

Poly lactide. II. Discontinuous Dry Spinning–Hot Drawing Preparation of Fibers

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SYNOPSIS

The mechanical properties and morphology of poly(L-lactide) fibers, prepared by the dry spinning–hot drawing process using different nonsolvent/chloroform spinning solutions, were studied in relation to fiber *in vitro* degradability. Acetone, methanol, ethanol, and cyclohexane were used as nonsolvents in the spinning mixture with as-polymerized PLLA, i.e., PLLA containing 10% of residual L-lactide. The tensile strength, structure, and degradability of obtained fibers were mainly governed by the nonsolvent volatility. Generally, the higher the volatility, the higher the strength, and the faster the degradation. The acetone/chloroform spinning system produced fiber with an increased degradation rate in comparison to the pure chloroform spinning system. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In many respects, poly(L-lactide) is an ideal material for medicinal use. Because of the nature of PLLA biodegradation, i.e., hydrolysis, there should be a relationship between the fiber morphology and the degradation rate. Porous fibers are supposed to degrade faster than the compact ones. One possibility to prepare porous fibers is dry spinning from a solvent/nonsolvent mixture.

In the first part of this study,¹ the PLLA fibers were prepared using the continuous dry spinning–hot drawing process. Mixtures of chloroform and cyclohexane were employed as a dissolution agent to secure a fiber porosity. A similar technique was used for reverse osmosis membrane preparation.² It appeared that the continuous process caused a thick, compact fiber skin that eventually led to hollow fibers. No increase of the degradation rate was observed except for the fibers formed from pure chloroform with a residual monomer at low drawing temperature. The question of the nonsolvent employed arose, too.

In this part, the fiber formation has been separated from the drawing and the polymer has been used as polymerized, i.e., with a residual monomer, only. The influence of the nonsolvent thermodynamical quality and volatility on the PLLA fiber morphology and the consequential degradability is the main subject of this article.

EXPERIMENTAL

Sample

The polymer was prepared as it was reported earlier.¹

Dry Spinning–Hot Drawing Process

The polymer was dissolved by stirring for 16 h at 50°C. After cooling to 33°C (2 h), the solution was spun at lab temperature through an orifice (0.28 × 7 mm) with an extrusion speed of 42.2 cm · min⁻¹ in a beaker 50 cm below. After achieving a constant weight, the filament was hot drawn in a 1 × 30 cm tube.

In vitro degradation and characterization of the fibers were the same as in the Introduction.¹

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Table I Spinning Solutions

System No.	Concentration of PLLA (g/mL)	Nonsolvents	Volume Ratio CHCl ₃ : Nonsolvent
1	0.133	—	Pure CHCl ₃
2	0.113	Ethanol	7 : 3
3	0.113	Cyclohexane	7 : 3
4	0.140	Methanol	7 : 3
5	0.126	Acetone	7.5 : 2.5

RESULTS AND DISCUSSION

Spinning Solutions

The spinning systems used are characterized in Table I. The effort to use spinning solutions of the same polymer concentration was limited by the different dissolution powers of the solvent mixtures.

In the case of the continuous fiber, preparation is an entrance speed of fibers in the drawing tube defined by the collection speed. For the discontinuous preparation, there is no limitation, and the entrance drawing speed would affect the fiber properties significantly. Therefore, the orientation study of the drawing behavior was made for system 3. The fibers formed from the mixture of chloroform and cyclohexane are typical skin fibers, and there is a presumption that results are transferable for the other systems.

