Stereocomplexation and Morphology of Polylactides

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ABSTRACT: Blends of isotactic polylactides of opposite configurations lead to the formation of stereocomplexes, provided the enantiomeric excess of the two homopolymers in contact is high enough. In this study, the stereocomplex formation between a poly(L-lactide) (100L) having an enantiomeric excess of 100% and a poly(D-lactide) having an enantiomeric excess of 80% (80D) has been investigated using differential scanning calorimetry and optical microscopy. These results have been compared to those obtained between two polylactides having both an enantiomeric excess of 100% (100L/100D blend). The melting temperatures of blends 100L/100D and 100L/80D are 230 and 208 °C, respectively. In both cases, the stereocomplex formation is preferred to the homopolymer crystallization and the stereocomplex controls the morphology of the blends over a wide range of concentrations. However, this control is more rigorous when the D component is 100% isotactic. This difference leads to a more complete crystallization of homopolymer 100L and to a greater influence of crystallization conditions in 100L/80D blends in comparison with 100L/100D blends. An epitaxial crystallization between the homopolymer 100L and the stereocomplex 100L/80D has also been observed at certain compositions.

Introduction

The mixing of two polymers can lead to the formation of a complex whose properties are usually very different from those of the parent homopolymers. Complexation can occur between polymers with different chemical natures, tacticities (i.e., between an isotactic and a syndiotactic polymer), or chiralities (two isotactic polymers of different configurations). In the last two cases, the process is often called stereocomplexation.

The first reported example of complexation between synthetic polymers involves poly(vinyl-*N*-butylpyridium bromide) and poly(sodium styrenesulfonate).[1] Many other systems have been investigated since, but fewer examples of complexation between polymers of different tacticities have been reported. In this category, the stereocomplex made of isotactic and syndiotactic poly(methyl methacrylate) is probably the best known.[2-5] Stereocomplexation also occurs in blends of isotactic polymers of opposite configurations, such as poly(*tert*-butylthiirane),[6] poly(isopropylthiirane),[7] poly(benzyl glutamate),[8] poly(α-methylbenzyl methacrylate),[9] poly(α-methyl-α-ethyl β-propiolactone)[10,11] (PMEPL), poly(β-(dichloroethyl)-β-propiolactone),[12] poly(β-(dichloropropyl)-β-propiolactone),[12] and more recently, polylactide.[13] However, mixing two polymers of opposite configurations does not always induce the formation of a stereocomplex, as shown, for instance, with poly(methylthiirane)[14] and poly(β-(trifluoromethyl)-β-propiolactone).[15]

The existence of a stereocomplex in mixtures of isotactic polylactides of opposite configurations has been reported by Murdoch and Loomis[13] and explored in greater detail by Tsuji, Ikada, *et al.* in a series of papers.[16-19] The melting temperature of the stereocomplex is 230 °C, approximately 50 deg above that of the corresponding homopolymer (179 °C). The stereocomplex crystallizes in a triclinic system in which the unit cell dimensions *a*, *b*, and *c* are respectively 0.916, 0.916, and 0.870 nm.[20] In comparison, the crystalline structure of poly(L-lactide) is pseudo-orthorhombic with unit cell dimensions of 1.07, 0.59, and 2.78 nm (*a*, *b*, and *c*).[21] The homopolymer chains form 10_3 helices; poly(L-lactide) is left-handed, while poly(D-lactide) is right-handed. In the stereocomplex, the chain conformation is rather a 3_1 helix, and each unit cell contains the same number of D and L units.[20] This general behavior is similar to that of PMEPL where the complex forms regular arrays of D and L units, leading to an expansion of the 2_1 chain conformation which goes from a 6.1 Å fiber repeat distance in the homopolymer to a 7.1 Å value in the stereocomplex.[22]

It has been reported that mixtures of two polylactides of opposite configurations but of lesser isotacticity also give rise to the formation of a stereocomplex.[19] The melting temperature and enthalpy of fusion of the stereocomplex drop, however, sharply with the overall isotacticity of the sample, no stereocomplexation occurring when the optical purity of the polylactide is below 72%. In contrast, Lavallée and Prud'homme[11] have observed the formation of PMEPL stereocomplexes in a large interval of compositions and isotacticities, including for the mixture of an isotactic polymer with an atactic one. They have also shown that the morphology of the system is controlled by the presence of the stereocomplex. This seems to be, in general, the case with polylactides,[23] although more limited results are available.

In this study, we will examine more deeply the influence of the composition, and overall enantiomeric excess, on the morphology of polylactide stereocomplexes. For this purpose, we have investigated blends made from a mixture of an isotactic poly(L-lactide), having an optical purity close to 100%, with a poly(D-lactide) having an optical purity of about 80% (100L/80D blends). The results will be compared with those obtained between two isotactic polylactides (100L/100D). The samples have been analyzed by differential scanning calorimetry and polarized optical microscopy.

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Table 1. Characteristics of the Polymers Used

polymer	[α], deg	[D], %	10^{-3} M_v	T_g, °C	T_f,[a] °C	ΔH_f,[a] J/g	M_w/M_n[b]
100L	−153	0	13.2	58	178	66	1.35
80D	124	90.5	44.2	57	135	16	1.65
100D	155	100	14.5	60	183	75	1.35

[a] First scan of the nascent polyester. [b] From size exclusion chromatography experiments, in tetrahydrofuran at 25 °C.[28] We believe that a large systematic error occurs in this sort of analysis of polylactides, and therefore, the M_w and M_n values are not reported; in our opinion, the polydispersity index remains, however, significant.

Experimental Section

The polylactides used in this study were prepared by ring-opening polymerization of lactide, in toluene at 70 °C, using aluminum isopropoxide as initiator.[24] The polymerization proceeds through a living mechanism, thus giving a polymer with a narrow polydispersity and a molecular weight that can be predicted from the monomer/initiator ratio. Three different polyesters have been used: two of them (100L and 100D) are completely isotactic but of opposite configurations, and the third one (80D) is of lower optical purity. Samples 100L and 100D were prepared from the direct polymerization of pure L- and D-lactide (CCA Biochem b.v.), respectively, while sample 80D was synthesized from a mixture of the two monomers in the appropriate molar ratio. The acronyms used in this study refer to the enantiomeric excess, ee, of the samples and mention the isomer in excess:

$$\mathrm{ee} = \frac{|D - L|}{D + L} \cdot 100 \tag{1}$$

where D and L correspond to the molar percent of each isomer in the polymer. For example, sample 80D contains 90% of the D isomer and 10% of the L isomer, giving an enantiomeric excess of 80% in D units (90% − 10%). The atactic polymer is thus characterized by an enantiomeric excess of 0%, while the isotactic component has a value of 100% (100L or 100D).

The optical purity (OP) of each polymer and, hence, its enantiomeric excess have been calculated using the specific optical rotation angle of the completely isotactic polymer ($[\alpha]_0$) and that of the polymer investigated ([α]):

$$\mathrm{OP} = \frac{[\alpha]}{[\alpha]_0} \cdot 100 \tag{2}$$

The value of $[\alpha]_0$ in chloroform was taken as ±154°.[25] A Jasco polarimeter, model DIP 360, operating at 598 nm at room temperature, was used for the measurements, which were done at a concentration of 10 g/L. The values obtained are given in Table 1.

