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Biodegradable fibres

Part I *Poly-L-lactic acid fibres produced by solution spinning*

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Fibres of about 620 000 viscometric molecular weight, M_V, were obtained by a spinning/drawing process using a poly-L-lactic acid/chloroform solution. Mechanical properties of fibres increased with draw ratio (DR) up to tensile modulus and strength of 10 GPa and 1.1 GPa, respectively. Moreover, draw ratio appeared to affect fibre structure and morphology, producing different amounts and types of crystallinity (characterized by two close but well distinct melting peaks, as revealed by DSC) or causing different failure modes in the stressed-up-to-break fibres. As demonstrated by scanning electron microscopy, a microfibrilar structure is developed for draw ratios higher than about 8.

1. Introduction

Polyglycolic acid fibres found the first industrial application as biodegradable polymers in 1967 [1]. Since then, many other polymers have been applied in the biomedical field, and polylactic acid represents one of the most important ones, being clinically used in orthopaedic surgery [2–5], in cardiovascular systems [6–8], and in drug delivery implants [9, 10]. In the last decade several researchers have focused their attention on poly-L-lactic acid (PLLA) fibres [11–17], in view of various possible applications as resorbable sutures [18], reinforcement for composites [19], and material for intravascular stents [20].

Previously we studied the effect of thermal treatments on the dynamic mechanical properties and crystallinity of different PLLAs [21, 22] and its *in vitro* degradation [23]. Aiming producing PLLA fibres suitable for the construction of different types of orthopaedic prostheses, our research moved to the processing and characterization of PLLA fibres, produced both by solution and melt spinning, starting from the interesting but not exhaustive information already reported in the literature [24]. In this first communication, production and characterization of high-strength solution spun PLLA fibres are reported.

2. Experimental procedures

2.1. Materials

A PLLA polymer, in the form of flakes, having viscometric molecular weight of 660 000, was purchased from PURAC (Gorinchem, The Netherlands), and dried in vacuum at 50 °C for 2 days before use. Differential scanning calorimetry (DSC) thermal analysis of the polymer showed a melting temperature of 184.9 °C and crystallinity content of 66.7%. Baker analysed chloroform was used as solvent.

2.2. Characterization

2.2.1. Molecular weight analysis

Viscometric molecular weight determinations were made by using diluted chloroform/polymer solutions and a Ubbelohde viscometer (type 0) at 25.0 °C. The viscometric molecular weight, M_V, was calculated from the intrinsic viscosity, $[\eta]$, by using the following equation [25]:

$$[\eta] = 5.45 \times 10^{-4} M_V^{0.73}$$

2.2.2. Thermal analysis

Differential scanning calorimetry (DSC) was performed using a Mettler DSC 30 calorimeter, covering 0 °C to 230 °C at 10 °C/min, on fibres (about 15 mg) wounded around a cylindrical metal wire and inserted in the aluminium pan of the calorimeter. The relative crystallinity content of the specimens was assessed by integrating the normalized area of the melting endotherm, determining the heat involved, and rating it to the reference 100% crystalline polymer (93.6 J/g) [26].

2.2.3. Mechanical properties

Mechanical properties of the fibres were measured at room temperature using an Instron tensile tester (model 4502) at a crosshead speed of 12 mm/min. Specimens with a gauge length of 25 mm were prepared using a thin paper test specimen mounting tab as recommended in standard ASTM D 3379. Fracture always occurred approximately in the centre of the fibre. All the reported tensile properties represent average values of at least five tests. Cross-sections were calculated from the fibre weight and length, measuring crystallinity content by DSC and assuming 1.248 and 1.290 g/cc for the amorphous and crystalline density, respectively.

2.2.4. Scanning electron microscopy

A Cambridge scanning electron microscope (SEM) model Stereoscan 200 was used to observe the surface

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topography and fracture surface of fibres. Fibres were examined using an accelerating voltage of 20 kV.

2.2.5. Draw ratio

Draw ratio, DR, was defined as $DR = S_{as}/S_d$, where S_{as} and S_d are cross-section of as-spun and drawn fibres, respectively.

3. Fibre production

PLLA fibre was produced using a two-stage process, dry spinning followed by hot drawing. Initially, solutions at different concentrations of PLLA in chloroform were used to define the best concentration for the first-stage extrusion process. The extruded (as spun) fibres were then drawn at conditions determined by the experimental optimization of the draw ratio/drawing temperature conditions.

