Radiation effects on poly(lactic acid)

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The effect of γ-irradiation on poly(lactic acid), PLA, synthesized by the solution polymerization of lactic acid in air and N_2 atmosphere, is studied. From the intrinsic viscosity and average molecular weight data of γ-irradiated samples, radiation chemical yields $G(s)$ and $G(x)$ for chain scission and crosslinking respectively were determined. Results indicate that the presence of air causes a decrease in both chain scission and crosslinking. Furthermore, the melting temperature decreased with dose and by using the Flory equation, the value of G (crystalline units) was estimated in air and N_2 atmosphere as 19 and 14 respectively.

Keywords Poly(lactic acid); crosslinking; chain scission; radiation degradation; radiochemical yields; crystallinity change

INTRODUCTION

Poly(lactic acid) (PLA) is known to be a biologically active compound[1]. It has found its use as a biodegradable implant material[2,3] in dentistry[4], orthopaedics[5,6], drug delivery[7], and biodegradable synthetic suture material in surgery[8]. However, the material is hydrolytically unstable. There is very little information available in open literature regarding the molecular, compositional and morphological structure of this polymer, but some data is available within the classified and patented literature.

The thermal and hydrolytic stability of this polymer has been studied by many workers[9–13] and it is found to undergo random chain scission. T.g.a./d.t.a. studies reveal that in presence of air, PLA undergoes thermal oxidative degradation with an activation energy of 22–28 kcal mol^{-1}. It is also observed that during thermal oxidative degradation, the molecular weight changes due to the scission of bonds at various weak links and chain stiffening of chains occur due to the reduction in the number of polyester linkages. Gilding *et al.*[13] studied biodegradable polymers for use in surgery and their studies included g.p.c., d.s.c., t.g.a. and n.m.r. techniques and concluded that through degradation lactide is the product. In order to use the sutures in surgery, sterilizing effects of γ-rays on polyglycollide (PGA) sutures were also studied by Gilding *et al.*[13].

During studies on the radiation degradation of polymers which have oxygen atoms in the main chain, e.g. polyoxymethylene[14], it has been reported that these polymers exhibit exceptionally high sensitivity to radiation [$G(s)=11.1$]. Similar studies on the polymers containing oxygen in the backbone have also been made[15]. It is observed that the quaternary C atom plays an important role during the radiation degradation of such biodegradable polymers. Thus it was considered to be of some interest to study the effects of radiation on PLA and the results are reported here.

EXPERIMENTAL

Polymer preparation

Poly(lactic acid) (PLA) was synthesized by solution polymerization of lactic acid catalysed with zinc oxide[10,12]. PLA was separated from the catalyst by repeated solutions in benzene and precipitation in ethanol and dried in dry air. ($[\eta]^{30}=16\,\mathrm{cm^3\,g^{-1}}$ in benzene, melting temperature 148°C and average molecular weight 6340.)

γ-Ray irradiation

Powdered dry PLA samples in a pyrex glass tube open at one end, irradiated in a Co^{60}-γ source (Gamma cell 900 supplied by BARC, Bombay, India) at room temperature, at a dose rate of 2.6×10^{-3} MGy/h in air. The samples were also irradiated in a N_2 atmosphere, the samples were purged in N_2 gas and then sealed.

Number average molecular weight (end group analysis)

The number average molecular weight ($\bar{M}_n$) was determined by end group analysis of carboxyl group contents as reported[10].

Intrinsic viscosity and molecular weight

The intrinsic viscosities $[\eta]\,\mathrm{cm^3\,g^{-1}}$ in benzene at 30 ±0.1°C were measured by Tuan–Fuoss Viscometer and converted to viscosity average molecular weight, $\bar{M}_v$, using the relation[16]

$$[\eta]=2.27\times10^{-2}\,\bar{M}_v^{0.75} \tag{1}$$

Equation (1) is expressed in terms of $\bar{M}_n$ as

$$\frac{\bar{M}_v}{\bar{M}_n}=[\Gamma\sqrt{(a+2)}]^{1/a}$$

where a is 0.75 and the equation takes into account the most probable distribution of the molecular weight of the degraded polymer[8].

