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High-energy-ion-irradiation effects on polymer materials: 3. The sensitivity of cellulose triacetate and poly(methyl methacrylate)

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The changes in sensitivity of a cellulose triacetate (CTA) film dosimeter is reported as a function of linear energy transfer (LET). The change in molecular weight of poly(methyl methacrylate) (PMMA) is also reported. For both materials, little or no LET effect was observed up to a threshold LET, but the sensitivity or radiation yield decreased with increasing LET above this threshold level. The threshold LET level was similar for both polymers, occurring at around a few hundreds of MeV cm^2 g^{-1}, with this level probably corresponding to the overlapping of spurs along the ion's path. Copyright © 1996 Elsevier Science Ltd.

(Keywords: ion irradiation; cellulose triacetate; poly(methyl methacrylate))

INTRODUCTION

The present authors have been studying ion-irradiation effects on polymeric materials in order to investigate radiation effects on polymers, radiation resistance of polymers to ions, and the linear energy transfer (LET) effect of polymers in terms of changes in mechanical properties such as elongation or flexural strength at break. We have already found that there seems to be little or no LET effect on some polymers such as polyethylene (PE) and polytetrafluoroethylene (PTFE) for 10 MeV protons[1,2], and poly(methyl methacrylate) (PMMA), epoxy matrix resin glass fibre reinforced plastic (GFRP)[3,4], epoxy matrix resin carbon fibre reinforced plastic (CFRP)[5] and polyimide matrix resin CFRP[5] with high-energy protons of 30–45 MeV. On the other hand, other polymers such as poly(ether sulfone) (PES) and bisphenol A type polysulfone (UPS) show an LET effect for 10 MeV protons and 20 MeV He ions[1,2]. Similar tendencies were observed in other studies[6,7]. Our primary objectives are to study the changes in mechanical properties as a function of dose when using ion beams. For these studies, distributions in the dose or stopping power inside the specimens should be avoided, in order to properly evaluate the relationship between the change in mechanical properties and dose. For this reason, ions having larger penetration depths than the specimen thicknesses have been used so far, so that ions can pass through the specimens without a significant dose (or stopping power) distribution inside the samples. This necessitated the usage of relatively low LET ions, such as high-energy protons or helium ions, as compared with other studies which use heavy ions. Since many reports claim that LET effects exist for polymers, the discrepancy may be due to the LET range used in our previous studies. Namely, even though low LET ions have larger LET values than electrons, they may not have sufficiently high values to make a difference in terms of radiation effects.

We have used a typical cellulose triacetate film dosimeter[8,9] to investigate observed doses and their uniformities, prior to the irradiation of polymeric materials. Uniformity in dose is typically within 5% disturbance, which implies proper beam scanning. In addition, as reported previously[1–4,10] for the case of 10–45 MeV proton irradiation, a satisfactory agreement between the expected dose and the observed dose was obtained. Recently, we have begun to study heavy ion irradiations of polymers[3]. However, when heavy ions such as 220 MeV C^{5+} are used, CTA dosimeters show a non-negligible discrepancy, i.e. the observed dose was found to be smaller than the expected dose. Kojima *et al.*[11] also found such discrepancies and related them to the contribution of mass collision stopping power and the resolution of calculation. However, mass collision stopping power seems to have little contribution because it is negligibly small (by an order of magnitude) compared to the electronic stopping power. At first we

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had no idea what caused this difference, but eventually concluded that this phenomenon was due to an LET effect for CTA. In this present work, we report the changes in sensitivity of CTA as a function of LET. We also report the LET dependence of the scission probability for poly(methyl methacrylate) (PMMA). Although PMMA shows little LET effect for high-energy protons, we expect that an LET effect may appear in a higher LET range. The possibility of the existence of a so-called 'threshold LET' in the radiation effect on polymers is discussed.

EXPERIMENTAL

Materials

A cellulose triacetate (CTA) film dosimeter, with a thickness of 0.125 mm, developed by the Fuji Photofilm Co. Ltd, was used. Details of CTA film dosimeters have been reported elsewhere[8,9]. The CTA sheets were cut into $100 \times 100\,mm^2$ squares and irradiated.

