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Stereocomplex Formation between Enantiomeric Poly(lactic acid)s. 3. Calorimetric Studies on Blend Films Cast from Dilute Solution

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ABSTRACT: Blend films were obtained by casting mixed solutions of poly(D-lactic acid) (PDLA) and poly(L-lactic acid) (PLLA). Crystallization in these films was studied by differential scanning calorimetry (DSC). When the casting solution was dilute (1 g/dL), racemic crystallites of PDLA and PLLA were preferentially produced, as long as either PDLA or PLLA had a low molecular weight, e.g., 5×10^3. In contrast, crystallites of PDLA or PLLA homopolymers were predominantly formed when the molecular weight of both polymers was high, e.g., 1×10^5. Racemic crystallization, however, occurred more predominantly than homopolymer crystallization even for the pair of PDLA and PLLA with the high molecular weight when the solution was aged for a long time at 10 g/dL prior to casting. On the basis of these DSC findings, a mechanism is proposed for the crystallization of enantiomeric poly(lactic acid)s when they are cast from dilute solution.

Introduction

The structure and properties of poly(lactic acid) (PLA) have been studied by numerous research groups,[1-7] but there are only a few studies on the racemic crystallization between poly(D-lactic acid) (PDLA) and poly(L-lactic acid) (PLLA). Recently, we reported that upon mixing their concentrated solutions, PDLA and PLLA can form racemic crystallites in solution.[8] The crystallite unit cell is arranged of PDLA and PLLA, packed side by side at a ratio of D-monomer unit to L-monomer unit of 1:1.[9,10] Poly(*tert*-butylethylene oxide)[11] and poly(*tert*-butylethylene sulfide)[12] are also reported to form racemic crystallites. Their melting behavior and wide-angle X-ray diffraction patterns differ from those of the homopolymers, similar to our PLA racemic crystallites.[13]

When racemic crystallites are formed from PDLA and PLLA in a concentrated solution kept at a constant polymer concentration, they act as cross-links and hence a three-dimensional gelation occurs.[8] Drying this swollen gel yields a brittle material with low crystallinity. The poor mechanical property is probably due to restricted molecular reorganization of the polymer chains to a more stable state. That is, chain mobility has been already largely restricted by formation of racemic microcrystallites in the gel phase, and further crystallization would be extremely difficult even after gel drying. The network will give rise to a decrease in enthalpy of fusion. Thus, to obtain a material with higher crystallinity and strength, it appears essential to allow further crystallization to take place during the drying process. Therefore, we have attempted to produce films composed of racemic crystallites by solution casting, where crystallization will take place during solvent evaporation. In this paper, we describe the effects of polymer molecular weight, casting solvent, and blending ratio of the isomers on the racemic crystallization of PDLA and PLLA.

Experimental Section

Materials. PDLA and PLLA were synthesized as previously reported.[14] Methyl D-lactate with an optical purity of 97% was supplied by Daicel Chemical Industries, Ltd., Japan, and hydrolyzed to D-lactic acid. L-Lactic acid with an optical purity of 98% was purchased in 90% aqueous solution from CCA Biochem BV, The Netherlands. Low molecular weight PLA was prepared by condensation polymerization of lactic acids and then thermally decomposed to yield the lactide monomers. Ring-opening polymerization of the lactides was performed in bulk at 140–220 °C using stannous octoate and lauryl alcohol as catalyst and initiator, respectively.[15] The resulting polymers were purified by repeated reprecipitation from the chloroform solution into methanol.

The viscosity-average molecular weight ($\bar{M}_v$) of the polymers was determined from their intrinsic solution viscosity $[\eta]$ in chloroform at 25 °C using the following equation:[16]

$$[\eta] = 5.45 \times 10^{-4} \bar{M}_v^{\,0.73} \qquad (1)$$

The specific optical rotation $[\alpha]$ of the polymers was measured in chloroform at a concentration of 1 g/dL at 25 °C using a Perkin-Elmer 241 polarimeter at a wavelength of 589 nm. The characteristics of the polymers used in this work are listed in Table I, together with the polymerization conditions. $[\alpha]^{25}{}_{\mathrm{D}}$ values of PDLA and PLLA were approximately +150 and −150°, respectively, in good agreement with literature values.[1]

