

# Resorbable Materials of Poly(L-Lactide). II. Fibers Spun from Solutions of Poly(L-Lactide) in Good Solvents

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## Synopsis

Fibers of poly(L-lactide) (PLLA) with a tensile strength up to 1.2 GPa and Young's modulus in the range of 12–15 GPa were obtained by a hot drawing of fibers spun from solution of PLLA in good solvents such as dichloromethane and trichloromethane. The tensile strength of fibers was strongly dependent on the molecular weight of PLLA and on polymer concentrations in the spinning solution. Changing of the polymer concentration in the spinning solution gives rise to formation of fibers with different shape and porosity. Fibers spun from 10–20% solutions at room temperature exhibit a regular structurization, due to the melt fracture. These fibers had knot strengths up to 0.6 GPa, whereas fibers with a smooth surface spun from more dilute solutions had weaker square knots up to 0.3 GPa.

## INTRODUCTION

In a previous paper of this series it was shown that poly(L-lactide) (PLLA) fibers could be produced by melt spinning and subsequent hot drawing, leading to a tensile strength of 0.5 GPa, and by solution spinning of PLLA in a poor solvent, toluene, at elevated temperatures, achieving a strength level of 1.0 GPa.<sup>1</sup>

In both cases the tensile strength of fibers increased with the draw ratio, and was found to be strongly dependent on the drawing temperature. Above a certain molecular weight ( $\bar{M}_v = 1.8 \times 10^5$ ), the tensile properties of the PLLA fibers improved on increasing the molecular weight of polymer. The melt spinning as well as the spinning of the PLLA solutions in toluene at 110°C decreased the molecular weight of PLLA fibers by 15%, while the hot drawing decreased the  $\bar{M}_v$  by 3–5% of an initial value.

It is the purpose of this paper to report some data on the PLLA fibers spun at room temperature from solutions of PLLA in good solvents. This procedure avoids degradation of the polymer by the high temperature spinning process and permits us to produce the PLLA fibers over a wide range of the molecular weights and concentrations.

It will be shown that the concentration of polymer solution has a strong effect on the shape and porosity of the as-spun fibers as well as on the tensile properties reached by the fiber after hot drawing.

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## EXPERIMENTAL

### Samples

Poly(L-lactide) with the viscosity-average molecular weight in the range of  $1.8\text{--}6.0 \times 10^5$  was obtained according to the procedure described previously.<sup>1</sup> The part of PLLA with  $\bar{M}_v = 5.3 \times 10^5$  was fractionated into two fractions with  $\bar{M}_v = 5.0 \times 10^5$  and  $6.0 \times 10^5$  by a fractional precipitation of the polymer at room temperature from 5% solution in dichloromethane-trichloromethane mixed in proportion of 1:1 v/v. Methanol-ethanol-acetone (1:0:6:0:4 v/v) mixture was used as a precipitant.<sup>2</sup>

The intrinsic viscosities of the polymer were measured in trichloromethane at 25°C. The viscosity-average molecular weight of PLLA was calculated according to the formula<sup>3</sup>:

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

### Solution Spinning of Fibers

Fibers of PLLA were obtained by extrusion of polymer solutions in dichloromethane or trichloromethane at room temperature, using the device shown in Figure 1. Polymer concentrations were in the range 1–20% w/v.

No degradation was found on extrusion of PLLA fibers under these conditions. Filaments were collected on a glass drum at a speed in the range of  $0.02\text{--}1.0 \text{ m}\cdot\text{min}^{-1}$ . No orientation was introduced in the filament during spinning.

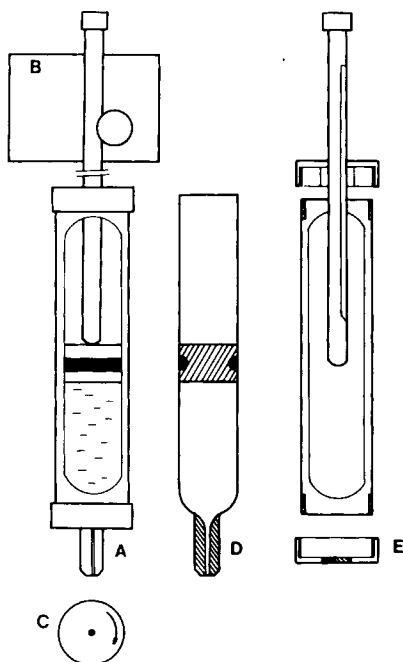


Fig. 1. Extruder for dry spinning of fibers: (A) general view; (B) motor drive; (C) collecting drum; (D) glass cylinder with capillary die of  $1 \times 25 \text{ mm}$ ; (E) cylinder holder.

### Hot Drawing

Hot-drawing experiments were carried out using a double-walled glass tube with a length of 1 m, heated with a kanthal wire wound against an outer surface of the tube. The heater was connected in the system with a platinum resistor thermometer-temperature regulator and temperature readout. Temperature in the tube was maintained within  $\pm 0.1^\circ\text{C}$ . Fiber was collected on the takeup bobin at a speed in the range of  $0.2\text{--}1\text{ cm}\cdot\text{s}^{-1}$ . The strain rate was in the range of  $10^{-3}\text{ s}$ .

### Characterization of the Fibers

Mechanical properties of PLLA fibers were measured at room temperature using a Zwick tensile tester at a crosshead speed of  $12\text{ mm}\cdot\text{min}^{-1}$ . The length of the specimen was 25 mm.

Melting characteristics of PLLA fibers in unconstrained form were obtained using a Perkin-Elmer DSC-2 apparatus at a scan speed of  $5^\circ\text{ min}^{-1}$ . A Jeol JSM-35C scanning electron microscope was used to characterize the fibre shape and morphology.

A Philips diffractometer and Ni-filtered  $\text{CuK}_\alpha$  radiation was applied to obtain wide-angle X-ray diffraction patterns of the as-spun fibers.

