

Orientation and relaxation 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 atactic polystyrene and poly(2,6-dimethyl 1,4-phenylene oxide) absorption bands provide a valuable method for the determination of orientation as well as relaxation of chains of both polymers during stretching of their compatible blends. Influence of strain rate, temperature of stretching, and molecular weight of the polymers on orientation of both polymer chains in blends containing up to 35% PPO has been studied. Orientation relaxation for both polymers has been analysed using Lodge's constitutive equation. Master curves have been obtained for PPO and PS in the blends at a reference temperature $T_0 = T_g + 10^\circ\text{C}$. Results are interpreted in terms of an hindrance of relaxation of PS chains induced by interaction with a highly-oriented PPO network which slowly relaxes.

Keywords PPO, PS; polymer blends; orientation; relaxation; Fourier-transform infra-red spectroscopy

INTRODUCTION

In a previous paper¹ it was pointed out that poly(2,6-dimethyl 1,4-phenylene oxide) (PPO) and atactic polystyrene (PS) chains orient in a different way when subjected to an uniaxial strain in spite of the compatible nature of the blend. Orientation of PS chains increases regularly with PPO content up to a limit concentration C_1 , then remains constant. However, PPO chain orientation remains constant over all the studied range of concentrations (0–35% PPO). It was expected that both polymers orient in the same way and the observed behaviour of PS and PPO chains, therefore, was surprising. As an explanation it was proposed that a gradual hindrance of PS chains relaxation occurs during the experimental stretching time period, induced by interchain interactions with PPO.

To improve understanding of the processes occurring at the molecular level, Fourier transform infra-red spectroscopy is used to study the influence of stretching parameters (temperature and strain rate) and molecular weight of the two polymers on orientation and relaxation of the two species.

THEORY

Vibrational spectroscopy is an established method for measuring orientation in polymers². Briefly, the information available by infra-red dichroism measurement is as follows. The orientation of a single unit of a polymer chain can be described by the three Eulerian angles θ, ϕ, ψ . The overall orientation is then described by an orientation distribution function $f(\theta, \phi, \psi)$ ³. For uniaxially-oriented systems, the orientation distribution function is expressed

as:

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

Where $P_n(\cos \theta)$ are the spherical harmonic functions:

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

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

etc.

For any absorption band, 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 of the orientation function by:

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

with $R_0 = 2 \cot^2 \alpha$, α being the angle between the dipole moment vector of the vibration and the chain axis and θ is the angle between the chain axis and the stretching direction. When it is possible to find non-overlapping absorption bands, dichroism measurements allow the overall orientation of any chemical unit in a blend, to be established.

EXPERIMENTAL

The characteristics of the polymers used are given in Table I. Other experimental details such as sample preparation

Table 1 Characteristics of PS and PPO samples

Sample	M_n	M_w	M_w/M_n	T_g (°C)	Origin
PS 1	149 800	254 200	1.70	105	CdF-Chimie Co.
PS 100	105 000	118 000	1.12	105	EAHP ^a
PS 900	891 000	999 000	1.12	105	EAHP
PPO 10	10 000	16 000	1.60	213	General Electric Co.
PPO 23	23 000	50 000	2.17	228	"
PPO 45	45 000	103 000	2.29	234	"

^a EAHP, Ecole d'Application des Hauts Polymères, Strasbourg, France

Table 2 Glass transition temperatures for each blend

PS (%)	3	6	10	15	20	25	30	35
T_g (°C)	105	108	110	113	119	123	128	130

and infra-red measurements are given in ref. 1. The 906 cm^{-1} absorption band is used for PS while the 1190 cm^{-1} , 1305 cm^{-1} and 865 cm^{-1} absorption bands are successively used as a function of PPO concentration in the blend¹. Glass transition temperatures were obtained using a Dupont 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 2. No significant change was observed as a function of the molecular weight of both polymers used in this study.

RESULTS AND DISCUSSION

All the samples were stretched at constant strain rate above the glass transition temperature. First consider the results obtained at a stretching temperature $T = T_g + 11.5^\circ\text{C}$ and a strain rate $\dot{\epsilon} = 0.026 \text{ s}^{-1}$, for different PS₁/PPO₂₃ blends.

