

# Degradation of Poly(D,L-lactic acid)-*b*-poly(ethylene glycol) Copolymer and Poly(L-lactic acid) by Electron Beam Irradiation

Peikai Miao,<sup>1,2</sup> Dimeng Wu,<sup>1</sup> Ke Zeng,<sup>1</sup> Chun'e Zhao,<sup>1</sup> Guoliang Xu,<sup>1</sup> Zhifu Huang,<sup>1</sup> Gang Yang<sup>1</sup>

<sup>1</sup>College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Application and Research Center for Electron Beams of College of Polymer-NHVC, Sichuan University, Chengdu 610065, People's Republic of China

<sup>2</sup>Technical R&D Department, R&D Center, Hunan Sokan New Materials Co., Ltd., Ningxiang 410600, People's Republic of China

Received 20 March 2010; accepted 12 August 2010

DOI 10.1002/app.33174

Published online 19 October 2010 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** This article investigated the effects of electron beam (EB) irradiation on poly(D,L-lactic acid)-*b*-poly(ethylene glycol) copolymer (PLEG) and poly(L-lactic acid) (PLLA). The dominant effect of EB irradiation on both PLEG and PLLA was chain scission. With increasing dose, recombination reactions or partial crosslinking of PLEG can occur in addition to chain scission, but there was no obvious crosslinking for PLLA at doses below 200 kGy. The chain scission degree of irradiated PLEG and PLLA was calculated to be 0.213 and 0.403, respectively. The linear relationships were also established between the

decrease in molecular weight with increasing dose. Elongation at break of the irradiated PLEG and PLLA decreased significantly, whereas the tensile strength and glass transition temperature of PLLA decreased much more significantly compared with PLEG. The presence of poly(ethylene glycol) (PEG) chain segment in PLEG was the key factor in its greater stability to EB irradiation compared with PLLA. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 509–517, 2011

**Key words:** biopolymer; crosslinking; degradation; electron beam irradiation; molecular structure

## INTRODUCTION

Biodegradable polymers have received much attention from the standpoints of pharmaceutical and biomedical applications and environmental application. Various properties such as good mechanical property, good biocompatibility, controlled degradability, and good safety are desired for biodegradable medical materials.<sup>1</sup> Poly(D,L-lactic acid)-*b*-poly(ethylene glycol) copolymer (PLEG) and poly(L-lactic acid) (PLLA) are the most widely utilized class of biodegradable and bioabsorbable polymers in the field of biomedical materials and have been used clinically in wound closure, tissue repair and regeneration, and drug delivery.<sup>2–5</sup> PLEG and PLLA are both hydrolytically unstable. Although insoluble in water, they degrade by hydrolytic attack of their ester bonds. Through this hydrolytic attack, random chain scission occurs in the polymeric biomaterial, causing it to degrade into lactic and ethylene glycol for

PLEG and lactic acid for PLLA. In human body, lactic and ethylene glycol enter the tricarboxylic acid cycle and are metabolized and subsequently eliminated from the body as carbon dioxide and water. The rate of degradation of PLEG and PLLA is dependent on their degree of polymer morphology and their glass transition temperature.<sup>6</sup> Conventionally, the degradation rate for these biopolymers is controlled by altering such chemical parameters as comonomer ratio and polymer molecular weight using chemical synthesis method.<sup>7–11</sup> However, this process is time-consuming, complexity of control and needs posttreatment.

Radiation has been known to alter the physical properties of polymers through main chain scission and crosslinking.<sup>12–14</sup> According to the principles of radiation chemistry, free radicals are formed when macromolecules of polymers are excited under ionizing radiation, where they are then free to react with one another or initiate further reactions among the polymeric chains, thus giving rise to changes in material properties. The combination of two radicals leads to crosslinking or recombination in the amorphous and crystalline regions, respectively, whereas chain transfer and the subsequent splitting results in chain scission. Usually, both these processes take place simultaneously for many polymers.<sup>15</sup> Especially, electron beam (EB) irradiation has been well

Correspondence to: G. Yang (yanggang65420@163.com).

Contract grant sponsor: International Cooperative Project with NHV; contract grant number: 08H0783.

known as a convenient, efficient, and environmental friendly tool for modification of polymers through degradation technique. Besides, EB irradiation can cause in parallel sterilization of the materials,<sup>16</sup> which is important for medical applications. Some people have studied the degradation behavior of gamma irradiated PLLA, reporting that PLLA has a high sensitivity to gamma radiation, whose thermal and mechanical properties decrease significantly due to the drastic decrease in the molecular weight.<sup>17–20</sup> Recently, some studies report an approach to control the degradation rate of PLLA and poly(lactide-co-glycolide) (PLGA) using EB irradiation under air atmosphere.<sup>6,15,21–23</sup> The results show that PLLA undergoes chain scission on irradiation but to a lesser degree compared with PLGA, and PLLA is of greater stability to EB irradiation compared with PLGA. Meanwhile, the relationship between irradiation dose and the degradation rate is also established.

It is widely accepted that PLEG and PLLA undergoes hydrolytic degradation, but to our best knowledge, no investigation has been reported so far regarding the differences in the effects of EB irradiation on properties of PLEG and PLLA under nitrogen atmosphere. In this article, average molecular weight ( $M_n$  and  $M_w$ ), mechanical properties, glass transition temperature ( $T_g$ ), and molecular structure were measured as a function of irradiation dose. The radiation chemical yields for chain scission ( $G_s$ ) and crosslinking ( $G_x$ ) were evaluated, and the relationships between the molecular weight and irradiation dose were also established.

## EXPERIMENTAL

### Materials

PLLA was purchased from Shenzhen Brightchina Industry (China). PLEG was synthesized according to our reported method.<sup>12</sup> Poly(ethylene glycol) with molecular weight 6000 (PEG6000) were purchased from Tianjin Bodi Chemical (China). Dichloromethane (DCM) was analytical grade and used without further purification.

The biopolymer films of PLLA and PLEG were prepared by a simple solvent casting method. PLLA and PLEG were first dissolved in DCM at a weight ratio of 1 : 4. Then, the polymer solution was spread over a glass plate to give a wet film. The solvent was evaporated slowly in air at room temperature for 12 h to prevent the formation of air bubbles. Finally, the polymer films were dried in a vacuum oven at 40°C for 36 h. The films were of approximately 50  $\mu\text{m}$  in dry thickness measured using a micrometer screw gauge (Nititoyo, Japan).