Drawing

System 3 fibers were drawn at 90, 125, and 165°C with the entrance speed of 2.2, 7.9, and 14.9 cm · min⁻¹. Table II shows values of the maximum

Table II Drawing Ratios of System 3 Fibers

Fiber No.	Drawing T (°C)	Entrance Speed (cm/min)	Lambda-max	MDR
3.1	90	2.2	5.7	6.4
3.2	125	2.2	7.6	9.7
3.3	165	2.2	10.0	13.5
3.4	90	7.9	5.6	6.6
3.5	125	7.9	6.8	8.6
3.6	165	7.9	8.5	9.9
3.7	90	14.9	5.5	7.2
3.8	125	14.9	6.5	9.5
3.9	165	14.9	7.4	10.8

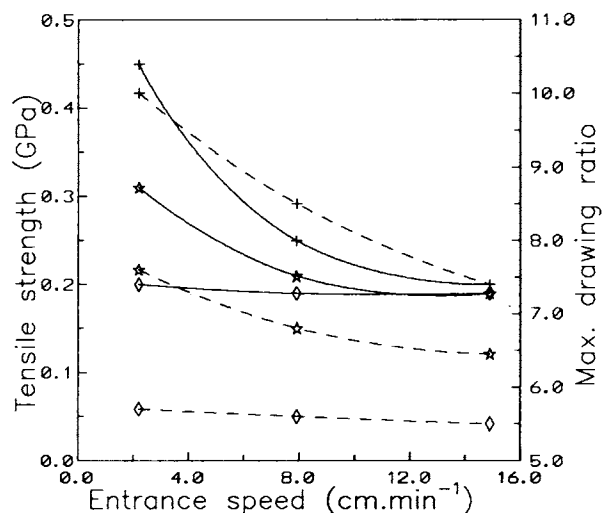


Figure 1 Dependence of the tensile strength and the maximum drawing ratio on the entrance speed. Tensile strength: (\diamond) 90; (\star) 125; (\pm) 165°C. Drawing ratio: (\diamond) 90; (\star) 125; (\pm) 165°C.

length drawing ratio (λ -max) and those of the maximum mass drawing ratio (MDR), which were calculated using the fiber weight *before* and *after* the drawing.

The highest differences between λ -max and MDR are about 40%, and they witness the mass loss during the drawing process. This mass loss is formed by the residual monomer evaporation. The most obvious differences appear to be at high temperatures and at low speeds, of course. Nevertheless, the divergences are relatively small, and the drawing mechanism is acceptably homogeneous in the studied range.

As is shown in Figure 1, the entrance speed of fibers in the drawing tube (i.e., drawing time) strongly affects the fibers' tensile strength, mainly at higher drawing temperatures. At 90°C, the drawing time has no influence on the fiber strength, though. At this temperature, the elastic part of deformation (i.e., drawing efficiency) is almost constant within the studied time range. The λ -max values at 90°C indicate that the drawing takes place under all but the same tension. At higher temperatures, the maximum drawing ratio increases with time of deformation (low speed), the elastic part of deformation increases too, and the drawing is more effective, even when the relaxation time of the elastic deformation is shorter.

On the other hand, the drawing was effective at higher temperatures if there was a sufficiently long time (Fig. 2). At the high entrance speed (short drawing time) and at the high drawing temperature,

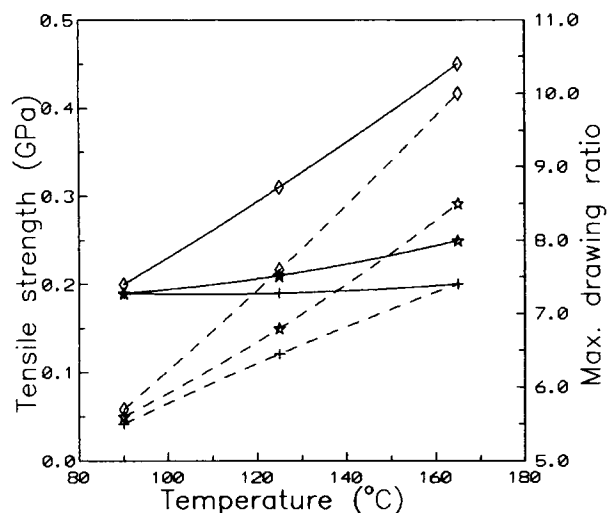


Figure 2 Dependence of the tensile strength and the maximum drawing ratio on the drawing temperature. Tensile strength: (◇) 2.2; (★) 7.9; (+) 14.9 $\text{cm} \cdot \text{min}^{-1}$. Drawing ratio: (◇) 2.2; (★) 7.9; (+) 14.9 $\text{cm} \cdot \text{min}^{-1}$.

there is a high part of plastic deformation, but the elastic (effective) quota stays low because of its time dependence. Therefore, the fiber strength does not

depend on temperature at the entrance speed of 14.9 cm/min , although the maximum drawing ratio does.

