

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/230412591>

Stereocomplex formation between enantiomeric poly(lactic acid)s. X. Binary blends from poly(D-lactide-CO-glycolide) and poly(L-lactide-CO-glycolide)

ARTICLE *in* JOURNAL OF APPLIED POLYMER SCIENCE · AUGUST 1994

Impact Factor: 1.77 · DOI: 10.1002/app.1994.070530808

CITATIONS

26

READS

31

2 AUTHORS, INCLUDING:



Yoshito Ikada

Nara Medical University

803 PUBLICATIONS 28,224 CITATIONS

SEE PROFILE

Stereocomplex Formation Between Enantiomeric Poly(Lactic Acid)s. X. Binary Blends from Poly(D-Lactide-co-Glycolide) and Poly(L-Lactide-co-Glycolide)

HIDETO TSUJI¹ and YOSHITO IKADA^{2,*}

¹Technology Development Center, Toyohashi University of Technology, Tempaku-cho, Toyohashi, Aichi 441, Japan, and ²Research Center for Biomedical Engineering, Kyoto University, 53 Kawahara-cho, Shogoin, Sakyo-ku, Kyoto 606, Japan

SYNOPSIS

Binary blend films from lactide-rich poly(D-lactide-co-glycolide) (PDLG) and poly(L-lactide-co-glycolide) (PLLG) were obtained by casting methylene chloride solutions of the two mixed copolymers with different D- and L-lactide contents (X_{DL} and X_{LL}), and their crystallization was studied by differential scanning calorimetry (DSC). Four combinations were selected from the binary (A-B) blends: mixing of the same polymer [$X_{DL}(A) = X_{DL}(B)$ or $X_{LL}(A) = X_{LL}(B)$], blending under $X_{DL}(B) = X_{LL}(A)$, blending of a D-lactide homopolymer [$X_{DL}(B) = 1$] with other PDLGs, and blending of a D-lactide homopolymer [$X_{DL}(B) = 1$] with other PLLGs. Racemic crystallites were exclusively formed between PDLG and PLLG when they had high lactide unit contents. The melting point and enthalpy of fusion of the racemic crystallites decreased with a decrease in X_{DL} of PDLG or X_{LL} of PLLG, suggesting that glycolide units in the polymer disturbed the growth of the racemic crystallites. A similar behavior was also observed for the homocrystallization in nonblended copolymer films. Homocrystallites composed entirely either of D-lactide unit or L-lactide unit sequences were formed when one component was crystallizable and the other component had the same sign of optical rotation or very different lactide content. An interesting finding was that even nonhomocrystallizable lactide-poor PDLG and PLLG could form racemic crystallites when both were blended. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In a series of studies on stereocomplexation (racemic crystallization) between poly(D-lactide) and poly(L-lactide) in solution,¹ we have investigated effects of various parameters such as mixing ratio of the isomers,¹⁻⁵ polymer molecular weight,²⁻⁵ polymer concentration,²⁻⁵ solvent nature,^{3,4} solution temperature,^{2,5} crystallization time,^{2,5} and polymer optical purity⁶ on stereocomplexation. All of these studies were carried out using lactide homopolymers¹⁻⁵ and random copolymers from D- and L-lactide.⁶

Stereocomplexation or racemic crystallization occurs if D-, and L-lactide unit sequences coexist

either in the same molecule or in different molecules.⁷⁻¹⁰ Indeed, stereocomplexation between D-lactide and L-lactide unit sequences has been reported for poly(D-lactide-*b*-L-lactide)⁷ and pairs of poly(D-lactide-co- ϵ -caprolactone) (PDLC) and poly(L-lactide-co- ϵ -caprolactone) (PLLC),^{8,9} and the poly(D-lactide) and poly(L-lactide-*b*- ϵ -caprolactone).¹⁰ Loomis et al. found that the critical lactide unit length needed for formation of the racemic crystallites was about 10 on the basis of a blending study of PDLC and PLLC.⁸ Murdoch et al. reported that the melting temperature of racemic crystallites decreased from 230 to 166°C when the lactide content of copolymers decreased from 1 to 0.8 for the blend of PDLC with PLLC having similar lactide contents.⁹ On the other hand, nonblended copolymers from L-lactide and D,L-lactide,^{6,11-13} glycolide,¹⁴ or ϵ -caprolactone^{9,15} form homocrystallites composed of L-lactide unit sequences if the copolymers

* To whom correspondence should be addressed.

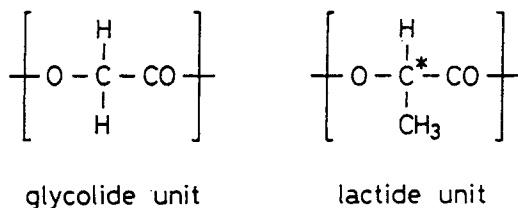
Journal of Applied Polymer Science, Vol. 53, 1061-1071 (1994)

© 1994 John Wiley & Sons, Inc.

CCC 0021-8995/94/081061-11

have high L-lactide unit fraction. Studies on poly(lactide) stereocomplex, except for those of D-rich and L-rich D,L-lactide copolymer⁶ and poly(D-lactide-*b*-L-lactide),⁷ employed an optically inactive comonomer unit having chemical structure different from that of lactide unit, e.g., ϵ -caprolactone, which has 5 carbon atoms between the neighboring ester groups, different from 1 of lactide unit.

On the contrary, the glycolide unit has a chemical structure similar to the lactide unit as given below:



As is seen, the glycolide unit has a proton instead of the α -methyl group of the lactide unit, which makes the lactide polymer optically active. Though the effect of copolymerization of L-lactide and glycolide on homocrystallization was studied by Gilding and Reed,¹⁴ no study has yet been reported on the effect of D- and L-lactide comonomer on racemic crystallization in binary blends. Therefore, the present investigation was undertaken to compare racemic crystallization between poly(D-lactide) and poly(L-lactide) with that between poly(D-lactide-co-glycolide) (PDLG) and poly(L-lactide-co-glycolide) (PLLG) in an attempt to get information about the effect of an optically inactive comonomer having a chemical structure similar to the optically active monomer on the racemic crystallization. Here also we use the terminology "homocrystallites" as the crystallites consisting entirely either of D- or L-lactide unit sequences, and "racemic crystallites" as the crystallites having the lattices in which D- and L-lactide unit sequences are packed side by side in parallel or antiparallel fashion in a ratio of 1 : 1.¹⁶ We have already reported that the homocrystallites have a melting point around 180°C,¹ which is lower than 230°C,¹ the melting temperature of the racemic crystallites (stereocomplex crystallites).

In this study we have investigated the racemic crystallization and homocrystallization of PDLG and PLLG with various glycolide contents synthesized by ring-opening polymerization of mixtures of D- or L-lactide and glycolide in binary blends. Blend films were obtained through casting the mixed solutions from PDLG and PLLG with different glycolide contents and crystallization was studied using differential scanning calorimetry (DSC).

