Crystallization under Strain and Resultant Orientation of Poly(ϵ-caprolactone) in Miscible Blends

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ABSTRACT: The crystallization of poly(ϵ-caprolactone) (PCL) in stretched miscible and amorphous blends containing 25−50 wt % of poly(vinyl chloride) (PVC) was monitored by infrared spectroscopy. It was found that, under most conditions, the crystallization under strain leads to a segmental crystalline orientation perpendicular to the strain direction, whereas a parallel crystalline chain orientation is observed under conditions where the crystallization is more rapid and the draw ratio higher. This orientation behavior was confirmed by X-ray diffraction measurements. The parallel orientation can be explained by an epitaxial growth of folded-chain lamellae from row nuclei. We suggest that the perpendicular orientation is mainly the result of the folding of oriented chains leading to lamellae aligned along the strain direction. Whatever the crystalline orientation direction, the crystallization of PCL under strain gives rise to nonspherulitic morphologies, different from those found when PCL is crystallized in unstretched blends. However, the magnitude of the resultant segmental orientation, both parallel and perpendicular, is similar to the orientation achieved by stretching crystalline PCL in the solid state at room temperature that is known to transform the spherulites into microfibrils.

Introduction

Crystallization from oriented (amorphous) chains has been investigated for a number of polymers including polyethylene (PE)[1−3] and poly(vinylidene fluoride) (PVF_2).[4] In those studies, the polymers were cross-linked in order to prevent the oriented samples from breaking, and the crystallization as well as the orientation was monitored mainly through X-ray diffraction and birefringence. Two slightly different approaches were utilized for observing the oriented crystallization. In the first case,[1] the cross-linked semicrystalline polymer was stretched in the solid state, then heated under strain to the liquid state, and subsequently cooled to allow the crystallization to occur. The second method[4] was to stretch directly the cross-linked polymer from its melt, followed by cooling the oriented polymer for its crystallization under strain. In essence, those studies show that the melt crystallization from oriented chains can result in orientation, crystalline textures, morphologies, and properties that are different from those obtained by stretching a semicrystalline polymer from the solid state. Generally, in those studies, the crystalline chain orientation was found to be parallel to the stretching direction, and questions remain about the interpretation of the occasionally observed perpendicular orientation.[2] Using cross-linked polymers, the degree of orientation can easily be controlled by the cross-link density and strain imposed on the sample. However, the interpretation of the data must take into account the effects of the network density and the possibly different behavior of the gel and sol fractions. It is also noted that orientation and crystallization of poly(ethylene terephthalate) (PET) have been extensively studied,[5,6] but those studies mainly dealt with stretching- or shear-induced crystallization.

In this paper, we report investigations on the crystallization from oriented and un-cross-linked poly(ϵ-caprolactone) (PCL) in its miscible blend with poly(vinyl chloride) (PVC). The reduced crystallization rate of PCL in the blend allowed us to stretch the amorphous PCL at room temperature and then, without changing the temperature, to follow the oriented crystallization under strain. The crystallization kinetics was monitored by infrared spectroscopy; the resultant chain orientation was measured by means of the infrared dichroism method. X-ray diffraction measurements were also used to analyze the crystalline orientation. We show that, depending on the blend composition, which influences the crystallization rate of PCL, the crystalline chain orientation can be either parallel or perpendicular to the stretching direction, but the perpendicular chain orientation is dominant in the stretched amorphous blends.

Experimental Section

The samples of PCL ($M_w \approx 65\,000$, $M_n \approx 42\,500$, $T_g = -65$ °C) and PVC ($M_w \approx 289\,000$; $M_n \approx 146\,000$; $T_g = 89$ °C) were purchased from Aldrich. PCL/PVC blends are known to be miscible over the whole range of compositions.[7] Generally, the crystallization of PCL takes place in blends containing 50 wt % or more of PCL. The crystallization leads to volume-filling spherulites, and the amorphous PCL and PVC are located in the interlamellar regions. The melt-crystallization rate of PCL is slowed by the presence of PVC. PCL/PVC blends containing 25−50 wt % of PVC were used in this study. Thin films about 30 μm thick, suitable for the infrared analysis, were prepared by casting THF solutions onto the surface of a glass plate and then dried under vacuum at 50 °C for 2 days.

The typical experimental procedure was as follows. A blend film was heated to 90 °C for 5 min (PCL crystals melted at about 60 °C), and then it was rapidly cooled to room temperature and stretched to a predetermined draw ratio (the film length after stretching over that before stretching). Unless otherwise stated, the same strain rate of 8 cm/min was used. The stretched film was held on a sample holder mounted inside

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the infrared spectrometer, and the spectra were recorded immediately after the stretching. To observe the crystallization of PCL in the blend under strain, 50 interferograms were averaged for each spectrum, which took about 2 min. In the case of the orientation measurements, each polarized spectrum was obtained from 50 scans, meaning that about 4 min was necessary to take the two polarized spectra used to calculate the orientation function, *F*. *F* can be determined from infrared dichroism through

