Orientation and miscibility of poly(ε-caprolactone)/poly(styrene-*co*-acrylonitrile) mixtures

Wenguang Li and Robert E. Prud'homme*
Centre de recherche en sciences et ingénierie des macromolécules, Department of Chemistry, Laval University, Québec (Que), Canada G1K 7P4
(Received 25 April 1993; revised 20 December 1993)

The relationship between orientation and miscibility in polymer blends has been investigated for blends of poly(ε-caprolactone)/poly(styrene-*co*-acrylonitrile) (PCL/SAN), containing from 23 to 38 wt% acrylonitrile. The miscibility of the blends was characterized by d.s.c. whereas the strain-induced orientation of both PCL and SAN chains, in blends containing between 2% and 20% PCL, was measured by Fourier transform infra-red (*FT*i.r.) dichroism. PCL orientation was observed in miscible matrices but not in immiscible SAN matrices, indicating that the miscibility leads to the orientation, and the maintenance of orientation, of the minor chain component, despite the fact that flexible chains are involved. In contrast, the major component, SAN, exhibits a similar orientation in the different PCL/SAN systems, and is little influenced by the addition of PCL. The results are discussed in terms of miscibility, chain entanglements, friction coefficients and chain flexibility.

(Keywords: orientation; miscibility; polymer blends)

INTRODUCTION

The general objective of this study is to investigate the relationship between orientation and miscibility in polymer blends. Let us first consider the general situation of a blend composed of a polymer A matrix containing a small amount of polymer B, both polymers having chain lengths sufficient to enable self-entanglement in the bulk. Depending upon the miscibility between the two polymers, polymer B can form isolated phases within the A matrix (*Figure 1a*) or distribute uniformly as isolated chains in the A matrix (*Figure 1b*). These two morphologies correspond to immiscible and miscible states, respectively. Since the B chains in both cases cannot be stretched directly, their possible orientation is driven by their interactions with the surrounding A chains when the matrix is deformed. In the case of model 1a, as they do not exhibit any interchain interaction with the surrounding A matrix, the B chains are not likely to be oriented, whatever the deformation of the A matrix (we exclude here the case where the matrix contains dispersed particles of a large size where the transfer of stress across the interface between the matrix and the dispersed phase may result in deformation and breakup of the dispersed phases). However, in the case of model 1b, the B chains may exhibit some molecular orientation with the deformation of the A matrix due to the existence of interchain interactions such as chain entanglements and specific interactions, which are often found to be at the origin of miscible polymer blends. Therefore, the miscibility may lead to isolated chains to be oriented in polymer blends. It should be noted that *Figure 1a* is not intended to imply that the B phase is made of one chain only. In fact, most of them are probably made up of several chains because, otherwise, their crystallization would be impossible, which is contrary to observation. However, the number and size of these phases strongly depend on the concentration of the B component in the blend.

Several studies have been carried out on the orientation of miscible polymer blends[1-7]. For a blend with specific molecular interactions, it was found that the orientation of the major component, which is higher than in the pure state, always depends on the composition whereas the orientation of the minor component is indeterminate since it changes from blend to blend. The behaviour of the major component was attributed to a modification of the friction coefficient due to the specific molecular interactions leading to a hindrance to chain relaxation[3,5-7]. Recently, Zhao *et al.*[8] proposed how chain entanglements, in addition to specific molecular interactions, may play an important role in the orientation behaviour of miscible polymer blends.

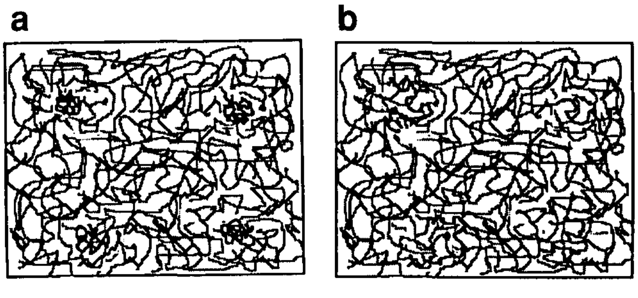

Figure 1 Schematic distribution of a small amount of polymer B in a polymer A matrix: (a) in the immiscible state; (b) in the miscible state

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* To whom correspondence should be addressed

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In immiscible polymer blends, it was found that the component of the continuous phase always orients to a higher degree than the component in the dispersed phase[9]. Several authors[10–12] also looked at immiscible systems induced by phase separation. Hsu *et al.*[10,11] compared the orientation of miscible and immiscible poly(vinyl methyl ether)/polystyrene (PVME/PS) blends. They found that the PS chains have a higher orientation in the miscible state than in the immiscible mixture, which was explained as being due to a greater interconnectivity of the chains in the former case. Abtal and Prud'homme[12] have also studied the orientation and phase separation of PVME/PS blends and found that, at a fixed stretching temperature, the magnitude of the PS chain orientation in immiscible blends is greater than that in the original blends, which is contrary to the results of the Hsu *et al.* but is in agreement with mechanical properties observed for the same system by Kim *et al.*[13], who reported that the tensile modulus and strength increase as phase separation occurs.

