Chain Orientation Resulting from the Crystallization Under Strain of Poly(ϵ-caprolactone) in Miscible Blends with Poly(styrene-*co*-maleic anhydride)

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ABSTRACT: Amorphous miscible blends of poly(ϵ-caprolactone) (PCL) with a random copolymer of styrene–maleic anhydride (SMA) were stretched at room temperature and the crystallization of PCL was allowed to develop under strain. The crystallization of PCL, from oriented amorphous chains, leads to macroscopic crystalline chain orientation. Using infrared dichroism and wide-angle X-ray scattering techniques, it was found that the resultant crystalline orientation of PCL is always parallel to the strain direction, regardless of the experimental conditions, which is in contrast with the PCL/poly(vinyl chloride) blend, where both parallel and perpendicular chain orientations can be induced. Furthermore, the degree of crystalline orientation of PCL is influenced by the initial stretching-induced amorphous chain orientation of the system.
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INTRODUCTION

In a previous study,[1] miscible blends of poly(ϵ-caprolactone) (PCL) with poly(vinyl chloride) (PVC) were used to study the crystallization of PCL in stretched films. It was found that such crystallization under strain is not only faster than the crystallization in nonstretched films but also leads to the development of a crystalline chain orientation. This chain orientation is as important as that obtained by direct cold drawing of crystalline PCL, which transforms crystal lamellae to microfibrils. More interestingly, this chain orientation can be either parallel or perpendicular to the strain direction. Parallel crystalline orientation is achieved under conditions that promote a high amorphous chain orientation induced by the stretching, whereas perpendicular crystalline orientation is observed under conditions that favor a lower amorphous orientation during the stretching. Those findings show that the crystallization of PCL in stretched blends can result in a variety of morphologies. To explain the observed results, possible mechanisms were discussed[1] based on studies of crystallization from oriented and crosslinked polymers[2–4]: the parallel chain orientation may result from row nucleation followed by epitaxial growth, whereas the perpendicular chain orientation may result from the folding of oriented chains, which leads to lamellae whose basal planes are aligned parallel to the strain direction. It should be noted that, here, we use the expression *crystallization under strain,*

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referring to a crystallization occurring after the end of the stretching process, instead of *strain-induced crystallization,* which generally refers to crystallization occurring during stretching.

In this investigation we report on a study, of the crystallization and orientation under strain, of PCL blended with a random copolymer of styrene–maleic anhydride (SMA), to verify whether the behavior observed for the PCL/PVC system represents a general feature for PCL crystallization under strain in miscible blends. Polarized infrared spectroscopy and wide-angle X-ray scattering (WAXS) were utilized to characterize the crystalline chain orientation resulting from crystallization under strain.

EXPERIMENTAL

Samples of PCL (M_n = 42,500; M_w/M_n = 1.7) and SMA (M_n = 110,000; M_w/M_n = 1.8) were purchased from Aldrich Chemicals (Milwaukee, WI). SMA contains 14 wt % of maleic anhydride distributed statistically on the chain. The miscibility of the PCL/SMA blend is known.[5] As in PCL/PVC blends, the presence of SMA slows down the crystallization rate of PCL and, eventually, prevents the crystallization when SMA exceeds about 60% in the blend. For PCL crystallized from nonstretched PCL/SMA blends, spherulites are formed with a miscible amorphous PCL/SMA phase located between the lamellae. To be able to perform ambient infrared measurements, conditions were sought for stretching amorphous blends at room temperature without inducing PCL crystallization during the stretching. Concentrations of SMA in the blends between 50 and 55% are suitable for this purpose. Below 50% of SMA, the stretching easily induces the crystallization of PCL, whereas above 55% of SMA, there is no noticeable crystallization of PCL that can develop under strain.