The viscosity-average molecular weight (M_v) of the polylactides was determined from their intrinsic viscosities ($[\eta]$), measured in tetrahydrofuran at 30 °C, using the Mark–Houwink equation:

$$[\eta] = KM_v^{\,a} \tag{3}$$

The a value is considered independent of the isotacticity of the polymer and was taken equal to 0.639 in all cases.[24] However, the K value varies from (5.49 to 9.62) × 10^{-2} for the atactic[24] and isotactic polymers, respectively. For the 80D sample, a value of 8.79×10^{-2} has been interpolated, assuming a linear relationship between K values and optical purity.

Blends were prepared by weighting the required amount of each polymer of opposite configuration and dissolving them in methylene dichloride at a total concentration of 20 g/L. After 1 night under stirring, the solvent was evaporated slowly at room temperature and the films thoroughly dried under vacuum, at least 1 week at room temperature.

Differential scanning calorimetry (DSC) measurements were conducted with a Perkin-Elmer DSC-4 apparatus equipped with a System-4 controller and calibrated with pure indium. Some of the films, called *cast films*, were scanned without any prior thermal treatment. Others were melted 10 min at 255 °C (blends 100L/100D) and isothermally crystallized for 1 h at 140 °C or, for blends 100L/80D, melted 10 min at 230 °C and isothermally crystallized for 1 h at 115 °C after fast cooling from the melting temperature. The melting temperature (T_f) was taken at the end of the melting peak, while the glass transition temperature (T_g) was recorded at the half-height of the heat-capacity jump, at a heating rate of 20 deg/min. The difference in crystallization temperature between the two series of blends was dictated by the difference in melting temperature between their 100D and 80D components. Finally, some samples of the two series were analyzed following a 2 min melting period instead of the 10 min used normally (same temperatures and cooling conditions as before); this shorter time led to similar DSC results.

The morphology of the samples was investigated with a Zeiss polarizing microscope equipped with a Mettler FP-5 hot stage. Films of blend 100/100D were melted 2 min at 255 °C to erase any prior thermal history, rapidly cooled to 225 °C to avoid degradation, and finally cooled at a rate of 1 deg/min; blends 100L/80D were melted 2 min at 230 °C and cooled rapidly to 215 °C before cooling slowly at a rate of 1 deg/min. This thermal treatment was preferred to the isothermal crystallization used in DSC analysis because it leads to the formation of larger spherulites, for all samples, and to an improvement in the morphological analysis.

Table 1 summarizes the characteristics of the polylactides used in this study. Sample 80D contains 90.5% D units and 9.5% L units. These L units are evenly distributed along the polymer chain, so that sample 80D can be considered as a statistical copolymer of D and L units.[26] Samples 100L and 100D have melting temperatures of 178 and 183 °C, respectively, and enthalpies of fusion of 66 and 75 J/g, respectively, similar to those obtained by Tsuji and Ikada[19] for completely isotactic polymers. Both parameters are lower for sample 80D; T_f = 135 °C and ΔH_f = 16 J/g. This behavior is typical of semicrystalline copolymers in which only one comotif can crystallize.[27] The incorporation of noncrystallizable units in a polymer chain leads to a decrease of the chemical potential of the melt to an exclusion of those units from the crystal, and to a decrease of the crystalline sequence length. Those factors lead to a drop in melting temperature and enthalpy of fusion. The T_f and ΔH_f values of sample 80D are consistent with the results of Tsuji and Ikada,[19] who reported that the crystallization of optically active polylactides becomes impossible when the mole fraction of the minority units exceeds 14–17%. In addition, Caron and Prud'homme[28] reported that the crystallization of polylactides proceeds with an exclusion from the crystals of the minor units.

Results and Discussion

DSC Analysis. Figure 1 shows the DSC melting curves of blend 100L/80D at different compositions, after crystallizing for 1 h at 115 °C. The occurrence of a stereocomplex is confirmed by the presence of a peak at approximately 208 °C (maximum at ≈195 °C) at every composition, even at that containing 10% 80D only, 30 deg above the melting temperature of sample 100L (179 °C). At mole fractions X_D of 80D between 10 and 40%, two distinct melting peaks are detected, indicating that there is simultaneous crystallization of constituent 100L and of the stereocomplex. When X_D exceeds 40%, no second melting peak can be detected because sample 80D does not crystallize under these conditions.

Figure 2 shows the melting temperature of the stereocomplex and of the homopolymer in excess as a function of the composition of blends 100L/80D; the corresponding values of blends 100L/100D are given for comparison. The melting temperature of these two stereocomplexes varies slightly with composition, exhibiting a maximum around 50%. In both cases, the

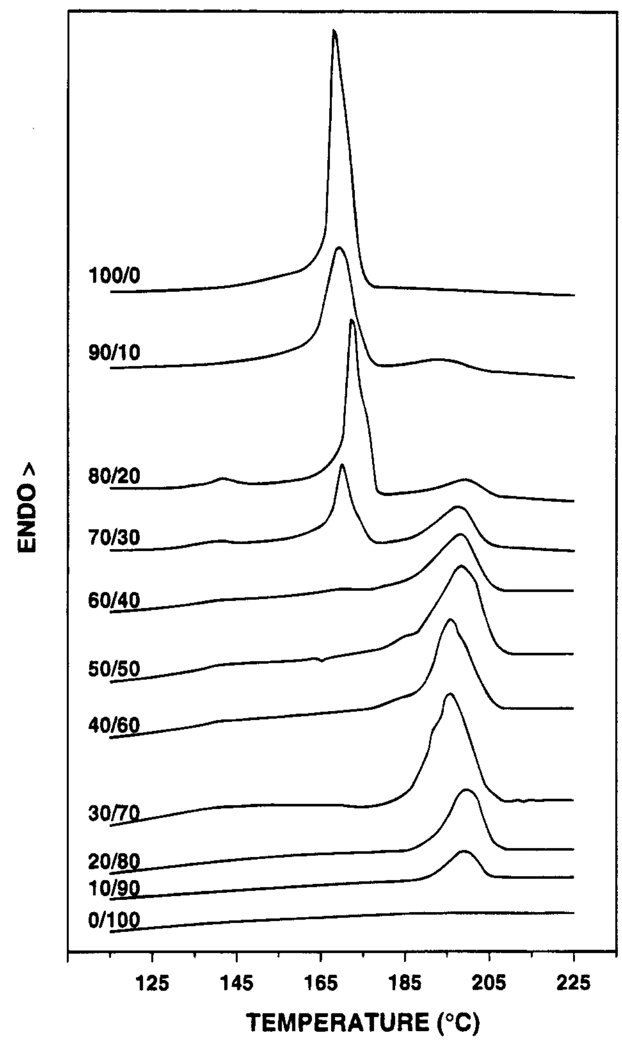


Figure 1. DSC curves of blends 100L/80D of different compositions crystallized for 1 h at 115 °C. Beside each curve, the mole fraction of the two polymers is indicated; i.e., 80/20 corresponds to a sample containing 20 mol % 80D.

melting temperature of constituent 100L decreases very slightly with an increase in the concentration of poly(D-lactide).

