Orientation and relaxation in uniaxially stretched poly(methyl methacrylate)-poly(styrene-*co*-acrylonitrile) compatible blends

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The orientation and relaxation of both polymer chains in compatible blends of poly(methyl methacrylate)-poly(styrene-*co*-acrylonitrile) (PMMA-SAN) have been studied using Fourier transform infra-red spectroscopy. The influence of strain rate and stretching temperature on orientation have been measured. In these blends, where inter-chain interactions are almost nonexistent, both polymers orient differently over the whole concentration range, with the PMMA chains being always more oriented than the SAN chains. Orientation relaxation master curves have also been established. A change in molecular weight between entanglements does not seem to be the main factor influencing orientation and relaxation, but use of the monomeric friction coefficient, which reflects local mobility and interactions, as a scaling factor allows one to obtain two general master curves which are representative of the overall behaviour of the PMMA and SAN chains in their compatible blends.

(Keywords: PMMA-SAN blends; orientation; relaxation)

INTRODUCTION

In previous work[1,2] on various compatible blends based on poly(methyl methacrylate) (PMMA), we pointed out that in PMMA-PEO (poly(ethylene oxide)) blends and in PPMA-PF$_3$E (poly(trifluoroethylene)) blends, chains orient in a different way when subjected to a uniaxial deformation, in spite of the compatible nature of the blend. These studies were limited to the high PMMA concentration range on account of the crystallization of the second component. In this range, PMMA orientation is concentration dependent and increases with an increase in PEO or PF$_3$E content; PEO remains unoriented while PF$_3$E orientation remains constant whatever the concentration. In these blends, compatibility arises from intermolecular interactions between dissimilar chains leading to negative values of the Flory–Huggins interaction parameter χ. The results were interpreted in terms of a modification of the friction coefficient that was due to the molecular interactions caused by compatibility. Therefore, it is interesting to examine the behaviour of polymer chains in blends for which compatibility does not result from an enthalpic character.

This present work deals with the study of orientation and relaxation of PMMA-poly(styrene-*co*-acrylonitrile) (SAN) blends using infra-red dichroism.

Compatibility of PMMA-SAN blends

The compatibility of PMMA-SAN blends (containing 9–28 wt% acrylonitrile) has been previously repeated in the literature by using various methods, including T_g measurements[3,4], electron microscopy[3,5], small-angle neutron scattering[6–8], pulsed n.m.r.[9] and cloud point measurements[8,10–12]. The Flory–Huggins parameter $\chi = -0.011$[13], with compatibility being assigned to repulsion between the styrene and acrylonitrile units in the copolymer[14].

In order to insure compositional uniformity and a single phase behaviour, we have chosen a SAN copolymer for this work which contains 25 wt% acrylonitrile.

EXPERIMENTAL

The PMMA used in this study was a pure polymer obtained by a radical chain polymerization process ($\bar{M}_n = 67\,000$; $\bar{M}_w = 111\,000$; $T_g = 123°C$; tacticity, triads *rr* = 55, *rm* = 39, and *mm* = 6%). The SAN sample was a commercial product obtained from Scientific Polymer Products Inc. ($\bar{M}_n = 63\,860$; $\bar{M}_w = 135\,800$; $T_g = 113°C$). Pichot and Pham[15] have shown that in a SAN copolymer containing 27 wt% acrylonitrile, the acrylonitrile (H) segments were completely located in styrene–acrylonitrile–styrene (SAS) triads. This result indicates that no long acrylonitrile sequences exist in the copolymer.

Sample preparation

Thin films of the blends, suitable for infra-red spectroscopy, were obtained by casting 6 wt% 2-butanone solutions onto a glass plate. Subsequent annealing was carried out under vacuum above the T_g in order to remove any traces of solvent and also to relieve internal stresses. The glass transition temperatures of the

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Table 1 Glass transition temperatures of the different PMMA-SAN blends

SAN content (wt%)	0	12	25	38	50	62	75	100
T_g (°C)	123	119	117	116	115	115	113	113

samples were obtained by using a Du Pont 1090 differential scanning calorimeter, at a heating rate of 20°C min^{-1}, with a sample weight of ~7 mg. The glass transition temperatures of the different blends are given in *Table 1*.

