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Stereocomplex Formation between Enantiomeric Poly(lactic acid)s. 6. Binary Blends from Copolymers

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ABSTRACT: Binary blend films from copolymers of D- and L-lactic acids were obtained by casting mixed solutions of the two copoly(lactic acid)s (PLA) with different D-contents (X_D) and were studied by differential scanning calorimetry (DSC). We selected four cases from the combinations of binary (A–B) blends: mixing the same polymer [$X_D(A) = X_D(B)$], cross blending under the condition that $X_D(A) + X_D(B) = 1$, blending between a D-polymer ($X_D = 1$) and other PLAs, and blending between a 1:1 DL-copolymer ($X_D = 0.5$) and other PLAs. Racemic crystallites were exclusively formed between D-rich PLA and L-rich PLA when they had high optical purities. The melting point and enthalpy of the racemic crystallites decreased with decrease in the optical purity of D-rich PLA or L-rich PLA, suggesting that a D-unit in the L-rich polymer or an L-unit in the D-rich polymer disturbed the growth of racemic crystallites. This behavior was very similar to the homocrystallization in nonblended films. Homocrystallites were formed only if one component was crystallizable and the other component was noncrystallizable or if both components were crystallizable but had a similar X_D content. The noncrystalline 1:1 DL-copolymer did not influence the crystallization of the other crystallizable polymer.

Introduction

It has been well established that stereocomplex formation takes place when a D-polymer is mixed with an L-polymer.[1-11] We have also demonstrated that racemic poly(lactic acid) (PLA) crystallites are preferentially formed as a result of stereocomplexation between D- and L-units when a concentrated mixture of D- and L-polymers is allowed to stand,[12] when polymer is cast from a dilute mixed solution[13] or precipitated into a nonsolvent from a dilute mixed solution,[14,15] or when the temperature of a dilute mixed solution is lowered.[16]

All of our previous studies on racemic crystallization were carried out using homopolymers of D- and L-monomers. The present investigation was undertaken to study the tacticity effect on the crystallization behavior through casting mixed solutions from lactic acid copolymers with different chemical compositions including D- and L-homopolymers. Although the effects of optical purity of PLA on homocrystallization were studied,[17-19] no study on the effects of optical purity of PLA on racemic crystallization in binary blends has yet been reported. As for poly(α-methyl-α-ethyl-β-propiolactones) (PMEPL), the effects of optical purity of the polymer on stereocomplexation have been studied for blends prepared keeping the optical purity of one component constant and changing the other one from the homopolymer to the completely random copolymer.[20] In this paper, we have synthesized PLAs of various D-contents, in other words, optical purities, by ring-opening polymerization of mixtures of D- and L-lactides and have investigated the racemic crystallization and homocrystallization in binary blends using differential scanning calorimetry (DSC).

Experimental Section

Materials. PLAs were synthesized as previously reported.[21] Methyl D-lactate with an optical purity of 97% was hydrolyzed to D-lactic acid. L-Lactic acid with an optical purity of 98% was of commercial grade. The lactide monomers were obtained by thermal decomposition of low molecular weight PLAs prepared by condensation polymerization of lactic acids. Ring-opening copolymerization of the mixture of D- and L-lactides was performed in bulk at 140 °C for 10 h using stannous octoate and lauryl alcohol as polymerization modulators.[22] To effect the polymerization sealed tubes containing the mixture of D- and L-lactides were vigorously shaken after melting of the monomers. The monomers in the resulting polymer were removed by repeated reprecipitation from chloroform solution into methanol. The following analyses were made on the residual polymers. Number-average molecular weight of the polymers (M_n) was evaluated from GPC obtained with a Shimadzu LC-6A system with SHIM pack columns (GPC806, GPC804, and GPC802) using polystyrene as standard. The polymers prepared from the mixture of D- and L-lactides in bulk have been reported to give a distribution curve of D- and L-units lying between the theoretical curves of the Bernoullian single- and pair-addition statistics, while the experimental curve approaches that of the pair-addition statistics, especially at L-unit contents above 80%.[19]

Intrinsic viscosities, [η], were measured in chloroform at 25 °C using an Ubbelohde viscometer.

