Orientation and relaxation in uniaxially stretched poly(*o*-chlorostyrene)–polystyrene blends

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Orientation and relaxation of polymer chains have been analysed in uniaxially stretched films of poly(*o*-chlorostyrene) (PoCS) and of compatible PoCS/polystyrene (PS) blends. The intrinsic birefringence of PoCS is derived from fluorescence polarization and birefringence orientation measurements. Further, using Fourier transform infra-red spectroscopy, we have determined the angle between the dipole moment vector of some infra-red vibrations of PoCS and the chain axis. The orientation of the benzene ring with respect to the chain axis in oriented PoCS samples is identical to that observed in PS. In PoCS/PS blends, infra-red and birefringence measurements show that chain orientation of both polymers is almost the same and independent of the presence of the second component, in agreement with mechanical relaxation measurements. This result is in contrast with previous data on PS/poly(phenylene oxide) and PS/poly(vinyl methyl ether) blends. It corroborates well the assumption that change in friction coefficients is responsible for the orientation behaviour of compatible blends in which strong enough polymer–polymer interactions develop.

(Keywords: orientation; polymer blends; poly(*o*-chlorostyrene); polystyrene; Fourier transform infra-red spectroscopy; fluorescence polarization; birefringence)

INTRODUCTION

In earlier studies on orientation of compatible blends of atactic polystyrene (PS) with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)[1-3] and poly(vinyl methyl ether) (PVME)[4], we have shown that polystyrene acquires a higher orientation in both blends as compared with the pure polymer. On the other hand, PPO is highly oriented in PS/PPO blends while PVME remains almost unoriented in PS/PVME blends. Such behaviour was interpreted in terms of hindrance of the relaxation of PS chains induced by a modification of friction coefficient due to the molecular interactions that are at the origin of compatibility. The time range covered in the experimental conditions does not allow detection of any change in PPO or PVME orientation. PPO chains keep the orientation that they have acquired during stretching, since their relaxation time is very long, while PVME chains, which have a very short relaxation time, remain unoriented.

It is interesting to examine the orientation behaviour in a compatible blend for which almost no interaction occurs between the two species. This is the case of PS/poly(*o*-chlorostyrene) (PoCS) blends, the compatibility of which originates mainly in the similarity of steric structures of both polymers[5]. The present work deals with the study of orientation of compatible PS/PoCS blends using fluorescence polarization, Fourier transform infra-red spectroscopy 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[6]:

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

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

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

$$P_4(\cos\theta)=(35\cos^4\theta-30\cos^2\theta+3)/8$$

etc.

Different techniques have been proposed for the measurement of the different moments $\langle P_n(\cos\theta)\rangle$ of the orientation function[7,8]. Among these techniques, fluorescence polarization using polymer chains labelled by a fluorescent molecule permits determination of the second and fourth moments of the orientation function.

If we consider two orthogonal axes Ox_1 and Ox_2 in the plane of a film, for uniaxial stretching along the Ox_1 axis, the fluorescence intensities I_{ij} measured with the polarizer along Ox_i and the analyser along Ox_j are given by[9]:

$$I_{11}=k\langle\cos^4\theta\rangle$$

$$I_{12}=I_{21}=k\langle\cos^2\theta\sin^2\theta\rangle/2$$

$$I_{22}=3k\langle\sin^4\theta\rangle/8$$

The second and fourth moments of the orientation distribution function can be calculated from the above

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intensities:

$$\langle\cos^2\theta\rangle = \frac{I_{11}+2I_{12}}{\frac{8}{3}I_{22}+4I_{12}+I_{11}}$$

$$\langle\cos^4\theta\rangle = \frac{I_{11}}{\frac{8}{3}I_{22}+4I_{12}+I_{11}}$$

On the other hand, 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:

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

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

$$\langle P_2(\cos\theta)\rangle = (3\langle\cos^2\theta\rangle - 1)/2$$
$$= (R-1)(R_0+2)/(R+2)(R_0-1)$$

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

For compatible blends of amorphous thermoplastics, a relationship holds between the final birefringence Δn and the individual orientation functions[10]:

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

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.