The blend films were obtained by the following casting method. Each solution of PDLA and PLLA was separately prepared to have a polymer concentration of 1 g/dL and then admixed with each other under vigorous stirring. Methylene chloride was used as the solvent unless otherwise specified. This solvent was chosen as it has a low boiling temperature (40 °C) and thus can be readily removed from the cast film by drying. The mixing ratio of the solutions was fixed at a 1:1 volume ratio, unless otherwise mentioned. The mixed solutions were cast onto a flat glass plate, and the solvent was allowed to evaporate at room temperature for approximately 1 week. The resulting films were dried in vacuo for another week and annealed under a nitrogen gas flow at 140 °C for 1 h prior to the differential scanning calorimetry (DSC) measurement. Chloroform, benzene, and dioxane were also used as casting solvents to evaluate the effect of the solvent on the racemic crystallization of PLA. When these solvents were used, the solvent molecules left in the cast films were extracted by methanol before drying in vacuo.

Measurements. The melting temperature (T_f) and the enthalpy of fusion (ΔH_f) were measured for the blend films with a Shimadzu DT-50 differential scanning calorimeter. Annealing was performed under a nitrogen gas flow at a heating rate of 10 °C/min. T_f and ΔH_f were calibrated with indium as a standard.

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Table I
Polymerization Conditions and Molecular Characteristics of the Polymers

	polymerization conditions				polymer		
code	LA,[a] wt %	SO,[b] wt %	temp, °C	time, h	$[\eta]$, dL/g	$\bar{M}_v$	$[\alpha]^{25}_D$, deg
D1	0	0.03	140	10	0.27	4.9×10^3	+153
D2	0	0.03	220	5	0.92	2.6×10^4	+154
D3	0.4	0.03	140	10	1.36	4.5×10^4	+155
D4	0	0.03	220	0.5	1.70	6.1×10^4	+154
D5	0	0.03	140	0.3	2.79	1.2×10^5	+156
D6	0	0.03	140	10	6.15	3.6×10^5	+153
L1	0	0.003	140	81	0.36	7.3×10^3	-147
L2	0	0.03	140	5	0.96	2.8×10^4	-153
L3	0.5	0.03	140	10	1.30	4.2×10^4	-154
L4	0	0.03	160	5	1.71	6.2×10^4	-151
L5	0	0.03	140	10	3.01	1.3×10^5	-153
L6	0	0.03	140	10	6.16	3.6×10^5	-153
L7	0	0.03	140	10	6.98	4.2×10^5	-157

[a] Lauryl alcohol. [b] Stannous octoate.

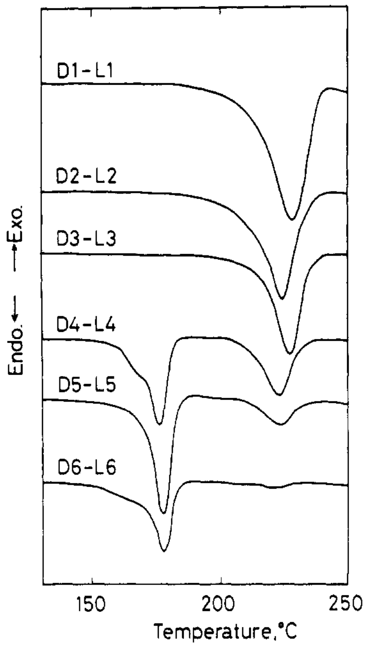

Figure 1. DSC thermograms of blend films of PDLA and PLLA with similar molecular weights.

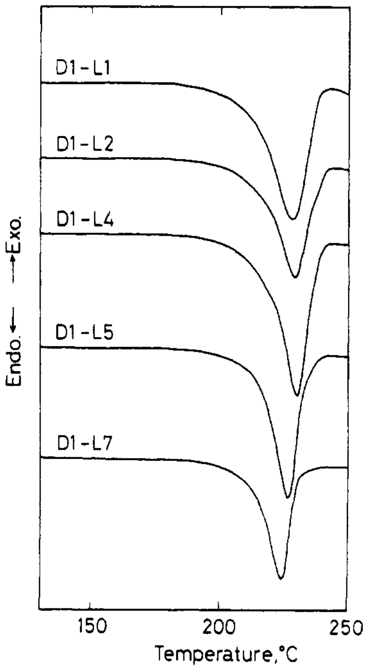

Figure 2. DSC thermograms of blend films of D1 and PLLA with various molecular weights.

