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Crystallization in Mixtures of Optically Active Polyesters

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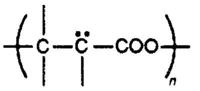
ABSTRACT: Melt-crystallized mixtures of isotactic poly(α-methyl-α-ethyl-β-propiolactone) (PMEPL) and isotactic poly(α-methyl-α-*n*-propyl-β-propiolactone) (PMPPL) are examined by solid-state ^{13}C nuclear magnetic resonance spectroscopy (NMR) and X-ray diffraction. These techniques reveal that, in such blends, the conformation and crystal structure found for isotactic PMEPL of a given chirality depend on the configuration of the PMPPL present. In samples containing PMEPL and PMPPL of the *same* configuration, the two polymers crystallize independently, to give forms identical to those obtained by melt crystallization in the pure states, i.e. PMPPL crystallizes as a helix whereas PMEPL adopts a planar zigzag conformation. In contrast, when blended with PMPPL of *opposite* configuration, isotactic PMEPL also crystallizes from the melt as a helix. Isotactic PMPPL crystallizes in the same conformation and crystal form in the two blends.

Introduction

Several optically active polyesters, including substituted poly(β-propiolactones)[1–5] and poly(lactides),[6–8] give rise to the formation of stereocomplexes. In these systems, blends composed of the isotactic polymers of opposite configuration crystallize in a form distinctly different from that found for each of the individual isotactic components. In the case of poly(α-methyl-α-ethyl-β-propiolactone) (PMEPL), the two crystal structures differ not only in packing but also in polymer conformation.[4] The stereocomplex is found to be composed of a mixture of left and right helices, where pure isotactic PMEPL crystallizes from the melt as a planar zigzag.

A variety of poly(β-alkanoates), including poly(pivalolactone),[9] poly(β-hydroxyvalerate),[10] and poly(β-hydroxybutyrate),[11] have been found to share a common 2_1 helical conformation, characterized by a fiber repeat distance of 6 Å. These polyesters are all based on the backbone which can be designated as



$$\left(\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{\ddot{C}}}-COO\right)_n$$

but differ in the nature of the substituents present at the α- or β-carbon. The same molecular conformation can accommodate variations in the size of the lateral groups because these substituents are disposed around the exterior of the backbone helix.[12] The similarity of polymer conformation exhibited within this family of polyesters is further manifested as isodimorphism in poly(β-hydroxybutyrate-*co*-hydroxyvalerate).[13] Depending on composition, these random copolymers crystallize in either the β-hydroxybutyrate or the β-hydroxyvalerate lattice. At all compositions, however, crystallinity remains high as each crystalline phase can accept the repeat unit of the other monomer as part of its organized structure.

The observations summarized above suggest that it may also be possible to incorporate variations in lateral substituents in the crystal lattice of a stereocomplex. This possibility is addressed in the present study of blends containing isotactic PMEPL and isotactic poly(α-methyl-α-*n*-propyl-β-propiolactone) (PMPPL).

Experimental Section

Isotactic PMEPL (MW 50 000) was prepared and characterized by Grenier et al.[14] The *R* and *S* isomers used in the present study have optical purities of 97 and 99%, respectively. Isotactic PMPPL of configuration *R* (optical purity 100%, MW 55 000) was synthesized in our laboratory by Ambeault.[15] Since isotactic PMEPL and isotactic PMPPL are both optically active, two distinct equimolar mixtures, differing in the relative configuration of the two components, can be prepared from these polymers. The results presented below concern two such mixtures. The first, denoted PMEPL(*R*)/PMPPL(*R*), is composed of PMEPL and PMPPL both of configuration *R*, and the second, denoted PMEPL(*S*)/PMPPL(*R*), contains the two polyesters of opposite configuration.

All samples were initially prepared as films cast from solution in hexafluoro-2-propanol. These films were subsequently heated, under vacuum, to temperatures 20 °C above the melting point, followed by cooling at 1–3 °C/min.

Solid-state ^{13}C CP/MAS NMR spectra were recorded with a 75-MHz Chemagnetics spectrometer. The standard pulse sequence for cross polarization with bilevel dipolar decoupling was employed with a contact time and recycle delay of 1 ms and 3 s, respectively. Chemical shifts were referenced to hexamethylbenzene at 17.4 ppm.