Orientation measurements were combined with mechanical relaxation. Dynamic shear experiments give the real $G'(\omega)$ and the imaginary $G''(\omega)$ parts of the complex modulus. The relaxation modulus can then be calculated from the formula of Ninomiya and Ferry[11]:

$$E(t) = G'(\omega) - 0.4G''(0.4\omega) + 0.014G''(10\omega)$$

with $\omega = 1/t$.

EXPERIMENTAL

The PS used in this study was atactic polystyrene ($\bar{M}_n = 150\,000$, $\bar{M}_w = 254\,000$, glass transition $T_g = 107$°C) from CdF-Chimie Co. PoCS was prepared by radical polymerization of *o*-chlorostyrene with azobisisobutyronitrile as initiator ($\bar{M}_n = 104\,000$, $\bar{M}_w = 199\,000$, $T_g = 134$°C). Thin films suitable for infra-red and fluorescence measurements were obtained by casting a 7% benzene solution on a glass plate.

Fluorescence polarization measurements were performed on a polarizing microscope developed in our laboratory[9]. A small amount (1 wt%) of anthracene-labelled polystyrene (PS*) ($\bar{M} = 316\,000$), prepared by deactivation of monofunctional living anionic PS chains by 9,10-bis(bromomethyl)anthracene[12], was added to the film as the fluorescent label.

Drawing experiments were performed using an apparatus developed in our laboratory, i.e. a stretching machine operating at constant strain rate and a special oven, designed to provide a very good temperature stability all over the sample (homogeneity is around 0.05°C). Other experimental details such as glass transition temperatures, infra-red and viscoelastic measurements are given in previous papers[1-4].

RESULTS

*Orientation of poly(*o*-chlorostyrene)*

The direct determination of the orientation of PoCS implies that either the intrinsic birefringence or the direction of the transition moment vectors are known. On account of the low degree of symmetry of the monomer unit, which belongs to the point group C_s, it is impossible to determine *a priori* the position of the transition moment vectors and Δ^0_{PoCS} is unknown.

In order to measure orientation in PoCS, we used fluorescence polarization. This method implies the use of a small amount of labelled chains dispersed in the polymer film. Under our experimental conditions, PS orientation measured by fluorescence polarization is in good agreement with infra-red results, as shown in *Figure 1*.

Ideally, the use of the same technique with PoCS would imply the use of labelled PoCS chains. Such labelled chains are not readily obtainable but PS* can be used considering the similarity of steric structure of both polymers. Furthermore, the molecular weights of PS* and PoCS fall in the range where $\langle P_2(\cos\theta)\rangle$ is independent of molecular weight[13].

Fluorescence polarization and birefringence data are given in *Table 1*. As shown in *Figure 2*, a linear relationship holds between $\langle P_2(\cos\theta)\rangle$ and birefringence, leading to a value $\Delta^0_{\mathrm{PoCS}} = -0.125$ for the intrinsic birefringence of PoCS, with a coefficient of determination $r^2 = 0.99$. Knowledge of the intrinsic birefringence makes it possible to calculate the angle ω between the chain axis and the perpendicular to the plane of the benzene ring.

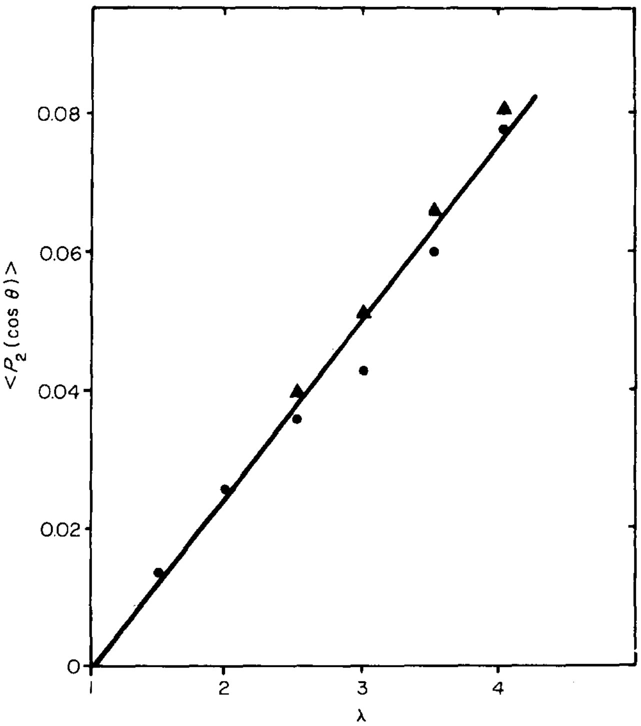

Figure 1 PS orientation measured by infra-red dichroism (●) and fluorescence polarization (▲)

