

# High-Strength Poly(L-Lactide) Fibers by a Dry-Spinning / Hot-Drawing Process. II. Influence of the Extrusion Speed and Winding Speed on the Dry-Spinning Process

A. R. POSTEMA,\* A. H. LUITEN, H. OOSTRA, and A. J. PENNINGS, *Department of Polymer Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands*

## Synopsis

This paper is concerned with the influences of the extrusion speed and the winding speed during dry spinning of 4 wt % solutions of poly(L-lactide) (PLLA) in mixtures of chloroform and toluene, on the ultimate fiber tenacities after hot drawing. It was found that high-strength PLLA fibers (1.5 GPa) can be produced at high spinning rates ( $> 180$  m/min) if rupturing of the entanglement network and oriented crystallization during spinning is suppressed. This could be accomplished by avoiding spinline stretching and applying low elongational deformation rates in the spinneret during spinning.

## INTRODUCTION

From studies on the gel spinning of ultra high molecular weight polyethylene,<sup>1-3</sup> it was shown that the extrusion rate and the winding speed may have a significant effect on the ultimate fiber properties. Adsorption of the extremely long molecules of polyethylene on the wall of the die and/or stretching of the spinline resulted in a severe rupturing of the entanglement network and had a lowering effect on fiber tenacity after hot drawing. Applying high spinning temperatures (above 200°C) suppressed the adsorption and prevented the introduction of flaws such as chain scission and tight knots. It was possible to spin filaments at speeds up to 1500 m/min without fracture of the spinline.

The aim of the present study is to investigate whether PLLA fibers can be prepared at higher spinning rates. In order to distinguish between effects originating from spinning conditions or hot-drawing conditions, the hot-drawing conditions were kept constant during this study. It will be shown that the shape of the spinneret and the size of the die exit have an enormous effect on the ultimate fiber properties. PLLA fibers can be spun at a rate of 180 m/min without loss of the tensile properties, provided that the right spinning conditions are applied.

\*Present address: Materials Department and Department of Chemical and Nuclear Engineering, University of California, Santa Barbara, CA 93106.

## EXPERIMENTAL

The preparation of the poly(L-lactide) and the spinning solutions used in this study have been published elsewhere.<sup>4</sup> The characterization of the fibers is described in Part I (this journal) of this study.

In a piston-cylinder apparatus the 4% (m/v) PLLA solution was conditioned at 70°C for 3 h. The solutions were extruded at 60°C through a stainless-steel, conical die (see Results and Discussion) and collected (at 20–22°C) on sand-blasted glass bobbins. The distance between die and bobbin was 6.5 cm. The extrusion rate could be varied. The as-spun fibers were dried on the bobbins at room temperature until constant weight was reached (usually about 40 h). There was no toluene left, which could act as a plasticizer during hot drawing.<sup>5</sup>

Wide-angle X-ray scattering (WAXS) experiments were carried out with a Statton Camera using  $\text{CuK}_\alpha$  radiation (0.154 nm) produced by a Philips X-ray generator connected to a closed cooling circuit and operated at 25 kV and 45 mA.

## RESULTS AND DISCUSSION

In previous studies,<sup>6–14</sup> the strength of polymeric fibers was found to be affected by the concentration of surface flaws and consequently by the surface area of the fibers. Thinner filaments usually yield higher values of the breaking strength. The thickness of the fibers will be determined by, for instance, the orifice diameter of the spinneret. For this reason the first experiments concerning the influence of winding speed and/or extrusion speed on the ultimate properties of PLLA fibers were performed by applying a spinneret with an exit diameter of 0.25 mm (Fig. 1). The entrance angle of this die was 43°.

At first we tried to increase the production rate by extruding at a constant extrusion speed of 30 m/min and varying the winding speed. In Figure 2 the

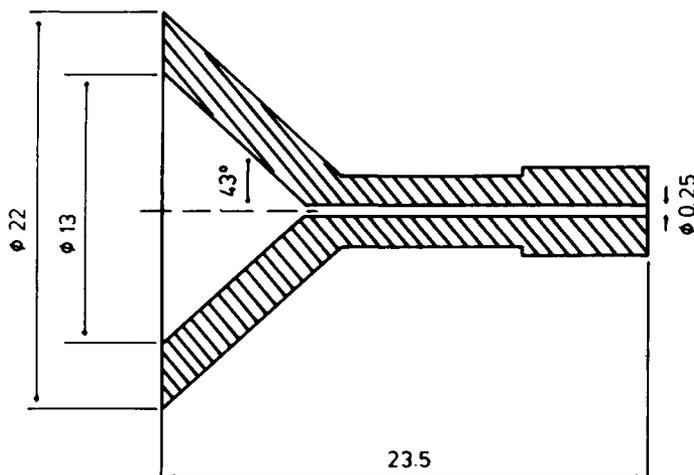


Fig. 1. A schematic representation of the conical die (length 23.5 mm; exit diameter 0.25 mm; entrance angle 43°).