EXPERIMENTAL SECTION

Materials

Poly(lactide-co-glycolide)s were synthesized as previously reported.¹⁷ 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 poly(lactide) prepared by condensation polymerization of lactic acids. Glycolide was obtained by the same procedure as that of lactide. Ring-opening copolymerization of the mixture of D- or L-lactide and glycolide was performed in bulk at 140°C for 10 h using stannous octoate and lauryl alcohol as polymerization initiators.¹⁸ For the polymerization, sealed tubes containing the mixture of D- or L-lactide and glycolide were vigorously shaken after melting the monomers. The monomer in the resulting polymer was removed by repeated reprecipitation from the methylene chloride solution into methanol. As copolymers polymerized in the feed having lactide contents below 0.65 were insoluble in methylene chloride, the following analyses were made on the copolymer polymerized in the feed having lactide contents above 0.68.

Number-average and weight-average molecular weights of the polymers (M_n and M_w) were evaluated from gel permeation chromatography (GPC) obtained with a Shimadzu LC-6A system with SHIM pack columns (GPC806, GPC804, and GPC802) using polystyrene as standard.

Lactide contents of the polymers were determined from 270-MHz ¹H-NMR spectra measured in a deuteriated chloroform by a Jeol JNM-GX270. The ratio of the integrated intensities at 5.2 ppm (CH group of lactide unit) to that at 4.8 ppm (CH₂ group of glycolide unit) was used to determine the chemical composition of these copolymers. It is expressed here by the mol fraction of D- and L-lactide unit in the polymers, X_{DL} and X_{LL} .

$$X_{\text{DL}} \text{ or } X_{\text{LL}} = \frac{\text{mole of lactide unit}}{(\text{mole of lactide unit}) + (\text{mole of glycolide unit})} \quad (1)$$

The specific optical rotation, $[\alpha]$, of the polymers was measured in chloroform at a concentration of 1 g/dL at 25°C using a JASCO DIP-140 polarimeter at a wavelength of 589 nm. The molecular characteristics are listed in Table I. As seen from Table I,

Table I Molecular Characteristics of the Polymers

Code Number	Monomer		Polymer				
	X_1^a	X_1^b	$[\alpha]_D^{25}$ (deg.)	M_n	M_w	M_w/M_n	M_{unit}
DG1 ^c	1.000	1.000	+156	2.47×10^4	4.35×10^4	1.76	72.1
DG2	0.939	0.939	+148	7.68×10^3	2.22×10^4	2.89	71.2
DG3	0.879	0.874	+145	6.54×10^3	2.42×10^4	3.70	70.3
DG4	0.849	0.835	+141	8.75×10^3	2.54×10^4	2.90	69.8
DG5	0.792	0.777	+135	8.01×10^3	2.37×10^4	2.96	69.0
DG6	0.763	0.745	+133	7.46×10^3	2.15×10^4	2.88	68.5
DG7	0.735	0.711	+129	6.07×10^3	2.38×10^4	3.92	68.0
DG8	0.707	0.689	+126	7.47×10^3	2.73×10^4	3.65	67.7
DG9	0.680	0.637	+118	7.10×10^3	1.86×10^4	2.62	67.0
LG1 ^d	1.000	1.000	-153	2.47×10^4	4.41×10^4	1.79	72.1
LG2	0.939	0.935	-148	1.41×10^4	4.47×10^4	3.17	71.2
LG3	0.879	0.875	-145	1.99×10^4	5.24×10^4	2.63	70.3
LG4	0.849	0.839	-143	1.41×10^4	4.76×10^4	3.38	69.8
LG5	0.792	0.774	-136	1.29×10^4	4.57×10^4	3.54	68.9
LG6	0.763	0.751	-134	1.17×10^4	4.01×10^4	3.43	68.6
LG7	0.735	0.727	-132	1.04×10^4	3.52×10^4	3.38	68.3
LG8	0.707	0.699	-127	1.08×10^4	4.34×10^4	4.02	67.9
LG9	0.680	0.675	-124	9.34×10^3	3.62×10^4	3.88	67.5

^a X_1 was calculated by

$$X_1 = \frac{w_1/72.1}{w_1/72.1 + w_g/58.0}$$

where w_1 and w_g are the weight fraction of lactide and glycolide, respectively, in the feed.^b X_1 was evaluated by ¹H-NMR measurements.^c DG: poly(D-lactide-co-glycolide).^d LG: poly(L-lactide-co-glycolide).

synthesized polymers have X_{DL} and X_{LI} similar to those in the feed. The polymers prepared from mixtures of L-lactide and glycolide in bulk have been reported to give a distribution curve different from that of the Bernoullian pair addition statistics because of higher reactivity of glycolide than lactide.¹⁴ $[\alpha]_D^{25}$ of D-lactide homopolymer (DG1) and L-lactide homopolymer (LG1) used in this study is +156 and -153, respectively, in good agreement with the reported value.¹⁹

The blend films were obtained by the following casting method. Each methylene chloride solution of the copolymers 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 DSC measurements.

DSC Measurements

The melting temperature (T_m) and the enthalpy of fusion (ΔH_m) 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_m and ΔH_m were calibrated using indium as standard.

In this study the unit of ΔH_m was expressed by kilocalorie per mole of repeating unit. ΔH_m (kcal/g of polymer) obtained from the DSC measurements was converted into ΔH_m (kcal/mol) using the following equation:

$$\begin{aligned} \Delta H_m \text{ (kcal/mol)} \\ = \Delta H_m \text{ (kcal/g of polymer)} / M_{unit,blend} \quad (2) \end{aligned}$$

where $M_{unit,blend}$ is the average mass per mole of repeating unit of blend. As polymers A and B are always mixed at a 1 : 1 weight ratio in this study, $M_{unit,blend}$ is given by:

$$M_{\text{unit,blend}} = M_{\text{unit}}(\text{A})R(\text{A}) + M_{\text{unit}}(\text{B})R(\text{B}) \quad (3)$$

$$R(\text{A}) = \frac{1/M_{\text{unit}}(\text{A})}{1/M_{\text{unit}}(\text{A}) + 1/M_{\text{unit}}(\text{B})} \quad (4)$$

$$R(\text{B}) = \frac{1/M_{\text{unit}}(\text{B})}{1/M_{\text{unit}}(\text{A}) + 1/M_{\text{unit}}(\text{B})} \quad (5)$$

where $M_{\text{unit}}(\text{A})$ and $M_{\text{unit}}(\text{B})$ are the average masses per mole of repeating unit of polymers A and B, respectively, which are given in Table 1, and $R(\text{A})$ and $R(\text{B})$ are the mole fractions of repeating unit assigned to polymers A and B in the blend, respectively. Equations (2) to (5) give (6):

$$\begin{aligned} \Delta H_m \text{ (kcal/mol)} \\ = \frac{2\Delta H_m \text{ (kcal/g of polymer)} M_{\text{unit}}(\text{A}) M_{\text{unit}}(\text{B})}{M_{\text{unit}}(\text{A}) + M_{\text{unit}}(\text{B})} \end{aligned} \quad (6)$$

From Eq. (6) we can get ΔH_m (kcal/mol) of the blend. For single polymer ($\text{A} = \text{B}$) Eq. (6) becomes

$$\begin{aligned} \Delta H_m \text{ (kcal/mol)} \\ = \Delta H_m \text{ (kcal/g of polymer)} M_{\text{unit}}(\text{A}) \end{aligned} \quad (7)$$

RESULTS

As 2 lactide homopolymers (DG1 and LG1) and 16 copolymers with different mole fractions of D-lactide and L-lactide unit were prepared, there are 18^2 combinations from two separated A and B groups for physical mixing even at the 1 : 1 weight ratio. Because of this too large combination number, we limited the mixing combination to four, as illustrated in Figure 1.