The enthalpy of fusion of films cast from blends 100L/100D and 100L/80D is shown in Figure 3, and that of isothermally crystallized samples, in Figure 4. For 100L/100D blends, the enthalpy of fusion of the stereocomplex increases linearly with the amount of poly(D-lactide) in the mixture. Since the homopolymers 100L and 100D have, by definition, the same enantiomeric excess, the maximnum in enthalpy is found at exactly the 50% composition. At the same time, the enthalpy of fusion of homopolymer 100L decreases with the addition of poly(D-lactide). This decrease is regular and the enthalpy of fusion goes to zero, i.e., no crystallization, at $X_D = 40\%$ (with a trace of crystallinity detected after annealing). These values indicate that the homopolymer in excess in the mixture, after the crystallization of the stereocomplex, does not crystallize as easily and as extensively as it would in the absence of stereocomplexation. This result is very similar to that observed before with PMEPLs.[10] No significant difference is detected between the enthalpy of cast and isothermally crystallized films of blend 100L/100D.

For 100L/80D blends, there is also a regular increase of the enthalpy of fusion of the stereocomplex for both cast and isothermally crystallized samples. However, in Figure 3, the maximum in ΔH_f is found at a mole fraction of approximately 65% in 80D, close but above the equimolar ratio (52%) of this mixture. Moreover, 100L crystals are detected up to 70% of constituent 80D (Figure 3). If stereocomplexation was complete, no crystalline 100L component should be detected for an 80D mole fraction greater than 50%. However, if the blends are isothermally crystallized for 1 h at 115 °C, the maximum in enthalpy of fusion (for the stereocomplex) increases from 25 to 48 J/g and appears at 56% instead of 65% (Figure 4), much closer to the 52% reference value. Furthermore, the crystallization of constituent 100L does not occur above a mole fraction of 50% in 80D. In view of these results, it can be concluded that isothemal crystallization of blends 100L/80D favors stereocomplexation, in contrast to blends 100L/100D where the extent of stereocomplex formation is independent of the crystallization conditions used. Crystallization at different temperatures leads to similar results, but the influence of temperature on the competitive processes of homocrystallization versus stereocomplexation is complex.[29] It should be noted that the isothermal crystallization of these samples does not give a significant variation of the melting temperature of the species involved, as compared to the casting procedure.

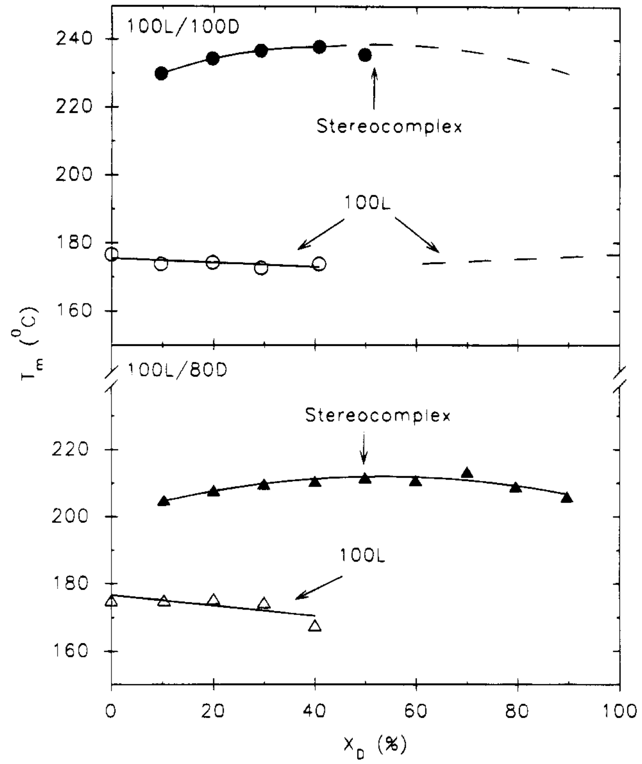


Figure 2. Melting temperatures of blends crystallized for 1 h at 140 °C (100L/100D) or 1 h at 115 °C (100L/80D). In the case of blend 100L/100D, the analysis of compositions between 60 and 100% 100D has not been performed, and their behavior (dashed line) is assumed to be the same as that of their symmetric counterpart, as has been shown before in the literature.[18,28] X_D is the mole fraction of D component in the mixture.

The difference in behavior between cast and isothermally crystallized films of blend 100L/80D may be related to the rate of crystallization of the species involved. It has been found[28] that the crystallization rate of the stereocomplex is much lower in blends 100L/80D than in blends 100L/100D, because the L units of sample 80D have to be excluded from the stereocomplex.

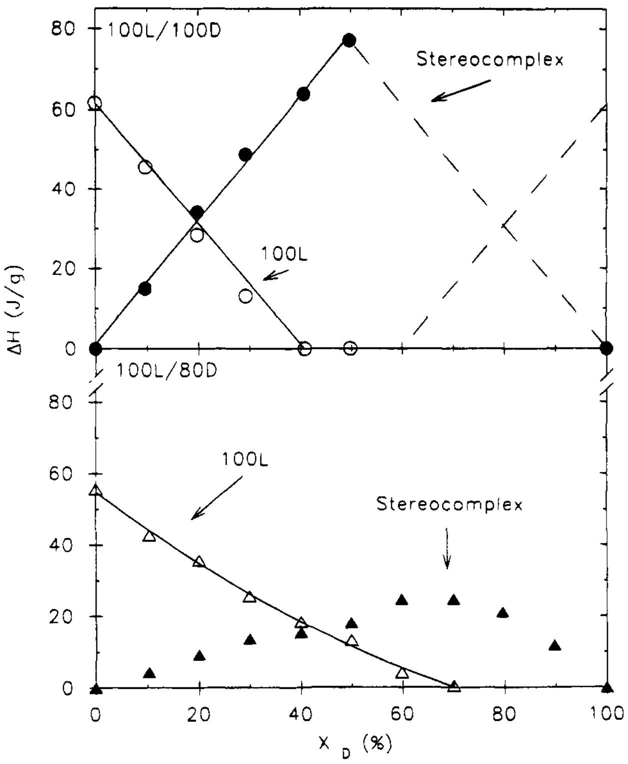


Figure 3. Enthalpy of fusion of casted blends 100L/100D and 100L/80D. In the case of blend 100L/100D, the analysis of compositions between 60 and 100% 100D has not been performed, and their behavior (dashed line) is assumed to be the same as that of their symmetric counterpart, as has been shown before in the literature.[18,28]

