General crystallization behaviour of poly(L-lactic acid)

B. Kalb* and A. J. Pennings

Department of Polymer Chemistry, State University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands
*(Received 1 June 1979)*

A study has been made of the general crystallization behaviour of poly(L-lactic acid), PLLA, and is intended to be the basis for further work on fibre formation processes. PLLA is shown to be a semi-crystalline polymer that may crystallize from the melt and from solution, and that may form fibres. Spherulites grown from the melt were negatively birefringent and grew at a rate similar to that for polypropylene. The equilibrium melting point and the glass transition temperature were found to be about 215°C and 55°C, respectively. Solution crystallization resulted in lamellar crystals about 10 nm thick and electron diffraction revealed a hexagonal unit structure with dimensions smaller than reported earlier. The equilibrium dissolution temperature in p-xylene and the end surface free energy at the fold surface amounted to 126.5°C and about 0.075 J m^{-2} respectively. Fibres of PLLA were formed by precipitation in a non-solvent; some of the fibres were highly porous with a pore size in the range 0.1—0.6 μm.

INTRODUCTION

In recent years, wide-spread attention has been paid to the formation of fibrous polymer crystals[1]. The investigations were mainly carried out using polyethylene and other synthetic polymers; exceptions are the studies on amylose[2] and cellulose[3]. However, since synthetic polymer products may cause considerable environmental problems in specific cases, studies on biodegradable polymers have become of increasing importance. In view of the possible decline in oil supplies in the future, renewable raw materials (e.g. lactic acid) may become more important. The present paper is concerned with preliminary investigations into the general crystallization behaviour of poly(L-lactic acid), PLLA. PLLA is biodegradable and biocompatible, with resultant environmental advantages over synthetic polymers. Since it is bioabsorbable[4,5], it may find medical application for sutures and surgical implants[4–8], where especially porous materials might be of importance.

PLLA can be produced by a cationic ring-opening polymerization[9–12] of the dilactide. It has the following chemical formula:
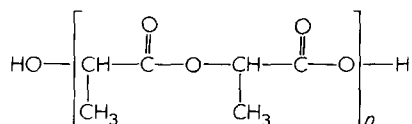
where *n* represents the degree of polymerization, which can be very large. The polymer has a high optical activity and is crystallizable.

Crystallization studies on lactide copolymers have been carried out earlier by Fischer *et al.*[13] in order to obtain information about the crystallization behaviour of these copolymers with different contents of non-crystallizable *DL*-lactide units. The distribution of the *DL*-units in

crystalline and amorphous regions depends strongly on the crystallization temperature. De Santis and Kovacs[14] showed that the unit cell of PLLA is pseudo-orthorhombic with dimensions of $a = 10.7$ Å, $b = 6.45$ Å, $c = 27.8$ Å and $\alpha = \beta = \gamma = 90°$, where the molecules assume a 10_3 helical conformation. The configuration of PLLA in solution was investigated by Flory's group[15,16]; their results indicate that the molecule is relatively flexible, as may be concluded from a comparison of the unperturbed dimension of this molecule with that of polyethylene. Other papers and patents[4–8] discuss the bioabsorbability and other properties of copolymers with $L(-)$- or *DL*-lactide. High shrinkage (*c.* 50% within 3 h) was reported[8] for amorphous poly(*DL*-lactide) fibres when exposed to physiological saline solutions. Attempts to improve the dimensional stability were unsuccessful.

The present study will deal with the crystallization of PLLA from bulk and solution, and estimates of the equilibrium melting and dissolution temperature will be made. After morphological investigations of lamellar crystals, some experiments on the fibre formation that yielded porous fibres will also be discussed. The study is intended to be the basis for further work on the fibre formation process of PLLA.