Oriented samples were obtained from the thin films by using an apparatus that had specially developed in our laboratory, namely a stretching machine operating at a constant strain rate combined with a special oven which allowed us to obtain a very good temperature stability over all of the sample specimen (homogeneity ~0.2°C). Draw ratios were measured by reference to ink marks on the samples, and all of the measurements were normalized to the T_gs.

Infra-red dichroism

Polarized spectra were obtained on either a Nicolet 7199 or a Nicolet 205 Fourier transform infra-red spectrometer, equipped with a SPECAC gold wire grid polarizer, set at the maximum transmission position. The samples, rather than the polarizer, were rotated through 90° in order to obtain the two polarization measurements. A total of 100 co-added interferograms were scanned at 2 cm^{-1} resolution. The infra-red dichroic ratio was calculated as $R = A_{\parallel}/A_{\perp}$ for the peak optical densities, $A_{\parallel}$ and $A_{\perp}$.

RESULTS

Orientation behaviour

Dichroic ratio measurements allow one to calculate the second-order moment of the orientation function, according to the relationship:

$$\langle P_2(\cos\theta)\rangle = \tfrac{1}{2}(3\langle\cos^2\theta\rangle - 1) = \left(\frac{R-1}{R+2}\right)\left(\frac{R_0+2}{R_0-1}\right) \tag{1}$$

where $R_0 = 2\cot^2\alpha$, with α being the angle between the dipole moment vector of the considered vibration and the chain axis, and θ the angle between the chain axis and the chain direction[16]. Although infra-red spectroscopy is an attractive method for deducing the chain orientations of the different polymers in a blend, absorption band overlapping may restrict the possibility of analysis. As shown in the PMMA and SAN spectra given in *Figure 1*, the absorption bands of both polymers badly overlap. However, the symmetric bending mode of the α-methyl group at 1388 cm^{-1} ($\alpha = 90°$) in PMMA[17] and the ν_{18a} in-plane ring vibration at 1028 cm^{-1} ($\alpha = 90°$) in SAN can be used to measure the orientation.

In a copolymer, on the other hand, the first question to ask is do both monomer units orient in the same way? In SAN, the CH$_2$ stretching absorption bands at 2930 and 2850 cm^{-1}, which belong to both monomer units, allow measurement of the overall orientation. The dipole moment vector of these vibrations should make an angle α of 90° with respect to the chain axis. In fact, an interaction between the stretching modes and an out-of-plane mode of the CH$_2$, which has been discussed in detail by Zbinden[18], induces a change in the α angle. An experimental value of $\alpha = 70°$ has been found in polyethylene[18] and polystyrene[19]. We have measured the values of the orientation function of eight SAN samples which have been stretched under the same conditions, by using the 2930, 2855 and 1028 cm^{-1} absorption bands. The results, given in *Table 2*, show that both monomer units orient in the same way, within the limits of experimental error.

The fact that both monomer units orient in a similar way makes possible the measurement of the α angle of the nitrile stretching mode, which can be deduced from the slope of the linear relationship:

$$\langle P_2(\cos\theta)\rangle_{1028} = f[(1-R)/(R+2)]_{2238} \tag{2}$$

where $f = [(R_0+2)/(R_0-1)]_{2238}$. The experimental results, given in *Figure 2*, lead to a value of α of 90°, showing that the dipole moment vector of this mode is perpendicular to the chain axis, as expected. It is interesting to note that in acrylonitrile, a delocalization of the dipole moment vector is observed ($\alpha = 70°$)[18,20], as well as an approximate 10 cm^{-1} wavenumber shift of the nitrile absorption band.