Because of the independence of the tensile strength on the entrance speed, the drawing temperature of 90°C was chosen for all the next experiments. In addition, this drawing temperature secures the influence of the residual monomer on the degradability, if there is any.

The fibrilaneous skin structure of final fibers is documented in Figures 3 and 4. The presence of the compact skin on these fibers is the reason for a modest degradation rate (Fig. 5). It is obvious that the drawing conditions do not affect the degradability. Although the fiber skin is much thinner than that via the continuous process, the degradation medium probably does not manage to penetrate it within the studied period. Therefore, the large inner surface area is not utilized.

Fiber Properties

The fibers' properties are characterized in Table III. According to the above stated expectations, the maximum drawing ratio of all fibers varied very little. Because of the different spinning solution con-

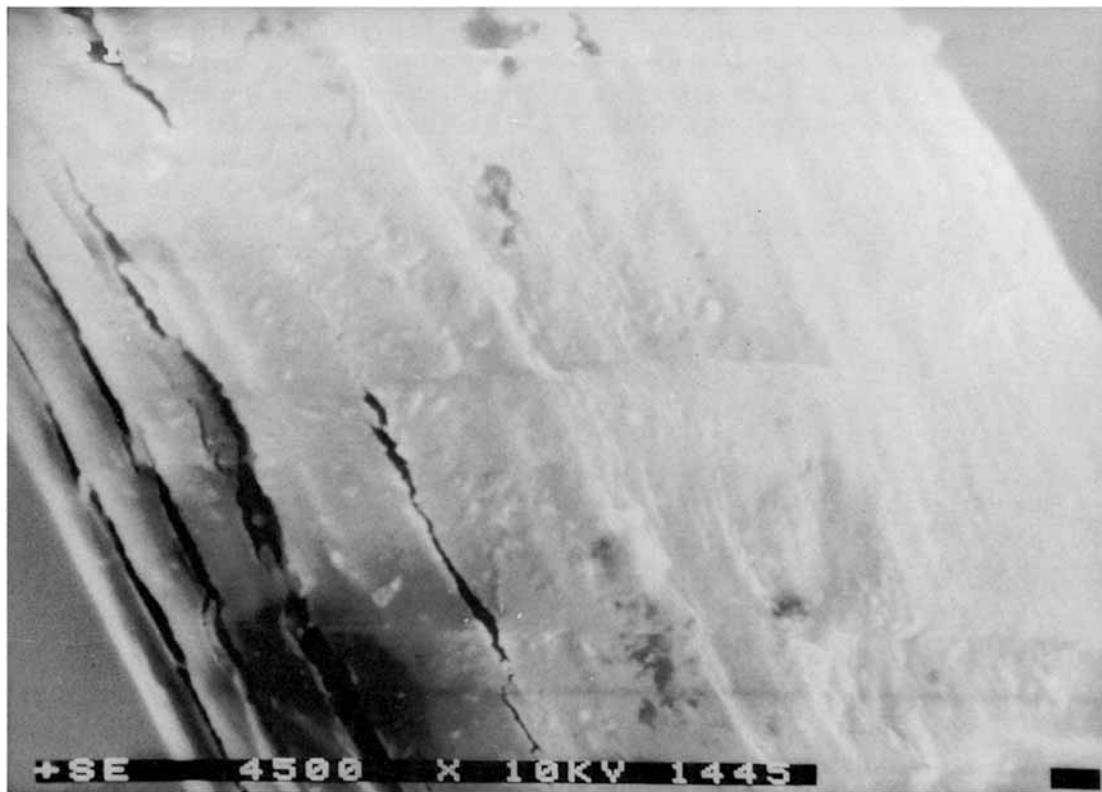


Figure 3 SEM micrograph of fiber 3.5 surface.

