine the second-order moment of the orientation function related to any chemical unit in a blend, providing it is possible to find non-overlapping absorption bands. The dichroic ratio:

$$R=A_{\parallel}/A_{\perp}$$

($A_{\parallel}/A_{\perp}$ being measured absorbance for electric vector parallel and perpendicular, respectively, to the stretching direction) is related to the second-order moment by the relation:

$$\begin{aligned}\langle P_2(\cos\theta)\rangle &= (3\langle\cos^2\theta\rangle-1)/2\\ &=(R-1)(R_0+2)/(R+2)(R_0-1)\end{aligned}$$

with $R_0=2\cot^2\alpha$, α being the angle between the dipole moment vector of the vibration and the local chain axis and θ being the angle between the local chain axis and the stretching direction.

On the other hand, for compatible blends of amorphous polymers, a relationship holds between the

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final birefringence Δ and the individual second-order moments[6]:

$$\Delta = f_1\Delta_1^0\langle P_2(\cos\theta)\rangle_1 + f_2\Delta_2^0\langle P_2(\cos\theta)\rangle_2$$

where f_i, Δ_i^0 and $\langle P_2(\cos\theta)\rangle_i$ are the volume fraction, intrinsic birefringence and orientation function of component i, respectively.

EXPERIMENTAL

The polymers used in this study were atactic polystyrene ($\bar{M}_n = 150\,000$, $\bar{M}_w = 254\,000$; $T_g = 107°C$) from Norsolor, and PPO ($\bar{M}_n = 23\,000$; $\bar{M}_w = 50\,000$; $T_g = 215°C$) kindly provided to us by R. P. Kambour (General Electric Co). Experimental details such as sample preparation and infra-red measurements are given in ref. 1. Details on birefringence measurements may be found in ref. 7.

Glass transition temperatures of the different blends were obtained using a Du Pont 1090 differential scanning calorimeter at a heating rate $20°C\,min^{-1}$; sample weight ≈ 7 mg. T_g values for each blend are given in *Table 1*.

Stretching machine

The stretching machine was designed and built in our laboratory. Its principle of operation is identical to that of a device previously described[8], but several components have been changed in order to improve the performance (speed, position). A schematic diagram is given in *Figure 1*. A feedback loop controls the displacement of a low friction double hydraulic plunger. A pump connected to a pressure accumulator is used to stock oil under pressure (200 bar). This oil then operates the plunger through the servovalve (flow). The plunger position is monitored by a displacement sensor (differential transformer). The voltage of this sensor is compared to that of an electronic ramp and the voltage difference between the two controls the flow rate of oil through the servovalve.

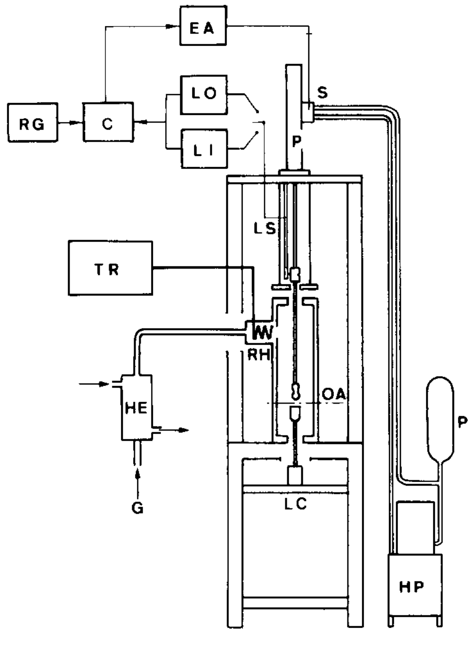

Figure 1 Stretching machine and temperature controlled chamber. HP, hydraulic pump; PR, pressure accumulator; S, servovalve; LC, load cell; IS, inductive sensor; P, plunger; HE, heat exchanger; G, gas; RH, resistive heater; TR, temperature regulator; OA, optical axis; RG, ramp generator; C, comparator; LO, logarithmic amplifier; LI, linear amplifier; EA, error amplifier

The plunger motion can be either linear or exponential by introducing the appropriate amplifier into the feedback control loop. The performance specifications of this equipment are: a 400 mm displacement; an 800 daN strain; a position known to ±0.1 mm with a displacement linearity of ±0.2%. The speed can vary from $0.5\,m\,s^{-1}$ to $5\times10^{-5}\,m\,s^{-1}$.

