Irradiation effects on aromatic polymers: 2. Gas evolution during electron-beam irradiation

El-Sayed A. Hegazy*, T. Sasuga, M. Nishii and T. Seguchi
Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, Watanuki-Machi, Takasaki, Gunma-ken, 370-12, Japan
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The gas evolution caused by electron-beam (e.b.) irradiation of aromatic polymers, such as polyimides (Kapton, Upilex-R and Upilex-S), poly(aryl ether ether ketone) (PEEK), poly(aryl ether sulphone) (PES), bisphenol A type Udel poly(aryl sulphone) (U-PS) and poly(aryl ester) (U-Polymer), has been quantitatively analysed. The radiation resistance in terms of gas evolution was in the following order: Upilex-R $\simeq$ Upilex-S $>$ Kapton $>$ PEEK $>$ PES $\gg$ U-PS $>$ U-Polymer. The component gases evolved from these aromatic polymers by e.b. irradiation were the same and possessed similar behaviour to those produced by gamma irradiation. But differences were found in the G values of some component gases evolved under e.b. irradiation compared with gamma irradiation due to the temperature rise caused by the high dose rate of e.b. irradiation. The effect of molecular structure and chemical unit linkages in the aromatic polymers on gas evolution was investigated. It was found that the biphenyl imide, tetracarboxylic acid anhydride imide, and aryl ether ketone unit linkages exhibited a protective effect against both e.b. and gamma irradiation. But aryl sulphone, isopropylidene aryl sulphone and aryl ester structures are sensitive to radiation. The polyimides and PEEK showed high radiation resistance, which can be of practical importance.

(Keywords: aromatic polymers; gas evolution; gas chromatography; electron beam irradiation)

INTRODUCTION

Recently, aromatic polymers have drawn much attention and gained wide practical use because of their excellent thermal and chemical stability, mechanical properties and radiation resistance. These polymers are of interest for various applications in areas with a high radiation field, such as in aerospace systems and around fusion reactors.

Radiation resistance is becoming an increasingly important consideration in the design of much equipment for nuclear instrumentation and for space technology[1]. Several of the aromatic polymers have already been employed in high-temperature apparatus[2], and these polymers should be important for such use in the nuclear energy field.

Polymeric materials are most sensitive to the environmental hazards of outer space, especially to ionizing radiation. Of particular concern is the electron radiation component, which will deposit in-depth radiation doses of up to 10 MGy during a typical 30 years exposure of materials used in satellites[3,4].

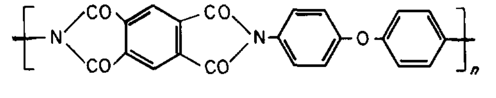
In a previous study[5], gas evolution produced by gamma irradiation of aromatic polymers has been investigated. It was found that polyimides and poly(aryl ether ether ketone) showed high radiation resistance to gamma irradiation. However, poly(sulphones) and poly(aryl ester) possessed much lower resistance; main-chain scission is probably the predominant process. To our knowledge, gas evolution from aromatic polymers by electron-beam (e.b.) irradiation has not been investigated and no information is available in the literature.

In this extension to our previous work, gas evolution produced by e.b. irradiation of aromatic polymers under vacuum was quantitatively analysed. A comparison between e.b. and gamma irradiation has been discussed.

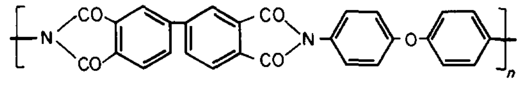
EXPERIMENTAL

The materials used are films of polyimides (Kapton, Upilex-R and Upilex-S), poly(aryl ether ether ketone) (PEEK-a, amorphous, and PEEK-c, crystalline), poly(aryl ether sulphone) (PES), bisphenol A type Udel poly(aryl sulphone) (U-PS) and poly(aryl ester) (U-Polymer). These aromatic polymers have the following chemical structures:

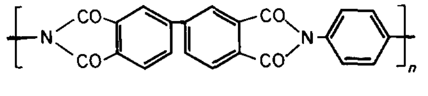
Kapton



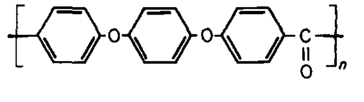
Upilex-R



Upilex-S



PEEK



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[*] To whom correspondence should be addressed. Present address: National Centre for Radiation Research and Technology, PO Box 29, Nasr City, Cairo, Egypt