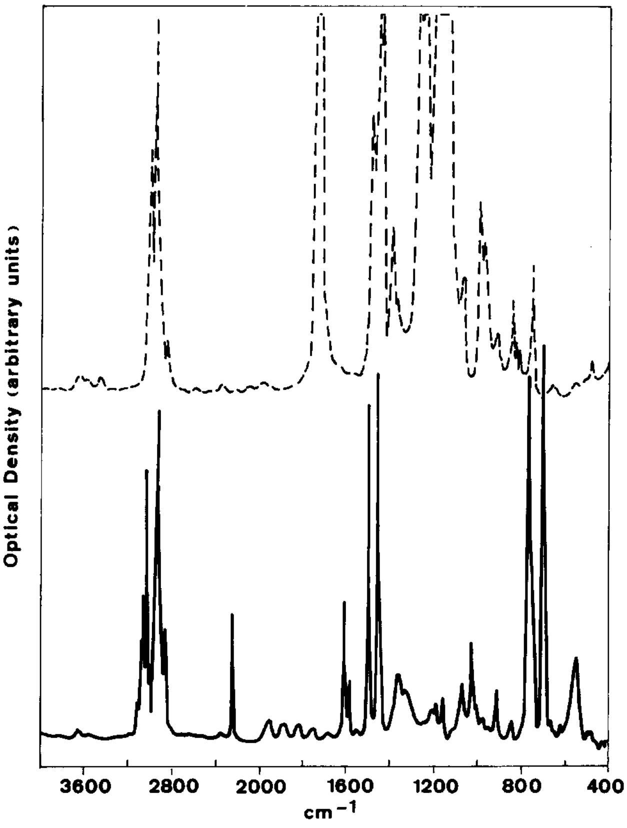

Figure 1 Infra-red spectra of PMMA (---) and SAN (——)

Table 2 Orientation function values obtained for different absorption bands in the SAN copolymer. Stretching temperature $T = T_g + 14$°C; strain rate = 0.026 s^{-1}; draw ratio, $\lambda = 3$

Absorption band (cm^{-1})	$\langle P_2(\cos\theta)\rangle$
2930	0.032 ± 0.006
2855	0.039 ± 0.009
1028	0.036 ± 0.006

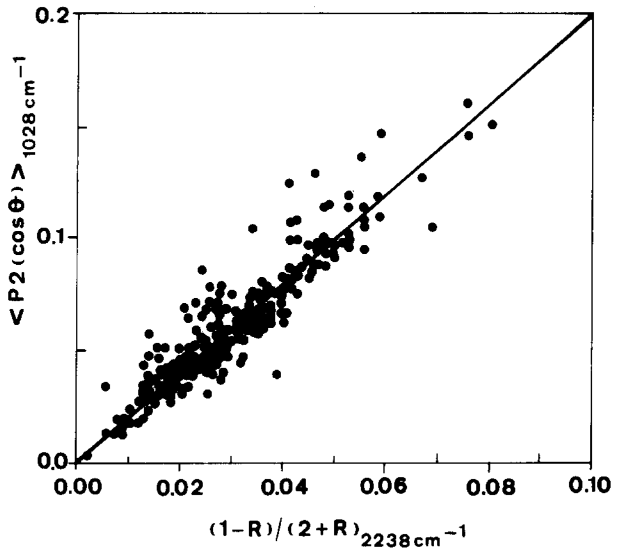

Figure 2 Plot for determination of the angle α of the C≡N 2238 cm^{-1} absorption band from $\langle P_2(\cos\theta)\rangle_{1028}$ (see equation (2))