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

where Θ is the angle between the chain axis and the reference direction, taken in this study as the stretching direction; *R* is the infrared dichroic ratio defined as $R = A_{\parallel}/A_{\perp}$, $A_{\parallel}$ and $A_{\perp}$ being the absorbances with the infrared beam polarized parallel and perpendicular, respectively, to the stretching direction, and $R_0 = 2 \cot^2 \alpha$ where α is the angle between the chain axis and the transition moment associated with the infrared (IR) band used for the orientation measurements. The orientation function *F*, ranging from −0.5 to 1, measures the average segmental orientation. A perfect orientation parallel to the stretching direction leads to $F = 1$, while a perfect perpendicular orientation gives $F = -0.5$; the random orientation is indicated by $F = 0$. Details about the IR measurements for the orientation of crystalline PCL, amorphous PCL, and PVC in the PCL/PVC blends are reported elsewhere.[8] Briefly, the 1295 cm^{-1} band arising from the crystalline PCL was used to determine the crystalline orientation function, whereas the carbonyl band around 1730 cm^{-1} for both crystalline and amorphous PCL was used to calculate the amorphous orientation function from the known crystalline orientation and the crystallinity of PCL. The orientation function of PVC in the blend was obtained from the band centered at 635 cm^{-1}. All IR spectra, with a 4 cm^{-1} resolution, were taken with a Bomem MB-102 FTIR spectrometer, and for the polarized spectra, a wire-grid polarizer was placed between the sample and the DTGS detector.

Differential scanning calorimetry (DSC) was employed to determine the weight-fraction crystallinity of PCL in blend samples, using 142 J/g as the enthalpy of melting for 100% crystallized PCL.[9] The crystallization kinetics of PCL in unstretched blend samples was also observed by DSC by measuring the enthalpy of melting as a function of crystallization time. The measurements were carried out on a Perkin-Elmer DSC-7 at a heating rate of 20 °C/min.

Wide-angle X-ray scattering (WAXS) measurements were made on a computer-controlled three-circle diffractometer (University of Reading, UK), using Cu Kα radiation with $\lambda = 1.5148$ Å produced by a Hiltonbrooks DG2 generator operating at 40 kV. By allowing the film to be rotated in its own plane, the diffractometer can measure the scattered intensity, at a fixed scattering vector *q*, where $q = 4\pi \sin \Theta/\lambda$ and 2Θ is the angle between the incident and scattered beams, as a function of α, which is the angle between the film stretching direction and the normal to the plane containing incident and scattered beams.[10] The measurements were carried out from $\alpha = 0°$ through $\alpha = 360°$ in steps of 5°.

Results

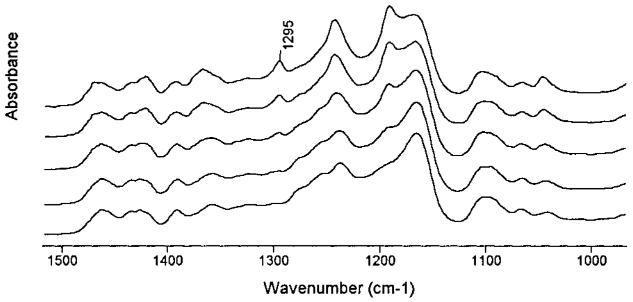

Figure 1. Infrared spectra, in the 1000−2000 cm^{-1} region, for a PCL/PVC-60/40 blend film after being stretched to $\lambda = 3$ at room temperature and held under strain for different times: 0, 0.5, 2, 4, and 6 h, starting from the bottom. The crystallization of PCL under strain is indicated by the increasing intensity of the 1295 cm^{-1} band.

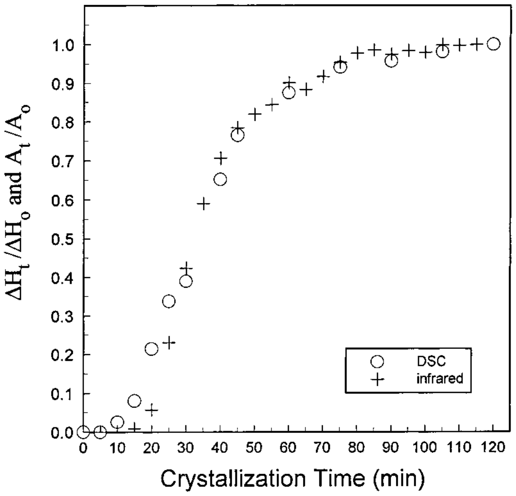

Figure 2. Crystallization development with time at room temperature for PCL in an unstretched PCL/PVC-65/35 blend as revealed by DSC and IR measurements.

Crystallization of PCL in Blends under Strain. The development of crystallization of PCL in stretched blend films was monitored by IR spectroscopy using the 1295 cm^{-1} band characteristic of the crystalline PCL. Figure 1 shows a set of IR spectra taken at different times after a PCL/PVC-60/40 blend film was stretched to $\lambda = 3$ (200% extension) and held under strain at room temperature. The spectrum at time zero was recorded immediately after stretching the film, which was cooled from the melt to room temperature. The 1295 cm^{-1} band is absent until about 30 min, indicating the amorphous nature of the blend during and after the stretching over that period of time. Then, the appearance of the 1295 cm^{-1} band and its increasing absorbance with time indicates the growth of the PCL crystals in the deformed blend. Furthermore, we have verified the validity of the IR analysis by using an unstretched blend sample for which both the IR and the conventional DSC measurements can be employed. Figure 2 compares the crystallization kinetics revealed by the IR and the DSC methods for an unstretched PCL/PVC-65/35 blend. The absorbances of the 1295 cm^{-1} band obtained at different times, A_t, are normalized to the absorbance after 2 h of crystallization, A_0, and the plot of A_t/A_0 as a function of the crystallization time t_c is compared to the plot of $\Delta H_t/\Delta H_0$ vs t_c, where ΔH_t is the enthalpy of melting measured at t_c and ΔH_0 is the enthalpy of melting after 2 h. It is seen that the IR approach gives rise to results similar to the DSC method. In the two cases, typical crystallization curves are observed; i.e., after a short induction period, the crystallization progresses, but it slows down at longer times, reaching a plateau after about 80 min. The sample was found to have a crystallinity of 38% after 2 h of crystallization, as determined from DSC. Assuming that there is no change of crystallinity of the sample when it was removed from the clamps and placed in the DSC apparatus, the A_t/A_0 values for samples under strain can be used to estimate the crystallinity. The crystallinity at the end of the crystallization period can be determined from a DSC