Commercial specimens of 3 mm thick poly(methyl methacrylate) (PMMA) were dissolved in chloroform and then solvent cast in a Petri dish to give a thin film (less than 0.01 mm) of PMMA. The PMMA films were dried under vacuum ($< 10^{-2}$ torr) for 48 h before irradiation. Gel permeation chromatography (g.p.c.) measurements showed that this treatment does not change the molecular weight of the pristine PMMA.

Irradiation

Details of the ion irradiation procedure are reported elsewhere[1-4,10]. An ion spot beam of 10 mm diameter from a cyclotron accelerator was scanned uniformly over a $100 \times 100\,mm^2$ area. The materials were positioned on a water-cooled holder and then irradiated at room temperature under vacuum. Ion currents were kept below 300 nA to avoid abrupt gas evolution which can deteriorate the vacuum in the chamber and accelerator. The linear energy transfer (LET) of ions to CTA or PMMA was evaluated with the TRIM (transport of ions in matter) code[12] and the absorbed dose was then calculated as the product of fluence and LET calculated from the TRIM code. The stopping powers, ranges and irradiation conditions are shown in *Table 1*. The stopping power for CTA was defined as the average between the initial LET (at the surface, i.e. incoming) and the final LET (at the opposite site side surface, i.e. outgoing), because the ion loses energy with depth and the LET becomes large (or in some cases, small, depending on the energy range). For the PMMA samples, however, the surface LET value was used as the stopping power, because the PMMA film used is so thin that little energy loss occurs with depth. The absorbed dose for PMMA was determined as the product of the LET at the surface and the fluence.

Table 1 Irradiated ions and LET values calculated by using the TRIM code[a]

Material	Ion	Energy (MeV)	LET ($MeV\,cm^2\,g^{-1}$)	Range (mm)
CTA	H^+	45	13.0	14.8
	H^+	30	18.1	7.07
	H^+	20	25.3	3.39
	H^+	10	44.2	0.978
	D^+	10	76.8	0.578
	He^{2+}	50	148.2	1.46
	He^{2+}	20	338[b]	0.288
	C^{5+}	220	969[b]	0.998
	O^{6+}	160	3190[b]	0.132
	O^{5+}	100	7380[b]	0.136
	Ar^{11+}	330	20900[b]	0.277
PMMA	C^{5+}	220	1010	1.03
	O^{5+}	100	4010	0.135

[a] All irradiations were carried out under vacuum at room temperature
[b] These values are the average between the LET at the incoming surface and the LET at the other, i.e. outgoing surface. The remaining ions have a much larger range when compared with the thicknesses of the materials, so that the distributions inside the specimens can be neglected

Measurements

The optical density (OD) of CTA at 280 nm was measured. The difference between the optical densities of unirradiated and irradiated CTA is known to be proportional to the absorbed dose[8,9], and was calibrated with electron beam irradiation. A conventional dosimeter gives the calibrated dose by using the formula,

$$\text{Dose} = K_{ele} \times (OD_{after} - OD_{before}).$$

The molecular weight of PMMA was measured by g.p.c. using chloroform as the solvent, as reported previously[3,4].

RESULTS AND DISCUSSION

Cellulose triacetate

Figure 1 shows the relationship between ion fluence ($ion\,cm^{-2}$) and the observed dose at 280 nm for CTA for H^+ (45 MeV), H^+ (30 MeV), H^+ (20 MeV), H^+ (10 MeV) and D^+ (10 MeV). The least-squares approximation method was used in order to get the best fit of the straight lines through the origin. The values of the slopes are shown in the figure near to each line, and refer to the apparent (i.e. experimentally observed) stopping powers, because the definition of the absorbed dose is the product of the fluence and the stopping power.

Figure 2 shows the relationship between fluence and dose based on the optical density at 280 nm for He^{2+}

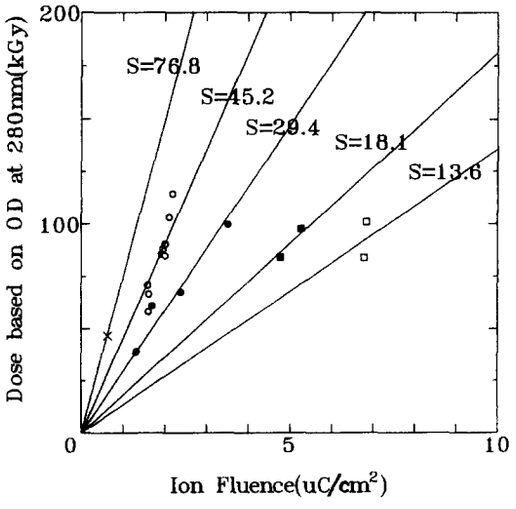

Figure 1 The relationship between ion fluence and observed dose at 280 nm for CTA: (□) H^+ (45 MeV); (■) H^+ (30 MeV); (●) H^+ (20 MeV); (○) H^+ (10 MeV); (×) D^+ (10 MeV)