Evaluation of G(s) *and* G(x)

For a polymer that undergoes chain scission and crosslinking simultaneously, the average molecular weight of the irradiated polymer[8] is expressed in terms of the initial weight average molecular weight $\bar{M}_{w,0}$, or number

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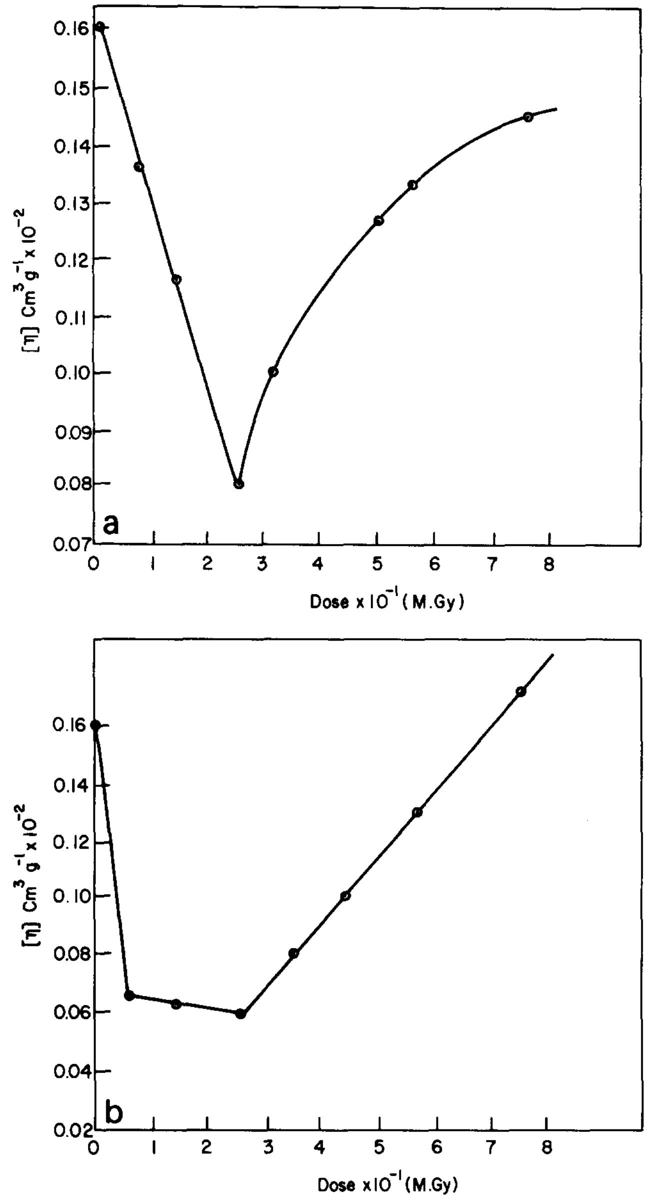

Figure 1 Variation of the intrinsic viscosity with dose: (a) air, (b) nitrogen atmosphere

average molecular weight, $\bar{M}_{n,0}$, the dose D, Avogadro number N_A, $G(s)$ and $G(x)$ where $G(s)$ and $G(x)$ are the G-values of chain scission and crosslinking per 100 eV of energy absorbed[17,18], respectively as follows

$$\frac{1}{\bar{M}_{w,t}}=\frac{1}{\bar{M}_{w,0}}+\frac{[G(s)-4G(x)]D}{200N_A} \qquad (2)$$

and

$$\frac{1}{\bar{M}_{n,t}}=\frac{1}{\bar{M}_{n,0}}+\frac{[G(s)-4G(x)]D}{100N_A} \qquad (3)$$

where $\bar{M}_{w,t}$ and $\bar{M}_{n,t}$ are the weight average and number average molecular weights after the sample is irradiated for time t. Radiation chemical yields for chain scission and crosslinking were determined from the slopes according to the equations (2) and (3).

RESULTS AND DISCUSSION

The intrinsic viscosity decreases rapidly on γ-irradiation in the cases of both air and nitrogen atmospheres and thereafter the intrinsic viscosity increases slowly (see *Figure 1*). Whereas the number average molecular weight as determined by end group analysis decreases rapidly, the viscosity average molecular weight $\bar{M}_{v,t}$ first decreases and then increases. The unexpected rapid fall of $\bar{M}_{n,t}$ rather than $\bar{M}_{v,t}$, suggests that random chain scission is not the primary mechanism of degradation. Even at very low dosages there is dramatic fall in $\bar{M}_{n,t}$; and this indicates that the large number of acid end groups are produced by an unzipping mechanism[13].

At higher dosages $\bar{M}_{v,t}$/or $[\eta]$ increases when the sample is irradiated with γ-rays where crosslinking and chain scission occur simultaneously. However, the continuous fall in $\bar{M}_{n,t}$ (by end group analysis) reveals that the crosslinking at higher dosages is not *via* the –COOH end group but is most probably at the quaternary carbon atom. This could only be if, during degradation, a free radical mechanism is favoured and these free radicals abstract hydrogen atoms at the quarternary C centres.