- Blend 1. Mixing of the same polymer [$X_{\text{DI}}(\text{A}) = X_{\text{DI}}(\text{B})$ or $X_{\text{LI}}(\text{A}) = X_{\text{LI}}(\text{B})$]. Blend 1 is not a blend, but we use the word *blend* here for simplicity and uniformity.
- Blend 2. Cross blending under the condition that $X_{\text{DI}}(\text{B}) = X_{\text{LI}}(\text{A})$.
- Blend 3. Blending of D-lactide homopolymer [$X_{\text{DI}}(\text{A or B}) = 1$, DG1] with 9 PDLGs or blending of L-lactide homopolymer [$X_{\text{LI}}(\text{A or B}) = 1$, LG1] with 9 PLLGs.
- Blend 4. Blending of D-lactide homopolymer [$X_{\text{DI}}(\text{B}) = 1$, DG1] with 9 PLLGs or blending of L-lactide homopolymer [$X_{\text{LI}}(\text{A}) = 1$, LG1] with 9 PDLGs.

These four combinations of blends were subjected to DSC measurements, from which melting temperatures of the homocrystallites (T_{m1}) and racemic crystallites (T_{m2}) were estimated in addition to their enthalpies of fusion (ΔH_{m1} and ΔH_{m2}).

Blend 1

As mentioned above, this case is not the true blending but a simple assembly of the same polymer chains. Figure 2 shows DSC thermograms of the films cast from 1 g/dL solution for 18 poly(lactide-co-glycolide) (blends 1₁ and 1₂). The polymers with the lactide mole fraction (X_1) below 0.75 exhibited neither endothermic nor exothermic peak. In addition, the melting peak of homocrystallites becomes smaller in area and shifts to lower temperature as X_1 deviates from 1. This suggests that a chemical potential of the melt or the crystalline size decreases as the optical activity of poly(lactide-co-glycolide) diminishes. T_{m1} and ΔH_{m1} evaluated from the DSC thermograms are plotted as a function of X_1 in Figure 3. It is seen that T_{m1} disappears and ΔH_{m1} goes

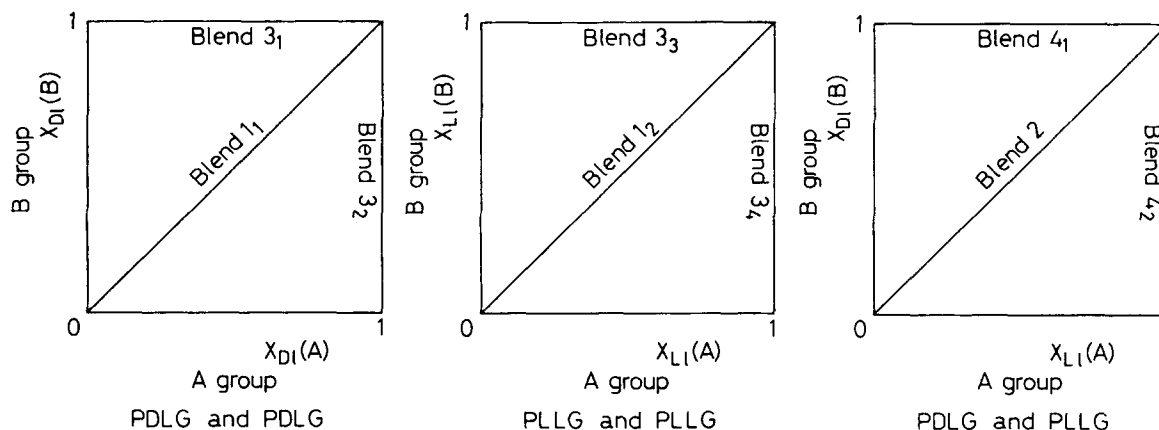


Figure 1 Binary blends used in this study.

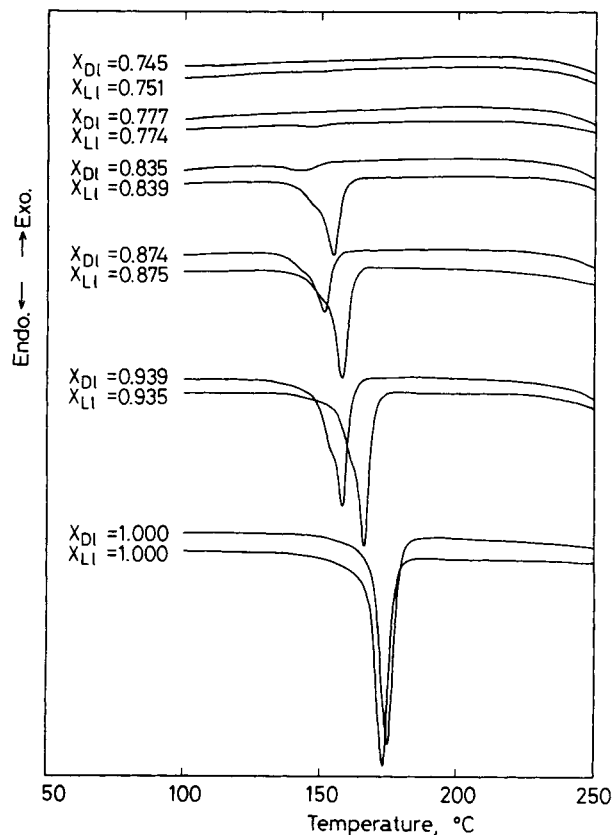


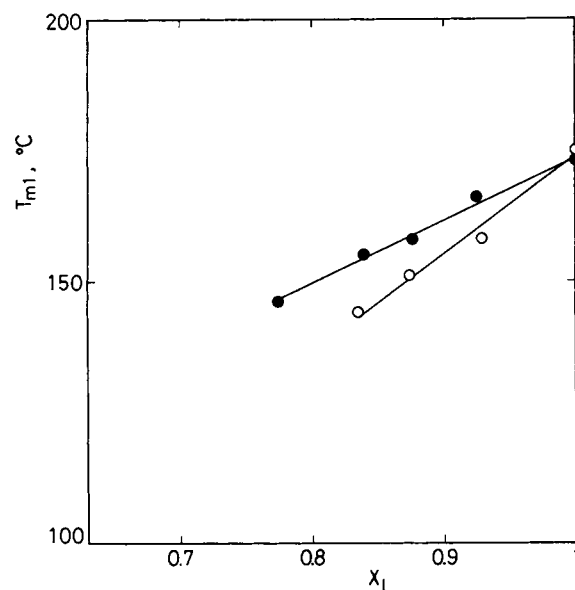
Figure 2 DSC thermograms of nonblended films from PDLG or PLLG (blends 1₁ and 1₂).

to zero long before X_1 reaches 0.5, implying that the glycolide unit in poly(lactide-co-glycolide) inhibits growth of the homocrystallites. ΔH_{m1} becomes zero at X_1 below 0.75, in other words, the cast films with X_1 below 0.75 are completely amorphous. The critical X_1 below which copolymer becomes noncrystallizable is in good agreement with that reported by Gilding and Reed ($0.75 \leq X_1 < 0.8$).¹⁴ Lower T_{m1} and ΔH_{m1} of PDLG than PLLG may be due to lower molecular weights of PDLG samples.