In order to clarify this behaviour, we looked for systems where the miscibility and phase behaviour could be easily controlled. For this purpose, poly(ε-caprolactone)/poly(styrene-*co*-acrylonitrile) (PCL/SAN) blends were selected. This system has several advantages. First, PCL is miscible with SAN copolymers within a certain range of acrylonitrile (AN) content[14,15]; thus, miscible and immiscible mixtures could be prepared at will simply by changing the AN content in the SAN copolymers. Second, the PCL/SAN blends exhibit a lower critical solution temperature (*LCST*)[14] and, therefore, immiscible systems could also be prepared by controlling the thermal history. Third, this system gives the opportunity to study the orientation behaviour of a system which exhibits repulsive interactions between styrene and AN[15]. Finally, both PCL and SAN possess characteristic absorption bands in their i.r. spectrum, which enable the chain orientation of each blend component to be measured.

In this study, three SAN copolymers, which contain 23, 28, and 38 wt% AN units, were mixed with PCL to make up two miscible systems, but with different levels of miscibility, as well as an immiscible system. The miscibility of the blends was characterized by d.s.c. Strain-induced orientation of both PCL and SAN chains in blends containing between 2% and 20% PCL was measured by Fourier transform infra-red (*FT*i.r.) dichroism. It will be shown, on the one hand, that the minor component of the immiscible blend does not orient and, on the other hand, that the orientation behaviour of both components in the miscible blends is determined by interchain interactions as well as chain flexibility.

EXPERIMENTAL

Sample preparation

The characteristics of the polymers used are given in *Table 1*. The weight-average molecular weight and polydispersity were determined by size exclusion chromatography relative to PS standards. The AN content of the SAN copolymers was determined by elementary analysis. PCL is semicrystalline and has a melting point (T_m) of 59.4°C whereas the SAN copolymers are amorphous.

Films for miscibility measurements were prepared by solvent casting from a 5% methyl ethyl ketone solution onto glass plates. After evaporation of the solvent at 45–55°C, the films were dried under vacuum at 65°C for 1 week. This procedure gives glass transition temperature (T_g) values for the different SANs which were 2 or 3°C below those of the initial pellets. However, for i.r. measurements, the films ($\sim 40\,\mu$m thick) were further annealed under vacuum at 120°C for 2 days.

Molecular orientation was induced by uniaxial extension at $T_g + 10$°C. The films (20 mm long, 6 mm wide) were stretched with an apparatus, constructed in our laboratory, that allows exponential deformation at a constant strain rate and a controlled temperature (± 0.5°C). A high draw rate of $0.115\,\mathrm{s}^{-1}$ was used in order to minimize possible chain relaxation during stretching.

For measurements of orientation as a function of the draw ratio λ (where λ is defined as $\lambda = l/l_0$, l_0 and l being the sample length before and after stretching, respectively), the sample was quenched to room temperature immediately after stretching, in order to retain the molecular orientation. The local macroscopic deformation was measured from small successive equidistant ink lines printed on the sample before stretching. This ensured that the i.r. measurements were taken at the desired λ for each example.

Immiscible mixtures were also prepared by holding PCL/SAN30 mixtures (10/90 v/v) at a constant temperature below and above the phase separation temperature (T_c), for a fixed period of 10 min; they were then quenched to room temperature, and stretched, by the method described above, to a λ of 2 at 100°C.

Orientation measurements

The second moment of the orientation distribution function, or Hermans' orientation function, $\langle P_2(\cos\theta)\rangle$, hereafter referred to as P_2, is obtained from i.r. dichroism through the relation:

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

where θ is the angle between the chain axis and the stretching direction, $R_0 = 2\cot^2\alpha$, where α is the angle between the transition moment vector of the vibration under consideration and the chain axis, and R is the i.r. dichroic ratio defined as $R = A_{\parallel}/A_{\perp}$, where $A_{\parallel}$ and $A_{\perp}$ are the measured absorbances parallel and perpendicular to the stretching direction, respectively.

The orientation function of SAN can be measured from the absorption band at $2238\,\mathrm{cm}^{-1}$. This band is attributed to the ν_{CN} stretching mode and it does not overlap with any absorption band of PCL, as shown in *Figure 2*.