X-ray diffraction powder patterns were recorded with a Rigaku Model RU200 rotating anode generator. Diffraction angles reported are for Cu Kα radiation.

Differential scanning calorimetry (DSC) thermograms were obtained with a Perkin-Elmer DSC 4 operated at heating and cooling rates of 20 °C.

Results and Discussion

Solid-State ^{13}C NMR Spectra. The solid-state ^{13}C NMR spectra of two equimolar blends of isotactic PMEPL and isotactic PMPPL are shown in Figures 2a and 3a. Although these two blends are identical except for the relative configuration of the two components, significant differences are evident between the spectra.

In the case of the blend containing PMEPL and PMPPL of configuration *R* (Figure 1a), all resonances can be easily identified by direct comparison to the spectra of the individual components (Figure 1b,c). As summarized in Table I, the resonances of melt-crystallized isotactic PMEPL and PMPPL appear unshifted in the spectrum of this blend.

Previous studies have indicated that the solid-state ^{13}C NMR spectra of the polyesters considered here are sensitive essentially to crystalline polymer conformation.[4] No signal is observed for the amormhous phase, presumably because of a large distribution of conformations leading to very broad peaks. The appearance of two distinct peaks for C2, C3, and C4 in the spectrum of isotactic PMEPL is related to the presence of a second, minority, crystal modification and will be discussed in further detail below. The observation that the NMR spectrum of PMEPL(*R*)/PMPPL(*R*) is identical to the sum of the spectra of the two-component polymers thus indicates that, in this blend, each polyester crystallizes in

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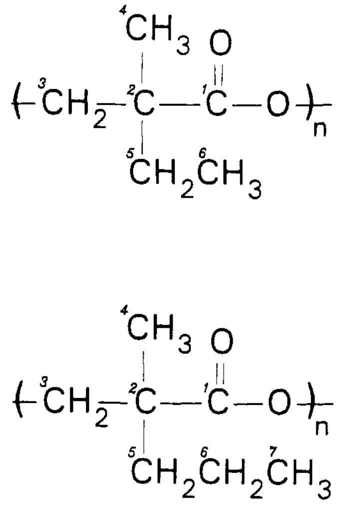

$\left({}^3CH_2-{}^2C({}^4CH_3)({}^5CH_2{}^6CH_3)-{}^1C(=O)-O \right)_n$

$\left({}^3CH_2-{}^2C({}^4CH_3)({}^5CH_2{}^6CH_2{}^7CH_3)-{}^1C(=O)-O \right)_n$

Figure 1. Chemical structure of PMEPL and PMPPL defining the carbon atoms referred to in the text.

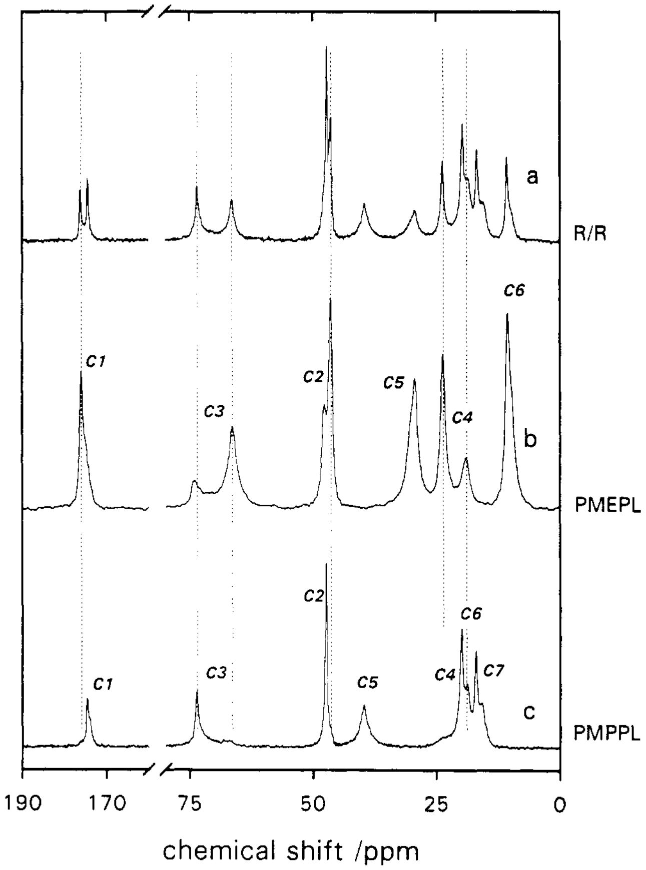

Figure 2. ^{13}C solid-state NMR spectra of melt-crystallized (a) PMEPL(*R*)/PMPPL(*R*), (b) isotactic PMEPL, and (c) isotactic PMPPL.