The specific optical rotation, [α], of the polymers was measured in chloroform at a concentration of 1 g/dL at 25 °C using a JASCO DIP-140 polarimeter at a wavelength of 589 nm. The blend films were obtained by the following casting method. Each methylene chloride solution of PLA was separately prepared to have a polymer concentration of 1 g/dL and then admixed with the other under vigorous stirring. The mixing ratio of the two solutions was always fixed at a 1:1 weight ratio. 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 prior to the DSC measurement. 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. Heating was performed under nitrogen gas flow at a heating rate of 10 °C/min. T_f and ΔH_f were calibrated using indium as standard.

Results

For this study 19 different PLAs were prepared, including 2 homopolymers and 17 copolymers with different D-unit (or L-unit) contents. The molecular characteristics are listed in Table I. The M_w/M_n ratio ranged from 2 to 4. The chemical composition of these PLAs is expressed here by the mole fraction of D-unit in the polymer, X_D.

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Table I
Molecular Characteristics of the Polymers

code	$[\eta]$ (dL/g)	M_n	$[\alpha]^{25}_D$ (deg)	X_D	OP[a] (%)
C-1	0.68	2.5×10^4	+156	1.000	100
C-2	0.72	2.6×10^4	+147	0.971	94
C-3	0.50	2.1×10^4	+142	0.955	91
C-4	0.73	2.9×10^4	+133	0.926	85
C-5	0.62	2.3×10^4	+130	0.917	83
C-6	0.65	2.3×10^4	+120	0.885	77
C-7	0.60	2.1×10^4	+119	0.882	76
C-8	1.74	7.9×10^4	+103	0.830	66
C-9	1.69	7.6×10^4	+86	0.776	55
C-10	0.88	3.7×10^4	0	0.500	0
C-11	1.64	4.7×10^4	-87	0.221	56
C-12	2.17	1.0×10^5	-111	0.144	71
C-13	1.26	4.9×10^4	-118	0.122	76
C-14	1.28	5.6×10^4	-122	0.109	78
C-15	1.25	5.2×10^4	-130	0.083	83
C-16	1.02	5.1×10^4	-133	0.074	85
C-17	1.41	4.3×10^4	-141	0.048	90
C-18	1.08	4.2×10^4	-145	0.035	93
C-19	0.56	2.5×10^4	-153	0.010	98

[a] Optical purity of polymers.

$$X_D = [\text{D-unit}]/([\text{D-unit}] + [\text{L-unit}]) \qquad (1)$$

$$= [[\alpha] - (-156)]/[156 - (-156)] \qquad (2)$$

where $[\alpha]$ is the specific optical rotation of the polymer. As $[\alpha]$ of the L-polymer is reported to be −156,[19] we assumed that the $[\alpha]$ values of the pure L- and D-polymers are −156 and +156, respectively.

There are $19^2/2$ combinations for physical mixing even at the 1:1 weight ratio from two separated A and B groups which has 19 different polymers for each. As this combination number is too large, we limited the mixing combination to four cases, as illustrated in Figure 1: blend 1, mixing the same polymer $[X_D(A) = X_D(B)]$ (blend 1 is not a blend, but we will use here the work "blend" for simplicity and uniformity); blend 2, cross blending under the condition that $X_D(A) + X_D(B) = 1$; blend 3, blending between D-polymer ($X_D = 1$, C-1) and 19 PLAs; blend 4, blending between 1:1 DL-copolymer ($X_D = 0.5$, C-10) and 19 PLAs.