Figure 1 shows the change of the $\langle P_2(\cos \theta) \rangle$ orien-

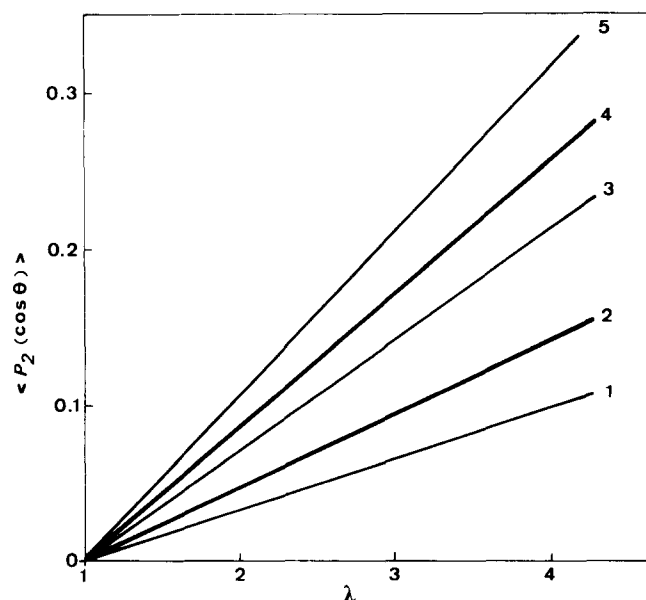


Figure 1 Orientation function of PS 1 in PS 1/PPO 23 blends as a function of draw ratio. Temperature of stretching $T = T_g + 11.5^\circ\text{C}$. Strain rate $\dot{\epsilon} = 0.026 \text{ s}^{-1}$. (1) pure PS; (2) blend 10% PPO; (3) blend 20% PPO; (4) blend 30–35% PPO; (5) PPO, any concentration

tation function relative to PPO and PS chains as a function of draw ratio and PPO percentage in the blend. A rectilinear relation holds for both polymers and any composition of the blend between $\langle P_2(\cos \theta) \rangle$ versus draw ratio.

It is interesting to describe the orientation behaviour^{1,4} by plotting the slope $d\langle P_2(\cos \theta) \rangle/d\lambda$ as a function of PPO percentage. Figure 2 shows that PPO orients in the same way up to 35%. PS orientation regularly increases up to a ratio of 25% PPO then remains constant, allowing definition of a limit concentration C_l , at and beyond which PS orientation is not sensitive to further addition of PPO.

The influence of strain rate on the function $d\langle P_2(\cos \theta) \rangle/d\lambda$ is shown in Figure 3. Orientation increases with strain rate for PPO. For PS, two effects are observed: for a given concentration, PS orientation increases with strain rate; the limit concentration, C_l , for which PS orientation becomes insensitive to further addition of PPO is shifted towards the low PPO concentration range with increasing strain rate. As expected from the time-temperature equivalency, similar behaviour is observed when the stretching temperature is closer to T_g , as shown in Figure 4.

In addition to the stretching parameters (λ , T , $\dot{\epsilon}$) it is interesting to examine the influence on orientation of the molecular weight of the two polymers. First consider the molecular weight of PS. Figures 5 and 6 show the change of the function $d\langle P_2(\cos \theta) \rangle/d\lambda$ versus PPO concentration for three different PS samples and two $T-T_g$ values for stretching temperature. When the stretching temperature is close to the glass transition temperature

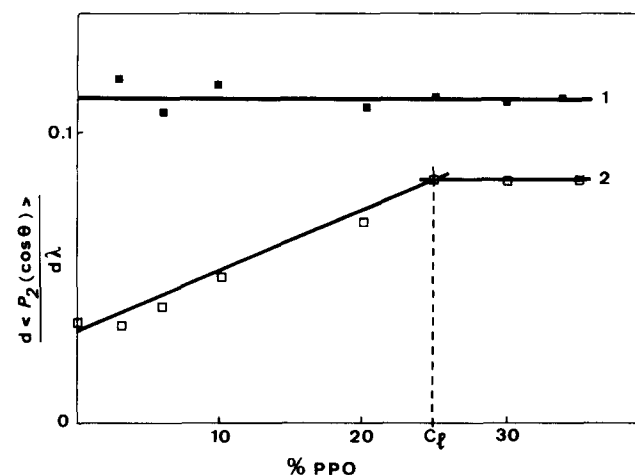


Figure 2 Slope of $\langle P_2(\cos \theta) \rangle = f(\lambda)$ as a function of PPO percentage. (1) PPO 23; (2) PS 1. Temperature of stretching $T = T_g + 11.5^\circ\text{C}$. Strain rate $\dot{\epsilon} = 0.026 \text{ s}^{-1}$