Films of PCL/SMA used for stretching were prepared by casting THF solutions (~ 5%) onto a glass plate. They were dried in a vacuum oven at 60°C for 2 days. Prior to stretching, all films were reheated to 70°C for at least 10 min, to ensure that they were amorphous and homogeneous. Under these conditions, the films were transparent and could easily be stretched at room temperature. A single T_g was found at around 17°C for both blends. Uniaxial stretching was carried out, using a laboratory-made device at a strain rate of 20 cm/min, immediately after cooling the sample from 70°C to room temperature, which took about 30 s. To monitor the crystallization development and the resultant chain orientation in the films under strain, the infrared band at 1295 cm^{-1}, which is assigned to crystalline PCL,[6] was used. Details about the use of infrared dichroism to measure the order parameter of crystalline PCL were previously reported.[1,7] As for SMA, the phenyl band at 1600 cm^{-1} was well suited for orientation measurement. Typically, immediately after the stretching, the film was transferred to a sample holder and placed inside the sample compartment of the FTIR spectrometer. A Bomem MB-102 FTIR (Quebec City, PQ) equipped with a wire-grid polarizer and a deuterated triglycine sulfate (DTGS) detector was used to record the spectra.

Wide-angle X-ray scattering measurements were performed in transmission with a Siemens/Bruker diffractometer equipped with a HiStar GADDS area detector. The scattered intensity was read from the two-dimensional detector. Scans of the X-ray images were made as a function of the scattering angle θ, or as a function of the azimuthal angle α at fixed scattering vector q = 1.5 $Å^{-1}$ (2θ = 21.42°), where $q = 4\pi \sin \theta/\lambda$, with 2θ the angle between the incident and scattered beams (110 plane) and λ the wavelength of the X-ray beam (1.542 Å). The thermal analysis was conducted on a Perkin–Elmer DSC-7 differential scanning calorimeter (Perkin–Elmer Cetus Instruments, Norwalk, CT) at a heating rate of 10°C/min. Using 190 J/g as the melting enthalpy of a PCL crystal,[8] the degree of crystallinity of PCL in blend samples could be measured.

RESULTS AND DISCUSSION

As previously shown for PCL/PVC blends,[1] the increase in absorbance of the 1295-cm^{-1} band can be used to monitor the rate of crystallization of PCL under strain by recording, with time, the infrared spectrum of a stretched film. At the end of the period of crystallization, the degree of crystallinity developed in the stretched film can be determined by DSC; then, the infrared data can readily be converted into curves of crystallinity versus time for the film under strain. Figure 1 shows a specific example, in which the degree of crystallinity is plotted as a function of time for PCL/SMA films of 50/50 composition, stretched to λ = 2.5 and λ = 3.5 and, for comparison, for a nonstretched film (λ = 1). It is seen that the

