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Epitaxial Crystallization in Mixtures of Optically Active Polyesters

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Introduction

Mixtures of optically active polyesters often lead to the formation of stable complexes in the presence of isotactic polymers of opposite configuration.[1−7] Such stereocomplexes exhibit a crystal structure which is different from that of their pure components. In the case of poly(α-methyl-α-ethyl-β-propiolactone) (PMEPL), whose repeat unit is $-(-CH_2-C(CH_3)(C_2H_5)-COO-)_n-$, the stereocomplex exhibits an orthorhombic unit cell composed of a mixture of left- and right-handed helices.[8,9] In comparison, isotactic PMEPL exhibits two distinct crystal modifications depending on its mode of preparation: an extended chain or all-trans conformation, hereafter called PMEPL-t, favored by melt crystallization,[9] and the energetically preferred and expected 2_1 helical conformation,[10] hereafter called PMEPL-h, and favored by solution casting.[8] Its helical handedness is imposed by the absolute configuration of the chiral center: the *R* configuration gives the left-handed helix, whereas the *S* configuration is associated with the right-handed helix.[8]

In the case of isotactic poly(α-methyl-α-*n*-propyl-β-propiolactone) (PMPPL), where the ethyl group has been replaced by an *n*-propyl group, crystallization gives a 2_1 helix from both modes of preparation (melt crystallization and solution casting). It also gives a stereocomplex with the mixture of the two polymers of opposite configuration. The orthorhombic unit cell of this isotactic polyester is very similar to that of PMEPL.[9] Since there is a difference of only a methylene group between the chemical structure of PMEPL and PMPPL, and since their crystal structures are very similar, isodimorphism could be expected, as has been reported with poly(β-hydroxybutyrate-*co*-hydroxyvalerate);[11] depending on composition, these random copolymers crystallize in either the β-hydroxybutyrate or the β-hydroxyvalerate lattice. Indeed, solid state ^{13}C NMR spectroscopy and X-ray diagrams of PMEPL/PMPPL mixtures, reported by Ritcey and Prud'homme,[12] show that isotactic PMEPL in the presence of a PMPPL of opposite configuration crystallizes from the melt in a helical conformation and, in the presence of a PMPPL of the same configuration, crystallizes from the melt in the all-trans conformation.

In order to explain the origin of the helical conformation of PMEPL from the melt, two possible mechanisms have been proposed. The first implies that PMEPL crystallizes epitaxially on lamellae of PMPPL; the second involves a cocrystallization of the two polyesters to form a single crystalline phase incorporating helices of both PMEPL and PMPPL. Differential scanning calorimetry (DSC) measurements are reported in this article and permit us to distinguish between these two possibilities.

Experimental Section

Isotactic PMEPL's of *R* (PMEPL(*R*), o.p. = 97%, M_n = 50 000) and *S* (PMEPL(*S*), o.p. = 99%, M_n = 50 000) configurations were prepared by Grenier and al.[13] Isotactic PMPPL of an *R* configuration (PMPPL(*R*), o.p. = 100%, M_n = 50 000) was synthesized in our laboratory by Ambeault.[14] Mixtures containing 50 wt % PMPPL(*R*) were prepared. Samples were initially cast at room temperature from hexafluoro-2-propanol solutions, which is the only known solvent for these polymers.

DSC measurements were conducted with a Perkin-Elmer DSC-4 apparatus calibrated with pure indium. The samples were scanned for the first time (from solution), melted at 180 °C for 5 min, cooled to 80 °C, and scanned again. Heating and cooling rates of 40, 30, 20, 10, 5, 3, and 1 °C/min were investigated, but unless indicated otherwise, all data reported in this article refer to 20 °/min heating and cooling rates. The melting and crystallization temperatures were recorded at the peak extrema, due to the difficulties associated with the location of the onset temperatures.[15]

Results and Discussion

The melting temperatures of the three pure isotactic polyesters, PMEPL-t (prepared from the melt), PMEPL-h (prepared from solution), and PMPPL, were recorded at several heating rates. At a rate of 20 °C/min, as shown schematically in Figure 1, the melting temperature of PMEPL-t (149.8 °C) is found to be 6.0 deg above that of PMEPL-h (143.8 °C), despite the fact that the all-trans conformation is unfavored.[10] In comparison, there is a slight difference of 4.6 deg between the melting temperatures of PMEPL-h and PMPPL (148.4 °C), both in the helical form, which is consistent with the similarity of their unit cell structure.