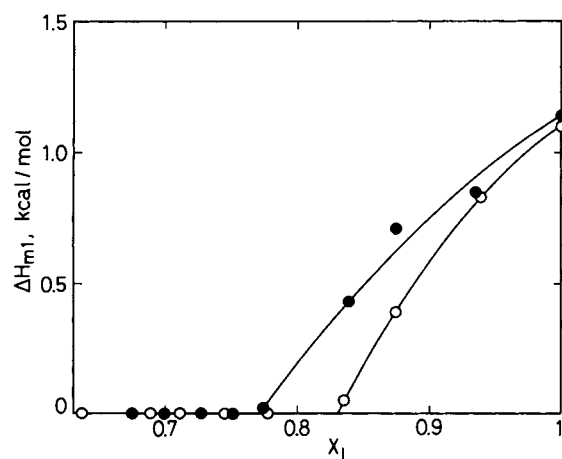
Blend 2

This case is the blending between PDLG and PLLG keeping $X_{DI}(B) = X_{LI}(A)$. Therefore, each of the counterparts has the same absolute value of $[\alpha]_{25}^D$. The polymer pairs employed include DG1·LG1, DG2·LG2, DG3·LG3, DG4·LG4, DG5·LG5, DG6·LG6, DG7·LG7, DG8·LG8, and DG9·LG9. DSC thermograms obtained for the blend films are illustrated in Figure 4. When D- and L-lactide homopolymers are blended [DG1($X_{DI} = 1$) and LG1($X_{LI} = 1$)], the melting peak appear around

230°C, which is equal to the melting point of racemic crystallites between poly(D-lactide) and poly(L-lactide) as demonstrated previously.¹ Apparently, only the melting peak corresponding to the racemic crystallites is observed for all the pairs, suggesting that only racemic crystallization occurs. The melting peak area of the racemic crystallites becomes smaller in size and shifts to lower temperature as X_1 of both groups approaches 0.5. This tendency is seemingly similar to the formation of homocrystallites in blend 1. Interestingly, racemic crystallites are formed from even PDLG and PLLG with X_1 below 0.75, although they cannot form homocrystallites by themselves



(a)



(b)

Figure 3 (a) T_{m1} evaluated from Figure 2 as a function of X_1 : (○) PDLG, (●) PLLG. (b) ΔH_{m1} evaluated from Figure 2 as a function of X_1 : (○) PDLG, (●) PLLG.

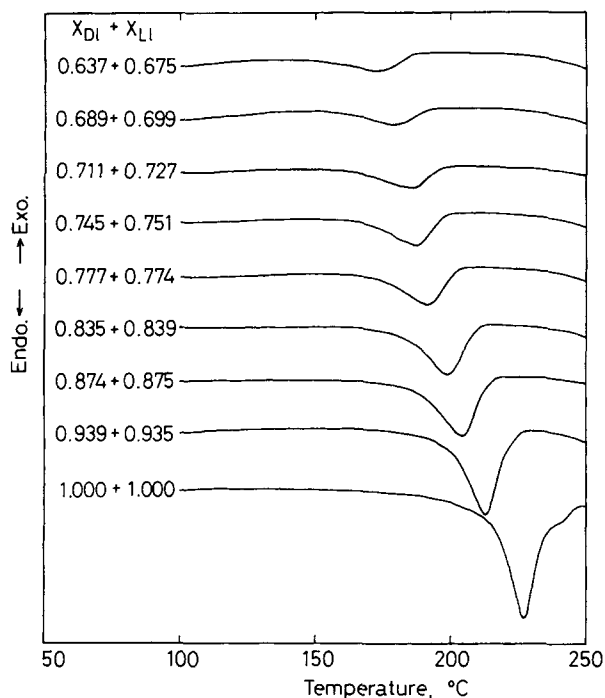


Figure 4 DSC thermograms of blend films from PDLG (DG1 to DG9, B) and PLLG (LG1 to LG9, A) (blend 2).

due to high glycolide contents. This is in contrast with the blend between D-rich and L-rich D,L-lactide copolymer, both with low optical purity, where both of racemic crystallites and homocrystallites were formed.⁶

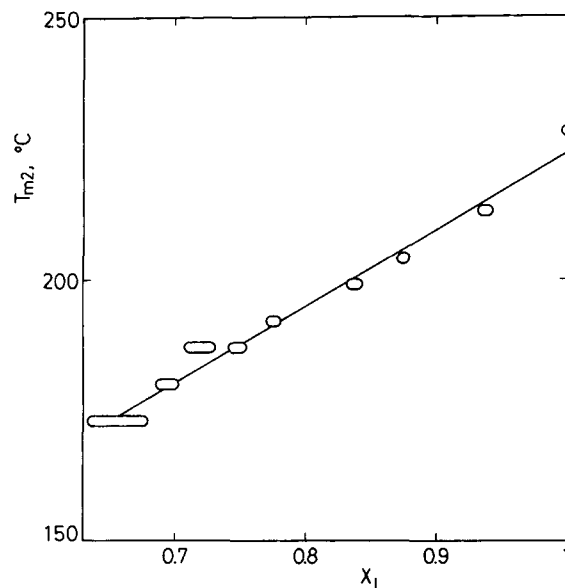
T_{m2} and ΔH_{m2} evaluated from Figure 4 are plotted as a function of X_1 of polymers in Figure 5. It is apparent that T_{m2} linearly decreases with the decreasing X_1 . Also, growth of racemic crystallites is hindered by the presence of glycolide unit. It is seen that ΔH_{m2} remains positive though it decreases with the decreasing X_1 .