Results

1. Blending of Polymers with Similar Molecular Weights. Figure 1 shows DSC thermograms of films cast from mixed solutions of PDLA and PLLA having similar molecular weights. The mixing ratio X_D, defined as [PDLA]/([PDLA] + [PLLA]), was fixed at 0.5 in all cases. A previous work has established that the peak at 180 °C is due to fusion of the homopolymer crystallites and that the peak at 230 °C is due to fusion of the racemic crystallites (stereocomplex crystallites).[13] These peak temperatures were assumed to be equal to the melting temperatures, T_{f1} and T_{f2}, of the homopolymer and the racemic crystallites, respectively. As is clearly seen, only T_{f2} is observed when the molecular weight of the polymers is below 4×10^4, whereas both T_{f1} and T_{f2} are observed for the polymers having molecular weights greater than 6×10^4. T_{f2} decreases with increasing molecular weight of the polymer, but T_{f1} remains almost unchanged. This implies that the average size of racemic crystallites decreases with increasing molecular weight of the polymers. Also, as the molecular weight of the polymer increases, the enthalpies of fusion at T_{f2} (ΔH_{f2}), estimated from the DSC peaks in Figure 1, become smaller and approach virtually zero at a molecular weight of 4×10^5. This indicates that racemic crystallization takes place exclusively for blends of polymers having molecular weight lower than about 4×10^4. Furthermore, the enthalpy of fusion at T_{f1} (ΔH_{f1}) becomes zero when the polymers have a molecular weight lower than 4×10^4 but approaches 40 J/(g-polymer) when the molecular weight of the polymers is greater than 6×10^4. Only ΔH_{f1} is observed for the polymer pair with the molecular weight of 3.6×10^5, indicating that the homopolymer crystallization prevails at this molecular weight. This is in contrast to solely racemic crystallization observed in the blend of PDLA and PLLA with the lowest molecular weight.

2. Blending of Polymers with Dissimilar Molecular Weights. The results of crystallization from pairs of the lowest molecular weight PDLA (D1) and PLLA of various molecular weights are illustrated in Figure 2. X_D is fixed at 0.5. It is seen that the main peak of fusion is observed at T_{f2} for all the polymer pairs, whereas no peak at T_{f1} is observed. T_{f2} monotonously decreases with an increase of the molecular weight of PLLA ($\bar{M}_v$(L)) in the region above 6×10^4. ΔH_{f2}, calculated from Figure 2, was approximately 70 J/(g-polymer) for PLLA with molecular weight less than 6×10^4 and 50 J/(g-polymer) for PLLA with molecular weight greater than 1×10^5. On the other hand, ΔH_{f1} was zero and independent of the mo-

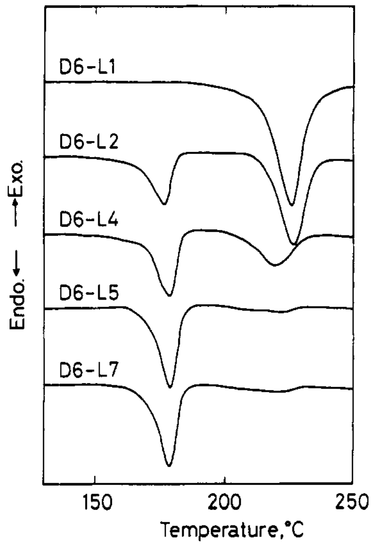

Figure 3. DSC thermograms of blend films of D6 and PLLA with various molecular weights.