The plots of $M_{n,0}/M_{n,t}$ vs. D and $M_{v,0}/M_{v,t}$ vs. D are essentially linear (*Figures 2* and *3*). However, in the low

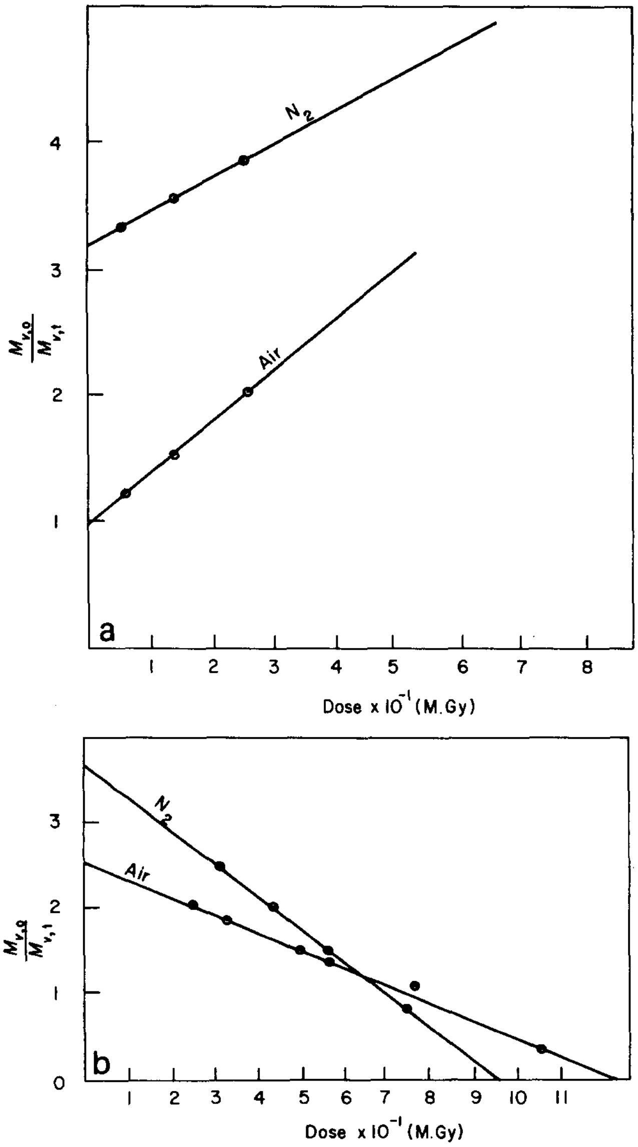

Figure 2 Ratio of the viscosity average molecular weight, $M_{v,0}/M_{v,t}$, as a function of dose: (a) dose<0.25 MGy, (b) dose >0.25 MGy (pregel region)

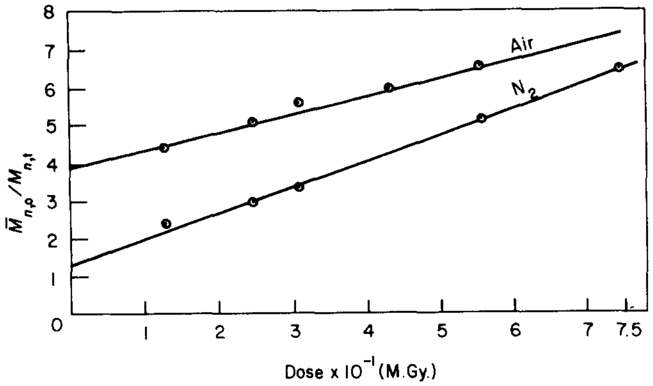

Figure 3 Ratio of the number average molecular weight $M_{n,0}/M_{n,t}$ as a function of dose

Table 1 $G(x)$ and $G(s)$ values in N_2 and air atmosphere

	N_2 atmosphere		Air atmosphere	
	Low dose (<0.25 M Gy)	Pregel region	Low dose (<0.25 M Gy)	Pregel region
$G(s)$	26.5	40.5	14.5	23.0
$G(x)$	4.5	11.0	0.4	6.5

dose region where the most dominant process is chain scission, the departure of the ratio, from 1 (from plot) when $t=0$ and $D=0$ may be due to the different mechanism of the chain scission and due to the change in the relative importance of chain scission and crosslinking as a function of radiation dose. These figures yield 1.23 M Gy and 0.97 M Gy for the gel dose, D_{gel}, in air and nitrogen atmospheres respectively. This indicates that γ-irradiation in nitrogen results in a much larger extent of crosslinking. The values of D_{gel} (from *Figures 2* and *3*) $G(x)$ and $G(s)$ in air and nitrogen atmosphere are recorded in *Table 1*.