Blend 3

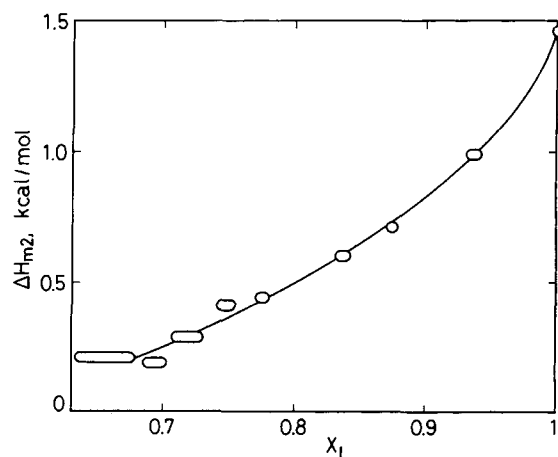
We present here only the results obtained for blend 3₁ illustrated in Figure 1, as blend 3₂, blend 3₃, and blend 3₄ will give the same results as blend 3₁. Blend 3₁ is blending of D-lactide homopolymer [DG1, $X_{Dl}(B) = 1$] with different 9 PDLGs. The observed DSC thermograms of the blend films are shown in Figure 6. As seen, the thermograms have only one main peak at approximately 174°C, irrespective of X_{Dl} of the counterparts of D-lactide homopolymer (DG1). The area of the peak at 174°C becomes smaller with a decrease in $X_{Dl}(A)$.

T_{m1} of the main peak and subpeak of the blend

films obtained for blends 3₁ is plotted as a function of $X_{Dl}(A)$ in Figure 7(a). Obviously, T_{m1} of the main peak remains constant around 174°C, independent of $X_{Dl}(A)$ in contrast with blend 1. The subpeak observed below 130°C for DG1·DG6, DG1·DG7, DG1·DG8, and DG1·DG9 decreases with the decreasing X_{Dl} of the counterparts of DG1. Although two kinds of polymers, D-lactide homopolymer (DG1) and one of PDLGs are present in the blend films, only one main peak is observed at 174°C in the $X_{Dl}(A)$ range from 0.637 to 1. This temperature is identical to the melting point of the



(a)



(b)

Figure 5 (a) T_{m2} evaluated from Figure 4 as a function of X_1 of PDLG and PLLG. (b) ΔH_{m2} evaluated from Figure 4 as a function of X_1 of PDLG and PLLG.

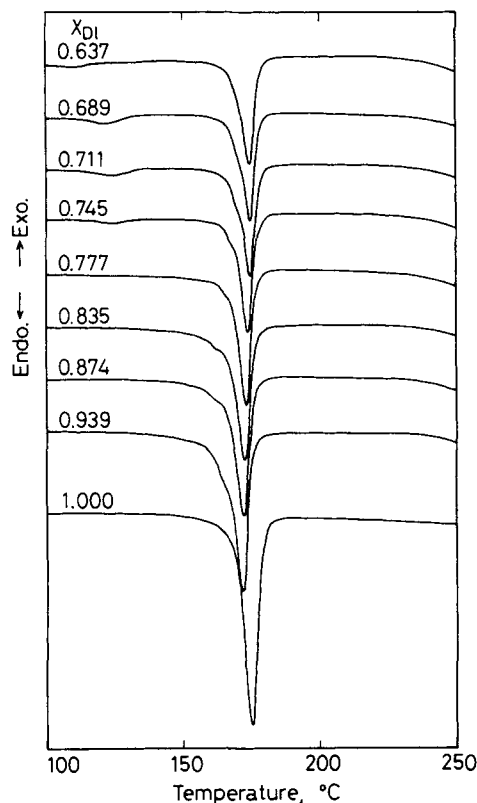


Figure 6 DSC thermograms of blend films from D-lactide polymer (DG1) and PDLGs (blends 3₁).

D-lactide homopolymer (DG1, $X_{D1} = 1$) as shown in Figure 3. This strongly indicates that only D-lactide homopolymer (DG1) can crystallize by itself, not with other PDLGs when $X_{D1}(A)$ is between 0.637 and 1. It follows that D-lactide homopolymer assembles itself to form homocrystallites without being affected by the existence of other PDLGs.

ΔH_{m1} of the main peak and subpeak and overall ΔH_{m1} evaluated from Figure 6 are given in Figure 7(b) against $X_{D1}(A)$. ΔH_{m1} of the main peak is seen to decrease from 1.10 to 0.53 kcal/mol when $X_{D1}(A)$ decreases from 1 to 0.637. Crystallization among PDLG chains may be denied because no peak is detected below 174°C in Figure 6. To confirm the occurrence of crystallization from PDLG, the enthalpy of fusion of the homocrystallites ($\Delta H_{m1,cal}$) was calculated from ΔH_{m1} in Figure 3(b) under the assumption that D-lactide homopolymer and PDLG crystallize separately without disturbing crystallization of the other constituent polymer. Then $\Delta H_{m1,cal}$ is given by the following equation:

$$\Delta H_{m1,cal} = \Delta H_{m1}(DG1)R(DG1) + \Delta H_{m1}(PDLG)R(PDLG) \quad (8)$$

where $R(DG1)$ and $R(PDLG)$ are the mole fraction of the repeating unit of DG1 and PDLG in the blend, respectively, as defined in Eqs. (4) and (5). Equations (4), (5), and (8) give (9):

$$\Delta H_{m1,cal} = \frac{\Delta H_{m1}(DG1)M_{unit}(PDLG) + \Delta H_{m1}(PDLG)M_{unit}(DG1)}{M_{unit}(PDLG) + M_{unit}(DG1)} \quad (9)$$

The broken line in Figure 7(b) shows $\Delta H_{m1,cal}$. It is interesting to note that the total ΔH_{m1} is higher

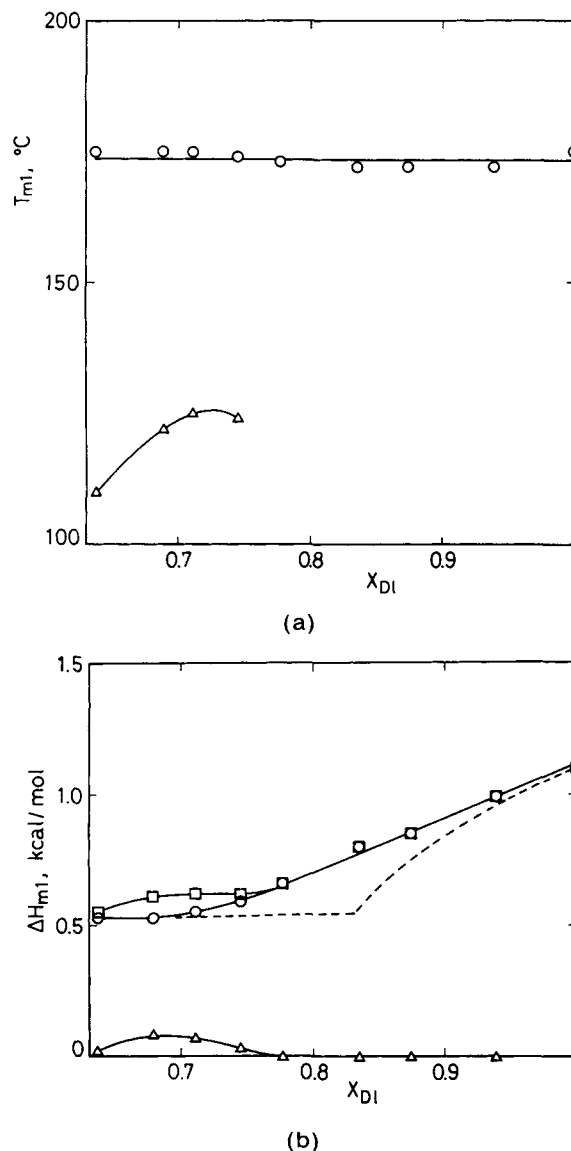


Figure 7 (a) T_{m1} of (O) main peak and (Δ) subpeak evaluated from Figure 6 as a function of X_{D1} of the counterpart of DG1. (b) ΔH_{m1} of (O) main peak and (Δ) subpeak and (□) overall ΔH_{m1} evaluated from Figure 6 as a function of X_{D1} of the counterpart of DG1. Broken line gives $\Delta H_{m,cal}$.