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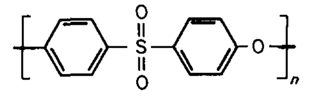
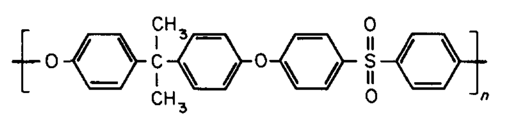
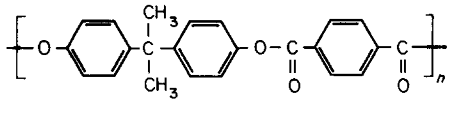
PES



U-PS



U-Polymer



Irradiation and gas analysis

A steel vessel was designed for the e.b. irradiation of film samples under vacuum, as shown in the schematic diagram (*Figure 1*). About 1 g of the film sample of thickness 100 μm was placed in the steel vessel between two steel plates of thickness 50 μm, sealed under a vacuum better than 10^{-3} Pa and then subjected to e.b. irradiation (2 MeV and 1 mA) at a dose rate of $1.7 \mathrm{kGy\,s^{-1}}$. The dose rate was determined at the sample position by measuring the change in the optical density of a cellulose triacetate (CTA) film dosimeter. The absorbed dose is determined using the following equation[6]:

$$\text{absorbed dose} = (OD_{\text{irr}} - OD_0)/0.063$$

where OD_{irr} and OD_0 represent the optical density of the irradiated and unirradiated CTA films, respectively.

To minimize the heat rise during e.b. irradiation at such a high dose rate, the vessel containing the film samples was cooled by placing it in a steel tray, which was continuously water cooled, under the e.b. scanner. The upper half of the vessel towards the direction of the e.b. scanner was kept free from water. Therefore, there was no restriction of the beam current penetration through the film samples. The gaseous products evolved from aromatic polymers by e.b. irradiation were then analysed by gas chromatography as described in the previous study[5].

