

Molecular orientation in crystalline miscible blends

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Abstract

The orientation induced by stretching uniaxially in the solid state two semi-crystalline miscible blends of poly(ϵ -caprolactone) (PCL) with poly(vinyl chloride) (PVC) and poly(styrene-*co*-acrylonitrile) (SAN) was investigated by infrared dichroism. In both cases, the deformation of the solution-cast films, having a high PCL crystallinity degree of about 50% and containing up to about 40 wt% of PVC or SAN, leads rapidly to a very high segmental orientation for the crystalline PCL as a result of a structural transformation from lamellae to microfibrils. Meanwhile, the amorphous components, being miscible and located in the interlamellar regions inside the spherulites, show a much lower orientation as compared with the crystalline PCL regardless of the blend composition. SAN is found to orient to the same degree as the amorphous PCL in the PCL/SAN blends, while the orientation of PVC is higher than that of the amorphous PCL in the PCL/PVC blends. Furthermore, the slow crystallization of PCL in blends containing around 40% of PVC made it possible to follow the orientation behaviour as a function of the crystallization time by stretching a series of films before and after the crystallization of PCL started. It was found that, even with as little crystalline PCL as 5% of the total blend weight, the stretching-induced crystalline orientation is almost as high as for the samples with high degrees of crystallinity. A stretching-induced crystallization forming microfibril-like crystallites of PCL is suggested to be at the origin of the high crystalline orientation for those blends, which have a dominant proportion of amorphous components during the stretching, instead of the transformation of existing lamellae to the microfibrillar structure for stretched highly crystalline blends. © 1998 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Among the large number of studies dedicated to polymer blends, the molecular orientation induced by uniaxial stretching has been investigated for miscible and amorphous systems by means of the infrared dichroism technique [1–3]. It is now well-known that the two polymer components in such a system can orient differently despite their miscibility, as reflected by a single composition-dependent glass transition temperature, T_g . The orientation behaviour of the components can also be different from that of the individual polymers when compared at the same stretching temperature T normalized to the T_g , i.e. same $T - T_g$ [2–4]. Those observations were mainly interpreted in terms of the chain orientation induced by the stretching and the simultaneous relaxation of the oriented chains. Two key parameters are believed to play an important role in this process. The first comprises the specific intermolecular interactions between the two components generally found and thought of as

responsible for the blend miscibility, since it can modify the characteristic relaxation times of the components. The second parameter is the entanglement spacing in the blends which determines the temporary network density for each component and, thereby, the chain orientation induced by the stretching.

The studies on the orientation behaviour of polymer blends have, till now, been focused on systems with two amorphous components. Only few studies involved blends containing one crystalline component [5]. In the case where one component is crystallizable, its concentration was usually kept low enough to prevent its crystallization [3,6]. Understandably, the crystallization is a complicating factor for the analysis of the effects of intermolecular interactions and entanglements. Nevertheless, in this study, we will look at the orientation behaviour in blends rich in the crystallizable component and, consequently, in which the crystallization occurred. New questions can be raised for such systems. For example, one would like to know if the orientation behaviour of the crystallizable component changes when increasing the amount of the amorphous

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polymer in the blend. What is the orientation of the two components in the amorphous region and how does it compare to the miscible blend of the same polymers without any crystallization? Finally, what are the factors which effectively determine the orientation of the components in such blend systems?

Blends of poly(ϵ -caprolactone) (PCL) with poly(vinyl chloride) (PVC) and poly(styrene-*co*-acrylonitrile) (SAN) have been used in this study. The choice of these two systems was made for several reasons. First, the PCL/PVC and PCL/SAN (SAN with 8–28 wt% of acrylonitrile) blends are miscible for the whole range of composition [7,8]. The crystallization of PCL develops at high concentrations (generally 40 wt%), but there is always an appreciable amount of PCL remaining amorphous and mixed with the other component. Second, thin films of the blends rich in PCL can easily be prepared from solution-casting, and the cold-drawing of the films can be performed at room temperature, below the melting point of the crystallized PCL at about 60°C; this allows the infrared dichroism method to be utilized for the orientation characterization. Finally, the orientation studies of some amorphous PCL/PVC and PCL/SAN blends containing less than 30% of PCL have already been reported [1,3], and these results could be used for comparison. In this context, the present work is complementary to the previous ones but deals with a different situation where the crystallization of PCL takes place in these blends.

2. Experimental

Samples of PCL ($M_w \approx 65\,000$; $T_g = -65^\circ\text{C}$), PVC ($M_w \approx 161\,000$; $T_g = 89^\circ\text{C}$) and SAN containing 25% of acrylonitrile ($M_w \approx 165\,000$; $T_g = 108^\circ\text{C}$) were purchased from Aldrich. Thin blend films of thickness 20–40 μm were prepared by dissolving both polymers in THF and then casting the transparent solution onto the surface of a glass plate. The films were dried under vacuum at 45°C for 2 days. Before the stretching and the orientation measurements, the weight-percentage crystallinity of PCL in all films was measured by differential scanning calorimetry (Perkin-Elmer DSC-7, heating rate: 20°C min⁻¹), using 142 J g⁻¹ as the melting enthalpy for 100% crystallized PCL [9]. Unless otherwise stated, the films were uniaxially stretched, at room temperature, on a stretching apparatus at a rate of about 20 mm min⁻¹, and the orientation measurements followed immediately. In addition to pure PCL, blends of PCL containing 10, 20, 25, 30, 35, 40 and 50 wt% of PVC and SAN were investigated.