For these four blending combinations we have conducted DSC measurements and estimated melting temperatures of homocrystallites (T_{f1}) and racemic crystallites (T_{f2}) as well as their enthalpies of fusion (ΔH_{f1} and ΔH_{f2}) from the DSC thermograms. We have already reported that the racemic crystallites from the mixture of homopolymers of D-lactide and L-lactide have a melting point around 230 °C, which is higher than 180 °C, the melting temperature of the homocrystallites from either homopolymer of D-lactide or L-lactide.[14] We use the terminology "homocrystallite" for the crystallite consisting entirely of either D-monomer unit or L-monomer unit sequences.

Blend 1. As mentioned above, this case is not a true blending but a simple assembly of the same polymer chains. Figure 2 shows the DSC thermograms of films cast from a 1 g/dL solution for 19 PLAs. The polymer whose X_D ranges from 0.14 to 0.83 exhibited neither an endothermic nor an exothermic peak. As seen in Figure 2, there is no melting peak of racemic crystallites but only that of homocrystallites, which becomes smaller and shifts to lower temperature as X_D approaches 0.5. This means that the crystalline size decreases as the PLA polymer loses optical purity. T_{f1} and ΔH_{f1} evaluated from the DSC thermograms are plotted as a function of X_D in Figures 3 and 4. It is seen that T_{f1} as well as ΔH_{f1} goes to zero long before X_D approaches 0.5, implying that the D-unit in L-rich PLA or the L-unit in the D-rich polymer inhibits the growth of homocrystallites. ΔH_{f1} becomes zero at $0.14 \leq X_D \leq 0.83$ to show that the cast films contain no crystallites.

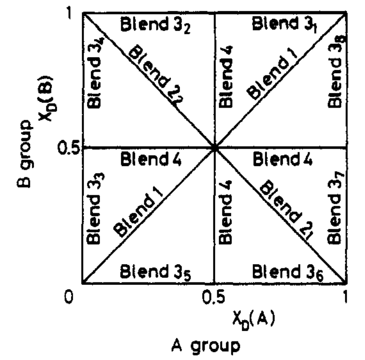

Figure 1. Binary blends used in this study.

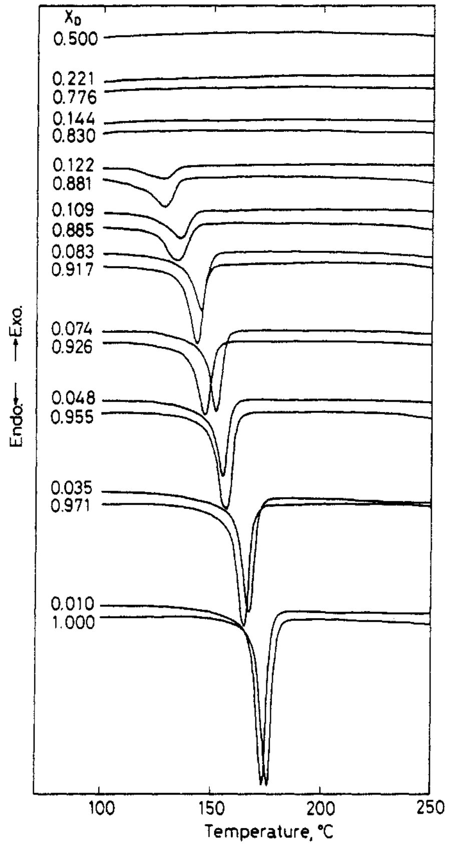

Figure 2. DSC thermograms of films cast from 1 g/dL solutions for C-1 to C-19 (blend 1).

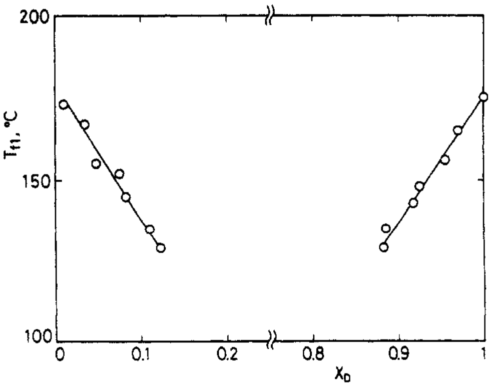

Figure 3. T_{f1} evaluated from Figure 2 as a function of X_D.