The crystallization temperatures of these two polyesters are found at, respectively, 119.5 and 104.0 °C, with a difference of 15 deg (N.B.: the two PMEPL samples, prepared from solution or from the melt, give the same crystallization temperature because the all-trans conformation is the sole PMEPL conformation obtained from the melt). Upon subsequent melting, the PMEPL peak occurs at 150 ± 1 °C, confirming that this polymer is in the all-trans conformation, in agreement with NMR and X-ray results.[12]

After solution casting, as given in Figure 2, the DSC melting curve of a mixture containing 50% of PMEPL and PMPPL, both having the same configuration, *R*, shows three overlapped peaks with three maxima at 144.2, 147.9, and 152.7 °C (reported schematically in Figure 1), corresponding, respectively, to the melting temperatures of PMEPL-h, PMPPL, and PMEPL-t, the last peak being less intense than the other ones. The presence, from solution casting, of the two helicoidal structures was expected, but not the all-trans conformation. This point is noted but remains unexplained at this moment. Subsequent scans give a single peak at 149.2 °C (Figure 1), without any shoulder, a temperature intermediate between those of PMEPL-t and PMPPL; the absence of a PMEPL-h peak, at lower temperatures, is noteworthy. It must be noted that measurements made at lower (1, 3, 5, and 10 °C/min) and higher (30 and 40 °C/min) scanning rates also give the three peaks reported in Figure 2, at roughly the same positions. Therefore, we excluded the possibility that the 152.7 °C peak could be due to melting/recrystallization processes and assigned it to the presence of PMEPL-t even if it is slightly shifted as compared to that found for a PMEPL crystallized from the melt (Figure 2, top curve).

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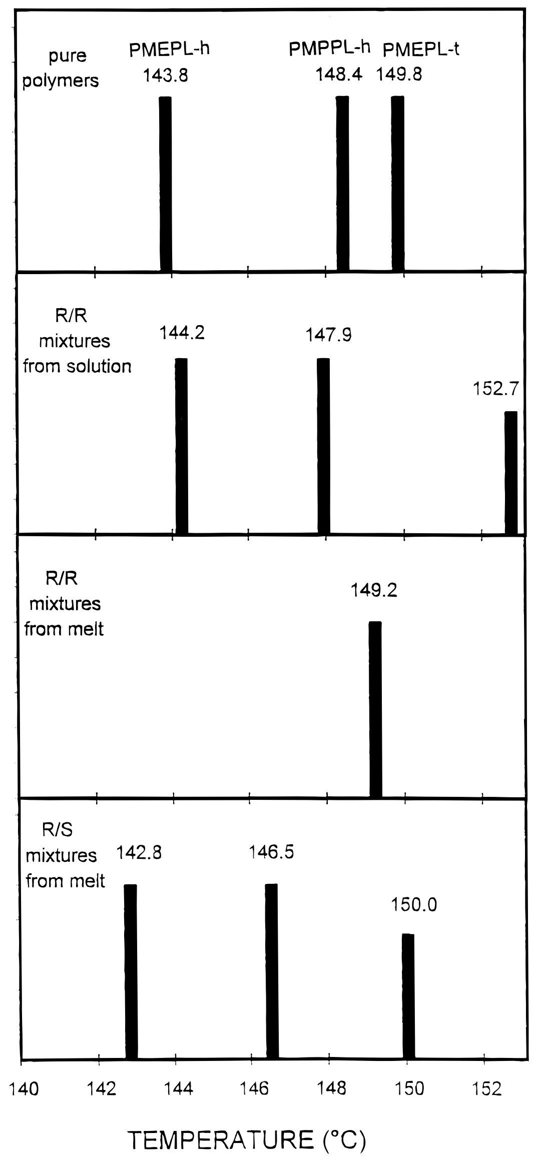

Figure 1. Temperature scale established from the DSC melting curves recorded at scanning rates of 20 °C/min. The melting points measured (at the maximum of the peaks) for pure PMEPL-h (solution), PMEPL-t (melt), and PMPPL are given in the top frame for reference. Values for *R*/*R* mixtures prepared from solution, for *R*/*R* mixtures prepared from the melt, and for *R*/*S* mixtures prepared from the melt are given in the following frames, from top to bottom.

