Thermal stability of poly(lactic acid) before and after γ-radiolysis

A Babanalbandi, DJT Hill,* DS Hunter and L Kettle

Polymer Materials and Radiation Group, Department of Chemistry, University of Queensland, Brisbane, QLD 4072, Australia

Abstract: The thermal degradation of poly(lactic acid) has been studied using thermal gravimetric analysis over the temperature range 300–700 K, and following a sterilization dose of 50 kGy under vacuum, nitrogen or air. Isothermal weight loss studies have been found to follow complex kinetics with activation energies determined by the MacCallum method for various fractional conversions in the range 72–103 kJ mol^{-1}. Dynamic thermogravimetric analysis at heating rates from 10 to 25 K min^{-1} showed the maximum rate of weight loss occurs in the range 550–650 K with the onset of degradation being in the range 450–500 K. The thermograms observed for the unirradiated polymer under a nitrogen atmosphere showed a very small shoulder on the low temperature side of the thermograms. The Kissinger expression, which is based on the temperature for the maximum rate of weight loss, yielded an activation energy of 109 kJ mol^{-1} for thermal degradation under nitrogen and 131 kJ mol^{-1} under oxygen. Compared with those of unirradiated samples, the weight-loss profiles under nitrogen for samples irradiated under vacuum or nitrogen were shifted towards higher temperatures, but the profiles for the samples irradiated in air did not change significantly. The shift to higher temperatures for the former two samples was attributed to modification of chain-end hydroxyl groups.
© **1999 Society of Chemical Industry**

INTRODUCTION

Poly(lactic acid) (PLA) and the copolymers of lactic acid with glycollic acid are biodegradable materials. Thus they have attracted considerable recent interest for a variety of applications, including those as broad as those of packaging materials and matrices for delivery of bio-active compounds. In some applications the polymers may be subjected to a sterilization dose of high-energy radiation, such as γ-radiation. It is therefore of interest to identify any changes in the polymer properties following γ-radiolysis, including changes in the thermal stability of the polymer.

The thermal degradation of PLA has been investigated by several workers[1–8] under a variety of experimental conditions, and it has been found to undergo thermal degradation in the temperature range 610–640 K with a reported activation energy in the range 92–117 kJ mol^{-1}. The degradation process has been reported to be a single-stage type, with lactide the major decomposition product.[2,4,6,7] However, it has also been reported that residual polymerization catalyst can accelerate the degradation, particularly if hydroxyl end-groups are present, leading to a two-stage degradation process.[6]

In PLA there are three chain linkages in the polymer which are all vulnerable to thermal scission; the —CH—O— linkage, the —CH—CO— linkage and the —CO—O— linkage. McNeill and Leiper[7,8] have postulated that the main route for degradation in an inert atmosphere is via a non-radical ester interchange reaction involving hydroxyl chain-ends. Kopinke *et al*[6] have also concluded that the major pathway for degradation involves an intramolecular transesterification reaction to form lactide. However, Gupta and Deshmukh[4] argued that the —CO—O— bond is the most likely site for chain scission, and that cleavage of this bond in air or oxygen would increase the total number of carbonyl end-groups in the polymer.

The γ-radiolysis of PLA under vacuum has been extensively studied by Babanalbandi and co-workers.[9,10] Radiolysis of PLA under vacuum was found to result in a loss of ester groups with the formation of new saturated and unsaturated aliphatic chain-ends, as well as chain-end aldehyde groups. The *G* value for chain scission was found to be 2.3, and the stable radicals observed at 300 K were reported to be alkyl chain radicals. These alkyl radicals would react with oxygen in air to form peroxy radicals, which could subsequently decompose to form carbonyl groups and other new functionalities in the polymer chains. Thus

radiolysis of PLA in air could lead to the formation of new chain-ends which could provide sites for the initiation of thermal degradation.

In the present work the thermal sensitivity of PLA under nitrogen following radiolysis under vacuum, in nitrogen and in air at 300 K have been examined using thermogravimetric analysis. These results have been compared with those obtained in corresponding studies on the unirradiated polymer under nitrogen and oxygen atmospheres.

