Thermal characterization of polylactides

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Three important thermal characteristics of polylactides have been measured and discussed. These are glass transition temperature, melting temperature, and degradation behaviour. The glass transition temperatures at infinite molecular weight for L- and D,L-optical isomers were 58 and 57°C, respectively. Melting temperature for the crystalline L-isomer was 184°C at infinite molecular weight. Number-average molecular weight, melt viscosity, differential scanning calorimetry, infra-red analysis and thermogravimetric analysis were used to study the degradation behaviour under different conditions. Polylactides were found to be highly sensitive to heat, especially at temperatures higher than 190°C. Most of the degradative reactions were thought to involve the highly concentrated ester bond on the main chain. These reactions included thermohydrolysis, depolymerization and cyclic oligomerization, intermolecular and intramolecular transesterifications. Low molecular weight compounds associated with the polymer seemed to play an important role in lowering the molecular weight at high temperatures, as well as the hydroxyl end group of the main chain. The compounds include water, monomers, oligomers, and polymerization catalysts. Removal of the non-polymeric contents and blocking the hydroxyl end-group enhanced the thermal stability of the polymers. The increased amount of the polymerization catalyst in the end product contributed to the degradative reactions.

(Keywords: polylactides; thermal properties; degradation; glass transition temperature; melting temperature)

INTRODUCTION

Interest in medical applications of polylactide materials has developed over the last two decades due to their favourable chemical, biological, and mechanical characteristics. These characteristics include structural simplicity, comparatively easy synthesis, compatibility with biological tissues, applicability of mechanical characteristics, and a simple degradation mechanism with no complex products. However, successful clinical applications for these polymers are yet to emerge.

Physical property studies of polylactides include: crystalline structure[1,2], crystallization and crystalline phase transition[3–5], eutectic crystallization of poly-L-lactide with pentaerythrityl tetrabromide[6], *p*-hydroxybenzoic acid, and hexamethylbenzene[7], and stereocomplexation between L- and D-enantiomers[8].

A preliminary study has shown that polylactides belong to the group of polymers with poor thermal stability. Surprisingly little attention has been paid to the thermal properties of these polymers. Kishore *et al.* recently reported[9] the isothermal melting behaviour of poly-L-lactide. Following an attempt by Chujo *et al.*[10] to enhance the thermal stability of polyglycolide, Cooper *et al.* conducted a series of studies[11] of the thermal degradation of poly-α-esters including polyglycolide and polylactides. Mass spectroscopic analysis has been applied[12,13] to find the thermal oxidative degradation mechanism of lactide–glycolide copolymers, while the thermal oxidative degradation of poly-D,L-lactic acid has been the subject of other investigations[14,15]. The thermodynamic equilibrium between D,L-lactide monomer and the high polymer was studied by Kulagina *et al.*[16].

This paper reports the ultimate glass transition temperature of polylactides using various methods of analysis. Thermal degradation, determined by the change in molecular weight (M_w), for original and modified polymers is also described.

EXPERIMENTAL

L- and D,L-lactic acids were obtained commercially from C.V. Chemie Combinatie Amsterdam CCA, The Netherlands (90% aqueous solution, edible type; 97.5% optical purity by enzymatic assay) and Shimakyu Pure Chemicals, Japan (90% aqueous solution), respectively.

Unfractionated samples of poly-L-lactic acid (PLLA: the term polylactic acid will be used for both polymers prepared by condensation and ring-opening polymerization) and poly-D,L-lactic acid (PDLLA) were synthesized by methods described elsewhere[17]. Molecular weights were determined by gel permeation chromatography at 40°C using four columns of Microstyrogel of 10^6, 10^5, 10^4 and 10^3 Å normal pore size, with tetrahydrofuran as the mobile phase. Polystyrene standards were used to calibrate the results. The samples used in this study are given in *Table 1*. All the solvents used for the experiments were purified according to the standard procedures.

Sample films of 20–200 μm thickness for studying mechanical properties were prepared by casting 2 wt% solutions in chloroform onto a glass plate. Air- and vacuum-dried films were prepared. The residual solvent was removed by heating at 70°C for 15 h *in vacuo* prior to the measurement.