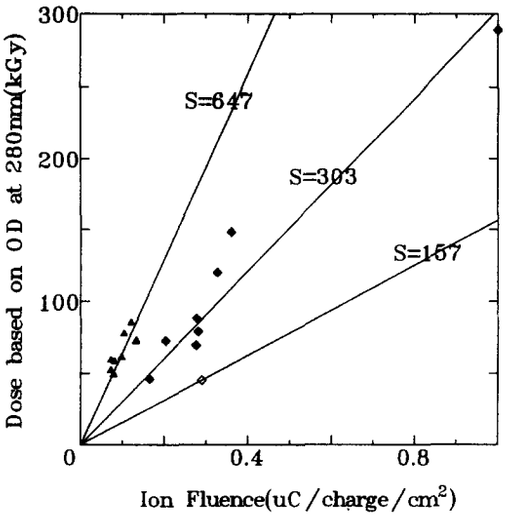

Figure 2 The relationship between ion fluence and observed dose at 280 nm for CTA: (◇) He^{2+} (50 MeV); (◆) He^{2+} (20 MeV); (▲) C^{5+} (220 MeV)

(50 MeV), He^{2+} (20 MeV) and C^{5+} (220 MeV), while *Figure 3* shows similar data for O^{5+} (160 MeV), O^{5+} (100 MeV) and Ar^{11+} (330 MeV). The calculated observed stopping powers are shown in the figures near to each of the lines. Some data at higher doses show scatter, but these were neglected because the recommended range of the CTA dosimeter is ~50–200 kGy[9]. *Figure 4* shows the sensitivity, defined as the ratio of the observed stopping power to calculated stopping power (by TRIM code), of the CTA film dosimeter as a function of calculated stopping power (by TRIM code). (The symbols used are the same as those used in *Figures 1–3*.) As we have reported previously[1–4,10], 45, 30, and 10 MeV protons show good agreement between the observed dose and expected dose, so that the observed stopping powers and the calculated stopping powers agree with each other, and thus the sensitivity is almost unity. When heavy- and high-LET ions are used for irradiation, the observed dose is less than the calculated dose, which in this case gives sensitivities which are less than unity. The decrease

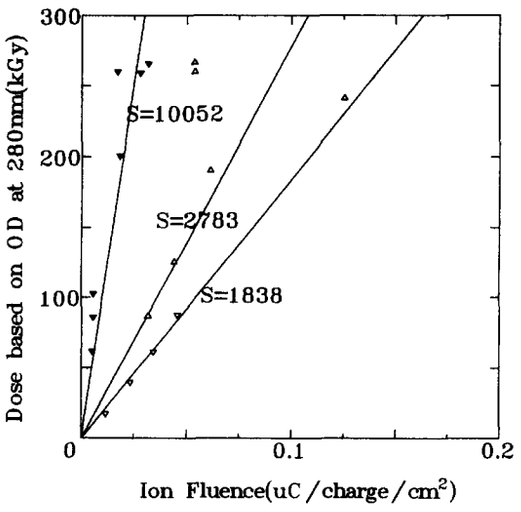

Figure 3 The relationship between ion fluence and observed dose at 280 nm for CTA: (▽) O^{6+} (160 MeV); (△) O^{5+} (100 MeV); (▼) Ar^{11+} (330 MeV)