Blend 2. This case is the blending between D-rich PLA and L-rich PLA keeping $X_D(A) + X_D(B) = 1$, in other words, the blending under the condition that both of the

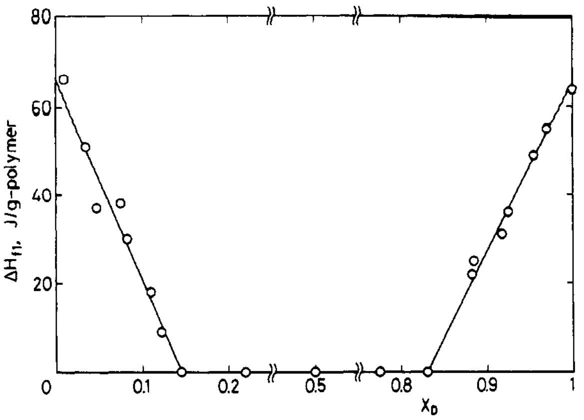

Figure 4. ΔH_{f1} evaluated from Figure 2 as a function of X_D.

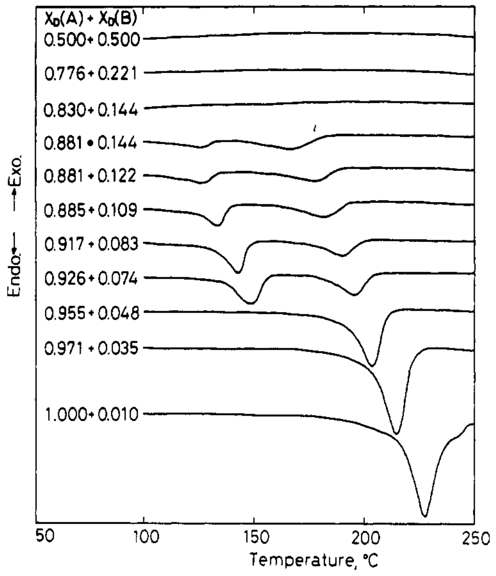

Figure 5. DSC thermograms of blend films from D-rich PLA (C-1 to C-9, A) and L-rich PLA (C-11 to C-19, B) (blend 2_1).

groups have the same optical purity. As it is practically too difficult to satisfy strictly this blending condition, we selected the most appropriate pairs from our PLA samples. The polymer pairs employed include C-1•C-19, C-2•C-18, C-3•C-17, C-4•C-16, C-5•C-15, C-6•C-14, C-7•C-13, C-7•C-12, C-8•C-12, C-9•C-11, and C-10•C-10. Here we present only the data obtained at blend 2_1 in the blending diagram in Figure 1, as it is completely identical to blend 2_2. The DSC thermograms obtained for the blend films are illustrated in Figure 5. When D- and L-polymers are blended [C-1 (X_D = 1.00) and C-19 (X_D = 0.01)], the melting peak appears around 230 °C, which corresponds to the melting point of racemic crystallites as demonstrated previously.[14] Apparently, the peak of the racemic crystallites becomes smaller and shifts to lower temperature as X_D of both groups approaches 0.5 and finally disappears when C-8 (X_D = 0.83) and C-12 (X_D = 0.14) are mixed. This tendency is seemingly very similar to the formation of homocrystallites in blend 1. Interestingly, the homocrystallite peak also appears on the thermograms from the C-4 (X_D = 0.93)•C-16 (X_D = 0.07) pair but disappears for the C-8 (X_D = 0.83)•C-12 (X_D = 0.14) pair.