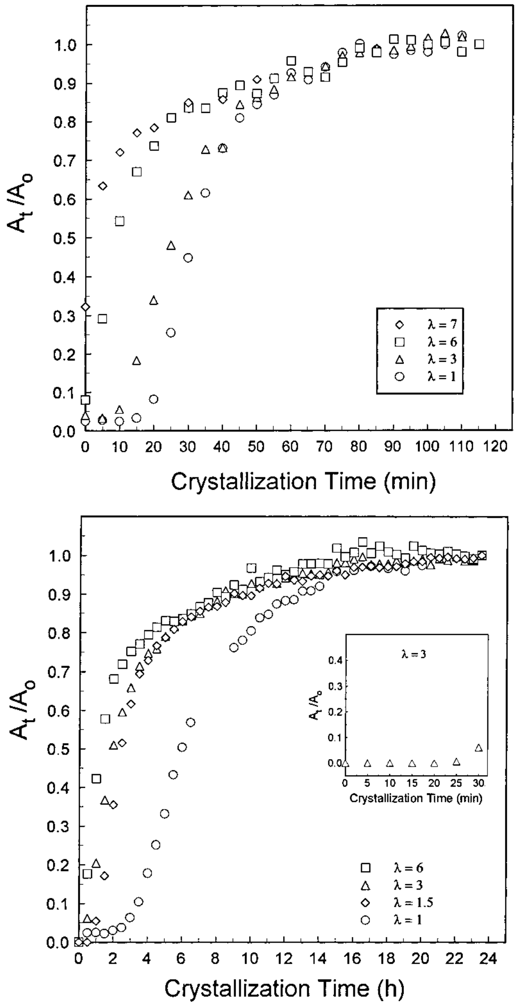

Figure 3. Crystallization development with time at room temperature for PCL, measured from IR spectroscopy, in (a, top) PCL/PVC-65/35 and (b, bottom) PCL/PVC-60/40 blends stretched to various draw ratios and held under strain. The inset in (b) shows data for the first 30 min at $\lambda = 3$.

measurement on the stretched sample released from the stretching apparatus.

Typical results for the crystallization of PCL under strain at room temperature in PCL/PVC blends are shown in Figure 3 using PCL/PVC-65/35 and PCL/PVC-60/40 blends. With 5 wt % more of PVC, the crystallization rate of PCL in the PCL/PVC-60/40 blend is much slower than that in the PCL/PVC-65/35 blend as can be noticed from the different experimental time scales. Therefore, the IR absorbances measured at different times are normalized to that after 2 h for the PCL/PVC-65/35 blend (Figure 3a) and to that after 24 h for the PCL/PVC-60/40 blend (Figure 3b). In both cases, however, when the blend film is stretched and held under strain, the crystallization of PCL becomes faster as compared to the unstretched blends ($\lambda = 1$). The effect is more drastic in the blend containing 40% of PVC, for which no crystallization can be observed until about 3 h for the unstretched sample, but it is seen within 1 h once the blend is stretched, even at the low draw ratio of 1.5. The results also show that the increase in the crystallization rate is more important for films stretched to higher extensions, but apparently, it is not linearly related to the draw ratio λ. However, it was found that the stretching increases the crystallization rate of PCL in the blends but does not increase its crystallinity. Actually, a PCL degree of crystallinity of about 38% is found for both PCL/PVC-65/35 after 2 h and PCL/PVC-60/40 after 24 h and for the unstretched as well as all the stretched samples used for the measurements shown in Figure 3. Finally, the blend films under strain, at least for extensions up to $\lambda = 3$, unambiguously exhibit an induction time after the stretching. This time is about 10 min in the case of the PCL/PVC-65/35 blend and as long as 30 min for the PCL/PVC-60/40 blend. (The data of the first 30 min under strain, at $\lambda = 3$, are shown in the inset of Figure 3b.) These results are important since they ensure not only that stretching is made on amorphous blends but also that PCL crystallizes essentially from oriented and amorphous chains, giving rise to the chain orientation behaviors shown below. This is different from stretching PCL crystals in semicrystalline PCL/PVC blends.