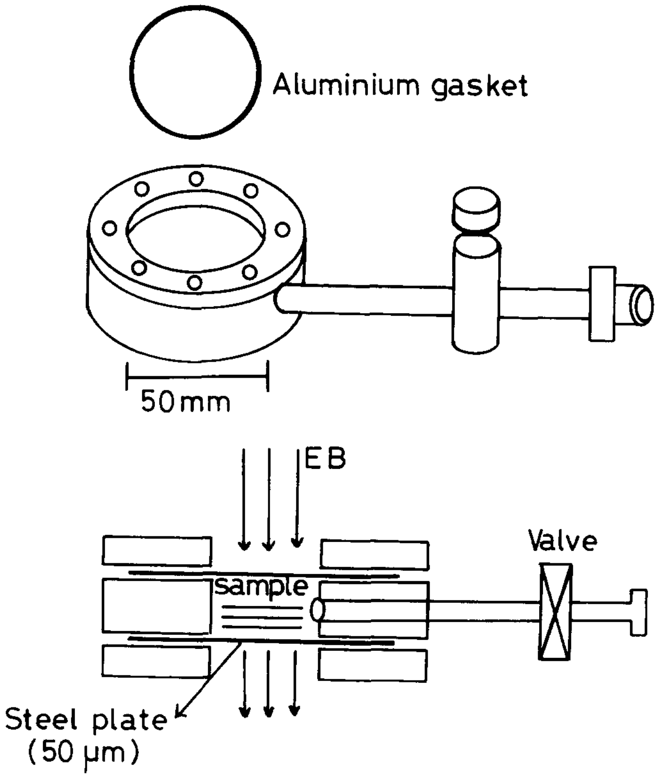


Figure 1 Schematic diagram of the steel vessel used for e.b. irradiation

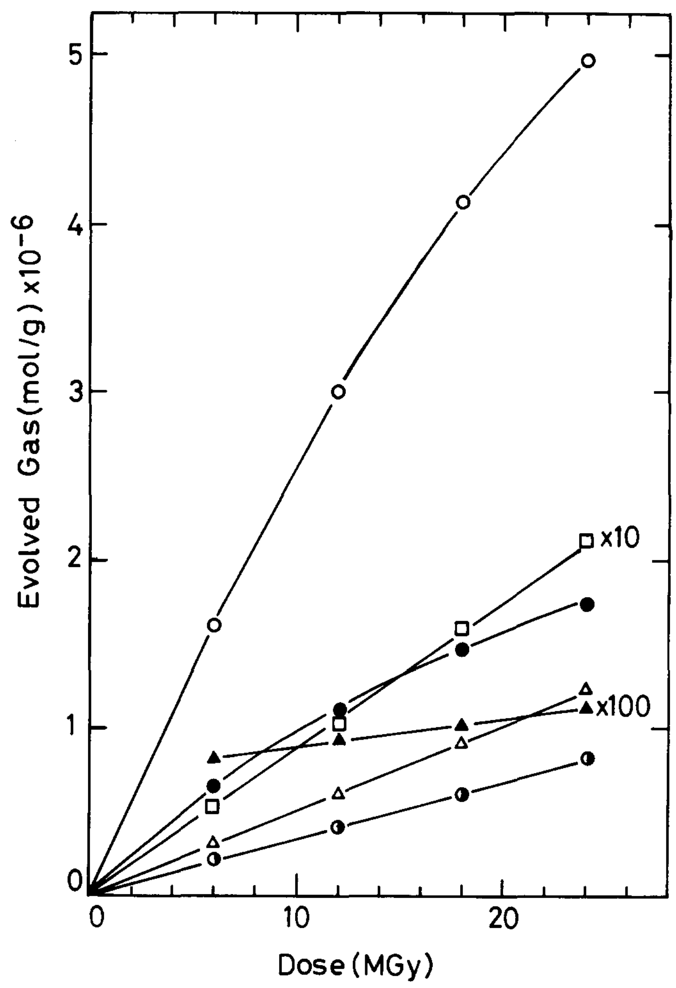


Figure 2 Yield of evolved gases vs. dose for Kapton on e.b. irradiation: (○) total gas, (△) H_2, (□) CH_4 (observed value × 10), (◐) CO, (●) CO_2 and (▲) N_2 (× 100)

RESULTS AND DISCUSSION

Polyimides

The yield of evolved gases from Kapton, Upilex-R and Upilex-S by e.b. irradiation as a function of dose is shown in *Figures 2*, *3* and *4*, respectively. The total gas increases proportionally with dose in the initial stage, but the yield per unit dose tends to decrease at higher doses. The yield of component gases from Kapton are in the order $CO_2 > H_2 > CO > CH_4 > N_2$, as can be seen from *Figure 2*. The evolution of H_2, CO and CH_4 increases linearly with dose, but CO_2 shows the same behaviour as the total gas. The yield of N_2 is almost constant with dose and is significantly reduced under e.b. irradiation as compared with gamma irradiation[5].

The gas evolution from Upilex-R is about half of that from Kapton. The component gases from Upilex-R are in the order $CO_2 > CO > H_2 > N_2 > CH_4$. All of these component gases increase linearly with dose, except N_2, which levels off at higher doses (*Figure 3*). The gas

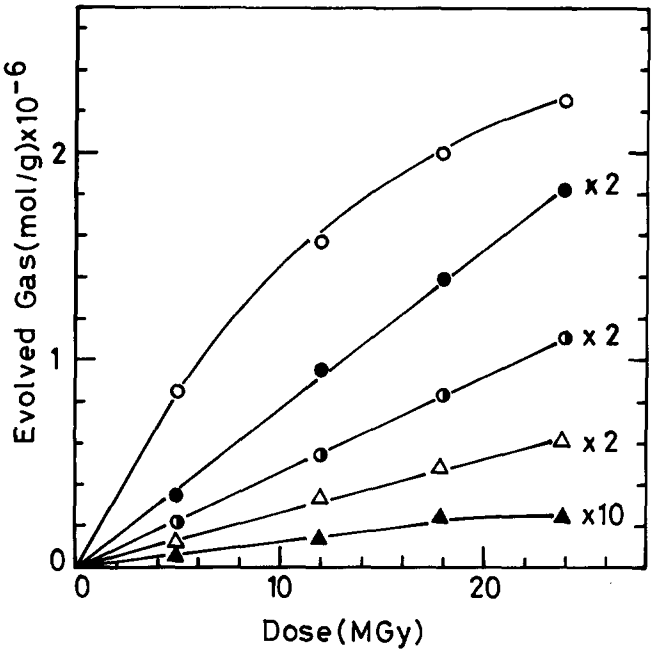


Figure 3 Yield of evolved gases vs. dose for Upilex-R on e.b. irradiation: (○) total gas, (△) H_2 (observed value ×2), (◐) CO (×2), (●) CO_2 (×2) and (▲) N_2 (×10)

evolution from Upilex-S is about 0.75 times that of Kapton. It can be seen from *Figure 4* that, at low doses, the total gas from Upilex-S is almost the same as that from Upilex-R. At higher doses, however, the gas evolution from Upilex-S is about 1.7 times that from Upilex-R. The component gases evolved from Upilex-S are in the order $CO_2 > CO > H_2 > N_2 > CH_4$. The evolution of H_2 and N_2 shows the same behaviour as the total gas, but CO_2, CO and CH_4 increase linearly with dose.