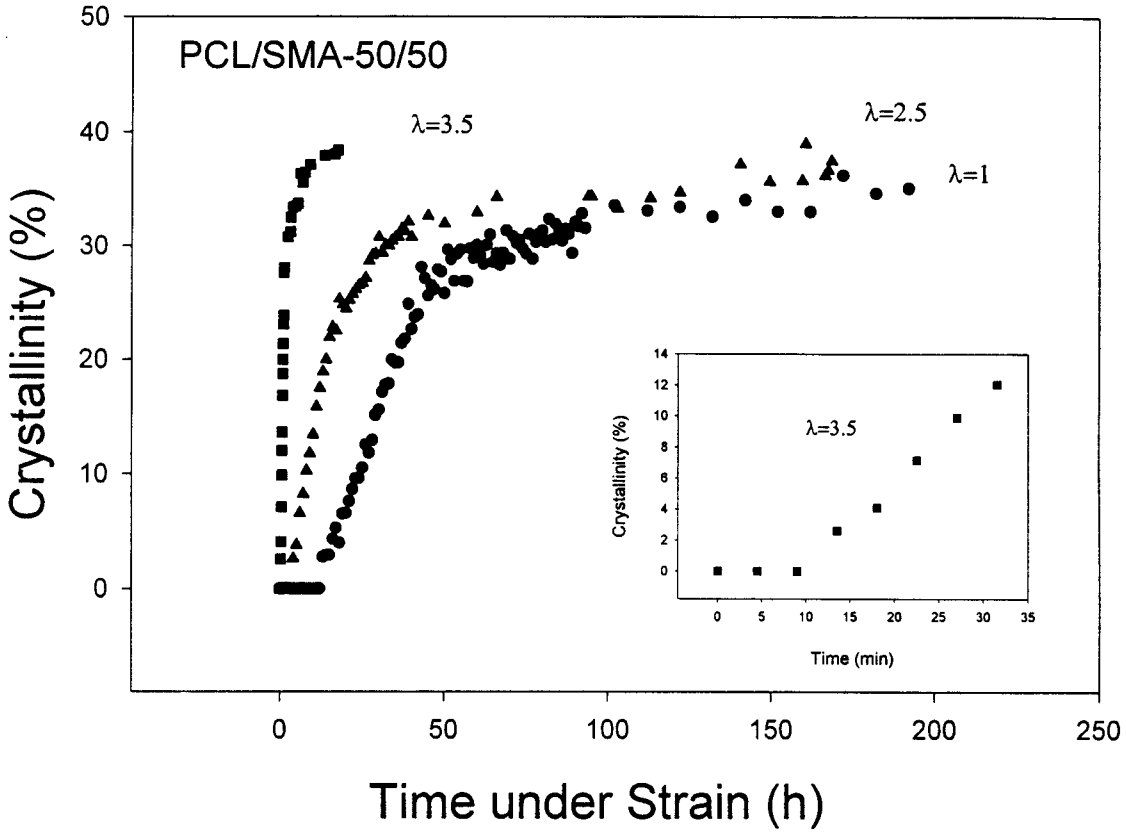

Figure 1 Degree of crystallinity as a function of time at room temperature, measured by infrared spectroscopy, for PCL/SMA–50/50 blend films under various draw ratios. The inset shows data for the first 35 min at $\lambda = 3.5$.

crystallization of PCL is slow in the nonstretched film, but it becomes faster for stretched samples, of which the increase in the rate of crystallization is greater for the film under the higher extension ($\lambda = 3.5$). It is important to emphasize that, even at $\lambda = 3.5$ (250% extension), there is no sign of crystallization occurring during the stretching; the crystallization shows up several minutes after the stretching is completed under the specific conditions of strain rate and temperature used here (inset of Fig. 1).

Figure 2 shows the degree of crystallinity versus draw ratio measured by DSC for films immediately after stretching (it took actually several minutes to install the film in the DSC pan and to start the measurement), and films held under strain for a period of time. In the case of PCL/SMA films of 50/50 composition, the stretching-induced crystallization is indeed detectable at draw ratios of $\lambda > 3$ (DSC heating curves display a melting endotherm at around 45°C). The degree of crystallinity achieved by stretching reaches about 10% (at very short times) for films stretched to $\lambda = 5.5$. In comparison, after 4 days of crystallization under strain, a degree of crystallinity of about 35% is obtained for the nonstretched and all stretched films, regardless of the draw ratio. For PCL/SMA blends of 45/55 composition, the crystallization of PCL is more difficult to develop and no stretching-induced crystallization was noticeable by DSC at draw ratios between 1 and 6 immediately after the stretching. For the films under strain, after 15 days, the degree of crystallinity increases with extension, but it always remains much below the 35% value found for PCL/SMA–50/50.

Infrared dichroism was used to characterize the crystalline chain orientation of PCL resulting from crystallization under strain. The measurements show that, similar to PCL/PVC, crystalline chain orientation develops in stretched films but, unlike PCL/PVC, whatever the stretching conditions used, this chain orientation is always parallel to the strain direction. The average degree of orientation seems to be even greater than that obtained by stretching crystalline PCL, and a sys-

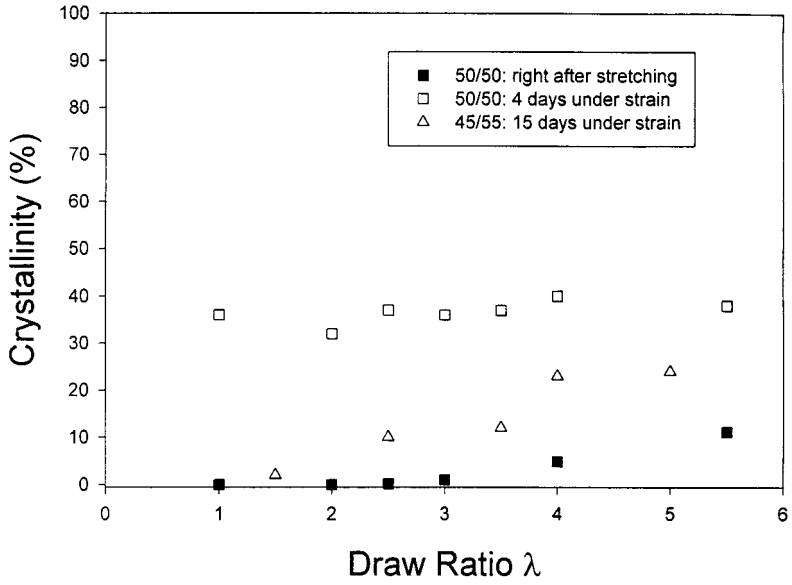

Figure 2 Degree of crystallinity as a function of draw ratio, measured by DSC, for PCL/SMA of 50/50 and 45/55 compositions, immediately after the stretching or after several days of crystallization under strain.