## RESULTS AND DISCUSSION

### Fiber Morphology

It was observed that the morphology of the poly(L-lactide) fibers produced by dry spinning from dichloromethane or trichloromethane solutions at room temperature depend, to a great extent, on the polymer concentration. The fibers obtained from 2% solutions were flat and exhibit a smooth surface, while the fibers spun from 10–20% solutions were cylindrical in shape and had a characteristic “structured” surface. This surface structurization may very well be due to “melt fracture,” a phenomenon that has been observed for a number of polymers<sup>4–8</sup> and is related to flow instabilities in the die arising from the elastic character of polymer melts and solutions. A typical example of a poly(L-lactide) PLLA fiber exhibiting a “melt-fracture” surfaces is shown by the scanning electron micrograph of Figure 2(A). This fiber was spun from a 20% solution of PLLA with a viscosity average molecular weight  $\bar{M}_v = 6.0 \times 10^5$  in trichloromethane. Due to the influence of elasticity on the flow behavior, the fiber turned out to be regularly “coarse threaded.” It was found that, for a given concentration, the pitch of the thread decreased on increasing the pressure applied to the polymer solution. Rates of extrusion were varied in the range of  $0.1\text{--}0.5\text{ m}\cdot\text{min}^{-1}$ . Figures 2(B), 2(C), and 2(D) show scanning electron micrographs of the fiber surface after stretching to draw ratios of 2, 10, and 20, respectively. The last two draw ratios were obtained by drawing at  $200^\circ\text{C}$ .

It can be seen that even hot drawing at high draw ratios does not completely remove the surface structure. Fiber stretching results in an extension of the pitch of the helix, indicating that the drawing does not proceed by a neck formation. In between the helical pitch, the surface of the fiber appears to be rather smooth

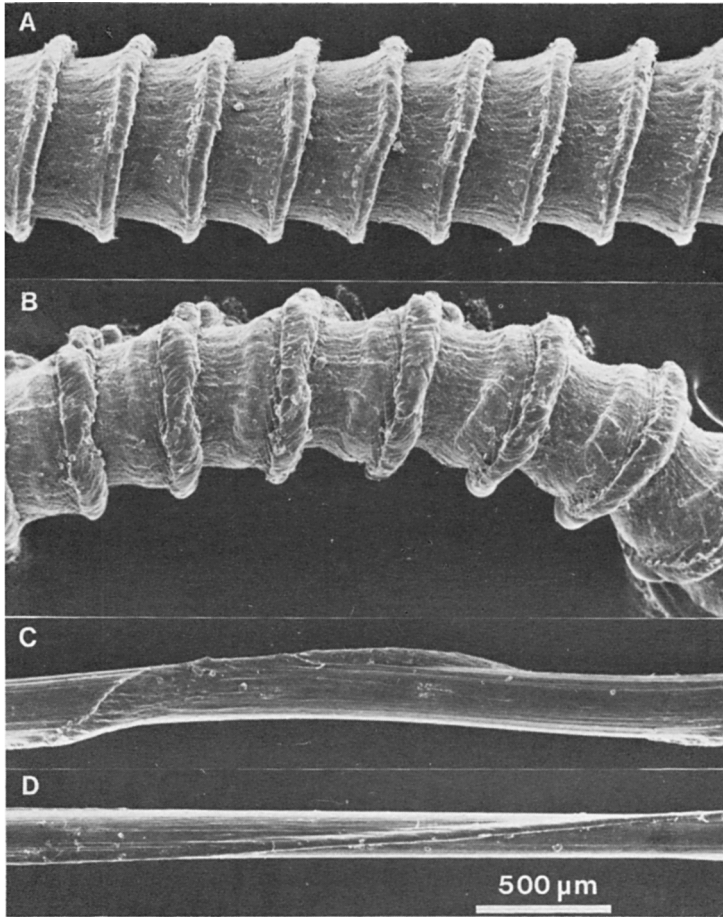


Fig. 2. PLLA fiber extruded from 20% solution in trichloromethane at room temperature: (A) as-spun fiber; (B) fiber cold-drawn 2X; (C and D) fiber hot-drawn at 200°C 10 and 20 times, respectively.

and fibrillated as disclosed by the scanning electron micrographs of Figures 3(A) and 3(B). This fiber was spun from a 20% solution of PLLA in trichloromethane and drawn at 200°C to the maximum draw ratio  $\lambda$  of 20.

The deformation of the extended helical surface-structure upon drawing is clearly illustrated by the model in Figure 4. When the "structured" fiber broke during hot drawing and the extended part was removed from the oven, the same helical structure was regained. This suggests that hot drawing does not lead to a fully reorganization at a molecular level but that a strong "memory effect" occurs that is likely to be associated with the remains of entanglements.

Figures 5(A), 5(B), 5(C), and 5(D) illustrate this "memory effect" for the fiber spun from a 20% solution of PLLA in trichloromethane and drawn at 200°C to the maximum draw ratio  $\lambda$  of 20. Fiber was broken on the takeup bobbin. By lowering the polymer concentration to 7%, melt fracture could be avoided and the fiber that was spun through a single die seems to be monolithic, although it was found to be composed of two almost separated fibers as is demonstrated in Figure 6(A). Hot drawing of this fiber at 200°C to  $\lambda_{\max}$  equal to 20 resulted in

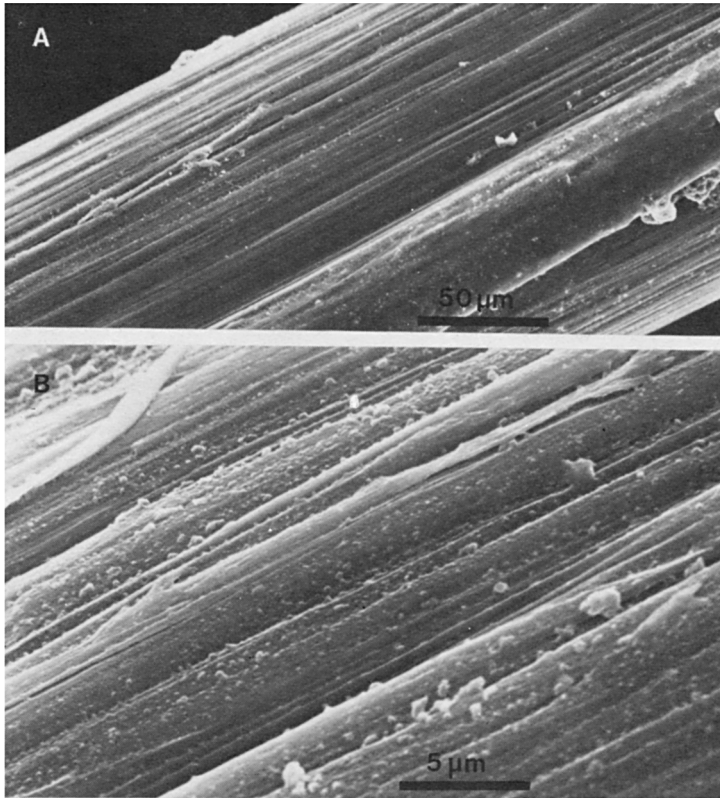


Fig. 3. Surface of PLLA fiber extruded from 20% solution in trichloromethane and drawn at 200°C to  $\lambda_{\max} = 20$ .