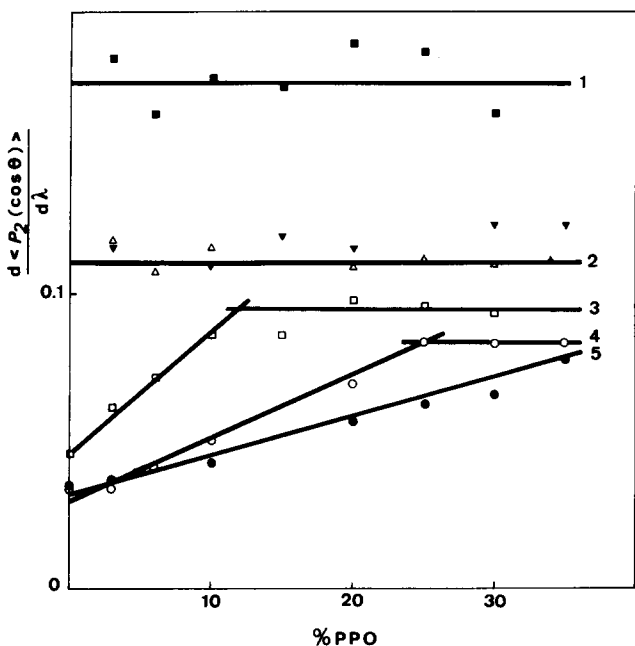


Figure 3 Slope of $\langle P_2(\cos \theta) \rangle = f(\lambda)$ as a function of PPO percentage and strain rate. Temperature of stretching $T = T_g + 11.5^\circ\text{C}$. (1) PPO 23, $\dot{\epsilon} = 0.115 \text{ s}^{-1}$; (2) PPO 23, $\dot{\epsilon} = 0.008-0.026 \text{ s}^{-1}$; (3) PS 1, $\dot{\epsilon} = 0.115 \text{ s}^{-1}$; (4) PS 1, $\dot{\epsilon} = 0.026 \text{ s}^{-1}$; (5) PS 1, $\dot{\epsilon} = 0.008 \text{ s}^{-1}$

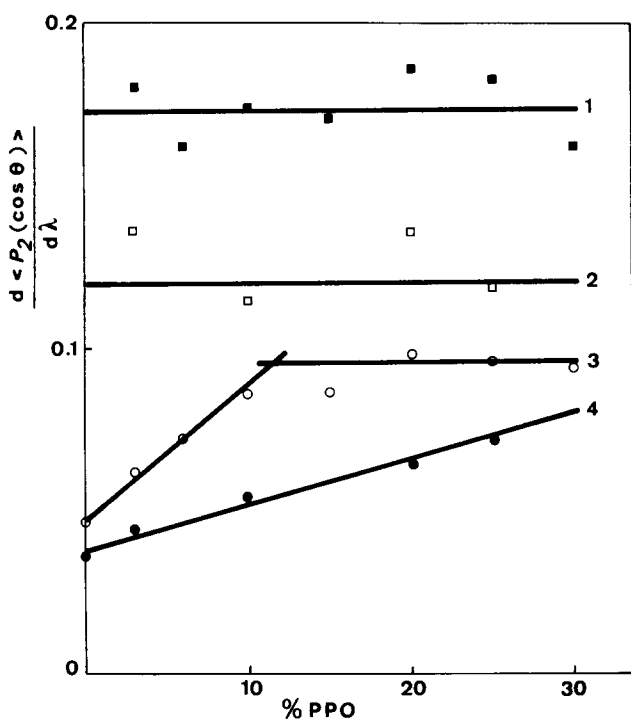


Figure 4 Slope of $\langle P_2(\cos \theta) \rangle = f(\lambda)$ as a function of PPO percentage and stretching temperature. Strain rate $\dot{\epsilon} = 0.115 \text{ s}^{-1}$. (1) PPO 23, $T = T_g + 11.5^\circ\text{C}$; (2) PPO 23, $T = T_g + 17^\circ\text{C}$; (3) PS 1, $T = T_g + 11.5^\circ\text{C}$; (4) PS 1, $T = T_g + 17^\circ\text{C}$