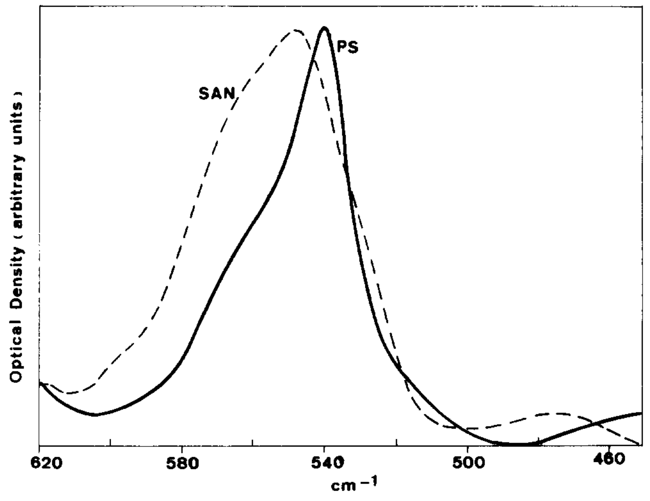

Figure 3 SAN and PS spectra in the out-of-plane ν_{16b} ring vibration region

On the other hand, for SAN, (see *Figure 3*), a shift towards the higher wavenumber range and a broadening of the absorption bands are observed in the 460–620 cm^{-1} region, which corresponds to the ν_{16b} out-of-plane mode of the styrene benzene ring. This mode, which is particularly sensitive to the conformational structure, is observed at 540 cm^{-1} when the benzene ring is linked to at least four aliphatic bonds in the *trans* conformation. A shift towards the higher wavenumber range is observed for the benzene rings when linked through *gauche–gauche* and *trans–gauche* conformations of the aliphatic chain[21]. The spectrum observed for SAN suggests that an increase in the amount of *gauche* conformational structures is induced by the presence of nitrile groups.

SAN orientation behaviour

A report of PMMA orientation behaviour has already been published[22] and it is therefore interesting to characterize the orientation achieved in SAN. The samples were stretched at different temperatures over the range from $T=T_g+3°C$ to $T=T_g+21°C$, and at two strain rates, namely 0.115 and 0.026 s^{-1}. From the different

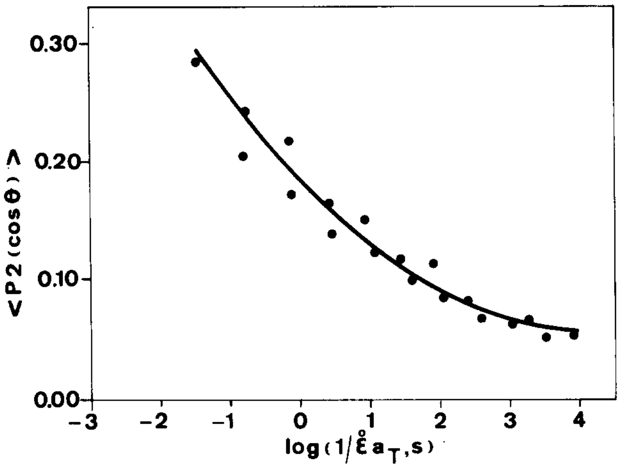

Figure 4 Master curve of orientation relaxation in SAN at a reference temperature $T=T_g+11°C$ and a draw ratio $\lambda=4$