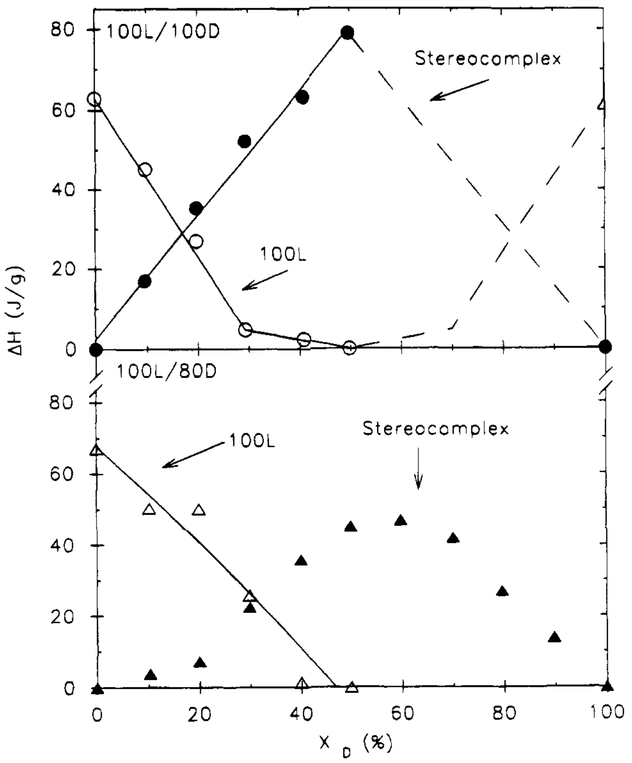


Figure 4. Enthalpy of fusion of blends 100L/100D and 100L/80D crystallized, respectively, at 140 and 115 °C for 1 h. In the case of blend 100L/100D, the analysis of compositions between 60 and 100% 100D has not been performed, and their behavior (dashed line) is assumed to be the same as that of their symmetric counterpart, as has been shown before in the literature.[18,28]

Therefore, if it is assumed that the evaporation of the solvent in blends 100L/80D (casted method) is fast as compared to the stereocomplex formation, the medium can be frozen in before all units of a given configuration come in contact with those of opposite configuration. This hypothesis is further supported by the fact that the diffusion of the chains in blends 100L/80D should be slower than in blends 100L/100D, due to the higher molecular weight of sample 80D (44×10^3) as compared to those of polymers 100L and 100D (13×10^3 and 14×10^3, respectively). The fusion of blends 100L/80D, followed by isothermal crystallization at 115 °C, can thus give the chains the opportunity to rearrange themselves in a suitable position to form the stereocomplex, provided the crystallization (or melting) time is long enough. In blends 100L/100D, no noticeable difference between the quantity of stereocomplex formed in cast and isothermally crystallized samples can be observed, probably because of the faster rate of stereocomplexation and the lower molecular weights (and diffusion rates) of the poly-D constituent.

We have already emphasized the minute variation of the melting temperature of constituent 100L as a function of the blend composition (Figure 2). Tsuji *et al.*[18,23] obtained similar results for blends of isotactic polyactides of opposite configurations, with various enantiomeric excesses. This composition behavior is also similar to those reported by Grenier and Prud'homme,[10] and Lavallée and Prud'homme[11] for mixtures of PMEPLs of opposite configurations. This common behavior of homopolymer/stereocomplex mixtures during crystallization may indicate that the two species are not well mixed in the melt but tend rather to form separate domains. If they would mix and form a homogeneous mixture, a larger temperature dependence, as in the case of copolymers,[27] would be expected.

In general, the results presented in Figures 1–4 with 50/50 mixtures are in agreement with those of Tsuji and Ikada:[18,23] a similar decrease of the melting temperature and enthalpy of fusion of the stereocomplex when going from the 100L/100D to the 100L/80D blend. However, our results emphasize the importance of the thermal history since the respective amount of homopolymer and stereocomplex crystals can be modified with crystallization time and temperature, as illustrated in Figures 3 and 4. Furthermore, our results demonstrate that similar variations in thermal stability (related to the melting temperature) and degree of crystallinity (proportional to the enthalpy of fusion) can be generated either by changing the enantiomeric excess of the polymers involved, as Tsuji and Ikada have done, or by taking one pair of polymer, i.e., especially with the 100L/80D blend, and changing its ratio, as done in this study. These variations are accompanied with important modifications in morphology, as reported in the following section.

Morphology. The morphology of slowly cooled 100L/100D blends of different compositions is shown in Figure 5. Sample 100L and the stereocomplex are both characterized by highly birefringent spherulites of radii of about 50 μm for sample 100L and 80 μm for the stereocomplex with a non-negligible distribution in size in both cases. The morphology of blend 100L/100D 90/10 is characterized by small and not-well-defined birefringent structures, looking somewhat like axialites.[27] The morphology of the mixtures having a mole fraction of constituent 100D between 20 and 50% is clearly spherulitic. Moreover, the size of those spherulites is

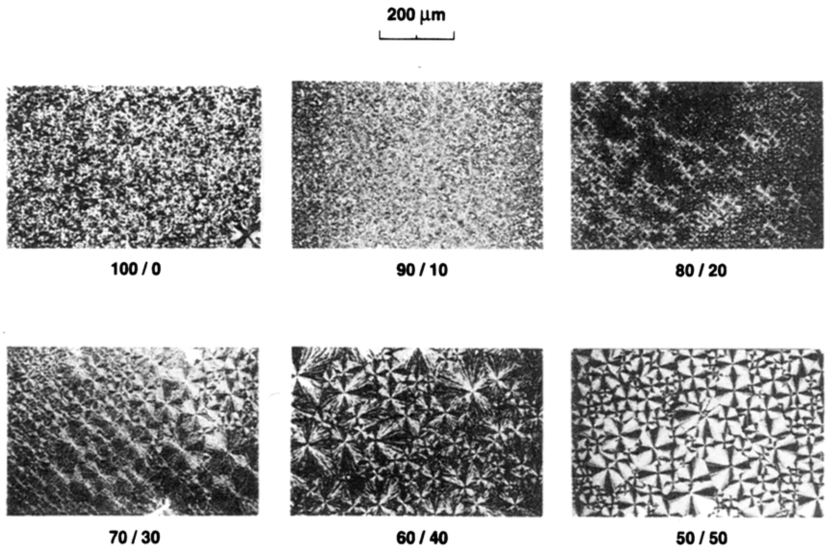


Figure 5. Photomicrographs of blends 100L/100D of different compositions prepared by slow cooling at 1 deg/min.