tematic calculation of the order parameter proved to be unnecessary, simply because it is apparently close to unity within experimental error. To illustrate this feature, a series of polarized infrared spectra, with infrared beam polarized parallel and perpendicular to the strain direction, is shown in Figure 3 for a PCL/SMA film of 50/50 composition stretched to $\lambda = 2$ at room temperature. Examining the parallel 1295-cm^{-1} band (marked by an arrow in the figure), the increase of its absorbance indicates the growth of crystalline PCL in the blend. It can be noticed that the crystallization is detectable about 0.5 h after the stretching and develops with time. However, the increase of crystalline PCL is observable only from the parallel absorbance; the perpendicular

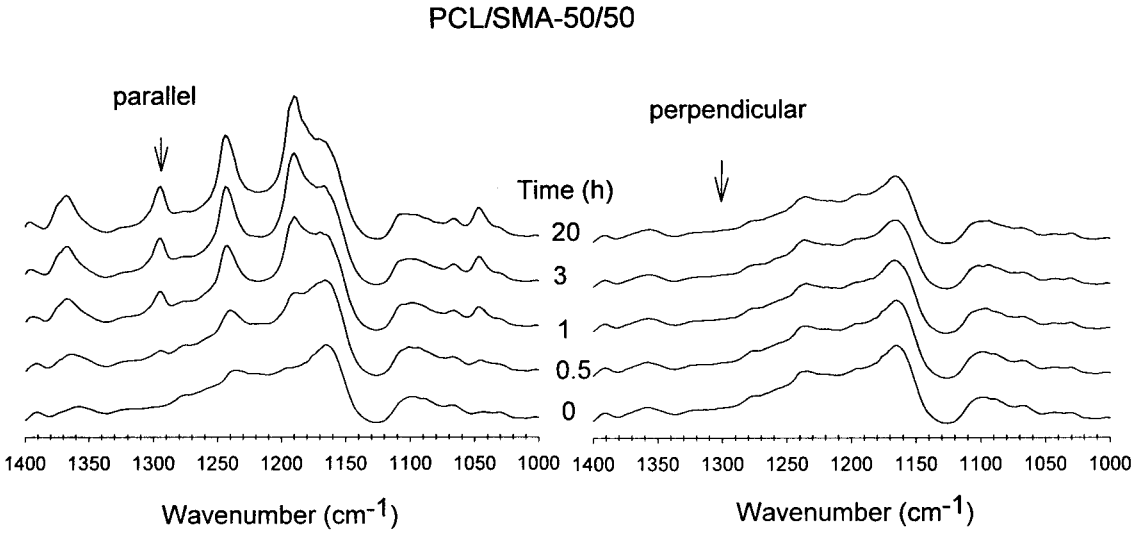

Figure 3 Polarized infrared spectra for a PCL/SMA–50/50 blend film stretched at room temperature to $\lambda = 2$ and held under strain for the indicated times. The spectra were taken with the electric vector of the infrared beam parallel and perpendicular to the strain direction.