a filament composed of very thin connected fibrils with a strength of 1.2 GPa [Fig. 6(B)]. The connectivity of these fibrils seems to decrease upon subjecting the fibre to tensile testing. Figure 7(A) shows how the microfibril splits into

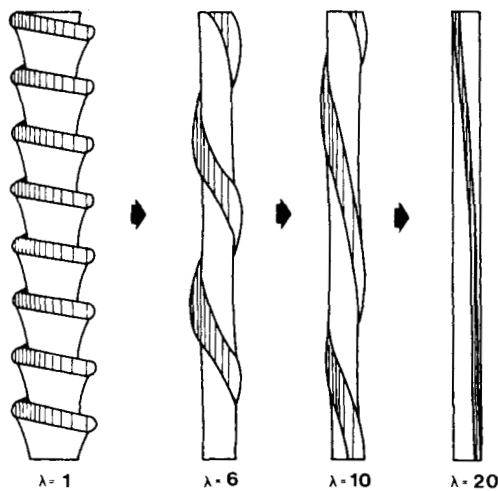


Fig. 4. Schematic illustration of the extension of the helix.

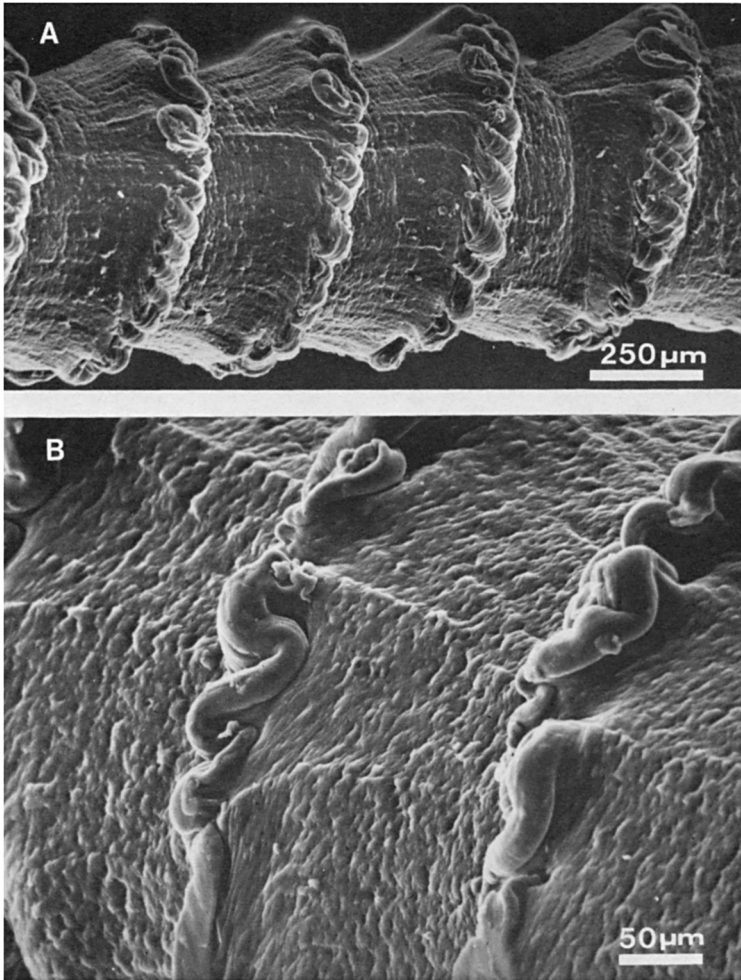


Fig. 5. Illustration of the “memory effect” in structurized PLLA fibers. Fiber was broken on the take-up bobbin after drawing at  $200^{\circ}\text{C}$  to  $\lambda_{\text{max}} = 20$  and passed back through oven: (A, B) side view; (C) view from below; (D) view from the top.

separate microfibrils in this deformation process and Figure 7(B) reveals the kink bands likely to be due to shearing. When concentration of the polymer solution was further reduced to 5%, the spun macrofiber seems to have a “TV cable” type of cross section with large holes and narrow capillary tubes running parallel to the fiber axis [Fig. 8(A)]. The surface of this fiber was found to be covered with ellipsoidally shaped cavities with dimensions of about  $1 \times 5 \mu\text{m}$  [Fig. 8(B)].

After hot drawing at  $198^{\circ}\text{C}$  to  $\lambda_{\text{max}}$  equal to 20 the cavities seem to be elongated and apparently separate the microfibrils more effectively as is shown by the scanning electron micrograph of Figure 9. Despite this more extensive voiding, the tensile strength of this fiber was still 1.1 GPa.