Temperature controlled chamber

Due to the high thermal sensitivity of the mechanical properties of polymers, it was necessary to build a controlled temperature chamber with a low thermal gradient. The design of this chamber is complicated by its large size, which is dictated by the high strain rates needed for our studies. A gas (air or nitrogen) at a controlled temperature is injected into the chamber by two vertical pipes having many small holes (0.3 mm in diameter). The distribution of holes and the injection pressure create a turbulent field which results in very good temperature homogeneity (±0.6°C at 200°C over 300 mm).

The gas is preheated or cooled by the heat exchanger before going through a regulated heating device which fixes the desired temperature. The injection pressure can be varied from 1 to 3 bar, and the preheating power may vary according to the experimental conditions.

The oven consists of many shells and can be completely opened on one side, and three windows enable optical measurements during the stretching. The nature of the materials used, the oven geometry and the choice of the gas allow one to obtain a wide range of operating temperatures (from −100°C to +300°C).

RESULTS

The determination of the orientation function using dichroic ratio measurements requires the use of well known absorption bands. In PS–PPO blends, up to a concentration of 80% of PPO, PS orientation can be satisfactorily analysed from dichroic ratios of the $906\,cm^{-1}$ absorption band. In the blend containing 90% of PPO, the absorbance of the $906\,cm^{-1}$ band is less than 0.02 and the dichroic ratio cannot be measured with accuracy. As far as PPO is concerned, the $860\,cm^{-1}$ absorption band was used in blends containing up to 30% of PPO[1]. When the PPO percentage is increased above 30%, this absorption band becomes too strong. We then used the $1115\,cm^{-1}$ absorption band for which we determined the dipole moment vector angle α with respect to the local chain axis. This determination was performed using infra-red and birefringence measurements in oriented PS–PPO blends containing 35% and 40% of PPO. The measurement of birefringence and of PS

Table 1 Glass transition temperature for each blend

PPO (%)	0	10	20	30	40	50	60	70	80	90	100
T_g (°C)	107	115	121	131	141	150	158	165	176	193	215

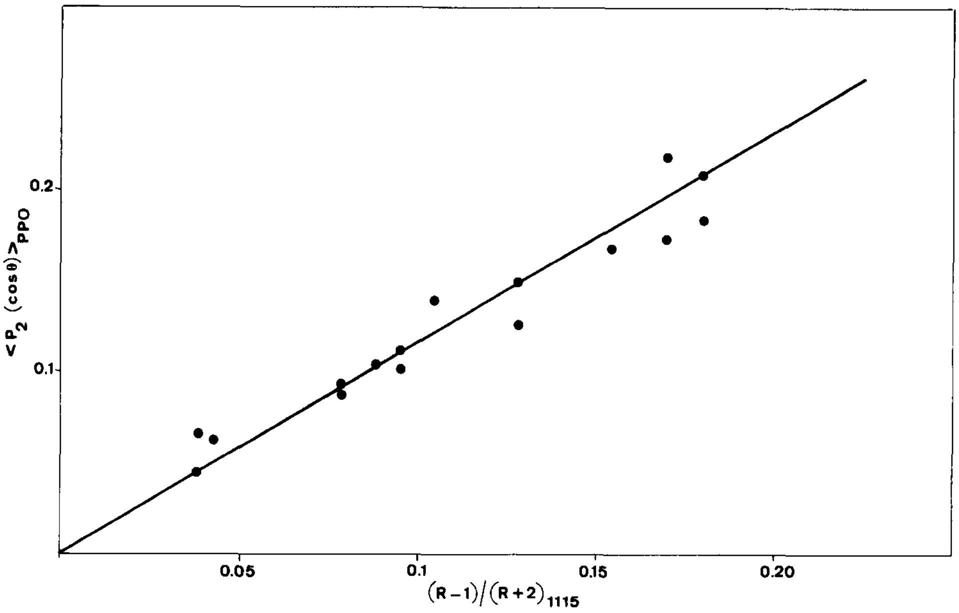

Figure 2 Determination of the angle α of the $1115\,cm^{-1}$ absorption band from $\langle P_2(\cos\theta)\rangle_{ppo}$