Table 1 Orientation function and birefringence of PoCS samples

Sample no.	1	2	3	4	5
$P_2(\cos\theta)$	0.07	0.11	0.12	0.17	0.18
$-\Delta_n \times 10^3$	8.38	12.2	15.3	19.3	24

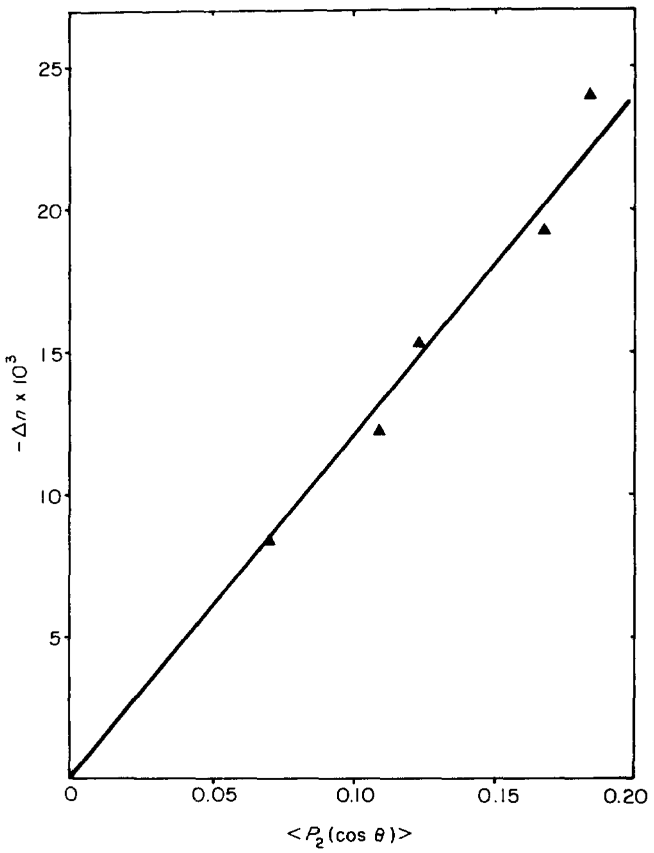

Figure 2 Birefringence *versus* PoCS orientation

Taking into account the polarizability of the bonds and the valence angles, Stein[14] obtained the relationship:

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

for polystyrene. Similarly, using the polarizability of the C–Cl bond given by Denbigh[15], we obtained the relationship:

$$\Delta^0_{PoCS} = 0.2449 - 0.6499\langle\cos^2\omega\rangle$$

using the density $\rho = 1.262$ derived from the literature data for PoCS[16].

We get $\omega = 41°$ in PoCS as compared with $\omega = 40°$ in PS[2]. This result shows that the *ortho* substitution by a chlorine atom does not noticeably affect the position of the benzene ring in oriented samples. The change of birefringence as a function of draw ratio for samples stretched at different strain rates at a temperature $T = T_g + 11.5°C$ is shown in *Figure 3*. In *Table 2*, the values of $\langle P_2(\cos\theta)\rangle$, calculated from birefringence data, are compared with the values of the orientation function of polystyrene samples stretched under the same conditions. Within the limits of the experimental error, both polymers develop the same orientation.

The infra-red spectra of PS and PoCS are given in *Figure 4*. An assignment of PoCS absorption bands based on *o*-chloroethylbenzene and *o*-chlorostyrene vibrational spectra[17] is given in *Table 3*. The knowledge of the second-order moments allows one to calculate the angle α between the dipole moment vectors of infra-red vibrations and the chain axis. The slope of the linear relation:

$$\langle P_2(\cos\theta)\rangle = (R-1)(R_0+2)/(R+2)(R_0-1)$$

gives R_0 and α.