EXPERIMENTAL
Materials

The poly(L-lactic acid) used in this study was obtained from Boehringer Ingelheim of Germany. Before use the polymer was powdered under a nitrogen atmosphere using a cryoscopic grinder. XPS studies on the polymer used in the study showed no evidence for the presence of any residual tin-based polymerization catalyst. Samples for γ-radiolysis were prepared in sealed glass ampoules, except for the experiments which were performed in air, in which case the ampoules were not sealed. For radiolysis under vacuum, the samples were evacuuated to a pressure less than 10^{-2} Pa for a period of 24h before the ampoules were sealed. The γ-radiolyses were carried out at ambient temperature using a ^{60}Co AECL Gammacell.

Thermogravimetric analysis

The thermally-induced weight loss for samples of PLA of approximately 5 mg were studied using a Perkin Elmer TGA7 thermogravimetric analyser. The experiments were conducted under a nitrogen or oxygen gas flow of $40 \, cm^{-3} \, min^{-1}$ over a range of heating rates from 10 to $25 \, K \, min^{-1}$. Derivative thermograms (DTG) were obtained using the Perkin Elmer TGA7 multi-tasking software kit.

RESULTS AND DISCUSSION
Isothermal study

The fractional isothermal weight loss X for unirradiated PLA was measured as a function of the degradation time t at 453, 473, 493, 513, 533 and 553 K. The plots of the fraction of polymer remaining $(1-X)$ versus time are shown in Fig 1. It can be seen that the weight reduction increases with temperature and time.

It was found that the weight-loss curves were not adequately explained by any simple kinetic model. Therefore, to calculate the activation energy E for the thermal weight loss process, the method recommended by MacCallum and co-workers[11–15] was used, according to whom the time t for a given fractional weight loss X can be expressed as a function of the temperature T through eqn (1) in which $F(1-X)$ is an undefined function of the conversion, A is a constant
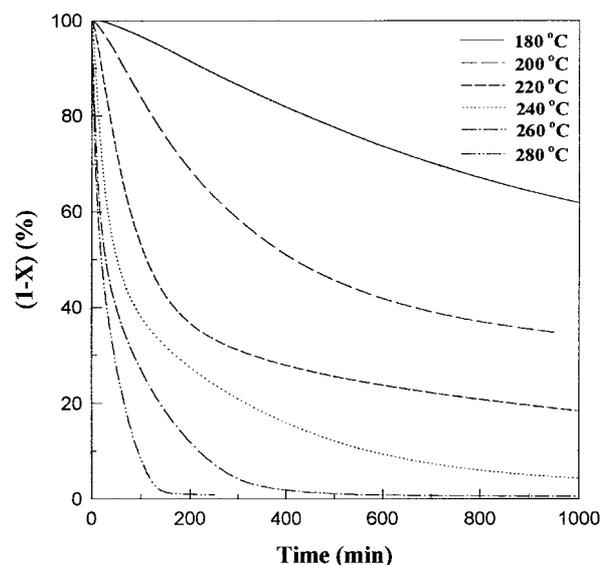
Figure 1. Isothermal weight loss curves for PLA, $(1-X)$%, versus time, at 180, 200, 220, 240, 260 and 280 °C (from top to bottom).

and R is the universal gas constant.

$$\ln(t) = \ln(F(1-X)) - \ln(A) + E/RT \qquad (1)$$

The data obtained at the various temperatures for a series weight loss fractions between 0.25 and 0.80 were fitted to eqn (1) using a regression analysis (see Fig 2) from which estimates of the activation energy were found. The values of E obtained for several weight-loss fractions are given in Table 1. (Values are not reported here for smaller weight-loss fractions because of the presence of the small shoulder in this region of the thermograms.) The estimates of the activation energies decrease initially as the weight loss
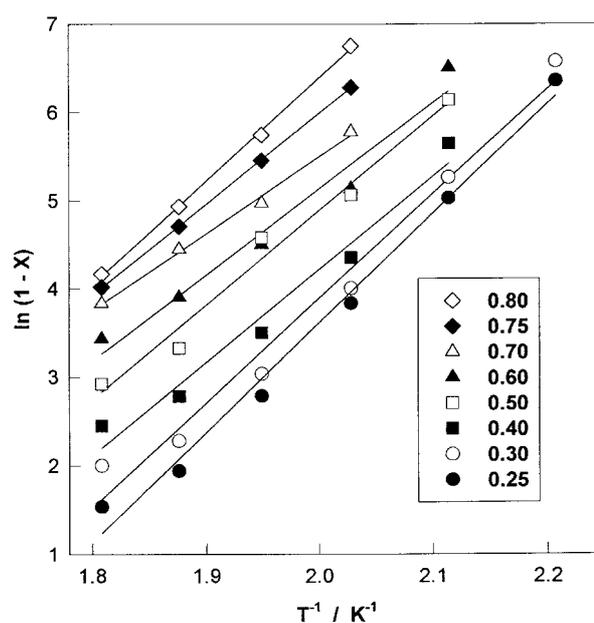