Upon cooling, two distinct peaks are observed at 108.0 and 112.5 °C, temperatures which are between those found for the pure isotactic polyesters. In order to verify that the high-temperature peak corresponds to the PMEPL(*R*) crystallization, the mixture was cooled to 117 °C, which corresponds to the onset of the crystallization of the high-temperature peak, kept there for 1 min, and remelted. The resulting melting temperature, 149.8 °C, is found to be equal to the PMEPL-t melting temperature. This observation confirms that the two polymers possessing the same configuration crystallize separately. ^{13}C NMR and X-ray diffraction results corroborate this conclusion, since spectra of the mixture are the sum of the spectra of the two polyesters taken separately.[12] It is noted that, in this mixture, the dilution of PMEPL(*R*) by PMPPL(*R*) leads to a decrease of the PMEPL(*R)* crystallization temperature whereas the presence of PMEPL(*R*) crystals leads to an increase of the PMPPL(*R*) crystallization temperature.

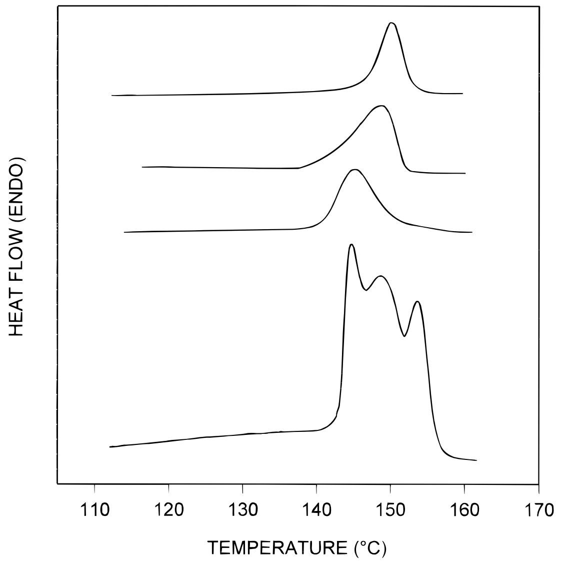

Figure 2. From top to bottom, DSC curves, obtained at 20 °C/min, for PMEPL-t (melt), PMPPL, PMEPL-h (solution), and a 50/50 mixture of PMEPL(*R*) and PMPPL(*R*).

^{13}C NMR and X-ray spectra of 50/50 mixtures prepared from the melt of the two polyesters with opposite configurations reveal the presence of PMEPL(*S*) and PMPPL(*R*), both in the helical form. A third component was reported but not identified.[12] The corresponding DSC curve shows a broad melting peak with two shoulders; there is obviously an extensive overlap between the melting curves of the three species present. The derivative of this curve gives three peaks located at 142.8, 146.5, and 150.0 °C (minor peak). A comparison between the position of these peaks with those of the pure polymers, as shown schematically in Figure 1, indicates the presence in the mixture of the two PMEPL conformations, PMEPL-t and PMEPL-h, in addition to PMPPL. The occurrence of PMEPL in the helical form at 142.8 °C should be emphasized since the crystallization of isotactic PMEPL from the melt does not give this structure nor the crystallization of a mixture of PMEPL(*R*) and PMPPL(*R*), as seen in the previous paragraph, but PMEPL in the extended chain conformation. Despite the overlap between peaks, the amount of the helicoidal form is observed to be more important than that of the trans form. It should be noted that DSC melting curves of mixtures prepared from solution casting were not reproducible, probably because traces of solvent were trapped in the crystals. Finally, the cooling curve of this mixture exhibits two poorly resolved peaks, whose maxima occur at 113.0 and 115.5 °C, slightly shifted upward as compared to the peaks found for the PMEPL(*R*)/PMPPL(*R*) mixture. The fact that ($T_f - T_c$) [T_f is the maximum of the melting curve and T_c the maximum of the crystallization curve found under the 20 °C/min conditions used here] equals 33.5 °C for this mixture whereas it equals 27.3 °C for PMEPL-h could be taken as an indication that there are interactions in the mixtures, between PMEPL and PMPPL, if this difference can be considered as significant in view of the rapid scanning rates used here.