T_{f1} and T_{f2} evaluated from Figure 5 are plotted as a function of X_D in Figure 6, where it is clear that both T_{f1} and T_{f2} decrease with decreasing X_D(A) or increasing X_D(B). T_{f1} appears in the very narrow range from 0.88 to 0.93. The relation between T_{f1} and X_D is almost identical to that given in Figure 3. This means that the sizes of the homocrystallites in blend 2 are similar to those in blend 1 and homocrystallization is not influenced by racemic crystallization. Figure 7 shows ΔH_{f1} and ΔH_{f2} as a function of X_D. It is seen that ΔH_{f2} decreases linearly with decreasing X_D(A) until 0.93, remains almost constant at 10 J/(g of polymer) for X_D(A) from 0.92 to 0.88, and finally becomes zero when X_D(A) is below 0.83. On the other hand, ΔH_{f1} has definite values only in the X_D range where ΔH_{f2} remains constant. Apparently, the homocrystallization and the racemic crystallization are concurrently taking place in this X_D region. When X_D was below 0.83, neither homocrystallization nor racemic crystallization occurred.

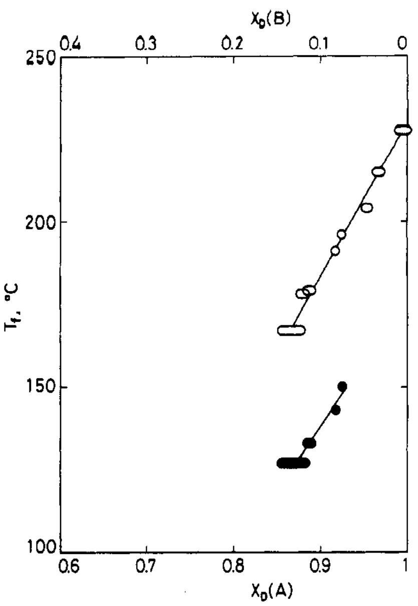

Figure 6. T_{f1} (●) and T_{f2} (○) evaluated from Figure 5 as a function of X_D(A) and X_D(B).

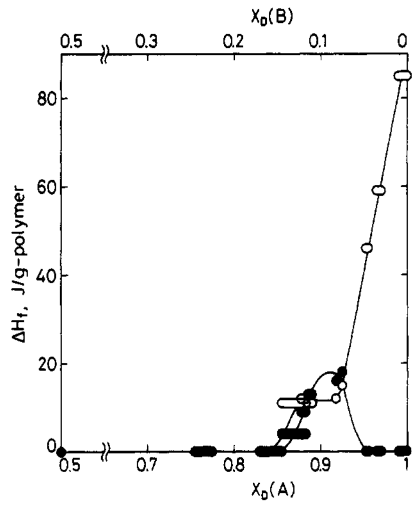

Figure 7. ΔH_{f1} (●) and ΔH_{f2} (○) evaluated from Figure 5 as a function of X_D(A) and X_D(B).

Blend 3. We present here only the results obtained in blend 3_1 and blend 3_2 illustrated in Figure 1. Clearly, blend 3_3, blend 3_5, and blend 3_8 will give the same results as blend 3_1, while blend 3_4, blend 3_6, and blend 3_7 will give the same results as blend 3_2. Blend 3_1 and blend 3_2, to be described below, correspond to the blending of D-polymer [C-1, X_D(B) = 1] with all 19 PLAs. The observed DSC thermograms of the blend films are shown in Figure 8. The thermograms have only one main peak at approximately the same temperature of 180 °C when the X_D of the counterparts of the D-polymer, X_D(A), is above 0.22. The area of the peaks at 180 °C becomes smaller with a decrease in X_D(A), irrespective of the shoulder. On the other hand, when X_D(A) is lower than 0.22, that is, the

