Stereocomplex Formation between Enantiomeric Poly(lactic acid)s. 5. Calorimetric and Morphological Studies on the Stereocomplex Formed in Acetonitrile Solution

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ABSTRACT: Precipitates from acetonitrile solutions of poly(D-lactic acid) (PDLA) + poly(L-lactic acid) (PLLA) mixtures were studied by differential scanning calorimetry and scanning electron microscopy. Precipitation was carried out under various conditions by changing the mixing ratio of the isomers, the polymer concentrations, the molecular weights of the polymers, and the solution temperature. It was found that the precipitates contained only racemic crystallites (stereocomplexes) consisting of equimolar amounts of D-monomer and L-monomer units, independent of the PDLA content in the initial acetonitrile solution. The enthalpy of fusion of the racemic crystallites was higher than that of the stereocomplexes obtained by casting a methylene chloride solution of the PDLA + PLLA mixture or precipitating a methylene chloride solution into methanol, provided the precipitation temperature of the acetonitrile solution was kept at 80 °C. The precipitates were either platelets or micron-sized spherical particles, depending on the precipitation parameters. When the equimolar polymer mixture was allowed to crystallize in acetonitrile solution below 1 g/dL at 80 °C, platelet-type precipitates were formed, while isolated and unified sphere-type precipitates were observed at 10 and 30 g/dL, respectively. It was concluded that the platelet-like and the sphere-like precipitates consist of racemic crystals from the PDLA + PLLA stereocomplex.

Introduction

We have already reported that poly(lactic acid) (PLA) stereocomplex is formed upon physical blending of poly(D-lactic acid) (PDLA) and poly(L-lactic acid) (PLLA) in solution.[1] The PLA stereocomplex has a racemic crystalline structure, in which PDLA and PLLA are assumed to be packed side-by-side.[2,3] The PLA complexation is likely to occur via the racemic crystallization process, because the complexation of PLA in concentrated chloroform solutions resulted in gelation, probably through cross-links composed of racemic microcrystallites.[4] However, such PLA racemic crystallites (PLA complexed crystallites) were not formed in dilute chloroform solutions below a critical concentration.[4] We have found that racemic crystallization (complexation) of PDLA + PLLA mixtures takes place in acetonitrile even when their solution concentration is as low as 0.1 g/dL. When complexation occurred, the solution became turbid and slow sedimentation of precipitates was observed. It is interesting to note that the solution of a single polymer, PDLA or PLLA, remains homogeneous at the same concentration and temperature.

In this study the racemic precipitates are investigated by differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). In addition, polarimetric studies on the precipitates are conducted to determine the PDLA/PLLA ratio in the precipitates. From electron diffraction analysis and the dependences of the precipitate morphology on the molecular weight of the isomers, the polymer concentration, the mixing ratio of the isomers, and the crystallization temperature, it is concluded that the precipitates are composed of racemic single crystals or their assembly.

Experimental Section

Materials. PDLA and PLLA were synthesized by the method previously reported.[5] 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 wt % aqueous solution from CCA Biochem BV, The Netherlands. A low molecular weight PLA was prepared by condensation polymerization of the free acids and then thermally decomposed to yield the lactide monomers. Ring-opening polymerization of the lactides was performed in bulk at 140 °C using stannous octoate (0.03 wt %) and lauryl alcohol as polymerization catalyst and initiator, respectively.[6] The resulting polymers were purified by repeated reprecipitation from methylene chloride solution into methanol.

The viscosity-average molecular weights ($\bar{M}_v$) of the polymers were determined from their intrinsic solution viscosities ([η]) in chloroform at 25 °C using the following equation:[7]

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

The specific optical rotations ([α]) of the polymers were measured in chloroform at a concentration of 1 g/dL and 25 °C using a Perkin-Elmer Model 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. The determined $[\alpha]^{25}_D$ was ca. +150° for PDLA and −150° for PLLA, in good agreement with the literature values.[8]

PLA precipitates were obtained by the following method. Acetonitrile solutions of PDLA and PLLA were prepared separately at 80 °C and then mixed together at the same temperature. Glass ampules containing the mixed solutions were immersed in an oil bath thermostatically controlled at arbitrary constant crystallization temperatures (T_c) between 0 and 80 °C for ca. 1 week. The formed precipitates were separated from the solution by filtration and extracted twice with fresh acetonitrile at T_c to remove the noncomplexed single polymers. For complete drying of the precipitates, acetonitrile left in the materials was extracted with methanol. Drying was performed in vacuo for ca. 1 week before the following physical measurements and microscopic observation.

DSC Measurement. The melting temperatures (T_f) and the enthalpies of fusion (ΔH_f) of the precipitates were measured with a Shimadzu DT-50 differential scanning calorimeter in the same manner as reported elsewhere.[9,10] Heating was performed under nitrogen gas flow at a rate of 10 °C/min, unless otherwise noted. T_f and ΔH_f were calibrated using indium as a standard.