The *G* values of evolved gases from polyimides by e.b. irradiation are shown in *Table 1*. The *G* value for total gas in Upilex-R decreases gradually as the dose increases, but it is almost constant for Kapton and Upilex-S. The *G* values for H_2, CO and CO_2 in all of the polyimides are nearly constant with dose. The $G(H_2)$ for Kapton is about twice that of Upilex-S and four times that of Upilex-R. The $G(CO)$ is the same for Upilex-R and Upilex-S, but it is higher for Kapton by 1.5 times. However, $G(CO_2)$ of Upilex-S is a little higher than that of Kapton and almost twice that of Upilex-R.

Based on the gas evolution from polyimides, a comparison can be made between e.b. and gamma[5] irradiation, summarized as follows:

(1) The behaviour of gas evolution from polyimides by both irradiation types is nearly the same.

(2) For Kapton, total gas evolution at low doses is almost the same for both e.b. and gamma irradiation, but at higher doses total gas evolution for e.b. is twice that for gamma radiation. The N_2 evolution is reduced significantly for e.b. to 2% of that for gamma irradiation. However, no significant changes in the *G* values of the other component gases are observed between both irradiation types.

(3) For Upilex-R, total gas evolution is similar for e.b. and gamma irradiation. The H_2 evolution for e.b. irradiation is about three times of that for gamma, but N_2 is only 2% of that evolved for gamma irradiation. The yield of other component gases is found to be almost the same for both irradiation types.

(4) For Upilex-S, the gas evolution is very significantly reduced for e.b. to about 20% of that for gamma irradiation. The evolution of H_2 and N_2 is also reduced by the same proportion as the total gas, but CO_2 is half of that obtained by gamma irradiation. However, the

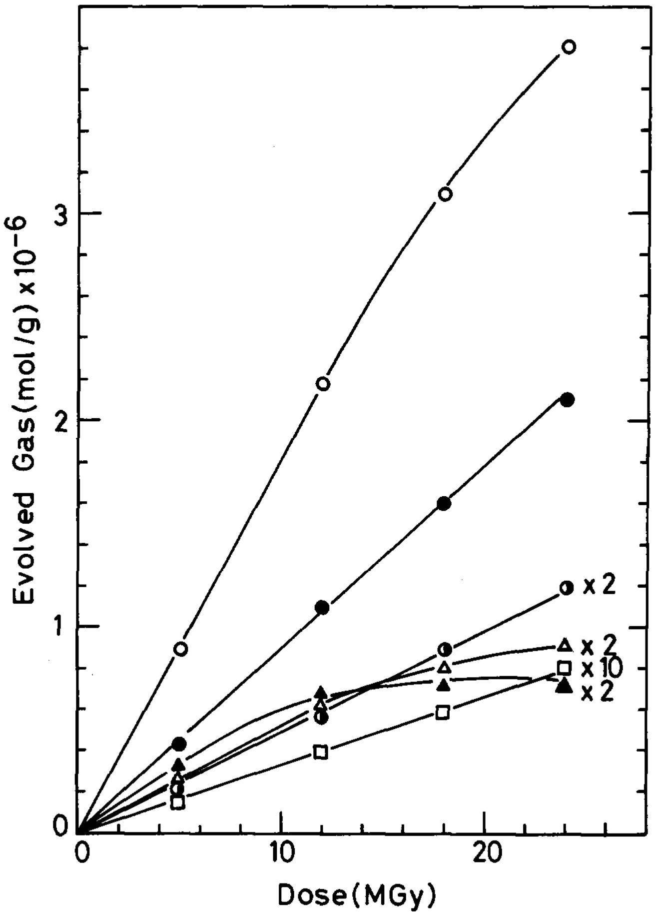


Figure 4 Yield of evolved gases vs. dose for Upilex-S on e.b. irradiation: (○) total gas, (△) H_2 (observed value ×2), (◐) CO (×2), (●) CO_2, (▲) N_2 (×2) and (□) CH_4 (×10)

Table 1 The *G* values of evolved gases from polyimides and PEEK on e.b. irradiation at a dose rate of 1.7 kGy s^{-1}

Polymer	Dose (MGy)	*G* value (10^{-4}) of component gas Total	H_2	N_2	CO	CO_2	CH_4
Upilex-R	0[a]	17	1.3	0.10	2.2	3.9	–
	5	16	1.3	0.10	2.1	3.4	0.07
	18	11	1.3	0.12	2.2	3.7	0.08
Upilex-S	0[a]	18	2.4	2.8	2.4	8.8	0.31
	5	17	2.3	2.9	1.9	8.2	0.27
	18	17	2.1	1.9	2.4	8.6	0.31
Kapton	0[a]	25	4.9	0.16	3.4	10	0.82
	6	27	4.8	0.15	3.5	11	0.89
	18	22	4.8	0.05	3.2	7.6	0.86
PEEK-c	0[a]	31	10	–	5.1	9.5	0.17
	5.8	25	7.5	–	3.4	11.3	0.16
	18	31	10	–	5.4	8.7	0.17
PEEK-a	0[a]	39	12	–	5.5	16	0.19
	6	39	12	–	5.2	16	0.22
	18	34	12	–	5.9	9.8	0.20