orientation by infra-red allows one to calculate PPO orientation from the relation:

$$\langle P_2(\cos\theta)\rangle_{ppo} = (\Delta - f\Delta^0_{PS}\langle P_2(\cos\theta)\rangle_{ps})/(1-f)\Delta^0_{ppo}$$

where f is the volume fraction of PS, $\Delta^0_{PS} = -0.10$ and $\Delta^0_{ppo} = 0.21$ are the intrinsic birefringences of PS and PPO, respectively[7]. Once $\langle P_2(\cos\theta)\rangle_{ppo}$ is known, one can deduce the value of α from dichroic ratio measurements on the $1115\,cm^{-1}$ absorption band. *Figure 2* shows that a linear relationship holds between $\langle P_2(\cos\theta)_{ppo}\rangle$ and $(R-1)/(R+2)_{1115}$. The slope of this straight line leads to a value of $\alpha = 18°$.

Orientation behaviour of PS–PPO blends

All the samples were stretched at constant strain rate above the glass transition temperature. First consider the results obtained at a stretching temperature $T = T_g + 11.5°C$ and a strain rate $\dot{\varepsilon} = 0.026\,s^{-1}$, for blends containing more than 35% of PPO. As shown in *Figure 3*, a rectilinear relation holds for both polymers and any composition of the blend between $\langle P_2(\cos\theta)\rangle$ *versus* draw ratio λ, similarly to the behaviour previously observed for blends containing up to 35% of PPO (ref. 2). Consequently,

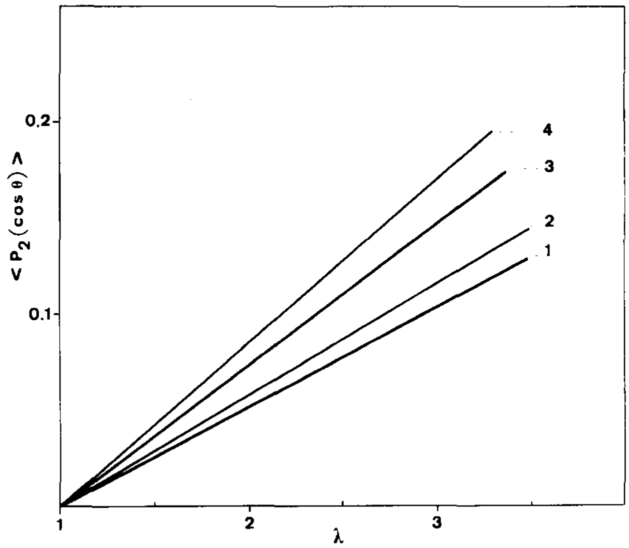

Figure 3 PS and PPO orientation in PS–PPO blends at different compositions. Temperature of stretching $T = T_g + 11.5°C$. Strain rate $\dot{\varepsilon} = 0.026\,s^{-1}$. (1) pure PPO; (2) PS in blends containing more than 35% of PPO; (3) PPO in the 70% PPO blend; (4) PPO in 40–60% PPO blends