DSC curves then confirm (Figure 1), for a broad range of cooling rates, i.e., 1, 3, 5, 20, 30, and 40 °C/min, that PMEPL-h is the predominant structure when a mixture of PMEPL(*S*) and PMPPL(*R*) is crystallized from the melt. Because of the indentification of this PMEPL-h structure, we can exclude one of the two hypotheses mentioned before from ^{13}C NMR and X-ray analyses,[12]

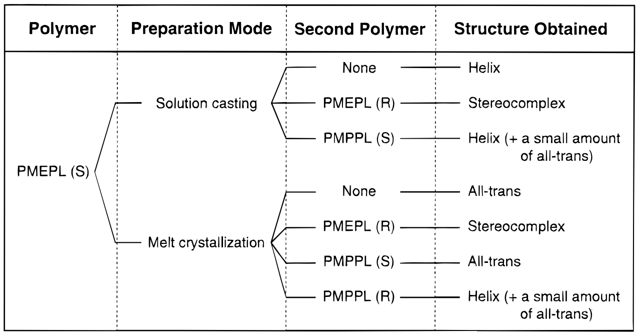

Figure 3. Summary of the different conformations generated by a combination of PMEPL with PMEPL or PMPPL of different configurations, taking into account the effect of crystallization conditions (melt or solution).

i.e., that there is formation of a PMEPL(*S*)/PMEPL(*R*) mixed stereocomplex. A small peak of PMEPL-t, the third unidentified component of the previous study,[12] has also been found.

The presence of a polyester of opposite configuration is then found to have a profound influence on the crystallization of PMEPL. Alone, or even in the presence of PMPPL of the same configuration, it crystallizes from the melt in the all-trans conformation (Figure 3). However, in the presence of PMEPL of opposite configuration, it gives a stereocomplex where chains are in the helical conformation[8,9] whereas, in the presence of PMPPL of opposite configuration, it also crystallizes in the helical conformation (Figure 3), but without the formation of a stereocomplex. How can PMPPL induce this change in crystallization behavior? It can be by strong interactions in the melt or by epitaxy. We believe that strong interactions would lead to the formation of a stereocomplex where the packing of right- and left-handed helices gives a compact structure having a high melting temperature, as it does between PMEPL(*R*) and PMEPL(*S*) chains. Weaker interactions lead to the separate crystallization of the molecules involved, i.e., a mixture of PMEPL and PMPPL of similar configuration where PMEPL is found in the same all-trans crystalline conformation as in the absence of PMPPL. However, in the case of the mixture of PMEPL and PMPPL of opposite configurations, PMPPL has an unquestionable influence on the crystallization of PMEPL, since it results in its crystallization in a different conformation, as normally observed for PMEPL crystallized from the melt. This influence is related to the fact that the crystallization curves of PMEPL and PMPPL, while apart by 15 deg when crystallized separately, are brought close to each other when crystallized together (Figure 1). In other words, in such a mixture, the formation of PMEPL crystals, presumably in the all-trans form, leads to the crystallization of PMPPL at high temperatures (as compared to the situation in the absence of PMEPL (Figure 1)) in its usual helical conformation, and the presence of helicoidal PMPPL crystals drives the crystallization of PMEPL in helical conformation by a mechanism which appears to be epitaxy in view of the similarity of the crystal structures of PMEPL-h and PMPPL. This model then accounts for the small amount of PMEPL-t found here and from previous measurements.[12] The same phenomenon does not occur during the crystallization of PMEPL and PMPPL of similar configurations because, presumably, efficient epitaxial interactions require chains of different handeness.

Our findings can then be summarized as follows (Figure 3). Alone, isotactic PMEPL crystallizes in the helical form from solution, and in the all-trans conformation from the melt. In the presence of PMEPL chains of opposite configurations, it gives a stereocomplex. In the presence of PMPPL chains of the same configuration, it gives mainly the all-trans conformation from the melt. However, in the presence of PMPPL chains of opposite configurations, its crystallization is modified by epitaxy to give mainly a helical conformation.

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