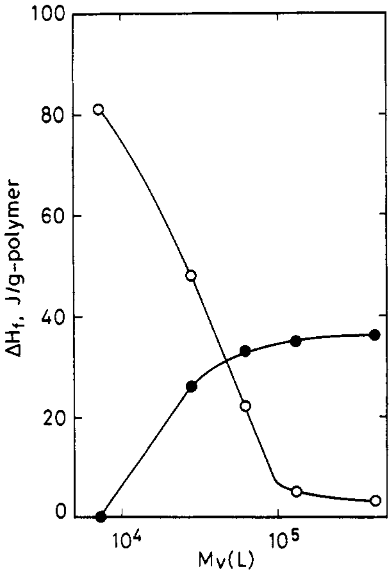

Figure 4. ΔH_{f1} (●) and ΔH_{f2} (○) calculated from Figure 3 as a function of PLLA molecular weight.

lecular weight of the PLLA. These results suggest that, when the molecular weight of at least one of the components in the PDLA and PLLA blend is sufficiently low, racemic crystallites are preferentially formed with virtually no homopolymer crystallites.

To confirm this finding we further studied the crystallization between PDLA with the highest molecular weight (D6) and PLLA of various molecular weights. Figure 3 shows the DSC thermograms of the blend films from these polymer pairs. Apparently, the result is similar to that shown in Figure 1. Figure 4 presents ΔH_{f1} and ΔH_{f2} calculated from Figure 3. It is seen that ΔH_{f1} gradually increases with increasing molecular weight of PLLA, approaching 35–40 J/(g-polymer), whereas ΔH_{f2} monotonously decreases with increasing molecular weight of PLLA and becomes virtually zero at a molecular weight of 1×10^5. This result also supports the assumption that racemic crystallites are formed preferentially to homopolymer crystallites if the molecular weight of at least one component of the PDLA and PLLA blend is sufficiently small.

3. Influence of Blending Ratio. Figure 5 shows the peak temperatures, T_{f1} and T_{f2}, as a function of X_D for the blend films of D2 and L2. When X_D is between 0.1 and 0.3 and between 0.7 and 0.9, both T_{f1} and T_{f2} can be observed. Only T_{f2} appears for films whose X_D is in the range from 0.4 to 0.6, whereas only T_{f1} is observed at X_D = 0 or 1 (pure PDLA or PLLA). T_{f2} remains almost unchanged over the X_D range from 0.1 to 0.9, implying that the average size of racemic crystallites is practically constant. ΔH_{f1} and ΔH_{f2} for blend films of D2 and L2 are plotted as a function of X_D in Figure 6. It is obvious that the maximum of ΔH_{f2} is observed exactly at X_D = 0.5. This finding is similar to that observed in our previous work where the induction time of the viscosity rise occurring upon mixing of concentrated solutions of PDLA and PLLA was studied as a function of X_D.[8]

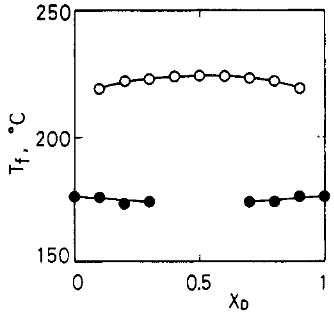

Figure 5. T_{f1} (●) and T_{f2} (○) as a function of X_D for blend films of D2 and L2.

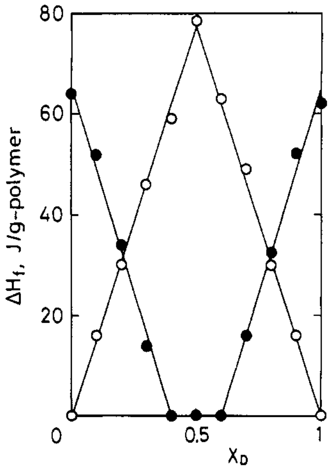

Figure 6. ΔH_{f1} (●) and ΔH_{f2} (○) as a function of X_D for blend films of D2 and L2.

The dependence of T_f and ΔH_f on X_D was different for different pairs of PDLA and PLLA. For instance, the blend films of D6 and L6 exhibited a much larger endothermic melting peak around T_{f1} than around T_{f2}, irrespective of X_D, as shown in Figure 7. This must be ascribed to the very high molecular weight of D6 and L6, thereby resulting in insignificant formation of racemic crystallites, as demonstrated earlier. Figure 7 shows that ΔH_{f1} remains almost constant for X_D in the range between 0.1 and 0.9, whereas ΔH_{f2} is quite small in this range. ΔH_{f1} of the homopolymer films is slightly larger than that of blend films, suggesting that the homopolymer crystallization is slightly reduced by the racemic crystallization.

