Communications to the Editor

Dual Growth Rates and Morphologies of Isothermally Crystallized Miscible Polymer Blends

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The study of the crystallization of semicrystalline polymers can be considered as a mature field. According to the secondary nucleation theory, the temperature dependence of the polymer growth rate can be expressed by two exponential functions: one expressing the nucleation rate with its characteristic activation energy and the other the transport of molecular segments to the crystallization sites.[1,2] The convolution of these two functions gives a bell-shaped temperature dependence for the growth rate that has been observed for a large number of polymers.[3,4]

Growth rates are often measured by following the radial expansion of spherulites in the melt. In the case of an A/B miscible polymer blend where A is semicrystalline and B amorphous, it is well-known that the growth rate of A decreases with the addition of B.[5] In fact, at a given temperature, the decrease is directly proportional to the reduction in concentration of A in the mixture and is further decreased by an additional entropy contribution due to the presence of B.[5,6] However, the growth rate of A in an A/B miscible polymer blend follows essentially the same temperature dependence as in pure A.

Here, we report, two distinct growth rates in the same sample of a miscible blend of crystallizable polycaprolactone (PCL) and amorphous poly(vinyl chloride) (PVC) crystallized at constant temperature. This unexpected behavior was observed in thick films of the order of several microns for the blend but not for pure PCL. Different morphologies are also associated with the two types of observed spherulites.

PCL and PVC were purchased from Aldrich Chemicals and were used without further purification. The glass transition temperatures of PCL and PVC were found at −60 and 80 °C, respectively, using a Perkin-Elmer DSC-7 calorimeter at a heating rate of 20 °C/min. The melting point of PCL was found at 60 °C. To prepare films, pure PCL, or PCL/PVC mixtures, were dissolved in tetrahydrofuran for at least 24 h, at room temperature, in the absence of light. Polymer solutions, with concentrations adjusted to the thickness desired, were poured into Petri dishes in which microscope cover glasses lie flat. The solvent was slowly evaporated for at least 5 days. The cover glasses, on which a thick polymer film was deposited, were then carefully removed from the Petri dishes.

A Zeiss Axioscop polarizing microscope was used to follow the growth of the spherulites, using a Linkam THMS600 hotstage, temperature controller, and cooling unit. Microphotographs were recorded with a Toshiba HV-D27 3CCD camera and analyzed with the Image Pro Plus 4.0 software. Samples were melted at 100 °C for 10 min under a nitrogen atmosphere—no coverslip was added on top of the polymer films—and, then, cooled at a rate of 50 °C/min to the crystallization temperature (which was held constant to within ±0.1 °C). Each sample was used only once, at one crystallization temperature. For each sample, the surface of several spherulites, observed in bright field, was measured with the Image Pro Plus 4.0 software, for at least 20 microphotographs taken at regular time intervals before impingement. From these surfaces, an average radius was calculated assuming a circular geometry. The radius was then plotted as a function of time, and the slope of these straight lines was calculated: this is the average radial growth rate. Bright field and polarized light (crossed polars) microscopies were used to make morphological observations, during and after isothermal crystallization.

Bright field optical microphotographs of two neighboring spherulites that develop at different growth rates and with different morphologies are shown in Figure 1. By adjusting the focus, it was observed that these two spherulites nucleated and developed in the 30 μm film at different depths: one near the air−polymer interface (film surface), labeled S-spherulites, and one in the core of the film, labeled C-spherulites. From bright field microphotographs, such as those shown in Figure 1A,B, radial growth rates can be measured. As an example, Figure 2 plots the radius of the two spherulites of Figure 1 as a function of time. In both cases, there is a linear increase of the radius with time for a period of more than 18 h (at 40 °C), with high correlation coefficients, as is usually observed for spherulitic crystallization.

For this blend containing 60% PCL and 40% PVC, it is calculated from Figure 2 that the S-spherulites grow at a rate of 0.67 nm/s (±0.04) and the C-spherulites at a rate of 0.26 nm/s (±0.02), a difference by a factor of 2.5. All spherulites observed in the sample are either S-type or C-type, meaning that they exhibit, within experimental error, one of the two growth rates reported above and one of the two morphologies described below. We never found spherulites having an intermediate growth rate.