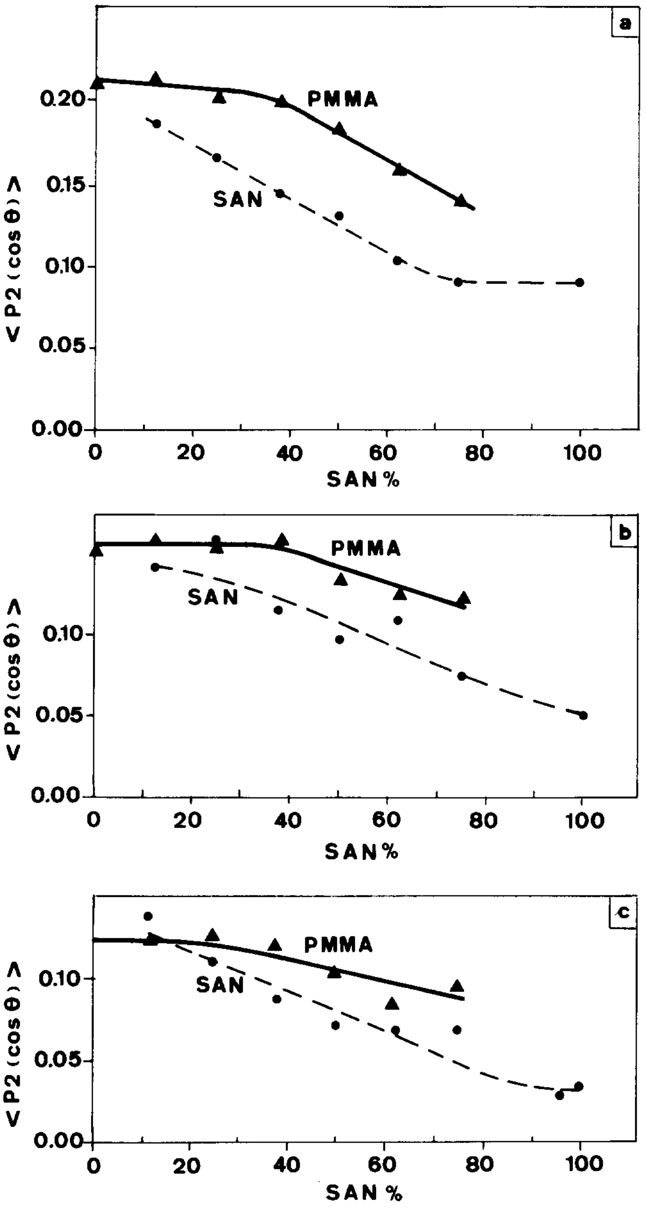

Figure 5 Orientation of PMMA and SAN in PMMA-SAN blends as a function of the SAN content, measured at a draw ratio $\lambda=4$, and a stretching temperature $T=T_g+14°C$. Strain rates: (a) 0.115; (b) 0.026 and; (c) 0.008 s^{-1}

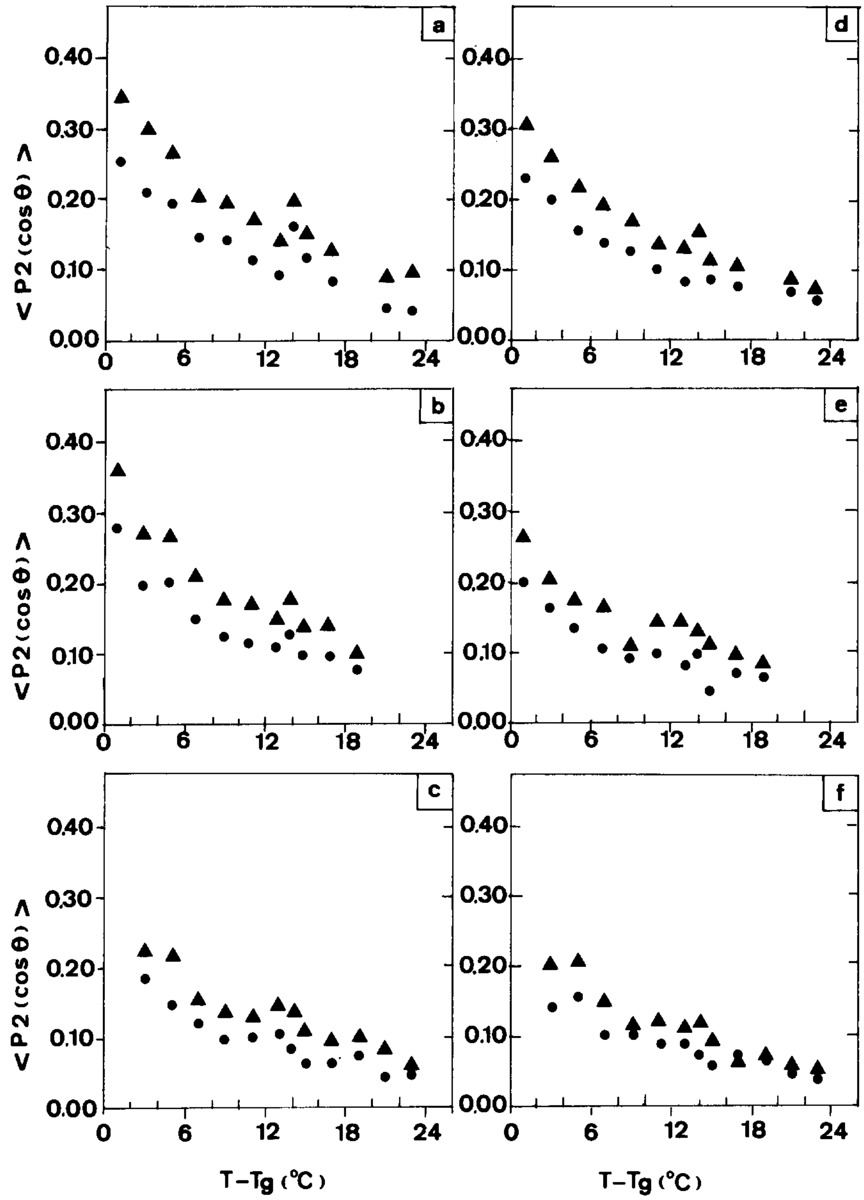

Figure 6 Influence of the stretching temperature and strain rate on the orientation of PMMA-SAN blends at a draw ratio $\lambda=4$; (▲) PMMA and; (●) SAN. Strain rate, 0.115 s^{-1}: (a) 25; (b) 50 and; (c) 75 wt% SAN. Strain rate, 0.026 s^{-1}: (d) 25; (e) 50 and; (f) 75 wt% SAN