### EB irradiations

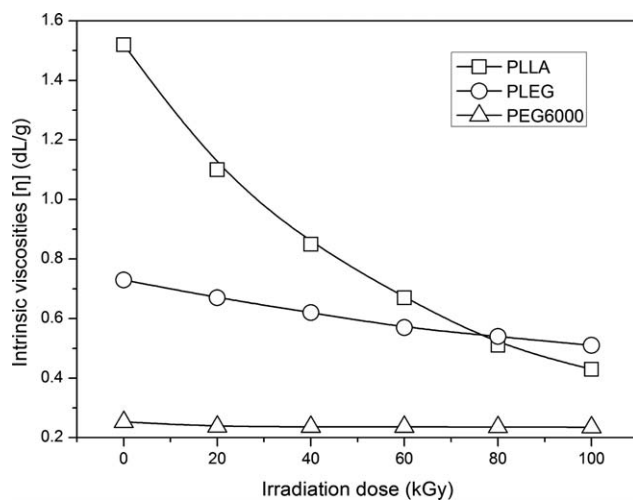
The film samples were irradiated by a Curetron EBC-200-AB-TW EB accelerator (NHV, Japan). The accelerating voltage was 150 kV with a beam current of 5 mA. A transport system was used with a conveyor speed of 27  $\text{m min}^{-1}$ . The dose rate was 20 kGy per pass. The irradiation doses of the samples were calculated by multiplying 20 kGy by the number of passes irradiated. The irradiations of the samples were performed at room temperature under the nitrogen atmosphere with the content of oxygen of less than 100  $\text{mg L}^{-1}$  detected by an instrument on this EB accelerator. About 30  $\text{m}^3$  nitrogen was used during irradiation. The purity of nitrogen was 99.999%, and its flow rate was more than 7  $\text{Nm}^3 \text{h}^{-1}$ . According to the reported literature,<sup>18</sup> the radicals can be decayed completely for at least a week after poly(lactic acid) was irradiated. Therefore, in this work, the irradiated samples were kept in sealed packages at room temperature for at least a week to decay radicals completely and dried in vacuum before measuring the properties.

### Measurements

The intrinsic viscosity  $[\eta]$  was determined at a concentration of 0.125  $\text{g/dL}$  in DCM at 30°C using an Ubbelohde viscometer with capillary diameter of 0.38 mm (Shanghai Shenyi Glass Products, China). Molecular weights were determined by a Waters gel permeation chromatography (GPC). The analyzer was composed of a Waters 1515 isocratic HPLC pump and a Waters 2415 refractive index detector. Samples were dissolved in tetrahydrofuran (THF) at a concentration of 1  $\text{mg mL}^{-1}$ . A Waters Styragel HT 4 THF column (7.8  $\times$  300 mm) with linear range of molecular weight from 5,000 to 600,000  $\text{g mol}^{-1}$  was used in series with HPLC grade THF as eluent at a flow rate of 1.0  $\text{mL min}^{-1}$ . The internal and column temperature were kept constant at 35°C. Calibration was accomplished with polystyrene standards. Molecular weights were determined by Empower 2 software.

According to ISO 1184, mechanical properties were analyzed with a KD III-500 electron tensile testing machine (Shenzhen Kaiqiagli Testing Instruments, China) at room temperature. The rectangular strip-shaped specimens were extended at a cross-head speed of 50  $\text{mm min}^{-1}$ . The tensile property values represented an average of the results from tests run on three specimens. The data were analyzed with KPTest V4.0 controlling software supplied by Shenzhen Kaiqiagli Testing Instruments.

Calorimetric studies were carried out on a DSC Q200 thermal analyzer (TA Instruments) by using nitrogen as a purge gas (50  $\text{mL min}^{-1}$ ) at scan rate



**Figure 1** The relationship of  $[\eta]$  and irradiation dose.

of  $10^{\circ}\text{C min}^{-1}$  from  $-10$  to  $160^{\circ}\text{C}$ . The instrument was calibrated with an indium standard (melting temperature  $156.6^{\circ}\text{C}$ ,  $\Delta H_f = 28.45 \text{ J g}^{-1}$ ), and an empty pan was used as reference. The samples ( $\sim 6$  mg) were tested in hermetic TA aluminum pans. Thermograms were analyzed with Universal Analysis 2000 software (Version 4.4A, TA Instruments).

Attenuated total reflection infrared (ATR-IR) spectra of films were measured on Thermo Nicolet 380 Fourier Transform Infrared Spectrometer (Thermo Electron) at  $4000\text{--}400 \text{ cm}^{-1}$  in air atmosphere. The spectra profile was recorded by using OMNIC software supplied by Nicolet Instrument.  $^1\text{H-NMR}$  spectra were recorded at room temperature using a 300-MHz Bruker spectrometer.  $\text{CDCl}_3$  was used as the solvent; chemical shifts ( $\delta$ ) are given in parts per million using tetramethylsilane as an internal reference.

## RESULTS AND DISCUSSION

### Intrinsic viscosity of irradiated samples

The changes in intrinsic viscosity  $[\eta]$  of PLLA, PLEG, and PEG6000 under EB irradiation are shown in Figure 1. At doses from 0 to 100 kGy, the irradiation caused a drastic decrease in PLLA's  $[\eta]$  from 1.52 to 0.45 dL/g. However, a slight decrease in PLEG's  $[\eta]$  from 0.73 to 0.52 dL/g was observed. Meanwhile, it can be seen that PEG6000's  $[\eta]$  almost did not change as a function of EB irradiation. Therefore, PLEG had a better radiation resistance compared with PLLA mainly due to the PEG6000 chain segment in PLEG.