We calculate the angle α for three vibrational modes: the 17b out-of-plane mode of the benzene ring (940 cm^{-1}) and the in-plane 9a (1160 cm^{-1}) and 18a (1130 cm^{-1}) modes. In *Figures 5* and *6*, the $\langle P_2(\cos\theta)\rangle$ function is plotted against the dichroic ratio, $(R-1)/(R+2)$, of the

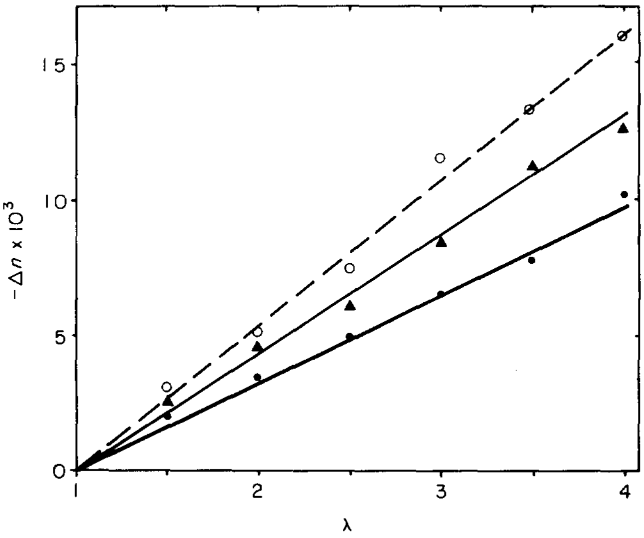

Figure 3 PoCS orientation *versus* draw ratio. Stretching temperature: $T = T_g + 11.5°C$. Strain rates: (○) 0.115 s^{-1}; (▲) 0.026 s^{-1}; (●) 0.008 s^{-1}

Table 2 Comparison of the orientation functions $\langle P_2(\cos\theta)\rangle$ of PoCS and PS for a stretching temperature $T = T_g + 11.5°C$ at three different strain rates $\dot{\varepsilon}$

	$\dot{\varepsilon} = 0.008\,s^{-1}$		$\dot{\varepsilon} = 0.026\,s^{-1}$		$\dot{\varepsilon} = 0.115\,s^{-1}$	
λ	PoCS	PS	PoCS	PS	PoCS	PS
1.5	0.02	0.01	0.02	0.02	0.02	0.02
2.0	0.03	0.02	0.04	0.03	0.04	0.04
2.5	0.04	0.03	0.05	0.05	0.06	0.06
3.0	0.05	0.04	0.07	0.06	0.09	0.08
3.5	0.06	0.06	0.09	0.08	0.10	0.11
4.0	0.08	0.07	0.10	0.10	0.13	0.13

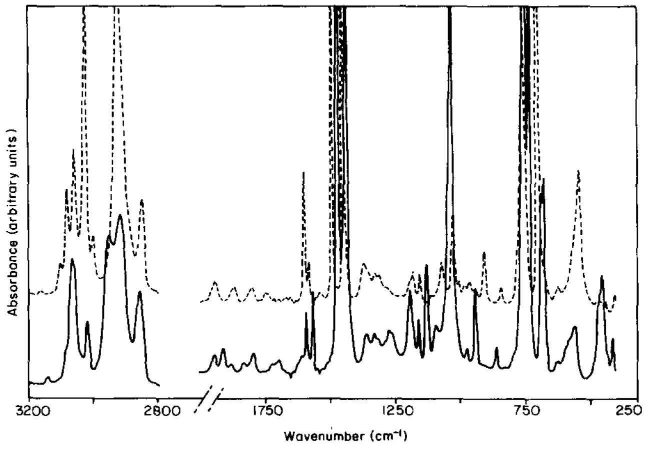

Figure 4 Infra-red spectra of PS (– – –) and PoCS (—)

Table 3 Vibrational spectrum of PoCS

Infra-red (cm^{-1})	Polarization	Assignment
460 m	π	16b a″
560 m	π	16a a″
675 s	σ (?)	
685 s	σ	6a a′
735 vs	π	4 a″
750 vs	π	11 a″
860 w	σ (?)	17a a″
940 m	π	17b a″
1035 vs	σ	1 a′
1130 m	σ	18a a′
1160 m	σ	9a a′
1192 m	π (?)	13 a′
1260 w	σ	3 a′
1275 w	σ	14 a′
1332 w	σ	$\gamma_s CH_2$
1362 w	σ	δCH
1440 vs	σ (?)	19a a′
1470 vs	σ (?)	19b a′
1570 m	σ	8a a′
1595 m	σ	8b a′
2856 m	σ	$\nu_s CH_2$
2915 s	σ	$\nu_{as} CH_2$
2950 s	σ	$\left\{\begin{array}{l}2 \times 19b \text{ Fermi resonance} \\ \text{with } \nu_{as} CH_2\end{array}\right.$
3018 m	σ	7b a′
3060 s	σ	2 a′