Morphological differences between the two types of spherulites can also be detected in Figure 2. In bright field, the C-spherulites show a tight structure whereas the S-spherulites show an open structure[7] with clearly visible large fibrils. The third microphotograph, Figure 1C, which was taken between crossed polars just a few

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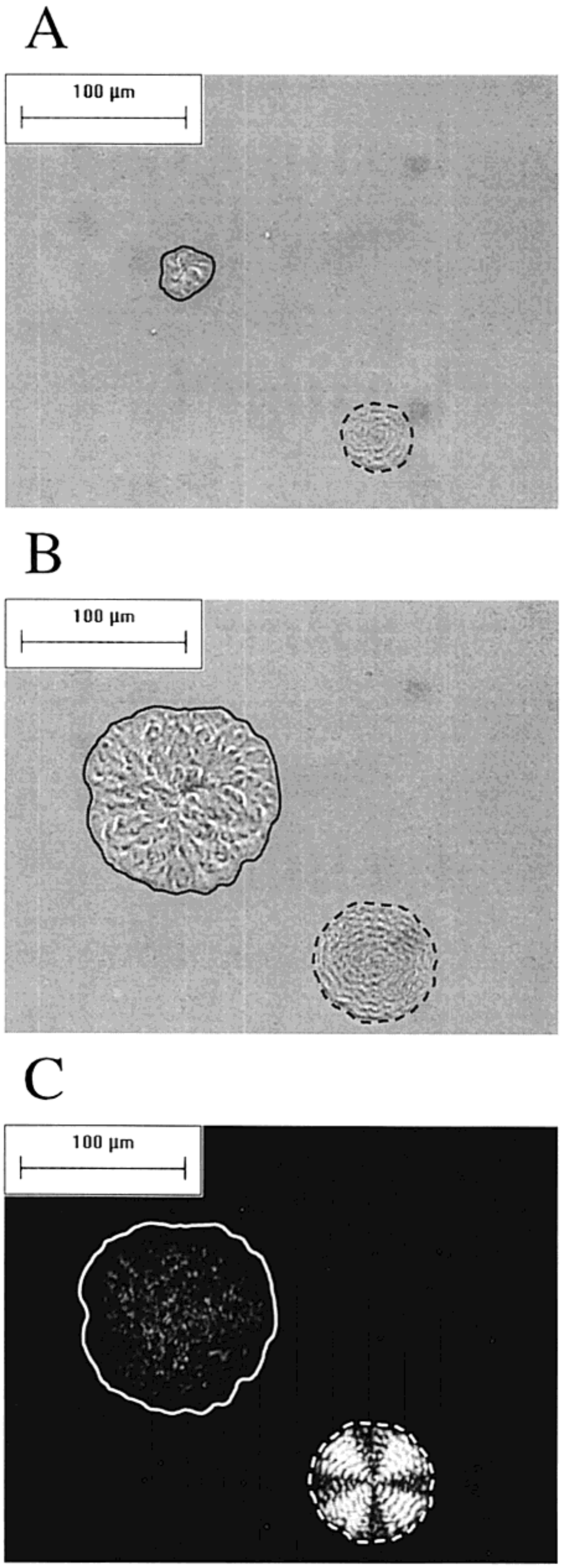

Figure 1. Microphotographs of S-type (circled by a full line) and C-type (circled by a dotted line) spherulites in a 30 μm thick film of a 60/40 PCL/PVC blend, at a crystallization temperature of 40 °C. (A) Bright field image taken at 30.85 h with a S-spherulite of 32 μm in diameter and a C-spherulite of 44 μm in diameter. (B) Bright field image taken at the same position as (A) 18 h later; the S-spherulite now has a diameter of 121 μm and the C-spherulite one of 74 μm. (C) Image taken between crossed polars at the same position as (B) a few seconds later. The S- and C-spherulites do not exhibit the same birefringent pattern.