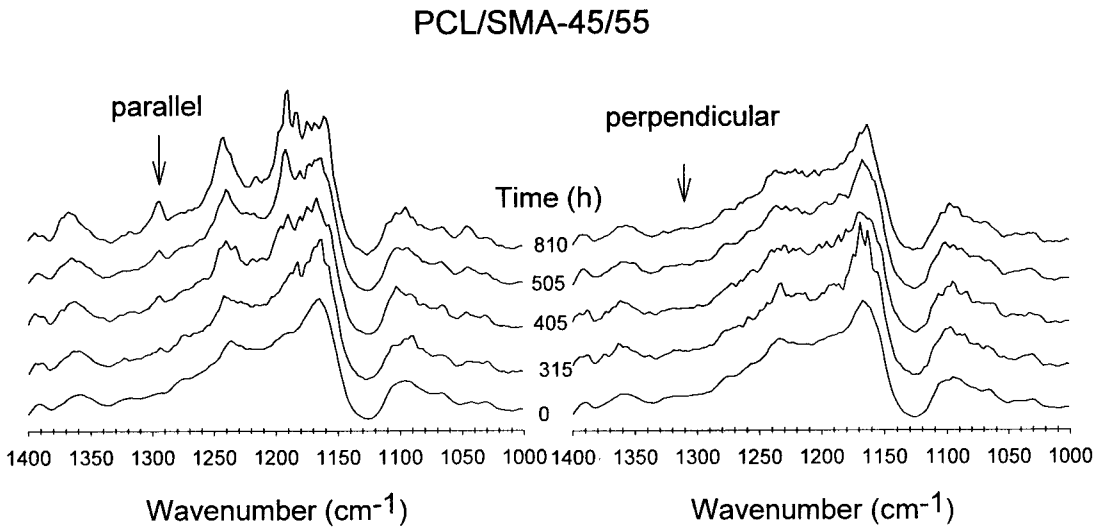

Figure 4 Polarized infrared spectra for a PCL/SMA–45/55 blend film stretched at room temperature to $\lambda = 2$ and held under strain for the indicated times.

absorbance remains close to zero, even after 20 h of crystallization. This result suggests that the crystallites of PCL formed in the blend under strain have their chain segments well aligned in the strain direction. Figure 4 shows an example for a PCL/SMA film of 45/55 composition; the spectra were also taken on a film stretched to $\lambda = 2$ with crystallization times indicated in the figure. The same above-noted observations can be made, except for the rate of crystallization of PCL, which is much lower than that in the previous PCL/SMA blend. Actually, the crystallization in this stretched film lasted more than 1 month but, even with such a slow crystallization, the formed crystallites are very well oriented.

X-ray measurements confirm the infrared results, as can be seen from Figure 5 for a film of PCL/SMA of 50/50 composition stretched to $\lambda = 4$ at room temperature. The first pattern recorded after 0.2 h under strain shows no detectable orientation (IR spectroscopy indicates that this blend is amorphous at this point). The measurement taken after 1.2 h shows two small peaks around 0 and 180°, indicating an increase in the orientation, which becomes more and more prominent with time. At the same time, IR spectroscopy as well as the development of crystallization peaks in the 2θ scans (not shown) indicate an increase in the degree of crystallinity. This result indicates that both the 110 plane and the 200 plane are perpendicular to the strain direction, as observed from measurements performed at $q = 1.68$ Å^{-1} (not shown). They indicate a perpendicular orientation for the a and b axes and, therefore, confirm that the crystalline chain (c axis) orientation is parallel to the strain direction. Furthermore, the width at half height of peak shows no significant change with time, which implies that the first crystallites formed under strain are already well oriented and, as the crystallization time increases, the amount of the oriented crystallites increases (the 2θ scans at $\alpha = 90°$ exhibit no crystallization peaks, even after 6.2 h of crystallization).

When amorphous PCL/SMA blends are stretched at room temperature (i.e., several de-

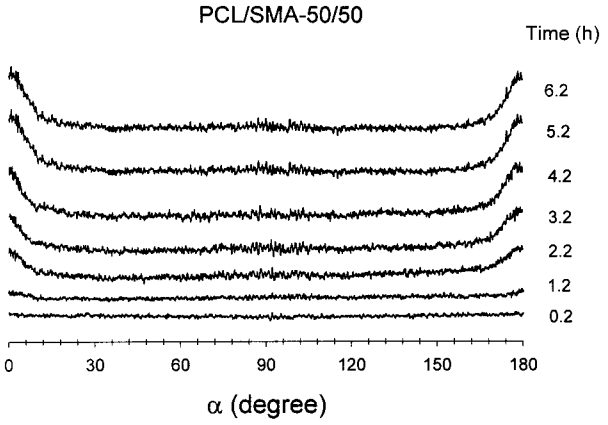

Figure 5 Scattered X-ray intensity ($q = 1.5$ Å^{-1}) as a function of azimuthal angle for a PCL/SMA–50/50 blend film stretched at room temperature to $\lambda = 4$ and held under strain for the indicated times.