results, using the Williams–Landel–Ferry (WLF) shift factor a_T measured by Wu[23], we obtained the orientation relaxation master curve given in *Figure 4*, for a reference temperature of $T=T_g+11$°C.

Orientation in PMMA-SAN blends

All of the samples were stretched at a temperature $T=T_g+14$°C and at three strain rates, namely 0.115, 0.026, and 0.008 s^{-1}. The results obtained for both blend components are presented in *Figure 5*.

The first point to note is that both polymers orient differently. As the SAN percentage in the blends increases, the PMMA orientation first remains almost constant and then decreases at a regular rate. Similarly, an increase in the PMMA concentration of the blend has no effect on the SAN orientation initially, but then the latter increases in a regular fashion. As expected, a decrease in the strain rate results in a decrease in the orientation.

The influence of the temperature of stretching on the orientation of both polymers is illustrated in *Figure 6* for three blends containing 25, 50, and 75 wt% SAN. The PMMA orientation always remains higher than the SAN orientation, whatever the temperature, with an increase in the stretching temperature resulting in a decrease in orientation.

The normalized orientation curves shown in *Figure 7* for the 25 wt% SAN blend show that the orientations of both of the blend components decrease in the same way when measured as a function of the stretching temperature. A similar behaviour was observed for all of the other blends that were studied.

Orientation relaxation in PMMA-SAN blends

Wu[23], in a rheological study of PMMA-SAN blends, has observed that a single WLF shift factor a_T was applicable for the blends, whatever the concentration, i.e.

$$\log a_T = -20.67(T-T_g)/(58.33+T-T_g) \qquad (3)$$

From the results obtained at different strain rates and different stretching temperatures, it is therefore possible to construct the orientation relaxation master curves for PMMA and SAN which are given in *Figure 8*.