[a] The *G* value obtained by extrapolation to zero dose

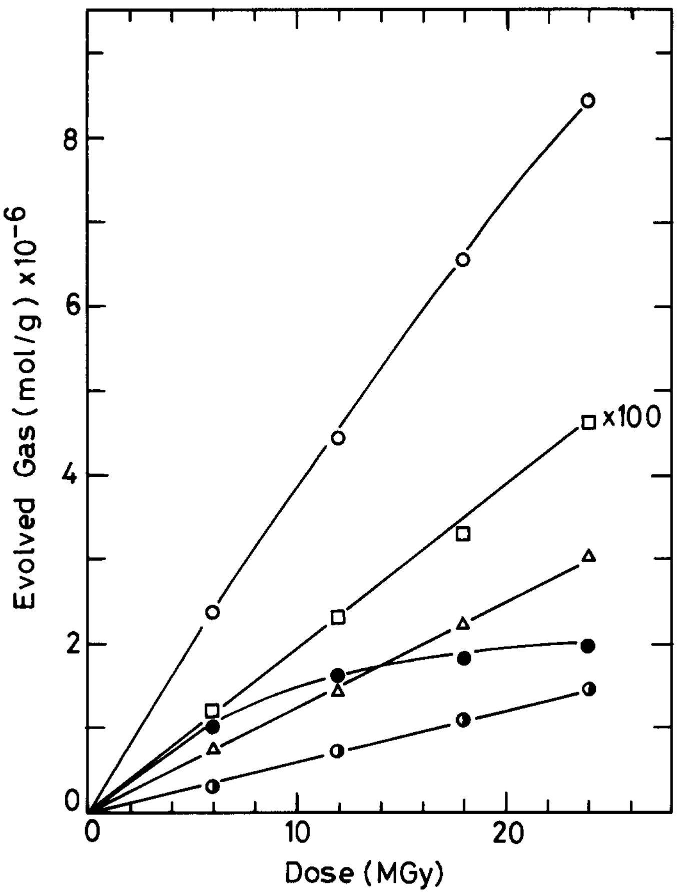


Figure 5 Yield of evolved gases vs. dose for PEEK-a on e.b. irradiation: (○) total gas, (△) H_2, (□) CH_4 (observed value × 100), (◑) CO and (●) CO_2

yield of CO and CH_4 is almost the same for both irradiations.

It can be assumed that the radiolysis mechanisms of polyimides for e.b. irradiation are the same as for gamma irradiation, as discussed in the previous paper[5]. The chemical structure and chemical unit linkages of polyimides have a great influence on the gas evolution and radiation resistance. The biphenyl unit linkages in Upilex-R and Upilex-S have a pronounced protective effect, which is higher than that of the tetracarboxylic anhydride imide units in Kapton. Furthermore, the presence of both biphenyl and phenyl ether unit linkages in Upilex-R produces a high resistance to radiation. Such aromatic units can act as energy transfer agents owing to their high resonance stabilities.

The temperature rise caused by high-dose-rate e.b. irradiation may have some effect on the evolution of gaseous products. The recombination of active sites is enhanced at higher dose rates; this leads to the reduction of some component gases, such as N_2 and CO_2. On the other hand, such recombination processes may favour the elimination of H_2 from aromatic rings. Elimination of H_2 is mainly by abstraction from phenyl rings, and therefore it is severely affected by such high dose rates. However, elimination of CO, CO_2 and N_2 is primarily from scission processes in imide end-groups. These processes may be significantly reduced by the higher probability of recombination at the high dose rate used in e.b. irradiations. The mechanism is not yet clear, and further investigations are necessary to clarify the effect of high-dose-rate irradiation and temperature rise.

Poly(aryl ether ether ketone)

The gas evolution of amorphous PEEK-a and crystalline PEEK-c by e.b. irradiation is shown in *Figures 5* and *6*, respectively. The component gases evolved from both polymers are in the order $H_2 > CO_2 > CO > CH_4$. For PEEK-a, the total gas, H_2, CO and CH_4 tend to increase linearly with dose, but CO_2 tends to level off above 6 MGy. In the case of PEEK-c, the total gas and component gases increase initially with dose and then the yield per dose decreases at higher doses. The gas evolution of PEEK-a is about 1.5 times that of PEEK-c, but the gas evolution of PEEK-c and PEEK-a is 2 and 2.7 times, respectively, that of Upilex-R.