### Melting Behavior

Figure 10 presents the melting endotherms of PLLA fibers with  $\overline{M}_v = 6.0 \times$

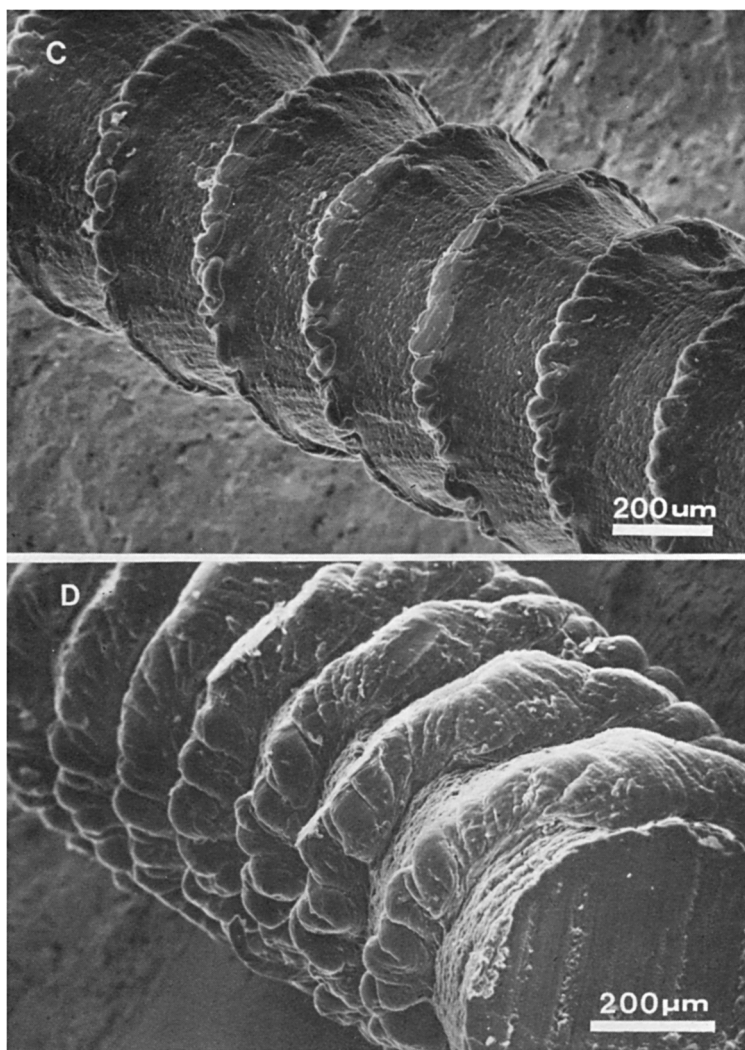


Fig. 5 (continued)

$10^5$  spun from 7% solution in trichloromethane. Endotherm 1 was recorded for the as-spun fiber. Endotherms 2, 3, and 4 were obtained for the fibers drawn at  $200^\circ\text{C}$  to different draw ratios. The tensile strength of these fibers was 0.1, 0.5, 0.8, and 1.2 GPa for 1, 2, 3, and 4, respectively. The broad melting endotherm of the as-spun fiber transforms into a high and narrow melting peak seen for all the hot-drawn fibers. The broad shoulder observed on the high temperature side of the endotherms, which almost disappeared when the fibers used for DSC measurements were cut to the small 2–3 mm pieces, is mainly due to a delayed randomization of the melt.<sup>1</sup> It can be seen in Figure 10 that, similar to that for nylon 6 fibers,<sup>9</sup> the melting temperature of unconstrained PLLA fibers is almost independent of the draw ratio. This is related to insensitivity of the melting temperature recorded for unconstrained fibers on the original structure of the sample.<sup>9</sup>

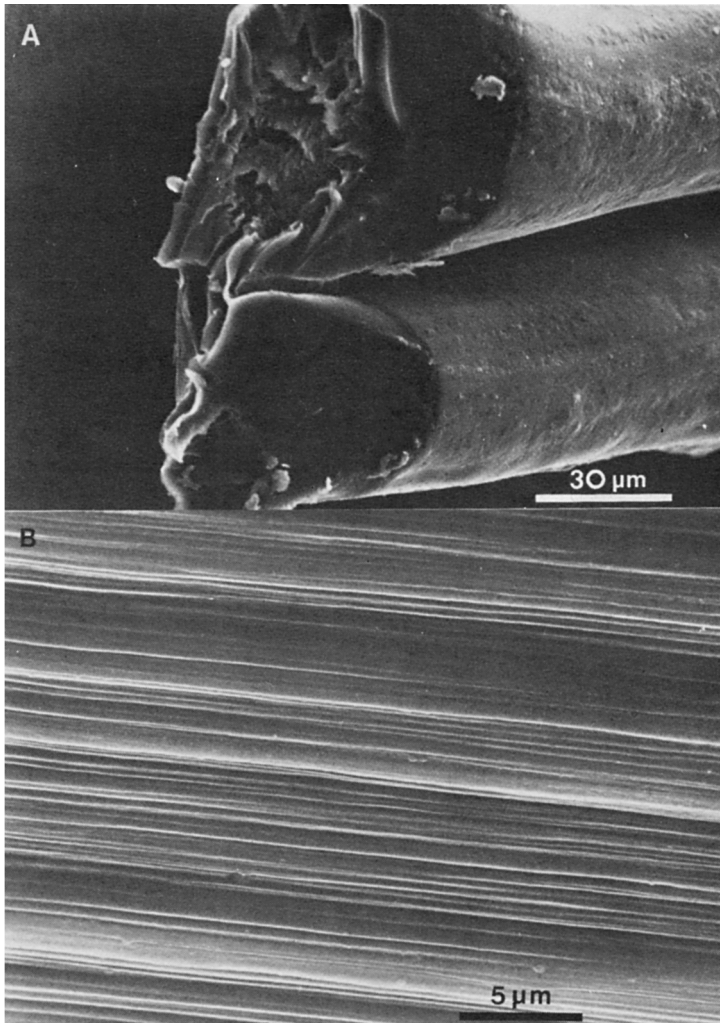


Fig. 6. PLLA fiber extruded from 7% solution in trichloromethane: (A) as-spun fiber; (B) surface of this fiber after hot-drawing at 200°C to  $\lambda_{\max} = 20$ .

On the other hand, it should be noted that the heat of fusion increases considerably upon hot drawing as is illustrated by the data of Table I. The  $\Delta H_m$  value for an as-extruded fiber was  $34.0 \text{ J}\cdot\text{g}^{-1}$  while after hot drawing at 200°C to  $\lambda_{\max} = 20$  the heat of fusion amounted to  $89.0 \text{ J}\cdot\text{g}^{-1}$ . Fischer et al.<sup>10</sup> calculated that the heat of fusion for fully crystalline poly(L-lactide) should be  $93.7 \text{ J}\cdot\text{g}^{-1}$ . Thus hot drawing under optimum conditions gives rise to an extension of the crystallites which can probably be correlated with the tensile strength as is indicated by the data summarized by Table I.