EXPERIMENTAL

The PLLA used in the present study had an intrinsic viscosity, $[\eta]$, in chloroform of about 10, which corresponds to a viscosity average molecular weight, M_v, of about 5.5×10^5 according to the relation[11]:

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

The polymer was stored over P_2O_5 to avoid absorption of water that may cause degradation when the sample is

---

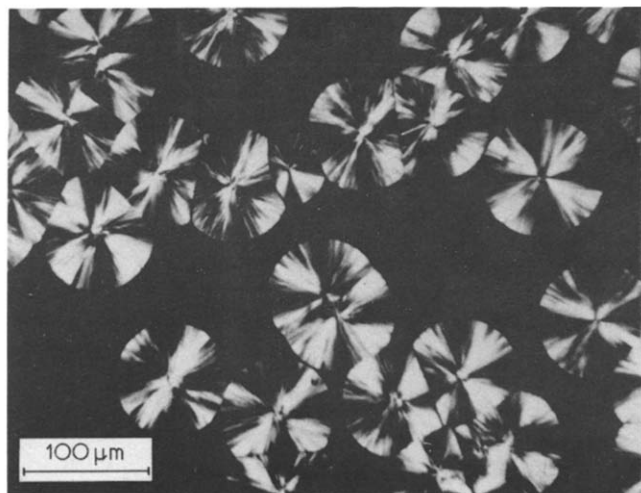* Present address: Bruckerstrasse 369, A-8101 Gratkorn, Austria.

Figure 1 Spherulites of PLLA grown at 120°C from the melt

used at higher temperatures, as frequently observed for polyesters[18]. Bulk crystallization experiments were performed on thin films of the polymer between microscope glass slides placed on a Mettler hot stage and a Zeiss optical microscope.

Stirring experiments were carried out in test tubes or glass beakers with glass or stainless steel stirrers.

For differential scanning calorimetry (d.s.c.), a Perkin Elmer DSC II was used, calibrated for the respective temperature ranges with indium, hexamethylbenzene, hexaethylbenzene and 1,2,4,5-tetramethylbenzene. D.s.c. scans of 3.4% (by wt) solutions of PLLA in p-xylene were performed by employing electrically welded steel pans[17] that contained higher volumes of the solution than pans normally used.

The examination of the solution-grown lamellar crystals and fibres was carried out by transmission (Philips EM 300) and scanning (Joel JSM-V3) electron microscopy.

RESULTS AND DISCUSSION

Crystallization from the melt

Thin films of PLLA were melted between glass slides at about 190°C, a temperature about 10°C above the original melting point of the supplied material. When cooled down to crystallization temperatures (T_c), spherulites started to grow after a short induction period (about 1 min at T_c = 120°C, obtained from an extrapolation to zero radius in the plot of spherulite radius versus time). *Figure 1* shows spherulites that were grown isothermally at 120°C; their growth rate was 10.6 μm min^{-1}, of the order of the growth rate of spherulites grown from polypropylene[19]. Examination in the polarizing microscope indicated the existence of negatively birefringent spherulites. Since fibres of PLLA have a higher refractive index in the axis direction, the present negative birefringence appears to be due to the fact that molecular chains are oriented in the direction orthogonal to the radius of the spherulites, which has already been found to be a general feature for spherulites[20]. It may be noted that similar spherulitic growth has also been observed in solutions of PLLA.

The relationship between crystallization and melting temperatures of PLLA was obtained from d.s.c. measurements

and is presented in *Figure 2*, where T_m represents the melting temperature. In these measurements, the thermograms were taken at a scan speed of 5°C min^{-1} after isothermal crystallization at T_c. The peak temperature was assumed to be the melting point of the sample. The straight line extrapolation of T_m versus T_c to the equilibrium melting point (T°_m), where $T_m = T_c$, carried out according to Hoffman and Weeks[21], yields T°_m = 488K (215°C). The error in this estimate of T°_m is expected to be about ±10°C, since the influence of the lamellar thickening process has been neglected.

The enthalpy of fusion (ΔH_f), as determined from the area under the melting peak, for a sample crystallized for 24 h at 149°C was calculated to be 50.7 J g^{-1}. This value of ΔH_f can be compared with those found by Fischer et al.[13], who estimated for an infinitely large crystal 81.3 to 93.0 J g^{-1}. Following this, the degree of crystallinity of PLLA might not reach values that are higher than about 0.6.

Further experiments on the d.s.c. revealed a glass transition temperature (T_g) for PLLA of about 55°C. The magnitude of the T_g is of significance for the mechanical properties of the polymer[22]. A very high T_g might give rise to small molecular mobilities and therefore to brittleness at room temperature. In the present case, the T_g is only slightly higher than room temperature.