3.1. Spinning

Dried polymer was dissolved in chloroform at different concentration (3–12 g/dl) by stirring the solution at room temperature for 1 week in a 50 ml sealed glass syringe. The syringe was then inserted in the thermostatic chamber of a solution spinning made-in-house apparatus. After 1 h of conditioning at 30 °C, fibres were finally extruded at room temperature through a needle (applied to the syringe) of length 15 mm and internal diameter 1 mm, at extrusion rates (length per unit of time of the fibre exiting from the die) varying in the range 1–200 cm/min. The as-spun fibres were collected on glass bobbins 65 mm away from the die, rotating at the same speed as the extrusion to avoid any stretching, and moving transversally to avoid fibre superposition.

3.2. Hot-drawing

As-spun fibres were stored at room temperature for different times, then drawn between two rollers positioned at the ends of a 1.6 m-long cylindrical hot-chamber flushed by dry nitrogen. Temperatures of 150–210 °C and an entrance fibre speed of 2.8 cm/min were used.

4. Results and discussion

Depending on the initial solution concentration (varying from 3 to 12 g/dl) different morphologies of the as-spun fibres were observed, similarly to the findings reported by Gogolewski and Pennings [27]. As summarized in Table I, the higher the concentration, the lower the maximum applicable extrusion rate and the larger the cross-section. Almost the same crystallinity content of about 15% was measured for all the fibres.

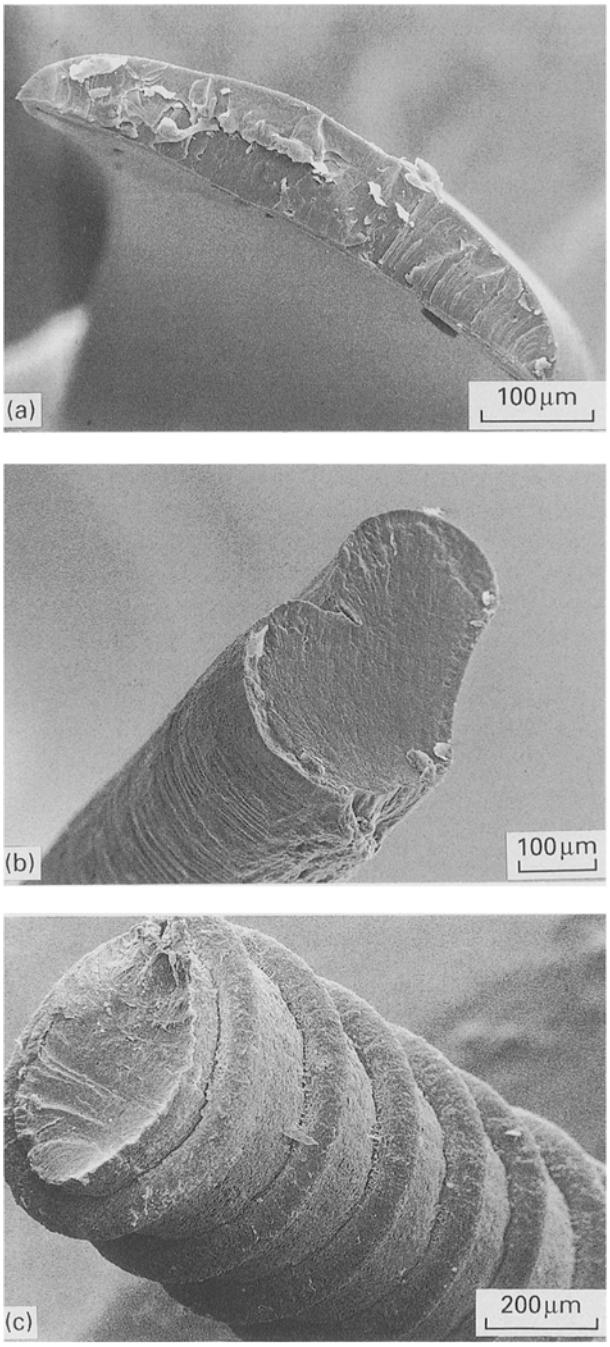

Figure 1 SEM micrographs of as-spun fibres obtained from solution of 5 g/dl (a), 7 g/dl (b) and 12 g/dl (c), and broken in liquid nitrogen.

TABLE I Morphology, cross-section and crystallinity of 620000 PLLA fibres extruded from solution in different conditions.