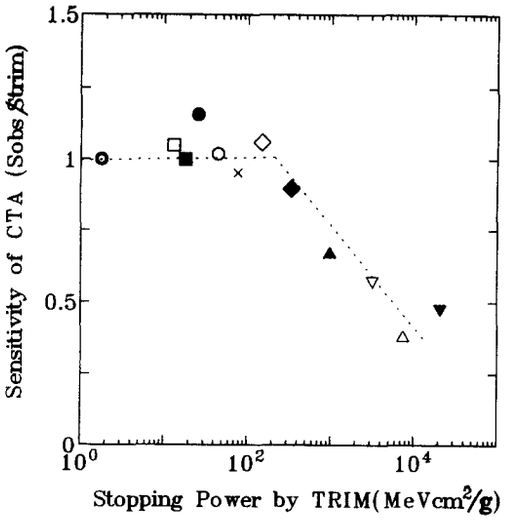

Figure 4 Sensitivity (the ratio of observed stopping power to the calculated stopping power) of the CTA film dosimeter as a function of calculated stopping power: (□) H^+ (45 MeV); (■) H^+ (30 MeV); (●) H^+ (20 MeV); (○) H^+ (10 MeV); (×) D^+ (10 MeV); (◇) He^{2+} (50 MeV); (◆) He^{2+} (20 MeV); (▲) C^{5+} (220 MeV); (▽) O^{6+} (160 MeV); (△) O^{5+} (100 MeV); (▼) Ar^{11+} (330 MeV)

seems to begin at ~300 MeV cm^2 g^{-1} (He^{2+} (20 MeV)), with the sensitivity decreasing in an approximately linear fashion with further increases in (logarithmic) LET. Because of this LET effect with CTA dosimeters, care must be taken when estimating doses using the CTA film dosimeter for high-LET radiation. This problem has been pointed out previously by Sunaga *et al.*[13] and Kojima *et al.*[11,14]

Poly(methyl methacrylate)

The results obtained in this work using C^{5+} (220 MeV) and O^{5+} (100 MeV) ions also showed that the molecular weight of PMMA decreases after irradiation, indicating that chain scission occurs. *Figure 5* shows the change in number-average molecular weight of the PMMA on irradiation (some data were taken from our previous work[4]). However, although M_n^{-1} increases linearly with dose, the probability of chain scission for the C^{5+} (220 MeV) and O^{5+} (100 MeV) ions is definitely less than

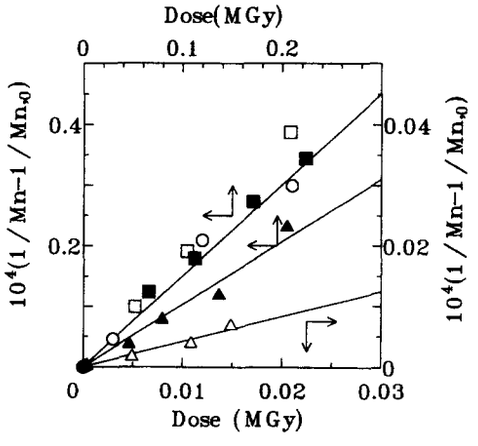

Figure 5 The change in number-average molecular weight of PMMA on irradiation (○, □, and ■ data taken from ref. 4): (○) ^{60}Co gamma rays; (□) H^+ (45 MeV); (■) H^+ (30 MeV); (▲) C^{5+} (220 MeV); (△) O^{5+} (100 MeV)

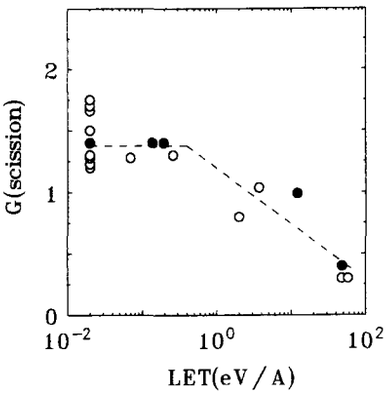

Figure 6 *G* (scission)-values for PMMA as a function of LET: (○) reported values taken from ref. 15; (●) this work (two sets of data in higher-LET region) and taken from ref. 4 (three sets of data in lower-LET region)

that found when using 45 and 30 MeV protons, and also gamma rays. The *G*-values of chain scission, calculated from the slopes of the lines in *Figure 5*, are 0.99 and 0.40 for C^{5+} (220 MeV) and O^{5+} (100 MeV) ions, respectively; these are smaller than those obtained for gamma rays, as well as 45 or 30 MeV proton irradiation.