Optical Rotation Measurement. Optical rotation was measured for the solution of dried precipitates and filtrates by

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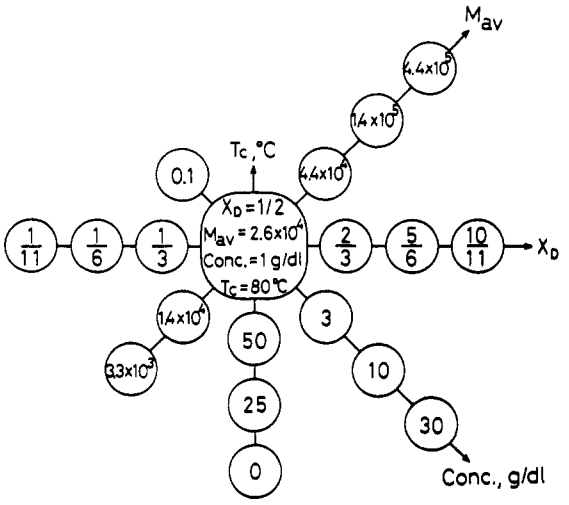

Figure 1. Crystallization conditions employed in this experiment.

Table I
Polymerization Conditions and Molecular Characteristics of the Resulting Polymers

	polymerization conditions		molecular characteristics		
code	lauryl alcohol, wt %	time, h	$[\eta]$, dL/g	$\bar{M}_v$	$[\alpha]^{25}_D$, deg
D1	5.0	10	0.20	3.3×10^3	+143
D2	2.0	10	0.61	1.5×10^4	+155
D3	0.5	10	0.89	2.5×10^4	+153
D4	0.4	10	1.36	4.5×10^4	+155
D5	0	1/3	2.79	1.2×10^5	+156
D6	0	10	7.32	4.5×10^5	+157
L1	3.0	10	0.20	3.3×10^3	−146
L2	1.0	10	0.56	1.3×10^4	−153
L3	0.6	10	0.93	2.7×10^4	−154
L4	0.5	10	1.30	4.2×10^4	−154
L5	0	10	3.24	1.5×10^5	−155
L6	0	10	6.98	4.2×10^5	−157

the same method as described above. Once the precipitates were formed, they could not be redissolved even after dilution with acetonitrile at 80 °C, but they were soluble in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) at room temperature. Therefore, HFIP was used as the solvent to measure $[\alpha]^{25}_D$ of the dried precipitates and filtrates. The relation between $[\alpha]^{25}_D$ and PDLA content, X_D (=PDLA/(PDLA + PLLA)), was obtained by measuring $[\alpha]^{25}_D$ of the HFIP solution of the PDLA + PLLA mixture with a given X_D. This relation was used to determine the X_D value of the precipitates and filtrates.

Electron Microscopic Observation. The morphology of the precipitates was observed with a Model S-2300 scanning electron microscope manufactured by Hitachi Ltd., Tokyo, Japan, after the samples were coated with a thin layer of carbon using a VX-10A Ion-coater (Eiko Engineering, Tokyo, Japan). Transmission electron micrographs (TEM) and electron diffraction patterns were obtained with a JEOL JEM-200CS electron microscope.

Results

The racemic crystallization of PDLA and PLLA from their mixed solution is influenced by their molecular weights, blending ratio, solution concentration, and temperature. As there are many combinations among these variables, we set up a standard condition for the racemic crystallization for simplicity. The standard condition is described in the large circle in Figure 1. The average molecular weight, M_{av}, is defined as $[\bar{M}_v(\text{PDLA}) + \bar{M}_v(\text{PLLA})]/2$. T_c is the crystallization temperature. Below we show the DSC results and SEM photographs of the precipitates obtained by changing one variable, keeping the others fixed, as illustrated in Figure 1.

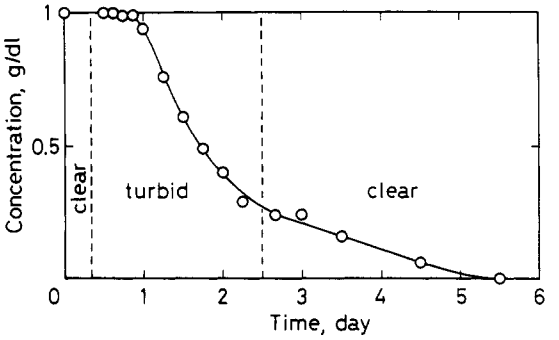

Figure 2. Polymer concentrations of the supernatants obtained from the solution of the D3–L3 mixture against time ($X_D = 1/2$, 80 °C, 1 g/dL).