The *G* values of evolved gases from PEEK by e.b. irradiation are listed in *Table 1*. The $G(CO_2)$ of PEEK-a is about 1.5 times that of PEEK-c, and it decreases as the dose increases for both polymers. The $G(H_2)$ of PEEK-a is a little higher than that of PEEK-c, and it is almost constant with dose. The $G(CO)$ and $G(CH_4)$ are almost the same for both polymers and they are constant with dose.

By comparing the gas evolution from e.b. and gamma irradiation of PEEK, some differences can be observed. Gamma irradiation resulted in a little higher gas evolution from both polymers compared with e.b. irradiation, especially at low doses. The *G* value of component gases of PEEK-a for gamma irradiation is a little higher than that for e.b. irradiation. For PEEK-c, the $G(H_2)$ and $G(CO_2)$ for e.b. irradiation are about 1.5 times those for gamma rays. In contrast, the $G(CO)$ for e.b. irradiation is reduced to half of that for gamma rays, but $G(CH_4)$ is the same for both irradiations.

Based on gas evolution, PEEK-a and PEEK-c possessed high resistance to e.b. irradiation, but less than polyimides. The crystalline PEEK-c showed higher resistance than PEEK-a. This can be attributed to the lower

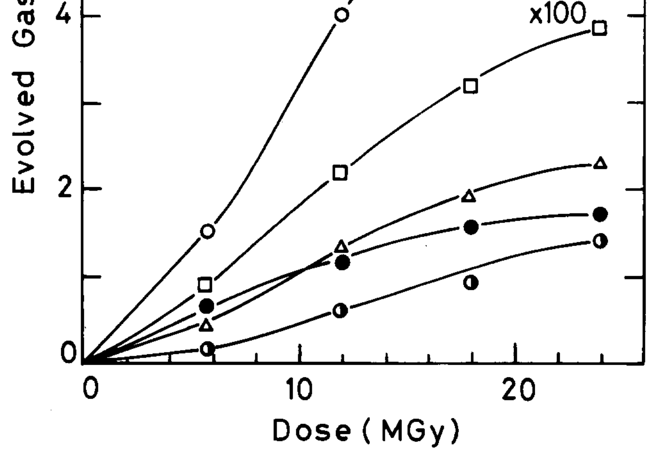
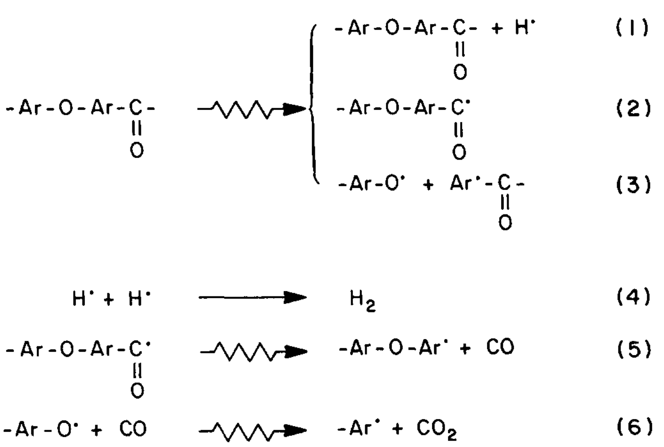


Figure 6 Yield of evolved gases vs. dose for PEEK-c on e.b. irradiation: (○) total gas, (△) H_2, (□) CH_4 (observed value × 100), (◑) CO and (●) CO_2

mobility of active sites in the crystalline regions. The higher mobility in the amorphous regions of PEEK-a has a large influence on the reactivity of active sites, which seems to enhance gas evolution from the ketone groups of its structure. Differences between PEEK-a and PEEK-c in total gas could also arise partly from the 'cage effect' being more effective in crystalline regions so that more recombination occurs in PEEK-c. The molecular configuration and mobility of lengths of polymer chain are very different in crystalline and amorphous regions; the latter may in some respects be considered as limited regions of liquid structure[7]. It was also reported that the higher probability of crosslinking in the amorphous structure would compensate for the degradation process by scission in ether and ketone linkages[8]. Consequently, the evolution of CO and CO_2 is enhanced from PEEK-a. This is in good agreement with the results obtained for their gamma irradiation[5]. On the other hand, the small difference between the gas evolution produced by e.b. and gamma irradiation of PEEK can be attributed to the temperature rise caused by the high dose rate of e.b. irradiation. But such differences are not as large as those observed in polyimides. These results suggest that the radiolysis mechanism for PEEK is almost the same for gamma and e.b. irradiations.