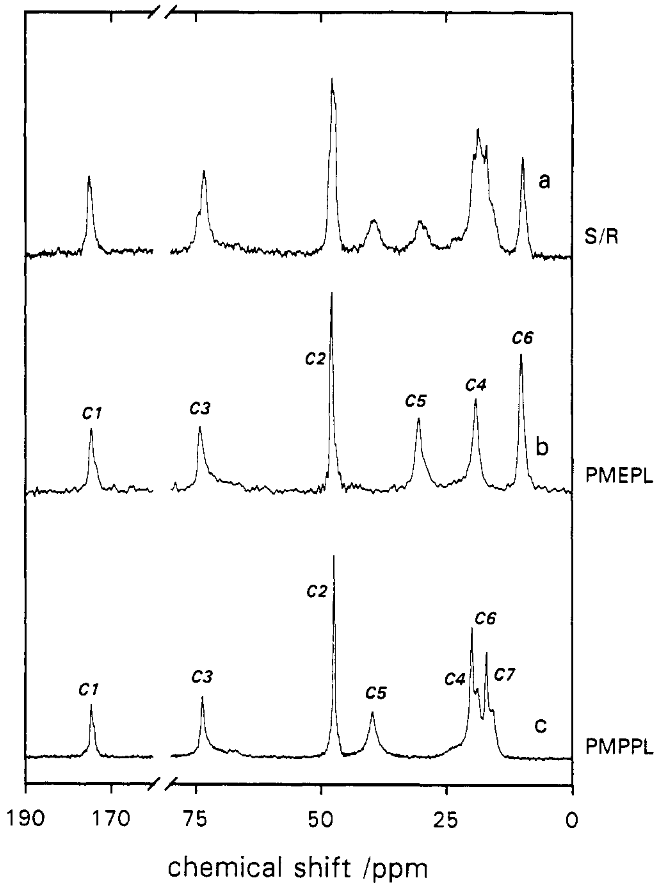

Figure 3. ^{13}C solid-state NMR spectra of (a) melt-crystallized PMEPL(*S*)/PMPPL(*R*), (b) solution-cast isotactic PMEPL, and (c) melt-crystallized isotactic PMPPL.

Table I
Chemical Shifts (in ppm) and Peak Assignments for Solid-State ^{13}C NMR Spectra[a]

	PMEPL[4]	PMPPL[4]	PMEPL(*R*)/ PMPPL(*R*)	PMEPL(*S*)/ PMPPL(*R*)
C1	176.0		176.2	
		174.7	174.5	174.4
C2	47.7[b]	47.1	47.2	47.7
	46.3		46.3	
C3	74.2[b]	73.5	73.5	73.4
	66.4		66.4	
C4	23.6		23.7	
		19.8	19.6	19.7
	18.9[b]		18.6	18.8
C5		39.7	39.7	39.6
	29.2		29.4	29.4
C6		18.8	18.6	18.8
	10.5		10.7	10.7
C7		16.9	16.7	16.8
		15.9	15.5	16.0

[a] The numbering of carbon atoms is defined in Figure 1. [b] Minor components.

the same conformation as when crystallized independently in its pure state.

Peak assignment for the solid-state NMR spectrum of the second blend, PMEPL(*S*)/PMPPL(*R*), is less obvious. Although the resonances attributed to isotactic PMPPL can be clearly identified, signals arising from carbon atoms C1, C2, C3, and C4 of PMEPL are shifted relative to their positions in the pure melt-crystallized polymer. In this blend, the carbonyl carbon, C1, and the tertiary carbon, C2, of PMEPL appear unresolved from the corresponding PMPPL resonances at 174.4 and 47.7 ppm, respectively. More striking changes in peak position are found for the main-chain methylene carbon, C3, and α-methyl carbon, C4. In the spectrum of pure melt-crystallized PMEPL (Figure 2b), the signal corresponding to C3 is manifested as a peak pair, with major and minor components located at 66.4 and 74.2 ppm, respectively. Similarly, C4 is present as two resonances at 23.6 and 18.9 ppm. In the spectrum of the PMEPL(*S*)/PMPPL(*R*) blend (Figure 3a), both of these carbon atoms appear as single peaks, occuring at the positions of the minor components of the corresponding peak pairs observed for pure melt-crystallized PMEPL.