I.r.: vs, very strong; s, strong; m, medium; w, weak. Polarization: σ, perpendicular; π, parallel

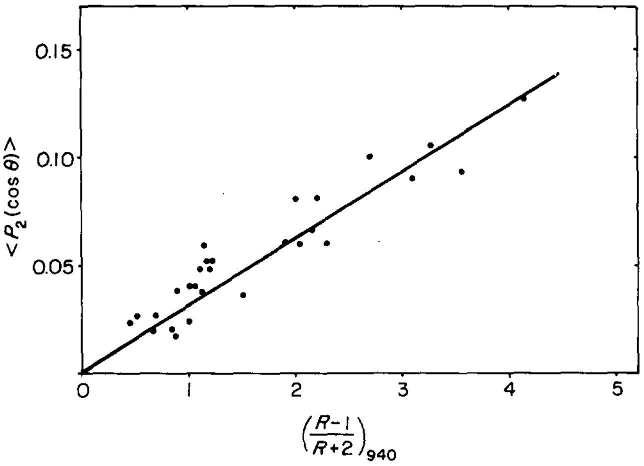

Figure 5 Determination of the angle α between the dipole moment vector of the 940 cm^{-1} vibration and the chain axis

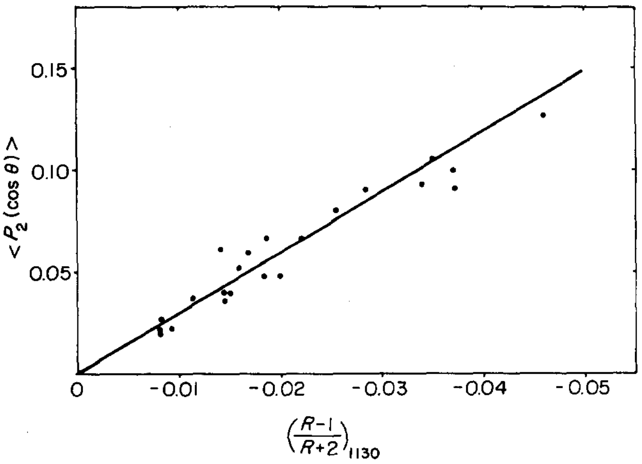

Figure 6 Determination of the angle α between the dipole moment vector of the 1130 cm^{-1} vibration and the chain axis

infra-red 940 cm^{-1} and 1130 cm^{-1} bands. The angle values are given in *Table 4*. It is worth noting that the angle value $\alpha = 41°$ obtained for the dipole moment vector of the out-of-plane mode (which is theoretically perpendicular to the benzene ring) is in good agreement with the value deduced from birefringence. *Ortho* substitution by a chlorine atom does not noticeably affect the orientation of the benzene ring with respect to the chain axis in oriented PoCS samples as compared with polystyrene. Conformational energy calculations performed on PS and PoCS model molecules[18] lead to the same conclusion.

Orientation in compatible PS/PoCS blends

On account of compatibility considerations, only blends containing less than 15 wt% of PoCS have been studied. The glass transition temperatures for each blend are given in *Table 5*. All the samples were stretched at a temperature $T = T_g + 11.5°C$ and stain rates $\dot{\varepsilon} = 0.008\ s^{-1}$, $0.026\ s^{-1}$ and $0.115\ s^{-1}$.

The infra-red spectra of both components badly overlap in the blends and infra-red dichroism only allows measurement of the orientation of PS using the 906 cm^{-1} absorption band. *Figure 7* illustrates the results obtained with a blend containing 10% of PoCS. As pointed out elsewhere[4], a rectilinear relationship holds between orientation function and draw ratio in the present experimental conditions. Accordingly, the slope $d\langle P_2(\cos\theta)\rangle/d\lambda$ is defined and gives the orientation behaviour of one component *versus* draw ratio. This slope for PS orientation *versus* blend composition is given in *Figure 8* for three different strain rates. In contrast with other blends studied[3,4], PS orientation is roughly independent of the presence of the second component.