(Figure 5), the molecular weight of PS has no influence on orientation of either PS as PPO. However, when the stretching temperature increases (Figure 6) PS orientation is slightly sensitive to molecular weight. Under the experimental conditions used in the present work, the C_1 concentration also remains constant.

The influence of PPO molecular weight is shown in Figure 7. When the molecular weight of this polymer is

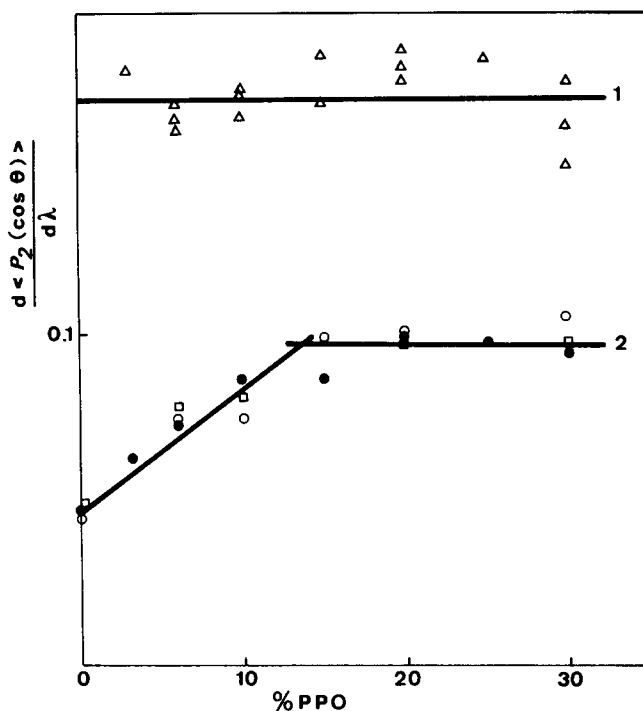


Figure 5 Slope of $\langle P_2(\cos \theta) \rangle = f(\lambda)$ as a function of PPO percentage and PS molecular weight. Temperature of stretching $T = T_g + 11.5^\circ\text{C}$. Strain rate $\dot{\epsilon} = 0.115 \text{ s}^{-1}$. (1) PPO 23, any blend; (2) PS: ● PS 1; □ PS 100; ○ PS 900

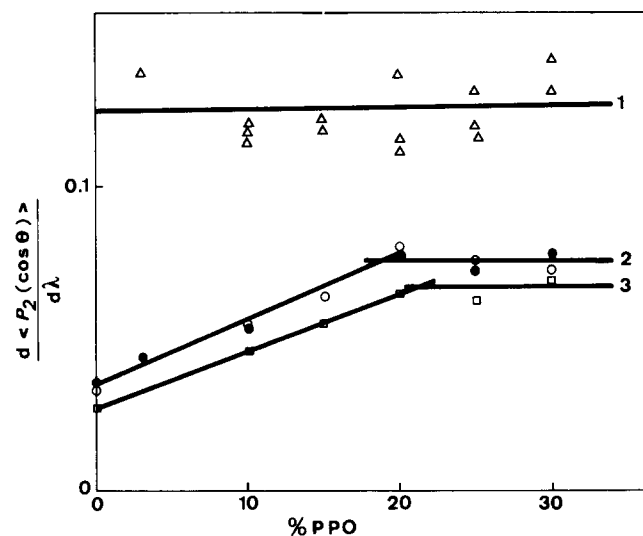


Figure 6 Slope of $\langle P_2(\cos \theta) \rangle = f(\lambda)$ as a function of PPO percentage and PS molecular weight. Temperature of stretching $T = T_g + 17^\circ\text{C}$. Strain rate $\dot{\epsilon} = 0.115 \text{ s}^{-1}$. (1) PPO 23, any blend; (2) PS: ● PS 1; ○ PS 900; (3) PS 100

higher than the average molecular weight spacing between entanglement points ($M_c = 9100$)⁵, the orientation of both PS and PPO are unaffected. However, when the molecular weight of PPO is of the same order of magnitude as M_c , a decrease of orientation of both polymer chains is observed. A shift of the C_1 concentration towards the high PPO concentration range also occurs. It is interesting to analyse the previous results in terms of orientation relaxation. Previously, for orientation and relaxation of uniaxially stretched atactic PS⁴, the Lodge constitutive equation⁶ was used to relate the second-order moment of the orientation function to an orientation