Some of the thermograms showed sharp endothermic peaks at the glass transition, especially for samples that were kept for more than a week at room temperature or overnight at about 45°C. Other samples that were crystallized or quenched in the d.s.c. prior to the T_g-scan did not show a pronounced endothermic peak. Similar peaks to the above-mentioned were also reported for other polymers[19,23] and may be related to stress—relaxation phenomena. Stresses in the polymer sample may arise from differences in the thermal expansion coefficient of amorphous and crystalline phase and the existence of tie-molecules between the crystallites. It appears that samples, which have been quenched shortly before the d.s.c.-scan, did not have time to relax internal stresses sufficiently, while those annealed for a longer period (equivalent to storing at room temperature) became completely relaxed. Accordingly, the polymer in which stress—relaxation was completed will again accumulate regional stresses on heating. Hutchinson and Kovacs[23] were able to explain the apparent first order transition at T_g theoretically using free volume relaxation kinetics. The influence of crystallinity, crystallite dimensions and other parameters on this relaxation process is open for further investigation.
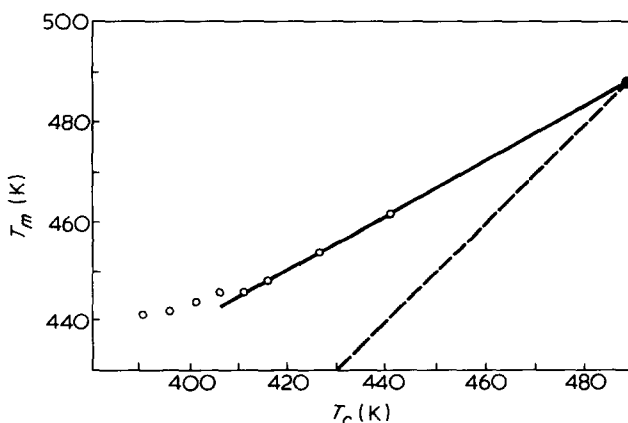

Figure 2 The crystalline melting point, T_m, of PLLA as a function of the crystallization temperature, obtained from d.s.c. measurements. The extrapolation of the data to $T_m = T_c$, − − − − −, yields an equilibrium melting point, T°_m, of about 488K, shown as ●

Crystallization from solution

Spherulites of PLLA were also grown from solutions in chloroform or *m*-cresol. The growth process was initiated by the absorption of water when the polymer solutions were exposed for several weeks to air humidity. In most cases,
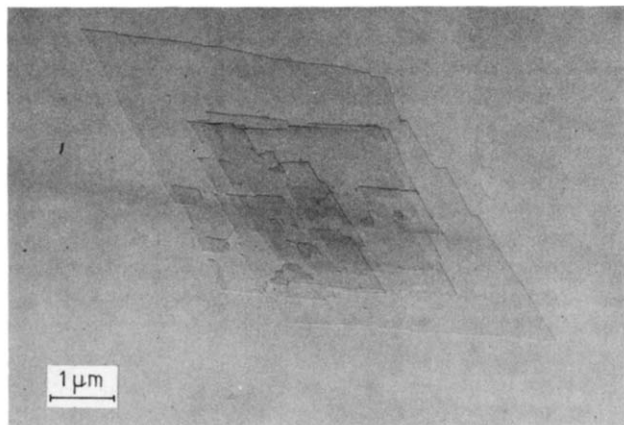

Figure 3 Transmission electron micrograph of lamellar crystals of PLLA grown from a 0.08 % (by wt) solution in toluene at 55°C

crystallization started at the edge of the glass slides and proceeded towards the centre of the sample. Similar observations of oriented growth have been made by crystallization of polypropylene in a temperature gradient[24].

Crystallization experiments using dilute solutions (about 0.08% by wt) of PLLA in toluene and *p*-xylene yielded large lamellar single crystals. *Figure 3* shows a microphotograph of single crystals crystallized at 55°C from toluene. The lamellae are lozenge-shaped and have a thickness of about 10 nm, as can be discerned from the length of the shadow in the electron micrograph. In *Figure 4*, single crystals prepared from *p*-xylene at 90°C are presented; the thickness of these lamellae is about 12 nm. The growth of the crystals now occurred along six planes, in contrast to the four planes in *Figure 3*, and a truncated lozenge has been formed.