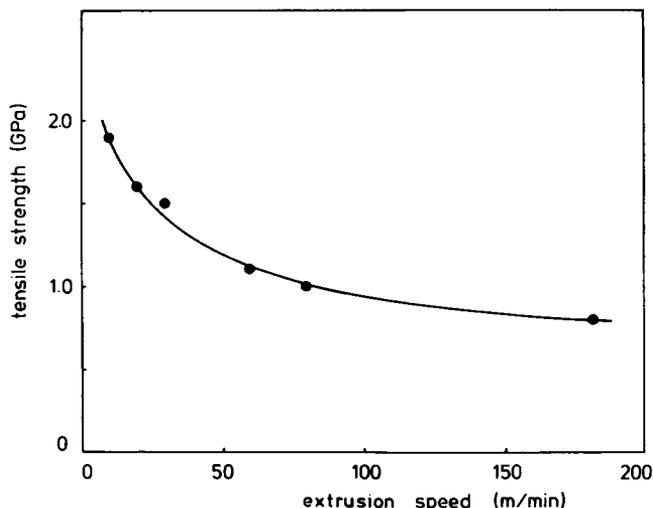


Fig. 2. Ultimate tensile strength of PLLA fibers as a function of the winding speed during spinning of 4 wt % solutions of PLLA in chloroform/toluene (40/60). The filaments were extruded at 30 m/min (die: see Figure 1).

ultimate tensile strength of the PLLA filaments is presented as a function of the winding speed. The tensile strength decreased from 1.9 GPa at a winding speed of 10 m/min to 0.8 GPa at a winding speed of 182 m/min. At higher winding speeds the spinline broke. DSC measurements on the as-spun fibers indicated a reduction of the heat of fusion for higher winding speeds (Table I). This reduction of the heat of fusion may be correlated to the number of entanglements and the amount of topological constraints.<sup>14-16</sup> Due to larger amounts of topological constraints it is not possible to acquire a high tensile strength after hot drawing. This is affirmed by a reduction in the maximum draw ratio of the as-spun fiber at higher winding speeds (Table I). Fibers produced at a winding speed of 10 m/min could be hot-drawn to a maximum draw ratio of 16, whereas fibers produced at a winding speed of 182 m/min could only be hot-drawn to a draw ratio of 9. The origin of the topological constraints, which are most likely the reason for the decrease in tensile strength, may be associated with the adsorption of the polymer chains on the wall of the die. The network is stretched on one end while the other end is anchored by the adsorbed layer on the wall of the die.<sup>2,8</sup> This may give rise to

TABLE I  
Heats of Fusion and Maximum Draw Ratios of As-Spun PLLA Fibers<sup>a</sup>

$V_{\text{wind}}$ (m/min)	$\Delta H$ (J/g)	$\lambda_{\text{max}}$ (hot draw)
10	45.0	16
20	40.1	13
30	36.1	13
60	34.4	10
80	27.2	9
182	21.8	9

<sup>a</sup> Extrusion speed: 30 m/min; die: see Figure 1.

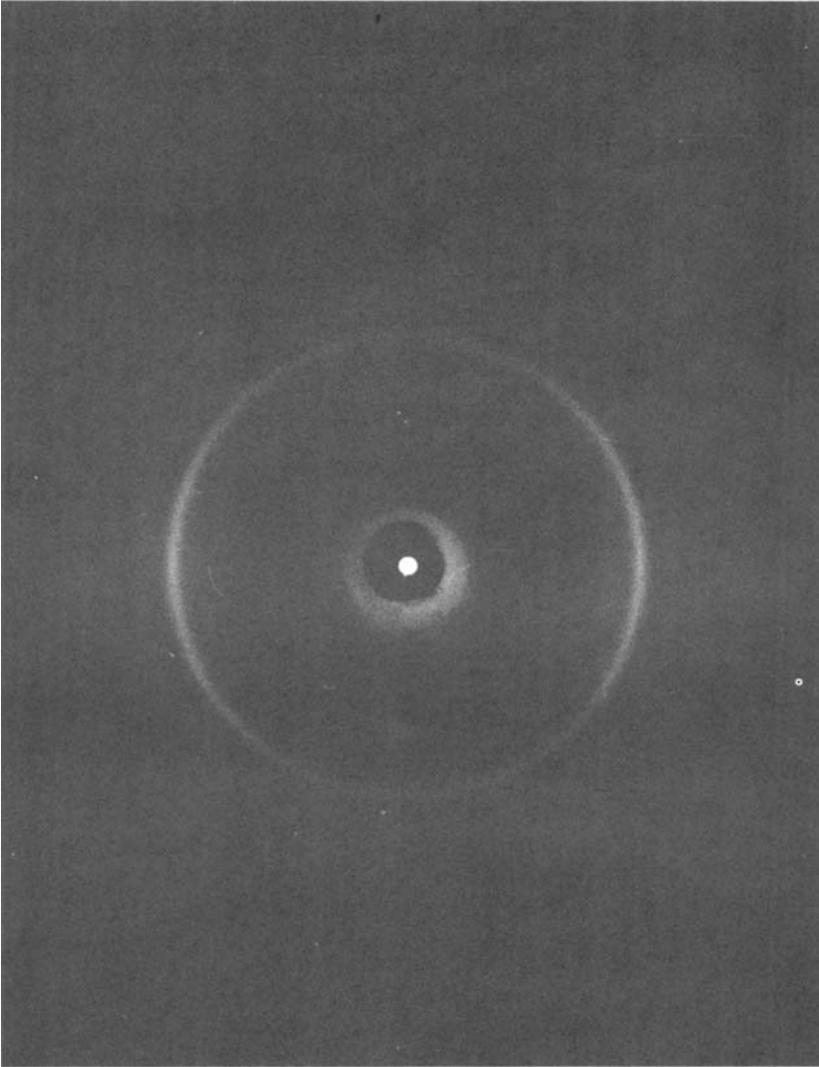


Fig. 3. WAXS pattern of a PLLA filament, extruded at 30 m/min and wound at 182 m/min (die: see Figure 1).

