

Stereocomplex Formation Between Enantiomeric Poly(lactic acid). VIII. Complex Fibers Spun from Mixed Solution of Poly(D-lactic acid) and Poly(L-lactic acid)

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SYNOPSIS

To obtain poly(lactic acid) (PLA) complex fibers, spinning was performed by wet and dry methods from 5–10 g/dL chloroform solutions of poly(D-lactic acid) (PDLA) and poly(L-lactic acid), both with a viscosity-average molecular weight of 3×10^5 . The dope was extruded from a mono-hole nozzle into coagulation baths from ethanol and chloroform for wet spinning and into a drying column kept at 60°C for dry spinning. Scanning electron microscopic observation of the as-spun fibers showed that the surface of the wet-spun fiber had large basins with diameters of 50–100 μm and many pores with diameters from sub μm to 10 μm , whereas the surface of dry-spun fiber had a microporous structure with the pore diameter of 1–3 μm . The tensile strength of the wet-spun complex fiber was very low and could not be drawn at high temperatures, in contrast to the dry-spun fiber. The tensile strength of dry-spun complex fiber increased upon hot drawing and showed the tensile strength of 94 kg/mm² by drawing at 160°C to the draw ratio of 13. Differential scanning calorimetry revealed that the complex fibers contained both the stereocomplex crystallites (racemic crystallites) and the crystallites of the single polymers, PDLA and PLLA, regardless of the spinning methods. The ratio of the racemic crystallites to the single-polymer crystallites increased with the draw ratio of the complex fiber. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In the series of our study on the stereocomplexation between poly(D-lactic acid) (PDLA) and poly(L-lactic acid) (PLLA),^{1–9} it has been found that racemic crystallites are formed in addition to crystallites of each of single polymers when the mixed solutions of PDLA and PLLA are (1) kept at a constant temperature and a high polymer concentration,⁴ (2) cooled at a low polymer concentration,⁷ (3) cast to dryness,^{5,8} and (4) poured into a precipitant.^{1,6} One of the most interesting findings in these studies is that the racemic crystallites have a much higher melting temperature (T_m) than that of single

polymers, which is around 180°C and lower by 50°C than the T_m of the racemic crystallites. This means that PLLA plastics may be reinforced by blending with the stereocomplex fiber because it has higher T_m than that of the PLLA matrix.

If this expectation is realized, a breakthrough will be given to biodegradable biomaterials that are currently applied for tissue healing as temporary scaffold and fixation. The most widely used synthetic biodegradable polymer is aliphatic polyesters such as poly(glycolic acid) and poly(lactic acid) (PLA). The largest drawback of these polymers when applied to fractured bone fixation to replace the currently used metals is the low mechanical strength in comparison with the cortical bone. Therefore, some attempts have been made to improve the mechanical properties of crystalline PLLA, for instance, by fibrillation^{10–15} and chain orientation.¹⁶ Composites of PLLA are also made using glass and carbon fibers,¹⁷ but they are not biodegradable.

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The object of this study was to make fibers from a mixed solution of PDLA and PLLA by wet and dry spinning. So far, only patents have been published on the spinning of complex from PDLA and PLLA.^{18,19}

EXPERIMENTAL

Materials

Synthesis of PDLA and PLLA

PDLA and PLLA were synthesized with the method previously reported.²⁰ Methyl-D-lactate with an optical purity of 97% was supplied by Daicel Chemical Industries, Japan, and hydrolyzed to D-lactic acid. L-Lactic acid with an optical purity of 98% was purchased as a 90 wt % aqueous solution from CCA Biochem, The Netherlands. The oligomeric PLAs prepared by condensation polymerization of the free acids were thermally decomposed to yield the lactide monomers. Ring-opening polymerization was performed for each lactide in bulk at 140°C for 10 h using stannous octoate (0.03 wt %) and lauryl alcohol as the polymerization modulator.²¹ The polymerization conditions were the same for D- and L-lactides and the resulting polymers were purified by the reprecipitation method using methylene chloride as solvent and methanol as precipitant.