Also shown in *Figure 4* is an example of an electron diffraction pattern of such a crystal, which indicates an almost hexagonal unit cell structure. From 9 diffraction diagrams on various single crystals obtained from toluene and *p*-xylene, it was concluded that the crystal lattice spacing is 5.17 ± 0.08 Å for all reflections in the spot pattern. The calibration for the given spacings was carried out with gold. Another calibration using molybdenum oxide yielded only 1.3% larger spacings, and indicated an accuracy of the diffraction
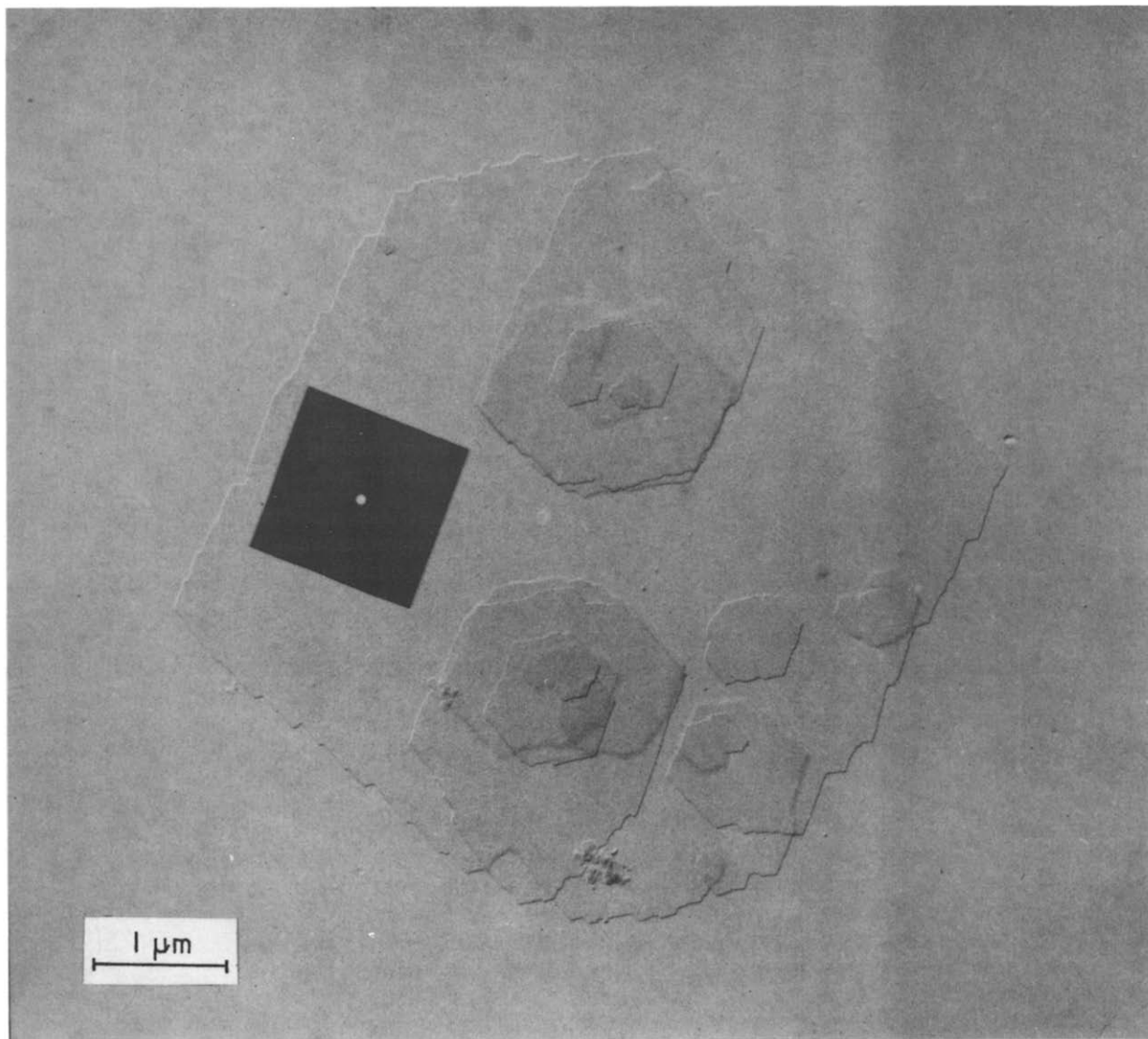