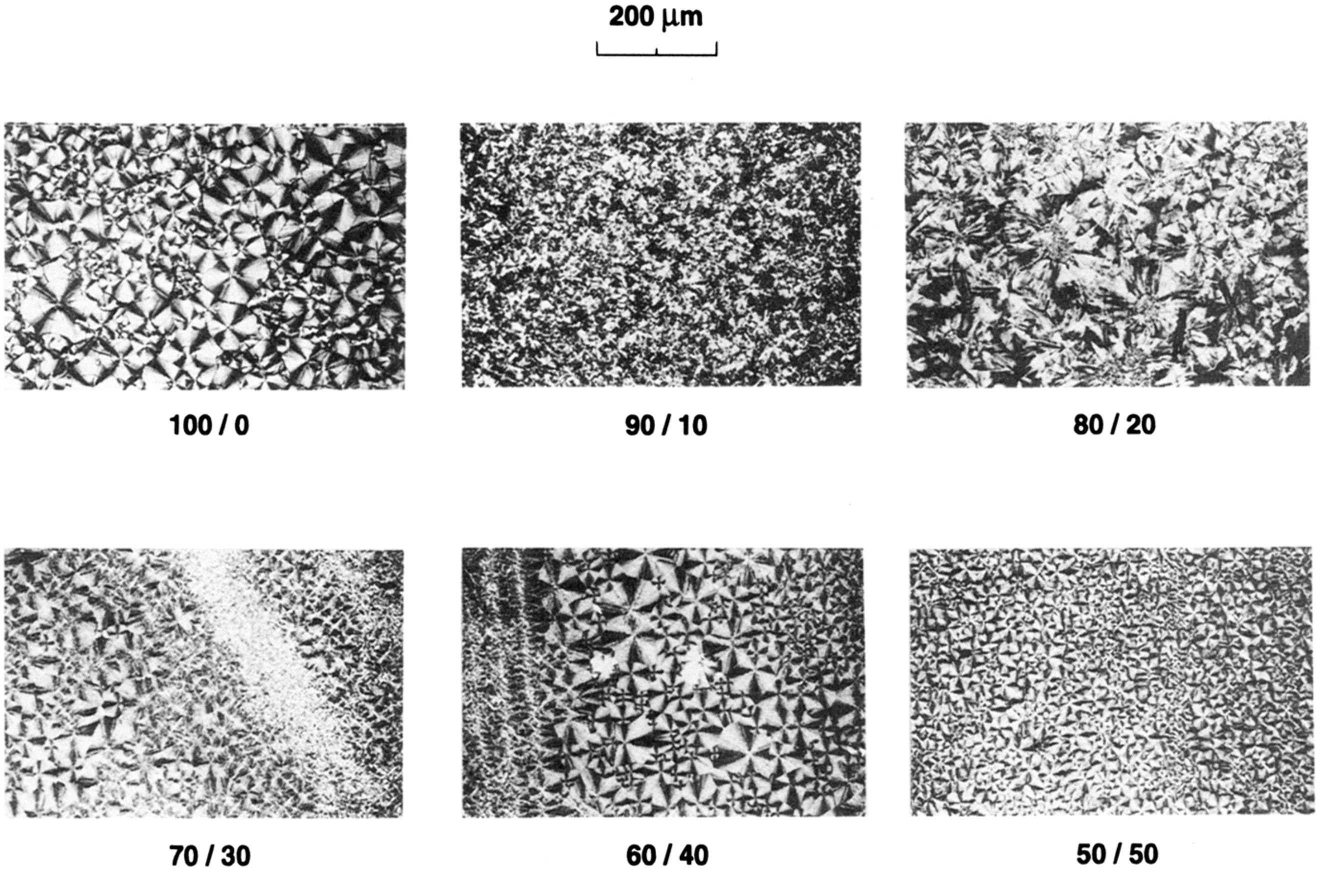
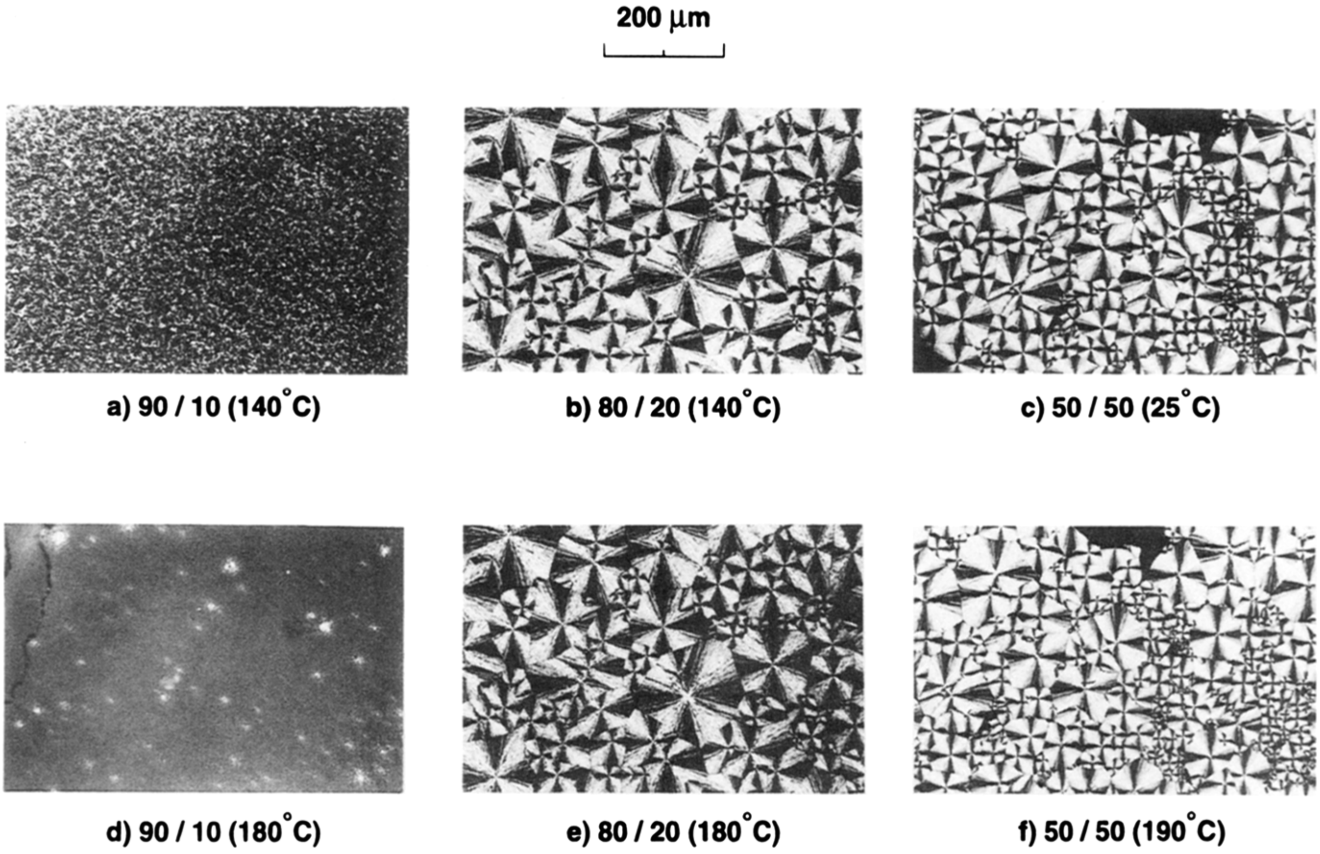


Figure 6. Photomicrographs of blends 100L/80D of different compositions prepared by slow cooling at 1 deg/min.

of the same order of magnitude as those of the stereocomplex.