The glass transition temperature (T_g) and melting temperature (T_m) were measured with a Perkin-Elmer (DSC-1B) differential scanning calorimeter using the

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Table 1 Molecular weights for lactic acid polymers obtained by polycondensation (PC) or ring-opening polymerization (ROP)

	$\bar{M}_n$	
	PC	*ROP*
D,L-polymers	430	10 900
	1650	12 620
	2900	18 130
	3470	19 200
	8500	20 270
		21 870
		22 730
		22 940
		24 550
L-polymers	1850	16 000
	2170	21 400
	3150	58 800
	4040	123 000
	5700	192 500
	7220	
	8570	

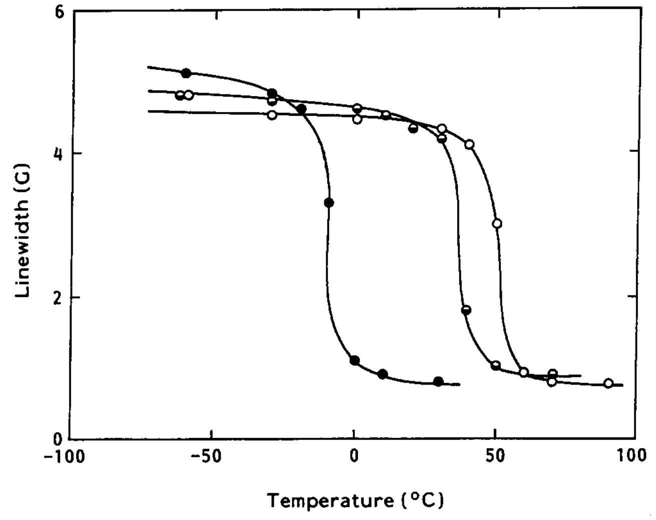


Figure 1 N.m.r. linewidth-transition method for determination of T_g of poly-D,L-lactic acid with different number-average molecular weights: ●, 430; ⊖, 3470; ○, 22 730

method of initial deviation from the base. Heating was performed under helium at a flow rate of 10°C min^{-1}.

Proton nuclear magnetic resonance (n.m.r.) spectra were obtained on samples in sealed, evacuated glass tubes (10^{-3} mmHg) using the 60 MHz proton broad-line n.m.r. spectrometer (JNM-PW-60, Jeol).

Specific optical rotation, [α], was measured at 25°C and a concentration of 0.82 g dl^{-1} in dioxane, with a Perkin-Elmer spectropolarimeter (model 241) at a wavelength of 578 nm.

The dynamic mechanical relaxation behaviour was measured with a Vibron DDV-2 (Toyo Baldwin) at a frequency of 110 and 11 Hz and a heating rate of 1°C min^{-1} over a temperature range of -100 to $+80$°C.

Hydroxyl end group acetylation was conducted homogeneously. A 5 wt% chloroform solution of the polymer was heated to 60°C under dry nitrogen. Acetic anhydride was added as the end-capping agent (5 wt%), followed by the addition of 2.5 wt% pyridine to catalyse the reaction. The reaction was continued for 5 h while stirring, and was terminated by cooling the solution to room temperature and separating the treated polymer by precipitation with excess amount of methanol. The double-precipitated polymer was dried and kept at 70°C in a vacuum oven for 24 h.

Removal of non-polymeric contents of the polymerization products was performed by repeated precipitation of the polymer solution in chloroform (*ca.* 5 wt%) with an excess amount of methanol at room temperature.

Thermal degradation of the polymers was investigated by thermogravimetric analysis (t.g.a.) by using the Perkin-Elmer TGS-1 automatic recording thermobalance at a heating rate of 5°C min^{-1} under nitrogen. The purity of the polymers was also examined by t.g.a.

The melt flow behaviour of PLLA samples was studied by using a flow tester at a constant pressure of 30 kg cm^{-2} and a heating rate of 6°C min^{-1}.