Figure 2. Activation energy plots for isothermal weight loss for unirradiated PLA according to eqn (1).

**Table 1.** Activation energies (*E*) for various weight loss fractions (*X*) under nitrogen for unirradiated PLA

X	*E* (kJ mol^{-1})
0.25	103
0.30	99
0.40	87
0.50	89
0.60	81
0.70	72
0.75	86
0.80	97

Figure 3. (A) TGA curves for unirradiated PLA. Duplicate studies under nitrogen (—, ··—··) and under oxygen (····). Heating rate 10 K min^{-1}. (B) DTG curves for unirradiated PLA under nitrogen (—) and oxygen (– – –). Heating rate 10 K min^{-1}.

fraction increases, as shown in Table 1, but at weight-loss fractions greater than 0.7 the values tend to increase. These observations are consistent with the complex nature of the weight-loss process, which is characterized by a continuously changing sample composition. The values for the activation energies given in Table 1 are lower than those reported previously by McNeill and Leiper[7] of 119 kJ mol^{-1} and Kopinke *et al*[6] of 110 kJ mol^{-1}, but these literature values were calculated using the assumption that the degradation reaction is first order in the early stages, even though there is good evidence that the degradation process follows more complex kinetics,[6] even at low conversions.

Dynamic thermal analysis

Dynamic thermogravimetric measurements on PLA were carried out under nitrogen at heating rates of 10, 15, 20 and 25 K min^{-1}. Typical thermograms are shown in Fig 3A for a heating rate of 10 K min^{-1}. Duplicate measurements under nitrogen showed good reproducibility (Fig 3) with evidence for a very small shoulder on the low temperature side of the major decomposition curve, which could be indicative of a two-stage process. The DTG curve corresponding to one of the weight-loss curves in Fig 3A is shown in Fig 3B where it is shown that the temperature at the maximum rate of degradation was 627 K for a heating rate of 10 K min^{-1}, which compares favourably with a value for PLA of 623 K reported by Kopinke *et al*[6] for a heating rate of 5 K min^{-1} in an inert atmosphere. However, the DTG curve in Fig 3B showed no evidence for a significant low temperature contribution from a first-stage process, and certainly there is no clear maximum in the DTG curve at 569 K for the first-stage process reported by Kopinke *et al*,[6] which they attributed to a catalysed degradation reaction associated with the presence of some residual polymerization catalyst.