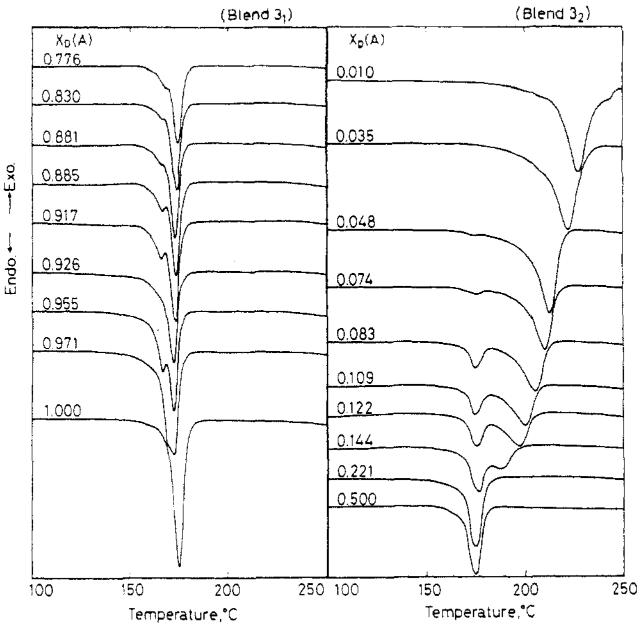

Figure 8. DSC thermograms of blend films from D-polymer (C-1, B) and all PLAs (C-1 to C-19, A) (blends 3_1 and 3_2).

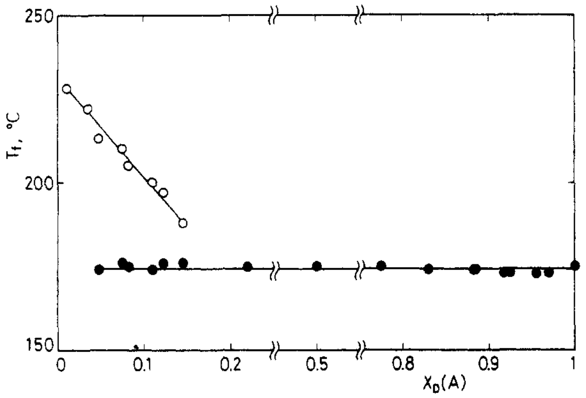

Figure 9. T_{f1} (●) and T_{f2} (○) evaluated from Figure 8 as a function of X_D of the counterpart of C-1, $X_D(A)$.

D-polymer is blended with L-rich PLAs (blend 3_2), the peak corresponding to the racemic crystallites appears while that of the homocrystallites gradually disappears. The $X_D(A)$ range, where only the melting peak of the racemic crystallites is observed, is below 0.04, whereas peaks for both homocrystallites and racemic crystallites are seen for $X_D(A)$ from 0.05 to 0.14, similar to blend 2, having $X_D(A)$ from 0.88 to 0.93. Homocrystallites with only one peak are observed for blend 3_2 with $X_D(A)$ of 0.22, but not with $X_D(A)$ of 0.14. To determine more precisely the critical $X_D(A)$ for formation of the two crystallites, DSC of the blend film from the L-polymer (C-19) and a D-rich PLA with X_D of 0.83 (C-8) was performed, as the blend film from the D-polymer and an L-rich PLA with X_D of 0.17 was not available. The DSC thermogram showed peaks of both racemic crystallites and homocrystallites, suggesting that the D-polymer and the L-rich PLA [$X_D(A) = 0.17$] could form both types of crystallites. Therefore, racemic crystallites and homocrystallites were found to simultaneously form for the D-polymer with PLAs having $X_D(A)$ ranging between 0.05 and 0.17.

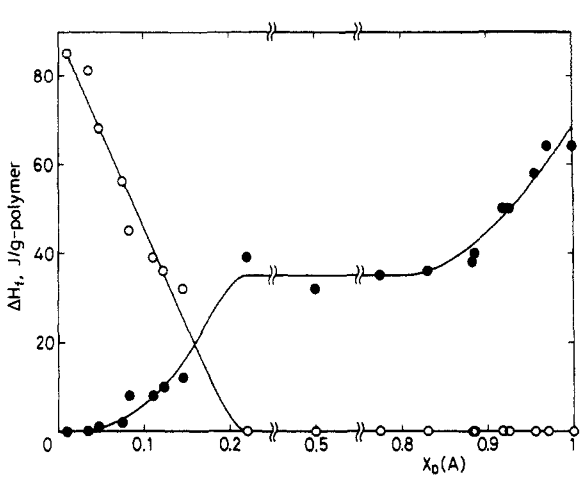

Figure 10. ΔH_{f1} (●) and ΔH_{f2} (○) evaluated from Figure 8 as a function of X_D of the counterpart of C-1, $X_D(A)$.