### Molecular weight of irradiated samples and degree of chain scission and crosslinking

A common phenomenon in radiation-induced processing of polymers is the scission of weaker bonds

in macromolecules. The energy supplied by radiation is absorbed by exposed material and the excited macromolecules are produced. The GPC plots for PLLA and PLEG samples under EB irradiation are shown in Figure 2. The plots suggested several insights into the irradiated samples. First, it can be seen that the retention time of irradiated PLEG and PLLA increased with increasing irradiation dose, which can indicate the reduction of molecular weight. Second, the GPC flow curve of PLEG had a symmetrical peak. After EB irradiation, a small shoulder on the low retention time side of the peak was observed at low dose of 20 kGy, and it increased with increasing dose. This indicated an approximate increase in molecular weight due to the formation of a small amount of crosslinking between PLEG molecular chains. However, for PLLA, no small shoulder on the low retention time side of the peak was observed at doses below 200 kGy. Therefore, irradiation of PLLA caused mainly chain scission, for higher doses, a small shoulder on the low retention time side of the peak was observed. This change was probably attributed to crosslinking reactions of PLLA as a function of high doses, as reported by Gupta and Deshmukh.<sup>17</sup> Although chain scission reactions of the irradiated PLEG occurred at doses of 0–100 kGy, its crosslinking reactions increased with increasing dose. These results were consistent with the reported conclusion that the crosslinking to scission ratio for aliphatic polyesters increased on irradiation as a function of increasing  $-\text{CH}_2-$  to  $-\text{COO}-$  ratios in the main chain.<sup>24</sup>

Figure 3(a,b) plot the number and weight average molecular weight ( $M_n$  and  $M_w$ ) of the irradiated PLEG and PLLA against dose, respectively. The results showed the decrease in average molecular weight with increasing dose. This indicated that chain scission was the dominant process on EB irradiation. It can also be observed that the extent of molecular weight decrease of irradiated PLEG was not so drastic. However, a drastic decrease in molecular weight of irradiated PLEG was observed as a function of dose. These phenomena were accordance with the variation trends of  $[\eta]$  in Figure 1. It could be explained as following two different radiation-induced mechanisms. The decrease in molecular weight was due to backbone main chain scission, where some long polymeric backbone chains broke into shorter chains, because the energy from the radiation exceeded the attractive forces between the atoms.<sup>25</sup> This happened because the excited states dissipated some of the excess energy by bond scission, resulting in the formations of alkyl free radicals in the polymer. Hydrogen abstraction was also a key radiation-induced scission mechanism. Due to a small quantity of oxygen diffused into the polymer,

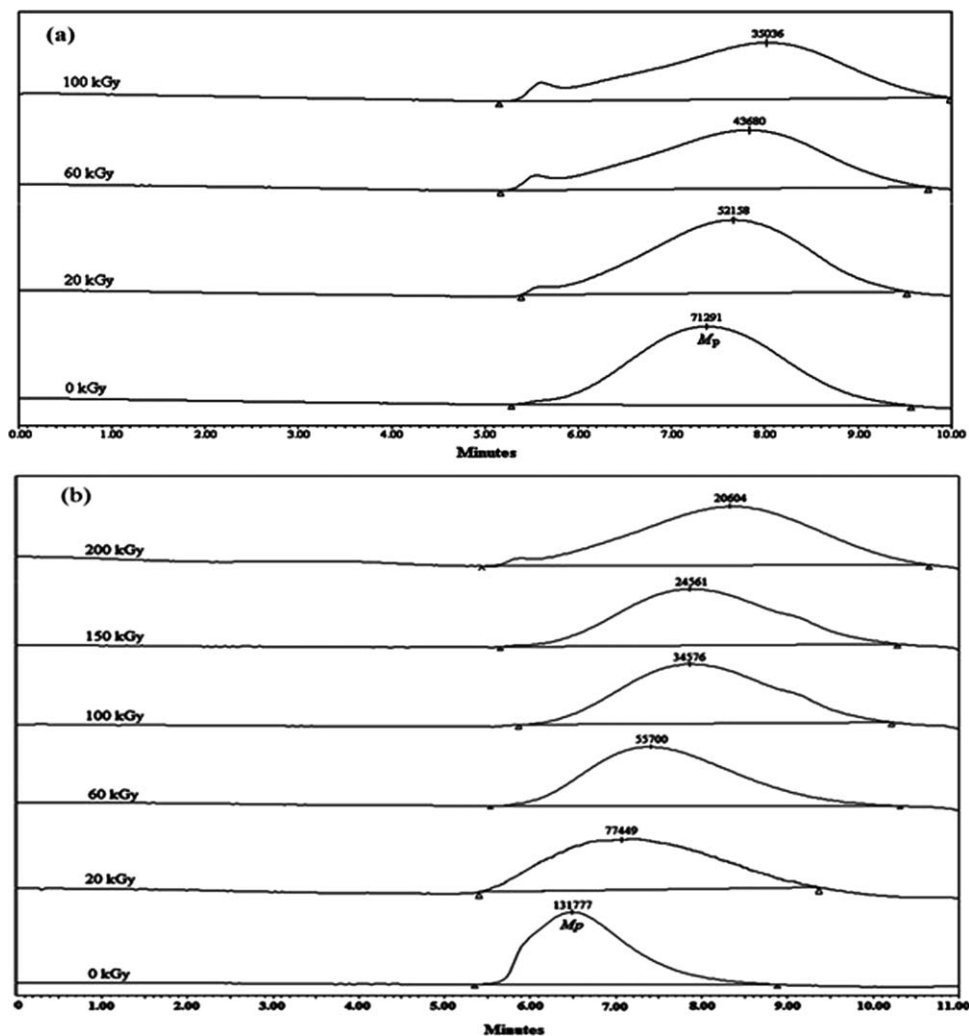
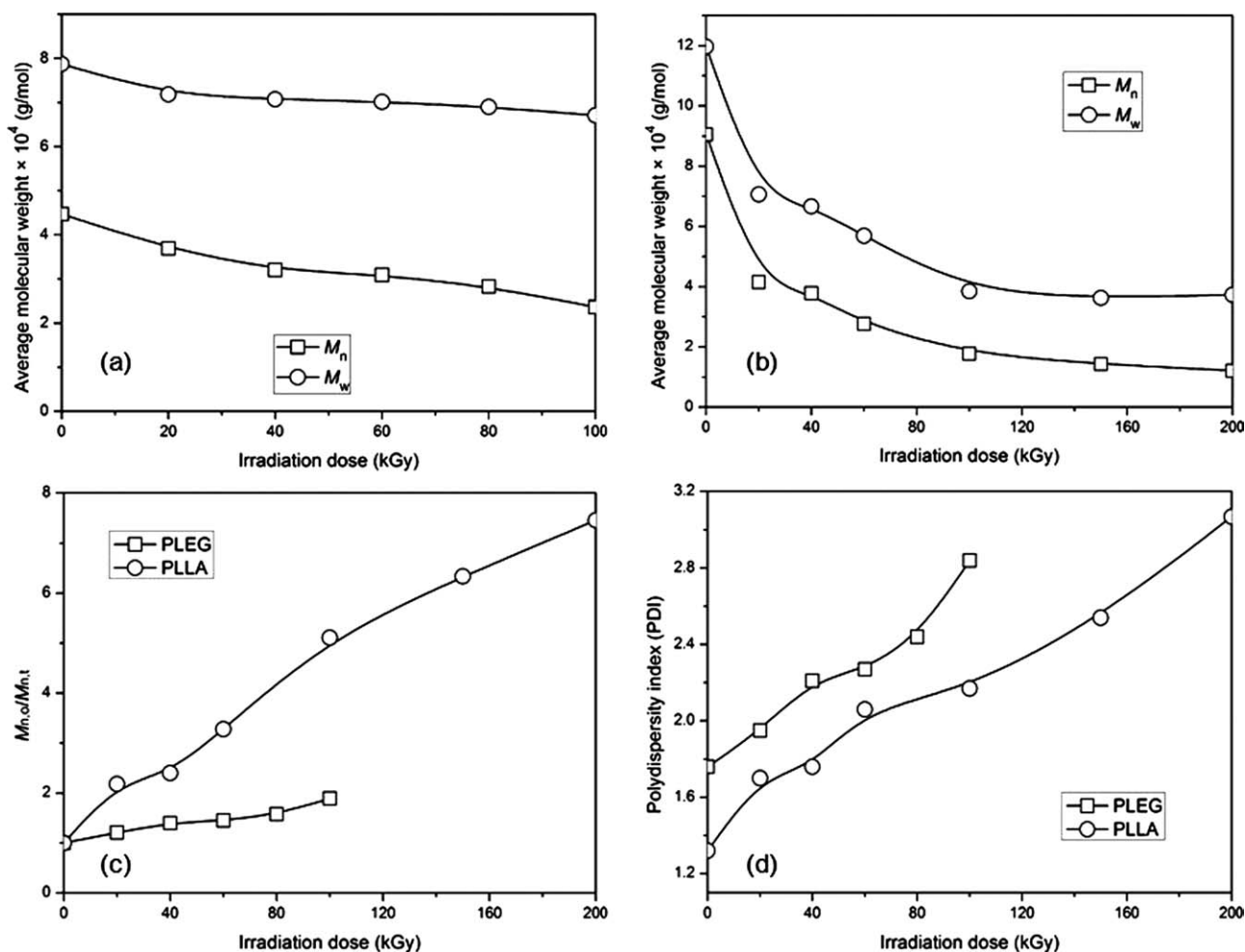