Previous analysis of the NMR spectra of PMEPL and PMPPL,[4] in conjunction with an electron diffraction investigation,[5] revealed that isotactic PMEPL crystallizes from the melt as an extended chain whereas PMPPL adopts a 2_1 helical conformation. It was thus demonstrated

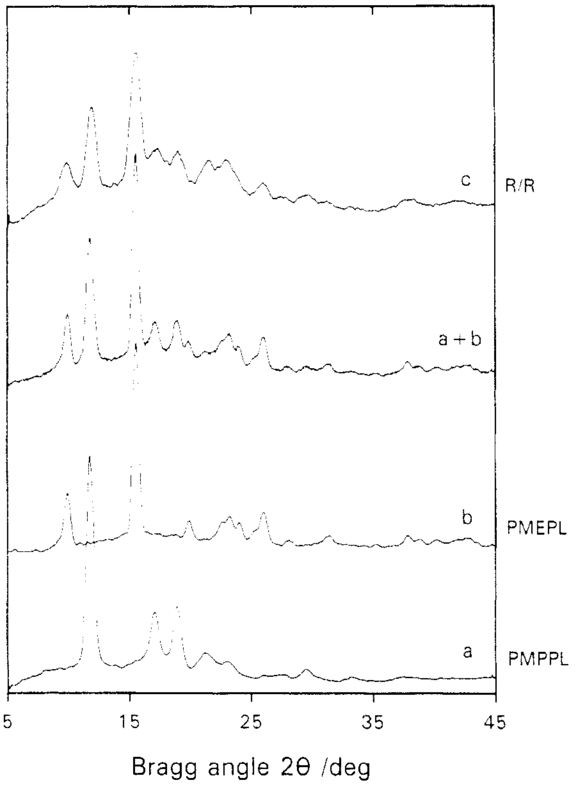

Figure 4. X-ray powder patterns of melt-crystallized (a) isotactic PMPPL, (b) isotactic PMEPL, and (c) PMEPL(*R*)/PMPPL(*R*). The sum of (a) and (b) is also shown.

that the two conformations can be distinguished by the position of the resonances corresponding to carbon atoms C2, C3, and C4 in the ^{13}C NMR spectrum. The chemical shifts reported in Table I for isotactic PMPPL are characteristic of the helical conformation whereas the extended chain is identified by those reported for PMEPL. The presence of minor peaks in the spectrum of melt-crystallized isotactic PMEPL thus indicates the presence of a minor crystalline phase composed of helices. Such a polymorph has been obtained as the major phase by solution casting and the corresponding NMR spectrum is shown in Figure 3b.

The NMR spectra of the two blends considered in the present study can be interpreted as follows: Isotactic PMPPL crystallizes in both blends in the same helical conformation as when crystallized alone. In contrast, the crystalline conformation adopted by isotactic PMEPL depends on the relative configuration of the PMPPL present. When the two polyesters are of the same chirality, PMEPL crystallizes as an extended chain, implying that there is no interaction between the two components of the blend. However, when blended with PMPPL of opposite configuration, isotactic PMEPL crystallizes from the melt as a helix.