### Mechanical Properties

#### *Effect of Draw Ratio*

Figure 11 shows the stress-strain dependence for PLLA fibers with  $\bar{M}_v = 6$



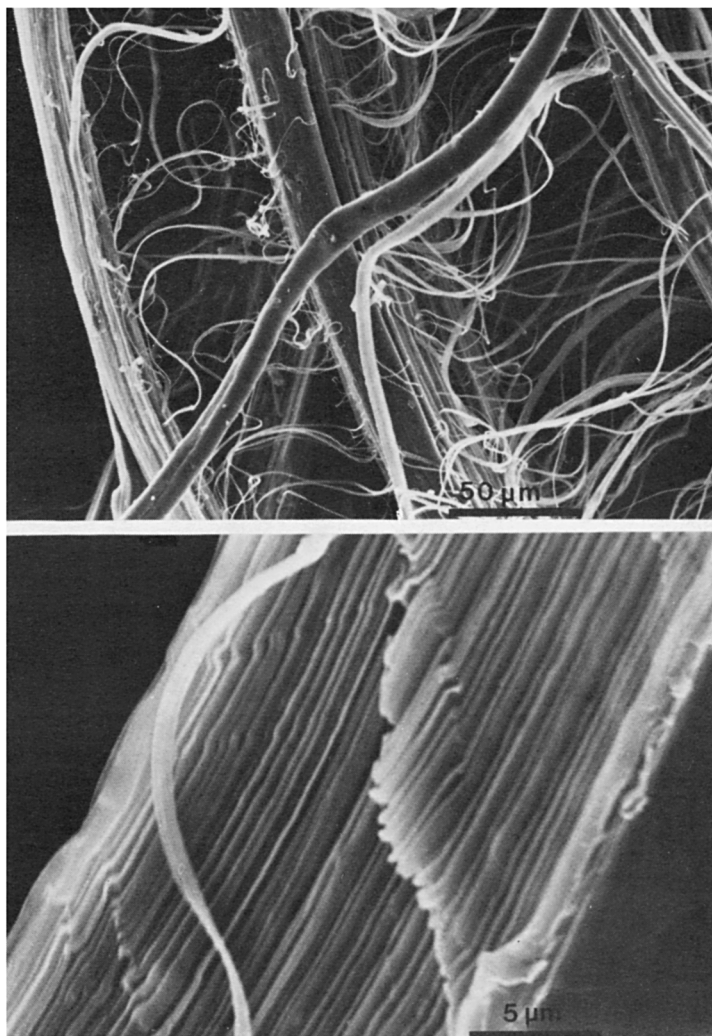


Fig. 7. PLLA fiber spun from 7% solution in trichloromethane and hot-drawn at 200°C to  $\lambda_{\max} = 20$  subjected to tensile testing. The kink bands can be observed in the bundles of split macrofibrils.

$\times 10^5$  spun at room temperature from a solution of the polymer in trichloromethane and subsequently hot-drawn at 200°C to various draw ratios. The diameter of these fibers was in the range of  $0.35\text{--}0.7 \times 10^{-4}$  m. The dashed line was drawn for the fiber spun at 110°C from PLLA solution in toluene and hot-drawn at 200°C to  $\lambda_{\max} = 18$ .<sup>1</sup>

It can be seen that, for the same draw ratio, the fibers spun from solution of PLLA in a good solvent exhibit better tensile properties than the fibers obtained from a poor solvent such as toluene. The initial modulus is again the same for all draw ratios but the strain at which the inflection point occurs increases with  $\lambda$ . Essentially one can distinguish two slopes in these stress-strain curves. This may be associated with a possible change in structure of the crystalline domains when PLLA is subjected to stress, similar to observations for poly(butylene

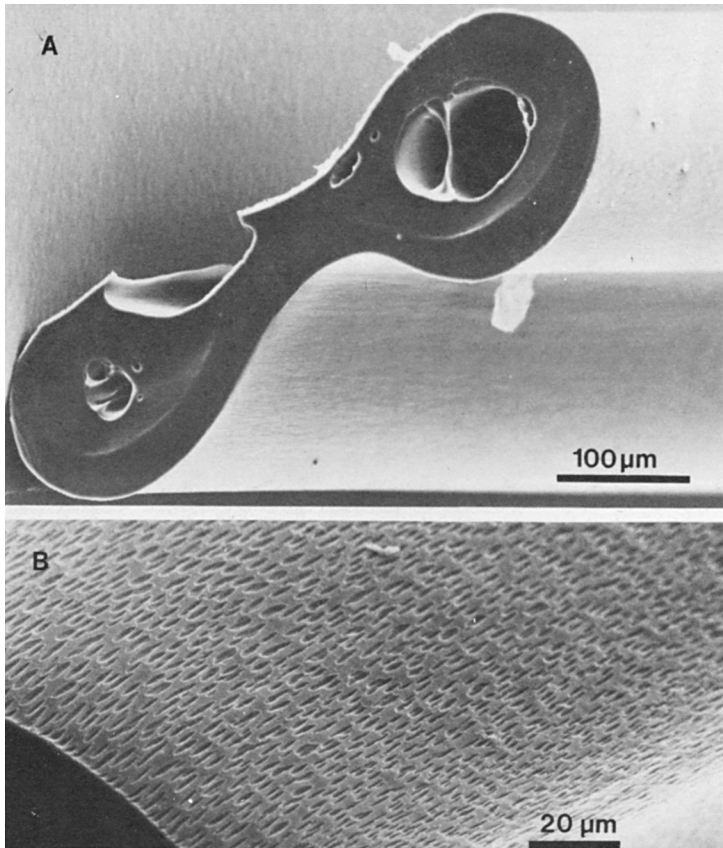


Fig. 8. PLLA fiber spun from 5% solution in trichloromethane: (A) general view; (B) ellipsoidal cavities present on the surface of the as-spun fiber.