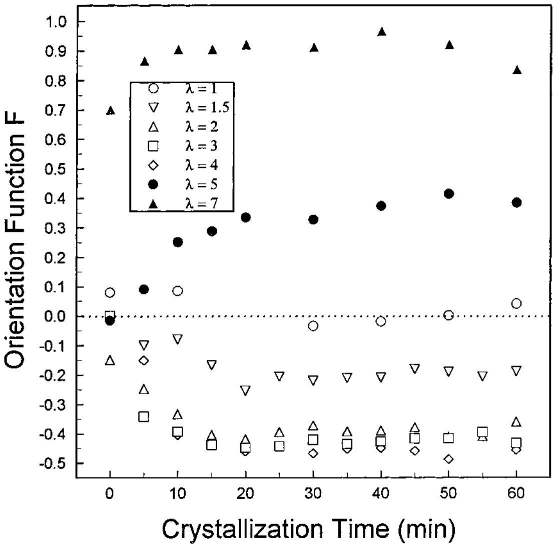

Figure 4. Crystalline orientation function of PCL as a function of time under strain for the PCL/PVC-65/35 blend stretched to various draw ratios at room temperature.

Chain Orientation Resulting from Crystallization under Strain. From unstretched and amorphous PCL/PVC blends with up to about 50% of PVC, the crystallization of PCL develops from unoriented chains, leading to volume-filling spherulites of PCL, while the amorphous PCL and PVC remain miscible and located in the interlamellar regions.[7] The resulting orientation functions for all components of the crystallized blend samples, including the crystalline PCL, are equal to zero, reflecting the absence of any macroscopically preferential chain orientation along a reference direction. For the stretched blends under strain, the crystallization of PCL is expected to start from the chains that have been oriented by the stretching, and similar to the melt crystallization from oriented cross-linked polymers,[1–4] it should result in macroscopic chain orientation for crystalline PCL. This is indeed the case.

Figure 4 shows the crystalline orientation function of PCL, which is plotted as a function of time, for the first 60 min after the stretching, for a PCL/PVC-65/35 blend stretched to and held at various draw ratios. Again, the data points at $t = 0$ min are those calculated from the two polarized spectra recorded immediately after the stretching. Starting with the unstretched blend ($\lambda = 1$), it is clear that, as expected, the orientation function is near zero showing no chain orientation as the crystallization of PCL develops. The scattering of

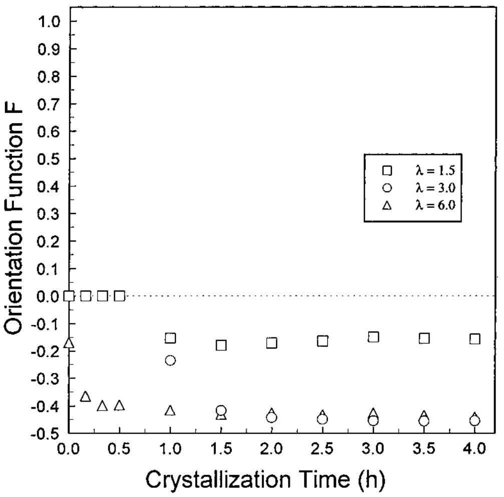

Figure 5. Crystalline orientation function of PCL as a function of time under strain for the PCL/PVC-60/40 blend stretched to various draw ratios at room temperature.

data actually indicates the uncertainty of the IR measurements. The error is larger for the orientation functions measured approximately 10−40 min after the stretching as the rapid increase in crystallinity (Figure 3a) contributes to the difference between the two IR absorbances; when the crystallization is slowed down at longer times, the error is smaller. In the case of stretched samples, the faster crystallization shown in Figure 3a means that significant errors could exist only at short times after the stretching, essentially over the first 20−30 min depending on the film extension.

The results in Figure 4 indicate that the crystallization of PCL in the stretched PCL/PVC-65/35 blend ($1.5 \leqslant \lambda \leqslant 7$) results in crystalline chain orientation. This orientation can either be perpendicular to the stretching direction (negative orientation function) for the samples stretched at draw ratios between 1.5 and 4 or be parallel to the stretching direction (positive orientation function) when the samples are stretched to $\lambda = 5$ or higher. Similar results were obtained for other blends containing less than 35% of PVC, showing PCL crystalline orientation parallel or perpendicular to the stretching direction depending on the draw ratio λ. In contrast, for the blends containing 40% or more of PVC, in which the PCL crystallization is much slower due to the higher PVC concentration, the crystalline orientation was found to be always perpendicular to the stretching direction regardless of the sample extension. This behavior is illustrated in Figure 5 using the PCL/PVC-60/40 blend as an example. It is seen that the crystalline orientation is perpendicular to the stretching direction even at $\lambda = 6$. For both blends, basically, the draw ratio determines the orientation of the amorphous polymers after stretching; i.e., a higher draw ratio leads to a higher amorphous orientation from which PCL crystallizes. This is confirmed by the plots, shown in Figure 6, of the orientation functions of amorphous PCL and PVC as a function of λ, determined at $t = 0$ min. The orientation of PCL is very small, while PVC is more oriented. Within experimental error, no significant difference can be noticed between these two blends.