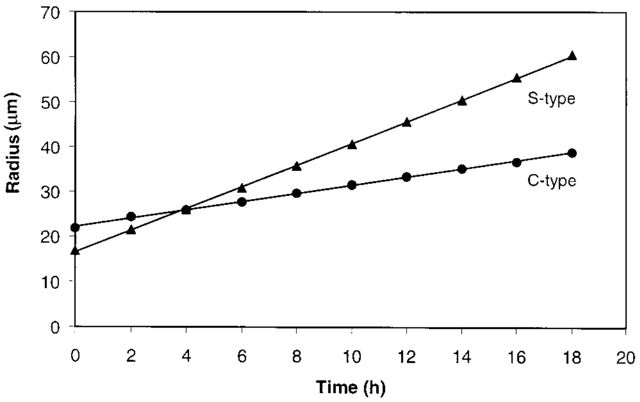

Figure 2. Radius of the S- and C-spherulites shown in Figure 1 as a function of the time of crystallization (shown respectively by triangles and disks). Same crystallization conditions as in Figure 1. Each data point was extracted from bright field optical microphotographs taken at 2 h intervals. Correlation coefficients greater than 0.999 were obtained, illustrating the linearity of the process. The growth rate is the slope of these lines.

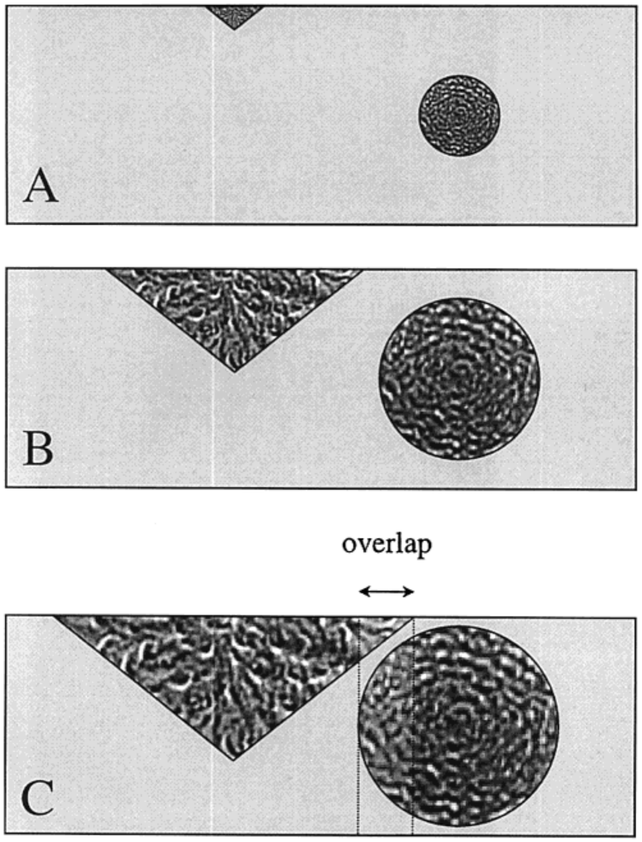

Figure 3. Schematic diagram of the crystallization process observed for PCL/PVC blends. The top surface of the film corresponds to the air−polymer surface, which is enriched in PCL as compared to the bulk composition of the film and where the S-spherulites (triangle) nucleate: (A) beginning of the crystallization, (B) intermediate crystallization stage, (C) overlapping stage where the microphotographs show a superposition of the two types of spherulites. The motif in the triangles (S-spherulites) and disks (C-spherulites) indicates the occurrence of different morphologies as observed by the bright field optical microphotographs.

seconds after recording Figure 1B, at the same position on the polymer film, gives information about the organization of the spherulites. The C-spherulites exhibit the classical banded Maltese cross pattern observed