Table 1 Polymers used

Polymer	Acronym	AN (wt%)	M_w ($\times 10^{-3}$)	M_w/M_n	T_g (°C)
Poly(styrene-*co*-acrylonitrile)	SAN25	23.4	258	1.81	110
	SAN30	28.3	313	1.89	111
	SAN40	38.2	177	1.87	114
Poly(ε-caprolactone)	PCL	–	56	1.74	−65

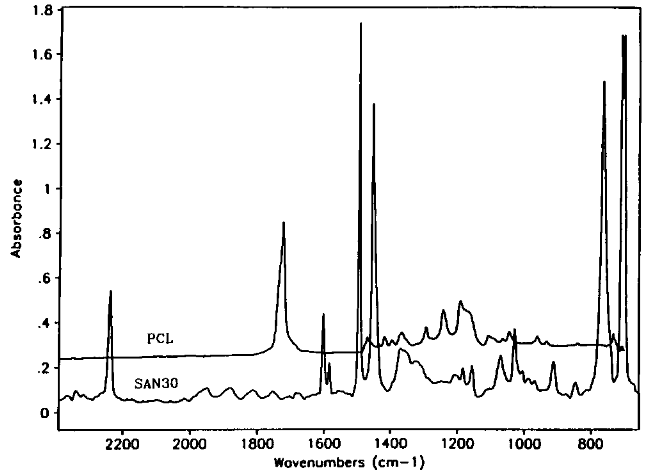

Figure 2 I.r. spectra of pure PCL and SAN30

The transition angle α between the CN moment vector and the chain axis was taken as 61.7° by Wang and Cooper[16] and 90° by Read and Stein[17], but 70.1° (average value) is found in the reference[18] cited by these two groups. Since, for a random AB copolymer, the average orientation of segments A and B is necessarily the same[19], we have used i.r. measurements of several SAN copolymers containing between 9% and 38% AN to determine the CN transition angle. A value of 90° was found[20] and used in our calculation.

For PCL, the orientation function can be measured from the absorption band at 1730 cm^{-1}, which is known to correspond to the symmetrical C=O stretching mode with a transition angle α of 78°[21]. This band, as shown in *Figure 2*, overlaps with the very weak absorption band of SAN at 1750 cm^{-1}, which is a combination of two out-of-plane ring modes[22]. The effect of this band, considered to have little significance, was neglected. For blends containing $\leqslant 10\%$ PCL, the absorbance value of the C=O band is below unity, and thus deviations from the Lambert-Beer law are avoided.

The polarized i.r. spectra were recorded with a Mattson Sirius 100 *FT*i.r. spectrometer, at a resolution of 4 cm^{-1}, from a total of 100 interferograms. The i.r. beam was polarized using a wire-grid polarizer with the sample rotated 90° in order to obtain the two polarization measurements. I.r. dichroism was calculated from the peak height intensity measured in absorbance when there was no shift of the bands in the two polarization measurements; otherwise, the integrated intensity was used. Each orientation value determined is an average of at least three measurements, taken of different areas of the stretched sample.

Intermolecular interactions in PCL/SAN blends were also investigated with a Bomem DA3.02 *FT*i.r. spectrometer equipped with a temperature controlled sample mount, at a resolution of 2 cm^{-1}. Dried films (~40 μm thick) containing 2% PCL in the SAN matrix (with AN contents from 0 to 38% in the SAN copolymers) were inserted between two KBr plates as a sandwich. The measurements were performed with 100 scans, at 65±0.2°C, which further ensures that the PCL chains remain amorphous in all SAN matrices. The position and width of the C=O band were analysed using a Spectra-Calc program and the centre of gravity of the C=O band (half-weight band position) rather than the band maximum is reported due to band broadening.

Miscibility measurements

The T_g and T_c values were used to characterize the miscibility of blends. The T_gs of the dried films were determined with a Perkin-Elmer DSC-4 apparatus, calibrated with indium. A heating rate of 20°C min^{-1} and a cooling rate of 320°C min^{-1} were used. The samples were first annealed for 5 min at a predetermined temperature (usually above the melting point of PCL but below the T_c of blends), quenched to −100°C, and then heated to measure the T_g of the sample. For phase separation measurements, the above procedure was repeated with successive increases in the annealing temperature until the observation of phase separation. Details of the method are given in reference 23.

RESULTS

Miscibility of PCL/SAN blends

The T_gs of PCL/SAN blends are shown in *Figure 3* as a function of blend composition. The occurrence of a single T_g with PCL/SAN25 and PCL/SAN30 blends indicates that the PCL is miscible with SAN25 and SAN30 whereas, for PCL/SAN40 blends, the presence of two T_gs, which are almost identical to those of the two pure components, clearly shows that the PCL is immiscible with SAN40.

It is difficult to distinguish between the two PCL/SAN miscible blends since their T_gs are identical, within experimental error. However, it is observed that the T_cs of PCL/SAN30 blends, which depend upon the blend composition, are as low as 65–130°C, whereas the T_cs of PCL/SAN25 mixtures are of the order of 230°C and, in fact, approach the thermal decomposition of the samples (using light scattering to measure cloud points, we found, at a heating rate of 1°C min^{-1}, that the samples gradually become yellow above 210°C, before phase separation). Therefore, this suggests that, despite the similarity in the T_gs of PCL/SAN25 and PCL/SAN30 blends, the level of miscibility in these two systems is different, as indicated by the differences in T_c, which is in agreement with the more negative interaction parameter B found for PCL/SAN25 blends as compared to PCL/SAN30 blends[15].