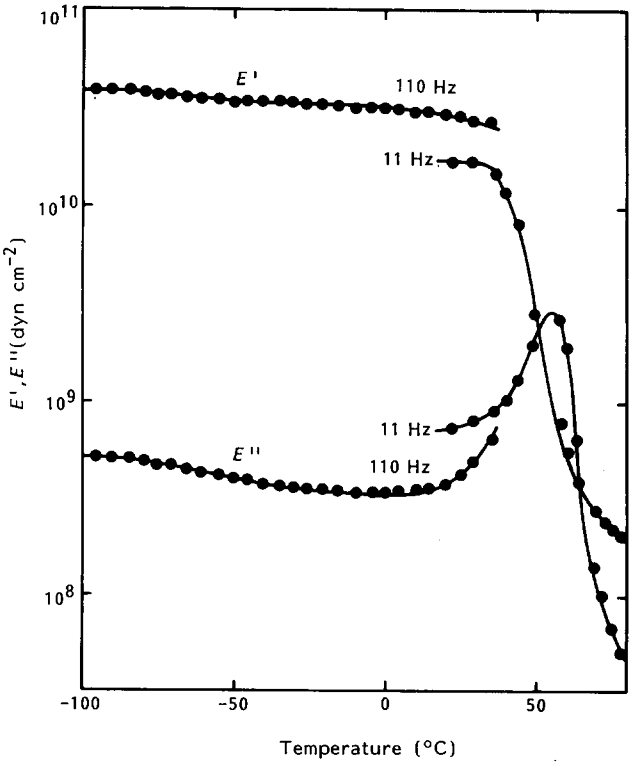


Figure 2 Dynamic viscoelastic analysis for determination of T_g of poly-D,L-lactide with number-average molecular weight of 22 730

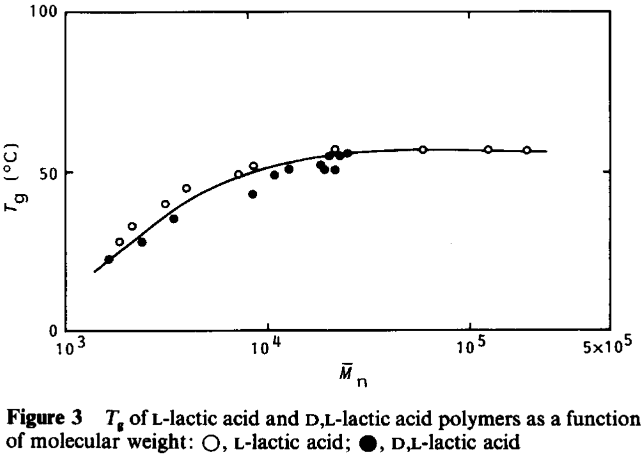


Figure 3 T_g of L-lactic acid and D,L-lactic acid polymers as a function of molecular weight: ○, L-lactic acid; ●, D,L-lactic acid

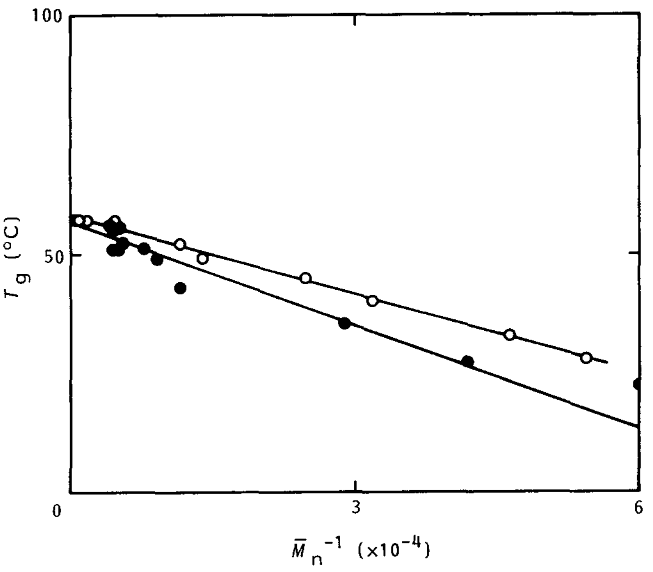


Figure 4 T_g vs. M_n^{-1} Fox–Flory relationship for L-lactic acid and D,L-lactic acid polymers: ○, L-lactic acid; ●, D,L-lactic acid