On the basis of the results in *Table 1*, it seems that the presence of air (oxygen) causes a decrease in both scission and crosslinking. Also, the ratio of $(M_{v,t}/M_{n,t})$ increases with the dose and this increase indicates that the radiation yields $G(s)$ and $G(x)$ are dose dependent.

The results indicate that the ratio of $G(s)/G(x)$ at low dosages in the case of air is much larger than in the nitrogen atmosphere where as in the pregel region the values are the same. The large value of $G(s)/G(x)$ at low dosages indicate negligible crosslinking in presence of air whereas in nitrogen the extent of crosslinking is much more marked. Thus initially, oxygen may act as free radical scavenger resulting in large chain scission whereas in nitrogen free radical centres will be deactivated by recombination. At higher dosages the same value indicates that the amount of air dissolved in the sample has probably been used up and no further scavenging of free radicals occurs, thereby giving the same ratio of $G(s)/G(x)$. These results clearly establish that radiation degradation is the predominant event.

In the case of PLA there are two sites of cleavage, at the C–O linkage and the oother quarternary carbon atom. It is known that glycosidic (oxygen)[19] links are favoured sites of scission in irradiated cellulose. Golden and Hazell[20] found evidence of cleavage at the ether and quarternary carbon atom in pentone. Pittman *et al.*[12] have suggested that the cleavage at the ester linkage is probably responsible for the low crosslinking in poly(α-hydroxy isobutyric acid) and the cleavage at the quarternary carbon is primarily responsible for the chain scission. Thus we can conclude that PLA undergoes both chain scission and crosslinking which may be due to the cleavage of the ester linkage (increase in COOH end groups) and hydrogen abstraction at the quarternary carbon atom sites.

Effect of radiation on the melting temperature

The melting temperature of the polymer decreases with dose suggesting thereby that the flexibility of the chains increases and the crystallinity decreases[17]. Thus according to the Flory equation, the mole fraction X, of the crystalline units are related to the melting temperature, $T_{m,D}$ at dose D as[21]

$$\frac{1}{T_{m,D}} - \frac{1}{T_{m,0}} = -\frac{R}{\Delta H}\ln X$$

where R and ΔH are the gas constant and the enthalpy of fusion per mole of crystalline units, respectively. The number of crystalline units excluded from the crystal per 100 eV of absorbed energy, G (crystalline units), can be calculated from the relation

$$G\,(\text{crystalline units}) = \frac{(1-X)N_A \times 100}{M \times D}$$

where M, average molecular weight of the repeat unit along the c-axis of the crystalline unit. Thus by plotting a graph of $\frac{1}{T_{m,D}}$ vs. D gives a straight line (*Figure 4*) the slope of which is used to calculate the value of G (crystalline units) and has values of 19 and 14 in air and nitrogen,

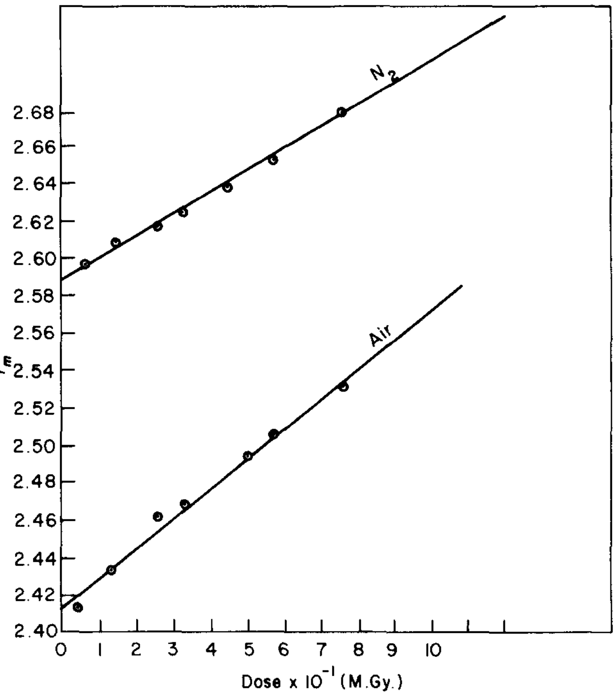

Figure 4 Reciprocal of the melting temperature of the irradiated PLA as a function of dose

respectively. In calculating the G (crystalline units), ΔH has been taken as 1.776 kcal mol^{-1} from the statistical entropy of fusion of similar molecules like POE, (the value of G (crystalline units) for PMMA = 10–30)[17].

Thus in conclusion PLA undergoes chain scission and crosslinking simultaneously in presence of air and nitrogen on irradiation with γ rays at room temperature and there is a decrease in crystallinity on irradiation.

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