The viscosity-average molecular weight (\bar{M}_v) of the polymers was determined from their intrinsic solution viscosity $[\eta]$ in chloroform at 25°C using the equation²²

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

The specific optical rotation $[\alpha]$ of the polymers was measured in chloroform at a concentration of 1 g/dL at 25°C using a Perkin-Elmer Polarimeter 241 at a wavelength of 589 nm. The characteristics of the polymers used in this work are listed in Table I, together with the polymerization conditions. $[\alpha]_D^{25}$ values were approximately +150° for PDLA and -150° for PLLA, in good agreement with the literature values.²³

Spinning of Complex Fiber

The dope used for both wet- and dry-spinning was prepared as follows: The chloroform solutions of PDLA and PLLA with a concentration of 5–10 g/dL were separately prepared and admixed at the equimolar ratio. The mixed solutions were stirred vigorously for 3 days for the thorough mixing of

Table I Characteristics of the Resulting Polymers Used for Spinning

Polymer	Molecular Characteristics		
	$[\eta]$ (dL/g)	\bar{M}_v	$[\alpha]_D^{25}$ (deg)
PDLA	5.40	3.0×10^5	156
PLLA	5.56	3.1×10^5	153

PDLA and PLLA molecules. The apparatus and conditions of wet-spinning are given in Figure 1 and Table II, respectively. The dope was extruded at a rate of 0.2 mL/min from a nozzle of a single hole with a diameter of 0.5 mm.

For wet-spinning, the dope with the concentration of 5–8 g/dL was first introduced into the mixture of nonsolvent and solvent, ethanol/chloroform = 10/3 (v/v) kept at 40°C, and then further into the second coagulation bath [ethanol/chloroform = 10/1 (v/v)] at 20°C to complete desolvation, followed by winding of the fiber. The first and the second coagulation paths were 30 and 40 cm, respectively. Dry-spinning of the complex fiber was performed under the conditions described in Table I by controlling the winding speed. The dope concentration was a little higher than that for the wet-spinning. The extruded dope was dried at 60°C in a column of 50 cm length. The complex fibers were drawn in a silicone oil bath thermostatically controlled at constant temperature of 120–160°C and annealed at the same temperature for 1 h in the drawn state.

Measurements

The T_m and the enthalpy of fusion (ΔH_m) of the complex fibers were measured with a Simadzu DT-50 differential scanning calorimeter (DSC) using indium as a standard. Heating was performed under a nitrogen gas flow at a heating rate of 10°C/min.

Morphology of the complex fibers was observed with a scanning electron microscope, Model S-450, manufactured by Hitachi, Tokyo, Japan, after coating the complex fiber with a thin layer of platinum using an Eiko IB-3 Ion-coater, Eiko Engineering, Tokyo, Japan.

Mechanical properties of the complex fibers were measured at 20°C and 65% relative humidity using a tensile tester at a crosshead speed of 100%/min. The initial length of the specimen was always 20 mm.