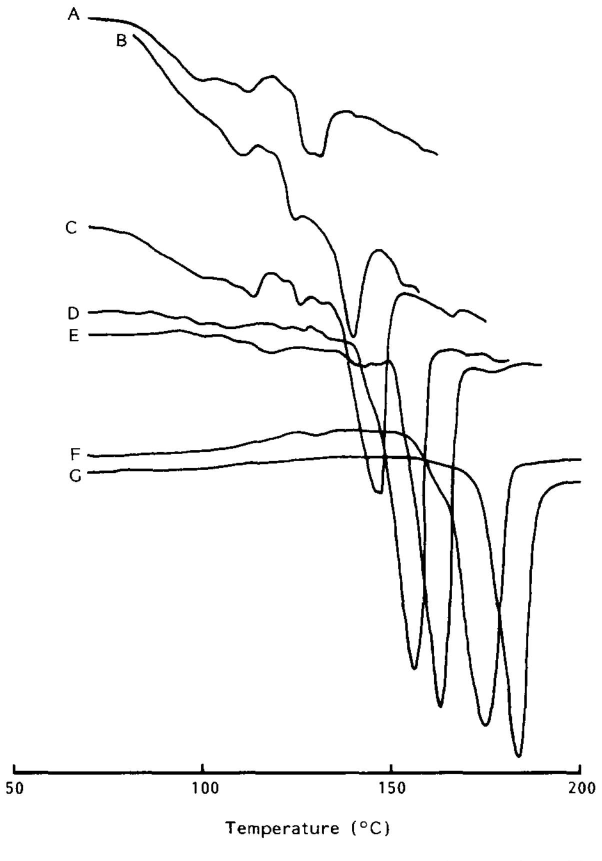


Figure 5 D.s.c. melting thermograms for poly-L-lactic acids with different $\bar{M}_n$: A, 1850; B, 2170; C, 3150; D, 5700; E, 8560, F, 21 400; G, 192 500

RESULTS AND DISCUSSION

Glass transition temperature

Broad-line n.m.r. and mechanical relaxation thermal behaviour were measured for PDLLA samples, and compared with the d.s.c.-based T_g values. *Figures 1* and *2* illustrate the n.m.r. linewidth and the dynamic modulus (E') and loss factor (E'') results. The lowest temperature at which the narrow component appeared in *Figure 1* was regarded as T_g. The T_g values read from *Figures 1* and *2* are compared in *Table 2*, together with those determined by d.s.c. It is seen that the T_g values determined by these three methods are in fairly good agreement. Thus, only the d.s.c. measurements were performed hereafter to obtain T_g.

Figure 3 shows the T_g values determined for PDLLA and PLLA plotted against the number-average M_W. T_g for PLLA is higher than that for PDLLA. This may be due in part to the difference in crystallinity between the two polymers, although PLLA samples were used after melt-quenching treatment. Segment mobility in the amorphous region of crystalline PLLA could be restricted by the crystalline regions, compared with that of the

Table 2 Comparison of glass transition temperature for poly-D,L-lactic acid of different molecular weights measured by different methods

$\bar{M}_n$	D.s.c. (°C)	N.m.r. (°C)	Vibron (°C)
430	−8.0	−9.0	–
3470	35.5	38.5	–
22 730	55.5	54.0	54.0

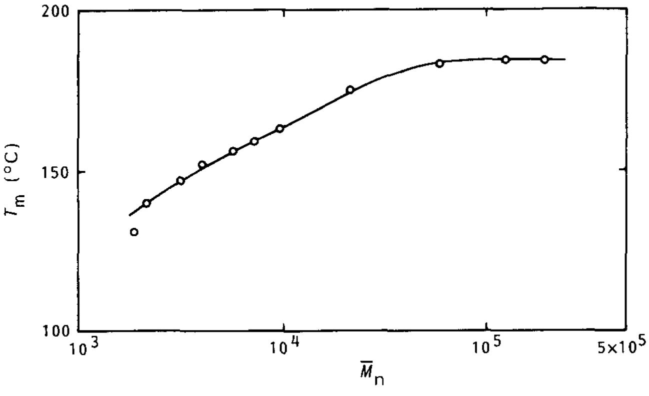


Figure 6 T_m of poly-L-lactic acid as a function of number-average molecular weight