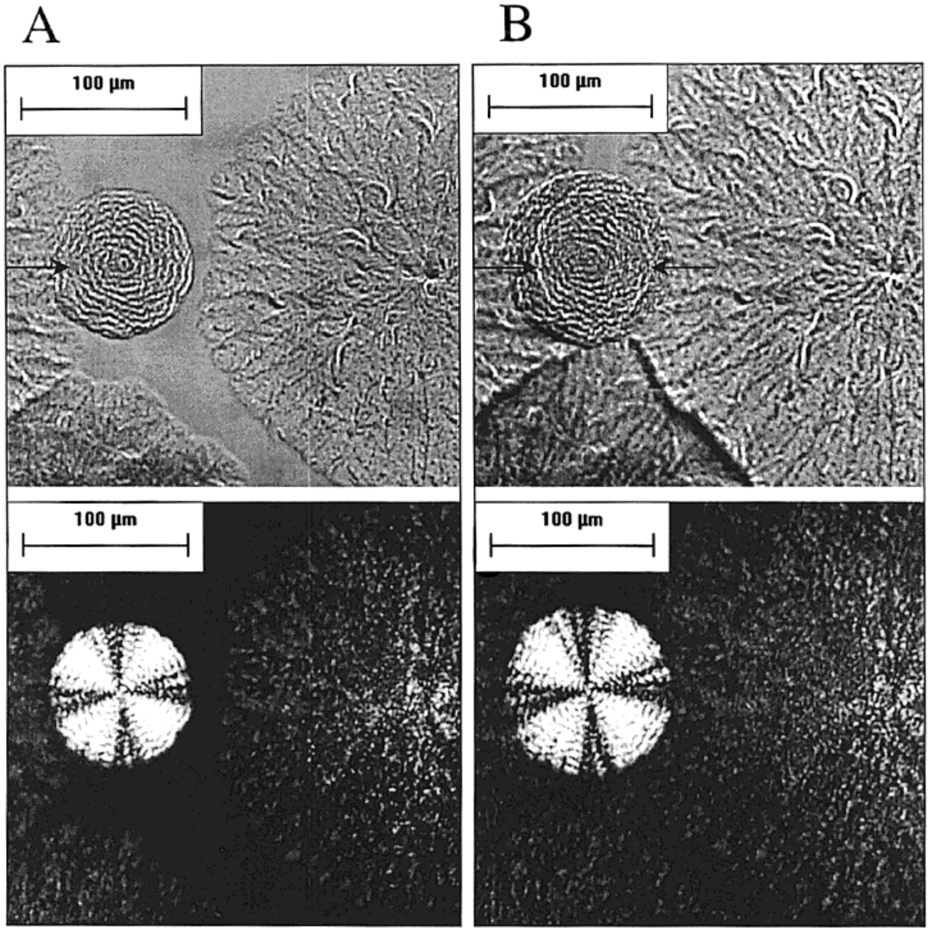

Figure 4. Microphotographs of an ensemble of S- and C-type spherulites. (A) Bright field and crossed polar images taken at 81.17 h at the same position. A slight overlap, highlighted by an arrow, can be detected on the left-hand side of the bright field image between the C-spherulite and one of the S-spherulites. (B) Bright field and crossed polar images taken 11.25 h later at the same position as (A). The overlap area has increased on the left-hand side of the C-spherulite and is now visible also on the right-hand side (arrows). Images under crossed polars reveal clearly the edges of the C-spherulite below the S-spherulites.

before in the literature for the PCL/PVC blends as well as for many other polymer blends and homopolymers.[8−11] The S-spherulites[12] exhibit a more diffuse and less birefringent pattern, indicating a much less organized structure.

It is emphasized that all S-spherulites are found to nucleate at the air−polymer surface and all C-spherulites in the core of the sample. This phenomenon can be correlated with observations made by Clark et al.,[13,14] who have reported a PCL surface enrichment (at the air−polymer interface) in PCL/PVC blends. We made similar observations using X-ray photoelectron spectroscopy on the same samples as used here.[15] This enrichment explains, at least in part, the development of faster growing spherulites at the surface than in the core, given that the surface of the film is enriched in PCL, and therefore, the dilution effect of the PVC component is less than it is in the core.