Concentration (g/dl)	Extrusion rate (cm/min)	Morphology	Cross section ($mm^2 \times 100$)	Crystallinity (%)
3	200	Substantial flatness and smooth surface	1.8	14.7
5	100	Flattened fibre and smooth surface	3.1	16.6
7	10	Bilobate section and rough surface	7	17.9
10	2.5	Bilobate section and structured surface	30	19.2
12	1	Circular section and helix shape	35	18.8

TABLE II Effect of drawing temperature on mechanical properties and crystallinity of fibres spun from 5 g/dl solution and drawn after 2 h at the maximum draw ratio

Temperature (°C)	Modulus (GPa)	Tensile Strength (GPa)	Melting temperature (°C)	Crystallinity (%)	Melting temperature (°C)	Crystallinity (%)
150	7.4	0.49	–	–	197.5	34.9
160	6.3	0.34	–	–	189.6	30.5
170	6.6	0.34	–	–	188.6	31.5
180	7.8	0.58	154.9	4.9	198.6	28.6
190	8.2	0.99	168.7	17.5	202.7	17.8
200	9.6	1.10	166.7	18.5	200.7	22.1
210	7.6	1.00	172.4	28.4	195.0	19.1

Due to the presence of solvent, fibre crystallinity was measured as described above, but subtracting the contribution of solvent evaporation to the endothermic peak and the solvent mass to the as-spun fibre weight. The heat of evaporation of chloroform from poly-lactic acid (205 J/g) was calculated from the endothermal peak and the mass loss of amorphous as-spun fibres of poly-D,L-lactic acid during a DSC scan in the range 70–140 °C. Fibre morphology changes (Fig. 1) as the PLLA solution concentration is varied. For instance, whereas extrusion from a 12 g/dl solution gave fibres having a helicoidal shape and rough surface, flattened more homogeneous fibres with a smooth surface and cross-section about ten times lower were spun from a 5 g/dl solution. In contrast, Gogolewski and Pennings [27] reported for the same 5 g/dl solution, a different cross-section morphology, having a "TV-cable" appearance, and presenting holes larger than 50 µm. Drawability of as-spun fibres was found also to be dependent on the amount of residual solvent (which acts as plasticizer) which, in the room temperature stored fibres, decreases very slowly with time. The residual chloroform contained in the fibre strongly affects drawability of fibres: 15 min after spinning at room temperature, fibres contained about 35% of solvent, this value dropping after two days to 20%. The result of a large number of experiments indicated that 2 h (when the as-spun 5 g/dl solution starting fibres possess a solvent amount equal to about 30%) was the most convenient after-spinning time to give reproducible drawing conditions.

The effect of the drawing temperature on the properties of fibres extruded from a 5 g/dl PLLA/chloroform solution and drawn at the maximum attainable draw ratio (DR_{max}) is shown in Fig. 2. After an initial decrease, drawability (maximum attainable draw ratio) of fibres increases with temperature, reaching a maximum at around 200 °C. Correspondingly, the tensile strength of fibres follows the maximum attainable draw ratio trend, going from a minimum of