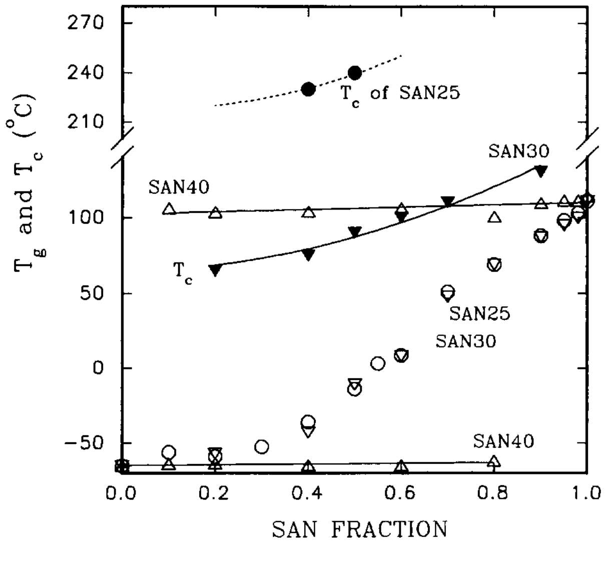

Figure 3 Phase diagram of PCL/SAN blends. T_gs of PCL/SAN25 (○), PCL/SAN30 (▽) and PCL/SAN40 (△). T_cs of PCL/SAN25 (●) and PCL/SAN30 ▼)

PCL orientation in PCL/SAN blends

First, it is necessary to describe the crystallization behaviour of the PCL in PCL/SAN mixtures in order to determine the orientation conditions of the samples. It was found that the PCL crystallization in the miscible blends depends upon its concentration, paralleling the behaviour of other PCL miscible blends[24–26]. The limiting concentration for PCL crystallization is 20% and, therefore, orientation measurements were limited to compositions containing between 0% and 20% of PCL where crystallization is avoided. However, in immiscible PCL/SAN blends, PCL crystallizes at room temperature even at concentrations as low as 2%. [For instance, concentrations of 2 and 10% PCL in PCL/SAN40 blends lead to enthalpies of fusion of 10.5 and 15.1 cal g^{-1}, respectively, values which are smaller than that found in bulk PCL (19.7 cal g^{-1}).]* Therefore, PCL chains inside the SAN matrix can crystallize before and after the deformation of the matrix, when the samples are kept at room temperature.

The orientation function of PCL in two miscible SAN matrices is shown in *Figure 4*. It is seen that it increases linearly with λ, reaching small values of the order of 0.05 even though the samples were stretched to a high λ (= 3.5) at a high draw rate (0.115 s^{-1}). Despite these small values, it is clear that the PCL chains do orient in the SAN matrix. It can also be observed from *Figure 4* that, within the range of compositions investigated, the magnitude of PCL chain orientation does not depend upon the blend composition in these two miscible systems.

In contrast, in immiscible blends, as shown in *Figure 4*, the orientation function of PCL chains is always close to zero, for all λ values and blend compositions investigated.

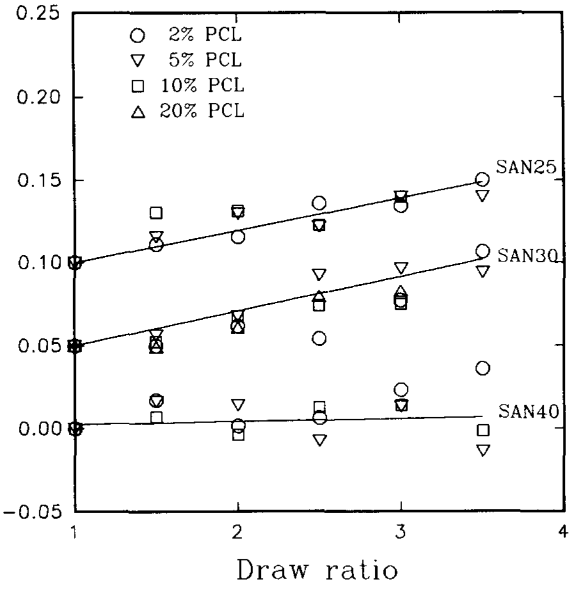

Figure 4 Orientation function of PCL as a function of draw ratio for PCL/SAN blends at different PCL concentrations. For clarity, the orientation function of PCL/SAN25 and PCL/SAN30 was shifted by 0.10 and 0.05 units, respectively

SAN orientation in PCL/SAN blends

Let us consider, as a point of reference, the SAN orientation in the bulk. It was found, under the stretching conditions used ($T - T_g = 10°C$, strain rate 0.115 s^{-1}), that the different SAN matrices (in pure form) exhibit the same orientation behaviour with λ, whatever the AN content in the SAN copolymer. As an example, *Figure 5* gives the orientation of SAN40.

Figure 5 also shows the orientation function of different SAN matrices in PCL/SAN blends. It is first observed that the orientation function of the SAN30 matrix, in blends containing between 2% and 20% PCL, increases linearly with λ, but each set of data (with 2, 10 and 20% PCL) is identical, within experimental error. It is also identical to the orientation of SAN in the pure SAN matrix (shown for the SAN40 matrix only). The same behaviour is found for the SAN25 orientation in blends containing 2 and 10% PCL, as shown in *Figure 5*. However, in PCL/SAN40 immiscible blends, the SAN orientation gradually decreases with an increase of the PCL concentration in the blend, for a given elongation (*Figure 5*).