The radiolysis mechanism of PEEK is suggested as follows:



$$-Ar-O-Ar-\underset{\underset{O}{\|}}{C}- \rightsquigarrow \begin{cases} -Ar-O-Ar-\underset{\underset{O}{\|}}{C}- + H^{\bullet} & (1) \\ -Ar-O-Ar-\underset{\underset{O}{\|}}{C^{\bullet}} & (2) \\ -Ar-O^{\bullet} + Ar^{\bullet}-\underset{\underset{O}{\|}}{C}- & (3) \end{cases}$$

$$H^{\bullet} + H^{\bullet} \longrightarrow H_2 \quad (4)$$

$$-Ar-O-Ar-\underset{\underset{O}{\|}}{C^{\bullet}} \rightsquigarrow -Ar-O-Ar^{\bullet} + CO \quad (5)$$

$$-Ar-O^{\bullet} + CO \rightsquigarrow -Ar^{\bullet} + CO_2 \quad (6)$$

Since the G value of CO_2 is almost twice that of CO, reaction (6) proceeds to form CO_2. The hydrogen radicals are abstracted from PEEK in reaction (1) and they recombine to form H_2. The CO is eliminated by the decomposition of radicals formed in reaction (2) as shown in reaction (5). The active sites formed by the reactions (1)–(6) result in crosslinking of polymer chains by their recombination.

Poly(sulphones)

The yield of evolved gases from PES and U-PS for e.b. irradiation as a function of dose is shown in *Figures 7* and *8*, respectively. The total gas initially increases proportionally with dose and then the yield per dose decreases at higher doses. The component gases evolved from both polymers are H_2, SO_2, CO_2, CO and CH_4. The yield of these component gases increases linearly with dose for both poly(sulphones). The component gases from PES are in the order $SO_2 > H_2 > CO_2 > CO > CH_4$. For U-PS, they are in the order $H_2 > SO_2 > CO > CO_2 > CH_4$. The gas evolution from U-PS is almost three times that of PES; this ratio is the same as that found for gamma irradiation[5].

The G values for evolved gases from poly(sulphones) for e.b. irradiation are listed in *Table 2*. It can be seen that the G values for all component gases evolved from both poly(sulphones) are almost constant with dose. The G value for total gas decreases gradually as the dose increases. It can also be seen that the G value for gas

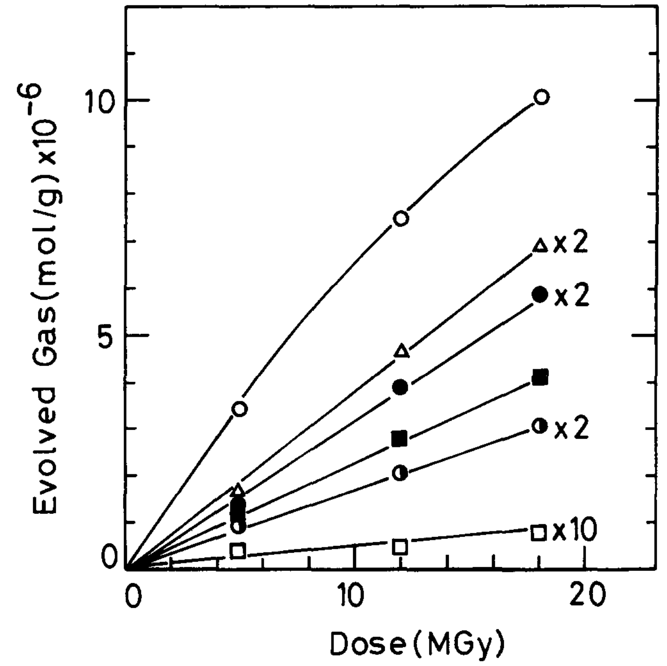


Figure 7 Yield of evolved gases vs. dose for PES on e.b. irradiation: (○) total gas, (△) H_2 (observed value ×2), (□) CH_4 (×10), (◑) CO (×2), (●) CO_2 (×2) and (■) SO_2