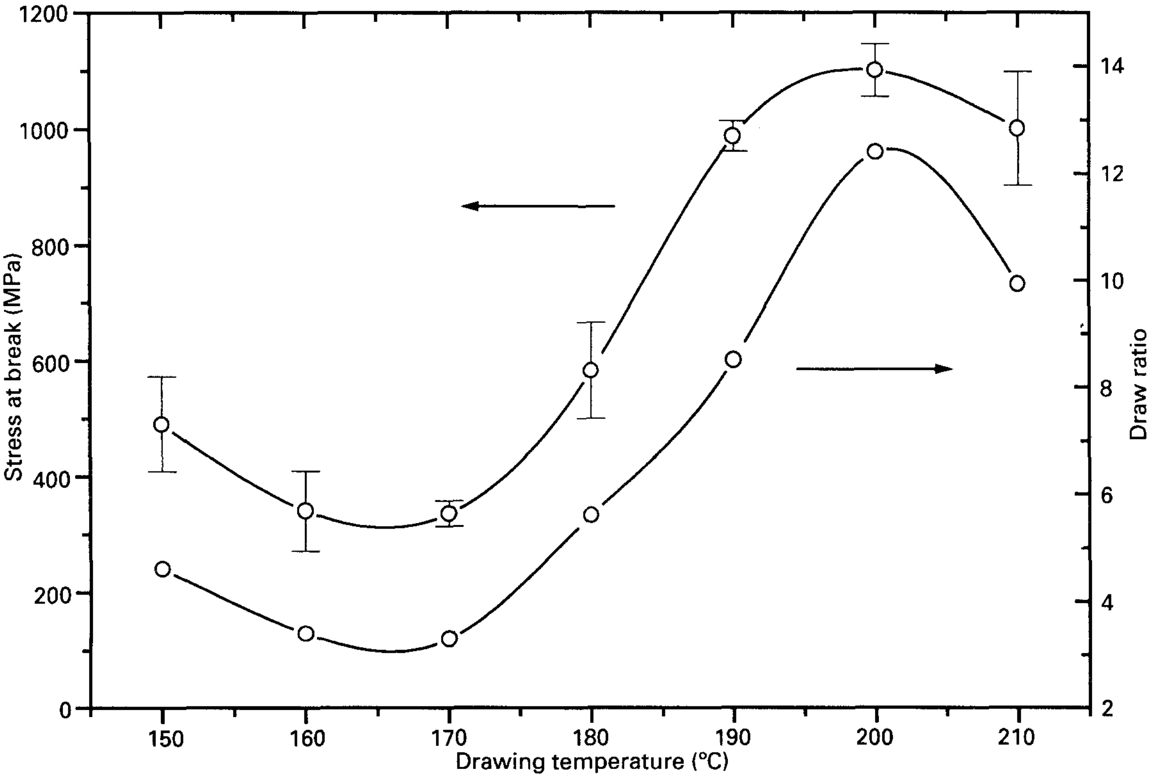

Figure 2 Stress at break and draw ratio of solution spun fibres as a function of drawing temperature.

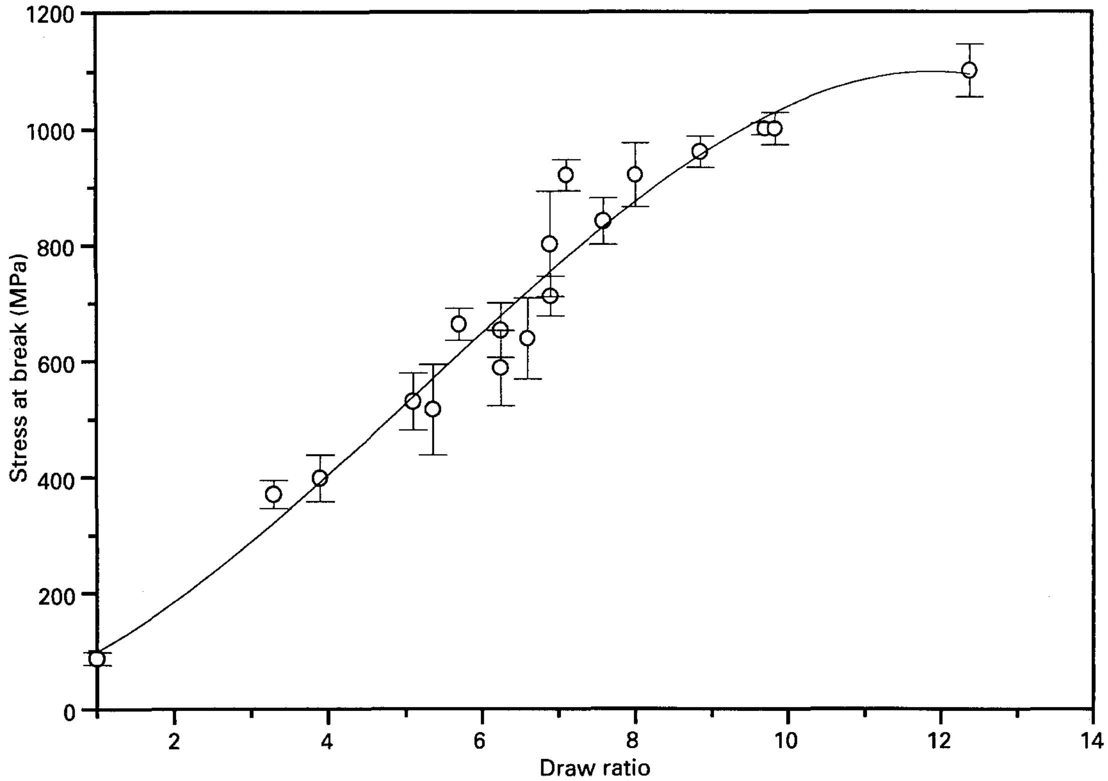

Figure 3 Effect of draw ratio on stress-at-break of solution spun fibres collected at a winding speed of 2 m/min and drawn at 200 °C.