stress-induced defects<sup>3</sup> and leads to heterogeneous network structures. Figure 3 shows a WAXS pattern of a PLLA fiber, extruded at 30 m/min and wound at 182 m/min. Enhanced intensities on the equator clearly illustrate improved orientation<sup>11-14</sup> of the PLLA molecules in the direction of the axis of the as-spun fiber. Figure 4 presents a scanning electron micrograph of a PLLA fiber, extruded at 30 m/min and wound at 80 m/min, showing shish-kebab-like structures. These structures arise if the winding speed is larger than the extrusion rate, and causes poor fiber properties after hot drawing.<sup>3</sup>

Another way of increasing the production rate of the PLLA fibers is to increase the extrusion rate. As is shown in Figure 2, at a constant extrusion speed the highest strengths were achieved by winding at a much smaller speed than the extrusion speed. A difficulty of this approach is the swinging of the

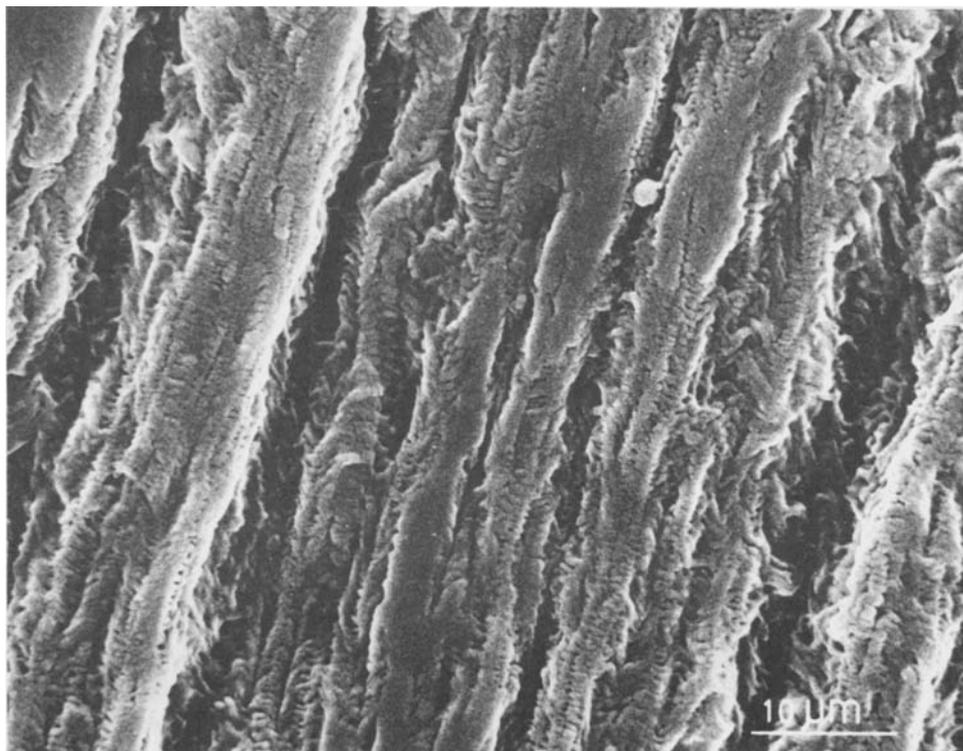


Fig. 4. SEM micrograph of a PLLA filament, extruded at 30 m/min and wound at 80 m/min (die: see Figure 1).

spinline at high extrusion rates which resulted in a complicated winding of the filaments. This could be avoided by taking the winding speed equal to the spinning speed. Figure 5 displays the ultimate tensile strength of PLLA fibers at various extrusion speeds. Increasing the extrusion speed resulted in a decreasing value of the fiber strength. The heats of fusion of the various filaments differed slightly, ranging between 36 and 42 J/g. The maximum draw ratio (Table II) during hot drawing reduced from 15 for a fiber spun at 3 m/min to 8 for a fiber spun at 200 m/min. Increasing the extrusion rate will induce a higher degree of orientation of the chains in the die,<sup>18-21</sup> leading to a greater degree of swelling of the extrudate when leaving the spinneret. This is shown in Figure 6, which presents the extrudate swell, defined as the measured weight of the fiber per unit length divided by the weight of the fiber per unit length as calculated from the spinneret dimensions and polymer concentration without extrudate swell, as a function of the extrusion speed (without winding). Above extrusion speeds of 150 m/min the extrudate swell had a value of around 6.0, indicating that by applying winding speeds equally to spinning speeds a “flow-induced” draw ratio of 6 is applied.

In the aforementioned described methods, it was recognized that in both cases of producing fibers at higher rates, the overall draw ratio increases at higher production rates. The overall draw ratio is defined as  $\lambda_{\text{ext}} \times \lambda_{\text{hd}}$ , in which  $\lambda_{\text{ext}}$  is the spinline draw ratio (winding speed divided by extrusion speed or the flow-induced draw ratio) and  $\lambda_{\text{hd}}$  is the maximum draw ratio

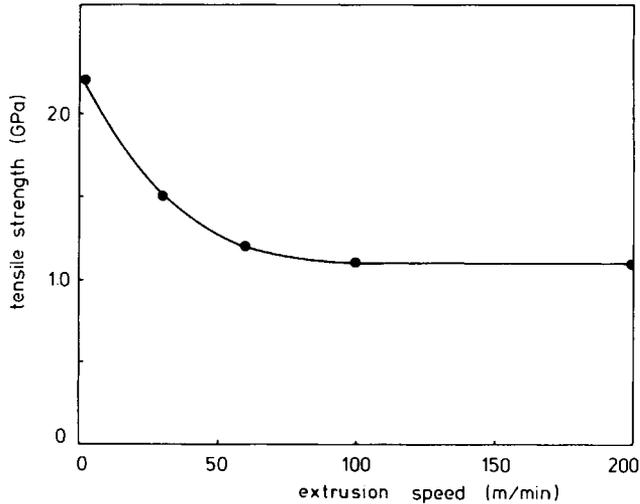


Fig. 5. Ultimate tensile strength of PLLA fibers versus extrusion speed during spinning of 4 wt % solutions of PLLA in chloroform/toluene (40/60). The applied winding speed was equal to the spinning speed (die: see Figure 1).