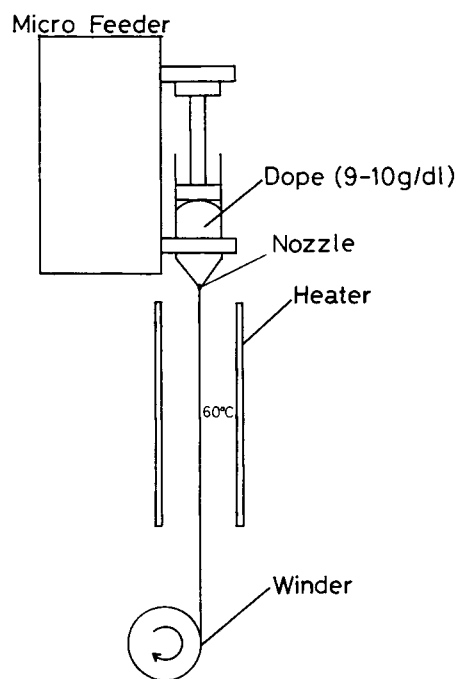
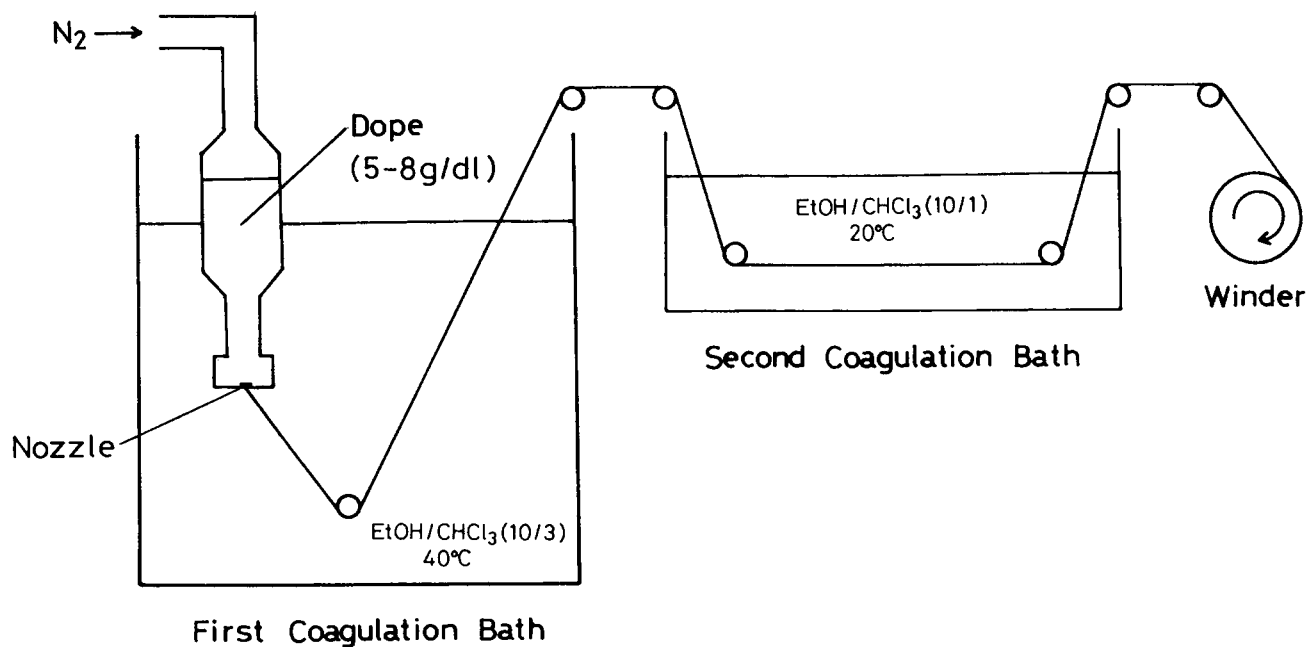


Figure 1 Apparatus of spinning used in this study.

RESULTS

Spinning

Solution spinning of the PDLA and PLLA mixture was too difficult when molecular weight of these

polymers was below 4×10^4 , since stereocomplexation occurred to yield a macrogel in the dope having high concentration appropriate for spinning.⁴ On the other hand, spinning of the complex fiber was possible when the polymer molecular weight was as high

Table II Conditions for Dry- and Wet-spinning of Complex Fibers

	Wet-spinning	Dry-spinning
Dope		
PDLA : PLLA	1 : 1	1 : 1
Concentration (g/dL)	5-8	9-10
Nozzle		
Type	Mono-hole	Mono-hole
Diameter of hole (mm)	0.5	0.5
Extrusion rate (mL/min)	0.2	0.2
First coagulation bath		
Composition	EtOH/CHCl ₃ = 10/3 (v/v)	—
Temperature (°C)	40	—
Path (cm)	30	—
Second coagulation bath		
Composition	EtOH/CHCl ₃ = 10/1 (v/v)	—
Temperature (°C)	20	—
Path (cm)	40	—
Drying column		
Temperature (°C)	—	60
Length (cm)	—	50
Wind-up speed (cm/min)	100	100

as 10^5 , since complexation between such high molecular weight PDLA and PLLA proceeded at a very slow rate even though the dope had such a high concentration as to exhibit an appropriate viscosity for spinning.⁵ Moreover, the extruded dope was easily broken by a low tensile force before solvent extraction or evaporation. Therefore, lowering the tensile force applied on the dope during spinning was essential to obtain the complex fiber. Moreover, too rapid desolvation will give the fiber having many voids. Only translucent fibers were obtained through wet-spinning, although we tried to lower the desolvation rate as much as possible. By contrast, dry-spinning gave apparently transparent complex fibers, suggesting that the dry-spun complex fibers had a small amount of voids, compared with the wet-spun fibers.