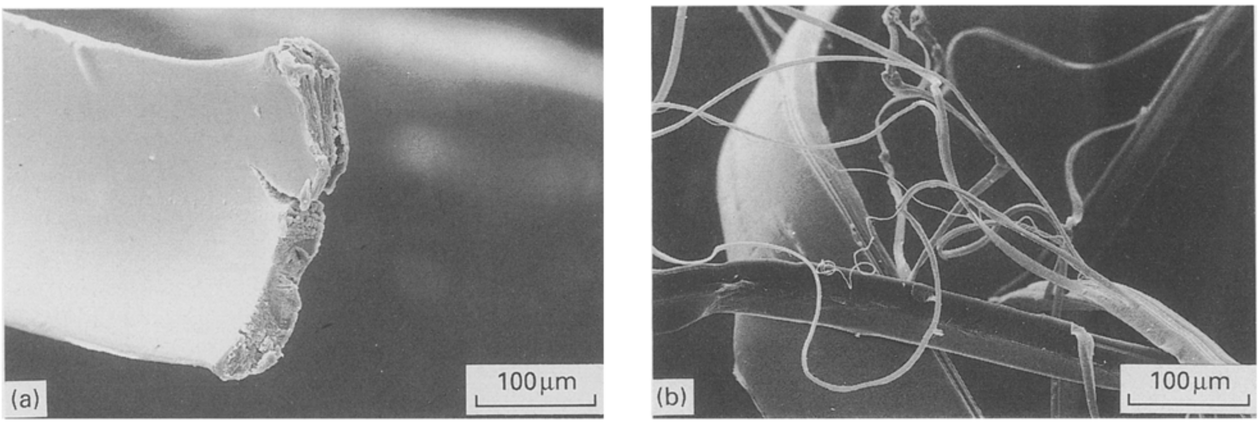

Figure 4. SEM micrographs of fracture surfaces of solution spun PLLA fibres drawn at 200 °C with a draw ratio of 6 (a) and 12.4 (b).

400 MPa to a maximum value of about 1.1 GPa, for fibres drawn at about 170 °C (DR_{max} = 4) and 200 °C (DR_{max} = 12.4), respectively. The tensile strength of fibres appeared strictly related to the size of a lower temperature melting crystalline peak, revealed by DSC. In fact, while the as-received polymer presents a unique well-defined melting peak [22], when drawn at temperatures higher than 180 °C (or, possibly, at DR higher than a not-yet-determined value) fibres present two distinct DSC melting peaks, related to two different crystalline phases, as reported in the literature [28] and confirmed in our case by preliminary X-ray diffractometry results.

Mechanical properties were found to be directly dependent on the DR, as reported in Fig 3 for the tensile strength of fibres drawn at different DR at 200 °C and reached an apparent plateau level for a DR of about 10. For draw ratios higher than about 8, fibres showed stress-at-break higher than 1GPa. At increasing DR, the failure mode of fibres changes. In fact whereas fibres obtained with a draw ratio of 6 showed a flat fracture surface (Fig. 4a), the failure of fibres drawn at a DR of 12.4 reveals that the fibre is composed of very thin connected micro-fibrils (Fig. 4b). The tensile strength of 1.1 GPa agrees with other values reported in the literature for fibres spun from chloroform solutions [11, 12, 16, 17, 27], but, in our case, at lower DR (12 versus 20) and crystallinity (41% versus 96%). By using toluene/chloroform solution and more complicated conditions, Leenslag [29] and Postema [14] produced fibres having a tensile strength higher than 2 GPa.

5. Conclusions

Poly-L-lactic acid fibres of high molecular weight were produced by a solution spinning process followed by hot drawing. In contrast to what happens with melt spinning, the two-stage solution spinning/hot drawing process did not provoke significant polymer degradation, giving a molecular weight for the fibres of 620 000, very close to the initial polymer M_V (660 000). Chloroform, still present in the as-spun fibres even after several months, improved drawability, with the best processing conditions (at each drawing temperature) being when the amount of solvent was around 30%.

The tensile strength of fibres increased with draw ratio, up to a maximum of 1.1 GPa, which was found for fibres drawn at a DR = 12.4 at 200 °C.

Depending on the drawing temperature, the polymer developed a double morphology, with the formation of low temperature melting crystalline regions. The role played in fibre properties by the two apparent crystalline phases detected in the polymer, as a function of the processing conditions is not completely clear. Although, the increase of fibre strength is accompanied by a corresponding increase of the lower melting temperature phase, whether or not this phase is responsible for the improvement of fibre properties remains as yet, an unanswered question. This finding, fibre degradation, and the effect of morphology on fibre degradation, are presently under study.