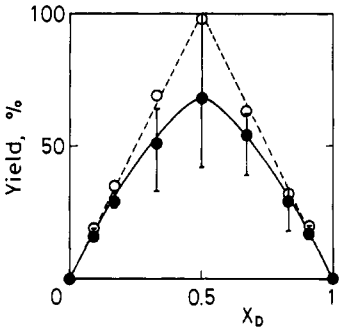

Figure 3. Yields of the complexed precipitates crystallized at 80 °C for 1 week from solutions of D3–L3 mixtures with various X_D (●), yields of the complexed precipitates crystallized at 0 °C for 2 days from solutions of D3–L3 mixtures with various X_D, followed by extraction of D3 and L3 polymers at 80 °C for 2 days (○), and the calculated yield (- - -).

1. Yield of Precipitates. When a 1 g/dL acetonitrile solution of D3 was mixed with that of L3 at the mixing ratio of 1:1 ($X_D = 1/2$) and kept at 80 °C, the solution became slightly turbid after 8 h and the apparent turbidity of the solution increased with time for 1–2 days. After that, precipitation started and precipitates deposited on the vessel bottom during 4–5 days. Figure 2 shows the decrease in supernatant concentration with time. As described in Figure 2, the solution became seemingly clear in ca. 2 days when the initial rapid decrease of the supernatant concentration came to an end. The subsequent slow decrease in polymer concentration of the supernatant lasted until the concentration reached practically zero, indicating that all particles were precipitated. In contrast to the solution of the PDLA + PLLA mixture, the single solution of PDLA or PLLA always remained homogeneous at 1 g/dL and 80 °C.

The yield of precipitates from the mixed 1 g/dL solutions kept at 80 °C for 1 week is shown in Figure 3 as a function of X_D. The pair used for this experiment is D3–L3. Clearly, the maximum yield is seen at $X_D = 1/2$. The broken line in Figure 3 represents the calculated yield under the assumptions that the precipitates contain equimolar amounts of D and L units and that precipitation lasts until one of the free PDLA or PLLA is entirely consumed by complexation. The observed yield is lower than that calculated, especially around $X_D = 0.5$, probably because the solution reached a quasi-equilibrium state at X_D around 0.5 after precipitation for 1 week. To accelerate the precipitation of particles, solutions of the D3–L3 mixture were quenched from 80 to 0 °C and kept at 0 °C for 2 days to force all the PLA molecules to precipitate. The temperature was then raised to and kept at 80 °C for 2 days to extract the noncomplexed single polymers. The yield obtained by this procedure is also given in Figure 3.

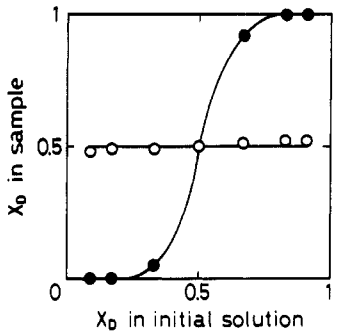

Figure 4. X_D of the precipitates (○) and the filtrates (●) obtained from solutions of D3–L3 mixtures with various X_D (1 g/dL, 80 °C).

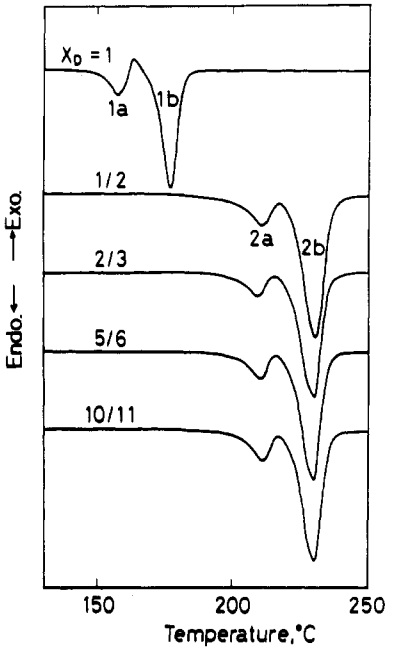

Figure 5. DSC thermograms of the precipitates from solutions of D3–L3 mixtures with various X_D (1 g/dL, 80 °C).

As is obvious, this yield is in good agreement with that calculated. It follows that the precipitates must be formed at the equimolar ratio of D-monomer and L-monomer units, regardless of X_D in the initial solution.

This assumption was confirmed by a polarimetric measurement of the precipitates and the dried filtrates obtained from solutions of the D3–L3 mixture with various X_D. Measurement was performed on the samples with the highest precipitation yield for each X_D. As is evident from Figure 4, the X_D value of the precipitates remains $^1/_2$, irrespective of X_D of the initial solution from $^1/_{11}$ to $^{10}/_{11}$, indicating that the precipitates contain equimolar amounts of D and L units. On the contrary, X_D of the polymers in the filtrates clearly approaches 0 or 1 as X_D of the initial solution deviates from $^1/_2$. This suggests that the excess PDLA or PLLA is left in solution without participating in stereocomplexation.