Figure 4 Transmission electron micrograph of lamellar crystals of PLLA grown from a 0.08 % (by wt) solution in *p*-xylene at 90°C. The insert shows an electron diffraction pattern of one of these crystals
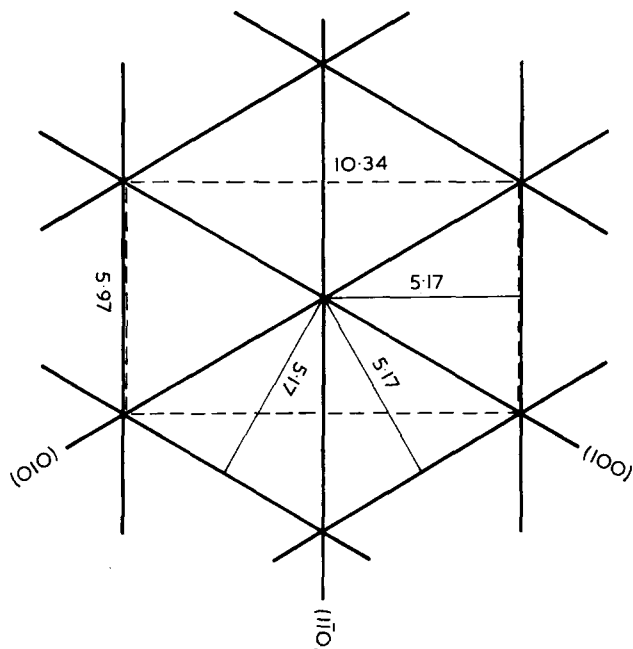
Figure 5 Schematic representation of the (hk0) planes for the crystal lattice of PLLA with spacings according to the present electron diffraction data. The unit cell appears to be hexagonal and may be compared with a previously obtained pseudo-orthogonal unit cell[12] by simple geometrical considerations (broken line). The numbers in brackets indicate crystal planes, while the other numbers represent dimensions in Å

technique that is within the error limits given above for the spacings. The electron diffraction results suggest that the molecular chains are oriented in the direction orthogonal to the basal plane of the crystal and that the unit cell is hexagonal having dimensions of $a = b = 5.9$ Å, $\alpha = \beta = 90°$ and $\gamma = 120°$. The magnitude of c cannot be derived from the present data but is expected to be similar to that given earlier[14]. A schematic representation of the (hk0) planes for the crystal lattice of PLLA with spacings according to the present data is shown in *Figure 5*. When the spacings are recalculated as illustrated in *Figure 5* by the broken lines for a pseudo-orthorhombic unit cell, which is the unit cell that was obtained earlier from X-ray fibre diagrams by de Santis and Kovacs[14] (where $a = 10.7$ Å, $b = 6.45$ Å, $c = 27.8$ Å, and $\alpha = \beta = \gamma = 90°$), then the dimensions are: $a = 10.34$ Å, $b = 5.97$ Å and $\alpha = \beta = \gamma = 90°$. The a and b unit cell dimensions calculated in the present study are substantially smaller than those suggested earlier. The discrepancy of 8% for b is too high to be accounted for by the experimental error given above. The only explanation at present is that the difference in the spacings might be due to different specimen morphologies (i.e. fibre and single crystal). In fibrous crystals used by the other authors, lattice expansion due to cumulative strain might have occurred (as discussed in Hoffman's theory of polymer fibril formation with cumulative strain[25]) therefore giving rise to larger cell dimensions than in the case of single crystals.

The observation of a hexagonal structure in this polymer is of significance since it may be connected to higher molecular mobility, as found for polyethylene fibres where a phase transition from an orthogonal to a hexagonal phase occurs at about $150°C$[26].