Figure 3 shows a schematic diagram modeling the development of the two types of spherulites observed. The cross-section representation highlights the fact that the two types of spherulites nucleate in two different regions of the film, at the air−polymer surface for the S-spherulites and in the core for the C-spherulites. Lamellae are shown to grow in three dimensions at the surface of the S-spherulites. In the *xy* plane of the film, where the microscopy observations are made and the growth rate measured, the growth is fast. However, in the *z* direction, the crystallizing front quickly meets the core of the film, where there is no PCL enrichment, and the growth rate presumably decreases to reach that of the C-spherulites. The faster growth rate of the lamellae that develop at the surface (as compared to those developing in the *z* direction) is likely to give a conic shape to the S-spherulites and a more or less triangular cross section as represented in Figure 3. However, Figure 1C shows clearly that the peculiar morphology of the S-spherulites is preserved at all times, even when the crystallization proceeds, at larger times, in the core of the sample. Similarly, the regular morphology of the C-spherulites, expressed in Figure 1C by the Maltese cross pattern, is preserved at all times; i.e., there is no indication of a different morphology when its crystallizing front reaches the surface of the sample. This latter observation can merely be the result of the thin enriched layer at the surface of the sample in comparison with the size of the observed spherulite. The morphological behavior of the S-spherulites is not well understood at this time and is still under study.

If the above-mentioned process involving the growth of spherical C-spherulites and conic-shaped S-spherulites is correct, it should be possible for C-spherulites to grow below S-spherulites, as shown schematically in Figure 3C, since the melted polymer is still present below the thin crystallized layer of the edges of the S-spherulites. As an illustration of this phenomenon, Figure 4 presents four microphotographs, two recorded in bright field and two others between crossed polars, all taken at the same position of the sample. The first pair (Figure 4A) shows a slight overlap on the left-hand side of the C-spherulite (highlighted by an arrow). The second pair (Figure 4B), taken 11.25 h later, shows that the C-spherulite is now growing below its three neighboring S-spherulites. The overlaps between the C-spherulite and the two larger S-spherulites growing on the left- and right-hand side are clearly visible (arrows) in real observations—and less clear in static pictures such as those of Figure 4—where the focus plane of the objective can be changed to detect which is above and which is below and where, using the software available, a sequence of pictures can be run. The concave shape of the growth fronts of the S-spherulites on top of the C-spherulite indicates that the C-spherulite has reached the surface and stopped any further growth of the S-spherulites on the surface. Crossed polar microscopy confirms that the C-spherulite develops below the S-spherulites since the characteristic Maltese cross pattern grows from Figure 4A to Figure 4B, and the C-spherulite keeps its circular outline in Figure 4B, which never occurs when two "classical" spherulites meet. It was noted that the growth of C-spherulites below S-spherulites eventually stops as the spherical C-spherulites meet the conic S-spherulites (but the S-spherulites continue to grow in other directions), leading to a fully crystallized sample in which there are C-spherulites dispersed into a matrix of S-spherulites.

Several of these blend samples were analyzed by X-ray diffraction, and the peaks observed correspond to those reported by Chatani et al.[16] for the orthorhombic structure of PCL, in complete agreement with those observed in a pure PCL sample. Similarly, DSC measurements exhibit only one melting peak, assigned to the melting of PCL. This peak is, however, shifted to lower temperatures by about 10 °C as compared to that of pure PCL due to the dilution effect brought by the presence of PVC, as it is well documented in the literature.[5] These two observations rule out the presence of a different crystalline form of PCL. Moreover, in a pure PCL sample, where a surface enrichment is not possible, all spherulites are C-spherulites.[15]

In summary, in thick films of PCL/PVC blends of 60/40 composition, we have shown that two well-defined families of spherulites exist. In a given sample, at a controlled temperature, two different growth rates are observed. Each of these spherulites exhibits a distinct morphology, one type located at the surface (showing a low birefringence) and the other in the core of the sample (with the classical Maltese cross pattern). Similar observations were made for other compositions of the same blend and other temperatures of crystallization. It appears that the initial morphology of the spherulite, once initiated, can propagate without disturbance. For example, the S-type spherulites retain their morphology even after leaving the surface of the sample when propagating in the z direction of the sample. Studies are being pursued to clarify this phenomenon.

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