Figure 6 gives the photomicrographs of slowly cooled 100L/80D blends having mole fractions between 0 and 50% in 80D. For any given composition, the morphology of blend 100L/80D is similar to that of blend 100L/100D since the samples are spherulitic, and their sizes are all of the same order of magnitude although the spherulites of the stereocomplex are slightly smaller than those of the 100L/100D complex. (The slight difference between the morphology of sample 100/0 shown in Figure 6 and that given in Figure 5 is due to a slightly different thermal treatment, as indicated in the Experimental Section: it was possible, in the mixtures involving sample 80D, to proceed at lower temperatures because the melting temperature of the stereocomplex is then lower, as indicated in Figure 2.) The blend of composition 80/20 is characterized by a more complex morphology, to which we will come back later. The morphology of blends 100L/80D containing more than 50% of 80D, not shown here, is similar to that of blend 50/50, except that the spherulites in blend 10/90 are not completely volume filling.[29]

In order to gain a better understanding of the influence of stereocomplexation on the morphology, each sample has been examined as a function of temperature.



a) 90 / 10 (140°C) b) 80 / 20 (140°C) c) 50 / 50 (25°C)

d) 90 / 10 (180°C) e) 80 / 20 (180°C) f) 50 / 50 (190°C)

Figure 7. Photomicrographs of blends 100L/100D of compositions 90/10 (a, d), 80/20 (b, e), and 50/50 (c, f) taken before and after heating the sample at 180 (d and e) and 190 °C (f). Blends a–c were prepared by slow cooling the samples from the melt at 2 deg/min.

Two photomicrographs of each sample have been taken: the first one at a temperature (25 or 140 °C) below the melting peak of the homopolymer 100L and the second one at 180 or 190 °C, above the melting peak of the constituent 100L but below the melting peak of the stereocomplex. The results for blends 100L/100D of compositions 90/10, 80/20, and 50/50 are given in Figure 7. It can be seen that the fusion of constituent 100L in blend 100L/100D 50/50 does not induce any noticeable change in the sample morphology. The same observation was made for blend 60/40 (not shown here).[29] In blends 100/100D of compositions 70/30 and 80/20 (only the second one is shown in Figure 7), the melting of homopolymer 100L causes a decrease of birefringence and even the appearance of a fluid in some areas. This effect is more pronounced at an 80/20 composition than at the 70/30 composition. Finally, in blend 100L/100D of composition 90/10, most of the birefringence vanishes when the sample is brought to 180 °C.

The consequences of the fusion of constituent 100L on the morphology of blends 100L/80D of different compositions have also been analyzed.[29] The corresponding photomicrographs are not shown because they are very similar to those presented in Figure 7. The fusion of homopolymer 100L in blend 100L/80D of composition 90/10 leads to the disappearance of most of the birefringence. For blends 100L/80D of compositions 70/30 and 60/40, at 180 °C, the birefringence of the samples decreases and a fluid becomes visible in some areas. This liquid phase is so important, in some cases, at the 70/30 composition, that blocks of spherulites can move; cracks also appear in some spherulites. Under the same conditions, no significant morphologic changes are noticed in blends containing more than 50% 80D, with the exception of a few liquid spots in blend 50/50. None of these blends exhibits a change in morphology when brought to a temperature between 135 and 170 °C, above the melting temperature of constituent 80D but below that of constituent 100L.

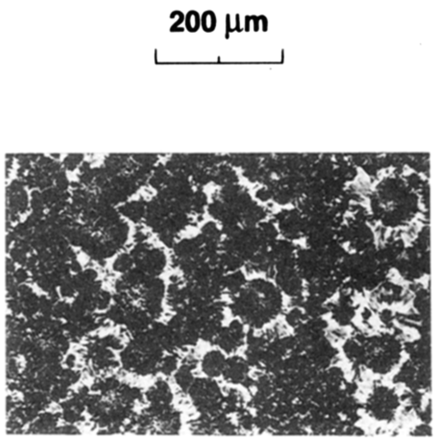
The above observations can be interpreted as follows. The spherulites of blends 100L/100D of compositions 50/50 and 60/40 are made of stereocomplex only, as can be deduced from the fact that no change in morphology occurs when these samples are brought above the melting temperature of the constituent 100L (Figure 7). This behavior is in agreement with DSC results (Figures 3 and 4), showing that the enthalpy of fusion of these blends is close to zero. In blends 100L/100D of compositions 70/30 and 80/20, the melting of homopolymer 100L induces a decrease of the birefringence of the sample, but most of the spherulites keep their initial shape and aspect (Figure 7). DSC results indicate that the amount of 100L crystals in these two blends is important enough to give rise to an endothermic peak at about 180 °C (Figures 3 and 4). In those blends, the proportion of uncomplexed 100L is of 40 and 60%, respectively. The chains of uncomplexed homopolymer 100L tend to form small spherulites between the stereocomplex lamellae. However, the development of large-scale homopolymer spherulites is impossible because the full volume is already occupied by the stereocomplex spherulites, as shown in Figure 7e. Finally, in blend 100L/100D of composition 90/10, the amount of stereocomplex becomes too small to produce a well-defined spherulitic morphology and most birefringence vanishes when the constituent 100L melts, leading to a relatively large enthalpy of fusion of constituent 100L as compared to that of the stereocomplex. The morphology of blends

100L/100D having a mole fraction of 100D larger than 20% is thus controlled by the stereocomplex, as in the case of poly(α-methyl-α-ethyl-β-propiolactones).[10,11]

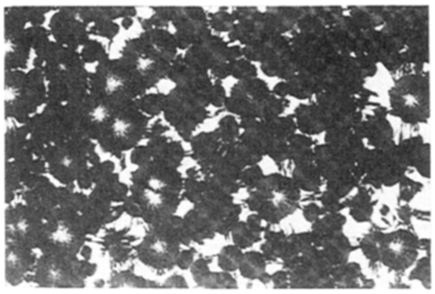
The change in morphology with composition of blend 100L/80D can be explained in the same way. However, since homopolymer 80D does not crystallize when slowly cooled from the melt,[28] the spherulites of blend 100L/80D having a mole fraction between 60 and 90% in 80D are made of stereocomplex only. In blends 100L/100D, the isotacticity of both homopolymers allows the crystallization of the homopolymer in excess (polylactide 100L or 100D). Furthermore, the appearance of a larger amount of fluid in blends 100L/80D as compared to blends 100L/100D when the melting temperature of constituent 100L is reached indicates that the fusion of constituent 100L, for a given composition, seems to influence the morphology more than it does in blends 100L/100D. This behavior suggests that the control of the morphology of the blend by the stereocomplex is less rigorous in blends 100L/80D than in blends 100L/100D.

In all those blends, when the temperature is decreased from the molten state, stereocomplexation becomes possible at a temperature above the crystallization of the homopolymers with the rearrangement of units of opposite configurations and the complexation of free adjacent units. The chains of constituent 100L in excess are then trapped between the stereocomplex lamellae inside the spherulites but can also form crystalline lamellae at lower temperatures. Indeed, Caron and Prud'homme[28] have reported that the crystallization of the stereocomplex begins at 195 °C, whereas the homopolymer does not crystallize above 155 °C in a few hours. It is thus probable, under the conditions used in Figure 5 and 6 that the stereocomplexation is completed even before the crystallization of the homopolymer starts. This results in the observation of a melting peak for constituent 100L in blends 100L/100D of compositions 80/20 and 70/30, in which the enthalpies of fusion are respectively 27 and 7.9 J/g for slowly cooled samples (see also Figures 3 and 4).