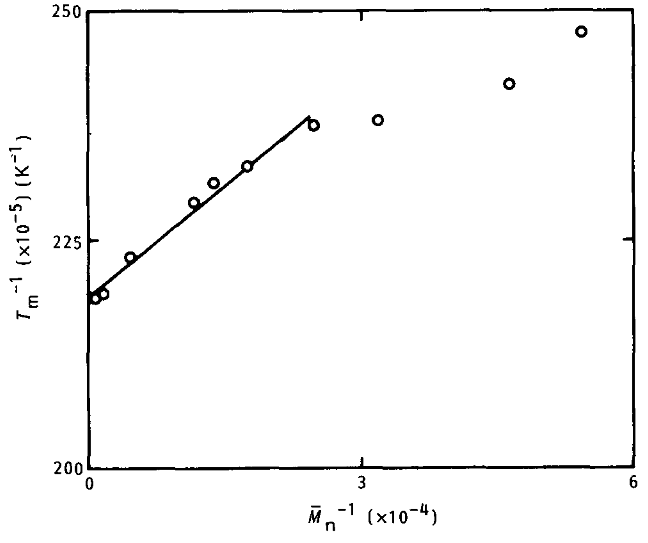


Figure 7 T_m^{-1} vs. M_n^{-1} relationship for poly-L-lactic acid

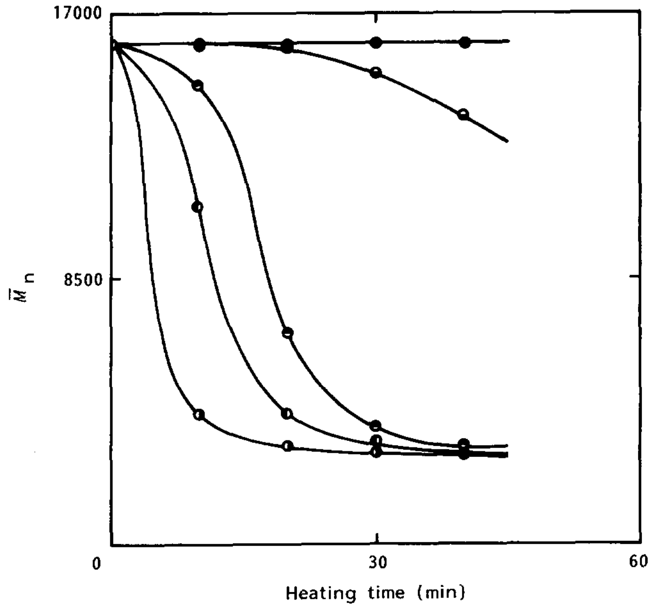


Figure 8 Thermal degradation of poly-L-lactide at different temperatures as a function of heating time: ●, 180°C; ⊖, 190°C; ◓, 200°C; ◐, 210°C; ◑, 220°C

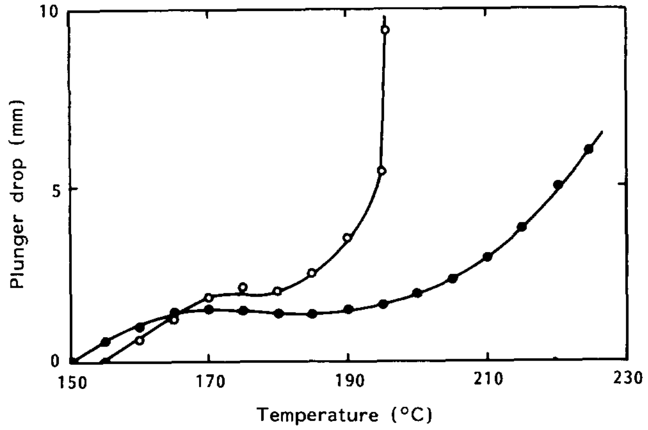


Figure 9 Effect of purification on the flow rate of poly-L-lactide as a function of heating temperature: ○, as-polymerized; ●, purified

amorphous PDLLA. In a previous study, we reported[18] that a PLLA fibre with a high degree of crystallinity showed a T_g of 68°C, as determined by the dynamic viscoelastic method.

The curve in *Figure 3* suggests that T_g of the polylactic acids approaches 57°C as the M_W becomes infinite. This is seen more clearly when the following Flory–Fox equation[19] is applied to the results:

$$T_g = T_g^{\infty} - K/\bar{M}_n \qquad (1)$$

Here T_g^{∞} is the T_g at the infinite M_W, and K is a constant representing the excess free volume of the end groups of polymer chains. The Flory–Fox plots for both polylactic acids are given in *Figure 4*; a linear relationship holds in both cases for all but the very low M_W samples. Such deviation from linearity has been also observed for other polymers[20]. The plots in *Figure 4* give $T_g^{\infty} = 58$°C and $K = 5.50 \times 10^4$ for PLLA and $T_g^{\infty} = 57$°C and $K = 7.30 \times 10^4$ for PDLLA.

Melting temperature

Figure 5 shows the d.s.c. curves for PLLA of different molecular weights. It is seen that polymers having M_W lower than 3000 exhibit weak endotherms at temperatures slightly lower than the main peaks. These broad peaks may be attributed to the unstable, crystallized region, and disappear with increasing M_W to give sharper single peaks. The T_m values read from the higher main peaks are plotted against the M_W in *Figure 6*. It is apparent that T_m approaches a constant value of 184°C as the M_W of the polymer increases.