Fiber Morphology

The SEM photographs of the wet- and dry-spun fibers are shown in Figure 2. It is seen that both the undrawn fiber surfaces are very irregular; the undrawn wet-spun fiber has basins with an average diameter of about 50 μm and a large number of pores with various sizes ranging from sub μm to 10 μm on its surface, whereas the undrawn dry-spun fiber has a lot of small size pores of 1-3 μm . The defective structure of the wet-spun fiber is probably due to the rapid desolvation from the extruded dope during

precipitation. The microporous structure of the undrawn dry-spun fiber may have resulted from the phase separation of the dope into concentrated and dilute regions during the solvent evaporation. As seen from Figure 2(E)-(H), a streaked surface appears upon hot-drawing of the dry-spun fiber, probably because of stretching micropores.

Thermal Properties of Fiber

DSC thermograms of the undrawn wet- and dry-spun fibers, together with those of the dry-spun fiber drawn to different ratios at 140°C, are given in Figure 3. The endothermic peaks around 180°C are ascribed to melting of the crystallites of the single polymers, PDLA and PLLA, and those around 230°C to melting of stereocomplex crystallites (racemic crystallites). The wet-spun fiber was too fragile to bear the hot-drawing, presumably because of many defects seen in Figure 2. Clearly, both the wet- and dry-spun complex fibers have both of the melting peaks, indicating that these fibers also contain both the racemic and single-polymer crystallites. Melting temperatures of the single-polymer crystallites (T_{m1}) and the racemic crystallites (T_{m2}) of the dry-spun fiber drawn at 140°C to different draw ratios are plotted as a function of draw ratio in Figure 4(a), together with those of the undrawn wet-spun fiber. It is seen that there is no significant difference in T_{m1} and T_{m2} between the wet-spun and