The molecular orientation averaged over all chain segments is usually characterized by the orientation function defined as

$$F = (3 \langle \cos^2 \Theta \rangle - 1)/2 \quad (1)$$

where Θ is the angle between the stretching direction and the chain axis. A perfect orientation along the stretching

direction corresponds to $F = 1$, while a perfect perpendicular orientation gives $F = -0.5$; random orientation or no macroscopic orientation results in $F = 0$. The orientation measurement of different blend components is made possible through the use of the infrared dichroism. This method allows for the determination of the orientation function through

$$F = (R_o + 2)(R - 1)/(R_o - 1)(R + 2) \quad (2)$$

where R is the measurable infrared dichroic ratio defined as $R = A_{\parallel}/A_{\perp}$, A_{\parallel} and A_{\perp} being the absorbance with the infrared beam polarized parallel and perpendicular, respectively, to the stretching direction, and $R_o = 2 \cot^2 \alpha$ with α being the angle between the chain axis and the transition moment associated with the infrared band used for the measurements. As an example, Fig. 1 shows the two polarized infrared spectra of a PCL/SAN 70/30 blend film stretched to a draw ratio λ of 2 (λ is defined as the ratio of the film length after stretching over the length before stretching). The 1295 cm⁻¹ band, displaying a strong parallel dichroism, is related to the C–C and C–O stretching vibrations of crystalline PCL [10] (it is totally absent in amorphous PCL). As it does not overlap any of the infrared bands of SAN or PVC, this band is well suited to the orientation measurement of crystalline PCL in the blends. Taking $\alpha = 0^\circ$, Eq. (2) leads to

$$F_{cr} = (R - 1)/(R + 2) \quad (3)$$

The carbonyl band of PCL around 1730 cm⁻¹ arises from both the crystalline phase (at 1724 cm⁻¹) and the amorphous phase (at 1737 cm⁻¹). Using the area under this band, it was used to determine the average orientation

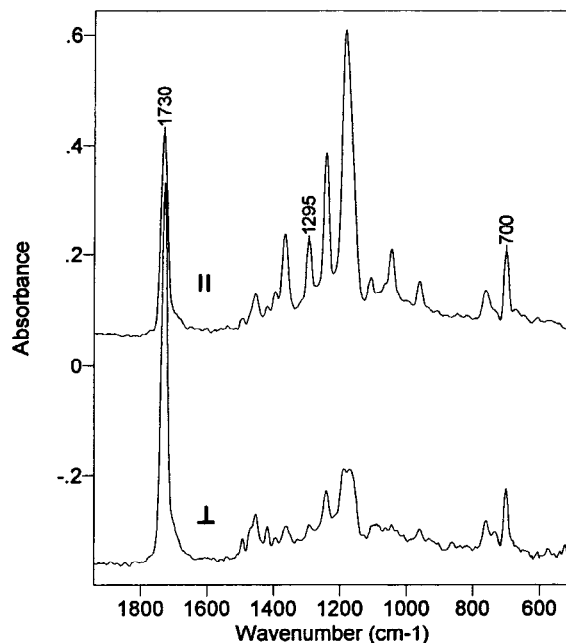


Fig. 1. Polarized infrared spectra of a film of PCL/SAN-70/30 stretched to $\lambda = 2$ with parallel (||) and perpendicular (\perp) polarization of radiation with respect to the stretching direction

function of PCL in both phases, i.e. F_{total} . As the α angle is generally cited [1] as 78° , we have

$$F_{\text{total}} = -2.3(R-1)/(R+2) \quad (4)$$

For a given sample, knowing F_{cr} , F_{total} as well as the degree of crystallinity, x , obtained from differential scanning calorimetry (d.s.c.), the orientation function of amorphous PCL, F_{am} , can be deduced from the following equation

$$F_{\text{total}} = xF_{\text{cr}} + (1-x)F_{\text{am}} \quad (5)$$

The orientation of SAN in the PCL/SAN blends was obtained by using the 700 cm^{-1} band (Fig. 1) which is assigned to the out-of-plane C–H bending vibration [11] ($\alpha = 0^\circ$), and the orientation of PVC in the PCL/PVC blends was estimated from the C–Cl stretching band [1] centred at 635 cm^{-1} ($\alpha = 90^\circ$). It should be mentioned, however, that these two bands are very weak for the blends, resulting in relatively large uncertainties in the data of the orientation function of SAN and PVC. Polarized infrared spectra were recorded with a 4 cm^{-1} resolution on a Bomem MB-102 Fourier transform infrared (FTi.r.) spectrometer using a wire-grid infrared polarizer placed between the sample and the DTGS detector. In most cases, 50 interferograms were averaged for each spectrum but, for some PCL/PVC samples, 200 scans were used in order to minimize the experimental errors in the measurement of the orientation of PVC.