Figure 2 GPC plots of samples irradiated at various doses (a) PLEG and (b) PLLA.

the alkyl free radicals reacted with oxygen to form peroxy free radicals.<sup>26,27</sup> These peroxy free radicals thereby caused chain scission through hydrogen abstraction. Unlike main chain scission, in which a drastic decrease in molecular weight was observed, the decrease in molecular weight by chain scission through hydrogen abstraction was less pronounced. Another possibility was that there was a relative increase of crosslinking to chain scission, which can be confirmed from the GPC plots [Fig. 2(a)]. The number of alkyl free radicals present was larger than the number of peroxy free radicals formed because of limited oxygen diffusion into the polymer. Alkyl free radicals were less effective in causing chain scission compared with peroxy free radicals, and they were more likely to recombine or crosslink in the polymer. Meanwhile, D'Alelio et al. had discussed in detail about the effect of ionizing radiation on a series of saturated polyesters.<sup>24</sup> It had been found that the scission to crosslinking ratio for aliphatic polyesters increased on irradiation as a

function of increasing  $-\text{COO}-$  to  $-\text{CH}_2-$  ratios in the main chain. In our work, the  $-\text{COO}-$  to  $-\text{CH}_2-$  ratios in PLLA main chain was larger than that in PLEG. Therefore, compared with PLEG, PLLA was more prone to chain scission as a function of dose because of the relatively high concentration of ester groups in PLLA backbone.<sup>28</sup>

The  $M_{n,o}/M_{n,t}$  ratio of molecular weight of the unirradiated sample ( $M_{n,o}$ ) to molecular weight of the irradiated sample ( $M_{n,t}$ ) showed the degree of degradation as a function of EB irradiation [Fig. 3(c)]. The deviation of  $M_{n,t}$  from  $M_{n,o}$  implied that a proper degradation had occurred, which resulted in an increase of  $M_{n,o}/M_{n,t}$  ratio. It can also be seen that the degree of degradation of PLLA was much more significant than that of PLEG. Figure 3(d) plots the polydispersity index of PLEG and PLLA against dose. The results showed the increase in polydispersity index for polymer with increasing dose. This was due to the poorer chain uniformity resulting from chain scission and chain branching. Chain



**Figure 3** Changes in the molecular weight and polydispersity indices of samples as a function of irradiation dose, (a) molecular weight of PLEG, (b) molecular weight of PLLA, (c)  $M_{n,o}/M_{n,t}$  and (d) polydispersity indices.

branching arose from the crosslinking or recombination of free radicals.