References

1. E. E. SCHMITT, US Patent 3 297 033, 1967 Jan 3.
2. L. GETTER, D. E. CUTTRIGHT, S. N. BHASKAR and J. K. AUGSBURG, *J. Oral Surg.* **30** (1972) 344.
3. M. VERT and F. CHABOT, *Makromol. Chem. Suppl.* **5** (1981) 30.
4. J. W. LEESLAG, A. J. PENNINGS, R. R. M. BOS, F. R. ROZEMA and G. BOERING, *Biomaterials* **8** (1987) 70.
5. D. G. TUNC, *Clinical Materials* **8** (1991) 119.
6. R. A. OLSON, D. L. ROBERTS and D. B. OSBON, *Oral. Surg.* **53** (1982) 441.
7. J. W. LEENSLAG, M. T. KROES, A. J. PENNINGS and B. VAN DER LEI, *New Polym. Mater.* **1** (1988) 111.
8. C. M. AGRAWAL, K. F. HAAS, D. A. LEOPOLD, H. G. CLARK, *Biomaterials* **13** (1992) 176.
9. S. YOLLES, US Patent 3 887 699 (1975), June 3.
10. D. H. LEWIS, in "Biodegradable polymers as drug delivery systems," edited by M. Chasin and R. Langer (Marcel Dekker, New York, 1990) p. 1.
11. B. ELING, S. GOGOLEWSKI and A. J. PENNINGS *Polymer* **23** (1982) 1587.
12. S. H. HYON, K. JAMSHIDI, Y. IKADA, in "Polymers as biomaterials", edited by S. Shalaby, A. S. Hoffmann, B. D. Ratner and T. A. Horbett (Plenum Press, New York, 1984) p. 51.
13. R. POSTEMA, A. J. PENNINGS, *J. Appl. Polym. Sci.* **37** (1989) 2351.
14. R. POSTEMA, A. H. LUITEN, A. J. PENNINGS, *ibid.*, **39** (1990) 1265.
15. M. DAUNER, E. MULLER, B. WAGNER, H. PLANCK, in "Degradation phenomena on polymeric biomaterials", edited by H. Plank, M. Dauner and M. Renardy (Springer-Verlag, Berlin, 1992) p. 107.
16. I. HORACEK and L. KUDLACEK, *J. Appl. Polym. Sci.* **50** (1993) 1.
17. H. TSUSJ, Y. IKADA, S-H-HYON, Y. KIMURA and T. KITAO *ibid.* **51** (1994) 337.
18. R. K. KULKARNI, E. G. MOORE, A. F. HEGYELI and F. LEONARD, *J. Biomed. Mater. Res.* **5** (1971) 169.
19. P. TORMALA *Clin. Mater.* **10** (1992) 29.
20. C. M. AGRAWAL, K. F. HAAS, D. A. LEOPOLD and H. G. CLARK, *Biomaterials* **13** (1992) 176.
21. C. MIGLIARESI, D. COHN, A. DE LOLLIS and L. FAMBRI. *J. Appl. Polym. Sci.* **43** (1991) 83.
22. C. MIGLIARESI, A. DE LOLLIS, L. FAMBRI and D. COHN, *Clin. Mater.* **8** (1991) 111.
23. C. MIGLIARESI, L. FAMBRI and D. COHN, *J. Biomater. Sci., Polym. Ed.* **5** (1994) 591.
24. C. MIGLIARESI, L. FAMBRI, A. PEGORETTI, S. D. INCARDONA, M. MAZZURANA and R. FENNER, in Transactions, 19th Annual Meeting of the Society of Biomaterials, Boston, MA (1994) p. 246.
25. A. SCHINDLER and D. HARPER, *J. Polym. Sci. Polym. Chem. Ed.* **17** (1979) 2593.
26. E. W. FISHER, H. J. STERZEL and G. WEGNER, *Kolloid Z. Z. Polym.* **251** (1973) 980.
27. S. GOGOLEWSKI and A. J. PENNINGS, *J. Appl. Polym. Sci.* **28** (1983) 1045.
28. W. HOOGSTEEN, A. R. POSTEMA, A. J. PENNINGS, G. TEN BRINKE and P. ZUGENMAIER, *Macromol* **23** (1990) 534.
29. J. W. LEENSLAG and A. J. PENNINGS, *Polymer* **28** (1987) 1695.