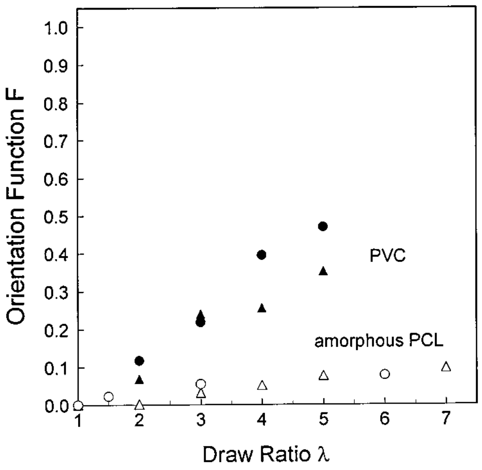

Figure 6. Amorphous orientation functions of PCL and PVC as a function of draw ratio for blends of PCL/PVC-65/35 (triangle) and PCL/PVC-60/40 (circle) blends, measured immediately after the stretching at $t = 0$ min.

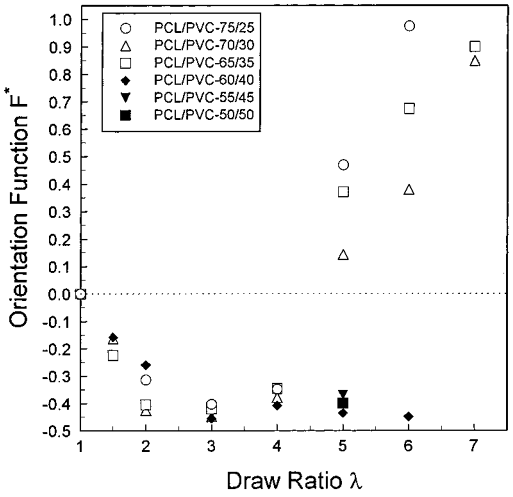

Figure 7. Maximum crystalline orientation function of PCL, achieved from crystallization under strain at room temperature, as a function of draw ratio for different PCL/PVC blends.

The results in Figures 4 and 5 show that both the direction and the magnitude of the crystalline orientation of PCL, after its crystallization under strain, depend on the concentration of PVC in the blend and the draw ratio λ. It is also clear that the maximum achievable crystalline orientation at each λ is given by the plateau value of the orientation function, denoted as F^*. Summarized in Figure 7 are the F^* values as a function of λ for various blends with the PVC content ranging from 25 to 45%. It can be seen that, under draw ratios below about $\lambda = 5$, the mechanism leading to the perpendicular crystalline chain orientation is dominant for all blends. At draw ratios above 5, while the crystalline orientation is still perpendicular for blends containing 40 and 45% of PVC, the parallel orientation is induced for the blends with 25−35% of PVC. The change of the orientation direction from perpendicular to parallel seems to take place in the vicinity of $\lambda = 5$ (400% extension). As the change of the orientation direction is abrupt at this critical λ, the corresponding F^* values bear large uncertainties for those blends due to the error in the measured draw ratio. The measured orientation can also be sensitive to small fluctuations of the room temperature, which can influence the crystallization tendency of PCL and, as will be discussed below, affect the induced orientation. It is interesting to note, from Figures 4 and 5, that both the parallel and the perpendicular crystalline orientations induced by the crystallization under strain are very high based on the observed orientation functions of $F^* \approx 0.9$ and F^*

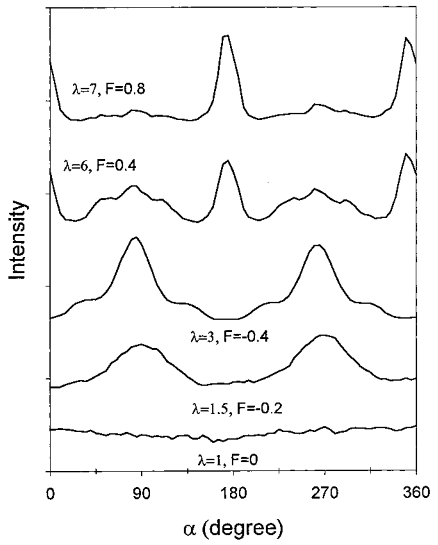

Figure 8. Scattered X-ray intensity as a function of angle between the film stretching direction and the normal to the plane containing incident and scattered beams. The measurements were made at fixed $q = 1.5$ Å^{-1} for films of PCL/PVC-70/30 crystallized under various draw ratios at room temperature. The draw ratios as well as the crystalline orientation functions determined from IR dichroism are indicated in the figure.

≈ -0.43 (except for samples under the low draw ratio of $\lambda = 1.5$). This level of orientation is similar to that produced by stretching the semicrystalline PCL or PCL/PVC blends from the solid state,[8] which transforms the crystalline structure from lamellae to microfibrils. In that case, the stretching-induced crystalline orientation is, however, always parallel to the stretching direction.