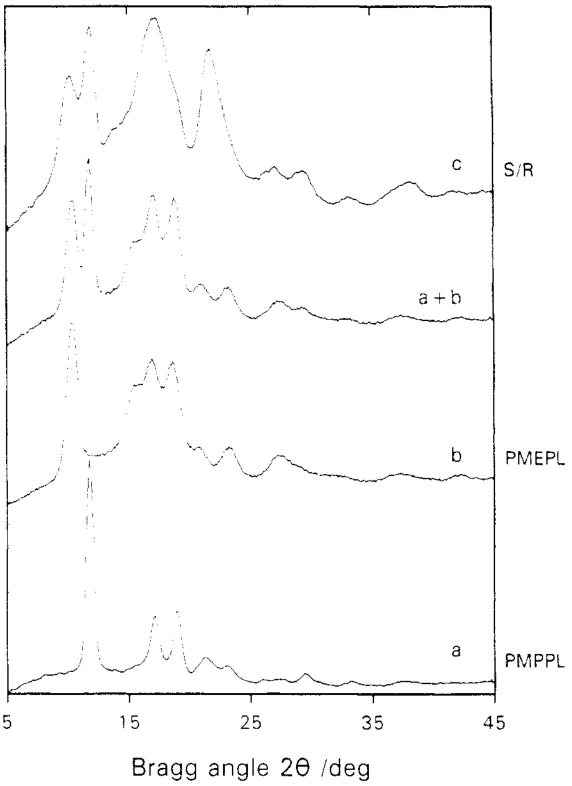

Figure 5. X-ray powder patterns of (a) melt-crystallized isotactic PMPPL, (b) solution-cast isotactic PMEPL, and (c) melt-crystallized PMEPL(*S*)/PMPPL(*R*). The sum of (a) and (b) is also shown.

Table II
X-ray Diffraction Data for Melt-Crystallized Samples[a]

Bragg angle 2θ			
PMEPL(*R*)/ PMPPL(*R*)	PMEPL(*S*)/ PMPPL(*R*)	PMEPL	PMPPL
9.7 (35)	10.0 (75)	9.7 (37)	
11.6 (75)	11.6 (95)		11.5 (100)
15.2 (100)		15.3 (100)	
16.9 (45)	16.9 (100)		16.8 (33)
18.6 (40)	18.7 (s)		18.6 (35)
		19.5 (19)	
21.1 (40)	21.3 (85)		20.9 (15)
22.5 (40)		22.2 (12)	22.7 (12)
		22.8 (16)	
		23.6 (13)	
25.5 (30)	25.7 (30)	25.5 (19)	25.4 (6)
27.0 (20)	26.5 (35)	27.4 (6)	26.7 (6)
29.0 (20)	28.6 (30)		29.0 (9)
30.6 (15)		30.7 (8)	
	32.5 (20)		32.7 (5)
37.2 (15)	37.4 (30)	37.0 (8)	36.7 (5)
		38.1 (6)	
		39.5 (6)	
41.3 (15)	41.0 (25)	41.8 (7)	40.6 (4)

[a] Relative intensities are indicated in parentheses, s signifying a shoulder.

X-ray Diffraction. The X-ray diffraction powder patterns of blends PMEPL(*R*)/PMPPL(*R*) and PMEPL(*S*)/PMPPL(*R*) are presented as Figures 4c and 5c. The corresponding diffraction angles are reported in Table II. Although the two diagrams possess several diffraction peaks in common, significant differences are apparent. For example, the intense peaks at 2θ = 16.9 and 21.3° evident in the spectrum of PMEPL(*S*)/PMPPL(*R*) are absent or of reduced intensity in that of PMEPL(*R*)/PMPPL(*R*). Similarly, the most intense reflection observed for PMEPL(*R*)/PMPPL(*R*) (at $2\theta = 15.2°$) appears only as a possible shoulder in the diagram of the other blend. A further difference to be noted is the position of the first reflection, located at 9.7° in the spectrum of PMEPL(*R*)/PMPPL(*R*) and 10.0° in that of PMEPL(*S*)/PMPPL(*R*).

As in the case of the ^{13}C NMR spectra, all reflections present in the X-ray powder diagram of the blend containing PMEPL and PMPPL of the same configuration can be identified in the diagrams of the pure polymers. In addition, Figure 4 illustrates that the relative intensities are unchanged and the sum of the powder patterns recorded for the individual components reproduces very well the diagram measured for the blend. It can therefore be concluded that each polymer crystallizes, not only in the same conformation as when crystallized alone but also in the same crystal form.

The X-ray spectrum of the second blend, PMEPL(*S*)/PMPPL(*R*) cannot be explained in this way. As indicated in Table II, the crystal form obtained when isotactic PMEPL is crystallized from the melt is characterized by an intense reflection at $2\theta = 15.3°$. This reflection is absent in the spectrum of the blend. Similarly, the powder diagram of the blend exhibits major peaks at $2\theta = 16.9$ and 21.3° that, although present, are of much lower intensity in the spectrum of pure PMPPL.