Dynamic TGA measurements on unirradiated PLA were also carried out under an oxygen atmosphere at heating rates of 10, 15, 20 and 25 K min^{-1}. A typical thermogram is shown in Fig 3A for a heating rate of 10 K min^{-1}, and the corresponding DTG curve is
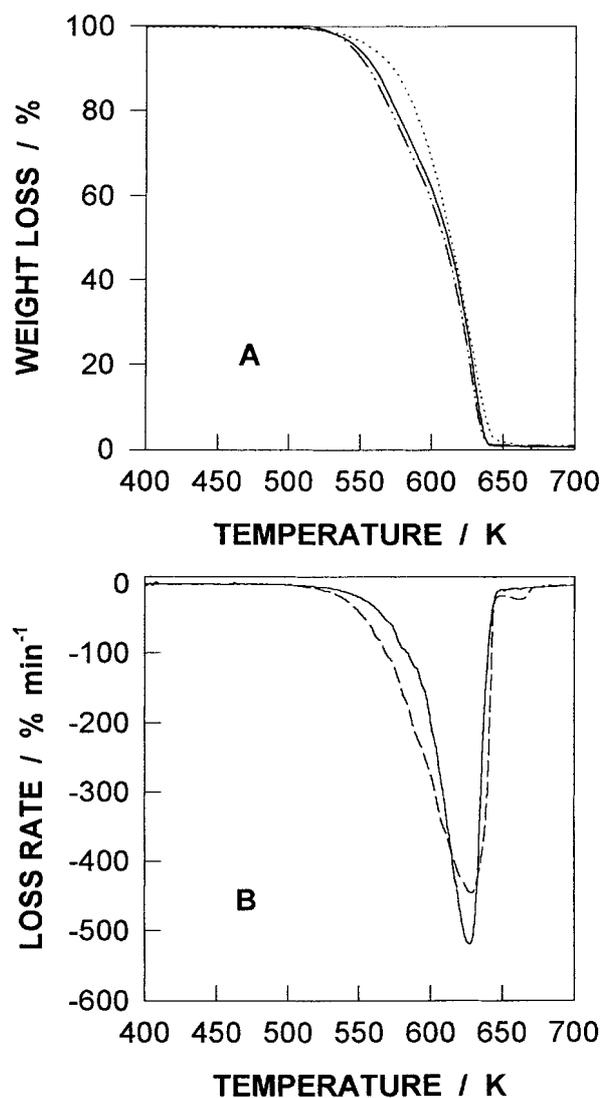
shown in Fig 3B. The curves in Fig 3 show that although the degradation under oxygen is initiated at a lower temperature than that under nitrogen, the temperature at the maximum rate of degradation (629 K) is close to that observed under nitrogen, suggesting that polymer oxidation does not play the major role in initiation of degradation. This observation is supported by the previous work of McNeill and Leiper[7] who observed that the temperatures for the maximum rates of degradation in nitrogen and air were similar.

The Kissinger method[16,17] for analysis of the DTG data obtained at the various heating rates was used to estimate the activation energy for the degradation reaction. The Kissinger expression[16] is

$$\ln\left(\frac{r}{T_{\mathrm{m}}^2}\right) = \ln\left(\frac{nRAW_{\mathrm{m}}^{n-1}}{E}\right) - \frac{E}{RT_{\mathrm{m}}} \qquad (2)$$

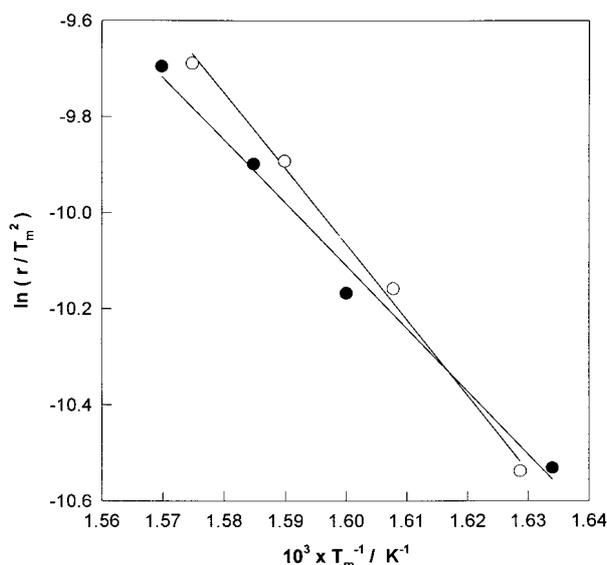where *r* is the heating rate in the TGA experiment, T_{m} is the temperature at the maximum rate of weight

Figure 4. Activation energy plots for unirradiated PLA according to the Kissinger relationship: nitrogen (●); oxygen (○).

Figure 5. TGA plots for PLA following γ-radiolysis. Heating rate $20\,\mathrm{K\,min^{-1}}$ under nitrogen.

reduction, R is the universal gas constant, E is the activation energy, A is the pre-exponential factor, W_m is the weight of the sample at the maximum rate of weight loss, and n is the apparent kinetic order of the degradation reaction.