2. DSC Study. (a) Mixing Ratio Effect. Figure 5 shows DSC thermograms of the precipitates obtained from 1 g/dL solutions of the D3–L3 mixture with various X_D, together with that of the precipitates from the acetonitrile solution of D3 (X_D = 1). This D3 precipitate was obtained by immersing the sealed glass ampule containing the 1 g/dL acetonitrile solution of D3 in a water bath kept at 0 °C. The DSC thermograms of the precipitates from the mixed solutions having excess L polymer were the same as those having excess D polymer. Therefore, Figure 5 shows only the results of the latter case. As seen from Figure 5, double endothermic peaks are observed at ca. 180 °C (1a and 1b) for the precipitates from the single polymer D3 and 230 °C (2a and 2b) for the precipitates from the mixed solutions. The peaks around 180 °C can be ascribed to the fusion of crystallites of PDLA or PLLA, while the peaks around 230 °C can be ascribed to the fusion of racemic crystallites (complexed crystallites).[1] The much higher melting point of the precipitates crystallized in the mixed solution than that of single PDLA or PLLA, irrespective of X_D, indicates that the racemic crystallites can be formed from all the mixed solutions of any X_D ratios.

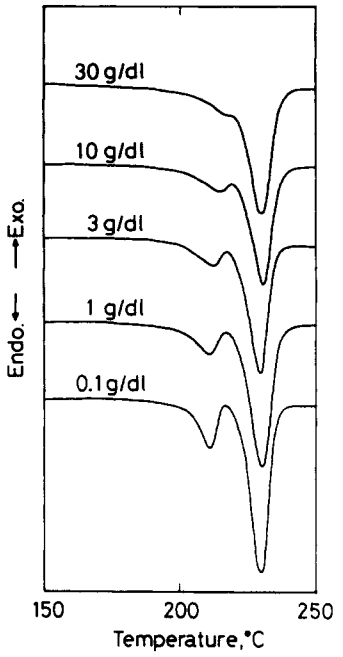

Figure 6. DSC thermograms of the precipitates from solutions of D3–L3 mixtures at various polymer concentrations (X_D = $^1/_2$, 80 °C).

(b) Polymer Concentration Effect. DSC thermograms of the precipitates obtained from solutions of D3–L3 mixtures at various concentrations are illustrated in Figure 6. Obviously, racemic crystallites are formed in the precipitates from all the solutions studied here. With increasing polymer concentration, peak 2a becomes smaller, shifting to higher temperature, and is finally absorbed in the main peak 2b, whereas T_{f2b} seems not to be influenced by the polymer concentration.

(c) Crystallization Temperature Effect. DSC thermograms of the precipitates from solutions of D3–L3 mixtures at various precipitation temperatures are shown in Figure 7. As is seen, a peak is present around 230 °C for all the precipitates. This means that the racemic crystallites are formed over the precipitation temperature range from 0 to 80 °C. Peak 2b is observed at almost the same temperature (230 °C) with the identical shape, independent of the precipitation temperature, while peak 2a becomes smaller, shifting to lower temperature with a decrease in precipitation temperature. The accompanying shoulders are not due to the crystallites of PDLA or PLLA but to the racemic crystallites, since peak 2a did not disappear even after extracting the precipitates with fresh acetonitrile at 80 °C. It is interesting to note that only the racemic crystallites were formed even below 25 °C in spite of the fact that the single polymer, PDLA or PLLA, is also crystallizable at 1 g/dL if the temperature is below 40 °C.

(d) Molecular Weight Effect. DSC measurements were performed on the precipitates from the mixtures of

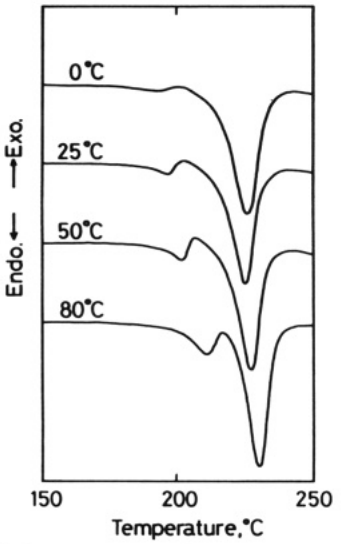

Figure 7. DSC thermograms of the precipitates from solutions of D3–L3 mixtures at various temperatures (X_D = $^1/_2$, 1 g/dL).