grees above T_g), chain orientation of both polymers should be induced right after the stretching. Unfortunately for PCL/SMA blends, the orientation of amorphous PCL could not be quantified from infrared dichroism because the C═O band of PCL overlaps with those from the maleic anhydride units of SMA. Nevertheless, on the basis of previous studies,[7] the amorphous orientation of PCL in miscible blends after stretching is expected to be small as a result of the fast chain relaxation. The orientation of SMA, on the other hand, can be estimated from the phenyl band at 1600 cm^{-1}. At room temperature its order parameter increases with draw ratio and reaches about 0.3 at $\lambda > 5$. The subsequent crystallization of PCL under strain takes place from oriented PCL chains that interact with oriented SMA chains. In other words, the amorphous chain orientation of the two components triggers the formation of oriented crystallites of PCL. To confirm that strain-induced chain orientation is the condition required for the development of oriented crystallites of PCL, the following experiments were performed on the PCL/SMA–50/50 blend.

A series of films were stretched at 100°C to $\lambda = 2$ and $\lambda = 5$. At this high temperature, which is above the T_m of crystalline PCL (~ 45°C), no crystallization is possible whatever the draw ratio and, as compared with stretching at room temperature, much more important orientation relaxation should occur during the stretching because of the short characteristic relaxation times. After the stretching, the films were kept at 100°C for different times and, thus, different chain relaxation occurred. Furthermore, once cooled to room temperature, the crystallization was allowed to develop under two different conditions: in one series of samples, the extension was held, and in a second series of samples, the films were allowed to retract freely. For those free films, there is more chain relaxation upon the film retraction, as expected. After 10 days of crystallization at room temperature, polarized infrared spectra were taken to measure the crystalline chain orientation of PCL. The results are summarized in Figure 6 by plotting the order parameter as a function of the relaxation time at 100°C. At $\lambda = 2$, chain orientation is small in films under strain and in free films. The small number of oriented crystallites is attributed to the low chain orientation induced by stretching under those conditions (high temperature for relaxation and small film extension). In the case of films stretched to $\lambda = 5$, for which a higher chain orientation is induced by stretching, the results are different. The crystalline orientation of PCL is observed, but the order parameter is no longer close to unity, as shown in Figures 3 and 4. As can be seen, for the series of films crystallized under strain, the orientation decreases for longer relaxation times at 100°C, although a significant orientation can still be observed after 30 min of relaxation at 100°C. In contrast, a high orientation is observed in the series of free films at 100°C only for short relaxation times (<3 min). All these results are consistent with the suggestion that the formation of oriented crystallites of PCL is directly related to the chain orientation of the two components, which remained in the initially amorphous miscible blends at the time of crystallization.

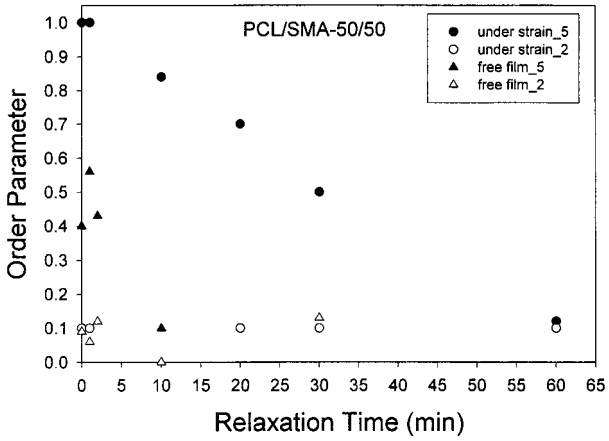

Figure 6 Order parameter as a function of relaxation time for PCL/SMA–50/50 blend films stretched to $\lambda = 2$ (open symbols) and $\lambda = 5$ (closed symbols) at 100°C. After stretching, the films were kept at 100°C for relaxation before being quenched to room temperature for crystallization either under strain (circles) or in free films (triangles).