than $\Delta H_{m1,cal}$ at X_{DI} , especially between 0.7 and 0.9. As seen in Figure 3(b), PDLG with X_{DI} below 0.75 produces no homocrystallites by itself. Therefore, this result indicates that even noncrystallizable PDLG can take part in homocrystallization and form homocrystallites with the size similar to that formed from the nonblended D-lactide homopolymer when blended with D-lactide homopolymer (DG1) as the melting point remains at 174°C in contrast to crystallization of PDLG without D-lactide homopolymer. This finding also suggests that glycolide unit in PDLG seems not to disturb homocrystallization when D-lactide homopolymer coexists. This homopolymer may promote homocrystallization of PDLG, probably because D-lactide homopolymer is supplying nuclei or growth sites of homocrystallites for PDLG.

Blend 4

Only the DSC thermograms of the blend films obtained by blending D-lactide homopolymer [DG1, $X_{DI}(B) = 1$] with all 9 PLLGs (blend 4₁) are shown in Figure 8, because blend 4₂ will give the same results as blend 4₁. As is seen, the peak of racemic crystallites alone is observed when $X_{LI}(A)$ is be-

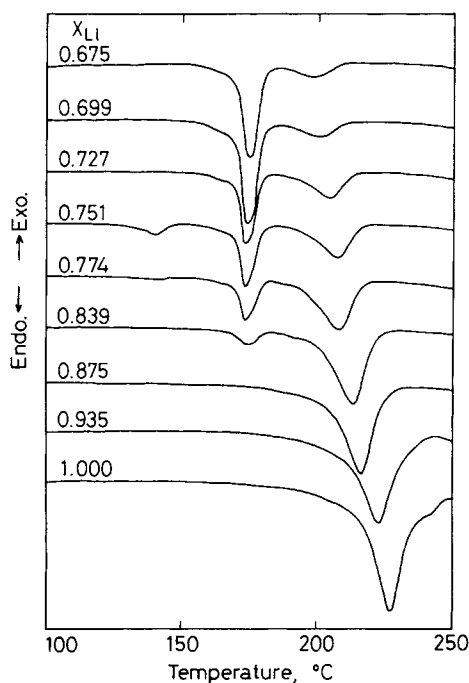


Figure 8 DSC thermograms of blend films from D-lactide polymer (DG1) and PLLGs (blend 4₁).

tween 0.875 and 1. At $X_{LI}(A)$ lower than 0.875, the peak corresponding to homocrystallites also appears and two kinds of peaks of homocrystallites are presented for the pairs of DG1·LG5 ($X_{LI} = 0.774$) and DG1·LG6 ($X_{LI} = 0.751$). Higher T_{m1} observed at X_{LI} below 0.839 may correspond to that of homocrystallites of D-lactide homopolymer (DG1), because this temperature agrees with T_{m1} of nonblended DG1 in blend 1. D-lactide homopolymer (DG1), which was added in excess and did not take part in racemic crystallization, will assemble itself to form homocrystallites because D-lactide homopolymer was mixed with PLLG with low X_1 . The weak subpeak observed below 150°C for X_{LI} of 0.774 and 0.751 may be due to homocrystallites composed of LG5 and LG6, respectively. Though LG5 and LG6 cannot form homocrystallites by themselves, blending may have induced homocrystallization of these noncrystalline polymers.

T_{m1} of the main peak and subpeak and T_{m2} observed for blends 4₁ are plotted as a function of $X_{LI}(A)$ in Figure 9(a). Obviously, T_{m1} of the main peak remains constant around 174°C when $X_{LI}(A)$ is below 0.835. Though there is a probability for formation of two kinds of homocrystallites composed of D-lactide homopolymer and PLLG in the blended films as mentioned above, only one peak is observed at 174°C, which is the melting point of the D-lactide homopolymer (DG1, $X_{DI} = 1$) as shown in Figure 3. It is seen in Figure 9(a) that T_{m2} linearly decreases from 224 to 198°C with the decreasing $X_{LI}(A)$ in contrast with T_{m1} . It follows that the chemical potential of the melt or the size of racemic crystallites must decrease as $X_{LI}(A)$ becomes lower, whereas the D-lactide homopolymer molecules, which did not take part in the racemic crystallization, assemble themselves to form homocrystallites without being affected by racemic crystallization. It should be noted that the slope of T_{m2} against $X_{LI}(A)$ in Figure 9(a) is smaller than that in Figure 5(a). This is probably because the chemical potential of the melt or the size of racemic crystallites formed from blend 2 more drastically decreases as X_1 of both PDLG and PLLG becomes smaller.

ΔH_{m1} of the main peak and subpeak and ΔH_{m2} , evaluated from Figure 8, are given against $X_{LI}(A)$ in Figure 9(b). ΔH_{m1} is seen to increase from zero to 0.5 kcal/mol when $X_{LI}(A)$ decreases from 1 to 0.7. On the other hand, ΔH_{m2} dramatically decreases with a decrease in $X_{LI}(A)$. Again, this indicates disturbance of racemic crystallization between D-lactide homopolymer and PLLG by the glycolide units in PLLG.