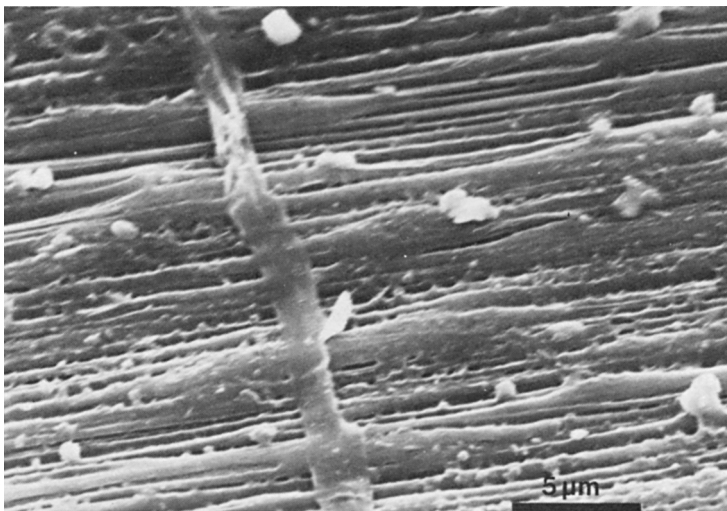


Fig. 9. Surface of PLLA fiber spun from 5% solution in trichloromethane. The fiber was hot-drawn at 200°C to  $\lambda_{\max} = 20$ .

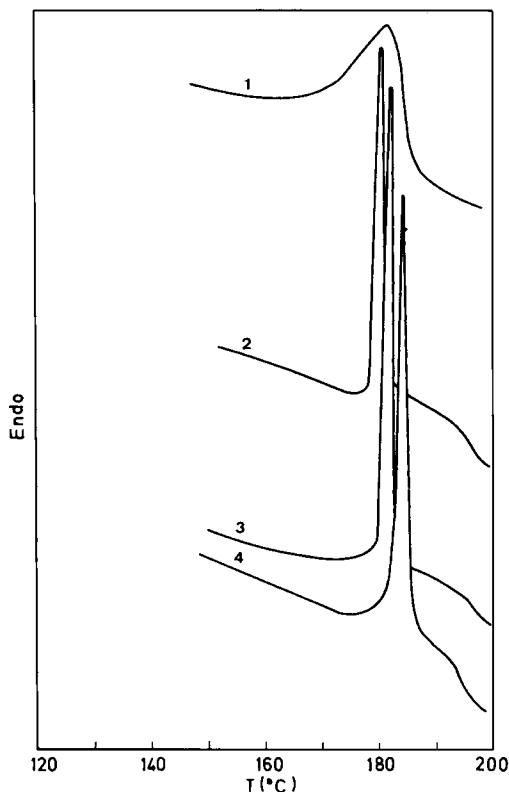


Fig. 10. Melting endotherms of PLLA fibers: (1) as-spun fiber; (2, 3, and 4) fibers drawn at 200°C to  $\lambda = 10, 16,$  and  $20,$  respectively.

terephthalate) as reported by Brereton et al.<sup>11</sup> Polyesters are known to exhibit solid-state transitions,<sup>12</sup> and in the case of PLLA it may be the transition from the  $\alpha$ -helical crystalline structure to the  $\beta$  crystalline structure, in which the chains assumed an extended, planar, zigzag conformation.<sup>13</sup>

The tensile strength at break seems to be rather strongly dependent on the draw ratio. Figure 12 illustrates the effect of the draw ratio on the tensile strength for PLLA fibers of a different molecular weight, spun from the 7% polymer solution in trichloromethane and hot-drawn at optimum drawing temperature. The character of this dependence is similar to that of found for PLLA fibers spun from the polymer solution in toluene and drawn at comparable temperature.<sup>1</sup> However, the trichloromethane-spun fibers reached a higher tensile strength and modulus than those of the similar initial molecular weight, spun from toluene. Young's modulus for trichloromethane-spun fibers subjected to hot drawing was usually in the range of 12–15 GPa while for toluene-spun fibers 7–10 GPa. Tensile strength of the fibers with similar molecular weight spun from PLLA solution in trichloromethane was on the average 0.2–0.4 GPa higher than the fibers spun from toluene.

It is conceivable that this marked difference in strength may be related to the fact that in a good solvent the more expanded coil will contain fewer topological irregularities, such as intramolecular entangled chain portions, than the polymer

TABLE I  
Heat of Fusion ( $\Delta H_m$ ) of PLLA Fibers with  $\bar{M}_v = 6.0 \times 10^5$  Spun from 5% Solution in Trichloromethane, Varying in Tensile Strength (TS)

TS (GPa)	Initial modulus	Draw ratio	Diameter ( $\times 10^{-4}$ m)	$\Delta H_m$ ( $J \cdot g^{-1}$ )
1.2	15	20	0.35	89.0
1.1	14	19	0.39	83.6
1.0	12	18	0.44	76.0
0.8	10	16	0.59	70.6
0.6	9	10	1.10	67.2
0.5	8	8	1.32	65.5

dissolved in a poor solvent. Such topological defects may not be removable upon hot drawing and will then lower the strength of the fiber. Obviously, there are many aspects involved in the early failure of fibers under load. One, for example, is the concentration of polymer chain end. In order to acquire some idea about the chain end concentration on the drawability and tensile strength, PLLA fibers with  $\bar{M}_v = 6.0 \times 10^5$  were, before hot drawing, extracted for 24 h with acetone at room temperature. Acetone is a good solvent for PLLA with a low molecular weight.<sup>14</sup> The fiber swells to a degree of swelling of about 5 and 5% of the smallest polymer molecules diffused out of the swollen fiber. The maximum draw ratio after extraction was considerably smaller, namely  $\lambda_{\max} = 11$ , than that for an unextracted fiber, which was  $\lambda_{\max} = 20$ . The tensile strength vs. draw ratio