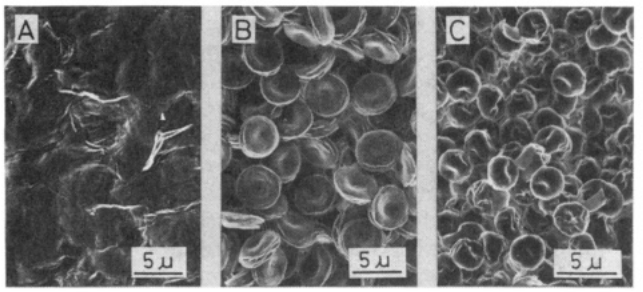

Figure 8. SEM photographs of the precipitates from mixed solutions of PDLA and PLLA with similar molecular weights (X_D = $^1/_2$, 1 g/dL, 80 °C): (A) D1–L1, (B) D3–L3, (C) D6–L6.

PDLA and PLLA having similar molecular weights, i.e., D1–L1, D2–L2, D3–L3, D4–L4, D5–L5, and D6–L6. Melting peaks were observed only around 230 °C for all the precipitates (data not shown), indicating that only the racemic crystallites could be formed from the PLA pairs with molecular weights ranging from 3×10^3 to 4×10^5.

3. SEM Observation. All the precipitates from the mixed solutions of PDLA and PLLA were studied with SEM. Typical SEM photos are shown below.

(a) Molecular Weight Effect. The effect of molecular weight on the shape of the precipitates from 1 g/dL solutions of equimolar PDLA + PLLA pairs having similar molecular weights is shown in Figure 8. Although the photograph in Figure 8A is not clear, closer inspection reveals that the precipitates from D1–L1 are composed of single-crystallite mats of various sizes. Magnification of the crystal in Figure 8A by 5 times is shown in Figure 9. In contrast to D1–L1, the particles from D3–L3 have a discoidal shape of 4-μm diameter and 1-μm thickness, while those from D6–L6 are a concaved sphere of 2-μm diameter. Thus it is likely that the precipitate shape approaches spherical particle as the molecular weights of the polymer pairs increase.

In the following experiments, the effect of variables on the precipitate shape was studied using only the D3–L3 pair, unless otherwise specified.

(b) Concentration Effect. Figure 10 shows SEM photographs of the precipitates from equimolar mixed solutions of D3 and L3 at different polymer concentrations from 0.1 to 30 g/dL. As is seen, the precipitates formed from 0.1 g/dL solution are similar to those from 1 g/dL solution, although the thickness of the round platelets

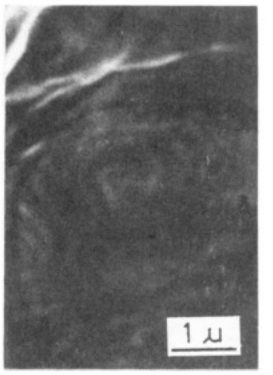

Figure 9. Magnification of one crystal in Figure 8A (×5).

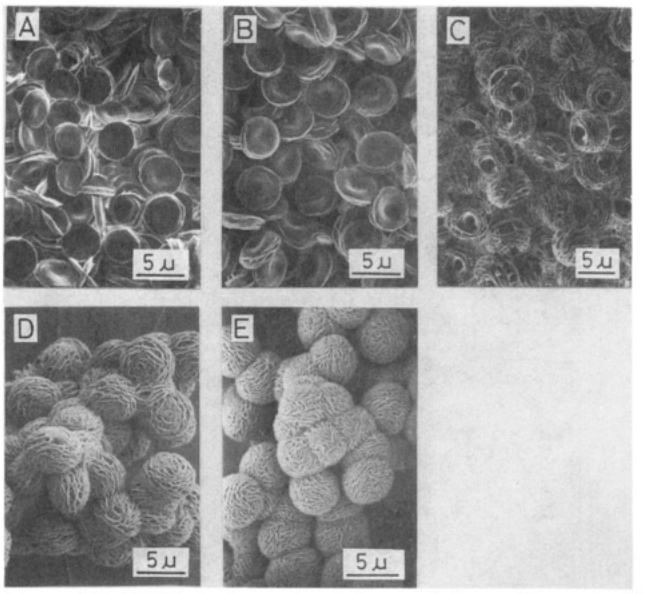

Figure 10. SEM photographs of the precipitates from mixed solutions of D3 and L3 at different concentrations (X_D = $^1/_2$, 80 °C): (A) 0.1, (B) 1, (C) 3, (D) 10, and (E) 30 g/dL.

formed from 0.1 g/dL solution is slightly smaller than that from 1 g/dL solution. As the solution concentration approaches 3 g/dL, spherical particles appear which have holes on both sides. The thickness of the particles increases with increasing solution concentration from 0.1 to 3 g/dL, but the particle diameter remains virtually unchanged. When the solution concentration is raised above 10 g/dL, the particles become more spherical but are unified with each other. At 30 g/dL, a three-dimensional network is finally formed by unification of the particles, making sedimentation of the particles impossible. Each of the particle units formed in concentrated solution is almost perfectly spherical and seems to be composed of many disks. Evidently, the average diameter of the particle units remains almost constant at ca. 4 μm and has a very narrow distribution over the concentration range from 0.1 to 30 g/dL, regardless of unification of the particles.