during hot drawing. This phenomenon was also observed by high-speed gel spinning of polyethylene.<sup>8</sup> In that case overall draw ratios were found in the range 1000–1500, which is much higher than the ratio of fully extended chain length to the radius of gyration of the random coil molecules. From this observation and from studies on the fiber morphology,<sup>15</sup> it could be concluded that, already at low flow rates, the molecular network splits up into long bundlelike flow units, each consisting of bundles of elongated chain parts connected via entanglements to large clusters of unoriented molecules. For this reason  $\lambda_{\text{ext}}$  is not a unique characteristic of the macromolecules in solution. The draw ratio of each macromolecule itself, will, of course, be much lower. At larger flow rates the original long flow units in the spinning solution are destroyed, due to the occurrence of elastic flow instabilities (elastic turbulence) in the solution.

High deformation rates, induced by high spinning speeds as well as high winding speeds, may induce chain scissioning,<sup>22–24</sup> which undoubtedly can give rise to a reduction of the tensile strength attainable after hot drawing.<sup>25–27</sup> This happens not to be the case during the PLLA spinning process. Table III shows the molecular weights of the PLLA in the as-spun

TABLE II  
Heats of Fusion and Maximum Draw Ratios of As-Spun PLLA Fibers<sup>a</sup>

$V_{\text{ext}}$ (m/min)	$\Delta H$ (J/g)	$\lambda_{\text{max}}$ (hot draw.)
3	36.6	15
30	36.1	13
60	40.2	9
100	42.5	9
200	38.5	8

<sup>a</sup> Winding speed = extrusion speed; die: see Figure 1.

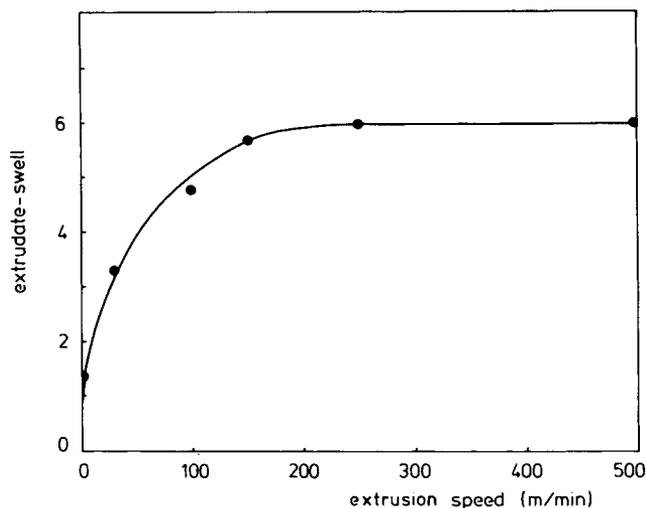


Fig. 6. Extrudate-swell of PPLA filaments, spun from 4 wt % solutions of PLLA in chloroform/toluene (40/60) as a function of the extrusion speed (die: see Figure 1).

fiber as obtained from viscosity measurements.<sup>4</sup> It is shown that the molecular weight is more or less independent of the extrusion rate. The only reduction in the molar mass was found during the preparation of the spinning solutions. By dissolving the PLLA in chloroform for 1 week the molecular weight decreased from  $9.1 \times 10^5$  to  $7.0 \times 10^5$  g/mol. After adding the toluene, the molecular weight remained constant. This decline in molecular weight could be suppressed by drying the chloroform on  $P_2O_5$  and preparing the solutions under dried nitrogen. Then the molecular weight only decreased to  $7.9 \times 10^5$  g/mol. This reduction can most likely be ascribed to traces of ethanol in the chloroform. The invariability of the molecular weight during extrusion implies that the splitting of the molecular network into long bundle-like flow units<sup>8</sup> has to go by disentangling rather than by chain scissioning.

The main reason for inferior fiber properties is most likely the breakup of the molecular network in the extrusion process. As a consequence of the converging flow lines in the die and the attachment of the long polymer molecules to the die wall by adsorption, the entanglement network will be effectively elongated.<sup>2,3</sup> At high deformation rates in the die, a rapid length increase of the molecular network may occur locally, which will not be compensated by a corresponding area decrement in the surrounding regions.

TABLE III  
Molecular Weight of PLLA in the As-Spun Fibers<sup>a</sup>

$V_{\text{ext}}$ (m/min)	$M_v$ (g/mol)
3	$6.5 \times 10^5$
30	$6.7 \times 10^5$
100	$7.0 \times 10^5$
200	$7.0 \times 10^5$

<sup>a</sup> Extrusion speed = winding speed; die: see Figure 1.

This may lead to flow instabilities (i.e., elastic turbulence)<sup>28,29</sup> from which voiding and cavitation occur, disrupting the entanglement structure completely and giving rise to anisotropic structures. As a result the coherence of the entanglement network in the as-spun fiber is lost and inferior fiber properties are found after hot drawing. This process may be intensified by phase separation, followed by partial crystallization (see Part I and Refs. 3, 30–34), induced by the effective orientation of the molecules, or parts of the molecules,<sup>35,36</sup> in the flow field. Quenching of these partly oriented solutions gives rise to partially fibrillar crystallization in the direction of the fiber axis. This is confirmed by WAXS measurements showing equatorial diffraction. Because of the increased melting temperature of these constrained fibrillar crystallites,<sup>37</sup> the alignment of the PLLA chains during hot drawing of the compositelike as-spun fiber is enormously disturbed and will yield inferior fiber properties.