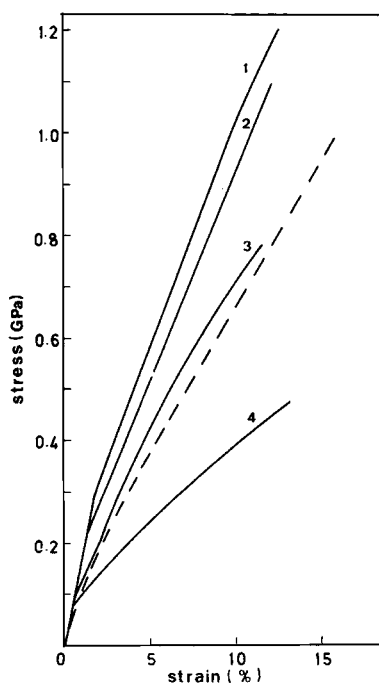


Fig. 11. Stress-strain dependence for PLLA fibers with  $\bar{M}_v = 6.0 \times 10^5$  spun from the polymer solution in trichloromethane and drawn at 200°C to different draw ratios: (1) 20; (2) 18; (3) 14, (4) 10. (---) Drawn for the fiber spun at 110°C from toluene and hot-drawn at 200°C to  $\lambda_{\max} = 18$ .

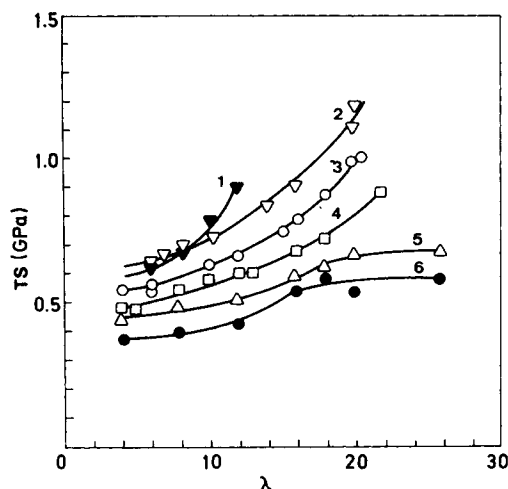


Fig. 12. Dependence of the tensile strength on the draw ratio for PLLA fibers with a different molecular weight: (1)  $6.0 \times 10^5$  (extracted fiber); (2)  $6.0 \times 10^5$  (nonextracted fiber); (3)  $5.0 \times 10^5$ ; (4)  $3.5 \times 10^5$ ; (5)  $2.5 \times 10^5$ ; (6)  $2.0 \times 10^5$ .

curves for the extracted fibers (1) and the unextracted fibers (2) are compared in Figure 12. Apparently, an amount of lower molecular weight polymer in the fiber is required in order to obtain high draw ratios, in agreement with observations by Capaccio and Ward for polyethylene.<sup>15,16</sup> These results also indicate that the tensile strength cannot be related in a unique way to the chain end concentration because the tensile strength of the extracted fiber is only 0.9 GPa whereas that for the unextracted one was 1.2 GPa. Since fibers of biodegradable polymers may find their way into use as suture material in surgery or as reinforcing elements for construction of surgical implants,<sup>17</sup> it was decided also to measure the knot strengths. The data on the strength of the square knots in smooth and structurized fibers are collected in Table II. It shows that the knot strength of the fibers with the surface structure is twice as large as the filaments with a smooth surface. In general, one may expect that the "melt-fracture" fiber irregularities may lead to poorer mechanical properties, but this turned out not to be the case for the PLLA fibers, as demonstrated by the data of Table II. Fibers with a smooth and with a helical surface structure were found to have very similar tensile strengths. The knot strengths of the former were about one third

TABLE II

The Tensile Strength (TS) and the Strength of Square Knots (KS) of PLLA Fibers with Smooth Surface and Structurized Surface Due to "Melt Fracture"

Smooth fibers		Structurized fibers	
TS (GPa)	KS (GPa)	TS (GPa)	KS (GPa)
0.5	0.2	0.5	0.3
0.7	0.3	0.7	0.5
0.8	0.3	0.8	0.5
0.9	0.3	0.9	0.6
1.0	0.3	1.0	0.6

of the fiber strength up to 0.3 GPa whereas the knot strength of the latter ranged up to 0.6 GPa.

### *Effect of Drawing Temperature*

The effect of drawing temperature on the tensile strength at  $\lambda_{\max}$  for PLLA fibers with different molecular weight spun from solution of the polymer in dichloromethane or trichloromethane was similar to that reported previously for the toluene-spun fibers.<sup>1</sup> Also in the present study two maxima separated by a minimum in the tensile strength vs. drawing temperature curve were observed. For the fibers with the molecular weight above  $4.0 \times 10^5$  the highest values of the tensile strength were found after drawing at temperature in the range 197–200°C, while, for the fibers with the molecular weight in the range  $1.2\text{--}3.5 \times 10^5$ , the maximum in the tensile strength was reached at 175–180°C. The reason is probably that, for a lower molecular weight polymer, the higher drawing temperature causes disordering and refolding of the chains into poor crystals with a lower melting temperature. Thus it seems that increasing of the drawing temperature above an optimum value results in the flow drawing rather than in the hot drawing, which could lead to the more or less oriented fibrillar crystals.<sup>18,19</sup>

On decreasing the polymer concentration of the spinning solution (which lowers the number of entanglements trapped in the as-spun fiber), the maxima in the tensile strength vs. drawing temperature curves shift 3–4°C towards lower temperatures.

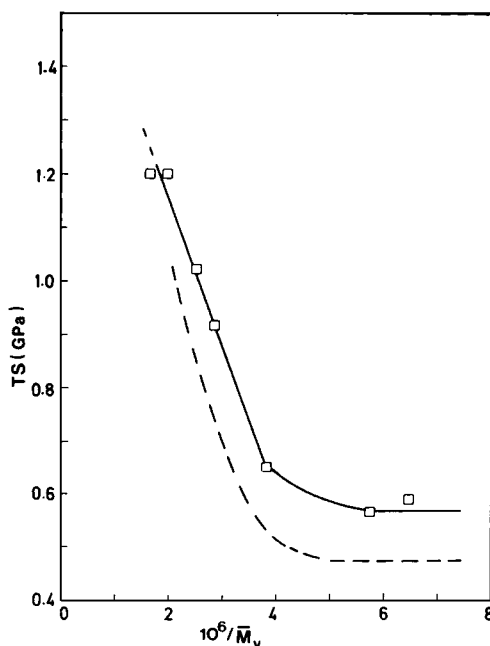


Fig. 13. Dependence of the tensile strength on the reciprocal of the molecular weight for PLLA fibers spun from 5% polymer solution in trichloromethane (—) and toluene (---). Both types of fibers were hot-drawn at optimum drawing conditions.