(c) Mixing Ratio Effect. As shown in Figure 11, the SEM observation on the precipitates obtained at different mixing ratios reveals that the racemic precipitates from mixed solutions of D3 and L3 at X_D = $^1/_{11}$ (PDLA/PLLA = $^1/_{10}$) and $^{10}/_{11}$ (PDLA/PLLA = $^{10}/_1$) are composed of relatively triangular platelets, which are slightly different from the round platelets from the mixed solution of D3 and L3 at X_D = $^1/_2$. Although there is a slight difference in shape, all the racemic precipitates seem to consist of a few stacked disks whose size is approximately 4 μm in diameter and 1 μm in thickness, regardless of X_D in the starting solutions.

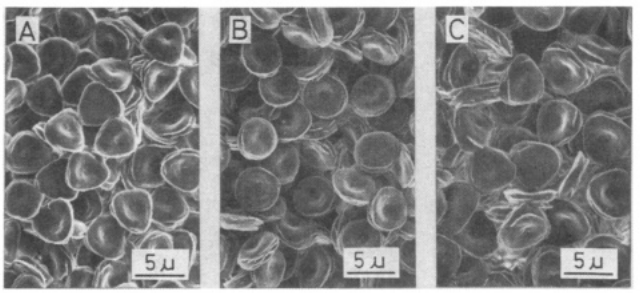

Figure 11. SEM photographs of the precipitates from mixed solutions of D3 and L3 at various X_D (1 g/dL, 80 °C): (A) $X_D = {}^1/_{11}$; (B) $X_D = {}^1/_2$; (C) $X_D = {}^{10}/_{11}$.

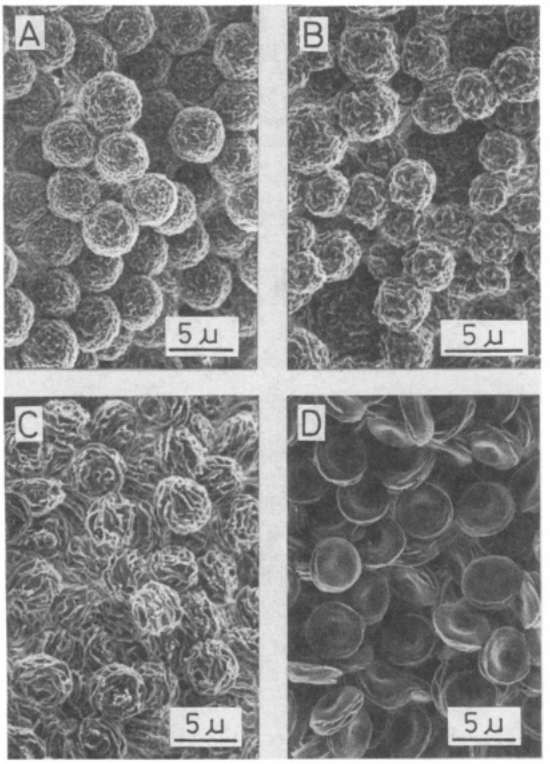

Figure 12. SEM photographs of the precipitates from mixed solutions of D3 and L3 at different temperatures ($X_D = {}^1/_2$, 1 g/dL): (A) 0, (B) 25, (C) 50, and (D) 80 °C.

(d) Crystallization Temperature Effect. The effect of crystallization temperature on the precipitate shape is shown in Figure 12. It is apparent that the precipitates from 1 g/dL mixed solutions of the equimolar D3–L3 pair at different T_c between 0 and 50 °C consist of spherical particles, in contrast with the discoidal particles formed at 80 °C. The racemic precipitates are composed of separate particles, regardless of T_c, though the appearance of particles depends on T_c.

Discussion

The boiling temperature of acetonitrile is 82 °C, which limits the upper crystallization temperature. When either PDLA or PLLA is dissolved in acetonitrile to give, for example, a 1 g/dL solution, it remains homogeneous and transparent, provided the temperature is kept above 60 °C, while racemically crystallized precipitates can be formed from mixtures of 1 g/dL PDLA solution and 1 g/dL PLLA solution kept above 60 °C, as demonstrated above. As shown in Figure 7, racemic crystallites are exclusively formed in the temperature range from 0 to 80 °C, indicating that racemic crystallization occurs in preference to crystallization of single polymers in dilute acetonitrile solutions of PDLA + PLLA mixture in this temperature range. In other words, the rate of nucleation and growth of the racemic crystallites is much higher than that of the crystallites of single polymers in acetonitrile.