Table 4 The angle α between the dipole moment vector of some vibrational modes of PoCS and the chain axis

Absorption band (cm^{-1})	940	1130	1160
α (deg)	41	73	67

Table 5 Glass transition temperature of PS–PoCS blends

PoCS (%)	0	5	10	15	100
T_g (°C)	107	109	109	110	134

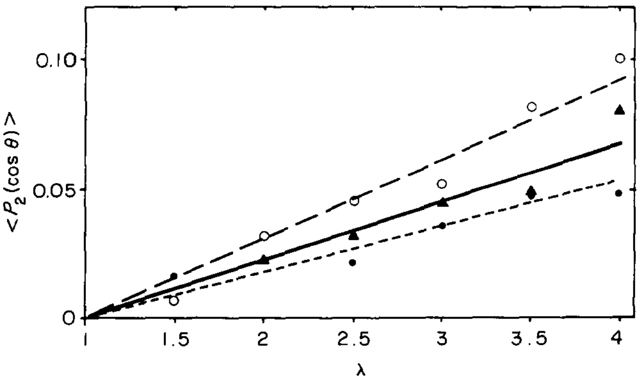

Figure 7 PS orientation in PS/PoCS (90/10) blend. Stretching temperature: $T = T_g + 11.5°C$. Strain rates: (○) $0.115\ s^{-1}$; (▲) $0.026\ s^{-1}$; (●) $0.008\ s^{-1}$

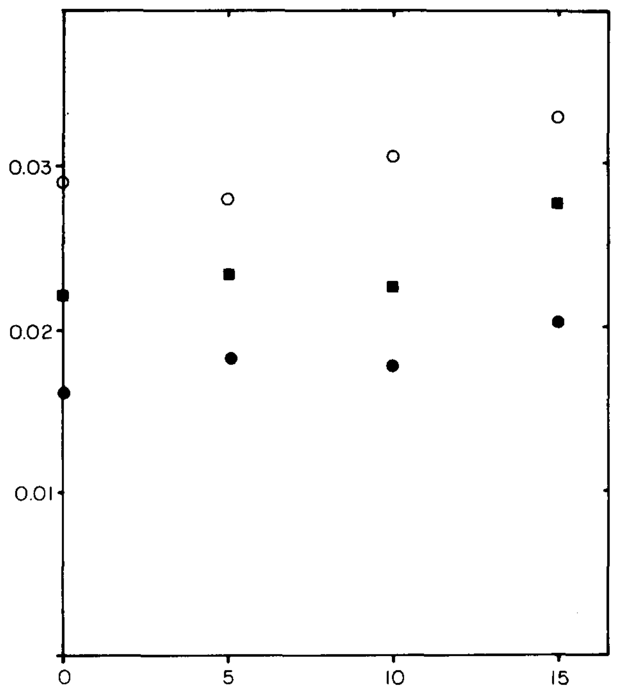

Figure 8 PS orientation *versus* blend composition. Stretching temperature: $T=T_g+11.5°C$. Strain rates: (○) $0.115\,s^{-1}$; (▲) $0.026\,s^{-1}$; (●) $0.008\,s^{-1}$

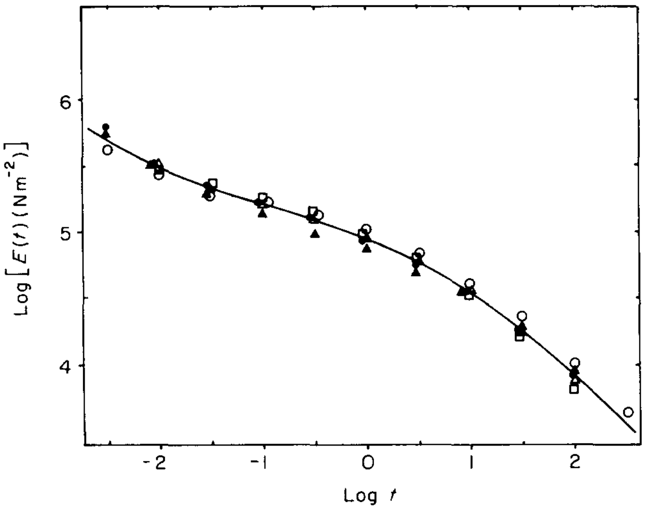

Figure 9 Master curve $\log E(t)$ *versus* $\log t$ for PS, PoCS and PS/PoCS blends. Reference temperature: $T=T_g+40°C$. PS (○); PoCS (▲); 5% PoCS (□); 10% PoCS (△); 15% PoCS (●)