Ionizing radiation causes the formation and breaking of polymer bonds as a result of intermolecular crosslinking and scission in the polymer. The radiation chemical yields for chain scission ( $G_s$ ) and crosslinking ( $G_x$ ), which is defined as the number of such reactions per 100 electron volts of absorbed energy, therefore determines the extent of chain scission and crosslinking during irradiation. It can be calculated approximately from the following equations<sup>29</sup>:

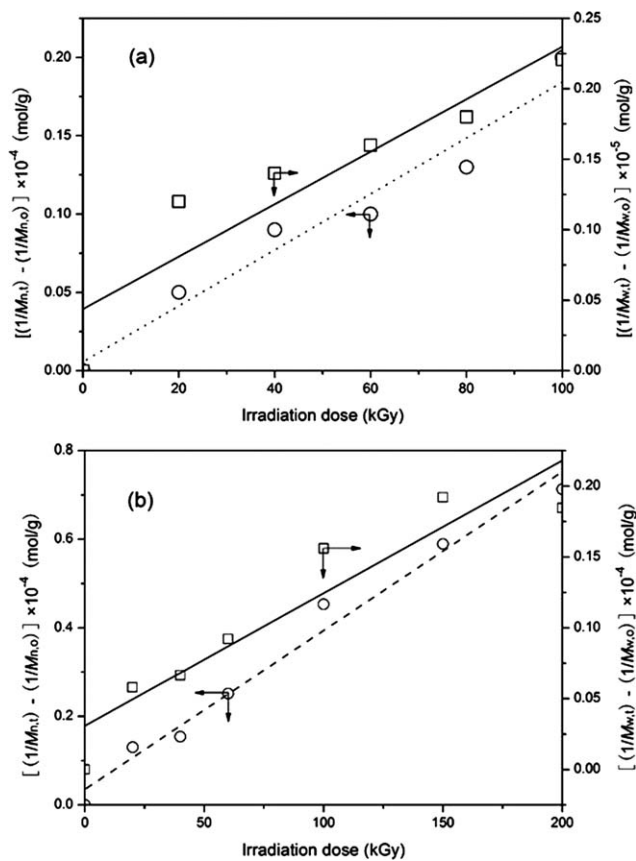
$$1/M_{w,t} = 1/M_{w,o} + (G_s/2 - 2G_x)D \times 1.038 \times 10^{-6} \quad (1)$$

$$1/M_{n,t} = 1/M_{n,o} + (G_s - G_x)D \times 1.038 \times 10^{-6} \quad (2)$$

where  $M_{w,o}$  and  $M_{n,o}$  are the weight and number average molecular weight of copolymer before irradiation.  $M_{w,t}$  and  $M_{n,t}$  are the number average molecular weight after irradiation.  $D$  is irradiation dose (kGy). A ratio of  $G_s/G_x$  greater than 4 would indicate that chain scission is more dominant.<sup>30</sup>

The plots of  $(1/M_{n,t}) - (1/M_{n,o})$  and  $(1/M_{w,t}) - (1/M_{w,o})$  against  $D$  gave linear relationships, as shown in Figure 4. From the slope of line: PLEG:  $1.79 \times 10^{-7}$  and  $1.86 \times 10^{-8}$ , respectively and  $3.59 \times 10^{-7}$  and PLLA:  $9.36 \times 10^{-8}$ , respectively. The values of  $G_s$  and  $G_x$  for irradiated PLEG and PLLA were obtained by using eqs. (1) and (2) and tabulated in Table I. The large  $G_s/G_x$  ratios, from Table I, further illustrated the dominance of chain scission in irradiated PLEG and PLLA samples, and this thereby increased the solubility of these polymers in DCM after EB irradiation.

The ratio of  $G_s/G_x$  differed for PLEG and PLLA, as shown in Table I. The results showed that PLLA had a higher  $G_s/G_x$  ratio compared with PLEG, indicating that PLLA was more susceptible to EB irradiation degradation than PLEG under nitrogen atmosphere. This can be explained in terms of their different structure, because PLEG contained long PEG chain segment, which had the ability of radiation resistance as a function of dose (Fig. 1).



**Figure 4** Plots of  $(1/M_{n,t}) - (1/M_{n,o})$  and  $(1/M_{w,t}) - (1/M_{w,o})$  of PLEG and PLLA against irradiation dose (a) PLEG and (b) PLLA.

Therefore, this factor played an important role in reducing the extent of EB degradation in PLEG.

When the reciprocal of number of average molecular weight was plotted against dose, as required in the calculation for  $G_s$  and  $G_x$ , a strong linear sample correlation coefficient of 0.98 and 0.99 for PLEG and PLLA respectively, was obtained (Fig. 4). This meant that the decrease in number average molecular weight can be quantified accurately with respect to dose. Using this linear equation, the change in  $M_{n,t}$  in terms of irradiation dose for this copolymer can be accurately determined. The equations obtained for PLEG [eq. (3), 0–100 kGy] and PLLA [eq. (4), 1–200 kGy] are as follows:

$$1/M_{n,t} = 1/M_{n,o} + (1.79D + 5.71) \times 10^{-7} \quad (3)$$

**TABLE I**  
Chain Scission ( $G_s$ ) and Crosslink ( $G_x$ ) Radiation Yields of EB Irradiated PLEG and PLLA

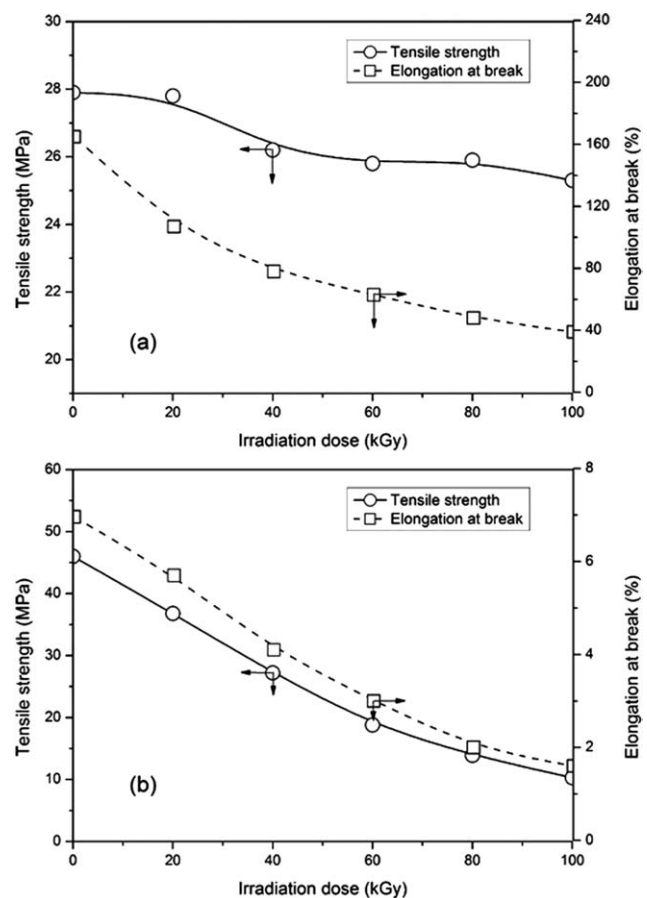
Polymer	$G_s$	$G_x$	$G_s/G_x$
PLEG	0.213	0.043	4.95
PLLA	0.403	0.053	7.60