X-ray Analysis. WAXS measurements were made on a series of PCL/PVC-70/30 blend films stretched to various draw ratios and crystallized under strain. The scattered intensity for an unstretched film, recorded over the range of $q = 0.5-6$ Å^{-1}, is similar to that for pure PCL. Two peaks appear at about 1.5 and 1.68 Å^{-1}, and they arise from the 110 and 200 diffraction, respectively, which are related to the *a*- and *b*-axis of the orthorhombic unit cell of crystalline PCL.[11] As the two peaks arise from the spatial correlation between the chain axes, recording scattered intensity while rotating the sample, at fixed $q = 1.5$ or 1.68 Å^{-1}, can reveal the presence of any macroscopic crystalline chain orientation of PCL in the blends. Figure 8 shows the results, obtained at $q = 1.5$ Å^{-1} (similar results were obtained at $q = 1.68$ Å^{-1}), by plotting the scattered intensity as a function of the angle α. The orientation functions of the films, determined from the IR measurements, are also shown in the figure. First, the different directions of the crystalline chain orientation, as revealed by infrared dichroism, are confirmed. Indeed, while the unstretched film ($\lambda = 1$) shows no macroscopic orientation, the film crystallized under $\lambda = 1.5$ gives maximum scattered intensity at α = 90° and 270°, indicating a crystalline chain orientation perpendicular to the stretching direction. This still is the case for the film crystallized under $\lambda = 3$, but the higher chain orientation is indicated by the narrowed scattering peaks. In contrast, a parallel crystalline chain orientation is evident for the films crystallized under $\lambda = 6$ and $\lambda = 7$, showing maximum scattering at α = 0° and 180°. (The slight shift of the peaks is due to the alignment of the film on the diffractometer.) Second, when increasing the film extension, the transition from perpendicular to parallel chain orientation is not discontinuous. For the film crystallized under $\lambda = 6$, it is clear that PCL crystals of both perpendicular and parallel chain orientation coexist. As IR dichroism yields the average chain orientation, it is not surprising to find $F = 0.4$ for this film, as compared to $F = 0.8$ for the film at $\lambda = 7$, for which the amount of crystals of perpendicular chain orientation becomes negligible. These X-ray results suggest that, for this blend, only the mechanism leading to a perpendicular chain orientation operates when crystallized under relatively low draw ratios ($\lambda \leqslant 4$); at very high draw ratios ($\lambda \geqslant 7$), the mechanism responsible for a parallel chain orientation prevails, whereas at some intermediate draw ratios ($\lambda = 5-6$), the crystallization develops from both mechanisms. It should be mentioned that the thin films used in this work, suitable for IR spectroscopy, made the measurements and analysis of small-angle X-ray scattering difficult; further X-ray investigations are underway.

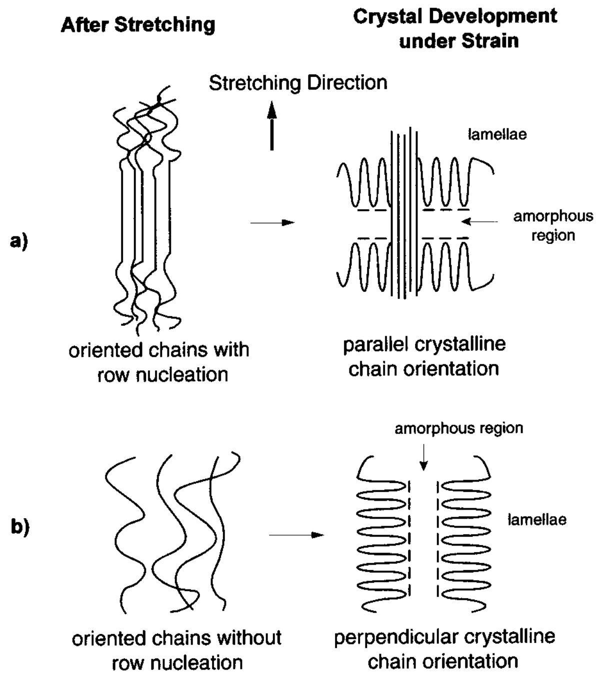

Figure 9. Schematic illustration of the two mechanisms of crystallization of PCL in stretched blends: (a) the mechanism leading to parallel crystalline chain orientation and (b) the mechanism leading to perpendicular crystalline orientation. See text for details.

Discussion

As mentioned in the Introduction, the crystallization of cross-linked polymers from oriented melt usually leads to a parallel crystalline orientation.[1-4] The established mechanism is based on a row nucleation under strain which produces linear nuclei parallel to the strain direction (the stretching direction in the present case); from the row nuclei, folded-chain lamellae can grow epitaxially with their chain axis (the crystal *c*-axis) parallel to the strain direction. This mechanism, as schematically illustrated in Figure 9a, is likely to be equally responsible for the observed parallel orientation of PCL crystallized under strain from the blends. Indeed, the fact that the parallel orientation is induced in the blend films under very large extensions and is observed for the blends having a relatively low concentration of PVC is indicative of this situation. On one hand, when a blend film is stretched to large extensions, greater chain orientation of PCL is expected; with the blend under strain, it would be easier for the, probably locally, highly oriented PCL chains to form row nuclei that contain fibrous chain backbones. On the other hand, we previously found[8] that stretching a PCL/PVC blend containing an amount of crystalline PCL as small as 5 wt % with respect to the total weight of the blend can still effectively give a deformation of the PCL crystals and lead to high chain orientation along the stretching direction. This means that, when a blend contains lesser PVC, like PCL/PVC-70/30, as the melt crystallization of PCL is relatively fast, some PCL crystallites can be formed during or even before the stretching, while after the stretching, those highly oriented crystalline chains can serve as row nuclei for subsequent growth of the PCL crystals. However, for blends having different concentrations of PVC, Figure 6 indicates a similar average orientation of amorphous PCL induced by the stretching. Should row nuclei or highly oriented fibrous regions were formed, their amount is too small to be revealed from the infrared dichroism of the carbonyl band. Another indication of this situation is that, right after the stretching, no clear crystalline band of PCL at 1295 cm^{-1} could be observed for infrared measurements.