The dissolution behaviour of lamellar crystals was studied in the DSC on 3.4% (by wt) solutions of PLLA in p-xylene and yielded a relationship between the dissolution temperature (T_d) and the crystallization temperature given in *Figure*

6. The experimental points follow a straight-line relationship of T_d versus T_c over the temperature range, which indicates that no significant lamellar thickening has occurred. An extrapolation of the data to infinite crystal size (intersection with $T_d = T_c$) results in an equilibrium dissolution temperature $T_d^\circ = 399.5K$ corresponding to $126.5°C$. Knowledge of the magnitude of T_d° is of relevance for fibre formation processes, since fibres grown from solution near this temperature have ultra-high strength properties[25].

In order to obtain a rough estimate of the surface free energy at the fold surface (σ_e), the following equation[21] can be employed:

$$\sigma_e = \frac{L\Delta h_f \rho_c (T_d^\circ - T_c)}{2T_d^\circ}$$

where L represents the thickness of the lamellar crystal (about 12 nm at a crystallization temperature of $T_c = 363K$); Δh_f and ρ_c are the enthalpy of fusion per mole repeat unit and the crystal density which were given by Fischer et al.[13] to be about 6200 J mol^{-1} and 1.29×10^3 kg m^{-3}, respectively. When further substituting in the above equation for $T_d^\circ = 399.5K$, the end surface free energy is calculated to be $\sigma_e = 75 \times 10^{-3}$ J m^{-2}. σ_e for this polymer is comparable with the value for polyethylene[27], which is in the order of 90×10^{-3} J m^{-2}. The lower fold surface free energy apparently originates in the higher flexibility[15] of the PLLA chain, and therefore from its greater ease of chain fold formation.

Fibre formation experiments

Stirring experiments with dilute and supercooled solutions of PLLA in toluene and p-xylene did not yield fibres, in contrast to observations on polyethylene. The reason for this phenomenon is not known, but might be related to the non-existence of high molecular weight fractions in the present sample of PLLA: the sample had been prepared by an ionic polymerization reaction.

In precipitation processes of PLLA, carried out by addition of droplets of polymer solution to a stirred coagulant, fibres such as shown in the scanning electron micrograph in *Figure 7* were formed. The polymer was dissolved in chloroform, and precipitated in a mixture of glycerol and ethanol (volume ratio of about 7:3, stirring rate 700 rpm). The
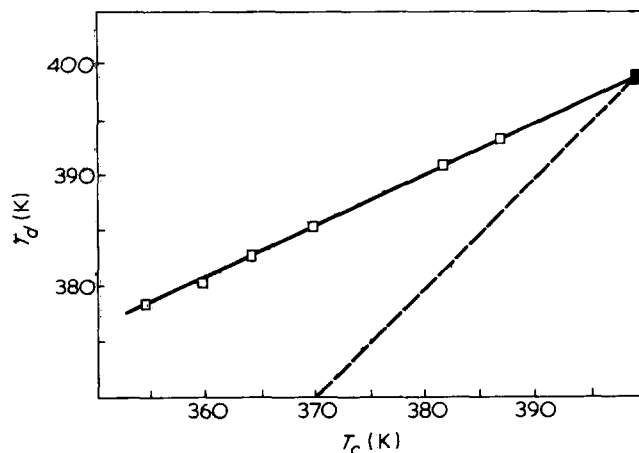