Another possible explanation for the destruction of the molecular network may be that the shearing of the molecular network over the sharp edges inside the orifice (see Fig. 1), combined with the acceleration of the solution at that specific place, might rupture the solution structure.

The flow disturbances can be suppressed in various ways. Adding lubricants, like aluminium stearate, to polyethylene solutions made it possible to collect gel filaments with takeup speeds up to 100 m/min having strengths of 3.0 GPa.<sup>8</sup> Increasing the extrusion temperature of polyethylene solutions<sup>2,3,38</sup> from 170 to 250°C resulted in a remarkable enhancement in stretchability of the spinline, as caused by a reduced tendency of the polymer molecules to be adsorbed on the wall of the die, yielding fibers of 3.5 GPa at winding speeds of 1000 m/min. Analogue improvements could not be applied to the dry-spinning process of PLLA. Added lubricants may reduce fiber strength (due to the incorporation into the crystal lattice) if not extracted from the as-spun fibers, whereas applying higher spinning temperatures is not possible, because of the low boiling temperature of the chloroform in the spinning solutions.

Another way of suppressing flow instabilities is changing the shape of the die. Both enlargement of the orifice diameter and reduction of the entrance angle will result in a smaller velocity gradient (deformation rate) in the orifice and thus may reduce partial crystallization and rupturing of the molecular network, due to phase separation. Orientation by a flow field can be obtained if the alignment of the polymer chains prevails over the relaxation of the deformed molecule. This is the case if  $\dot{\epsilon} \cdot \tau < 1$ ,<sup>39</sup>  $\dot{\epsilon}$  being the elongational deformation rate and  $\tau$  the relaxation time of the molecule. Moreover, the exposure time  $t$  of the molecules to the orientational action of the flow field should be long enough to achieve orientation. This is the case if  $\dot{\epsilon} \cdot t \gg 1$ . For this reason we replaced the spinneret in the previous experiments by a pseudohyperbolic die<sup>40</sup> (see Fig. 7) having an entrance angle of 3° and an exit diameter of 1.0 mm and carried out the experiments again with variable extrusion rates. Figure 8 presents the ultimate tensile strengths of PLLA fibers as a function of extrusion speed. A maximum extrusion rate of 180 m/min was the experimental restriction of our spinning apparatus. The applied winding speeds were equal to the spinning speeds. After hot drawing to a maximum draw ratio of 19, the tenacities of all the fibers appeared to be

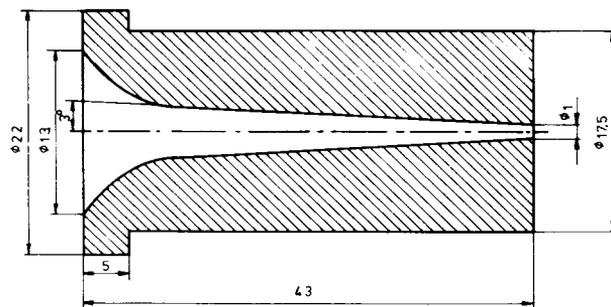


Fig. 7. A schematic representation of the pseudohyperbolic die (length 43.0 mm; exit diameter 1.00 mm; entrance angle  $3^\circ$ ).

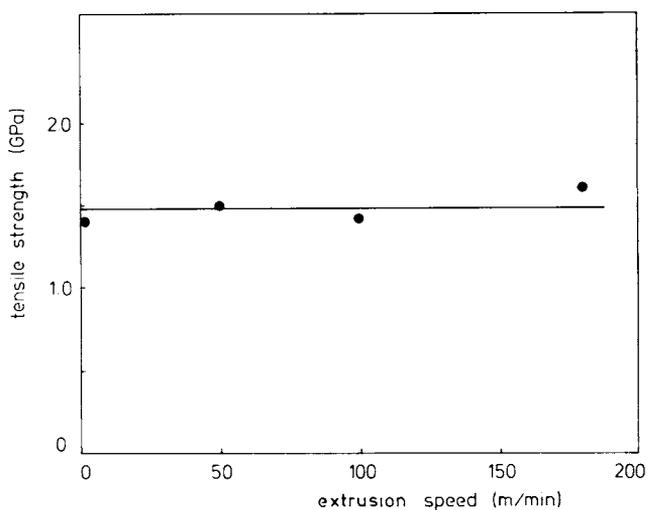


Fig. 8. Ultimate tensile strength of PLLA fibers versus extrusion speed during spinning of 4 wt % solutions of PLLA in chloroform/toluene (40/60). The applied winding speed was equal to the extrusion speed (die: see Figure 7)

TABLE IV  
Heats of Fusion and Draw Ratios of As-Spun PLLA Fibers<sup>a</sup>

$V_{\text{ext}}$ (m/min)	$\Delta H$ (J/g)	$\lambda_{\text{max}}$ (hot draw)
1	46.1	19
50	48.0	17
100	49.0	19
180	51.9	20

<sup>a</sup> Winding speed = extrusion speed; die: see Figure 7.