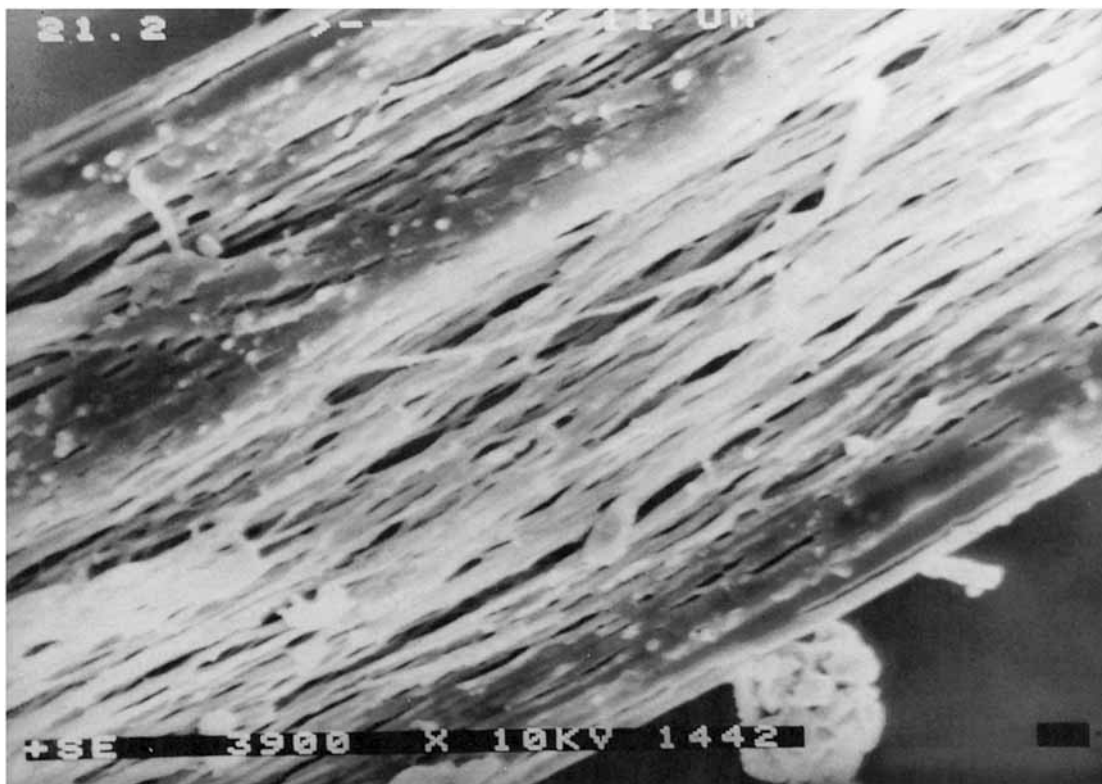


Figure 4 SEM micrograph of fiber 3.2 longitudinal cross-section.

centrations, the fiber diameters cannot be fully compared to each other. These values are only orientative. The (η) of PLLA in all mixture-solvents is lower than that in chloroform, i.e., there is always

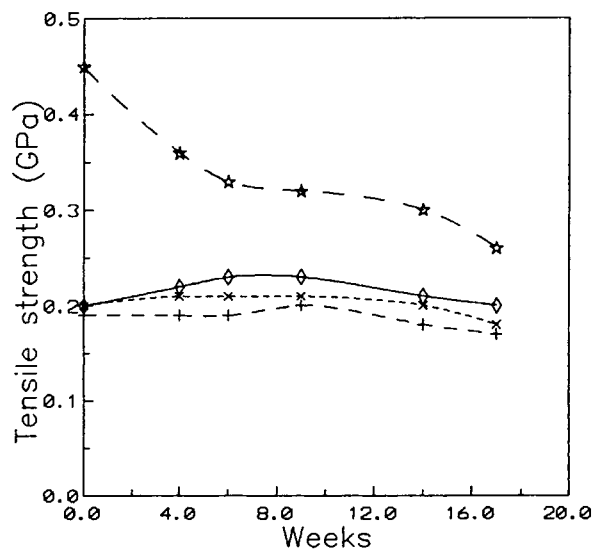


Figure 5 *In vitro* degradation of selected fiber 3: (◇) 3.1; (☆) 3.3; (+) 3.7; (×) 3.9.