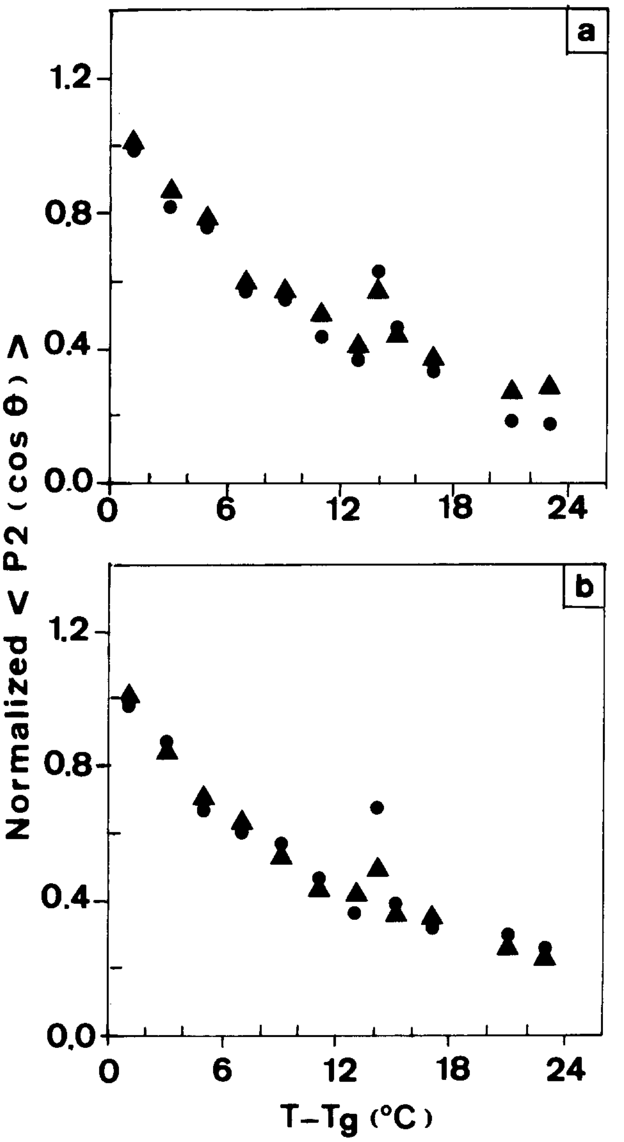

Figure 7 Normalized orientation function *versus* stretching temperature for the 25 wt% SAN blend at a draw ratio $\lambda=4$, measured for a strain rate of (a) 0.115 and (b) $0.026\,s^{-1}$: (▲) PMMA and; (●) SAN

DISCUSSION

These present results show that in PMMA-SAN blends stretched above the glass transition temperature both polymers orient differently, with PMMA always being more oriented than SAN. The change of orientation as a function of the concentration in the blends could be qualitatively explained by the change in molecular weight between the entanglements, M_e, as observed by Wu[23]. Thus, an increase in the amount of SAN, which induces an increase in M_e, also induces a 'fall-off' in the orientation of PMMA. However, it is interesting to note that the PMMA orientation remains almost constant up to 40 wt% SAN, while at the same time M_e increases from 9000 to $11\,700\,g\,mol^{-1}$, which makes the influence of M_e on orientation doubtful, at least on a large scale.

On the other hand, when considering orientation and relaxation phenomena, an important parameter is the monomeric friction coefficient ζ, which characterizes the resistance encountered by a monomer unit moving through its surroundings. The coefficient ζ can be determined from viscoelastic measurements on the melt. In PS and PMMA, chain orientation relaxations of both polymers stretched above T_g behave differently at a reference temperature $T=T_g+\text{constant}$, but are identical for the same ζ value[24].

In a compatible blend, an average friction coefficient ζ_r can be measured[25]. When the present results are compared at the same friction coefficient ζ_r, and by using the values given by Wu[25], one can obtain the two general master curves shown in *Figure 9*, which are representative of the orientation relaxation behaviour of PMMA and SAN in blends, whatever the concentration. This result