Viscoelasticity of PS/PoCS blends

Mechanical relaxation curves can be deduced from dynamic oscillatory measurements. For a given composition, six to ten different temperatures were swept. The time–temperature equivalence was used to reduce results to a reference temperature. The relaxation modulus was then calculated with Ninomiya and Ferry's relation[11].

In *Figure 9*, $\log E(t)$ is plotted *versus* time t for the pure polymers and three blends at equivalent reference temperature $T=T_g+40°C$. The choice of this temperature is arbitrary but it falls within the range of experiments so no extrapolated reduction is necessary. In contrast with other blends previously studied[3,4], mechanical relaxation of PS, PoCS and PS/PoCS blends is identical. Such behaviour is consistent with orientation measurements and suggests that the average molecular weight between entanglements is very similar in PS and PoCS.

DISCUSSION

In order to explain the orientation behaviour in PS/PPO and PS/PVME blends, we suggested an increase in the friction coefficients of each species induced by the molecular interactions that are at the origin of compatibility[4]. For a binary mixture of two polymers, the free energy of mixing ΔG is given by the familiar expression:

$$\Delta G/RT=(\phi_1/r_1)\ln\phi_1+(\phi_2/r_2)\ln\phi_2+\chi\phi_1\phi_2$$

where ϕ_i and r_i are the volume fraction and the degree of polymerization of the polymer i, respectively, and χ is the Flory–Huggins parameter.

Interaction forces are characterized by negative values of the parameter χ. Thus $\chi\simeq-1$ in PS/PPO blends[19] and $0<\chi<-0.4$ in PS/PVME blends[20–22]. On the other hand, blends of PS and PoCS constitute an example of miscibility without specific interactions, as confirmed by the value $\chi\simeq0$ (Ref. 23). Similarly, no phase separation occurs in PS/PPO blends while an increase in temperature induces phase separation in PS/PVME blends[21]. PS/PoCS blends are only compatible for mixtures containing a low percentage of PS or PoCS.

To break free from the influence of the number of interactions, it is interesting to plot PS orientation *versus* the ratio of monomer units K for the three blends studied. The results are shown in *Figure 10* for a strain rate $\dot{\varepsilon}=0.115\,s^{-1}$. PPO is more effective than PVME in increasing PS orientation in the low concentration range, while both polymers exhibit the same efficiency at higher concentrations. On the other hand, PoCS has almost no influence on PS orientation. Such results are consistent with a change of friction coefficients induced by compatibility in the blends for which polymer–polymer interaction occurs.

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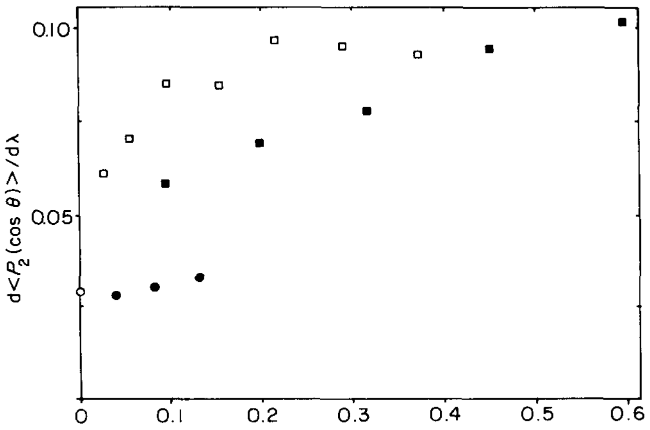

Figure 10 PS orientation *versus* ratio of monomer units K in PS/PPO (□), PS/PVME (■) and PS/PoCS (●) blends

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