a lower level of the polymer/solvent interaction, and, therefore, all mixture systems incline to phase separation when they are spun. Lower tensile strength of fibers from mix-solvents show the same tendency. However, the kinetic of phase separation, i.e., the resulting pore volume and skin density, does not depend on thermodynamic parameters only. The governing parameter seems to be the volatility gradient between solvent (chloroform) and nonsolvent. Therefore, the fibers 2 and 3.4 appear to have the lowest tensile strength, although (η) of system 3 is the nearest to that of system 1. Thus, fiber 2 (Figs. 6 and 7) appears to have similar sponge-skin structure as that of fiber 3.

In contrast, the structure of as-spun fiber 4 (from the thermodynamically worst solution) is similar and microscopically indistinguishable from the structure of fiber 1, as a consequence of the very near boiling points of chloroform and methanol.

This structure is seemingly very compact, but it becomes fibrillar after drawing. Surfaces of these fibers are cracked because of the presence of residual monomer in the polymer matrix, but not in the fiber pores (Fig. 8).

In the case of fiber 5, (η) of the polymer is higher than that for fiber 4, and the boiling point gradient

Table III Fiber Properties

Fiber No.	5	1	4	2	3.4
(η) (dL/g) ^a	3.67	5.19	2.48	3.98	4.87
Boiling point of nonsolvent (°C) ^b	56.3		64.5	78.4	81.4
Drawing T (°C)	90	90	90	90	90
ν_1 (cm/min) ^c	8.3	8.3	8.3	8.3	7.9
Lambda-max	5.3	4.7	5.4	5.2	5.6
Diameter (μm)	66	59	68	73	58
Tensile strength (GPa)	0.32	0.41	0.28	0.16	0.19
Elongation (%)	37	26	16	17	16

^a (η) of as-polymerized PLLA in the solvent mixture.

^b Boiling point of chloroform is 61.1°C.

^c ν_1 Entrance speed in the drawing tube.

is even negative. Therefore, the tensile strength of fiber 5 is higher than the strength of fiber 4, although both structures are very similar.

In vitro degradation of the all prepared fibers is shown in Figure 9. The fiber degradation profiles correspond very nearly to their microstructures. Fibers 2 and 3 lose their tenacity very slowly because of the compact skin presence. Fiber 1 degrades

faster, and this rate is in accord with that stated earlier.¹ The fiber 4 curve copies the character of fiber 1 degradation. This was expected according to the fibers' similar morphology. However, fiber 5 loses its strength completely within 18 wk of *in vitro* degradation, i.e., it degrades faster than fibers formed from pure chloroform with low molecular weight additive.