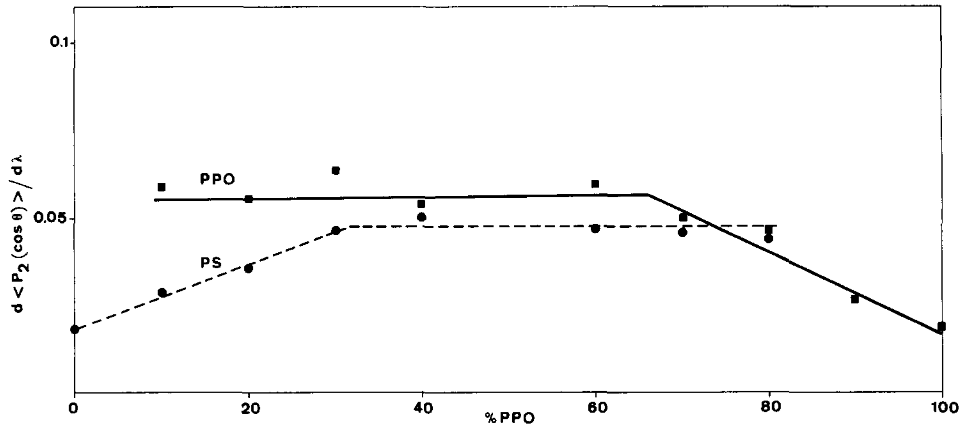

Figure 4 Slope of $\langle P_2(\cos\theta)\rangle = f(\lambda)$ as a function of the composition of the blends. Temperature of stretching $T = T_g + 20°C$; strain rate $\dot{\varepsilon} = 0.026\,s^{-1}$

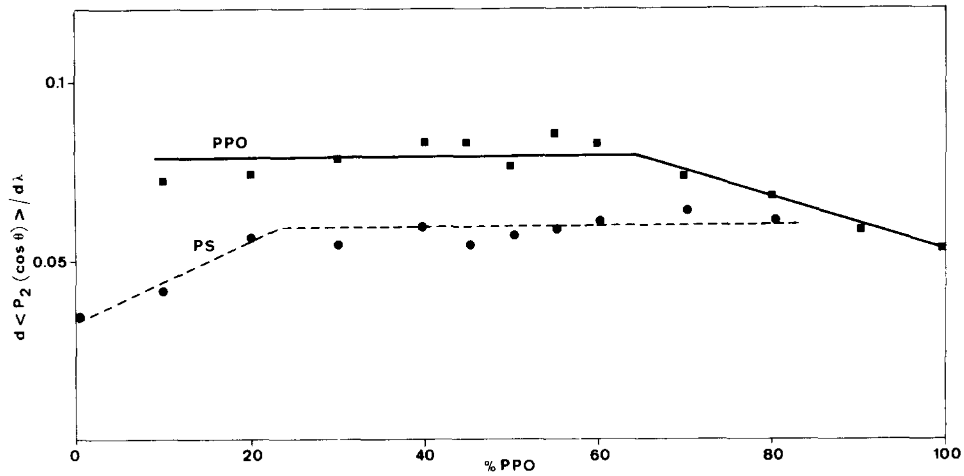

Figure 5 Slope of $\langle P_2(\cos\theta)\rangle = f(\lambda)$ as a function of the composition of the blends. Temperature of stretching $T = T_g + 11.5°C$; strain rate $\dot{\varepsilon} = 0.026\,s^{-1}$