The values of the activation energy for the degradations under nitrogen and oxygen were obtained from the linear regression plots of $\ln (r/T_m^2)$ versus $1/T_m$ shown in Fig 4. The values obtained from these plots were $109\,\mathrm{kJ\,mol^{-1}}$ for nitrogen and $131\,\mathrm{kJ\,mol^{-1}}$ for oxygen. These values are somewhat higher than those found from the isothermal measurements. However, the maximum rates of degradation occur at high weight-loss fractions, and therefore must be considered to be somewhat unrepresentative of the degradation process at lower weight-loss fractions. The isothermal studies showed that the activation energy tends to increase as the weight-loss fraction increases beyond 70%; thus the activation energies obtained from the Kissinger analysis support these observations. Kopinke *et al*[6] have also previously observed that the activation energy increases at higher degradation fractions, and they report values in the range $190–270\,\mathrm{kJ\,mol^{-1}}$.

Irradiated samples

Thermogravimetry measurements on irradiated samples of PLA (absorbed dose 50 kGy) were carried out at heating rates of 10, 15, 20 and $25\,\mathrm{K\,min^{-1}}$. Typical thermograms for samples which were irradiated under vacuum, nitrogen and air are shown in Fig 5 for heating rates of $20\,\mathrm{K\,min^{-1}}$. The thermograms for the samples irradiated under vacuum and nitrogen were almost identical, but they were shifted towards higher temperatures compared with the curve for an unirradiated sample. In addition, the comparision shows that the small shoulder on the low temperature side of
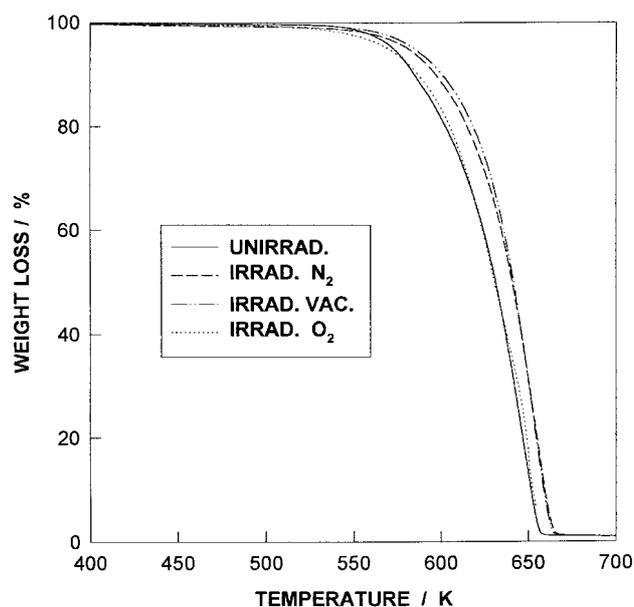
the latter curve is absent in the curves for the irradiated samples.

The absence of the shoulder and the shift of the TGA curves towards higher temperatures for the irradiated samples suggests that the radiolysis has removed those species which are responsible for initiation of the thermal degradation process at lower temperatures. Previous studies on the radiolysis of PLA[9,10] have demonstrated that it undergoes chain scission on γ-radiolysis, with the loss of ester links and the evolution of CO and CO_2. In addition, a range of new saturated and unsaturated chain-ends have been identified following radiolysis, but it is apparent that these new chain-ends are incapable of premature initiation of any thermal degradation reaction.

McNeill and Leiper[7] have observed that acetylation of the hydroxyl chain-end groups in PLA shifts the degradation endotherm by 26 K towards higher temperature. This shift is comparable with the 10–15 K shift observed here for the dynamic TGA curves following γ-radiolysis, suggesting the possibility that the γ-radiolysis causes a loss or modification of the chain-end hydroxy groups, so stabilizing the polymer.

The activation energies for the thermal degradation of PLA following radiolysis in vacuum and nitrogen were determined using the Kissinger method. The Kissinger plots are shown in Fig 6, from which the activation energy following vacuum radiolysis was found to be $111\,\mathrm{kJ\,mol^{-1}}$ and following radiolysis under nitrogen, $119\,\mathrm{kJ\,mol^{-1}}$. These values are of similar magnitudes to the values found for the unirradiated polymer using the same method of analysis.