3. Results and discussion

3.1. Crystallinity of PCL in the blends

For the reasons mentioned above, the degree of crystallinity of PCL in the blends is an important parameter for this study. The crystallinity development of PCL is known to be sensitive to preparation methods [12]. Generally, its crystallization is easy in solution-cast films since the PCL mobility is allowed by the low T_g due to the presence of the solvent during the film drying. In contrast, for melt-crystallization, a lower PCL crystallinity is expected because the crystallization takes longer times to complete. This is illustrated in Fig. 2 which shows the d.s.c. heating curves of solution-cast PCL/PVC 70/30 and PCL/SAN 70/30 films after a 2 day drying period in vacuum, denoted hereafter as as-cast films, as well as curves recorded from the second scan after cooling those films from the isotropic state, hereafter called recrystallized films. It is seen that the as-cast films exhibit a large endotherm corresponding to a degree of crystallinity of about 55%, while the subsequent heating results in a smaller endotherm indicating a lower degree of crystallinity of about 35%, which mainly develops during the heating as revealed by the exotherm at lower temperatures. The double endotherms for the as-cast films are known to be arising from a mechanism of melting and recrystallization during the heating scan [13].

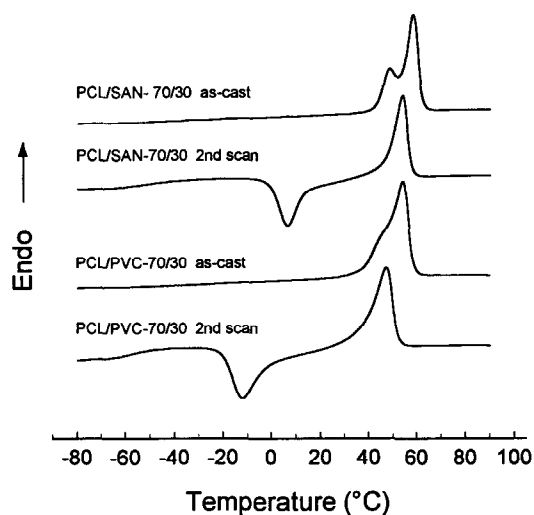


Fig. 2. D.s.c. heating curves for as-cast films of PCL/SAN-70/30 and PCL/PVC-70/30 and their second scan after being cooled from the liquid state

Fig. 3 shows the T_g and the degree of crystallinity of PCL in as-cast and recrystallized films for all investigated blends of PCL/PVC (Fig. 3a) and PCL/SAN (Fig. 3b). Some common features can be observed for both blend systems. First, the miscibility is confirmed by the presence of a T_g which increases on increasing the concentration of PVC or SAN. The T_g s of the as-cast films, especially for high PVC or SAN contents, were difficult to observe. However, it appears that the as-cast films have, for a given composition, a higher T_g than the recrystallized films, reflecting the greater crystallinity of PCL in these blends and, consequently, the smaller amount of amorphous PCL mixed with PVC or SAN. Second, except for PCL/PVC blends containing 40% or more PVC, the degree of crystallinity of PCL in the as-cast films remains almost constant at about 50%, regardless of the blend composition. On the other hand, the crystallinity of the recrystallized samples decreases rapidly with higher PVC or SAN concentrations and, apparently, drops to zero in the blends containing more than 40% of PVC or SAN, indicating a severe slow down of the crystallization rate in those blends. As already mentioned, the stretching experiments in this study were carried out on as-cast films having a relatively high PCL crystallinity degree. However, as will also be shown, the slow crystallization in the recrystallized blends with a high PVC concentration was also exploited to investigate the orientation behaviour of the samples as a function of the development of PCL crystallinity with time.

3.2. Orientation in stretched as-cast films

Pure PCL films can be cold-drawn at temperatures below the melting point of the PCL crystals at about 55°C . Fig. 4 shows the results obtained for PCL stretched at room temperature and 50°C , where the orientation function of both the crystalline and the amorphous PCL is plotted versus draw ratio up to $\lambda = 6$. At 50°C , which is close to the crystal melting, the PCL films generally broke at $\lambda > 4$. A similar

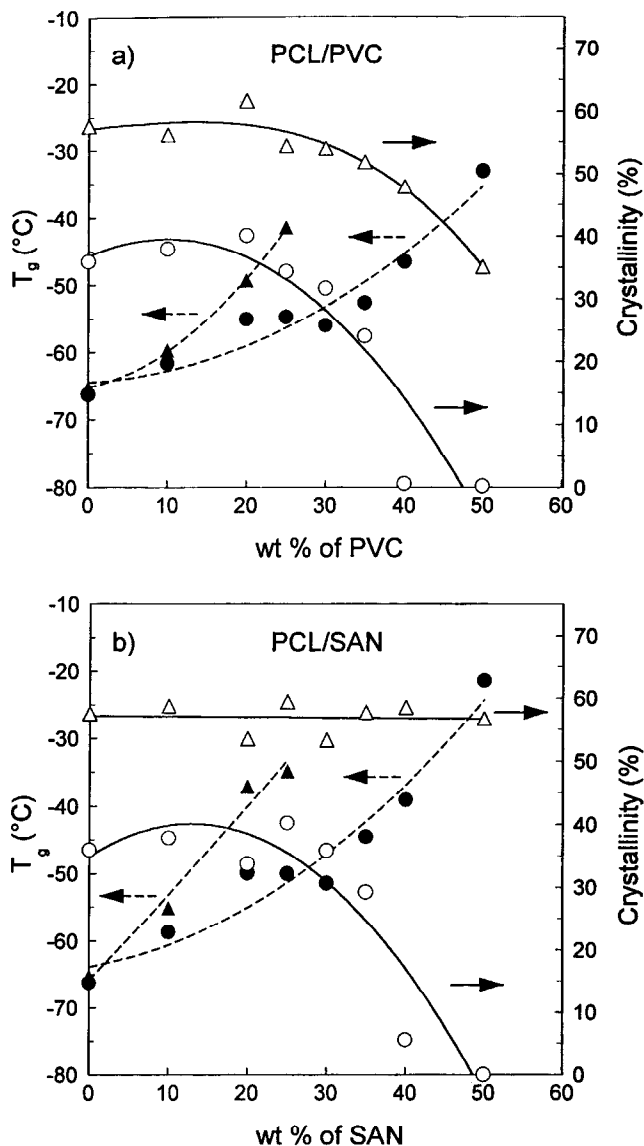


Fig. 3. Glass transition temperature and degree of crystallinity of PCL determined from as-cast films ($\blacktriangle, \triangle$) and their second scan (\bullet, \circ) for (a) PCL/PVC and (b) PCL/SAN