Finally, the orientation function of SAN30 in blends containing 10% PCL is given in *Figure 6* as a function of temperature, for samples annealed before stretching. It can be observed that the SAN orientation function is essentially constant for all samples annealed below 125°C (before phase separation), but increases slightly with an increase of the annealing temperature (after phase separation). It is then obvious that the phase separation of the blend results in changes in the SAN orientation behaviour.

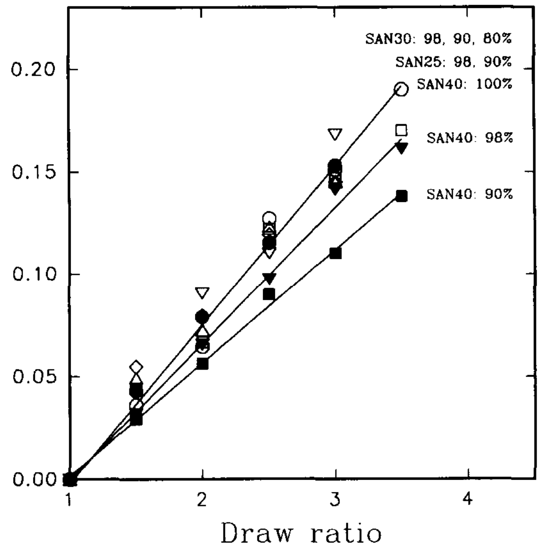

Figure 5 Orientation function of SAN as a function of draw ratio for different PCL/SAN blends at SAN concentrations: SAN30: 98 (○), 90 (▽) and 80% (△); SAN25: 98 (□) and 90% (◇); and SAN40: 100 (●), 98 (▼) and 90% (■)

DISCUSSION

With reference to *Figure 1*, the presence of specific intermolecular interactions and interchain entanglements provides the possibility for isolated chains to be oriented in miscible blends when the matrix is deformed. In contrast, isolated chains or small aggregates of chains in immiscible mixtures are not expected to orient due to the absence of interactions with the surrounding matrix. The results presented in *Figure 4* agree with this model: that is, PCL orientation is observed in the miscible PCL/SAN25 and PCL/SAN30 blends, whereas no orientation

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* 1 cal = 4.19 J

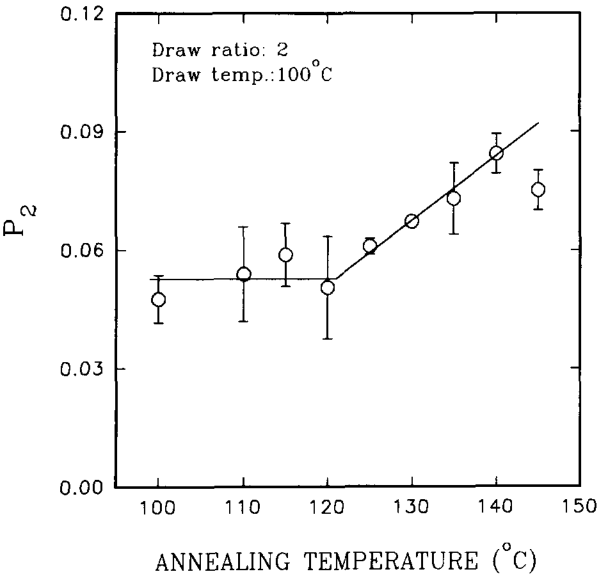

Figure 6 Orientation function of SAN in PCL/SAN30 blends containing 10% PCL as a function of annealing temperature. The annealed samples were drawn to a draw ratio of 2 at 100°C

could be detected in the immiscible PCL/SAN40 blends whatever the deformation of the matrix. It should be noted that the absence of orientation of PCL chains may also be due to their fast relaxation rate, after orientation, since the stretched samples are stored and measured at room temperature which is far above the T_g (−65°C) of PCL. Nevertheless, the results suggest that the miscibility between the two polymers leads to the orientation and maintenance of orientation of isolated chains in polymer blends, under the conditions used.

With this model in mind, it is speculated that the magnitude of the orientation of blend components is related to the strength of interchain interactions in the miscible blends. Indeed, it was proposed that the relaxation of chain orientation during stretching is hindered by the interactions, which modify the friction coefficient and lead to an increase in orientation of the components[3–5]. In miscible systems, the strength of interactions is usually characterized by negative values of the Flory–Huggins parameter χ. The more negative the parameter χ, the stronger is the interchain interaction. On the basis of this hypothesis, Faivre *et al.*[4] have compared the increase in orientation of the major component of three miscible PS-based blends, where $\chi = -1$ in poly(phenylene oxide) (PPO)/PS blends, $0 < \chi < -0.4$ in PVME/PS blends, and $\chi = 0$ in poly(*o*-chlorostyrene)/PS. They found that PPO is more effective than PVME in increasing the PS orientation, whereas poly(*o*-chlorostyrene) has almost no influence on PS orientation.