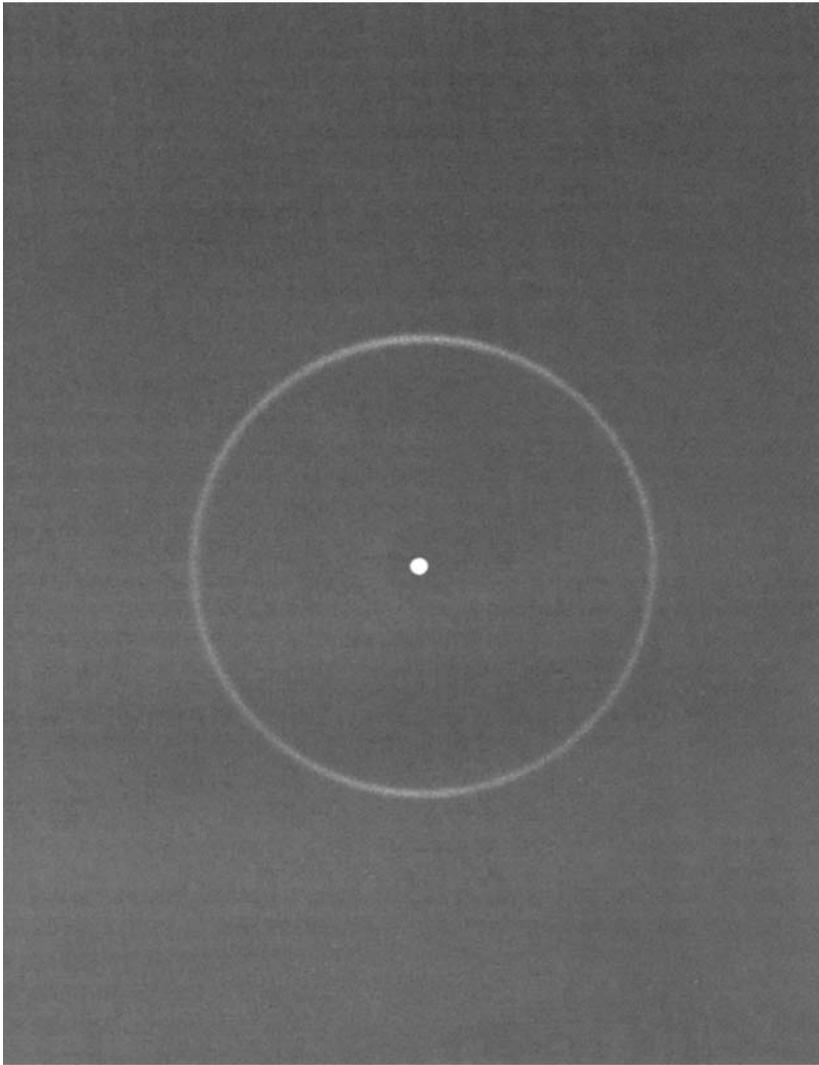


Fig. 9. WAXS pattern of a PLLA fiber extruded and wound at 180 m/min (die: see Figure 7).

about 1.5 GPa. There were some remarkable differences with the previous experiments (Table IV). The ultimately attainable draw ratio was much greater ( $\lambda = 19$ ) by applying the pseudohyperbolic spinneret with a large orifice diameter (1.0 mm), than ( $\lambda = 13$ ) by applying the conical spinneret with a small orifice diameter (0.25 mm). Additionally the heat of fusion of the as-spun filaments increased going to higher extrusion rates. Figure 9 presents a WAXS pattern of a PLLA fiber extruded and wound at 180 m/min, showing no preferential orientation of the PLLA chains.

At low extrusion rates, fibers spun through the pseudohyperbolic spinneret with a large orifice diameter and subsequently hot drawn had a tensile strength of 1.4 GPa ( $d = 41 \mu\text{m}$ ), whereas fibers spun through the conical spinneret with a small exit diameter were 2.2 GPa ( $d = 12 \mu\text{m}$ ) after hot

TABLE V  
Heats of Fusion, Draw Ratios, and Ultimate Tensile Strengths of PLLA Fibers Spun from Various Solvent Compositions<sup>a</sup>

Toluene (%)	$\lambda_{\max}$	$\Delta H$ (J/g)	$\sigma$ (GPa)
20	10	30.6	0.9
50	17	44.3	1.2
60	19	48.0	1.4
70	17	52.8	1.0

<sup>a</sup> Extrusion speed = winding speed = 100 m/min; die: see Figure 7.

drawing. This again demonstrates that the fiber diameter has a marked effect on the tensile strength.<sup>6-10</sup>

In a previous investigation it was found that the solvent composition during dry spinning of PLLA had a profound effect on the ultimate fiber properties.<sup>5</sup> Fibers spun from solutions of PLLA in mixtures of chloroform and toluene (40/60) had tensile strengths of 2.3 GPa after hot drawing.<sup>7</sup> These high tenacities could only be achieved at this specific solvent composition. At the other solvent compositions, flow-induced phase separation resulted in inferior fiber properties after drawing (see Part I). At higher production rates this solvent composition still appeared to be favorable. Table V displays the ultimate tensile strength which can be attained after spinning at 100 m/min