LET effects on PMMA have proved to be of considerable interest, with many studies have been carried out. Yates and Shinozaki[15], and Schnabel and Klaumunzer[16] reported that the *G* (scission)-values decrease with increasing LET. On the other hand, we reported that the *G* (scission)-value is almost constant over the LET range from 1.8 to 16 MeV cm^2 g^{-1}, i.e. from gamma rays to 30 MeV protons[3,4]. *Figure 6* shows the *G* (scission)-values for PMMA as a function of LET; these include the results obtained in this present work, our previous results[3,4] and values reported in ref. 15. It appears that the majority of the results imply that the *G* (scission) parameter is almost constant up to a few hundreds of MeV cm^2 g^{-1}, and then decreases at higher LET values. It is worth noting that almost the same behaviour is observed for both PMMA and CTA, with their 'threshold' LET values being quite similar.

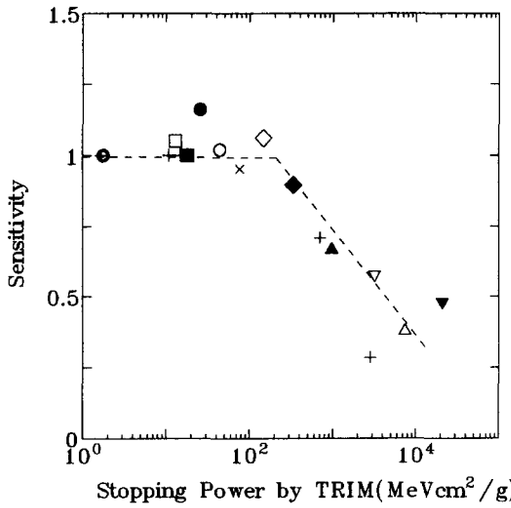

Figure 7 The sensitivity of CTA (the ratio of observed stopping power to the calculated stopping power) and the sensitivity of PMMA (the ratio of the *G* (scission)-value of the radiation of interest to the *G* (scission)-value for gamma rays) as a function of the calculated stopping power (by TRIM code): (+) PMMA, from this work and taken from ref. 4. The other symbols are for CTA: (□) H^+ (45 MeV); (■) H^+ (30 MeV); (●) H^+ (20 MeV); (○) H^+ (10 MeV); (×) D^+ (10 MeV); (◇) He^{2+} (50 MeV); (◆) He^{2+} (20 MeV); (▲) C^{5+} (220 MeV); (▽) O^{6+} (160 MeV); (△) O^{5+} (100 MeV); (▼) Ar^{11+} (330 MeV)

Threshold LET

Figure 7 shows the sensitivity of CTA (the ratio of observed stopping power to the calculated stopping power (by TRIM code for CTA)) and the sensitivity of PMMA (the ratio of the *G* (scission)-value for the radiation of interest to the *G* (scission)-value for gamma rays) as a function of the stopping power (calculated by TRIM code). Some data for PMMA were taken from refs 3 and 4. As mentioned above, the two polymers show almost the same LET dependence. Since PMMA undergoes chain scission as shown above, and CTA undergoes scission by gamma or electron beam irradiation[8], *Figure 7* indicates that the probability of scission decreases with increasing LET. The LET effect on polymeric materials is considered to be due to the high-density ionization and excitation in the localized area referred to as a track. As the LET increases, the recombination probability between intermediate species in a track is expected to increase, thus leading to a decrease in scission probability and an increase in crosslink density. The track itself can be considered as an overlapping of 'bead-like' spurs[17]. These spurs are considered to be isolated from each other in the case of low-LET irradiation such as gamma rays or electron beams, but the average distance between neighbouring spurs is expected to become smaller with increasing LET. Thus it is reasonable to conclude that, even if the LET of an ion beam is larger than that of gamma rays or electron beams, it may not be large enough for spurs to overlap, so that each spur will remain isolated, and the recombination probability will be insignificant. In such instances, the apparent radiation effects may not be very different for either ions, gamma rays or electron beams. The LET level at which spurs begin to overlap can be referred to as the 'threshold LET', below which the apparent radiation effects are identical with those of gamma rays or electron beams, and above which LET effects may appear (decreases in scission probability and increases in local crosslink density). The increase in crosslink probability for polystyrene observed in ref. 18, above a few eV A^{-1}, i.e. of the same order of the magnitude observed in this work, supports this idea. The threshold LET can be represented as the ratio of the energy required to form a spur to the spur radius, and according to the results given above, this is around 300 MeV g^2 cm^{-1} (ca. 2.5 eV A^{-1}) for CTA and PMMA. It seems reasonable that the spur formation energy and spur radius are of similar magnitudes for CTA and PMMA because both are solid-state aliphatic polymers containing C, H and O atoms. If we let the average spur formation energy be equal to 30–40 eV (a typical value) the spur radius is ~1–2 nm, which is in rough agreement with the experimentally estimated value[19] for alanine (radical formation, the change in radical yield per ion at higher fluence). Koizumi *et al.*[20] also found that the *G*-value for radical formation in alanine decreases with increasing LET over the region from 2 to 20 eV A^{-1}. However, it is worth noting when estimating the dimensions of a spur or track, that the overlap between spurs along one ion path