4. Influence of Solvent. We examined whether or not racemic crystallites were formed in solvents other than methylene chloride by casting solutions of PDLA and PLLA with similar molecular weights. Chloroform, benzene, and dioxane were used as solvents of PLA in addition to methylene chloride. Figure 8 shows the DSC thermograms of the blend films cast from 1:1 mixed solutions of D3 and L3 in these solvents. As is clearly seen, only the

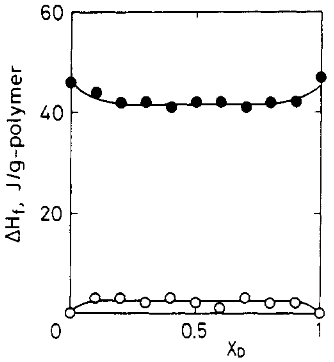

Figure 7. ΔH_{f1} (●) and ΔH_{f2} (○) as a function of X_D for blend films of D6 and L6.

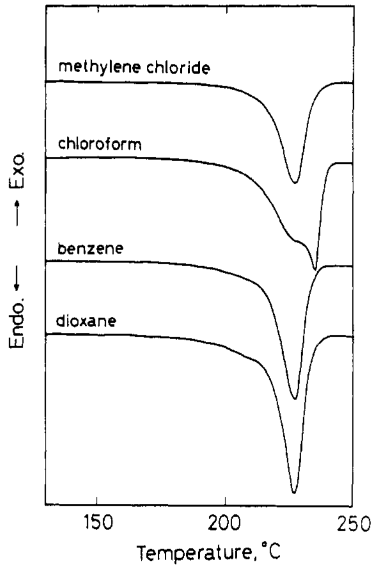

Figure 8. DSC thermograms of blend films of D3 and L3 cast from solutions in various solvents.

Table II
DSC Results on Blend Films Cast from Solutions in Various Solvents

		T_f		ΔH_f, J/(g-polymer)	
blend film	solvent	T_{f1}	T_{f2}	ΔH_{f1}	ΔH_{f2}
D3 + L3	methylene chloride		227		65
	chloroform		235		84
	benzene		228		80
	dioxane		228		88
D6 + L6	methylene chloride	178	221	42	4
	chloroform	178	223	34	2
	benzene	178	221	54	3
	dioxane	181	223	55	13

melting endotherm of the racemic crystallite (T_{f2}) is observed for all the solvents. The shape of the DSC curve for the blend from the chloroform solution is different from those of the methylene chloride, benzene, and dioxane solutions. The formation of a double peak was very reproducible. The values of T_f and ΔH_f calculated from the thermograms are given in Table II. It appears that the solvent used for casting does not greatly influence the formation of racemic crystallites.

Figure 9 gives the DSC thermograms of the blend films of D6 and L6 cast from the various solutions. Both polymers have a high molecular weight of 3.6×10^5. T_{f1}, T_{f2}, ΔH_{f1}, and ΔH_{f2} obtained from Figure 9 are listed in Table II. As seen from Table II, ΔH_{f2} is much lower than ΔH_{f1}, irrespective of the solvent used, indicating that the mixture of PDLA and PLLA, both of which have a high molecular weight, forms homopolymer crystallites preferentially over racemic crystallites in all solvents.

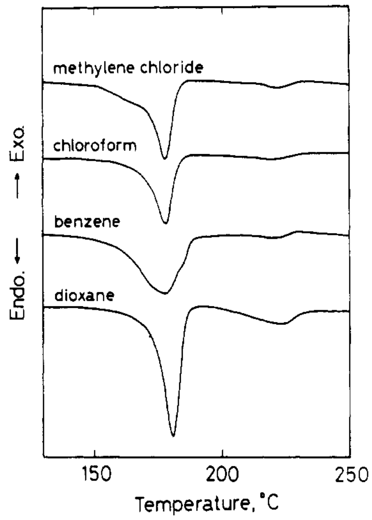

Figure 9. DSC thermograms of blend films of D6 and L6 cast from solutions in various solvents.