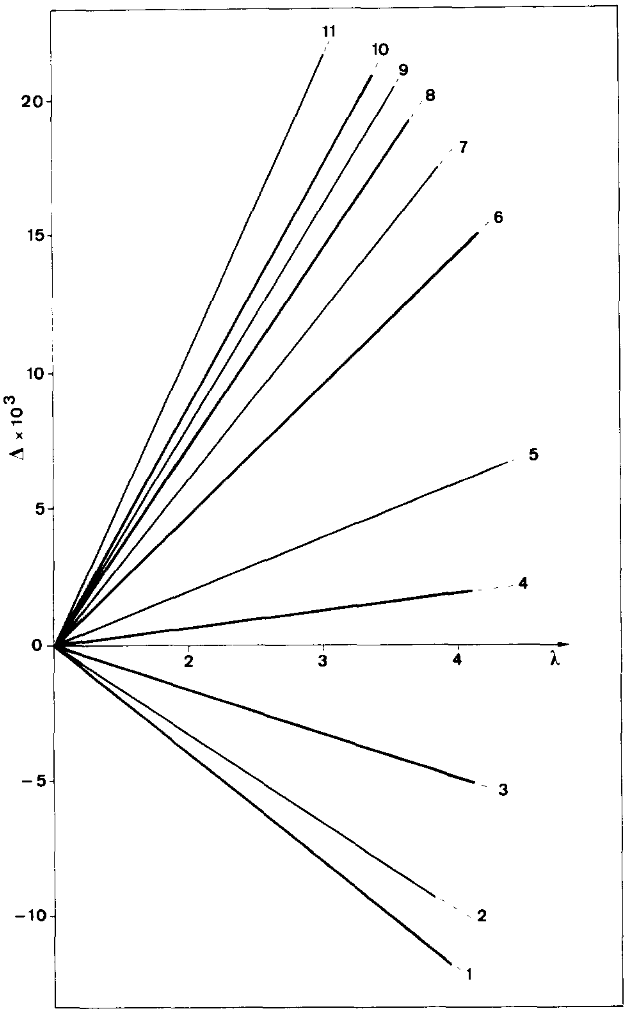

Figure 6 Birefringence of PS–PPO blends as a function of draw ratio. Temperature of stretching $T = T_g + 11.5°C$. (1) pure PS; (2) blend 10% PPO; (3) blend 20% PPO; (4) blend 30% PPO; (5) blend 40% PPO; (6) blend 50% PPO; (7) blend 60% PPO; (8) blend 70% PPO; (9) blend 80% PPO; (10) blend 90% PPO; (11) pure PPO

orientation can be described by plotting the slope $d\langle P_2(\cos\theta)\rangle/d\lambda$ as a function of PPO percentage. The results are given in *Figure 4*, for the whole range of concentrations. A similar behaviour is observed for both polymers. Orientation is concentration dependent when the corresponding component is present in a large amount, and one can observe a linear increase of the function $d\langle P_2(\cos\theta)\rangle/d\lambda$ up to a limit concentration C_l. In the present case $C_l \simeq 20\%$ of PPO for PS orientation and $C_l \simeq 25\%$ of PS for PPO orientation. Between these two values, orientation of both components is insensitive to the composition of the blend.

As shown in *Figure 4*, similar results are obtained when the blends are stretched at a temperature $T = T_g + 20°C$ and a strain rate $\dot{\varepsilon} = 0.026\,s^{-1}$. As previously observed[2], an increase in the stretching temperature induces a decrease of the orientation level of both polymers. The change in birefringence of the blends on the overall range of concentration as a function of draw ratio is shown in *Figure 6*, for a stretching temperature $T = T_g + 11.5°C$ and a strain rate $\dot{\varepsilon} = 0.026\,s^{-1}$.

DISCUSSION

The influence of different factors such as chain stiffness, chain entanglement, free volume or interchain friction may be considered to explain the orientation behaviour of polymer blends. Our previous studies on PS–PPO[1,2] and PS–poly(vinylmethyl ether) (PVME)[9] blends have clearly shown that orientation in a compatible blend cannot be related to the stiffness of the components. On the other hand, the increase of orientation of both PS and PPO in the blends with respect to pure polymers orientation cannot be related to an increase of chain entanglements. Wu[10] has recently shown that, in compatible blends, the specific interactions tend to align the chain segments for the interactions, thus locally stiffening the segments, reducing their convolution and resulting in reduced entanglements between dissimilar chains. Consequently, the orientation of the two components in a compatible blend should be lower than the orientation observed for the pure compounds. As far as free volume is concerned, the f/B WLF parameter, where f is the free volume and B a constant, is of the same order of magnitude in PS (4.21×10^{-2}), PPO (3.80×10^{-2}) and PS–PPO blends at the reference temperature $T = T_g + 11.5°C$. These values were calculated from the data of Prest and Porter[11].

In PS–PPO compatible blends there are strong interactions between the phenyl ring of PS and the phenylene ring of PPO[12]. Interactions greatly modify the molecular environment of polymer chains. Therefore mobility of the two polymer chains is hindered and the friction coefficient of each species is increased. Indeed, using the data of Prest and Porter[11], Wu[10] observed an increase in the interchain friction in PS–PPO blends as well as in other compatible blends. Furthermore, our own results on PS–PVME blends[9] were interpreted in terms of a hindrance of relaxation of PS chains induced by a modification of friction coefficients due to the molecular interactions. The increase in orientation observed in this work for both polymers in the blends when compared with the pure components is in good agreement with an increase in friction coefficient.

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