For the PCL/SAN mixtures, the interaction parameter B ($B = \chi RT/V_r$, where R is the gas constant, T the absolute temperature and V_r the molar volume of the statistical lattice units) was determined by the analysis of the melting point depression of PCL in blends, and was also calculated by using the mean field theory considering intrachain repulsive interactions in the system[15]. For comparison purposes, the orientation function of SAN25, SAN30 and SAN40 is shown in *Figure 7* as a function of the parameter B. For the two miscible blends, *Figure 7* gives the average value of the orientation function found at different blend compositions because the SAN orientation is composition independent (*Figure 5*). For the immiscible systems, as the SAN orientation function changes with concentration, the error bar for each elongation is used to indicate the range of values obtained. *Figure 7* shows that the SAN orientation is insensitive to the strength of interaction in the PCL/SAN system. The same conclusion can also be reached for the PCL orientation among PCL/SAN blends.

For immiscible blends, the decrease of the SAN orientation cannot be attributed to the change of the interaction parameter B since the semicrystalline PCL phase exhibits few, if any, interchain interactions with the SAN matrix. Thus, the orientation of SAN should not differ from that in the bulk, at the same stretching temperature. However, the relaxation of the oriented SAN matrix can be influenced by the crystallization of isolated PCL phases, which are liquid at the time of stretching and then gradually become semicrystalline after quenching to room temperature. The crystallization process can ease the surrounding stress applied to isolated PCL phases and, in turn, result in the relaxation of SAN chains near the interface. It is obvious that the larger the number of PCL domains in the SAN matrix, the greater the effect will be. This hypothesis is consistent with the results shown in *Figure 5*. Such a behaviour was also found in poly(methyl methacrylate)/poly(ethylene oxide) (PMMA/PEO) blends[6]. When the PEO is able to crystallize in the blend due to microphase separation, the orientation of PMMA chains decreases with PEO concentration.

In contrast, immiscible blends prepared by thermal phase separation above T_c of PCL/SAN30 blends containing 10% PCL result in a slight increase of SAN orientation, as shown in *Figure 6*. After phase separation, one PCL-rich phase appears while the original phase becomes richer in SAN, this tendency increasing with the annealing temperature. This process results in an increase of the T_g for the major phase of the blend (the SAN-rich phase). As the stretching experiment was carried out at a fixed temperature of 100°C, the demixed sample was in fact stretched at a temperature with a smaller $T - T_g$

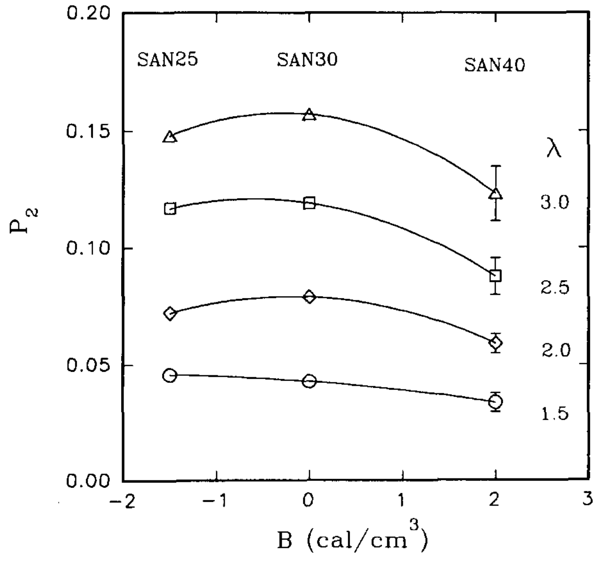

Figure 7 Orientation function of SAN as a function of the interaction parameter B for PCL/SAN blends at various draw ratios. The B values used are the experimental data determined by the melting point depression method[15]

difference compared to the miscible blend. The strong dependence of orientation on the stretching temperature results in an increase of the SAN orientation compared to the orientation observed before phase separation. This result is in agreement with that observed by Abtal and Prud'homme[12] for PVME/PS blends.

It was shown in *Figure 7* that the orientation of SAN and PCL does not change significantly with the strength of interaction. However, weak interactions must be present in PCL/SAN mixtures because distinct differences in phase separation temperatures (*Figure 3*) are observed between PCL/SAN25 and PCL/SAN30 blends. In order to characterize the specific intermolecular interactions in PCL/SAN blends, *FT*i.r. measurements have been carried out. It is known that the position and width of the C=O vibration band of PCL is sensitive to changes of its environment.