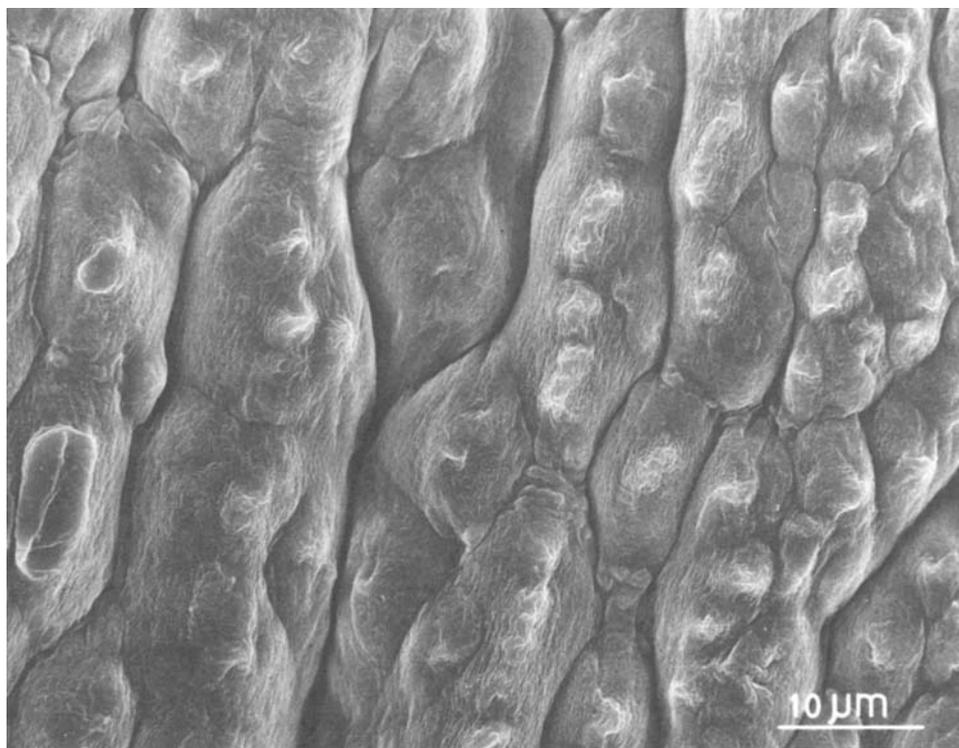


Fig. 10. SEM micrograph of a PLLA fiber, spun from a 4 wt % PLLA solution in a mixture of chloroform/toluene (50/50), at a speed of 100 m/min.

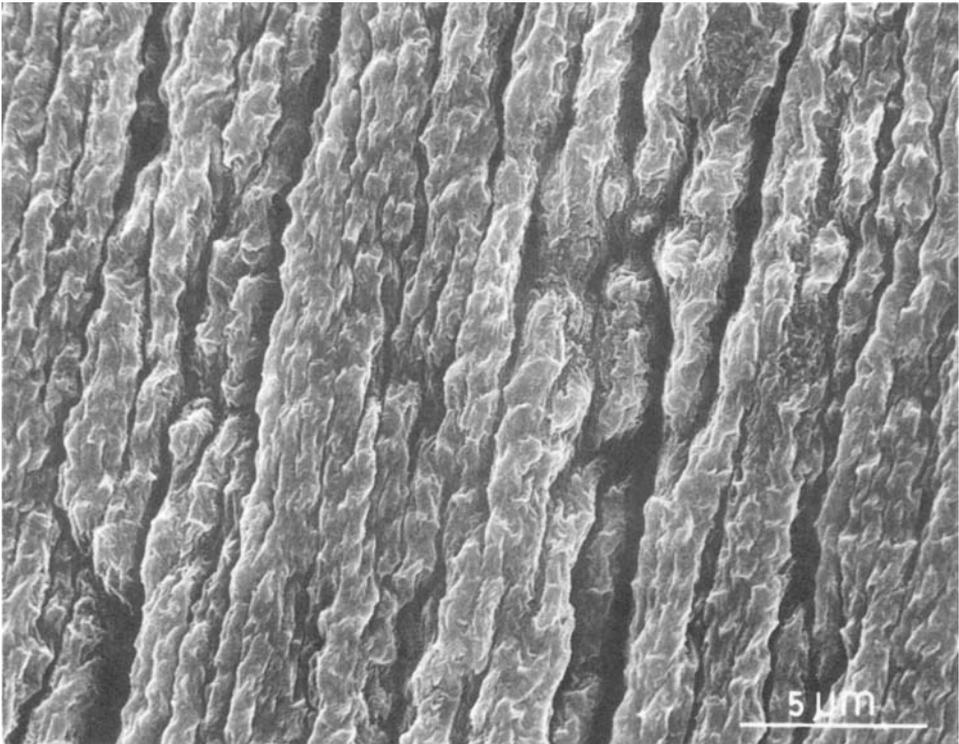


Fig. 11. SEM micrograph of a PLLA fiber, spun from a 4 wt % PLLA solution in a mixture of chloroform/toluene (40/60), at a speed of 100 m/min.

from PLLA solutions with different solvent composition. It shows that the strongest fibers were produced from PLLA solutions in mixtures of chloroform and toluene in a ratio of 40:60. This is also reflected in the ultimately attainable draw ratio. A maximal draw ratio of 19 was achieved at the 40/60 mixtures. Decreasing the solvent quality by adding a poor solvent (toluene) reduces the number of entanglements and thus must increase the heat of fusion of the as-spun filaments.

Small variations in solvent composition had a great effect on the morphology of the as-spun fibers. Figure 10 shows a scanning electron micrograph of a PLLA fiber spun from a chloroform/toluene (50/50) mixture. The fiber was extruded and collected at rates of 100 m/min. The fiber has a lumplike structure. Figure 11 is a scanning electron micrograph of a PLLA fiber extruded from a chloroform/toluene (40/60) mixture. This fiber was also spun and collected at 100 m/min. These changes in fiber morphology, induced by variation of solvent composition, can most likely be ascribed to the rate of phase separation (see Part I and Refs. 31–34), leading to heterogeneous fiber textures, which results in a reduced fiber coherence.

## CONCLUSIONS

From this study on the influence of the extrusion speed and winding speed during dry spinning of PLLA solutions, as reflected in the tensile strengths,

the following conclusions may be drawn:

PLLA fibers, having high tensile strengths (1.5 GPa), can be produced at high extrusion rates (> 180 m/min) by avoiding rupturing of the molecular entanglement network, due to phase separation and oriented crystallization.

