

# Poly lactide. III. Fiber Preparation by Spinning in Precipitant Vapor

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## SYNOPSIS

The mechanical properties and morphologies of poly(L-lactide) (PLLA) fibers, prepared by spinning in different vapor precipitants and hot drawing afterward, were studied in relation to fiber *in vitro* degradability. Petrolether, methanol, and ethanol were employed as precipitants. PLLA was used as-polymerized, i.e., with 10% of residual L-lactide. The tensile strength, structure, and degradability of obtained fibers were mainly governed by the nonsolvent concentration in the vapor phase. Using methanol as the precipitant for the fiber preparation, total tensile strength loss was achieved during 12 wk of *in vitro* degradation. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

PLLA was recognized as a potential biodegradable material for medical use in the early 1960s. For the last 30 years, the studies were for different biomedical applications, mainly for the surgical suture. So far, the main restriction for a practical use, i.e., the very low degradation rate, has not been satisfactorily solved yet.

In two previous parts of this study,<sup>1,2</sup> the degradability was studied in relation to morphology of fibers prepared by continuous and discontinuous processes using a mixture-solvent and a polymer with a residual monomer. The degradability increased along with the decrease of the phase separation rate. When this rate was too high, the compact skin fibers were formed. The skin presence prevented a degradation medium to utilize the inner porous surface for the reaction.

For the homogeneously porous fiber formation, it is necessary to achieve a very flat concentration gradient of a nonsolvent across the all-fiber diameter. This can be secured only when the diffusion resistance is out of the fiber. A vapor phase may

represent a diffusion resistance, as in the case of a reverse osmosis membrane formation.<sup>3</sup> Thus, the forming fiber is saturated by a nonsolvent in vapor phase. Because the nonsolvent concentration is very low, the skin formation is suppressed and the structure development is longer. It will be shown that this process may lead to a substantially enhanced *in vitro* degradation of the resulting fibers.

## EXPERIMENTAL

### Sample

The polymer was prepared as it was reported earlier.<sup>1</sup>

### Spinning-Hot Drawing Process

The two grams of as-polymer were dissolved in 15 mL of chloroform 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 × 26 mm) with an extrusion speed of 21.1 cm · min<sup>-1</sup>. The filament was led up through 2.5 × 10 cm glass tube and was collected on a steel drum 60 cm far away from the orifice. To the bottom of the tube, vapor of a precipitant was brought by a gentle stream of argon (30

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**Table I** Characterization of Fibers

Fiber No.	Vapor Phase	$T$ (°C)	$\nu_1/\nu_0$	Lambda-max	$d$ ( $\mu\text{m}$ )	$\sigma$ (GPa)	$\epsilon$ (%)
1	PeE	25	0.63	4.8	56	0.13	15
2	MeOH	25	1.03	4.8	46	0.27	35
3	EtOH	25	0.91	4.9	44	0.39	30

$\nu_0$ : extrusion speed.

$\nu_1$ : collection speed.

mL/min) from a tank, which was kept at 25°C. All the fibers were hot drawn to lambda-max after 48 h in a 1 × 30 cm drawing tube at 90°C with an entrance speed of 8.3 cm/min.

*In vitro* degradation and characterization of the fibers were the same as in Part 1.<sup>1</sup>