The plot of T_m against the reciprocal of the M_W is given in *Figure 7*. Flory has shown[21] the following equation will hold for the T_m of a polymer homologue with different M_W values.

$$1/T_m^{\infty} - 1/T_m = 2RM_0/\Delta H_m \bar{M}_n \qquad (2)$$

Here T_m^{∞} is the T_m at the infinite M_W, R is the gas constant, M_0 is the M_W of the repeat unit, and ΔH_m is the heat of fusion per mole of the repeat unit. The plot of T_m^{-1} against $\bar{M}_n^{-1}$ is expected to give a straight line with a slope of $2RM_0/\Delta H_m$ and an intercept of T_m^{∞}. It is seen from *Figure 7* that this Flory plot holds approximately well for polymers with high M_W. The T_m and ΔH_m values obtained from the plot are 184°C and 3.5 kcal mol^{-1}, respectively. This heat of fusion is comparable to that of polycaprolactone (3.0 kcal mol^{-1})[22].

Thermal degradation

Studies of thermal degradation of PLLA samples were carried out using an aluminium cell under nitrogen in

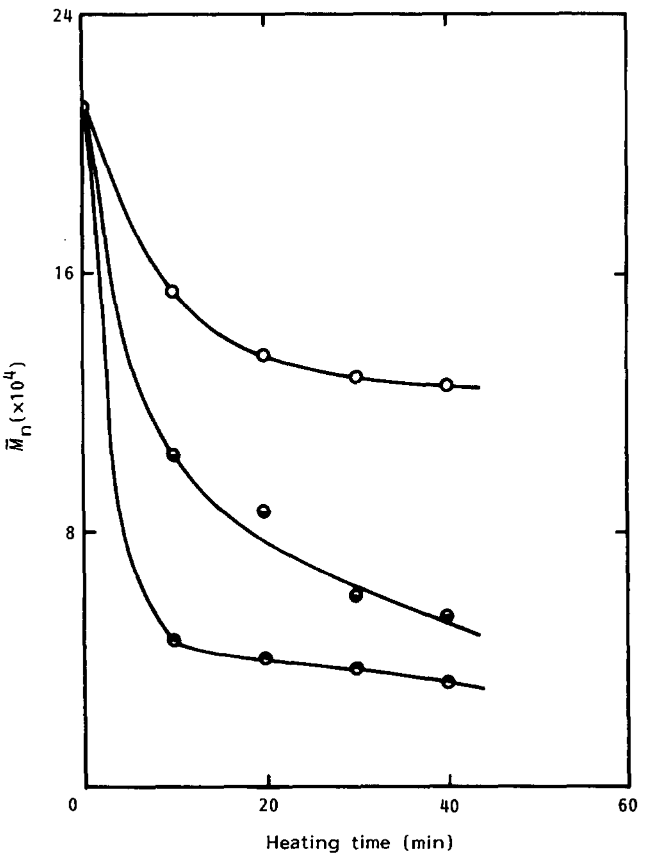


Figure 10 Effect of purification and end-capping on the thermal stability of poly-L-lactide at 200°C in N_2: ◓, as-polymerized; ⊖, purified; ○, acetylated

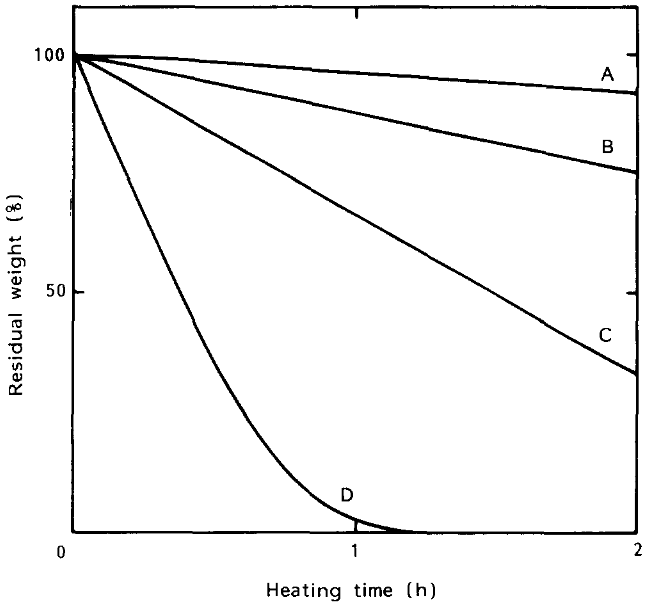


Figure 11 Effect of heating temperature on the weight loss of poly-L-lactide containing 5 wt% stannous octoate in N_2: A, 140°C; B, 160°C; C, 180°C; D, 200°C