By applying a pseudohyperbolic die, this destruction of the molecular network and phase separation can be suppressed substantially.

Independent of the production rate, maximal fiber strengths have been found by spinning PLLA fibers from solutions of PLLA in mixtures of chloroform/toluene (40/60).

The authors wish to acknowledge the AKZO, The Netherlands, for financial support. The assistance of W. Hoogsteen (WAXS) and H. Nijland (SEM) is gratefully acknowledged.

### References

1. J. Smook and A. J. Pennings, *J. Mater. Sci.*, **19**, 31 (1984).
2. A. J. Pennings, R. J. van der Hooft, A. R. Postema, W. Hoogsteen, and G. ten Brinke, *Polym. Bull.*, **16**, 167 (1986).
3. W. Hoogsteen, R. J. van der Hooft, A. R. Postema, G. ten Brinke, and A. J. Pennings, *J. Mater. Sci.*, to appear.
4. A. R. Postema and A. J. Pennings *J. Appl. Polym. Sci.*, to appear.
5. J. W. Leenslag and A. J. Pennings, *Polymer*, **18**, 1695 (1987).
6. J. W. Leenslag, S. Gogolewski, and A. J. Pennings, *J. Appl. Polym. Sci.*, **29**, 2829 (1984).
7. W. F. Christopher and D. W. Fox, *Polycarbonates*, Reinhold, New York, 1962, p. 159.
8. J. Smook, W. Hamersma, and A. J. Pennings, *J. Mater. Sci.*, **19**, 31 (1984).
9. L. R. McCreight, H. W. Rauch, and W. H. Sutton, *Ceramic and Graphite Fibres and Whiskers*, Academic, New York, 1965, Chap. IV.
10. H. v. d. Werff and A. J. Pennings, *Polym. Bull.* (1988), to appear.
11. S. Chen and J. E. Spruiell, *J. Appl. Polym. Sci.*, **33**, 1427 (1987).
12. J. E. Spruiell and J. L. White, *Polym. Eng. Sci.*, **15**, 660 (1975).
13. K. Katayama, T. Amano, and N. Nakamura, *Kolloid Z. Z. Polym.*, **226**, 125 (1968).
14. A. J. Pennings, *Makromol. Chem. Suppl.*, **2**, 99 (1979).
15. J. de Boer and A. J. Pennings, *Polymer*, **23**, 1944 (1982).
16. P. Smith, H. D. Chanzy, and B. P. Rotzinger, *Polym. Commun.*, **26**, 258 (1985).
17. H. M. Heuvel and R. Huisman, *High Speed Fiber Spinning*, A. Ziabicki and H. Kawai, eds., Wiley, New York, 1985, Chap. 11.
18. J. A. Brydson, *Flow Properties of Polymer Melts*, Butterworth, London, 1970, Chap. 5.
19. A. Ziabicki and H. Kawai, *High Speed Fiber Spinning*, Wiley, New York, 1985.
20. A. J. McHugh and J. M. Schultz, *Kolloid Z. Z. Polym.*, **251**, 193 (1973).
21. F. C. Frank, A. Keller, and M. R. Mackley, *Polymer*, **12**, 467 (1975).
22. J. A. Odell, A. Keller, and M. J. Miles, *Polym. Commun.*, **24**, 7 (1983).
23. J. A. Odell and A. Keller, *J. Polym. Sci. Polym. Phys. Ed.*, **24**, 1889 (1986).
24. A. F. Horn and E. W. Merrill, *Polym. Commun.*, **28**, 172 (1987).
25. Y. Termonia, P. Meakin, and P. Smith, *Macromolecules*, **18**, 2246 (1985).
26. A. J. Pennings, J. Smook, J. de Boer, S. Gogolewski, and P. F. v. Hutten, *Pure Appl. Chem.*, **55**, 777 (1983).
27. P. J. Flory, *J. Am. Chem. Soc.*, **67**, 2048 (1945).
28. C. D. Han, *Rheology in Polymer Processing*, Academic, New York, 1976.
29. J. H. Southern and R. L. Ballmann, *Text. Res. J.*, **53**, 230 (1983).
30. W. Hoogsteen, G. ten Brinke, and A. J. Pennings, *Polymer*, **28**, 923 (1987).
31. A. Silberberg and W. Kuhn, *J. Polym. Sci.*, **XIII**, 21 (1954).
32. B. A. Wolf, *Macromol. Chem. Rapid Commun.*, **1**, 231 (1980).
33. B. A. Wolf and H. Kramer, *J. Polym. Sci. Polym. Lett. Ed.*, **18**, 789 (1980).
34. H. Kramer and B. A. Wolf, *Macromol. Chem. Rapid Commun.*, **6**, 21 (1985).
35. D. G. Peiffer, M. W. Kim, and R. D. Lundberg, *Polymer*, **27**, 493 (1986).
36. G. Marrucci, *Polym. Eng. Sci.*, **15**, 229 (1975).

37. J. Smook and A. J. Pennings, *Coll. Polym. Sci.*, **262**, 712 (1984).
38. A. J. Pennings, *Proc. Fiber Prod. Conf., Greenville*, 1 (1986).
39. M. R. Mackley and G. S. Sapsford, *Developments in Oriented Polymers*, I. M. Ward, Ed. Applied Science, London, 1982, p. 201.
40. D. W. Ihm and J. A. Cuculo, *J. Polym. Sci. Polym. Phys. Ed.*, **25**, 619 (1987).

Received March 22, 1989

Accepted March 28, 1989