Figure 8 shows the centre of gravity of the C=O band in blends containing 2% PCL as a function of AN content. It is observed, except in a PS matrix (0% AN), that the C=O band in all SAN matrices (with 9–38% AN units) shifts to lower wavenumbers as compared to its position in the bulk (dashed line). The maximum shift of the C=O band occurs in the SAN matrix containing ~28% units, which is the highest AN content in SANs which form miscible mixtures with PCL. The shift of the C=O band in PCL/SAN systems may be due to the weak hydrogen bonding between C=O and α-hydrogen groups[27]. With an increase of AN units in SAN, the number of α-hydrogens increases, with the formation of a larger number of hydrogen bonds, which in turn results in a larger shift of the C=O band. However, this interaction cannot be considered as the cause of miscibility in PCL/SAN blends. First, the C=O band also shifts in immiscible SAN matrices (see the right-hand side of *Figure 8*); second, the minimum in position of the C=O band does not correspond to the composition where the miscibility is greatest (15–20% AN)[14,15]. It is thus concluded that the miscibility of PCL/SAN mixtures does not originate from the presence of specific interactions. It may be due to a combination of inter- and intrachain interactions suggesting, as predicted by the mean field theory[15], that the repulsive forces in dissimilar segments of the SAN copolymer play an important role in the miscibility of the system.

In order to explain the orientation behaviour of PCL/SAN blend components, the influence of chain entanglements must also be considered. It was proposed that, in amorphous polymers, chain entanglements can be considered as temporary networks, similar to crosslinked networks found in amorphous rubbers[28] where the molecular orientation is inversely proportional to the number of segments between two crosslink points[29–31]: the higher the crosslink density, the higher the molecular orientation induced by stretching. In the case of amorphous polymers, as the entanglement points are temporary and changeable, the average spacing between entanglements is an important molecular parameter influencing the orientation in the polymers. On the basis of this hypothesis, Zhao *et al.*[8] have suggested that, if two components in the bulk have very distinct entanglement spacings, entanglements with similar and dissimilar chains influence the orientation behaviour of the components differently: the orientation of a miscible component is composition-dependent when its entanglement spacing is influenced by entanglements both with similar and dissimilar chains; the orientation is composition-independent when its entanglement spacing is controlled by entanglements with the dissimilar chains only.

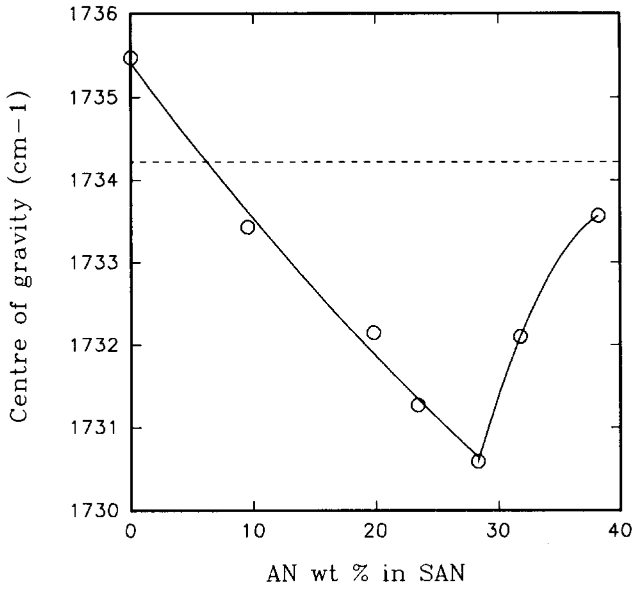

Figure 8 Position of the C=O band as a function of the AN content in SAN copolymers, for PCL/SAN blends containing 2% PCL

Table 2 Summary of chain parameters and entanglement data

Polymer	C_∞	M_e
Polystyrene	10.8	18 700
Poly(styrene-*co*-acrylonitrile) (SAN24)	10.6	11 500
SAN25 (23.4% AN)	–	11 680[a]
SAN30 (28.3% AN)	–	10 210[a]
Poly(ε-caprolactone)	5.9	1 160

[a] Values interpolated as indicated in the text

At first sight, the orientation behaviour of both SAN and PCL in PCL/SAN blends can be explained with this model since it does not change with the level of miscibility. As shown in *Table 2*, the PCL in bulk exhibits a molecular weight between entanglements (M_e) of 1160 (calculated from the PCL characteristic ratio C_∞ of 5.9[32] according to the relation between M_e and C_∞ proposed in the literature[33]), a value which is small as compared with that of a SAN containing 24% AN units, whose M_e is ~11 500[33]. For comparison, the M_e value of PS in the bulk (~18 700[33]) is also listed in *Table 2*. As the M_es between PS and SAN are not very different, to a first approximation, a linear relationship can be used to calculate the M_e of SANs with different AN contents; this leads to M_es of 11 680 and 10 210 for SAN25 and SAN30, respectively (*Table 2*). Thus, SAN (or PCL) in the two miscible PCL/SAN25 and PCL/SAN30 blends has a similar density of chain entanglements, in agreement with the similar orientation behaviour of SAN (or PCL) in PCL/SAN blends despite different levels of miscibility*.