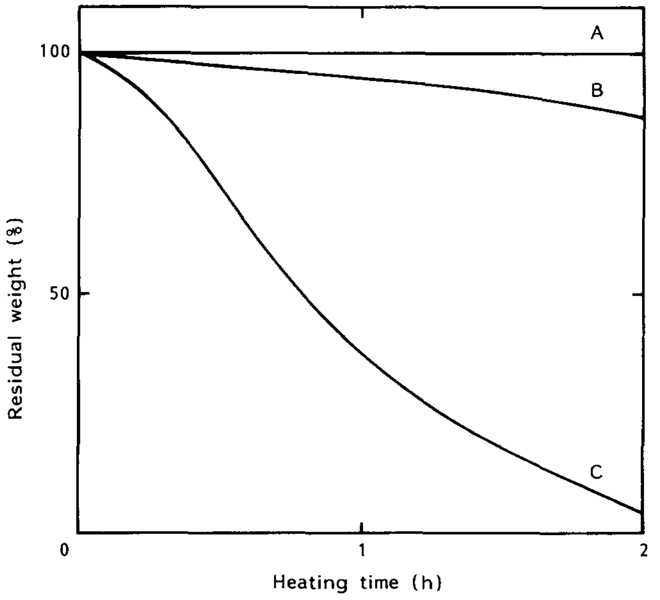


Figure 12 Effect of heating temperature on the weight loss of purified poly-L-lactide in N_2: A, 200°C; B, 220°C; C, 240°C

the temperature range 180–240°C. *Figure 8* shows the M_W change after heating at different temperatures for the as-polymerized, unpurified PLLA. It is seen that the polymer exhibits a noticeable decrease in M_W upon heating, even at as low a temperature as 190°C. This suggests that PLLA belongs to the group of polymers which are relatively sensitive to thermal degradation. Several reasons can be given for its poor thermal stability: (1) hydrolysis by trace amounts of water, catalysed by hydrolysed monomers (lactic acids); (2) zipper-like depolymerization, catalysed by the remaining polymerization catalyst; (3) oxidative, random main-chain scission; (4) intermolecular transesterification to monomer and oligomeric esters; and (5) intramolecular transesterification resulting in formation of the monomer and oligomeric lactides of low M_W. The transesterification may be accelerated by the polymerization catalyst, similar to the depolymerization[23].

It is difficult to decide which reactions dominate the thermal degradation of polylactide, because little information about degradation mechanisms is available. Oxidative degradation seems unlikely to play an important role in this temperature range, since no such indications were observed in the i.r. spectrum for the PLLA heated to 200°C for 1 h under nitrogen, air or oxygen, compared with that of the PLLA prior to heating. Moreover, no exothermic peaks, corresponding to oxidative decomposition, were observed on the d.s.c. spectra of polylactide up to 400°C, at least before the appearance of the endothermic thermal degradation peak. It is also noteworthy that the optical rotation of PLLA did not vary when the heating temperature was kept below 220°C. However, the specific optical rotation smoothly approached zero, as heating at 240°C was continued for 6 h. A rotation of about 30° was observed at this point.

We cannot discard the possibility of hydrolysis of main-chain ester bonds due to trace amounts of water[24]. However, this possibility proved to be insignificant, since the M_W decrease for a carefully dried sample was similar to that for a conventionally dried one.

To obtain better insight into the degradation mechanism, the product of ring-opening polymerization of L-lactide was purified by repeating precipitation to remove the remaining monomer and catalyst from the polymer, followed by extensive drying. The melt viscosity of the polymer, as measured by a plunger drop method, is plotted in *Figure 9* against temperature. A clear difference between the unpurified and the purified polymer is evident. A similar tendency was also observed with change in M_W (*Figure 10*).