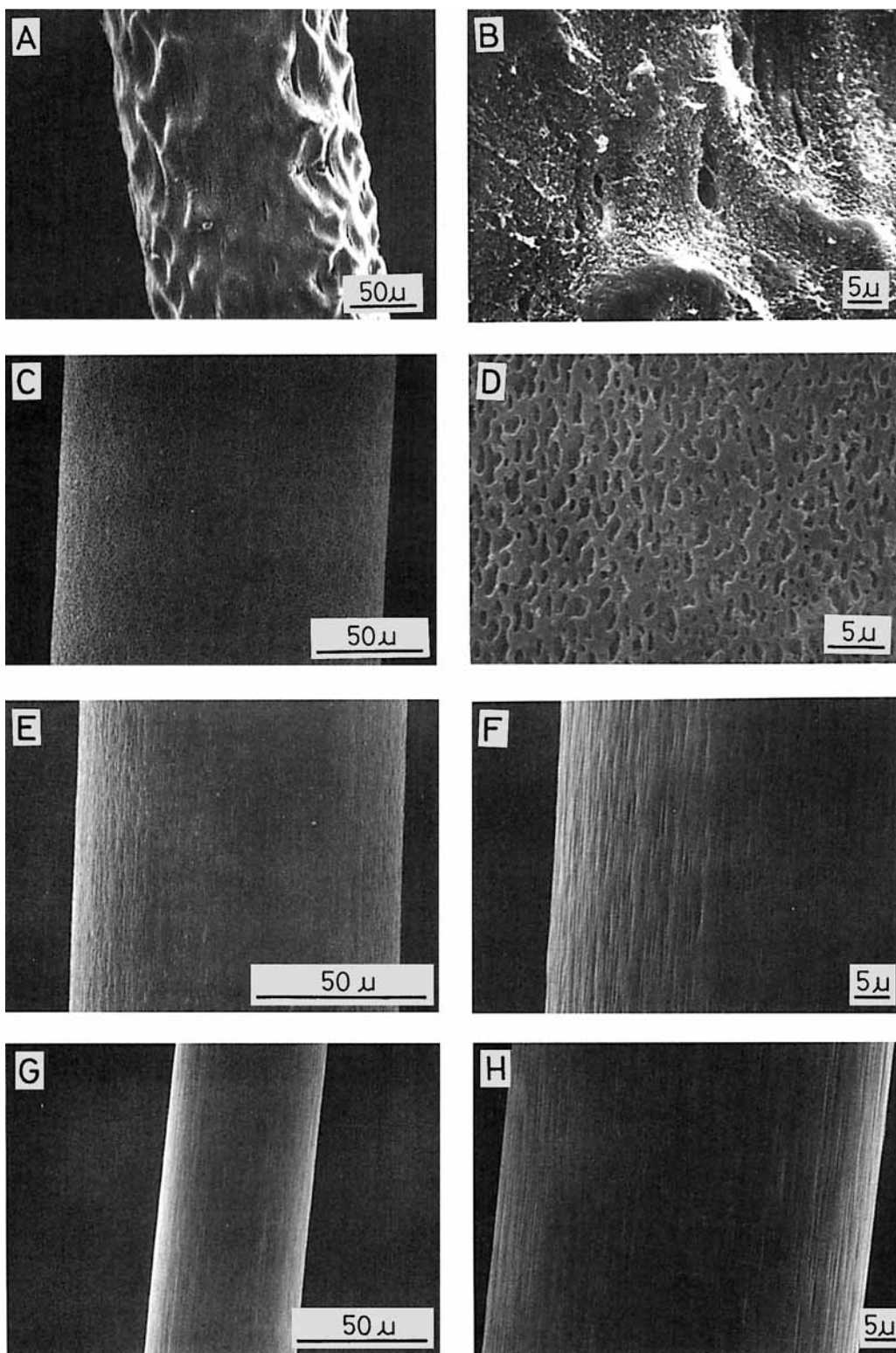


Figure 2 SEM photographs of the undrawn complex fibers and the dry-spun complex fibers drawn at 140°C to different draw ratios (annealed at 140°C for 1 h): (A,B) undrawn wet-spun fiber; (C,D) undrawn dry-spun fiber; (E,F) dry-spun fiber drawn to the ratio of 3; (G,H) dry-spun fiber drawn to the ratio of 9.

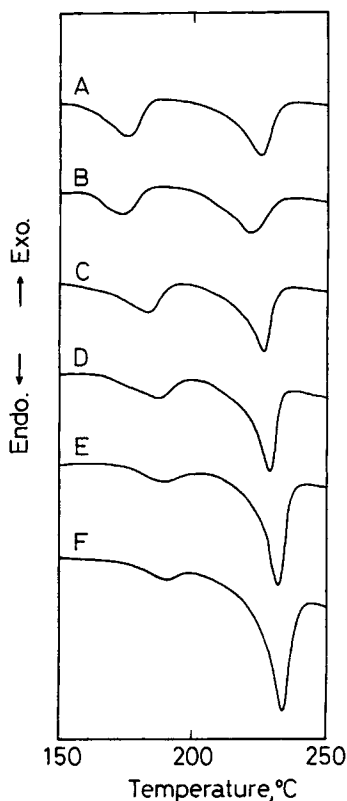


Figure 3 DSC thermograms of the undrawn complex fibers and the dry-spun complex fibers drawn at 140°C to different draw ratios (annealed at 140°C for 1 h): (A) undrawn wet-spun fiber; (B) undrawn dry-spun fiber; (C) dry-spun fiber drawn to the ratio of 3; (D) dry-spun fiber drawn to the ratio of 5; (E) dry-spun fiber drawn to the ratio of 7; (F) dry-spun fiber drawn to the ratio of 9.

the dry-spun fibers before drawing. For the dry-spun fiber, both T_{m1} and T_{m2} become higher with increasing draw ratio, as is common for crystalline polymers. Figure 4(b) shows the enthalpies of fusion of the single-polymer crystallites (ΔH_{m1}) and the racemic crystallites (ΔH_{m2}) for the complex fibers. It is apparent that ΔH_{m1} of the dry-spun fiber decreases with increasing draw ratio, in contrast to ΔH_{m2} . The increase in T_{m2} and ΔH_{m2} and the decrease in ΔH_{m1} upon the fiber drawing strongly indicate that hot-drawing increases the size and the fraction of the racemic crystallites, transforming a part of the single-polymer crystallites into other components such as noncrystalline and racemic crystalline.