Figure 6 The dissolution temperature, T_d, of PLLA in p-xylene as a function of the crystallization temperature, T_c. The extrapolation of the data to $T_m = T_c$, ――, yields an equilibrium dissolution temperature, T_d°, of 399.5K, shown as ■
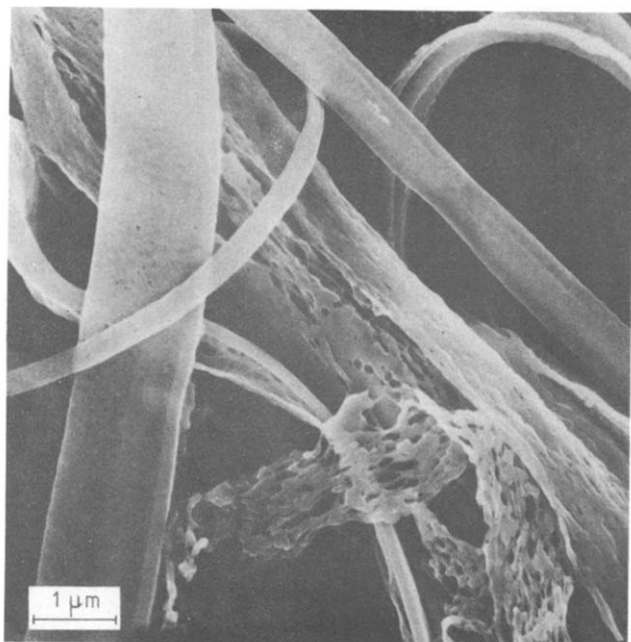
Figure 7 Scanning electron micrograph of PLLA fibres produced by precipitation of a chloroform solution in a coagulant of glycerol/ethanol stirred at 700 rpm. Note the appearance of porous material
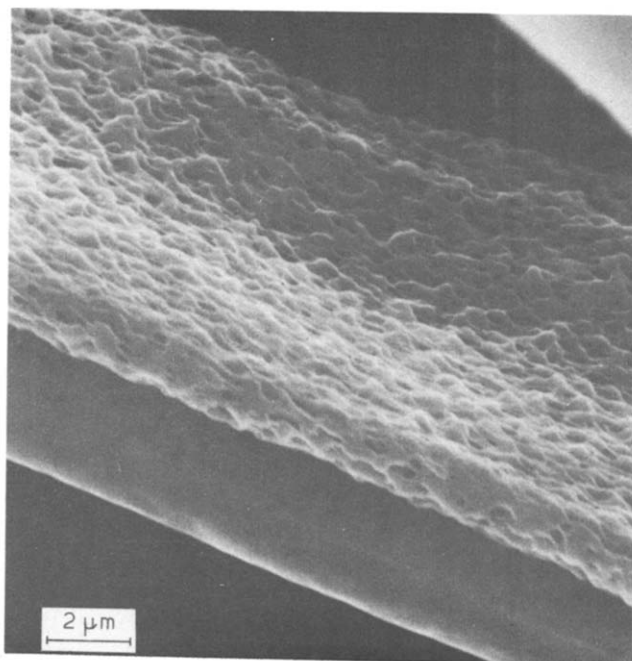

Figure 8 Scanning electron micrograph of a porous fibre produced by precipitation of a solution of PLLA in chloroform in a stirred coagulant of glycerol/ethanol. The size of the pores is in the range 0.1–0.6 μm

fibres formed bundles around the stirrer, which were carefully removed and thereafter washed and stored in ethanol. Flat fibres of various size have been produced predominantly, comparable to the experimental results on the fibre formation of cellulose[3] where stirred coagulants have also been used. The appearance of porous fibres in this study is a significant observation (*Figure 7;* at a higher magnification, *Figure 8*). The pores have a width of 0.1–0.6 μm. Porous fibres might be of particular importance for medical applications, where the rate of biological degradation can be controlled by the porosity of the fibres.

Observations in the optical microscope indicated that some of the fibres were considerably oriented. In other experiments with solutions of PLLA (in *m*-cresol; isoamyl alcohol; or a mixture of ethylene glycol/acetone) similar fibres to those presented above were formed.

Examination of mildly ultrasonicated fibre samples in the transmission electron microscope showed that the fibres consist of microfibres of about 20 nm in diameter. The microfibres had a shish-kebab appearance; however, no fibre pattern could be produced by electron diffraction which might be due to a relatively low crystallinity of the fibres.

CONCLUSION

PLLA is a semi-crystalline polymer, able to form spherulites, lamellar crystals and fibres.

Spherulites were grown from the melt and from solution and exhibit negative birefringence. The growth rate of melt-crystallized spherulites falls in the order of that of polypropylene. D.s.c. measurements yielded values for $T_m^\circ \simeq 215^\circ C$ and $T_g \simeq 55^\circ C$.