The strikingly very high perpendicular orientation of the crystalline PCL after its crystallization under strain must come from a different mechanism. The perpendicular orientation might emerge when there are no row nuclei formed by the stretching which, for the reasons explained above, is likely to be the case for blends under relatively low extensions or blends containing more PVC, like PCL/PVC-60/40, for which the crystallization of PCL is slow. In this case, the nucleation must develop from oriented and amorphous PCL chains. It can happen by the so-called intramolecular crystallization mechanism[1], which was proposed by Judge and Stein in 1961 to explain the observed perpendicular crystalline chain orientation of a cross-linked polyethylene under draw ratios below 3. In that hypothesis, the nucleation is achieved from the folding of chains initially oriented along the strain direction, resulting in lamellae that align along the same direction; consequently, the crystalline chain axes are perpendicular to the strain direction. This is sketched in Figure 9b. It is interesting to note that the intramolecular crystallization is more likely to occur in a stretched blend than in a stretched cross-linked polymer (a network). In the stretched PCL/PVC blends under strain, the oriented PCL chains are subjected to two tendencies: there is, first, some chain relaxation which involves longitudinal chain retraction and, necessarily, some kind of chain folding and, second, the crystallization which is based on chain folding. The nucleation by chain folding which initiates the subsequent growth of the crystal lamellae may well be the result of combining the two tendencies. In the case of a network under strain, in principle, the oriented chains only undergo transversal relaxation for uniform chain curvilinear density, and it is more difficult to picture the folded-chain nucleation; the intramolecular crystallization is more likely to be initiated by oriented chains in the sol fraction of the network.

This study suggests that the dominant mechanism for the crystallization from oriented PCL in its miscible blends with PVC is that leading to the perpendicular crystalline chain orientation, but a parallel orientation can be observed under conditions where some kind of row nuclei are formed after the stretching. For the perpendicular mechanism, it is expected that the crystalline chain orientation will be high from the very beginning of the crystallization under strain and will remain constant with the development of crystallinity that essentially increases the number of the lamellae along the stretching direction. This is indeed what we see. Using the PCL/PVC 65/35 blend crystallized under $\lambda = 3$ as an example, the PCL crystallinity increases continuously up to about 50 min (Figure 3a), while the crystalline chain orientation function reaches the plateau value of about -0.42 after only 10 min (Figure 4).

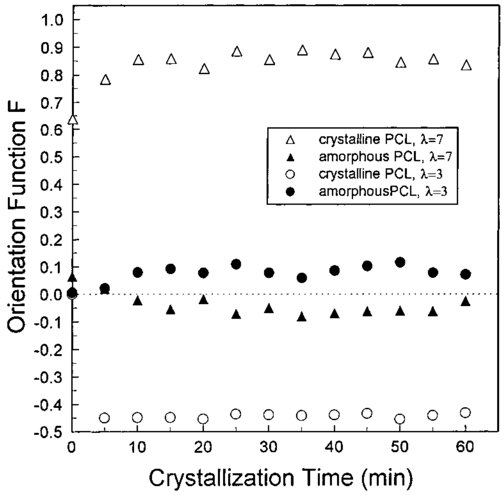

Figure 10. Crystalline and amorphous orientation function of PCL as a function of time under strain for a PCL/PVC-70/30 blend stretched to $\lambda = 3$ and $\lambda = 7$ at room temperature.

In addition, if the two mechanisms depicted in Figure 9 are correct, there should be differences between them in the orientation of the amorphous chains, which are constrained inside the interlamellar regions. In the case of a resultant perpendicular crystalline orientation (Figure 9b), the amorphous chains are located between lamellae aligned parallel to the stretching direction, and they undergo a constraining effect that tends to draw them along the stretching direction. However, in the case of a resultant parallel crystalline orientation with the lamellae grown epitaxially from row nuclei (Figure 9a), the constraining forces on the amorphous chains would be opposite. Figure 10 compares the crystalline and the amorphous orientation functions of PCL as a function of time under strain for the PCL/PVC-70/30 blend stretched to $\lambda = 3$ and $\lambda = 7$, respectively. At $\lambda = 3$, the crystalline chain orientation is perpendicular, but the amorphous chain orientation, although much lower, is clearly parallel. In contrast, at $\lambda = 7$, the resultant crystalline chain orientation is parallel while the amorphous chain orientation is perpendicular to the stretching direction. These observations support the models described above.

From the above, it is clear that all factors that normally influence the orientation and the crystallization kinetics of PCL in blends could affect the effective crystallization mechanism of PCL under strain. In other words, the conditions for the switching between perpendicular and parallel crystalline chain orientation may vary depending on those parameters. Generally, strain rate is an important factor for stretching-induced orientation of polymer blends, in contrast with cross-linked polymers. A higher strain rate means less chain relaxation during the stretching and, thereby, a greater chain orientation. All the results reported above were obtained using the same strain rate of 8 cm/min, which was quite rapid. We also performed some experiments on the PCL/PVC-70/30 blend using different strain rates. With a higher strain rate of 23 cm/min, a parallel crystalline chain orientation of PCL was observed at a draw ratio of $\lambda = 4.5$, while at $\lambda < 4$, the resultant orientation was perpendicular. With a lower strain rate of 3.5 cm/min, only perpendicular orientation was obtained even for $\lambda \geqslant 5$. These trends are consistent with the proposed conditions for the crystallization mechanism leading to parallel crystalline chain orientation of PCL; that is, strain rate should be high enough to promote the formation of some row nuclei or fibrous backbones at the end of the stretching process.