However, it is noticed that the enthalpies measured for this species in 100L/100D blends are smaller than expected on the basis of the amount not incorporated in the complex. For example, in Figures 3 and 4, one would expect for the mixture containing 20% 100D an enthalpy of $^3/_5 \times 66$ J/g, i.e., 39.6 J/g, whereas the two experimental values are below 30 J/g. This indicates that the crystallization of the homopolymer in excess, after the crystallization of the stereocomplex, is hindered due to the difficulty in transporting the chain segments to the crystallization site because of the presence of stereocomplex lamellae and spherulites. In solution-casted 100L/80D blends, the behavior is different: the enthalpy of fusion of homopolymer 100L is close to that calculated on the basis of the amount which is not incorporated into the stereocomplex. After annealing, the enthalpy of fusion (and amount) of stereocomplex increases, and the enthalpy of fusion of species 100L decreases but remains close to the value calculated. This behavior indicates a greater freedom for crystallization of the homopolymer in excess in 100L/80D blends as compared to 100L/100D blends. Even if spherulites are observed in both cases, and even if the above discussion indicates a greater rigidity in the stereocomplex spherulites in samples 100L/100D, the resolution given by the optical microscope did not permit us to visualize this phenomenon. Work is in progress in this area.



a) 118 °C

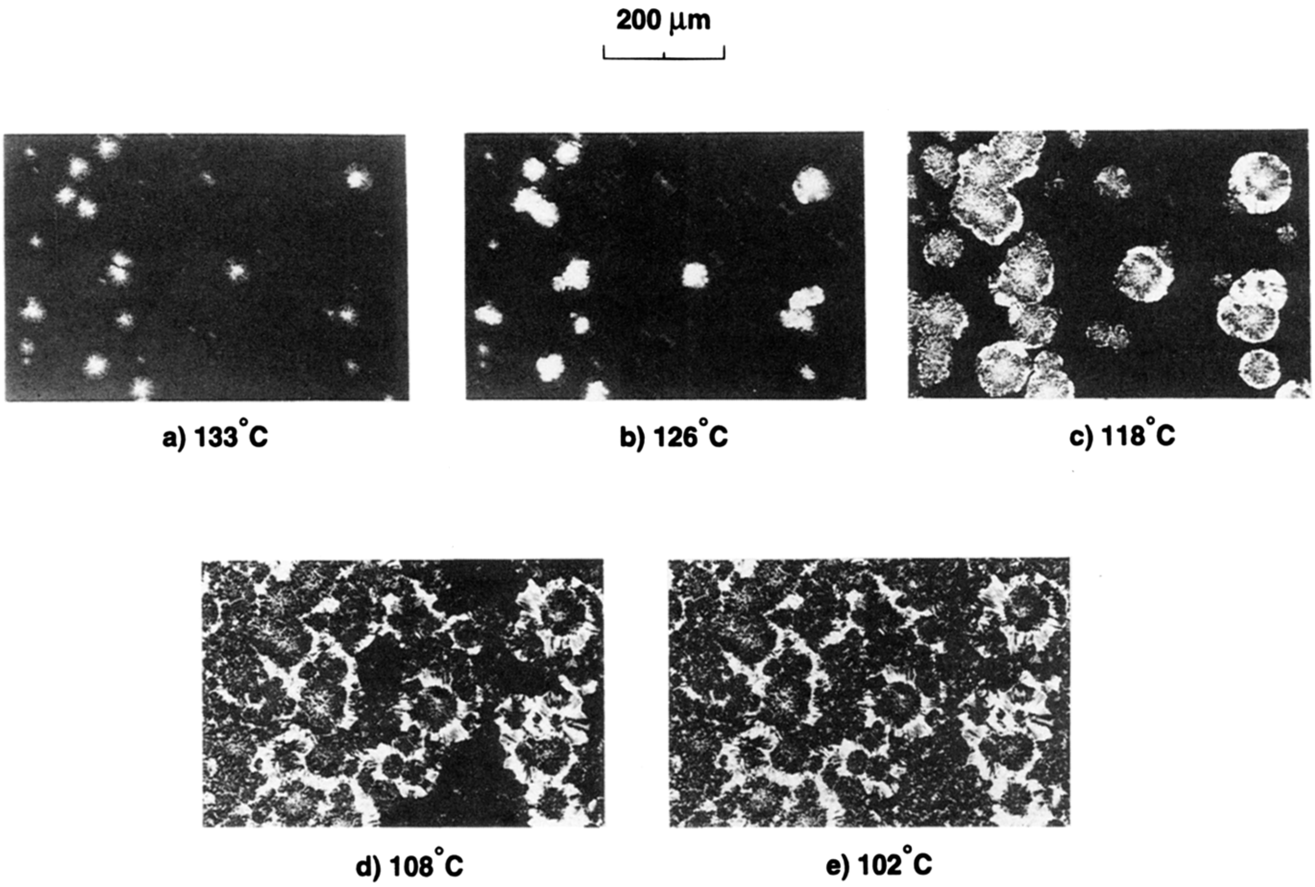


b) 171 °C

Figure 8. Photomicrographs of blend 100L/80D of composition 80/20 taken at (a) 118 and (b) 171 °C. The initial sample was prepared by slow cooling from the melt at 2 deg/min.

The behavior of blends 100L/100D and 100L/80D of composition 90/10 is different from those previously mentioned. These blends are made of homopolymer 100L in which can be found 20% stereocomplex, a fraction which is too small to control the sample morphology. However, the spherulites of the stereocomplex may act as nucleation sites for the homopolymer in excess in a process similar to that leading to the self-nucleation of polypropylene onto polypropylene crystals when the polymer is not totally melted, before crystallization.[31] This phenomenon appears possible in view of the similarity of the crystal structures of the two species involved. It would lead to the important decrease of the spherulites dimensions observed in those blends (Figures 5 and 6).

As mentioned above, blend 100L/80D of 80/20 composition is characterized by a peculiar morphology which has not been observed for any other system investigated in this article; its spherulites are usually ringed and slightly bigger than those found at other compositions. Strangely, a weakly birefringent area, more or less circular, is found at the center of most spherulites. Figure 8 shows photomicrographs of this blend taken at 118 and 171 °C, for a slowly cooled sample. The melting of homopolymer 100L at 171 °C (Figure 8b) leads to an important decrease of the birefringence of the sample and leaves behind small weakly birefringent spherulites whose presence was unnoticed. These small spherulites are surrounded by very bright rings. When the sample is heated to 200 °C, the spherulites and the bright rings which surround them vanish together.



a) 133°C b) 126°C c) 118°C

d) 108°C e) 102°C

Figure 9. Photomicrographs of blend 100L/80D taken at different temperatures (°C): (a) 133; (b) 126; (c) 118; (d) 108, and (e) 102. The initial sample was prepared by slowly cooling from the melt at 1 deg/min.

In order to identify the nature of the species involved, the same area of blend 100L/80D was photographed at different temperatures during its cooling from the melt at 1 deg/min. The initial spherulites, weakly birefringent, appear around 166 °C; the middle of some of them is, however, very bright. As shown in Figure 9, these highly birefringent areas grow faster than the other spherulites (Figure 9a,b). At approximately 118 °C (Figure 9c), the bright areas exceed the boundary of the initial spherulites and form the bright rings mentioned earlier (Figure 8). However, the growth of these bright rings seems to stop at about 108 °C (Figure 9d); the space still unoccupied is then filled with weakly birefringent matter (Figure 9e). When this sample is heated again at a temperature above the melting temperature of constituent 100L, a morphology similar to that shown in Figure 8b is obtained.