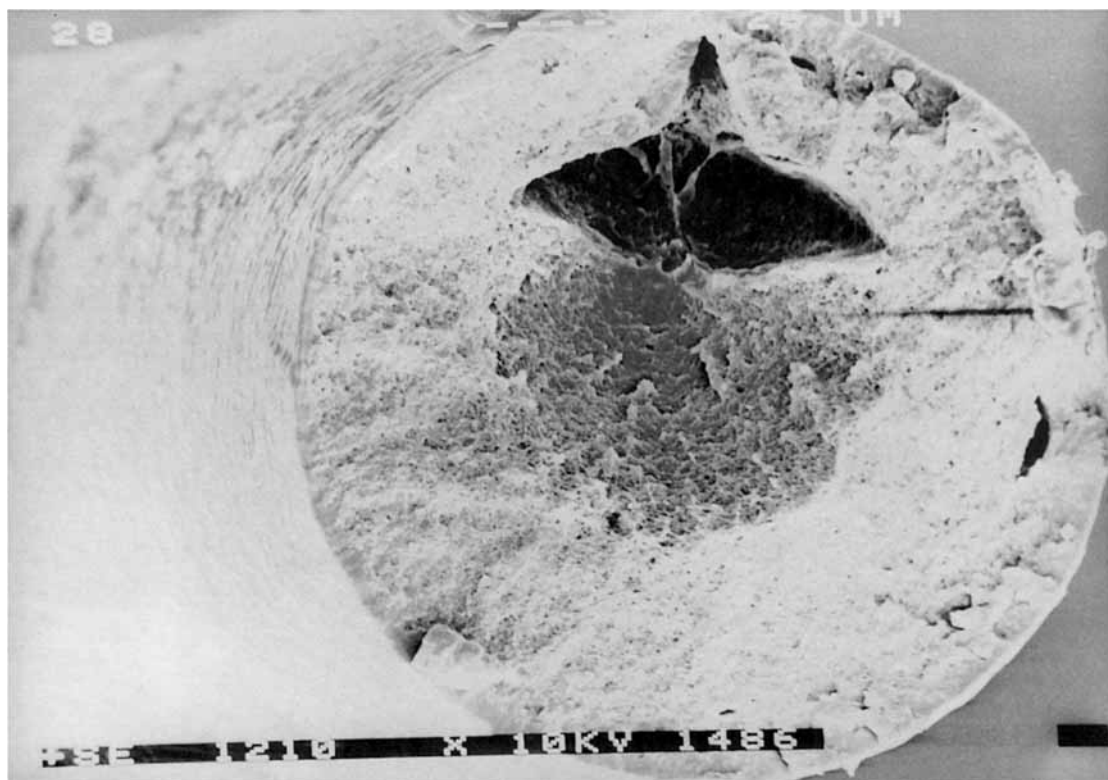


Figure 6 SEM micrograph of as-spun fiber 2.

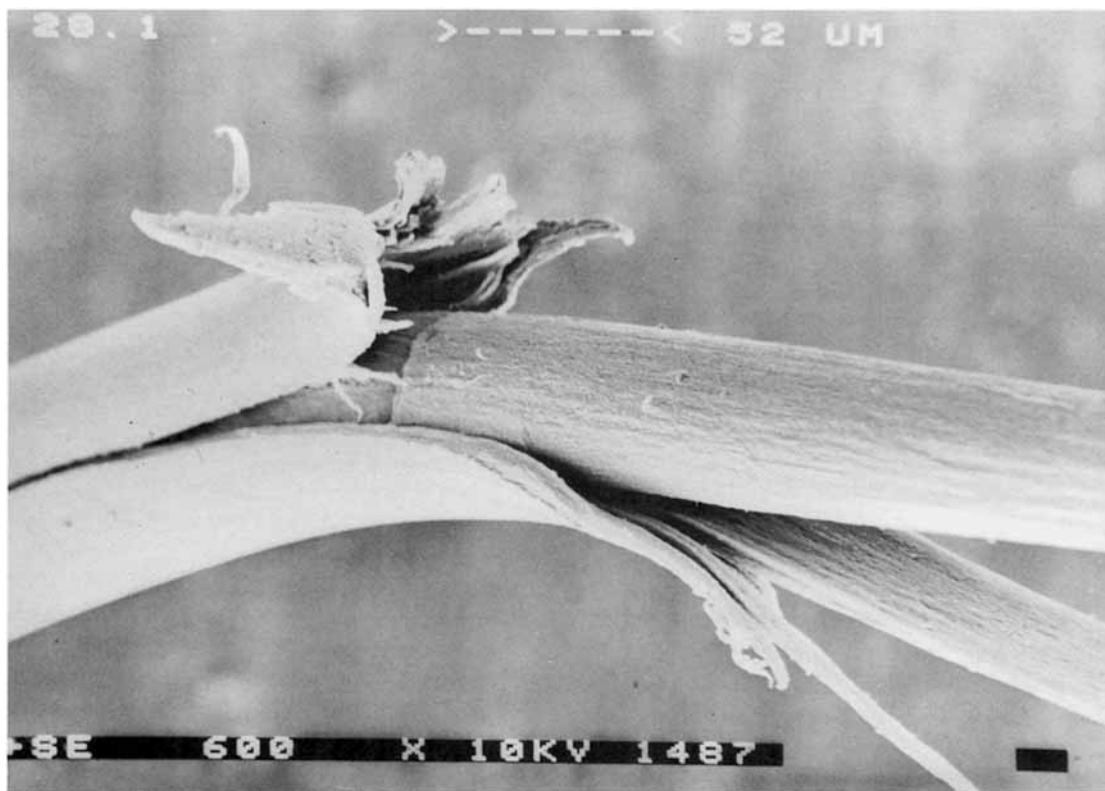


Figure 7 SEM micrograph of drawn fiber 2.