*Effect of Molecular Weight and Polymer Concentration*

Figure 13 shows the dependence of the tensile strength at  $\lambda_{\max}$  on the reciprocal of the viscosity-average molecular weight for PLLA fibers spun from the polymer solution in trichloromethane. The dashed line represents the same dependence for the PLLA fibers spun from toluene solutions at 110°C.<sup>1</sup> For the polymer with the molecular weight in the range of  $1.8\text{--}3.0 \times 10^5$ , the tensile strength is almost independent of the molecular weight, while above that range the tensile strength increases linearly with the molecular weight of polymer.<sup>20,21</sup> It can be seen that, for PLLA fibers with the same initial molecular weight, the fibers spun from good solvents have higher tensile strength than those spun from poor ones. Because the molecular weight of fibers spun at 110°C from toluene decreased by 15% from the initial value, while the  $\bar{M}_v$  of PLLA fibers spun from trichloromethane at room temperature did not change, one might attribute the decrease in tensile strength to the reduction in chain length. However, the same difference in tensile strength is found to exist and to be independent of molecular weight below  $\bar{M}_v = 3.0 \times 10^5$  for both the solvents. Therefore, it seems more likely that the enhanced tensile strength level for the fibers spun from trichloromethane solutions is associated with the topology of the entanglement network. Another observation pointing to the essential importance of the entanglement density in the spinning solution is the variation of the tensile strength with the polymer concentration. Figure 14 illustrates the dependence of the tensile strength of PLLA fibers of varying molecular weight on the reciprocal of the polymer volume fraction in trichloromethane solution. Tensile strength of PLLA fibers spun from the melt is nearly always independent of molecular weight of the polymer and has a value of 0.5 GPa. Schneider reported<sup>22</sup> that melt-spun PLLA fibers

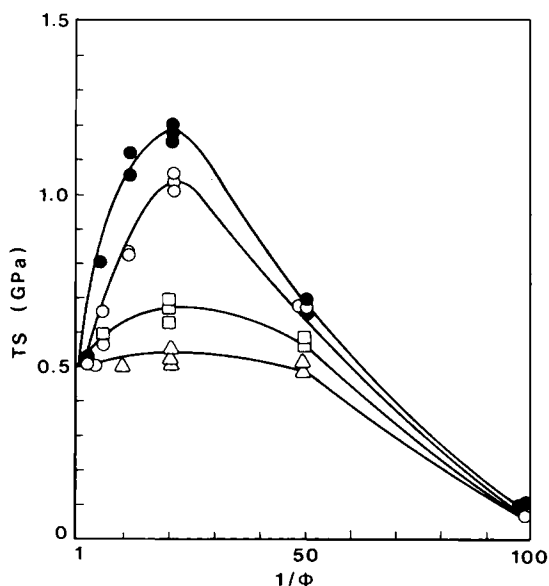


Fig. 14. Dependence of the tensile strength (TS) of PLLA fibers on concentration ( $\phi$ ) of the polymer solutions, used for spinning ( $\bullet$ )  $\bar{M}_v = 6.0 \times 10^5$ ; ( $\circ$ )  $\bar{M}_v = 5.0 \times 10^5$ ; ( $\square$ )  $\bar{M}_v = 3.5 \times 10^5$ ; ( $\Delta$ )  $\bar{M}_v = 1.8 \times 10^5$ .

with a molecular weight of  $3 \times 10^4$  had a tensile strength of 0.5 GPa, which is the same value as found in this study for PLLA with a molecular weight of  $6 \times 10^5$ . Apparently the chain end concentration is not the major factor controlling the strength.

The most pronounced influence of molecular weight on the tensile strength is found for 5% solution. Further reduction of the polymer concentration lowers the tensile strength and for 1% solution a tensile strength of 0.1 GPa is obtained. The molecular weight had no effect on the strength at this concentration. It is also pertinent that these fibers could be hot-drawn to a  $\lambda_{\max}$  of 20, but the heat of fusion had a very low value of  $50.4 \text{ J}\cdot\text{g}^{-1}$ . This poor crystallinity points to an imperfect chain alignment upon hot drawing. Chain extension occurs effectively if the polymer molecule participates by at least two firm entanglements in the transient network. Generally speaking, the mechanical properties are strongly dependent on the degree of crystallinity and on the concentration of crystal defects. The heats of fusion and tensile strength data collected in Table I clearly demonstrate the correlation between crystallinity and mechanical properties. The tensile strength of a PLLA fiber with a heat of fusion of  $89.0 \text{ J}\cdot\text{g}^{-1}$  is 1.2 GPa, whereas the weakest fiber, that having a tensile strength of 0.5 GPa, has a heat of fusion of only  $65.5 \text{ J}\cdot\text{g}^{-1}$ . Among the factors affecting the strength maybe the presence of flaws in the fiber surface. The fourth column in Table I shows that fiber strength decreases with increasing diameter. Higher draw ratios that are achievable for the higher molecular weights also yield thinner filaments and therefore less surface flaws per unit length.

## CONCLUSIONS

PLLA fibers of various shape can be produced by dry spinning of solutions of the polymer in good solvents at room temperature, over a wide range of molecular weights and concentrations.

The hot drawing of these materials at temperature close to the melting point yields fibers with the tensile strength up to 1.2 GPa and Young's modulus up to 15 GPa.

The tensile strength of the hot-drawn fibers increases with draw ratio and molecular weight.

For concentration of the spinning solution in the range of 5–100%, the tensile strength of PLLA fibers increases with decreasing concentration.

The rough surface of the "structurized fibers" obtained from concentrated solutions gives rise to considerably higher knot strength as compared with that for smooth fibers spun from dilute solutions. Since the higher knot strengths produced by melt-fracture spinning are of importance in surgical and other applications, it may be appropriate to reexamine this now generally relinquished technique for fiber production.

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