$$1/M_{n,t} = 1/M_{n,o} + (0.36D + 3.54) \times 10^{-6} \quad (4)$$

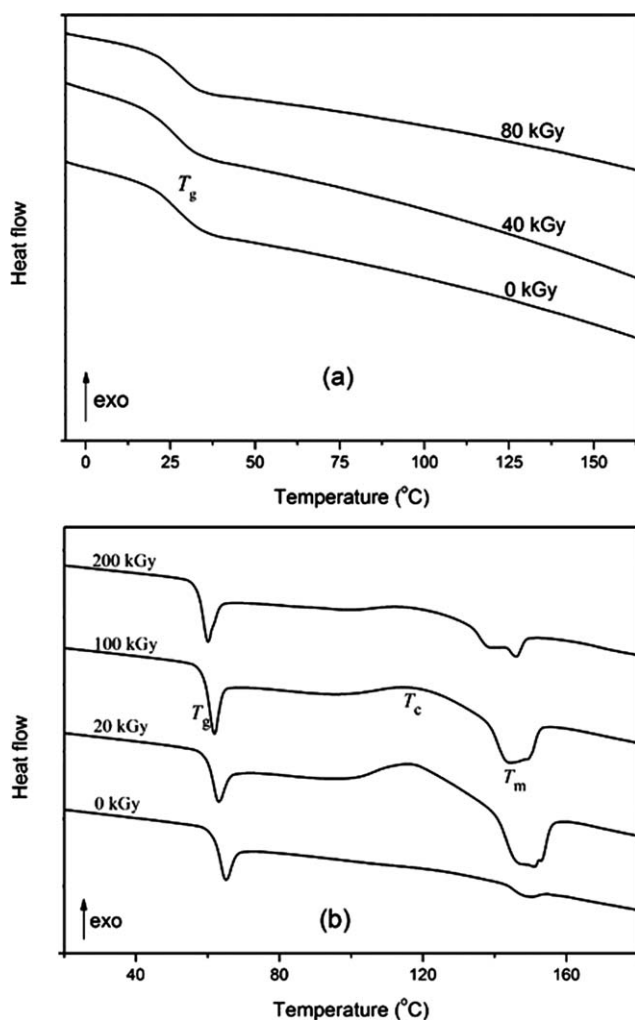
The standard deviation (SD) of this estimate was  $6.83 \times 10^{-6} \text{ mol g}^{-1}$  and  $3.93 \times 10^{-6} \text{ mol g}^{-1}$  for PLEG and PLLA, respectively. These equations would therefore allow for an accurate prediction of the resulting number average molecular weight after EB irradiation.

### Effects of irradiation on mechanical properties

The influence of irradiation on the mechanical properties of polymers differs widely depending on whether the polymer crosslinks or degrades. Radiation degradation almost always causes deterioration in the mechanical properties of polymers. Figure 5 shows the plots of tensile strength and elongation at break of PLEG and PLLA against dose. Elongation at break of PLEG and PLLA decreased sharply with increasing dose. Tensile strength of PLLA decreased from 46 MPa to 10.3 MPa on 100 kGy irradiation, about 77.6% loss compared with the sample before irradiation. Therefore, the mechanical performance of PLLA deteriorated severely with increasing



**Figure 5** Plots of tensile strength and elongation at break of samples against irradiation dose (a) PLEG and (b) PLLA.



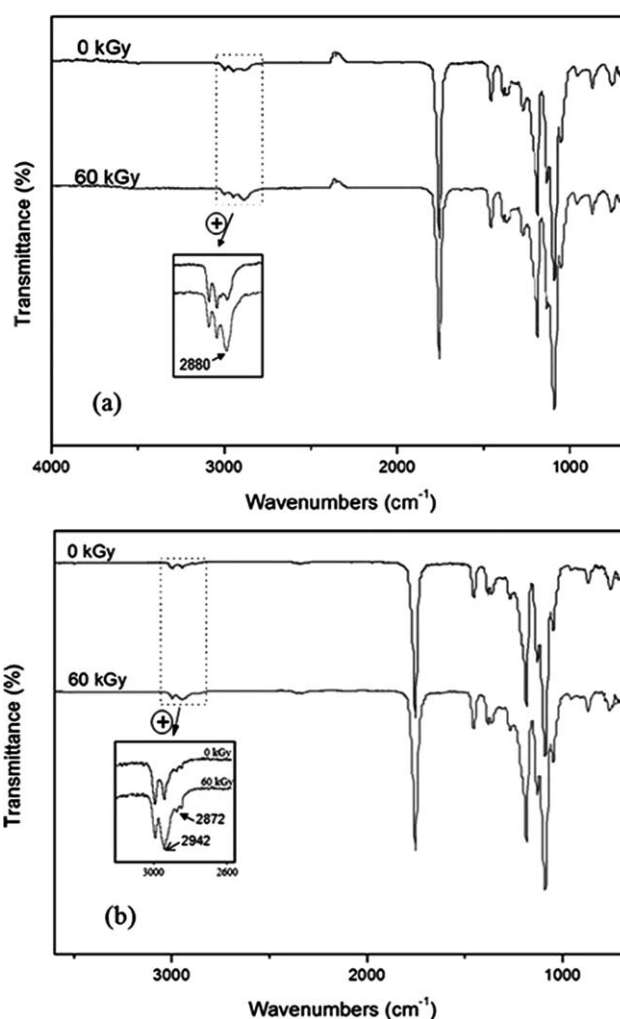
**Figure 6** DSC heating curves of samples irradiated at various doses (a) PLEG and (b) PLLA.

irradiation dose, mainly due to the sharp decrease of molecular weight of PLLA on irradiation. However, at doses from 0 to 100 kGy, the tensile strength of PLEG decreased slightly from 27.9 to 25.3 MPa, only 9.3% loss compared with the unirradiated sample. This was attributed to the fact that the crosslinking to chain scission ratio for irradiated PLEG aliphatic polyester increased as a function of increasing  $-\text{CH}_2-$  to  $-\text{COO}-$  ratio in the main chain.<sup>24</sup> Meanwhile, EB irradiation of PLEG with a lower concentration of ester groups in the backbone was prone to result in crosslinking of the polymer.<sup>31</sup> The GPC flow curves of PLEG under EB irradiation also confirmed this fact [Fig. 2(a)].