As is apparent from Figure 2, the rate of precipitation is low in comparison with that of conventional phase separation of dilute polymer solutions occurring upon a temperature drop or rise. This suggests that the precipitates are formed as a result of crystallization. The deposition speed of precipitates depends on their shape and size. As demonstrated in Figure 10, the precipitates formed from dilute acetonitrile solutions of PDLA + PLLA mixtures such as 1 g/dL had the shape of a single disk or sphere, while those from concentrated solutions were composed of connected microspheres, so that they could not deposit on the vessel bottom.

An important finding in the present work is the equimolar ratio of PDLA and PLLA in the precipitated particles, regardless of X_D in the initial mixed solutions. This strongly supports our assumption that the precipitates are an assembly of racemic crystallites which do not contain any crystallites of the single PDLA or PLLA polymer. The maximum yield of the complexed precipitates at $X_D = {}^1/_2$ is thus very reasonable. For concentrated chloroform solutions of PDLA + PLLA mixtures, the X_D value was also ${}^1/_2$, which gave the minimum induction period until the viscosity rise;[4] $X_D = {}^1/_2$ also gave the maximum enthalpy of fusion for the racemic crystallites prepared by casting and nonsolvent precipitation methods.[9,10] If the precipitated particles consist of both amorphous and crystalline parts, the amorphous part should also be composed of equimolar amounts of D-monomer and L-monomer units, similar to the crystalline part, because the overall ratio of D-monomer and L-monomer units in the particles is equimolar. As reported elsewhere, X-ray analysis has revealed that the racemic crystallites are composed of equimolar amounts of D-monomer and L-monomer units.[2,3]

To gain deeper insight into the physical structure of the racemic crystallites, a DSC study was carried out on the precipitated particles. ΔH_{f2} evaluated from the DSC curves remains as high as 91–102 J/g of polymer, so long as crystallization is allowed to proceed at 80 °C. This is in marked contrast with that of the crystallites prepared by casting and nonsolvent precipitation methods.[9,10] In the case of casting, racemic crystallites were formed in a small amount and the main product was the single-polymer crystallites, especially when the polymer pairs had high molecular weights,[9] whereas $\Delta H_{f2} = 47$ J/g of polymer was found for crystallites obtained by the nonsolvent precipitation.[10] These results imply that the degree of crystallinity of the racemically crystallized precipitates formed in acetonitrile at 80 °C must be high, irrespective of crystallization conditions such as X_D, polymer concentration, and PLA molecular weight. However, $\Delta H_{f2} = 78$ J/g of polymer was found for precipitates formed in acetonitrile at lower temperatures (0–50 °C). Probably less undercooling at higher temperatures will yield more perfect crystals and higher chain mobility at higher temperatures will allow the polymer chains in the precipitate to reorganize to a more stable state, resulting in a higher degree of crystallinity.

The precipitates from D3–L3 solutions with various X_D show similar T_{f2a} (210 ± 1 °C), T_{f2b} (230 °C), and ΔH_{f2} (96 ± 4 J/g of polymer), suggesting that the precipitates are equivalent with respect to crystalline size dispersion, degree of crystallinity, and crystallization process, independent of X_D of the initial solutions. In other words, it

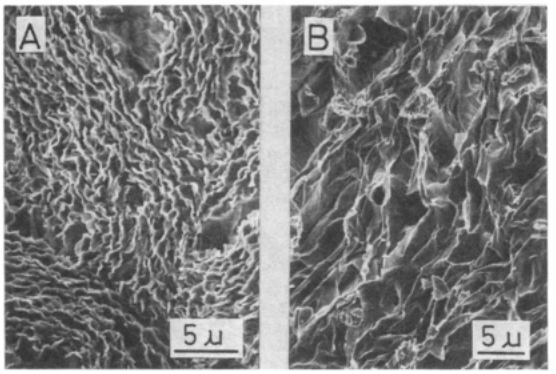

Figure 13. SEM photographs of the PDLA (D3) precipitates from 1 g/dL acetonitrile solutions at 0 and 25 °C: (A) 0 and (B) 25 °C.

seems likely that the excess D or L polymer does not disturb racemic crystallization between D and L polymers.

The racemically crystallized precipitates from D3–L3 solutions have double endothermic peaks, irrespective of X_D. Generally, such double melting peaks of crystalline polymers are ascribed to the presence of two different crystalline or morphological structures. Another interpretation is that the endothermic peak at the lower temperature is caused by the melting of the less perfect crystallites, which will be recrystallized during DSC scanning to join the more perfect crystallite with the higher melting temperature. The latter recrystallization mechanism seems more probable in the present case, because the X-ray diffraction profile of the racemically crystallized precipitates with double endothermic peaks was identical to that of the racemically crystallized film with a single endothermic peak (data not shown). This suggests that the racemically crystallized precipitates with double DSC peaks do not contain another type of crystallites. In addition, an exothermic peak is observed between two peaks, especially for the precipitates formed below 50 °C (Figure 7), implying that recrystallization during scanning occurs.