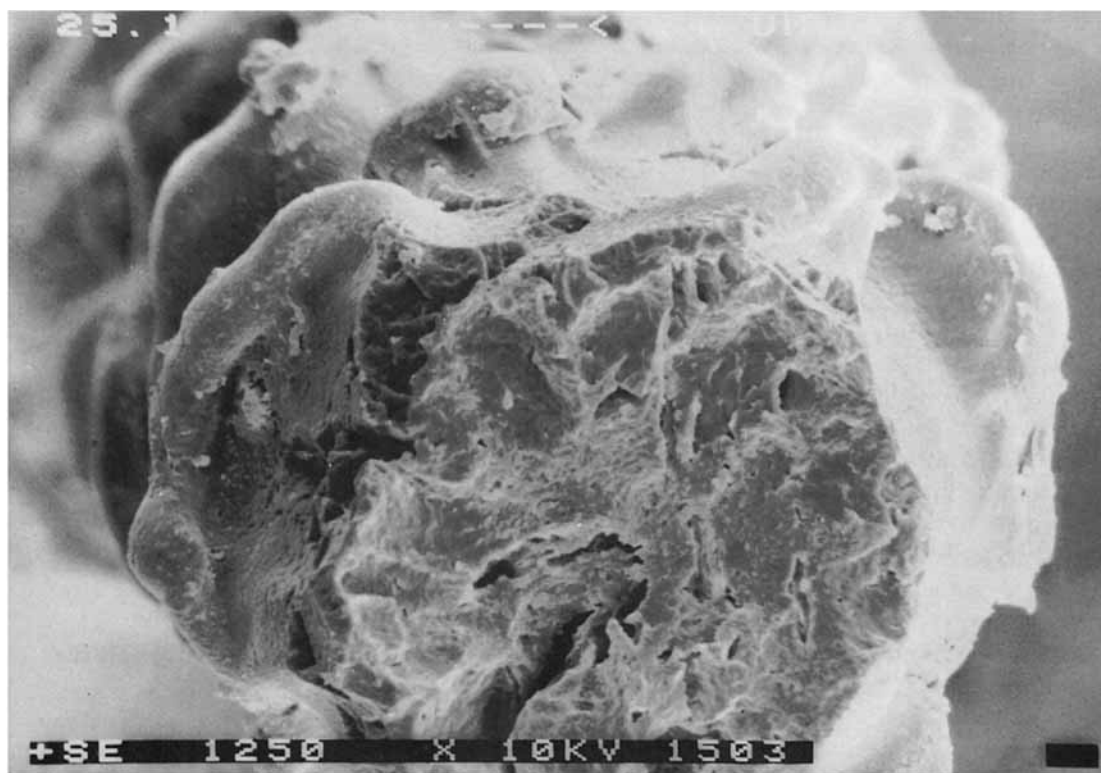
## RESULTS AND DISCUSSION

Because of the increasing tensile strength and the decreasing fiber diameter, it can be concluded that

the nonsolvent/fiber interaction declines from top to bottom in Table I.

This is in accord with the decreasing vapor concentration from petrolether to ethanol according to their boiling points. While petrolether acts like a liquid precipitant thanks to its high vapor concentration, ethanol seems to affect the fiber formation with difficulty, because the tensile strength of this fiber corresponds to that of the fiber from pure chloroform by the dry spinning.<sup>2</sup>

In Figure 1, the structure of as-spun fiber 1 is characterized by a non-regular skin and a porous inner part. It is obvious that phase separation was



**Figure 1** SEM micrograph of as-spun fiber 1.

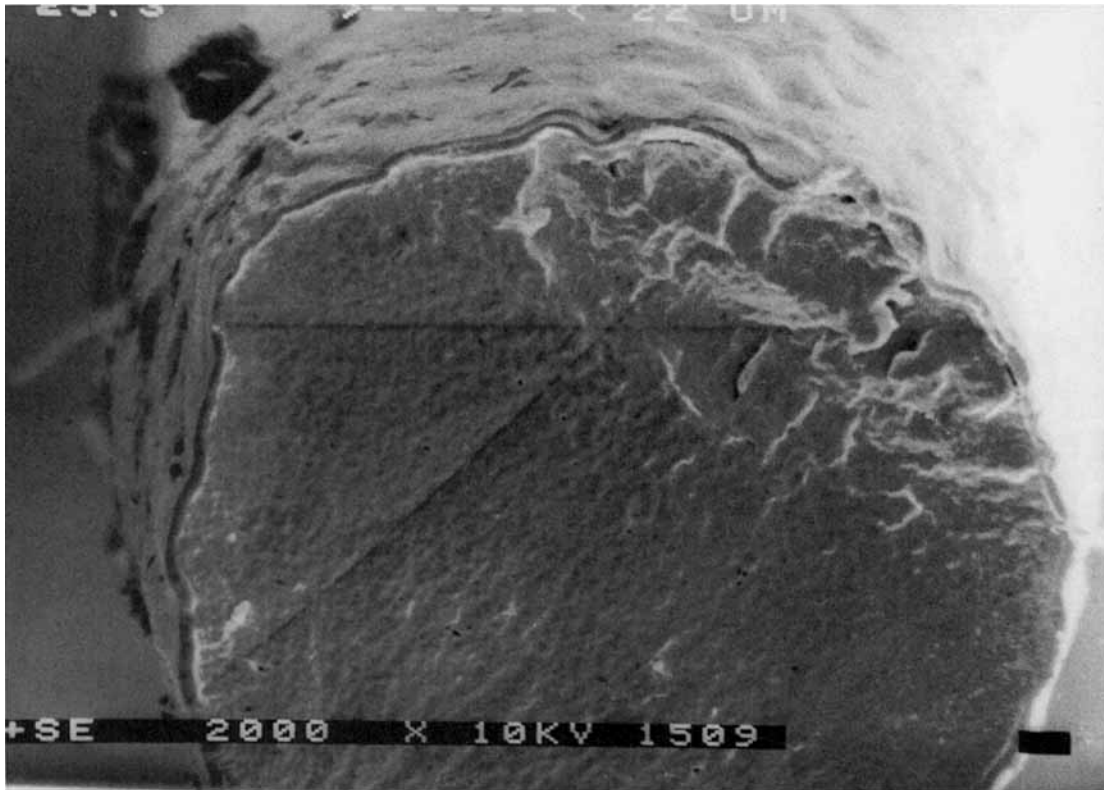


Figure 2 SEM micrograph of as-spun fiber 3.