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* This study deals mainly with blends containing a small amount of PCL (⩽10%). The chain entanglements of the blends, which are usually determined by viscoelastic measurements, are not considered because the individual chain entanglements in the blends play a more important role for determining the orientation of blend components

Furthermore, for a miscible system, it is expected from the entanglement model that the orientation of SAN (the major component in the blend) should be composition-dependent since the PCL and SAN chains have very distinct M_e values and its entanglement spacing should be influenced by entanglements both with SAN and with PCL chains. In comparison, the orientation of PCL should be composition-independent since the PCL concentration is so low that its chains entangle primarily with the surrounding SAN chains. Indeed, *Figure 4* shows that the orientation of PCL chains in the SAN matrix is indeed composition-independent in agreement with the entanglement model (this observation is possible despite the low orientation functions measured). However, the results in *Figure 5* disagree with the above prediction for SAN orientation since, within experimental error, the orientation of SAN chains in PCL/SAN blends is little influenced by the addition of PCL chains and, thus, apparently composition-independent. Therefore, it appears that the orientation of the SAN (or PCL) chains may not only be governed by interchain entanglement interactions, but also by other parameters.

In order to explain our results, we have considered the influence of friction coefficients on the orientation behaviour in blends, since Zhao *et al.*[34] have recently shown that the orientation of pure PS and pure PMMA is the same for a similar value of the friction coefficient. For PCL/SAN mixtures, it was reported[35] that the segmental friction coefficient of SAN decreases with the addition of PCL, in accordance with the additivity of free volume. Therefore, it can be assumed that, under a normalized stretching temperature (i.e. $T_g + 10°C$), the orientation and relaxation of SAN chains during stretching should not be hindered by the addition of PCL and that the friction coefficient of SAN should not be modified. Thus, the orientation of SAN chains should be the same as that in the bulk, which is in agreement with the results observed in this paper (*Figure 5*, SAN25 and SAN30).

Finally, we have to comment about the low orientation of PCL chains in SAN matrices. As compared to SAN (*Figure 5*), the PCL chains in SAN matrices (*Figure 4*) exhibit a very low, concentration-independent orientation in spite of high elongation and draw rates. Similar behaviour can be found for PVME in PVME/PS blends[3] and for PEO in PMMA/PEO blends[6]. In those cases, the low orientation of the minor component was attributed to its very short relaxation time as compared to the time frame of the experiment, which is reasonable since, under the stretching conditions used, PVME or PEO are kept at a temperature much above their T_g. However, if the minor component is kept at a temperature lower than its T_g, a high orientation function is expected, in agreement with the observation of isolated PPO chains in several matrices including PS, a PS copolymer and corresponding ionomer[8]. This means that chain flexibility is also an important factor influencing the orientation behaviour, especially in blends without strong interchain interactions. Interchain interactions in miscible blends should tend to restrict chain motions and result in more or less co-operative motions. However, such an effect depends upon blend composition and temperature, which in turn make it possible for the chains to exhibit their own flexibility. Thus, the orientation behaviour in blends is influenced by a combination of the interactions and chain flexibility. The influence of the latter factor in blends has been observed by other techniques[36,37]. Le Menestrel *et al.*[37] have shown by solid-state n.m.r. spectroscopy that the local chain motions of PVME and PS do not have the same frequency and temperature dependencies in PVME/PS blends. Similarly, Zawada *et al.*[38] have shown, using a new rheo-optical technique, that PEO and PMMA maintain distinct relaxation times in PEO/PMMA blends. All these findings strongly support the fact that the two components of miscible blends usually exhibit different orientation functions and relaxation times.

CONCLUSIONS

In the search for a relationship between orientation and miscibility in polymer blends, we selected a model system where the orientation of the minor component depends only upon its miscibility with the matrix, i.e. in PCL/SAN blends the miscibility can be controlled by changes of the composition of the SAN copolymer. Isolated PCL chains were observed to be oriented in miscible SAN matrices, whereas they exhibit no orientation in immiscible SAN matrices. From this result, we conclude that miscibility leads to the orientation and maintenance of orientation of isolated chains in blends.

The orientation behaviour of the major component of a blend is usually influenced by intermolecular interactions[3–5]. However, it was found that SAN exhibits a similar orientation in different PCL/SAN mixtures, and is little influenced by the addition of PCL, indicating that the intermolecular interactions in the PCL/SAN blends are not a major factor controlling the orientation behaviour. For immiscible blends induced by varying the temperature of phase separation, it was also observed that SAN exhibits a higher degree of orientation as compared to that in the original blends, at a given stretching temperature. This behaviour can be rationalized in terms of differences between the stretching temperature and the T_g of the major phase in the blend during the process of phase separation.

Finally, it can be concluded that the magnitude of orientation of the components in miscible blends is not only determined by the strength of interaction, but also by chain flexibility, especially for a component which is kept well above its T_g.

ACKNOWLEDGEMENTS

We are grateful to Drs Anna M. Ritcey and C. Geraldine Bazuin for reading critically the manuscript, and to Dr Yue Zhao for useful discussions. Financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Fonds pour la formation de chercheurs et Aide à la recherche (FCAR (Québec)) is acknowledged.

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