T_{f1} and T_{f2} of the films obtained in blends 3_1 and 3_2 are plotted as a function of $X_D(A)$ in Figure 9. Obviously, T_{f1} is constant around 174 °C, independent of $X_D(A)$. Although there are two kinds of polymer, that is, the D-polymer and one of the PLAs in the blended films, only one peak is observed at 174 °C in the $X_D(A)$ range above 0.15. This temperature is identical to the melting point of the D-polymer as shown in Figure 3. This indicates that only D-polymer can crystallize by itself, not with other PLAs when their $X_D(A)$ is higher than 0.15. It is seen in Figure 9 that T_{f2} linearly decreases from 230 °C with increasing $X_D(A)$, although T_{f1} remains constant around 174 °C, irrespective of $X_D(A)$. It follows that the size of racemic crystallites must decrease as $X_D(A)$ becomes higher, while the excess D-polymer assembles itself to form homocrystallites without being affected by racemic crystallization, as mentioned above. It should be noted that the slope of T_{f2} against $X_D(A)$ in Figure 9 is smaller than that in Figure 6, probably because the size of the racemic crystallites more drastically decreases as X_D of both PLAs approaches 0.5.

ΔH_{f1} and ΔH_{f2}, evaluated from Figure 8, are plotted against $X_D(A)$ in Figure 10, where ΔH_{f1} is seen to increase from zero to about 35 J/(g of polymer) when $X_D(A)$ increases from zero to 0.22 and then to remain almost constant at $X_D(A)$ below 0.89, followed by a steep increase to 64 J/(g of polymer), which is ΔH_{f1} of the homopolymer. If the D-polymer crystallizes only by itself even in the films blended with PLA, ΔH_{f1} should amount to 32 J/(g of polymer), which is half of ΔH_{f1} observed for the D-polymer. Indeed, the observed values are close to 32 J/(g of polymer) in the range from 0.2 to 0.8 but greatly deviate from 32 J/(g of polymer) when $X_D(A)$ is lower than 0.2 or higher than 0.8, suggesting that the D-polymer and D-rich PLAs together participate in crystallization to yield homocrystallites with the size similar to that from D-polymer at $X_D(A)$ higher than 0.8. On the other hand, T_{f2} and ΔH_{f2} dramatically decrease with increase in $X_D(A)$. Again, this indicates that the D-units in L-rich PLAs disturb the racemic crystallization between the D-polymer and the L-rich PLA of its counterpart.

Blend 4. DSC studies on the blend films from the noncrystalline 1:1 DL-copolymer (C-10, $X_D = 0.5$) and 19 PLAs have been performed. This blending corresponds to blend 4 in the diagram given in Figure 1. Only the homocrystallite peak was observed at X_D of the counterpart of C-10 below 0.12 or above 0.88 (data not shown). T_{f1} plotted as a function of X_D of the counterpart of C-10 is very similar to that in Figure 3, while ΔH_{f1} as a function of X_D of the counterpart of C-10 is just half the ΔH_{f1} in Figure 4 when they are compared at the same X_D. This means that only PLAs can crystallize without any disturbance by the noncrystalline 1:1 copolymer. In this blend system, the homocrystallites are formed only at X_D below 0.12 or above 0.88.

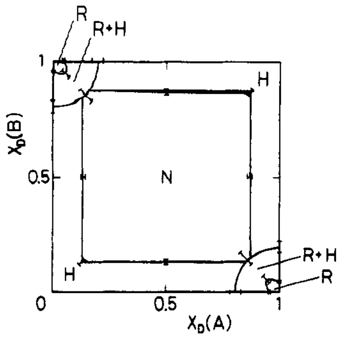

Figure 11. Schematic representation of the DSC results on binary blends of copolymers. R, racemic crystalline; R + H, racemic crystalline and homocrystalline; H, homocrystalline; N, noncrystalline.