Mechanical Properties of the Fiber

Tensile properties of the dry-spun fibers drawn at different temperatures are plotted against the draw

ratio in Figure 5. Fiber drawing was not possible at the temperature above 180°C, probably because of melting of the crystallites of the single polymers. The tensile strength of the dry-spun fibers rises with the draw ratio. At the same draw ratio, the tensile strength of the fiber drawn at lower temperature is larger than that drawn at higher temperature. It is obvious that the dependence of Young's modulus of the fiber on the drawing temperature and ratio is very similar to that of the tensile strength. On the contrary, elongation-at-break of the dry-spun fibers is practically independent of the drawing temperature, but depends on the draw ratio as seen in Figure 5(c). The undrawn fibers exhibit remarkably large elongation, which may be ascribed to the porous structure of the as-spun fibers.

In the present study, the highest strength and modulus were obtained when the dry-spun fiber was drawn at 160°C to the ratio of 13.

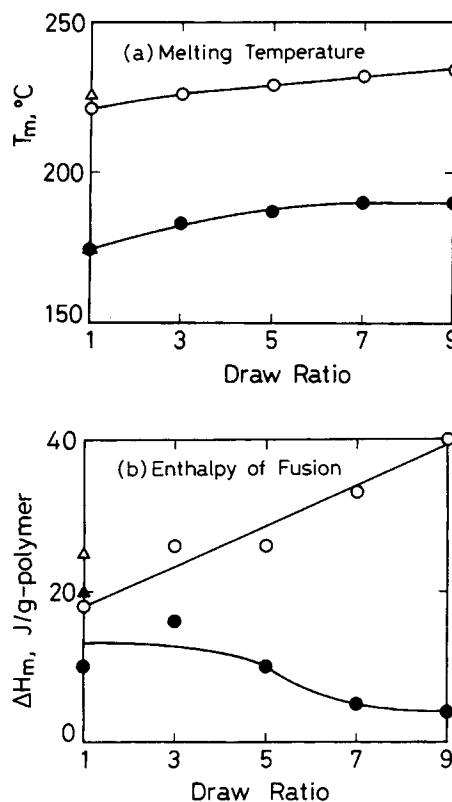
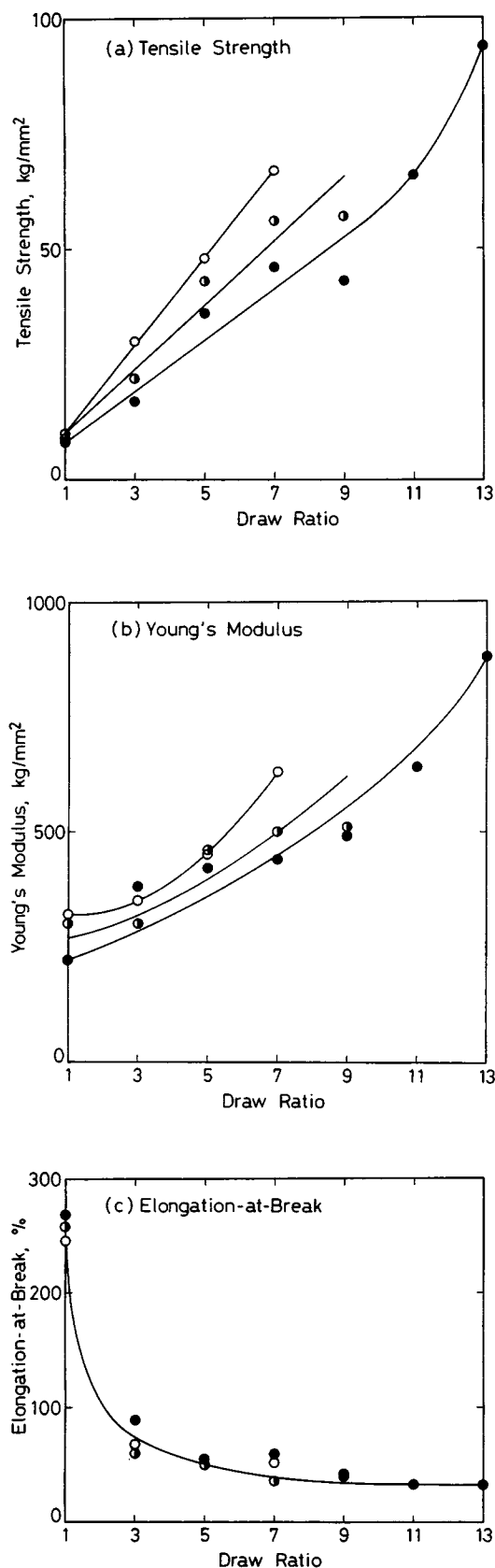