orientation development can be seen at both stretching temperatures. The crystalline orientation function increases rapidly upon extension and reaches a value of about 0.9 at $\lambda > 4$. This indicates a very high segmental orientation of the crystalline chains along the stretching direction. In terms of the crystalline structure of PCL, which has an orthorhombic unit cell with similar a and b dimensions as polyethylene [14], this means that the c -axis (fibre axis) is aligned parallel to the stretching direction while the a -axis and b -axis are perpendicular. The high crystalline orientation resulting from drawing in the solid state resembles the results often observed for other semi-crystalline polymers such as polyethylene. Basically, the stretching to high deformations transforms the initially lamellar structure into a microfibrillar structure [15].

On the other hand, the segmental orientation of

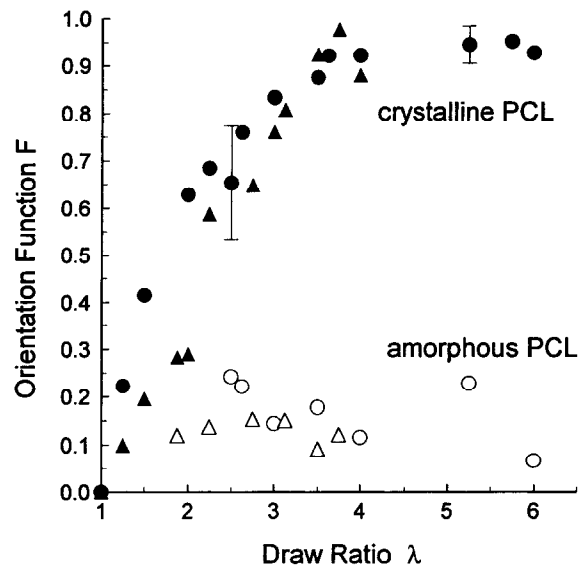


Fig. 4. Orientation function versus draw ratio for as-cast films of PCL stretched at room temperature (\bullet, \circ) and 50°C ($\blacktriangle, \triangle$)

amorphous PCL chains is much lower than the crystalline orientation. The orientation function has a value around 0.1 at $\lambda = 2$ and, within the experimental error, looks unchanged or even slightly decreased as the draw ratio increases. This amorphous orientation seems to be slightly lower than that of polyethylene whose amorphous orientation function was often found to be of the order of 0.3 at $\lambda = 5$ [15]. Nevertheless, the result is not surprising. The amorphous chains, which reside in the interlamellar regions inside the spherulites, can exist in various forms [16]: tie chains, cilia, loops and unattached chains. Starting the stretching, the spherulites initially deform, and then the lamellae are transformed into microfibrils. The resulting amorphous orientation can be very different depending on the type of amorphous chains [16]. Generally, the tie chains, interconnected by the crystal blocks, are expected to orient more than the cilia, loops and unattached chains that also relax more rapidly tending to recover the initial unoriented state. Consequently, the proportion of the different types of amorphous chains in a specific semi-crystalline polymer influences its amorphous orientation. In the case of PCL, the results in Fig. 4 suggest that the amorphous region includes an important number of cilia, loops or unattached chains which account for the low stretching-induced orientation accompanying the nearly perfect segmental orientation of the crystalline PCL.

We then measured the orientation functions for PCL/PVC and PCL/SAN blends whose films were stretched at room temperature. Before discussing the results obtained, let us recall that the degree of crystallinity of PCL in those as-cast films remains at about 50% for almost all the compositions investigated (Fig. 3). Also, it is known that, in these miscible blends, the amorphous PVC or SAN is incorporated in the interlamellar regions of the spherulites and mixed with the amorphous PCL. The spherulites in the blends are