Discussion

Binary blending from the D-polymer, the L-polymer, the 1:1 DL-copolymer, and the random copolymers yields three kinds of physical states: noncrystalline (amorphous), homocrystalline, and racemic crystalline (stereocomplexed). In the blend films, only one of these states or the mixed states are present, depending on the nature of blending polymers, as described above. As the crystallinity of any film is not 100%, the amorphous component must be present in every case. Figure 11 shows the schematic representation of the DSC results on binary blends when two random copolymers of D- and L-units are mixed at the 1:1 weight ratio in methylene chloride solution and cast to produce films. Although the molecular weights and the molecular weight distributions of the polymers are not identical, each region has a rather clear boundary for the three states. As can be seen, Figure 11 involves a mixed region of the racemic crystalline and the homocrystalline states, in addition to their single regions. It should be noted that the region where only racemic crystallites, not homocrystallites, are formed is limited to a very small region compared with others. Exclusive formation of the racemic crystallites between D- and L-units is not possible if the D- and the L-polymers contain the opposite monomer unit higher than 3 mol %, which corresponds to an optical purity of 94%. If the optical purity of PLA decreases further, the homocrystallites of D-monomer unit or L-monomer unit sequences start to form, together with the racemic crystallites. Our previous work has revealed that, when the D-polymer and the L-polymer, both with a sufficiently low molecular weight, are blended at a mixing ratio different from 1:1, racemic crystallites are preferentially formed and then followed by homocrystallite formation from the remaining D- or L-polymer. This clearly suggests that racemic crystallization more readily takes place than homocrystallization, so far as the conditions necessary for both crystallizations are satisfied. When a D-rich polymer and an L-rich polymer with much different optical purities are mixed at the 1:1 polymer weight ratio as in blend 3_2, the average X_D deviates from 0.5. In this case, a fraction of the component whose optical purity is higher than the other remains without taking part in racemic crystallization because of nonstoichiometric X_D, and the excess polymer will assemble itself to form the homocrystallites. This is the reason why the boundary of region where only racemic crystallites are formed approaches the point $[X_D(A), X_D(B)] = [0, 1]$ or $[1, 0]$. On the other hand, the coexistence of two different crystalline forms in blend 2 where the total X_D is always kept at 0.5 may be explained in terms of D-unit and L-unit distribution along the copolymer chain. As this copolymer is of the random type, it has a possibility that there is a continuing sequence of the same repeating units in the polymer chain. Thus, copolymer chains with a long continuing sequence will form racemic crystallites with the counterpart of chains with a long continuing sequence. On the other hand, chains with a short sequence of repeating units may assemble themselves to form their homocrystallites. Homocrystallization may become impossible if the minor repeating unit in copolymer is larger than 0.14–0.17 in the mole fraction or the optical purity is lower than 66–72%. If the content of the minor unit exceeds this threshold, even the homocrystallites cannot be formed, but the blend film becomes completely amorphous. It was reported that the other units were excluded from the homocrystallites formed in DL-copolymers to some extent.[17]

As mentioned above, Lavallée and Prud'homme have reported the effects of optical purity of PMEPLs on stereocomplexation in melt.[20] Stereocomplex can be formed from the mixtures of *R*-rich and *S*-rich PMEPLs even when either of the *R*-unit content (X_R = [*R*-unit]/([*R*-unit] + [*S*-unit])) of the copolymers approaches 0.5, in contrast with the blends of D-rich and L-rich PLAs. For example, complexation occurred between the homopolymer of (*R*)-MEPL ($X_R = 0.985$) and the 1:1 random copolymer of (*R*)- and (*S*)-MEPL ($X_R = 0.5$).

Finally, it should be pointed out that the polymer molecular weight and its distribution, the casting solvent and temperature, and the blending method must have substantial effects on the phase diagram of binary blends from PLA copolymers. They will be studied in the future.

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