The molecular weight of polymers is another factor that is known to have important effects on their flow-induced orientation and structures.[12] In particular, for samples containing a fraction of chains that are too short to be entangled, the orientation of those chains is much smaller than that of entangled chains. However, in this study, the molecular weights of PCL and PVC are expected to exert relatively little influence on the stretching-induced orientation for two reasons. First, the samples used of PCL and PVC have molecular weights well above their respective critical molecular weight for entanglement ($M_c \sim 2300$ for PCL[13] and $M_c \sim 6250$ for PVC[14]). It is reasonable to believe that few chains in the blends are not entangled. Second, the inherently very fast chain relaxation of PCL is the dominant factor for its low average orientation after stretching, as compared to the case of PVC. This is a typical situation in the orientation of miscible polymer blends containing a flexible component having a low T_g.[15,16] In other words, in this study, stretching was made on well-entangled polymers, and the difference in orientation after stretching arises mainly from the fast relaxation of PCL. Nevertheless, for comparison, some experiments were carried out using a PVC sample of lower molecular weight ($M_w \approx 102\,000$, $M_n \approx 67\,400$). Again, the PCL/PVC-70/30 blend was chosen. The orientation of the amorphous PCL after stretching was similar to that shown in Figure 6, while the orientation of PVC was smaller. After crystallization under strain, a perpendicular orientation of PCL was induced under most conditions, but with a strain rate of 8 cm/min, a parallel orientation was obtained for a film stretched to $\lambda = 5.5$, which is only slightly higher than the critical draw ratio found for the PCL/PVC-70/30 blend made of the PVC sample of larger molecular weight (Figure 7).

Another important question to be raised is whether the stretching can reduce the miscibility between PCL and PVC and, thus, contribute to the observed crystallization and orientation behaviors. Miscibility of polymer blends under shear flow has been extensively studied, and both shear-induced mixing and demixing were reported.[17,18] However, to the best of our knowledge, investigations on the miscibility of stretched blend films have not been reported. We have made some DSC measurements on stretched PCL/PVC films, but we could not unambiguously assess the effect of deformation on the blend miscibility. The crystallization of PCL makes the measurement of changes in T_g difficult. Judging from the large increases in the rate of crystallization of PCL in blends under strain, even for relatively small deformations such as $\lambda = 1.5$ (Figure 3), it seems possible to consider the contribution of factors other than stretching-induced chain orientation, but this is beyond the scope of this article.

Finally, it is interesting to mention some results obtained with the PCL/PVC-50/50 blend, for which the high concentration of PVC results in a very slow crystallization of PCL. When a film of this blend was stretched to $\lambda = 5$ and held under strain, no crystallization of PCL was detected before 20 h. At that time, the orientation of the amorphous PCL was very low with $F \approx 0.08$, but the orientation of PVC remained high with $F \approx 0.5$. Interestingly, even from such a low orientation of the PCL chains, 2 days later, the measurements showed a high crystalline chain orientation with $F \approx -0.4$, while the orientation of PVC was essentially unchanged during this period of time. These observations seem to indicate that, in the miscible PCL/PVC blend with one component, PVC, highly oriented and the other one, PCL, almost relaxed to an unoriented state, the intramolecular crystallization of PCL still takes place, giving rise to aligned lamellae with crystalline chains perpendicular to the stretching direction. These results suggest a possible role played by the highly oriented PVC chains, or an effect of the aligned environment, on the crystallization mechanism and the resultant orientation of PCL in the blend under strain. As can be noticed from Figures 4 and 5, when the PCL/PVC blends are stretched to a low extension of $\lambda = 1.5$, corresponding to low orientations of PCL and PVC as well, the resultant perpendicular crystalline orientation of PCL is actually low with $F \approx -0.2$.

Concluding Remarks

The reduced crystallization rate of PCL in its miscible blend with PVC makes it possible to investigate the crystallization of PCL in oriented blends and the resultant crystalline chain orientation. We found that the crystallization of PCL in the blends under strain results in crystalline chain orientations either parallel or perpendicular to the strain direction. Unlike cross-linked polymers, in these blends, the crystallization process leading to the perpendicular orientation is dominant, being observed for blends with a high PVC content of 40−50 wt % at all draw ratios and blends with a relatively low PVC content of 25−35 wt % at draw ratios below about 5. The parallel orientation is observed only for the blends with 25−35 wt % of PVC at draw ratios of 5 or higher. In fact, at draw ratios around 5−6, even if the average chain orientation is parallel, a substantial amount of crystals of perpendicular chain orientation can be present and coexist with crystals of parallel chain orientation. The parallel orientation can be explained by the established mechanism based on the row nucleation and the epitaxial growth of folded-chain lamellae. The perpendicular orientation can be explained, in contrast, by a mechanism based on the so-called intramolecular crystallization, proposed by Judge and Stein in 1961 for cross-linked polyethylene.[1] This mechanism could actually represent an important crystallization process for oriented chains in polymer blends. The intramolecular crystallization under strain results in lamellae that align along the stretching direction, which is different from what happens when the crystallization takes place in unstretched blends.

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