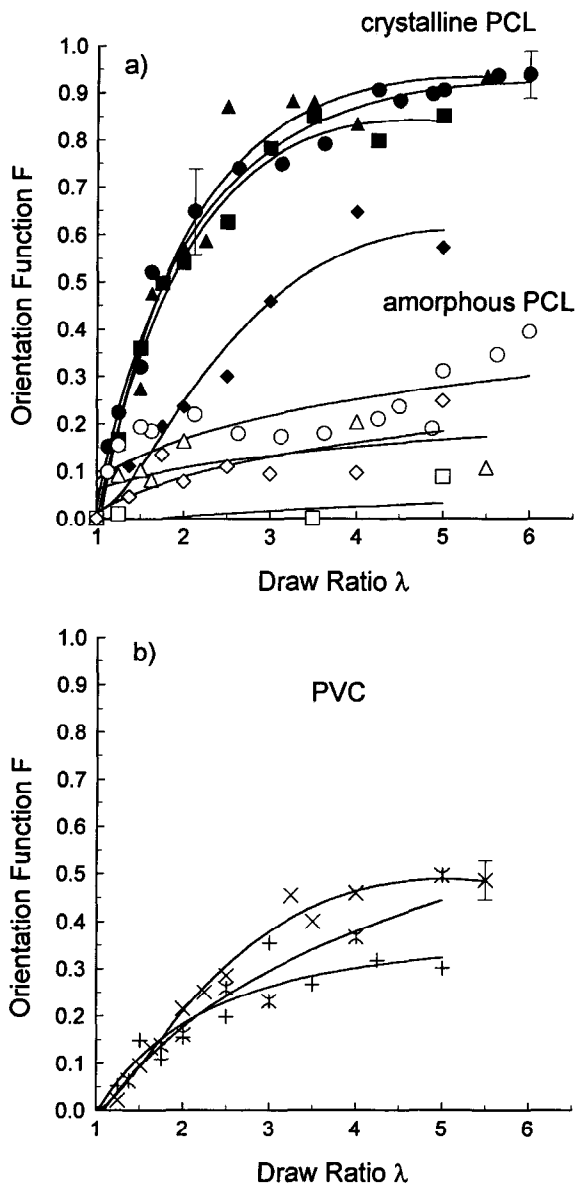


Fig. 5. Orientation function *versus* draw ratio for as-cast films of the PCL/PVC blends stretched at room temperature: (a) PCL orientation; (b) PVC orientation. The blends contain 20% (●,○), 30% (▲,△, ×), 40% (■,□, +) and 50% (◆,◇, ✕) of PVC

volume-filling, and the amorphous layers (interlamellar spacing) are thickened as the content of PVC or SAN increases, which is true up to about 50% of PVC in the case of PCL/PVC blends [16]. We made polarizing microscopy observations, confirming the presence of PCL spherulites in these blends. The results of the orientation measurements, at four different compositions for each system, are presented in Fig. 5 for PCL/PVC and in Fig. 6 for PCL/SAN blends. For clarity, the orientation functions of PVC and SAN are plotted separately from those of the crystalline and amorphous PCL. Unlike the PCL/PVC films, the PCL/SAN films with high concentrations of SAN broke quite easily during the stretching at $\lambda > 2$ and, therefore, the highest concentration of SAN shown in Fig. 6 is 30%. Overall, it can be

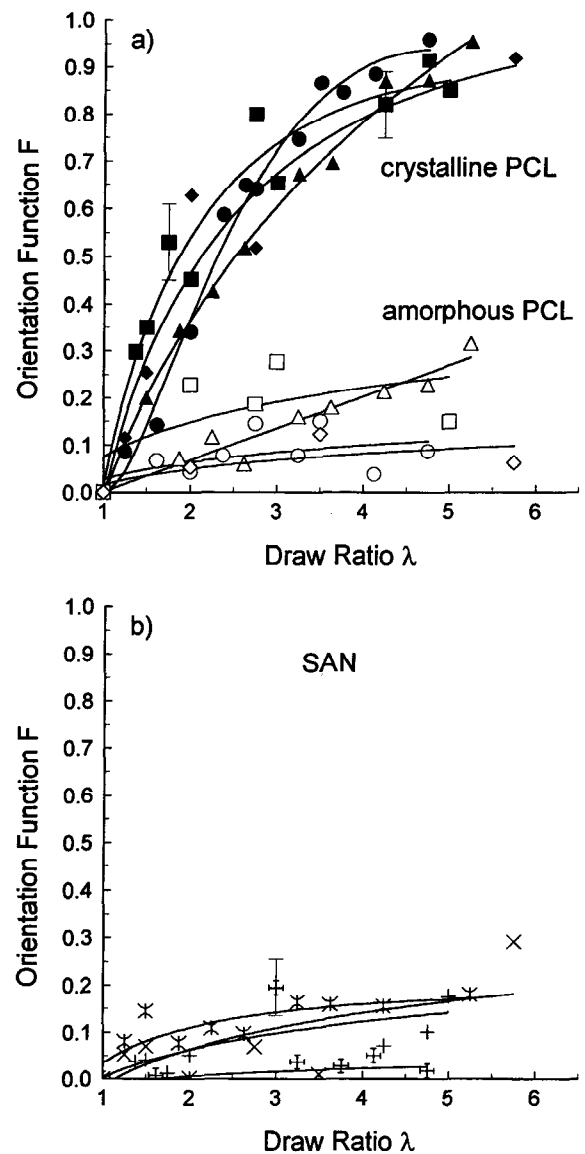


Fig. 6. Orientation function *versus* draw ratio for as-cast films of the PCL/SAN blends stretched at room temperature: (a) PCL orientation; (b) SAN orientation. The blends contain 10% (●,○, ✕), 20% (▲,△, ✕), 25% (■,□, +) and 30% (◆,◇, ✕) of SAN

seen that the two blend systems behave in a similar way. First, the development of the crystalline orientation of PCL shows no noticeable difference as compared with the pure PCL (Fig. 4); the only exception is the PCL/PVC 50/50 blend where the crystalline orientation is lower. Even with 40% of PVC or 30% of SAN, the crystalline orientation of PCL is similar to that of the pure PCL. This observation is interesting. Taking the PCL/PVC 60/40 blend as an example, the degree of crystallinity of PCL in the as-cast film was found to be 46% (Fig. 3); this means that the crystalline PCL accounts for only about 27% of the total weight of the blend (the remaining 73% is amorphous PCL and amorphous PVC). In other words, the ratio of the amorphous material (located in the interlamellar region) to the crystalline material (the lamellae) is roughly three for this blend in