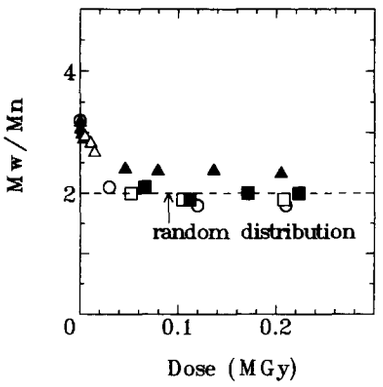

Figure 8 The molecular-weight distribution (the ratio of weight-average to number-average molecular weight) of PMMA after irradiation (○, □, and ■ data taken from ref. 4): (○) ^{60}Co gamma rays; (□) H^+ (45 MeV); (■) H^+ (30 MeV); (▲) C^{5+} (220 MeV); (△) O^{5+} (100 MeV)

occurs almost simultaneously, but also that the lifetime of a track should be taken into account when considering overlapping between tracks in high-fluence regions; this problem must have been avoided in the work of Koizumi *et al.*[20], because the radical in alanine has a very long lifetime[21] when compared to the irradiation time.

Since the probability of scission decreases and the crosslink density increases above the threshold LET, a conversion from scission-type polymers to crosslink-type polymers is expected. It is reported that polycarbonate becomes insoluble in dichloromethane after ion irradiation with 4×10^{11} cm^{-2} at an LET of 16.3 MeV mg^{-1} cm^2 (ca. 140 eV A^{-1}; Ar^{11+}, 6.9 MeV per nucleon)[22], while the polymer is completely soluble in the solvent before irradiation and undergoes scission by gamma[23,24] or electron irradiation[25]. We have also found another example of this conversion in bisphenol A type polysulfone (UPS)[1,2,6,7], where scission is predominant for electron beam irradiation but gelation occurs for ion irradiation (H^+ (10 MeV), ca. 0.4 eV A^{-1}, above 1 MGy). Moreover, the molecular-weight distribution (the ratio of weight-average molecular weight to number-average molecular weight) of PMMA remained at around 2.3 after C^{5+} (220 MeV) irradiations (as shown in *Figure 8*), indicating that non-random scission occurs. Some crosslinking is expected for PMMA for higher-LET irradiation. However, since the commercial PMMA used in this work contains some monomer and has an initial polydispersity of ~ 3, further analysis is too complex, and therefore inappropriate. Simpler materials (for example, pure and monodispersed polymer) would be better candidates for further analysis. Other questions still remain; while the threshold LET values for CTA and PMMA occur at similar values, at ~ 2.5 eV A^{-1}, why does UPS show the LET effects even for H^+ (10 MeV), for which the LET is ~ 0.4 eV A^{-1}? Perhaps the threshold LET varies among different polymers, and is dependent upon the nuclei contained, the number of single, double or conjugate bonds, etc. These parameters can affect the mean excitation potential and also perhaps the spur formation energy. The electron mobility (or diffusion constant) in polymers may also affect the spur radius. However, we are not sure at this present time what determines the spur radius and the threshold LET. The 'aromaticity' of polymers has been pointed out previously[1,2,6,7]. It is likely that aromaticity affects the electron mobility of polymers as well as the mean excitation potential. Further studies on the existence of the threshold LET, its dependence on the polymer's characteristics (mean excitation potential, electron mobility, etc.), the behaviour of the G (scission) or G (crosslink) parameters as a function of the LET over a wide range, and the question of whether the conversion from a scission- to a crosslinked-type material can be observed in other polymer systems, are all of interest.

CONCLUSIONS

High-energy-ion-irradiation effects on CTA and PMMA were studied by following changes in the optical density and molecular weight. Both polymers showed little LET dependence below a few (ca. 2.5) eV A^{-1}, but above this threshold value, the sensitivity decreases with increasing LET, implying a lower probability of scission. The threshold LET indicates the overlap of spurs.

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