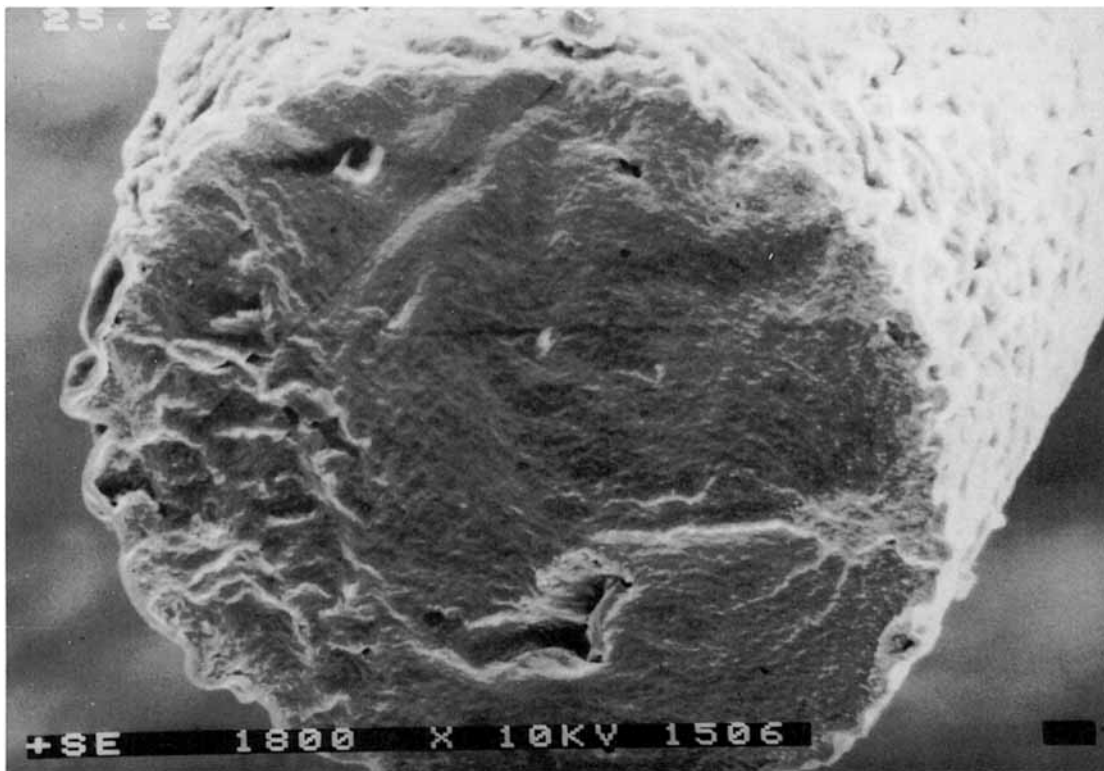


Figure 3 SEM micrograph of as-spun fiber 2.