Lamellar crystals of about 100 Å in thickness were obtained from dilute solutions in toluene and *p*-xylene and appear to have a hexagonal molecular structure with dimen-

sions smaller than those calculated elsewhere[14]. The equilibrium dissolution temperature was found from d.s.c. data to be $T_d^\circ = 126.5^\circ C$ for PLLA in *p*-xylene; and the same data reveal an end surface free energy of the folded chain crystals of $\sigma_e \simeq 0.075$ J m^{-2}. The relatively low value of σ_e compared with lamellar polyethylene is explained as being due to a higher flexibility[15] of the PLLA molecule.

Fibre formation experiments with PLLA from supercooled solutions were unsuccessful, apparently because of the absence of extremely high molecular weight fractions in the present cationically polymerized sample.

The precipitation of PLLA solutions in a stirred nonsolvent resulted in the formation of fibres with a variety of dimensions within the sample. Some of the fibres showed a porous structure with a pore size in the range 0.1–0.6 μm. The fibres are birefringent and have a smaller optical refractivity in the fibre axis direction; some of the fibres seemed to be considerably oriented.

ACKNOWLEDGEMENTS

REFERENCES

1   Peterlin, A. *Polym. Prepr.* 1975, **16**, 315
2   Bolhuis, H. H. and Pennings, A. J. *J. Macromol. Sci. Phys. Edn* 1975, **11**, 455
3   Kalb, B. *PhD Thesis*, McGill University, Montreal, Canada, 1978
4   Schindler, A., Jeffcoat, R., Kimmel, G. L., Pitt, C. G., Wall, M. E. and Zweidinger, R. 'Contemporary Topics in Polymer Science' (Eds. E. M. Pearce and J. R. Schaefgen) Plenum Press, New York, Vol 2, 1977

5 Canadian Patent. 863 673. B. Schneider, Feb 16, 1971

6 US Patent 3 636 956, B. Schneider, Jan. 25, 1972

7 US Patent 3 982 543, Schmidt *et al.* Sept. 28, 1976

8 Hodge Jr, J. W. *US Army Medical Biochem. Res. Lab. Report* **7105**, 1971

9 Kleine, J. and Kleine, H. -H. *Macromol. Chem.* 1959, **30**, 23

10 Dittrich, W. and Schulz, R. C. *Ang. Makromol. Chem.* 1971, **15**, 109

11 Tsuruta, T., Matsuura, K. and Inoue, S. *Macromol. Chem.* 1964, **75**, 211

12 Schlindler, A. and Harper, D. *J. Polym. Sci., Chem. Edn.* in press

13 Fischer, E. W., Sterzel, H. J. and Wegner, G. *Koll.-Z. Z. Polym.* 1973, **251**, 980

14 De Santis, P. and Kovacs, A. J. *Biopolymers* 1968, **6**, 299

15 Tonelli, A. E. and Flory, P. J. *Macromolecules* 1969, **2**, 225

16 Brant, D. A., Tonelli, A. E. and Flory, P. J. *Macromolecules* 1969, **2**, 228

17 Schouteten, C. J. H., Bakker, S., Klazema, B. and Pennings, A. J. *Anal. Chem.* 1977, **49**, 522

18 Kohan, M. I., ed., 'Nylon Plastics', Wiley–Interscience, New York, 1973

19 Wunderlich, B. 'Macromolecular Physics', Academic Press, New York, Vol 1, 1973, Vol 2, 1976

20 Keller, A. *J. Polym. Sci.* 1955, **17**, 351

21 Hoffman, J. D. and Weeks, J. J. *J. Res. Nat. Bur. Std.(A)* 1962, **66**, 13

22 Van Krevelen, D. W. 'Properties of Polymers', Elsevier, Amsterdam, 1976

23 Hutchinson, J. M. and Kovacs, A. J. *J. Polym. Sci. (Polym. Phys. Edn)* 1976, **14**, 1575

24 Smith, P. and Pennings, A. J. *Eur. Polym. J.* 1976, **12**, 781

25 Hoffman, J. D. to be published

26 Zwijnenburg, A. *PhD Thesis*, State University of Groningen, The Netherlands, 1978

27 Hoffman, J. D., Frolen, L. J., Ross, G. S. and Lauritzen, Jr., J. I. *J. Res. Nat. Bur. Std. A*, 1975, **79**, 671