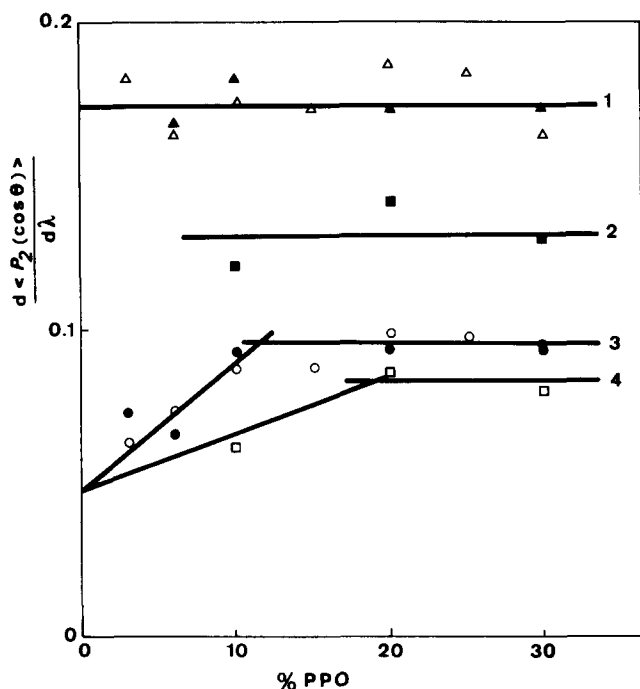


Figure 7 Slope of $\langle P_2(\cos \theta) \rangle = f(\lambda)$ as a function of PPO percentage and molecular weight. Temperature of stretching $T = T_g + 11.5^\circ\text{C}$. Strain rate $\dot{\epsilon} = 0.115 \text{ s}^{-1}$. (1) \blacktriangle , PPO 45; \triangle , PPO 23; (2) PPO 10; (3) PS in PS 1/PPO 45 and PS 1/PPO 23 blends; (4) PS in PS 1/PPO 10 blend

relaxation function $\theta(t)$:

$$\langle P_2(\cos \theta) \rangle_{av} = \sum_i \theta_i \left[\frac{3\dot{\epsilon}\tau_i}{(1-2\dot{\epsilon}\tau_i)(1+\dot{\epsilon}\tau_i)} - \frac{2\dot{\epsilon}\tau_i e^{2\dot{\epsilon}t} e^{-t/\tau_i}}{1-2\dot{\epsilon}\tau_i} - \frac{\dot{\epsilon}\tau_i e^{-\dot{\epsilon}t} e^{-t/\tau_i}}{1+\dot{\epsilon}\tau_i} \right]$$

Where θ_i and τ_i originate from a decomposition of the orientation relaxation function $\theta(t)$ in a sum of exponentials:

$$\theta(t) = \sum_i \theta_i e^{-t/\tau_i}$$

Choosing arbitrarily $\theta(t) = \sum_{i=-1}^{+3} \theta_i e^{-t/10^i}$, an orientation

relaxation master curve was obtained. Comparison with the mechanical relaxation modulus master curve at the same reference temperature showed that a constant factor, similar to the 'stress optical coefficient' holds between the two sets of results, supporting the use of an orientation relaxation function.