Figure 7 shows the results of X-ray measurements for the series of films stretched to $\lambda = 5$ and allowed to crystallize under strain at room temperature. The relaxation time at 100°C, before cooling, is indicated in the figure. Similar to the infrared results, the X-ray results indicate that the crystalline chain orientation developed under strain is sensitive to amorphous chain orientation prior to crystallization (as in Fig. 5, the 2θ scans at $\alpha = 90°$ show no sign of crystallinity, whereas those at $\alpha = 0$ or 180° exhibit clear crystalline peaks at $q = 1.50$ and 1.68

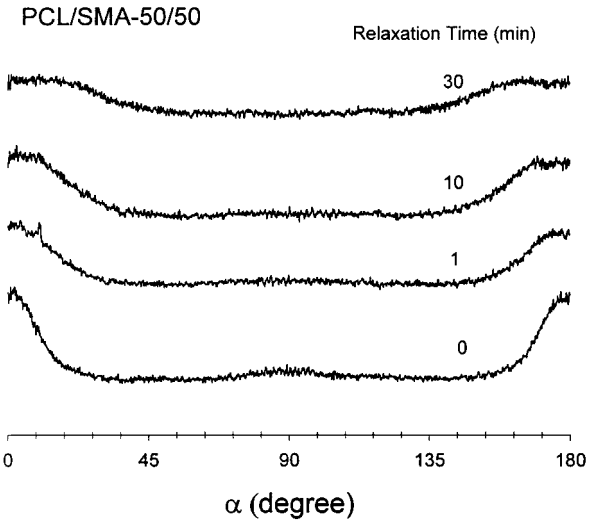

Figure 7 Scattered X-ray intensity (q = 1.5 Å^{-1}) as a function of azimuthal angle for PCL/SMA–50/50 blend films stretched to λ = 5 at 100°C and kept at this temperature for relaxation for the indicated times before being quenched to room temperature for crystallization under strain.

Å^{-1}). Judged from the broadened peaks, the crystalline orientation is smaller for longer relaxation times at 100°C. Even for the film quenched immediately after stretching at 100°C (0 min relaxation), the peaks are clearly wider than those for the film stretched at room temperature to λ = 4 (Fig. 5), which is attributed to chain relaxation during the stretching at 100°C. All these results imply that the oriented crystallites would be formed from oriented PCL chains, and that the orientation of SMA chains may also play a role in the crystallization of PCL. It is worthwhile mentioning that the X-ray technique has a higher sensitivity than does infrared dichroism for detecting differences in the crystalline chain orientation of PCL. In Figure 7, the difference between the two films kept at 100°C for 0 and 1 min is clear, whereas the infrared dichroism does not enable this difference to be measured within experimental error.

The preceding results show that the behavior of crystalline chain orientation of PCL in stretched blends can be either parallel or perpendicular to the stretching direction. In PCL/PVC blends, it can be one or the other, whereas in PCL/SMA blends, it is always parallel. The question is how to explain these different behaviors. In both systems, there is miscibility between the two blend components, which is responsible for the reduced rate of crystallization of PCL. Also, the orientations of the two amorphous components right after stretching are similar, showing a low orientation of PCL and a higher orientation of PVC or SMA. However, the specific intermolecular interactions accounting for the miscibility between PCL and PVC, and PCL and SMA, can be different. The miscibility of the PCL/SMA blend seems to be not as good as that in the PCL/PVC blend. A qualitative indication is given by the ease with which the crystallization of PCL can be induced during the stretching process at room temperature. In the case of PCL/PVC blends, the strain-induced crystallization was detected only for blends containing less than 40% of PVC and this only under high film extensions. By contrast, for the PCL/SMA blend, if the concentration of SMA is below 50%, a modest draw ratio can readily lead to crystallization of PCL in the course of the film stretching and result in parallel chain orientation. As greater miscibility is generally promoted by stronger intermolecular interactions acting between the two components, the specific interactions between PCL and PVC may play a role in the mechanism, leading to perpendicular crystalline chain orientation. More studies are under way to understand the crystallization mechanisms of PCL in stretched miscible blends.

CONCLUSIONS

The crystalline chain orientation of PCL resulting from crystallization under strain is different in PCL/SMA and PCL/PVC blends. In contrast to PCL/PVC, for which the developed orientation can be either parallel or perpendicular to the strain direction, in PCL/SMA the orientation is always parallel, whatever the conditions used. For PCL/SMA films stretched at room temperature, even with a very slow rate of crystallization, the increase in the degree of crystallinity is accompanied by a high and almost constant chain orientation, suggesting that well-oriented crystallites are formed during the whole crystallization process. However, if the strain-induced chain orientation of the amorphous blend is allowed to relax at high temperatures before the crystallization under strain, the developed crystalline chain orientation decreases.

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