CONCLUSIONS

A structure, mechanical properties, and *in vitro* degradability of PLLA fibers prepared by dry spinning process from mixtures of chloroform/nonsolvent in the presence of residual monomer are affected by

the dissolution power of the mixture, mainly by the volatility gradient between nonsolvent and chloroform. Therefore, the higher boiling nonsolvents (i.e., ethanol and cyclohexane) cause similar fiber properties, although the spinning solutions are thermodynamically different. These fibers were char-

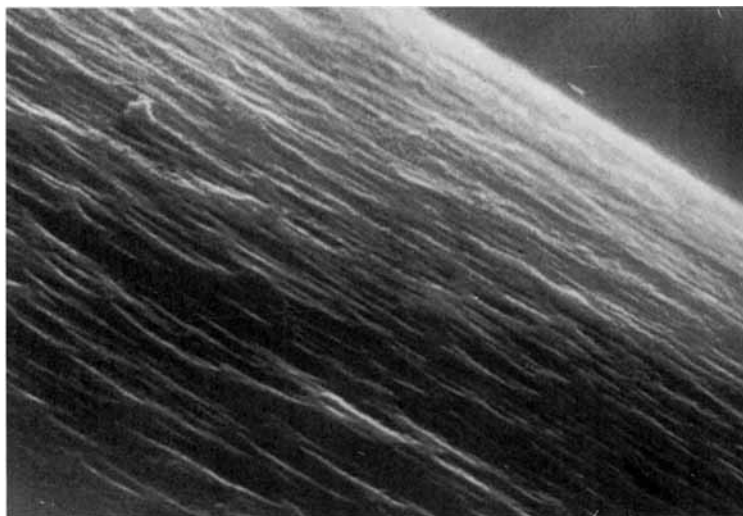


Figure 8 SEM micrograph of drawn fiber 1 (1,250 \times magnification).

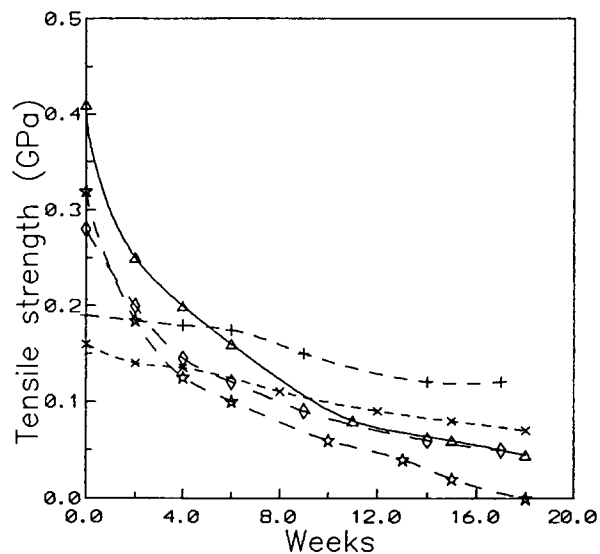


Figure 9 *In vitro* degradation of prepared fibers: (Δ) 1; (\times) 2; (+) 3.4; (\diamond) 4; (\star) 5.

acterized by a pore skin structure and low degradability. A low volatility gradient (methanol) results in a fiber similar to that from pure chloroform, but with lower tensile strength. At the negative boiling point difference of nonsolvent (acetone) and chloroform, it is possible to track down a combined influence of phase separation and residual monomer. This fiber appears to have an increase *in vitro* degradability in comparison to that of those from pure chloroform with a low molecular additive.

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