A similar procedure was used here. Using five different temperatures of stretching for each blend and five strain rates ($\dot{\epsilon} = 0.008; 0.026; 0.059; 0.086$ and 0.115 s^{-1}) a set of curves is obtained which represent the change of the $\theta(t)$ function versus time for PPO and PS. Figure 8 shows the results obtained for PS in the PS 1/PPO 23 blend containing 20% of PPO. From these results, it is possible to obtain a master curve for the orientation relaxation functions. Curves from Figure 8, shifted using the WLF coefficients previously obtained by Prest and Porter⁷ results in the curve shown in Figure 9 for a reference temperature $T_R = T_g + 10^\circ\text{C}$. Figure 10 shows the change of the orientation relaxation function of PPO versus time

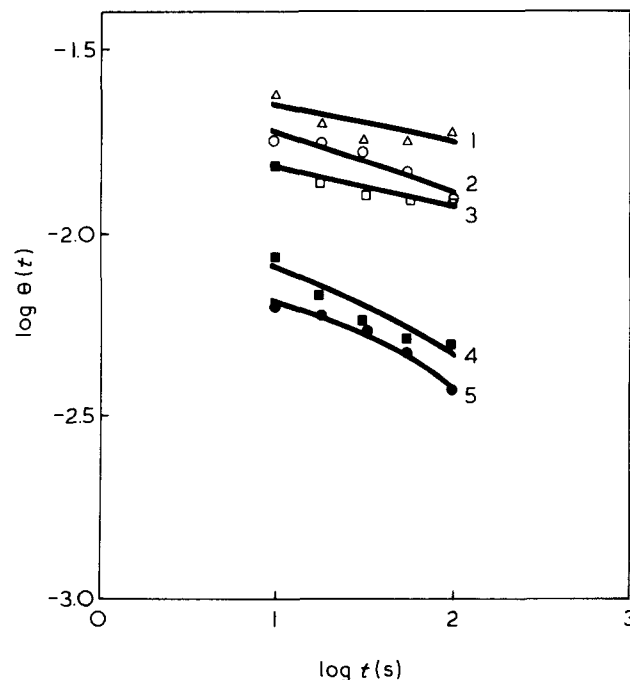


Figure 8 $\log \theta(t)$ vs. $\log t$ for PS 1 in 20% PPO 23 blend. (1) 123.5°C ; (2) 126.5°C ; (3) 130°C ; (4) 135.5°C ; (5) 142°C

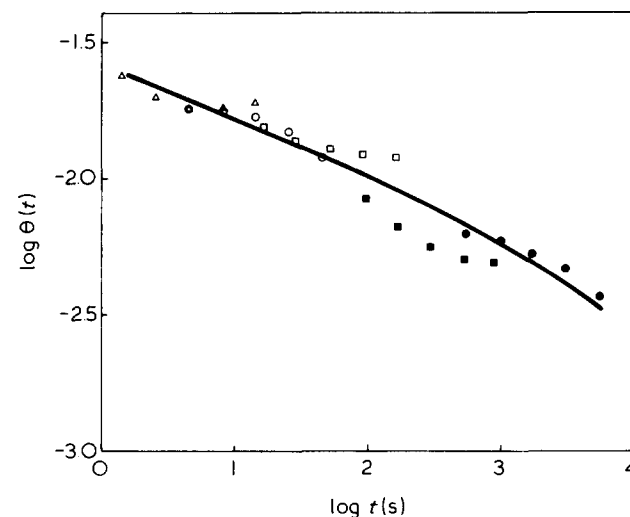


Figure 9 Master curve $\log \theta(t)$ versus $\log t$ for PS 1 in 20% PPO 23 blend between 123.5° and 142°C . Reference temperature $T_0 = 128.5^\circ\text{C}$

in different blends. Although the experimental points are relatively scattered, only one curve is obtained whatever the concentration. Figure 11 shows that PS orientation relaxation is a function of PPO concentration in the blend. For short relaxation times the function $\theta(t)$ is independent of PPO concentration $> 10\%$ and the observed value is larger than that for pure PS. For longer relaxation times, the PS orientation relaxation function increases with PPO concentration.

Such orientation relaxation results explain reasonably well the orientation behaviour previously observed. If the experimental conditions correspond to short relaxation times, e.g. $\log t = 0$, $\theta(t)$ functions have the same value for blends containing 10–30% PPO. Thus, the limiting concentration C_1 for which no influence of further addition of PPO on PS orientation is observed will be $0\% < C_1 < 10\%$.