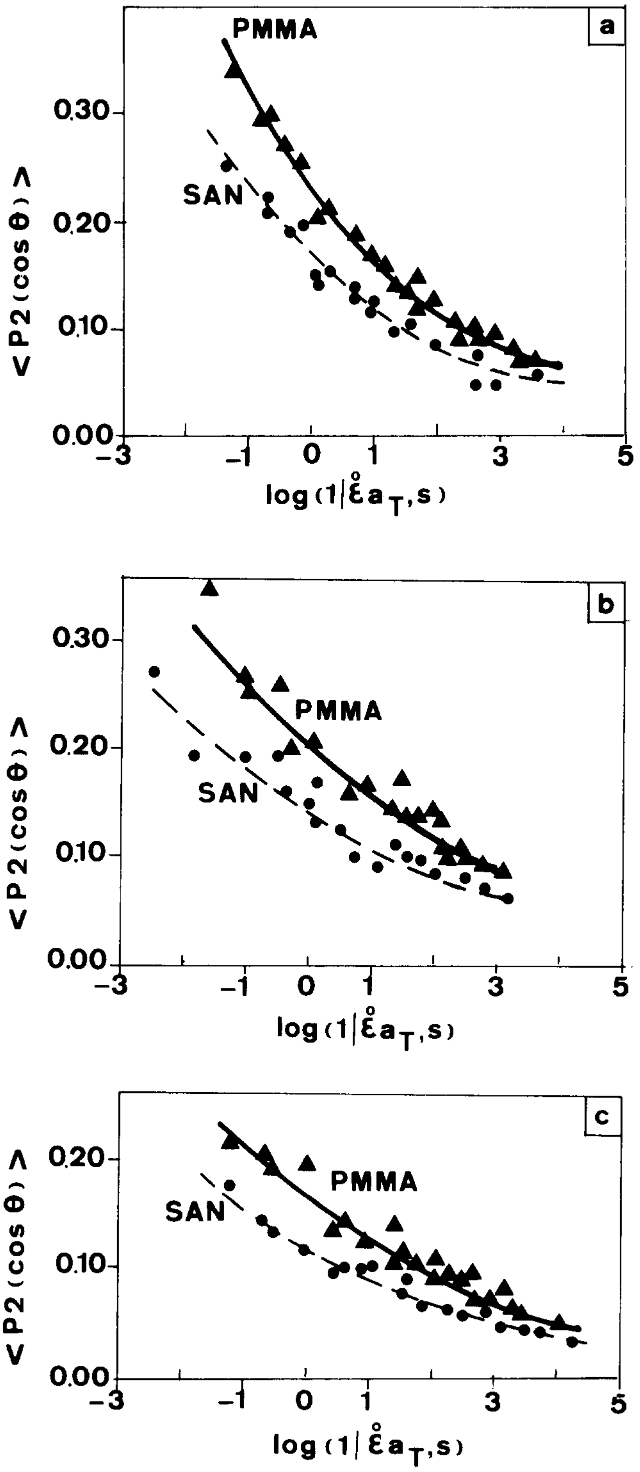

Figure 8 Orientation relaxation master curves of PMMA (▲) and SAN (●) in PMMA-SAN blends at a draw ratio $\lambda=4$, and a reference temperature $T=T_g+11°C$: (a) 25; (b) 50 and; (c) 75 wt% SAN

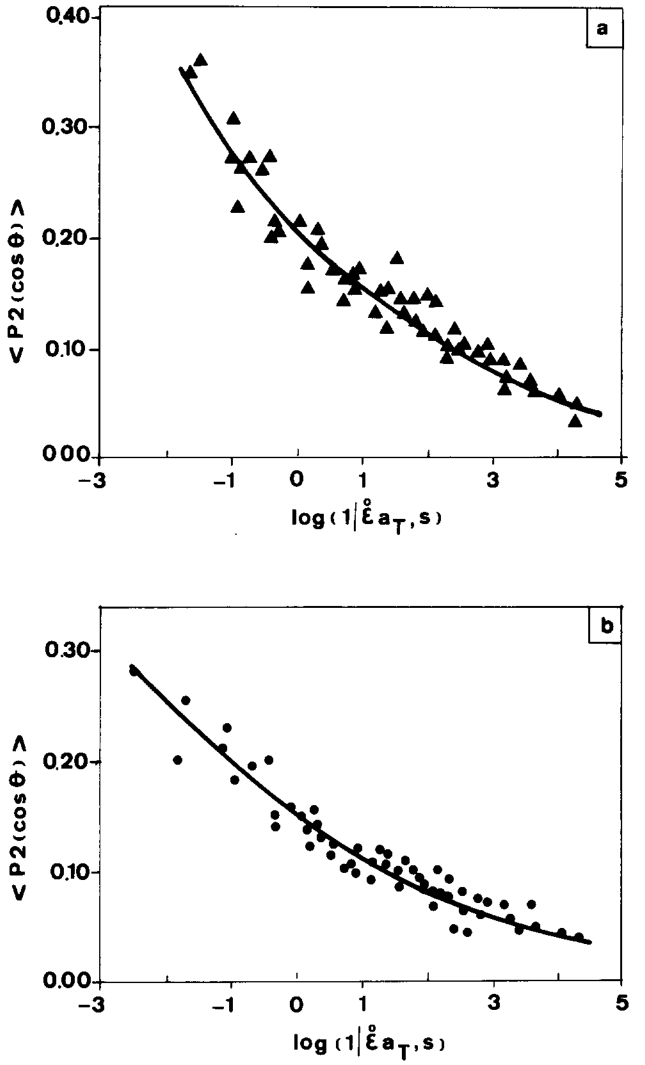

Figure 9 General orientation relaxation master curves of PMMA (a) and SAN (b) in PMMA-SAN blends at the same friction coefficient (ln ξ (N s m^{-1}) = 1.56) and a draw ratio $\lambda = 4$

emphasizes the importance of friction coefficients when considering the orientation and relaxation phenomena in compatible polymer blends.

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