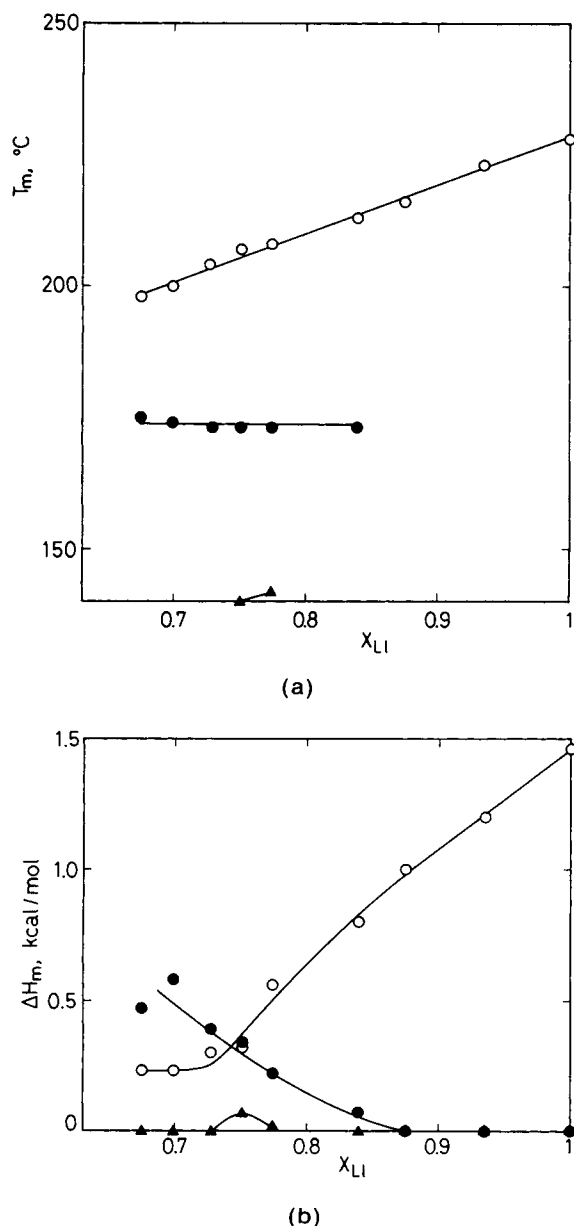


Figure 9 (a) T_{m1} of (●) main peak and (▲) subpeak and T_{m2} (○) evaluated from Figure 8 as a function of X_{LI} of the counterpart of DG1. (b) ΔH_{m1} of (●) main peak and (▲) subpeak and ΔH_{m2} (○) evaluated from Figure 8 as a function of X_{LI} of the counterpart of DG1.

DISCUSSION

Based on the results described above, the X_1 ranges forming racemic crystallites and homocrystallites are illustrated in Figure 10. The variation of T_m with X_1 is also denoted in Figure 10. Figure 10 shows only the X_1 range below which copolymers are no more

soluble in methylene chloride. As points A and B in Figure 10 have not yet been determined experimentally, the boundary of respective regions containing these points are not certain. As is obvious from the results of blends 2 and 4, mixtures of PDLG and PLLG result in formation of racemic crystallites even when X_{DI} and X_{LI} are below 0.7. An interesting finding in this study is that racemic crystallization can occur even from the noncrystallizable PDLG and PLLG, which have X_1 below 0.75, when they are blended. This result denotes that the critical D- and L-lactide unit sequences needed for racemic crystallization between PDLG and PLLG are smaller than that for homocrystallization of nonblended PDLG and PLLG. As reported in a previous study, the pair of D-rich and L-rich D,L-lactide copolymers gave a different result that only the pair of homocrystallizable D-rich and L-rich D,L-lactide copolymers could form racemic crystallites.⁶ In addition, this suggests that the critical D- and L-lactide unit sequences needed for racemic homocrystallization were almost equal to those for homocrystallization of either nonblended D-rich or L-rich D,L-lactide copolymers.

Homocrystallization of PDLG (PLLG) in the presence of D-lactide (L-lactide) homopolymer is also interesting. As seen in Figure 7(b), the overall ΔH_{m1} of the blend from PDLG and D-lactide homopolymer was larger than the sum calculated from ΔH_{m1} of nonblended D-lactide homopolymer and PDLG. Thus, glycolide units in PDLG seem not to disturb homocrystallization of D-lactide homopolymer in blend. More important is that homocrystallization of PDLG was promoted by the presence of D-lactide homopolymer, resulting in an increase of ΔH_{m1} . The results shown in Figures 3(b) and 7(b) suggest that noncrystallizable PDLG took part in homocrystallization, promoted by the presence of D-lactide homopolymer. In the case of homocrystallization of the mixtures from D-rich D,L-lactide copolymer and D-lactide homopolymer, the overall ΔH_{m1} of the blend was approximately equal to the calculated ΔH_{m1} sum of nonblended D-rich D,L-lactide copolymer and D-lactide homopolymer.⁶

To investigate the effect of the presence of D- or L-lactide homopolymer on racemic crystallization we calculated the heat of enthalpy per mole of lactide repeating unit excluding excessive D-lactide or L-lactide repeating units ($\Delta H_{m2, \text{lactide}}$) for comparison of blend 2 with blend 4₁. Blend 2 is a blend from PDLG and PLLG, whereas blend 4₁ from D-lactide homopolymer (DG1) and PLLG. This calculation was done using the following equation (10) under

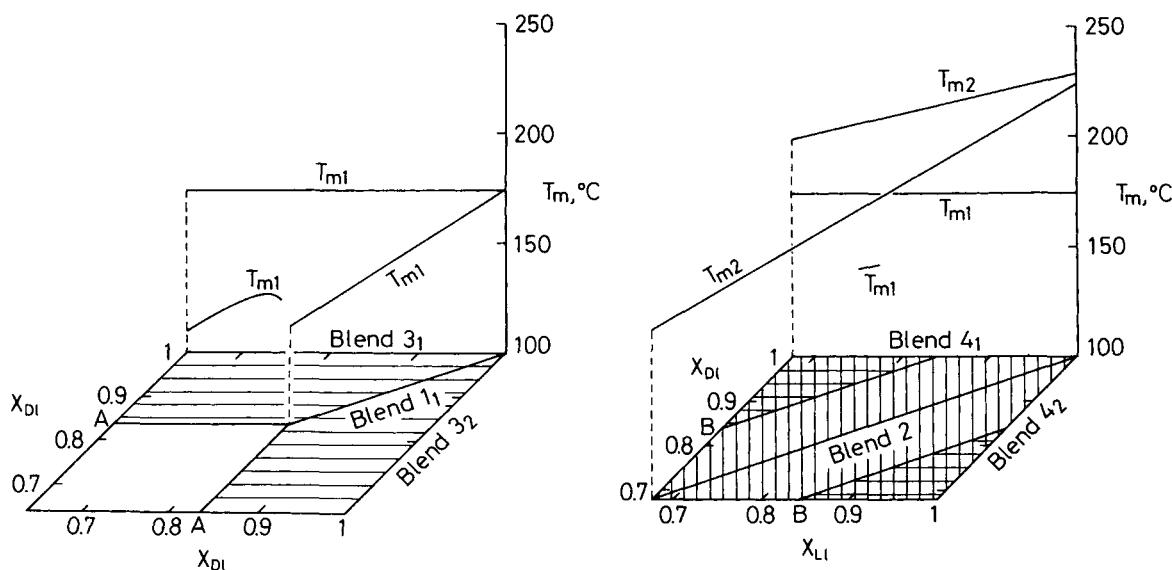


Figure 10 Schematic representation of the X_1 range for crystallization of binary blends from copolymers: (▨) racemic crystalline, (▤) racemic crystalline and homocrystalline, (▥) homocrystalline, and (□) noncrystalline.

the assumption that racemic crystallites contain equimolar D- and L-lactide units and that excessive D- or L-lactide units in the blend cannot take part in racemic crystallization.

$$\Delta H_{m2, \text{lactide}} = \frac{\Delta H_{m2} \text{ (kcal/mol) of blend}}{2R(A)X_1(A)} \quad (10)$$

where $R(A)$ is the mole fraction of the repeating unit assigned to polymer A in the blend and $X_1(A)$ is the mole fraction of the lactide unit in polymer A. Here we assume that polymer A has smaller X_1 than polymer B. The calculated values are plotted as a function of X_1 of polymer A in Figure 11. As is seen, $\Delta H_{m2, \text{lactide}}$ of the blend from DG1 and PLLG (blend 4₁) is larger than that of the blend from PDLG and PLLG (blend 2) in the X_1 range between 0.75 and 1, indicating the promoted racemic crystallization by D-lactide homopolymer. However, this relation is reversed at X_1 below 0.75. Low miscibility between D-lactide homopolymer (DG1) and PLLG having low X_1 may disturb association of the two polymers, resulting in low $\Delta H_{m2, \text{lactide}}$.