comparison with approximately one for the pure PCL. The results show that, despite the increasing volume of the amorphous region inside the spherulites as the content of PVC or SAN increases in the blends, the stretching remains effective for transforming the lamellar structure to the microfibrillar structure, characterized by the rapidly reached very high crystalline orientation upon extension. In the case of the PCL/PVC 50/50 blend which shows a smaller crystalline orientation (Fig. 5a), the degree of crystallinity of PCL in the as-cast film was exceptionally lowered to only 34% (Fig. 3), and the above defined amorphous-to-crystalline ratio becomes five. It is no surprise to see that the stretching transforms less efficiently the lamellae to microfibrils, since a more important 'direct' stretching of the amorphous chains is likely to occur and contribute to the sample's elongation. Nevertheless, the still relatively high value of the orientation function ($F = 0.5\text{--}0.6$) indicates that, even when the PCL lamellae represent as low as 17% of the total weight of the blend, the transformation of the lamellae under the stretching remains the dominant process.

On the other hand, the orientation of the amorphous PCL in both blend systems behaves essentially like that of pure PCL, the orientation function being of the order of 0.1. Considering the uncertainties in the data due to the fact that the amorphous orientation was calculated indirectly as described in Section 2, these results show no significant composition-dependence of the amorphous PCL orientation.

Finally, the orientation functions of PVC and SAN are shown in Fig. 5b and Fig. 6b. The orientation of PVC increases continuously with extension, particularly before $\lambda = 4$, and reaches a value of about 0.3 at $\lambda = 4$. The orientation of SAN is much lower compared to that of PVC. Apparently, the orientation of SAN is basically similar to that of the amorphous PCL in the blends, with an orientation function of about 0.1. Again, due to the relatively large experimental uncertainty, no attempt was made to analyse any possible influence of the blend composition on the orientation of PVC and SAN.

Comparing the orientation of amorphous components in these crystalline blends with that of amorphous blends is of interest. In the case of amorphous PCL/PVC blends, Hubbell and Cooper [1] have reported, for a blend containing 25% of PCL, an orientation function of PCL ranging from about 0.15 to 0.25 over $\lambda = 2.5\text{--}4$, and have concluded that the chain segments of isotactic PVC orient as PCL while the segments of syndiotactic PVC show a higher orientation. In the present study, the infrared band employed, centred at 635 cm^{-1} , leads to the average PVC orientation over all chain segments (it was not possible for us to distinguish between the orientation of segments of different tacticities). The results shown in Fig. 5 suggest that, in the crystalline PCL/PVC blends, the orientation behaviour in the amorphous region is similar to the orientation in amorphous PCL/PVC blends, i.e. the orientation of the amorphous PCL is low and the overall orientation of PVC is higher.

In the case of amorphous PCL/SAN blends, an infrared study [3] on an amorphous blend containing 20% of PCL gives an orientation function of about 0.15 for both PCL and SAN at $\lambda = 3.5$, a value which is fairly comparable to the results presented in Fig. 6. For amorphous blends, it is now well established that the measured orientation depends much on the relaxation of the chains oriented in response to the stretching. The stretching temperature is a key parameter that influences the orientation relaxation. A higher stretching temperature with respect to the T_g means a greater chain mobility and, thus, faster relaxation of the oriented chains resulting in a lower orientation. In the study on amorphous PCL/PVC [1], the stretching was apparently performed at room temperature, which was very close to the T_g of the blend (around 25°C). In the study of the amorphous PCL/SAN [3], the stretching temperature was also close to the T_g of the blend, at $T_g + 10^\circ\text{C}$, whereas in our study the situation is different since all the films of the crystalline PCL/PVC and PCL/SAN blends were stretched at room temperature, i.e. some $30\text{--}70^\circ\text{C}$ above the T_g of the amorphous mixtures in the interlamellar regions. At those temperatures, important chain relaxation is expected. In other words, for these crystalline miscible blends, the orientation of the amorphous PCL or PVC or SAN should be still smaller than what is shown in Figs 5 and 6 if the orientation was dictated by the same factors as in the corresponding amorphous blends, without crystallization. From this sort of consideration, the results in Figs 5 and 6, which indicate comparable orientation as compared with amorphous blends stretched at lower temperatures, suggest a distinct influence of the crystalline phase on the orientation behaviour in the amorphous regions. Indeed, the following qualitative analysis easily shows this possibility.

The very high crystalline orientation observed for almost all the investigated blends suggests that the stretching involves primarily the structural transformation of the crystalline PCL from lamellae to microfibrils. This implies that the amorphous polymers in the interlamellar regions, in particular the tie chains which are part of the amorphous PCL blended with PVC or SAN, would orient, and that this orientation will not be relaxed in the same way as in the amorphous blends. The tie chains are interconnected by the PCL crystal blocks and, consequently, the orientation shows limited relaxation. At the same time, the PVC or SAN chains and the other types of amorphous PCL chains can orient through possible routes like an orientation coupling between those chains and the tie chains of PCL owing to the miscible nature. The possible effects of the entanglements in the amorphous regions certainly cannot be ruled out, and temporary networks arising from entangled polymer chains inside the interlamellar regions can contribute to the amorphous orientation upon extension, but the orientation relaxation can be different from the amorphous blends. For instance, it is not unreasonable to believe that the oriented amorphous chains of both components could be trapped by the oriented crystallites of PCL, restricting the relaxation.