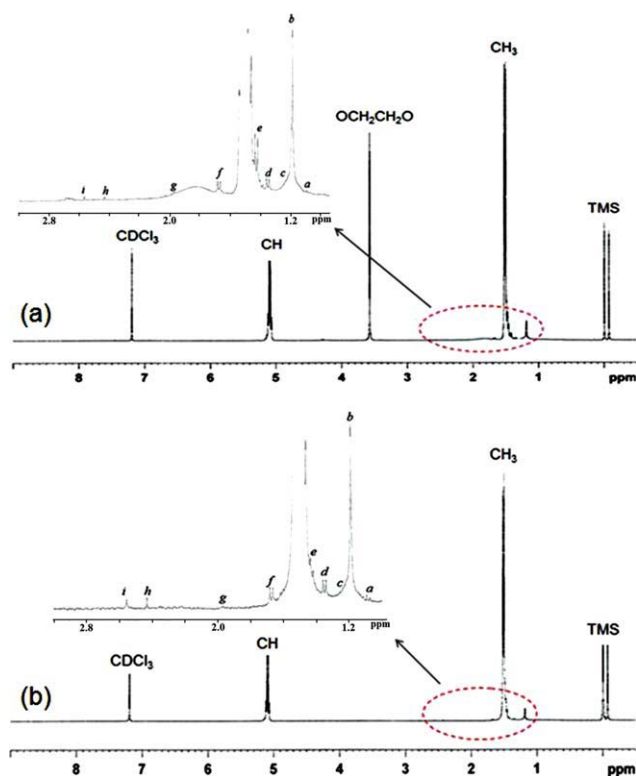
### Thermal transition properties

The quantitative evaluation of thermal transitions of irradiated PLEG and PLLA samples with various doses was investigated by DSC. Figure 6 shows the DSC heating curves of PLEG and PLLA. The unirra-

diated PLEG showed only a glass transition temperature ( $T_g \sim 27^\circ\text{C}$ ), without any exothermic peak of crystallization and melting peak. Similar observations were made for PLEG irradiated at 40 and 80 kGy, and  $T_g$  was found to be  $\sim 27.2^\circ\text{C}$  and  $\sim 27^\circ\text{C}$ , respectively. This meant that EB irradiation had little effect on  $T_g$  for this copolymer. It was due to the simultaneous occurrence of chain scission and crosslinking in copolymer chains, as shown in Figure 2(a). At doses below 100 kGy, there was an obvious decrease in  $T_g$  for PLLA due to the drastic decrease in its molecular weight. On the other hand, the unirradiated PLLA showed a single melting peak, but the irradiated PLLA thermogram showed additional cold crystallization ( $T_c$ ) peak and a double melting peak. Chain scission of PLLA during EB irradiation gave rise to shorter polymer chains, which had better mobility and were able to align themselves and pack more easily to form a crystalline phase, and thus also resulting in the formation of a  $T_c$  peak. With increasing dose, more chains were scission,



**Figure 7** ATR-IR spectra of samples before and after EB irradiation (a) PLEG and (b) PLLA.



**Figure 8**  $^1\text{H-NMR}$  spectrum of samples irradiated at 60 kGy (a) PLEG and (b) PLLA. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

promoting crystallization and increasing the degree of crystallinity in PLLA. But at higher dose, the degree of crystallinity of PLLA decreased due to the significant decrease in molecular weight with radiation dose. The melting peaks shifted to a lower temperature and became broader as the irradiation dose increased. According to Hoffman-Weeks' equation, the decrease in  $T_m$  was caused by a decrease in heat of fusion and/or increase in end surface free energy unless the crystal thickness changes.<sup>32</sup> Therefore, the differences in doublet melting peak temperatures were caused by the introduction of two kinds of irregularities, i.e., larger and smaller ones into crystalline surfaces and inside. The peak appearing at the lower temperature side corresponded to a typically degraded crystal component with larger irregularities, whereas the peak appearing at the higher temperature side corresponded to a less-degraded crystal component with smaller irregularities.<sup>18</sup>

#### ATR-IR spectra

Figure 7 plots the percentage of transmittance of infrared against the infrared frequency for samples. There were some distinctive differences in the ATR-IR spectra of PLEG and PLLA before and after EB irradiation. Irradiation resulted in the increase in

**TABLE II**  
Identification of the Possible Chemical Structures of the New Peaks Formed on the  $^1\text{H-NMR}$

Peak/ $\delta$	Proposed structure
a/1.10	
b/1.19	
c/1.23	
d/1.38	
e/1.45	
f/1.68	
g/1.95	
h/2.43	
i/2.54	



peak intensity for peak  $2880\text{ cm}^{-1}$  (PLEG) and  $2872, 2942\text{ cm}^{-1}$  (PLLA). The increase in peak intensity mainly corresponded to an increase in  $-\text{CH}_2-$  and  $-\text{CH}_3$  groups formed during irradiation.

### $^1\text{H-NMR}$ spectra

Figure 8 plots the  $^1\text{H-NMR}$  spectra of PLEG and PLLA irradiated at 60 kGy, which was found to be similar to the  $^1\text{H-NMR}$  spectra of unirradiated samples. For PLEG, the bands at 1.56 and 5.17 ppm were attributed to the methyl and methine protons, 3.64 ppm was characteristic of main chain methylene in the PEG blocks. For PLLA, the signals of the methine bond and methyl group were located at 5.11 and 1.50 ppm, respectively. The magnification of  $^1\text{H-NMR}$  spectra of irradiated samples from 1.0 to 2.8 ppm was observed, where the only difference between the unirradiated samples and irradiated samples. Each of the labeled peaks (*a-g*) indicated the formation of a new chemical bond formed during irradiation. Table II summarizes the possible chemical structures for each of these  $^1\text{H-NMR}$  peaks, arising possibly due to free radical recombination.<sup>15</sup> The proposed chemical structures had been reconfirmed with the  $^1\text{H-NMR}$  simulation software ChemDraw Ultra 8.0 (CambridgeSoft), and the simulated parts per million values were close matches to the actual  $^1\text{H-NMR}$  peak parts per million values.