As mentioned above, a second crystal modification, prepared by solution casting, has been previously identified for isotactic PMEPL. Furthermore, in this polymorph, PMEPL crystallizes as a helix, and the corresponding X-ray powder pattern can therefore be compared to that obtained for the PMEPL(*S*)/PMPPL(*R*) blend. The result of this comparison is presented in Figure 5. The spectrum of the blend is found to share many features with the sum of the diagrams of melt-crystallized PMPPL and solution-cast PMEPL. Differences in resolution are, however, apparent, and more importantly, the presence of an intense reflection at $2\theta = 16.9°$ in the diffraction pattern of the blend is left unexplained. One possible interpretation of the diffraction pattern of the blend is the simultaneous occurrence of three crystal forms; the pure helical PMEPL and PMPPL modifications and a new form corresponding to a mixed stereocomplex.

The observations outlined above can be interpreted as follows: It is clear that isotactic PMEPL, in the presence of PMPPL of opposite configuration, crystallizes from the melt in a helical conformation similar to that obtained for the pure polymer only by solution casting. Two possible mechanisms can be proposed by which this helical conformation is induced by the presence of PMPPL. The first possibility is that PMEPL crystallizes epitaxially on lamellae of isotactic PMPPL, and for reasons of lattice matching, the polymorph of PMEPL composed of helices is favored over the extended chain modification obtained upon melt crystallization in the pure state. A second possible mechanism would involve the cocrystallization of the two polyesters to form a single crystalline phase incorporating helices of both PMEPL and PMPPL. Unfortunately, the data available at this time are insufficient to distinguish between these two hypotheses. It is, however, interesting to note that this phenomenon is stereospecific, that is, only one of the two blends examined exhibits behavior different from that of constituent polymers. This observation indicates that the relevant interactions involve intimate contact between the chains and thus supports the formation of a single crystalline phase.

The above discussion is based on the supposition that the parameter responsible for the differences between the two blends is the *chirality* of the isotactic PMEPL present. This assumption is soundly supported by previous studies[14] which reveal that no significant differences in molecular weight, optical purity, crystal structure, or crystallization kinetics exist between the two PMEPL isomers employed in this investigation. Unfortunately, isotactic PMPPL of configuration *S* of sufficiently high optical purity is not available for the preparation of blends of PMEPL(*R*)/PMPPL(*S*) and PMEPL(*S*)/PMPPL(*S*).

Differential Scanning Calorimetry. DSC thermograms of both blends, PMEPL(*R*)/PMPPL(*R*) and PMEPL(*S*)/PMPPL(*R*), show single unresolved melting endotherms centered near 150 °C. When the same experimental conditions are employed, individual samples of PMPPL and PMEPL melt at 148° and 155 °C, respectively.

Table III
Enthalpies of Fusion and Crystallization Recorded with Heating and Cooling Rates of 20 °C/min

	ΔH_f/J mol^{-1}	ΔH_c/J mol^{-1}
PMEPL isotactic	62	−55
PMPPL isotactic	45	−42
PMEPL(*R*)/PMPPL(*R*)	40	−46
PMEPL(*S*)/PMPPL(*R*)	46	−43

The crystallization exotherms of PMEPL and PMPPL, recorded upon cooling from the melt, exhibit maxima at 116 and 100 °C, respectively. Two peaks can be identified at corresponding temperatures in the cooling curve of PMEPL(*R*)/PMPPL(*R*), providing further evidence that the two components of this blend crystallize independently. Unfortunately, the crystallization exotherm recorded for the second blend, PMEPL(*S*)/PMPPL(*R*) is less reproducible and variations in both peak shape and position of maxima were noted from one sample to another.

The specific heats of fusion and crystallization for the various samples are presented in Table III. The values found for the two blends agree well with those found for the pure polymers, indicating that both PMEPL and PMPPL crystallize in the blends to approximately the same extent as in their pure state. Furthermore, the degree of crystallinity of the blends does not depend on the relative configuration of the two constituent polymers.

Conclusions

The conformation and crystal structure adopted by isotactic PMEPL when crystallized from the melt in the presence of isotactic PMPPL depend on the relative configuration of the two optically active polyesters. In samples containing PMEPL and PMPPL of the *same* configuration, the two polymers crystallize independently, to give forms identical to those obtained by melt crystallization in the pure states. In contrast, when blended with PMPPL of *opposite* configuration, isotactic PMEPL crystallizes in a different modification, composed of helices. The observation that the crystalline conformation of PMEPL is altered uniquely in blends composed of PMEPL and PMPPL of opposite chirality suggests that, in such blends, both polyesters are incorporated in a single crystal form.

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