Figure 4 Melting temperature (T_m) and enthalpy of fusion (ΔH_m) evaluated from Figure 3 as a function of the draw ratio of the fiber for the crystallites of the single polymers [(▲) wet-spinning; (●) dry-spinning] and the racemic crystallites [(△) wet-spinning; (○) dry-spinning] in the fibers.



DISCUSSION

As is apparent from the DSC results, the fiber containing a large amount of racemic crystallites and a very small amount of crystallites of the single polymers could be obtained by hot drawing of the as-spun fibers. ΔH_{m2} of the dry-spun complex fiber drawn at 160°C finally reached 40 J/g-polymer, which is much larger than that obtained by casting 1 g/dL chloroform solution (3 J/g-polymer),⁵ but lower than that obtained by precipitation from acetonitrile solution (100 J/g-polymer), when compared for the polymer pair with similar molecular weight as that used in this study.⁷

The attained maximum tensile strength and Young's modulus of the dry-spun complex fiber were 94 and 880 kg/mm², respectively. This tensile strength value is comparable with those obtained by hot drawing of the dry-spun fibers from the single solution of PLLA in a good solvent (1.2×10^2 kg/mm²)¹¹ and in a poor solvent (1.0×10^2 kg/mm²),¹⁰ respectively. The maximum tensile strength of the hot-drawn fibers from PLLA with \bar{M}_v of 3.5×10^5 , which is similar with that used in this study, was 85 kg/mm² in a good solvent¹¹ and 80 kg/mm² in a poor solvent.¹⁰ The maximum Young's modulus of the hot-drawn complex fibers is also similar with those of the hot-drawn PLLA fibers, i.e., 1.5×10^3 (PLLA fibers with \bar{M}_v of 6.0×10^5 in a good solvent),¹¹ 9×10^2 (PLLA fiber with \bar{M}_v of 5.3×10^5 in a poor solvent),¹⁰ and 1.0×10^3 (PLLA fiber with \bar{M}_v of 3.5×10^5 in a poor solvent).¹⁰

The high elongation-at-break of the complex fiber at low draw ratio is probably due to its microporous structure, which may be formed as a result of phase separation of the dope into dilute and concentrated regions, when the dope was brought into the drying column. It is interesting to note that the porous structure of the undrawn dry-spun fiber [Fig. 2(C) and (D)] is very similar to that of the dry-spun PLLA fiber from the solution in a good solvent.¹¹ This suggests that the phase separation during spinning might not be specific to the dope from PDLA and PLLA but common to the PLA dope in a good solvent.

In this study, we utilized the solution spinning method at room temperature to avoid thermal de-

Figure 5 Tensile properties of the dry-spun complex fibers drawn at different temperatures [(○) 120°C; (◐) 140°C; (●) 160°C] as a function of the draw ratio (annealed at the drawing temperature for 1 h).

composition of constituent polymers. However, by employing melt-spinning, the complex fiber without pores may be obtained, since phase separation will not occur in the melt.

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