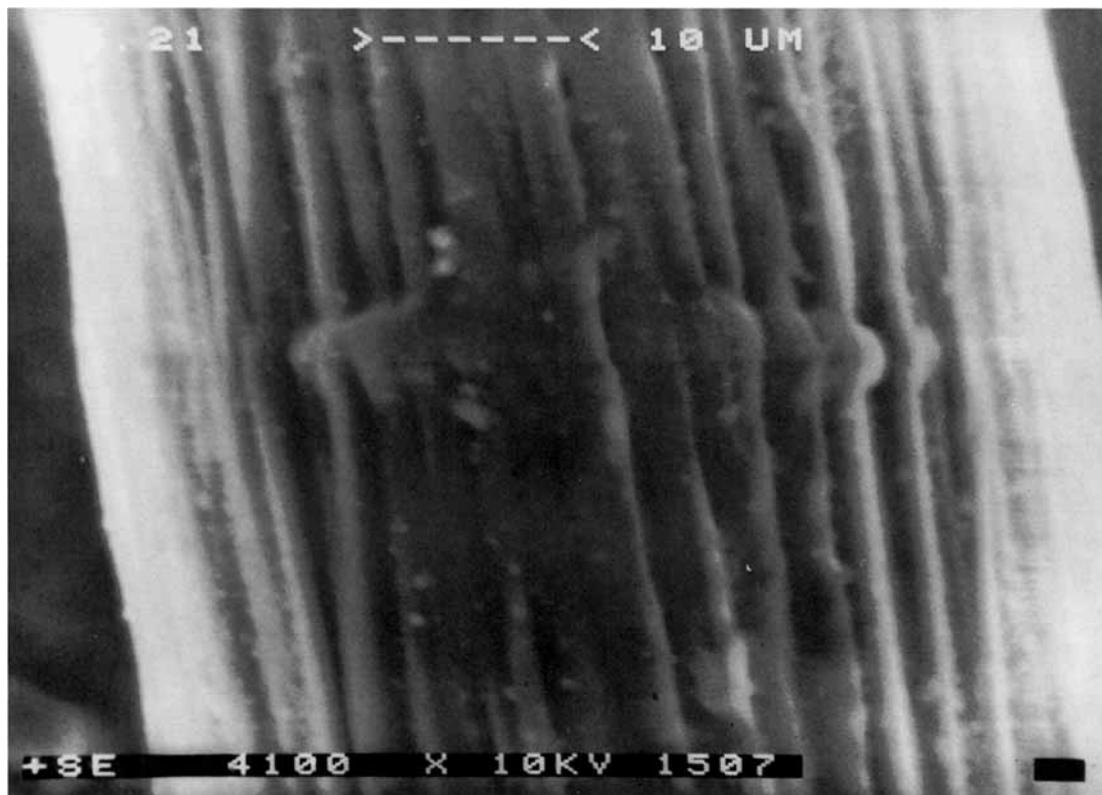


Figure 4 SEM micrograph of final fiber 2.

too fast and after the skin formation, the syneresis of the core causes the fiber deformation and an introduction of weak spots. These deformations can-

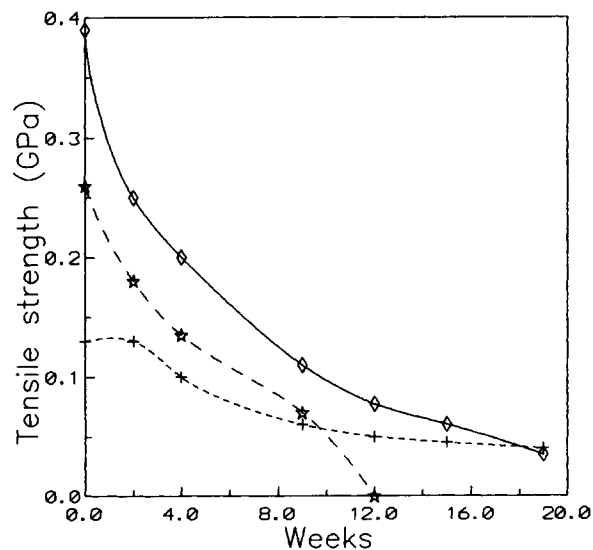


Figure 5 *In vitro* degradation: fiber 3 (◇); fiber 2 (☆); fiber 1 (+).

not be removed by drawing, and therefore the tensile strength is so low. The degradation rate can also be expected to be very low.

Figure 2 reveals the next similarity between fiber 3 and the fiber formed from pure chloroform by the dry spinning process. The amount of ethanol absorbed during the fiber passing through the vapor zone is probably too low to introduce phase separation, and it is almost evaporated in the dry zone before the fiber solidification.

The structure of fiber 2 (Fig. 3) lies in the center. The as-spun fiber does not have an apparent skin, the surface is perforated, and the fiber shape is regular. It suggests that some phase separation takes place during the spinning. After drawing (Fig. 4), the fiber appears to have a pseudofibrillar surface, and it is reasonable to presume a higher water penetration in the fiber by the degradation.

*In vitro* degradation test confirms the above stated expectations (Fig. 5). While fiber 1 loses its strength very slowly, fiber 3 degrades analogically to that fiber from pure chloroform by the dry spinning process. However, fiber 2 lost its tensile strength during 12 wk. Therefore, it is possible to

presume that the fiber structure in Figure 4 approaches the effective structure, which allows the more successful contact between the fiber and the degradation medium. There is a reason to believe that the fiber degradability results from both the residual monomer presence and the method of preparation, as when the purified polymer was primarily employed, the fiber failed to degrade at all.

*In vitro* degradability of fiber 2 is fully comparable with commonly used PDS (Ethicon, Inc.) of similar starting properties.

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