### CONCLUSIONS

PLEG and PLLA degraded through chain scission when exposed to EB irradiation under nitrogen atmosphere. This caused a decrease in average molecular weight ( $M_n$  and  $M_w$ ), and thus a corresponding decrease in glass transition temperature, mechanical properties of the biopolymers. With increasing dose, recombination reactions or partial crosslinking of PLEG can occur in addition to chain scission, but there was no obvious crosslinking for PLLA at doses below 200 kGy. The decrease in molecular weight was observed to have a linear relationship with dose. EB irradiation caused the formation of crystalline phase in PLLA but no crystallinity for PLEG. Compared with PLEG, PLLA was more susceptible to EB irradiation degradation, because PLEG contained long PEG chain segment, which had the ability of radiation resistance as a function of dose. ATR-IR and  $^1\text{H-NMR}$  spectra indicated the formation of a new chemical bond during EB irradiation mainly due to the chain scission of lactic acid units in PLEG and PLLA backbone.

We thank Sichuan Santai Gurui Enterprise (People's Republic China) for the ATR-IR, GPC, and DSC measurements.

### References

- Okada, M. *Prog Polym Sci* 2002, 27, 87.
- Drumright, B. R. E.; Gruber, P. R.; Henton, D. E. *Adv Mater* 2000, 12, 1841.
- Krikorian, V.; Pochan, D. J. *Chem Mater* 2003, 15, 4317.
- Ruan, G.; Feng, S. S. *Biomaterials* 2003, 24, 5037.
- Ren, J.; Hong, H. Y.; Ren, T. B.; Teng, X. R. *React Funct Polym* 2006, 66, 944.
- Loo, J. S. C.; Ooi, C. P.; Boey, Y. C. F. *Polym Degrad Stab* 2004, 83, 259.
- Lewis, D. H. *Biodegradable Polymers as Drug Delivery Systems*; Marcel Dekker: New York, 1990, p 1.
- Sawhney, A. S.; Chandrashekhar, P. P.; Hubbell, J. A. *Macromolecules* 1993, 26, 581.
- Metters, A. T.; Anseth, K. S.; Bowman, C. N. *Polymer* 2000, 41, 3993.
- Saha, S. K.; Tsuji, H. *Polym Degrad Stab* 2006, 91, 1665.
- Wang, Z. Y.; Zhao, Y. M.; Wang, F. *J Appl Polym Sci* 2006, 102, 577.
- Miao, P. K.; Zhao, C. E.; Xu, G. L.; Fu, Q.; Tang, W. R.; Zeng, K.; Wang, Y. P.; Zhou, H. F.; Yang, G. *J Appl Polym Sci* 2009, 112, 2981.
- Miao, P. K.; Wu, D. M.; Zhao, C. E.; Xu, G. L.; Zeng, K.; Wang, Y. P.; Fu, Q.; Yang, G.; *e-Polymers* 2010, no. 006.
- Miao, P. K.; Wu, D. M.; Zeng, K.; Xu, G. L.; Zhao, C. E.; Yang, G. *Polym Degrad Stab* 2010, 95, 1665.
- Loo, J. S. C.; Ooi, C. P.; Boey, F. Y. C. *Biomaterials* 2005, 26, 3809.
- Haji-Saeid, M.; Sampa, M. H. O.; Chmielewski, A. G. *Radiat Phys Chem* 2007, 76, 1535.
- Gupta, M. C.; Deshmukh, V. G. *Polymer* 1983, 24, 827.
- Nugroho, P.; Mitomo, H.; Yoshii, F.; Kume, T. *Polym Degrad Stab* 2001, 72, 337.
- Kantoglu, Ö.; Güven, O. *Nucl Instr Meth B* 2002, 259, 197.
- Milicevic, D.; Trifunovic, S.; Galovic, S.; Suljovrujic, E. *Radiat Phys Chem* 2007, 76, 1376.
- Loo, J. S. C.; Ooi, C. P.; Boey, F. Y. C. *Biomaterials* 2005, 26, 1359.
- Loo, J. S. C.; Tan, H. T.; Ooi, C. P.; Boey, Y. C. F. *Acta Biomaterialia* 2006, 2, 287.
- Loo, J. S. C.; Tan, Z. Y. S.; Chow, Y. J.; Lin, S. L. I. *J Pharm Sci* 2010, 99, 3060.
- D'Alelio, G. F.; Häberli, R.; Pezdirtz, G. F. *J Macromol Sci A* 1968, 2, 501.
- Carlsson, D. J.; Scott, G. *Mechanisms of Polymer Degradation and Stabilization*; Elsevier: London, 1990, p 109.
- Kelen, T. *Oxidative Degradation and Polymer Degradation*; VNR: New York, 1983, p 107.
- Montanari, L.; Cilurzo, F.; Valvo, L.; Faucitano, A.; Buttafava, A.; Groppo, A.; Genta, I.; Conti, B. *J Control Release* 2001, 75, 317.
- Södergård, A.; Stolt, M. *Prog Polym Sci* 2002, 27, 1123.
- Schnabel, W.; Güven, O.; In *Cross-Linking and Scission in Polymer*, NATO ASI Series; Kluwer Academic Publishers: The Netherlands, 1988, p 15.
- Şen, M.; Uzun, C.; Kantoglu, Ö.; Erdoğan, S. M.; Deniz, V.; Güven, O. *Nucl Instr Meth Phys Res B* 2003, 208, 480.
- Nijenhuis, A. J.; Grijpma, D. W.; Pennings, A. *J Polymer* 1996, 37, 2783.
- Hoffman, J. D.; Weeks, J. J. *J Res Natl Bur Stand A* 1962, 66A, 13.