Discussion

As is evident from the above DSC results, racemic crystallization takes place more readily than homopolymer crystallization, if both PDLA and PLLA have a low molecular weight and are mixed together at X_D close to 0.5. The crystallization is schematically depicted in Figure 10(1). In this case, the nucleation and growth of the racemic crystallites appear to come to completion readily by solvent evaporation within a short period of time. If solutions of PDLA and PLLA, both with a low molecular weight, are mixed at a nonequimolar ratio, racemic crystallites are formed, but the excess component of PDLA or PLLA will be left without participating in the racemic crystallization. This remaining homopolymer component may aggregate and form homopolymer crystallites when the solution is condensed. Thus, both the homopolymer and the racemic crystallites are formed at these mixing ratios as schematically illustrated in Figure 10(2).

When PDLA and PLLA with dissimilar molecular weights are mixed, the lower molecular weight component may diffuse to the higher molecular weight one, resulting in the nucleation and growth of racemic crystallites as shown in Figure 10(3). On the other hand, a solution of PDLA and PLLA, both with a high molecular weight, may not be microscopically homogeneous because of enthalpic repulsions between the dissimilar molecules of such a high molecular weight, resulting in preferential homopolymer crystallization. Therefore, the racemic crystallization must take place only in the overlapped region of PDLA and PLLA molecules. This is depicted in Figure 10(4).

However, there is a probability of the growth of racemic crystallites by chain reordering, provided the mixed solution is allowed to stand at a high constant concentration for a sufficiently long time for the dissimilar polymer chains to frequently interact, as is illustrated in Figure 10(5). To verify this assumption, we studied the crystallization of a polymer pair, keeping the solution at a constant concentration for a prolonged time. Figure 11 shows the DSC thermogram of a sample prepared by the following method. First, each of 10 g/dL (not 1 g/dL) chloroform solutions of D6 and L6 was mixed together at X_D of 0.5. The mixed solution was sealed in a test tube and kept at room temperature for 3 years. Gelation took place and the gel became turbid in 3 years, suggesting that cross-

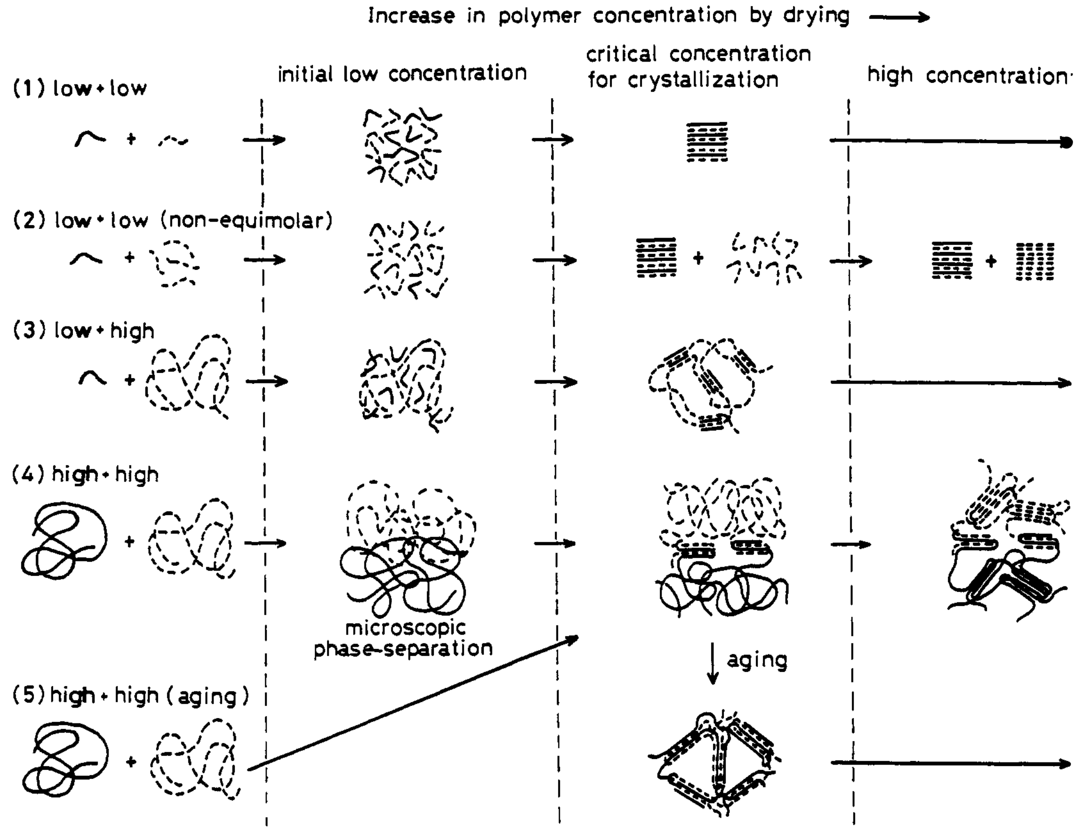

Figure 10. Schematic presentation of PLA crystallite formation between polymer pairs with different molecular weights cast from solution.