3.3. Orientation in stretched films with varying crystallinity of PCL

Due to the miscibility of the system, the crystallization rate of PCL is reduced in the PCL/PVC and PCL/SAN blends. This effect is more prominent for the PCL/PVC blends. Fig. 7 shows the evolution of PCL crystallinity degree with time, determined from d.s.c. at room temperature, for the blends containing 40% of SAN, 35% of PVC and 40% of PVC. It is seen that the crystallization of PCL is faster in the blend containing SAN than in the blends containing PVC. The degree of crystallinity of PCL reaches 30% after about 50 min in the PCL/PVC 65/35 blend and after 5 h in the PCL/PVC 60/40 blend (data not shown in Fig. 7). For these two blends, the slow crystallization makes it possible to stretch the films when the blends are amorphous, i.e. with no crystallization has occurred yet, or when there is just a small amount of crystals. When the blends are still amorphous, the orientation behaviour should essentially reveal the effects of entanglements and intermolecular interactions as we usually expect for miscible amorphous blends. When the crystallization of PCL starts, stretching the blends with varying degrees of crystallinity of PCL should show the interplay between the parameters governing the orientation in amorphous blends and the crystalline structural transformation. Thus, with PCL/PVC blends, we can have, in principle, a complete picture of the orientation passing from amorphous to crystalline blends.

The experiments were performed by stretching films retained at 90°C for 5 min for equilibrium and then cooled to room temperature for the crystallization of PCL. Measurements were first made on the PCL/PVC 65/35 blend. Films were stretched to $\lambda = 3$ after being left at room temperature for different times. Plotted in Fig. 8 are the orientation functions versus the crystallization time. Before

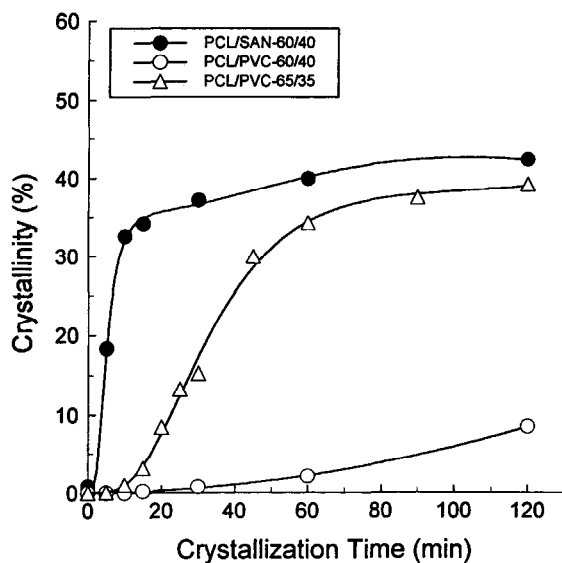


Fig. 7. Crystallinity development with time for PCL melt-crystallized at room temperature in three blends

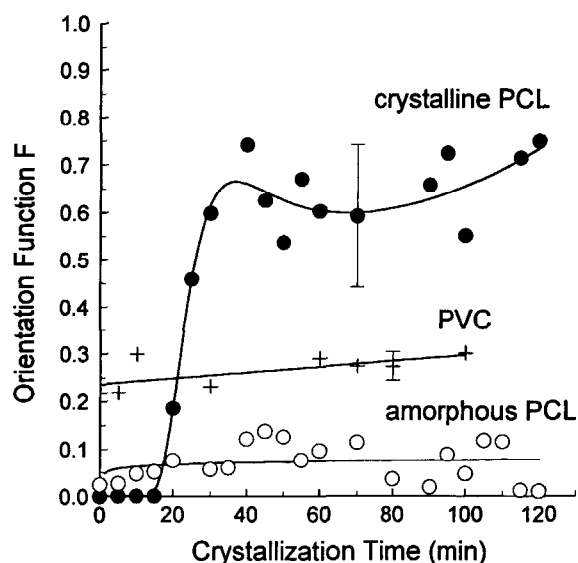


Fig. 8. Orientation function versus crystallization time before the film stretching to $\lambda = 3$ for the PCL/PVC 65/35 blend

20 min, no crystalline PCL could be detected in the blend since the infrared band at 1295 cm^{-1} was absent; the orientation of the amorphous PCL is very weak, if not negligible, while the orientation of PVC is higher. After 20 min at room temperature, the infrared band of the crystalline PCL becomes detectable. Although the absorbance is very weak at this point, the dichroism is clear giving rise to $F \approx 0.2$. This result suggests that from the first moment of the appearance of PCL crystals, even with a very low crystallinity degree, the crystalline PCL is oriented in the stretched films. Then, as the crystallization of PCL develops with time in the blend film before stretching, the orientation of the crystalline PCL induced by the stretching increases rapidly. For films crystallized for 40 min or longer, the crystalline orientation reaches the level found for the as-cast films at the same draw ratio, i.e. $F \approx 0.7$ (Fig. 5a). It is interesting to note, from Fig. 8, that along with the high orientation of the crystalline PCL, the orientation of the amorphous PCL and PVC also increases a little and remains at a level similar to the as-cast films. This result may reflect the influence of the crystalline orientation on the orientation of the amorphous components in crystalline miscible blends, but no clear conclusion can be drawn here because of the small level of orientation combined with a large experimental uncertainty, due to the fact that each data point corresponds to the stretching of a different sample to $\lambda = 3$. At about $\lambda = 3$, the orientation is still very sensitive to the film extension (Figs 5 and 6) and, as a consequence, any error for the exact deformation arising from, for example, a heterogeneous local film stretching, can lead to quite different values for the orientation function.