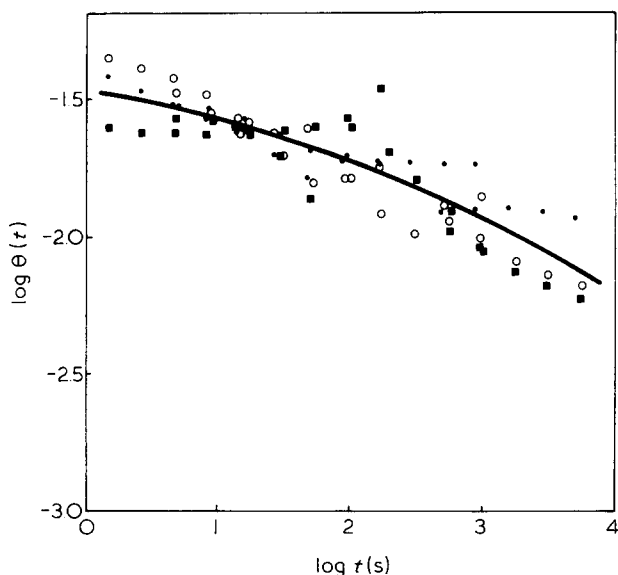


Figure 10 Master curve $\log \theta(t)$ versus $\log t$ for PPO 23 in PS 1/PPO blends any percentage. Reference temperature $T_0 = T_g + 10^\circ\text{C}$

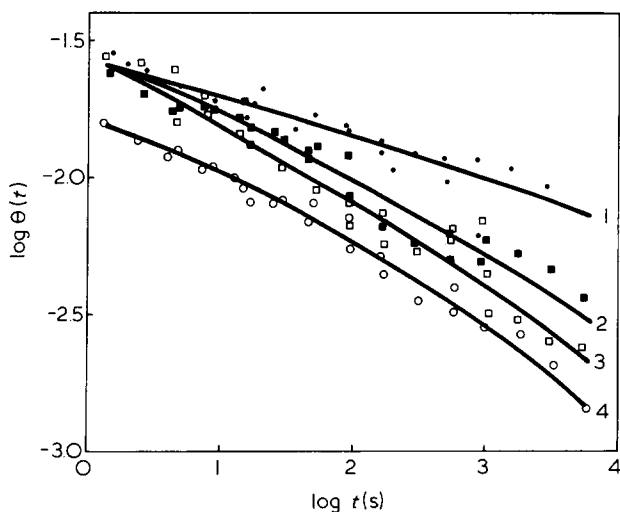


Figure 11 Master curve $\log \theta(t)$ versus $\log t$ for PS 1 in PS 1/PPO 23 blends. (1) Blend 30% PPO; (2) blend 20% PPO; (3) blend 10% PPO; (4) 0% PPO. Reference temperature $T_0 = T_g + 10^\circ\text{C}$

If the experimental stretching conditions correspond to longer relaxation times, e.g. $\log t = 2$, similar orientation relaxation function values are observed for 20 and 30% PPO while the value of this function is lower for 10%

PPO. In this case, the limit concentration C_1 will be close to 20%. Similarly, for $\log t = 3$, C_1 will be >30% PPO.

It is reasonable to consider that the orientation behaviour observed in PPO/PS blends is related to the high stiffness of PPO chains⁶. Owing to this stiffness, PPO chains relaxation after deformation occurs at much longer times than those in the experimental conditions chosen here, resulting in a high level of orientation. On account of entanglements, it is apparent that after deformation, PPO chains participate in a highly-oriented physical network. Interaction between PS and PPO chains hinders PS relaxation over all the studied time scale. For short relaxation times, the interaction factor certainly prevails to hinder local motions of PS chains. For longer relaxation times, in addition to the interaction term, important motions of PS chains are hindered by the highly-oriented PPO network which slowly relaxes.

The influence of the molecular weight of the two polymers also supports such a scheme. When the molecular weight of PPO is close to the critical M_c value, chains no longer overlap and the PPO oriented network is not achieved. Both PS and PPO chain orientation decreases with increase in PS chain relaxation. However, PS orientation and C_1 concentration are practically independent of the molecular weight of this polymer. This result is easily explained considering that hindrance of relaxation of PS chains is mainly introduced by the oriented PPO network which appears to be insensitive to PS chains.

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