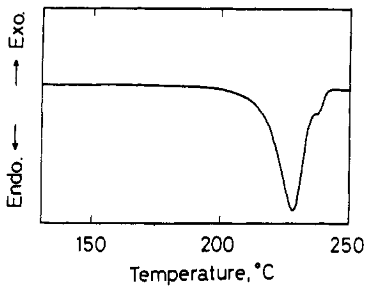

Figure 11. DSC thermogram of a blend film of D6 and L6 whose solution was kept at 10 g/dL and room temperature for 3 years.

links or racemic crystallites were formed in the solution. Then, following the evaporation of the solvent, drying and annealing were performed on this material prior to the DSC measurement by the same method as described in the Experimental Section. The dried film was flexible. As seen from Figure 11, only racemic crystallites are formed. The ΔH_{f2} value was calculated from the peak to be 74 J/(g-polymer), which is approximately the same as that of the film cast from the pair of D3 and L3 (84 J/(g-polymer) in Table II). This indicates that the blend film of D6 and L6 obtained after aging the solution prior to casting has a high degree of crystallinity, similar to that of D3 and L3. This finding supports the assumption that racemic crystallites can be formed from a mixed solution of PDLA and PLLA over the entire molecular weight range if the solution is allowed to stand at a high concentration for a prolonged period of time prior to solvent evaporation. However, as long as the conventional casting method is used, the evaporation rate seems too high for the PDLA and PLLA molecules with a high molecular weight to form racemic crystallites.

As was shown previously, racemic crystallites were also formed from the mixture of PDLA and PLLA if the solution concentration was kept constant above a critical polymer concentration for gelation (C_c).[8] In the case of casting, the concentration of mixed polymer solutions gradually increases, finally approaching the dried polymer density, as the solvent evaporates. Racemic crystallization can take place when the solution concentration exceeds C_c, but the concentrated solution may undergo microscopic phase separation into a PDLA-rich and a PLLA-rich phase, especially when the molecular weight of both polymers is high. In addition, racemic crystallization proceeds slowly as was shown previously.[8] Thus, homopolymer crystallization may dominate racemic crystallization, if both the PDLA and PLLA have a molecular weight high enough for microscopic phase separation. In other words, the X_D values must deviate locally from 0.5 although the overall X_D is 0.5 when the mixed cast solution of PDLA and PLLA with a high molecular weight becomes concentrated as the solvent evaporates. Probably, the rate of racemic crystallization is quite low compared to that of the solvent evaporation, although racemic crystallization proceeds more quickly than homopolymer crystallization in microscopically well mixed solutions.

Conclusion

No significant crystallization takes place at the moment of mixing of two dilute solutions of PDLA and PLLA, but both racemic and homopolymer crystallization may occur in the course of solvent evaporation because of the solution concentration. However, there is a critical molecular weight below which racemic crystallites are obtained. For instance, this molecular weight is approximately 6 × 10^4 for formation of racemic crystallites in methylene chloride allowed to evaporate from the mixture for 1 week at room temperature. Racemic crystallites of PDLA and PLLA are predominantly formed below the critical molecular weight, while homopolymer crystallization of PDLA or PLLA is predominant above the critical molecular weight. On aging the solution at a high constant concentration before casting, however, racemic crystallites can be formed even from the pair of PDLA and PLLA with a higher molecular weight. These results indicate that materials containing only intermolecular crystallites can be obtained by racemic crystallization for all molecular weights of PLA. Racemic crystallites are more stable than homopolymer crystallites in mixed solutions of PDLA and PLLA.

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Registry No. (PDLA)(PLLA) (copolymer), 127514-57-2.