Two reasons may be given for the purification-enhanced thermal stability of polylactide: the removal of catalyst

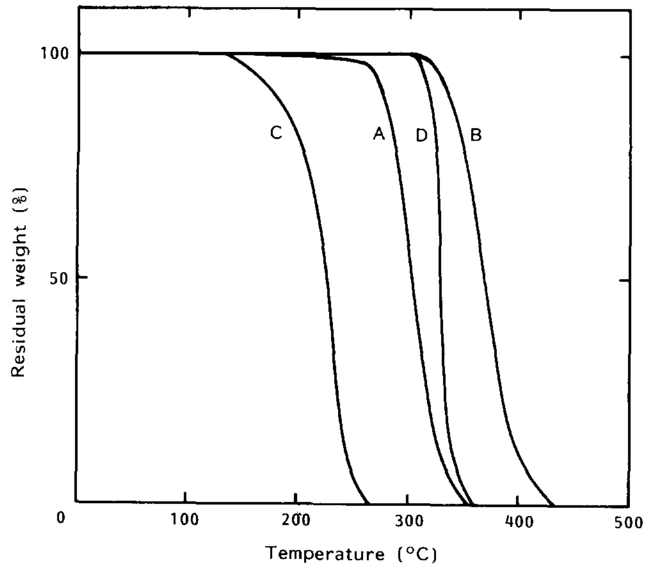
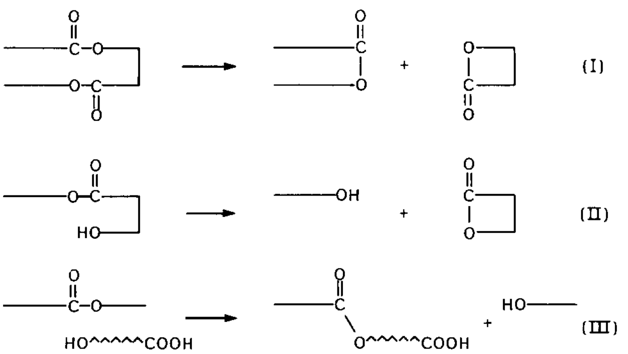


Figure 13 Effect of stannous octoate and end-group capping of poly-L-lactide on thermogravimetric analysis running at 5°C min^{-1} in N_2: A, purified; B, purified and acetylated; C, purified and 5 wt% stannous octoate added; D, purified, acetylated, and 5 wt% stannous octoate added

and the removal of monomer. To examine the former effect, we added 5 wt% of stannous octoate catalyst to the purified polymer and again heated the samples at different temperatures. The weight loss determined by t.g.a. is shown in *Figure 11*. Clearly, the thermal degradation is accelerated by addition of the catalyst, even at temperatures as low as 160°C. This indicates that the catalyst has a strong effect on thermal degradation. Therefore, the remarkable weight loss observed at high temperatures for the purified polymer (*Figure 12*) can also be explained in terms of the catalyst. A trace amount of catalyst must still remain unremoved, although the polymer was subjected to the purification procedure. The effect of the residual monomer on thermal degradation is difficult to study, because monomer may again be produced upon heating the polymer, even if monomer had been completely removed from the starting polymer.

It is also not easy to examine in detail the transesterification reactions which might lead to M_W reduction. The main reactions for the thermal degradation of polylactides may be represented as:



Reaction I, resulting in the formation of monomer and cyclic oligomers, is catalysed by the polymerization catalyst, as discussed above. Reactions II and III are brought about by the terminal hydroxyl groups of the same chain or of monomeric and oligomeric acids produced by eventual hydrolysis of their precursors^{25}.

Reactions I and II lead to the production of low M_W compounds which will evaporate due to the high temperature. Therefore, a reduction in weight of the polymer should be easily observed. On the other hand, the random scission nature of reaction III suggests that a sharp drop in M_W will occur. Removal of the low M_W compounds, as well as the polymerization catalyst in reaction I, will most likely suppress these degradative reactions. Deactivation, however, of the hydroxyl end-group seems necessary to stop reaction II. Therefore, we attempted to study the effect of end blocking of the purified polymer. The result is shown in *Figure 10*. Obviously, acetylation inhibits the thermal degradation of the purified polymer to a significant extent. Weight loss at high temperatures should also be inhibited by acetylation. *Figure 13* shows that the thermal degradation is effectively slowed down by the acetylation, as expected.

In conclusion, the residual catalyst influences the thermal degradation of polymer by catalysing reaction I, while end blocking and purification of the polymerization product may stop reactions II and III, respectively, leading to an increase in thermal stability of the polymer.

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