To compare with the SEM photographs of the racemically crystallized particles, single polymers of D3 were precipitated from a 1 g/dL acetonitrile solution at 0 and 25 °C. SEM photographs of D3 are shown in Figure 13. D3 can crystallize only below 40 °C at 1 g/dL in acetonitrile, and the PDLA precipitates were formed as a lump of millimeter order at the inner surface of the glass vessel containing the solution. As is apparent from Figure 13, the shape of single-polymer precipitates is different from that of racemic precipitates, revealing that the particle formation is specific to the racemic crystals from the acetonitrile solutions. It seems highly possible that the racemic precipitates are an assembly of single-crystal lamella. If this is true, the term "disk" used to describe the fine structure of the platelets shown in Figure 10 should be changed to "lamella". We have already reported that the racemic single crystal can be readily formed from the diluted mixed solution of PDLA and PLLA in acetonitrile.[2] TEM photographs of the single crystal and the complex disk obtained from D3 and L3 under the standard condition are presented in Figure 14. The electron diffraction pattern of the complex disk is identical with that of the single crystal (Figure 14). This strongly supports that the complex particle is composed of single crystals or lamellas.

Immediately after formation of a nucleus in the mixed solutions of PDLA and PLLA, the racemic lamella will grow rapidly under formation of lamella dislocation. This may result in formation of disk-type precipitates and

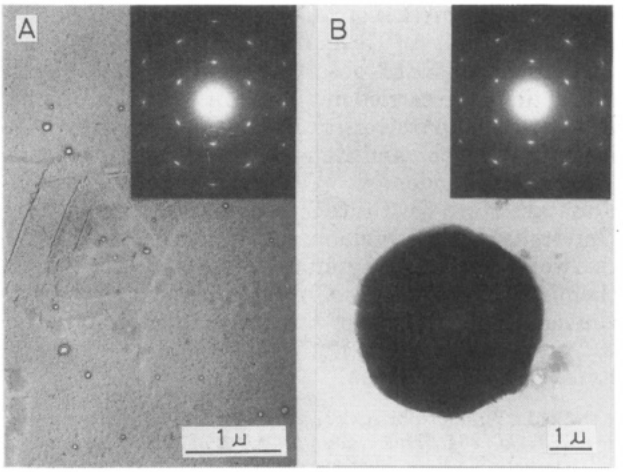

Figure 14. TEM photographs and electron diffraction patterns of complexes: (A) racemic single crystal; (B) precipitate from mixed solution of D3 and L3 obtained under the standard condition ($X_D = {}^1/_2$, $M_{av} = 2.6 \times 10^4$, 1 g/dL, 80 °C).

finally of spherical particles. If the racemic crystallization is allowed to take place in more favorable environments such as at lower temperature and higher polymer concentration, more complete spherulite-like particles will be formed. The single particles will be unified to give a network as a result of collision with each other as the solution concentration becomes higher. This is a well-known phenomenon in the case of conventional spherulite growth from melts and concentrated solutions of crystalline polymers. Our stereocomplex particles were too small to be observed by polarization microscopy.

It has been reported that a dilute solution of st- and it-PMMA in a so-called strongly complexing solvent (type A solvent) becomes turbid,[11–13] followed by sedimentation of the aggregated complexed particles.[14] The diameter of the PMMA complexed particles is estimated to be 10–30 nm,[14–18] which is much smaller than that of PLA complexed particles (3–5 μm). Observation of two melting peaks for the PMMA complexed precipitates during DSC[19–22] is also similar to the case for the PLA complexed precipitates. These two peaks have been ascribed to decomplexation of the complexed sections, partly organized into a fringed micellar cluster, and simultaneous decomplexation and melting of lamellarly crystallized complexes.[22] In PMMA complexation in dilute solution the complexation between segments and the crystallization of complexed sections can be clearly separated,[18] whereas only the racemic crystallization has been observed for PLA complexation in dilute acetonitrile solution so far.

It may be concluded that the round precipitates formed from the solution of PDLA + PLLA mixtures in acetonitrile in the temperature range from 0 to 80 °C are composed of racemic crystallites of equimolar amounts of D and L units not only in the crystalline but also in the noncrystalline region, regardless of X_D in the initial solution. The DSC thermograms suggest that the racemically crystallized precipitates have high crystallinity, irrespective of the crystallization conditions such as X_D, polymer concentration, and PLA molecular weight. Such high crystallinity could not be obtained by casting and nonsolvent precipitation methods.

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Registry No. PDLA (homopolymer), 106989-11-1; PDLA (SRU), 26917-25-9; PLLA (homopolymer), 26811-96-1; PLLA (SRU), 26161-42-2.