The thermograms for samples irradiated in air were similar to those obtained for the unirradiated polymer under oxygen. There was no significant shift in the curves towards higher temperatures following radiolysis. This observation is probably a result of the
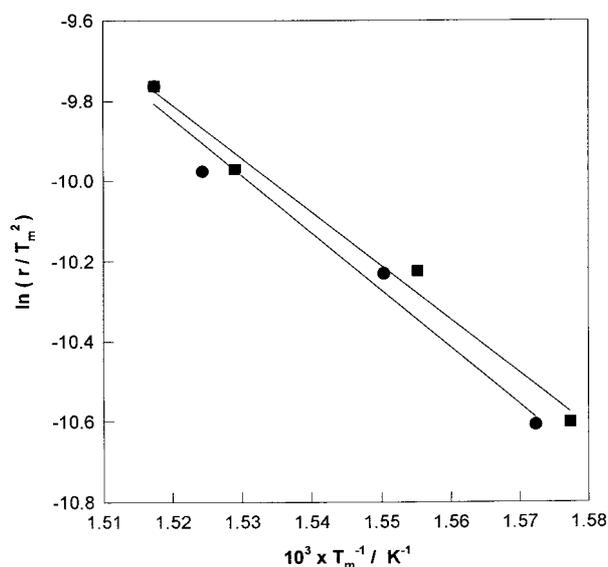
Figure 6. Activation energy plots according to the Kissinger relationship: irradiated under nitrogen (●) and undes vacuum (■).

formation of peroxy radicals and a variety of other new thermally sensitive groups during the radiolysis process in air. Thus, although the chain-end hydroxyl groups initially present may have been modified by the radiation, some of the new groups introduced in the polymer chains would appear to be capable of initiating degradation reactions.

Thus radiolysis of PLA with a sterilization dose of 50 kGy under vacuum or nitrogen at ambient temperature increases the thermal stality of the polymer by approximately 10–15 K, but radiolysis in air had little or no effect on its overall thermal stability.

CONCLUSIONS

The isothermal degradation of PLA over the conversion range 25–80% was found to have an activation energy in the range 72–103 kJ mol^{-1}, and a dynamic TGA study showed little difference between the thermal weight-loss curves under nitrogen and oxygen.

Following the γ-radiolysis of PLA under vacuum or nitrogen, the TGA curves were shifted towards higher temperature; thus has been attributed to the modification of hydroxyl chain-end groups. However, γ-radiolysis in air did not result in a comparable shift in the TGA curves and this was attributed to the formation of peroxides during the radiolysis.

REFERENCES
1 Schindler A and Harper D, *J Polym Sci Polym Chem Edn* **17**:2593 (1979).
2 Gilding DK and Reed AM, *Polymer* **20**:1459 (1979).
3 Gupta MC and Deshmukh VG, *Colloid Polym Sci* **260**:308 (1982).
4 Gupta MC and Deshmukh VG, *Colloid Polym Sci* **260**:514 (1982).
5 Gupta MC and Deshmukh VG, *Polymer* **24**:827 (1983).
6 Kopinke F-D, Remmler M, Mackenzie K, Moder M and Wachsen O, *Polym Degrad Stab* **53**:329 (1996).
7 McNeill IC and Leiper HA, *Polym Degrad Stab* **11**:267 (1985).
8 McNeill IC and Leiper HA, *Polym Degrad Stab* **11**:309 (1985).
9 Babanalbandi A, Hill DJT, O'Donnell JH, Pomery PJ and Whittaker AK, *Polym Degrad Stab* **50**:297 (1995).
10 Babanalbandi A, Hill DJT and Whittaker AK, *Polym Degrad Stab* **58**:203 (1997).
11 MacCallum JR, in *Comprehensive Polymer Science*, vol 1, Thermogravimetric Analysis, Ed by Allen G and Bevington JC, Pergamon, Oxford, p 903 (1988).
12 MacCallum JR and Write WW, *Polym Degrad Stab* **3**:397 (1981).
13 Atkinson J and MacCallum JR, *Eur Polym J* **8**:809 (1972).
14 MacCallum JR and Tanner J, *Eur Polym J* **6**:970 (1970).
15 MacCallum JR and Tanner J, *Eur Polym J* **6**:1033 (1970).
16 Kissinger H, Mronga S and Gemmecker G, *Magn Reson Chem* **29**:527 (1991).
17 Cheng HN, in *Modern Methods of Polymer Analysis*, Ed by Barth HG and Mays JW, Wiley, New York. p 409 (1991).