These initial weakly birefringent spherulites can be associated with the stereocomplex, which crystallizes at a higher temperature than the homopolymer. The bright zones in the middle of several spherulites are due to homopolymer 100L crystallization since they vanish when the sample is brought to 171 °C (Figure 8b). The bright rings surrounding the weakly birefringent spherulites are probably made of both stereocomplex and homopolymer crystals because, on the one hand, there is a decrease of the birefringence when the melting temperature of the homopolymer is reached and, on the other hand, there is a simultaneous melting of the bright rings and the weakly birefringent spherulites at 200 °C, at the melting temperature of the stereocomplex 100L/80D.

The start of the homopolymer crystallization at 165 °C is surprising, considering that the sample 100L requires more than a few hours to crystallize at temperatures above 155 °C.[28] Figure 10 shows the DSC melting curve of sample 100L crystallized for 1 h at 150 °C and those of blends 100L/80D of compositions 80/20 and 60/40 prepared under the same conditions. It can be seen that the crystalline fraction of constituent 100L in the 80/20 and 60/40 blends at about 173 °C is much larger than that in sample 100L. Therefore, the spherulites of stereocomplex 100L/80D seem to act as nucleation sites for the homopolymer 100L which can, in turn, crystallize at a faster rate than the stereocomplex.

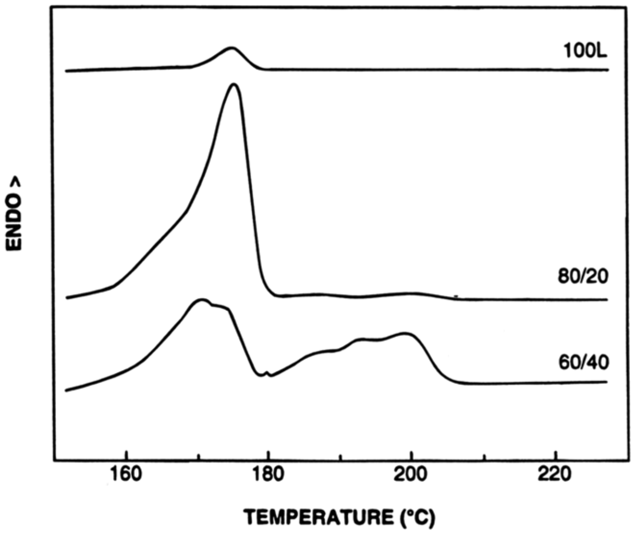


Figure 10. DSC curves of homopolymer 100L and of blends 100L/80D of compositions 80/20 and 60/40 crystallized for 1 h at 150 °C.

It is then concluded that the crystallization rate of each constituent controls the morphology of the blend. The stereocomplex 100L/80D crystallizes at a higher temperature than the homopolymer 100L, but at a slower rate.[28] Homocrystallization can then take place on the stereocomplex lamellae, as in an epitaxial crystallization.[27] In such a process, the action of the substrate is to enhance the nucleation of a second crystalline phase by lowering its free energy of activation. An epitaxial crystallization originates frequently from a specific interaction between the functional groups of each constituent in relation to their spacial arrangement. Several examples of epitaxial crystallization can be found in the literature. An epitaxial crystallization between a stereocomplex and one of its constituents has been recently reported in the literature by Soldera and Prud'homme[30] who have observed that poly(α-methyl-α-propyl-β-propiolactone) of *R* configuration crystallizes epitaxially onto poly(α-methyl-α-ethyl-β-propiolactone) of *S* configuration. Here, one composition only of blend 100L/80D has been studied in this respect. It is probable that this type of crystallization also occurs, to a lesser extent, in blends 70/30 and 60/40, as suggested by the enhancement of homopolymer crystallization in a blend of composition 60/40, in comparison with sample 100L (Figure 10). The observation of these blends in polarized light reveals in fact the existence of a morphology similar to that of a blend of composition 80/20, but less frequent.

The epitaxial crystallization observed in blends 100L/80D of different compositions is probably due to the combination of several factors. The simultaneous crystallization of the stereocomplex and constituent 100L is possible because the difference between their respective melting temperatures (208 versus 178 °C) is relatively small. Since the crystallization rate of the homopolymer is larger than that of the stereocomplex, the development of homopolymer crystals becomes predominant once the nucleation step is completed. However, no epitaxial crystallization has been observed for 100L/100D blends under the conditions used. The difference of melting temperatures between the homopolymer (178 °C) and the stereocomplex (235 °C) is rather high, and their crystallization rates are similar.[28] It is thus probable that crystallization of the stereocomplex is complete before that of the homopolymer begins, reducing the possibility of an epitaxial crystallization.

It is indicated in Table 1 that the molecular weight of sample 80D is larger than those of homopolymers 100D and 100L. Now, Tsuji *et al.*[18] have observed that complexation is favored if the molecular weights of the components are below 6×10^3 whereas homocrystallization is favored if they are above 1×10^5. However, no significant change in T_f was observed for the homopolymer between 4.9×10^3 and 4.2×10^5 whereas the decrease in T_f for the stereocomplex with increasing molecular weight was found to be significant but remained modest.[18] In this study, it can therefore be expected that the T_f values would be almost the same if both samples had similar molecular weights. In other words, the difference of 48° reported in Table 1 between homopolymer 100D and copolymer 80D is almost exclusively due to their difference in optical purity. The difference in molecular weight between samples 80D and 100D can also have a modest influence on the rate of crystallization, as will be discussed in a forthcoming article,[28] and on ΔH_f. Tsuji *et al.*[18] have shown that ΔH_f of homopolylactides increases with molecular weight, whereas the ΔH_f of the stereocomplex decreases. This behavior means that the amount of stereocomplex in 100L/80D blends would be higher if the molecular weight of copolymer 80D was smaller, all other conditions being equal; this behavior also means that the spherulitic morphology shown in Figures 5–9 could be more developed with a smaller molecular weight copolymer. However, our results suggest that the limitation imposed on the stereocomplex formation by the molecular weight of the components can be overcome, at least partially, by optimizing the crystallization conditions.

Conclusions

In summary, our results have permitted us to compare two polylactide mixtures, one where the two polymers are 100% isotactic (100L/100D blends) and a second one where one of the two polylactides has a smaller enantiomeric excess (100L/80D blends).

(a) They have shown that blends 100L/80D give, as a function of composition, spherulites which are similar, under polarized microscopy observation, to those found in 100L/100D blends.

(b) However, a closer analysis as a function of temperature indicates that the stereocomplexation process leads to a more rigid structure in the second case, and to a more flexible assembly with 100L/80D blends. This situation allows an easier crystallization of the homopolymer in excess in 100L/80D blends and, at the same time, the possibility of improving the stereocomplexation by isothermal crystallization.

(c) In the same blend, at a 80/20 composition, a phenomenon of epitaxial crystallization is observed when the stereocomplexation is slow and the rate of crystallization of the homopolymer is rapid.

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