In order to observe more accurately the orientation behaviour in the amorphous-to-crystalline transition zone, the PCL/PVC 60/40 blend, where the crystallization of PCL is still slower at room temperature, was also studied. For this

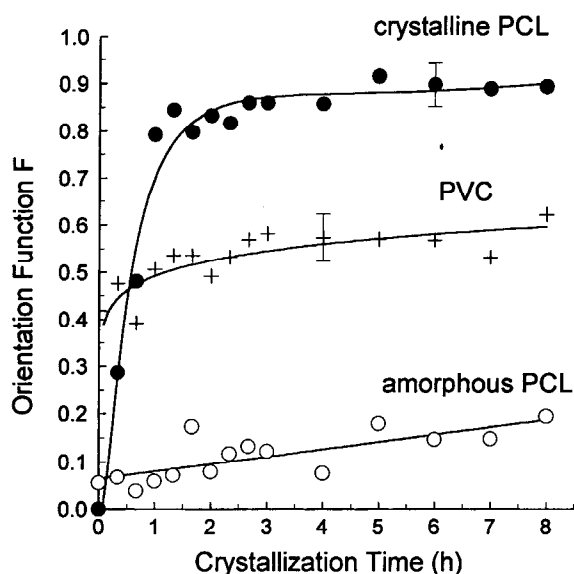


Fig. 9. Orientation function *versus* crystallization time before the film stretching to $\lambda = 6$ for the PCL/PVC 60/40 blend

series of experiments, the films were stretched to $\lambda = 6$. The results are shown in Fig. 9. Surprisingly, the crystalline orientation of PCL is detected for the film annealed for 20 min even though no PCL crystallization was found in the blend at this time before the stretching (Fig. 7). This result suggests a crystallization of PCL induced by the stretching, which is not peculiar at a draw ratio of 6. This suggestion was readily confirmed by a d.s.c. measurement on the stretched film which shows a small melting endotherm around 50°C corresponding to a degree of crystallinity of about 3%. D.s.c. measurements were thus systematically made for all the stretched films, and the stretching-induced PCL crystallization was further demonstrated. For instance, the film shows a PCL crystallinity degree of 2% before stretching and 8% after stretching, after being annealed for 60 min. In this stretched film, the crystalline orientation function of PCL already reaches the plateau value of about 0.8, as can be seen from Fig. 9. With longer annealing times, the degree of crystallinity of PCL develops in the blend, but the achievable crystalline orientation remains essentially constant. The orientation of the amorphous PCL is similar to that found for the PCL/PVC 65/35 blend, but the orientation of PVC is more important due to the high draw ratio of 6. Again, the orientation of the amorphous components seems to be a little higher with the crystallization of PCL.

For the PCL/PVC 60/40 blend before the stretching, when the crystallinity degree of PCL is of the order of 5%, the blend certainly does not have the same morphology as the as-cast film with volume-filling spherulites. The PCL crystallites are instead in the form of lamellae dispersed in the amorphous and miscible PCL/PVC matrix. When such a film is stretched, it is reasonable to expect that the amorphous polymers support most of the stress and their orientation along the stretching direction accounts for the

elongation of the sample. This model cannot explain the results in Figs 8 and 9 which indicate a constantly high crystalline orientation of PCL even with few PCL crystals in the blends. We suggest that this high crystalline orientation is related to the stretching-induced crystallization. It is reasonable to believe that the PCL chains which form the crystals during the stretching are those already aligned along the stretching direction prior to the crystallization; these crystallizing chains have the potential to form microfibril-like crystallites of PCL. In other words, stretching a PCL/PVC blend in the solid state always results in a nearly perfect segmental orientation of the crystalline PCL regardless of the crystallinity; but, depending on the amount of crystalline PCL in the blend, the main orientation process is different, being either the transformation from existing lamellae to microfibrils or the formation of microfibrils from amorphous PCL chains which crystallize during the stretching.

4. Conclusion

The results of this study show that, when the degree of crystallinity of PCL is high in PCL/PVC or PCL/SAN blends, an uniaxial stretching in the solid state always leads to a very high segmental orientation for the crystalline PCL. This behaviour is observed for blends containing up to 40% of PVC or 30% of SAN, for which the spherulites are volume-filling and the stretching results in the crystalline structural transformation from lamellae to microfibrils. In contrast with this large crystalline orientation, the amorphous components situated in the interlamellar regions orient little. For all the blends investigated, the orientation of the amorphous PCL is similar to that found for the pure PCL. SAN orients in the same way as the amorphous PCL, while the orientation of PVC is higher than that of the amorphous PCL. Orientation measurements as a function of crystallization time in two blends containing 35% and 40% of PVC reveal a surprisingly high crystalline orientation of PCL in the stretched films containing few PCL crystals, even for films in which the amount of the crystalline PCL represents as little as 5% of the total weight of the blend. In those blends, a transformation of the existing lamellae to microfibrils is unlikely due to the dominant proportion of the amorphous components supporting most of the extensional force. Instead, the stretching-induced crystallization of PCL is suggested to be at the origin of the high crystalline orientation; during the extension, the crystallizing PCL chains may form microfibril-like crystallites.

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