For nonblended lactide copolymer the T_{m1} decrease with the increasing comonomer fraction is more remarkable for poly(D-lactide-co- ϵ -caprolactone) (PDLG) and poly(L-lactide-co- ϵ -caprolactone) (PLLG) than for PDLG and PLLG. T_{m1} of nonblended PDLG and PLLG was reported to be 113 ($X_{DI} = 0.778$) and 118°C ($X_{LI} = 0.769$),⁹ lower than 146°C of PLLG ($X_{LI} = 0.774$). Here X_{DI} and

X_{LI} were obtained by substituting mole of glycolide unit in Eq. (1) with mole of ϵ -caprolactone unit. Vion et al. reported that the critical X_{LI} below which copolymer loses homocrystallinity is between 0.70 and 0.79 for PLLC,¹⁵ similar to that for PLLG.

In case of the blend 2, the T_{m2} decrease with a decrease in X_1 of copolymer was larger for PDLG and PLLG than for PDLG and PLLG.⁹ For example, T_{m2} for PDLG ($X_{DI} = 0.778$) and PLLG ($X_{LI} = 0.769$) was reported to be 166°C, much lower than 192°C for PDLG ($X_{DI} = 0.777$) and PLLG ($X_{LI} = 0.774$). In case of the blend 4, the T_{m2} decrease

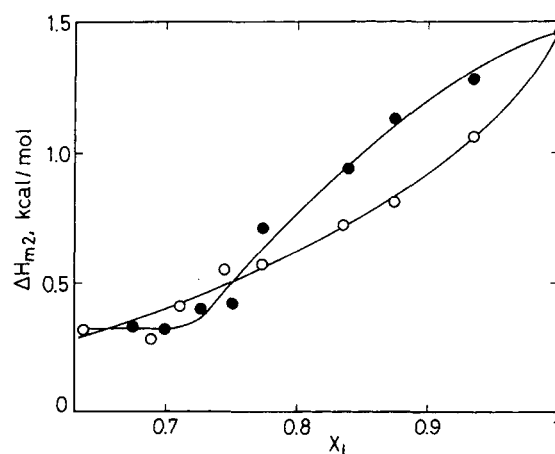


Figure 11 $\Delta H_{m2, \text{lactide}}$ for the blend of PDLG and PLLG (○) (blend 2) and blend of DG1 and PLLG (●) (blend 4₁).

with the decreasing X_1 for racemic crystallites formed between L-lactide homopolymer and PDLC or D-lactide homopolymer and PLLC is greater than that of D-lactide homopolymer and PLLG when compared at the similar X_1 of copolymers.⁹ These suggest that the influence of comonomer unit on racemic crystallization is greater for the ϵ -caprolactone than for the glycolide unit, similar to that on homocrystallization. The slope of T_{m2} against X_1 was larger for the pair of PDLC and PLLC than the pair of D-lactide homopolymer and PLLC or the pair of L-lactide homopolymer and PDLC,⁹ similar to our results.

We are indebted to Dr. Suong-Hyu Hyon (Research Center for Biomedical Engineering, Kyoto University) for supplying glycolide. Acknowledgments are due to Dr. Shin-ichi Itsuno (Department of Materials Science, Toyohashi University of Technology) for the use of polarimeter and NMR facilities, and to Mr. Masahiro Takayama (Department of Materials Science, Toyohashi University of Technology) for useful suggestions in NMR measurements.

REFERENCES

1. Y. Ikada, K. Jamshidi, H. Tsuji, and S.-H. Hyon, *Macromolecules*, **20**, 904 (1987). This is the first paper of this series.
2. H. Tsuji, F. Horii, S.-H. Hyon, and Y. Ikada, *Macromolecules*, **24**, 2719 (1991).
3. H. Tsuji, S.-H. Hyon, and Y. Ikada, *Macromolecules*, **24**, 5651 (1991).
4. H. Tsuji, S.-H. Hyon, and Y. Ikada, *Macromolecules*, **24**, 5657 (1991).
5. H. Tsuji, S.-H. Hyon, and Y. Ikada, *Macromolecules*, **25**, 2940 (1992).
6. H. Tsuji and Y. Ikada, *Macromolecules*, **25**, 5719 (1992).
7. N. Yui, P. J. Dijkstra, and J. Feijen, *Makromol. Chem.*, **191**, 481 (1990).
8. G. L. Loomis, J. R. Murdoch, and K. H. Gardner, *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)*, **31**(2), 55 (1990).
9. J. R. Murdoch and G. L. Loomis, U.S. Pat. 4,719,246 (1988).
10. P. J. Dijkstra, A. Bulte, and J. Feijen, The 17th Annual Meeting of the Society for Biomaterials, May 1-5, 1991, p. 184.
11. E. W. Fisher, H. J. Sterzel, and G. Wegner, *Kolloid Z. Z. Polym.*, **251**, 980 (1973).
12. M. Vert and F. Chabot, *Macromol. Chem., Suppl.*, **5**, 30 (1981).
13. F. Chabot, M. Vert, S. Chapelle, and P. Granger, *Polymer*, **24**, 53 (1983).
14. D. K. Gilding and A. M. Reed, *Polymer*, **20**, 1459 (1979).
15. J.-M. Vion, R. Jérôme, P. Teyssié, M. Aubin, and R. E. Prud'homme, *Macromolecules*, **19**, 1828 (1986).
16. T. Okihara, M. Tsuji, A. Kawaguchi, K. Katayama, H. Tsuji, S.-H. Hyon, and Y. Ikada, *J. Macromol. Sci.-Phys.*, **B30**, 119 (1991).
17. W. R. Sorenson and T. W. Campbell, Eds., *Preparative Methods of Polymer Chemistry*, Wiley, New York, 1961.
18. S.-H. Hyon, K. Jamshidi, and Y. Ikada, in *Polymers as Biomaterials*, S. W. Shalaby, A. S. Hoffman, B. D. Ratner, and T. A. Horbett, Eds., Plenum Press, New York, London, 1984, pp. 51-65.
19. A. E. Tonelli and P. J. Flory, *Macromolecules*, **2**, 225 (1969).

Received September 13, 1993

Accepted January 22, 1994