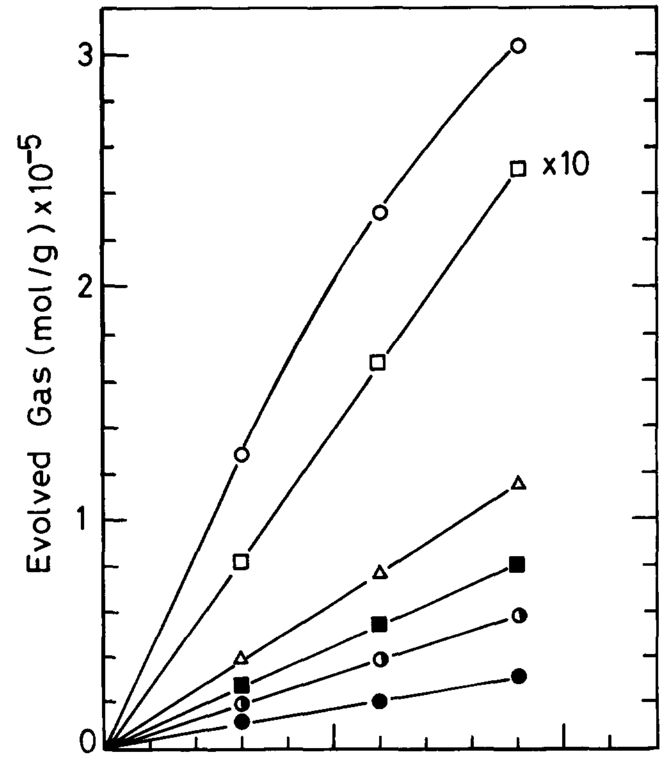


Figure 8 Yield of evolved gases vs. dose for U-PS on e.b. irradiation: (○) total gas, (△) H_2, (□) CH_4 (observed value ×10), (◑) CO, (●) CO_2 and (■) SO_2

Table 2 The G values of evolved gases from poly(sulphones) and U-Polymer on e.b. irradiation at a dose rate of 1.7 kGy s^{-1}

Polymer	Dose (MGy)	G value (10^{-3}) of component gas						
		Total	H_2	SO_2	CO	CO_2	CH_4	C_2H_6
PES	0[a]	6.9	1.9	2.3	0.83	1.6	0.04	–
	5	6.6	1.6	2.2	0.77	1.3	0.05	–
	18	5.5	1.5	1.8	0.70	1.4	0.04	–
U-PS	0[a]	21	6.2	4.3	3.2	1.6	1.3	–
	6	20	6.1	4.2	2.9	1.6	1.3	–
	18	17	6.1	4.3	3.0	1.7	1.3	–
U-Polymer	0[a]	46	8.0	–	22	12	3.2	–
	5	48	5.6	–	16	11	1.7	0.1
	18	43	7.0	–	20	11	2.6	0.1

[a] The G value obtained by extrapolation to zero dose

evolution from poly(sulphones) is higher than that of polyimides and PEEK by one order of magnitude.

The isopropylidene aromatic unit linkage of the U-PS structure is sensitive to radiation. Consequently, a higher yield of gas is evolved from U-PS compared with PES. It can be reasonably assumed that main-chain scission is occurring in the isopropylidene and C–S aromatic unit linkages. As a consequence, $G(H_2)$ and $G(CO)$ from U-PS are almost three times those of PES, and $G(SO_2)$ is twice that of PES. The degradation of isopropylidene unit linkages has enhanced the evolution of CH_4 in U-PS; its G value is about 30 times that from PES. These results provide strong evidence for such chain scission degradation, since isopropylidene units are the only aliphatic part in the U-PS chemical structure. The C–S main-chain scission also occurs, resulting in the liberation of SO_2 as one of the major component gases. The radiolysis mechanisms of PES and U-PS have been discussed in the previous study of gas evolution during gamma irradiation.

The lack of protective units, such as biphenyl imide, tetracarboxylic acid anhydride imide and aryl ether ketone, in the molecular structure of PES and U-PS brings about a pronounced degradation in their structures upon irradiation. Therefore, the gas evolution of PES and U-PS is about 4 and 15 times that of polyimides, respectively. This result was also found previously for gamma irradiation[5] of the same materials.

Comparison can be made between gas evolution from e.b. and gamma irradiation of PES and U-PS. The e.b. irradiation of both polymers leads to a slightly higher gas evolution compared with gamma irradiation, and a marked difference is observed for SO_2 evolution. The $G(SO_2)$ of PES and U-PS for e.b. is 1.5 and 3 times, respectively, that for gamma irradiation. This may be attributed to the enhancement of C–S scission due to the temperature rise that occurs in e.b. irradiation.

U-Polymer

Figure 9 shows the yield of evolved gases from U-Polymer as a function of dose. The component gases from U-Polymer for e.b. irradiation are in the order $CO > CO_2 > H_2 > CH_4$. The total gas, CO_2 and H_2 increase linearly with dose. The yield of CO and CH_4 initially increases proportionally with dose and then tends to level off around 18 MGy.

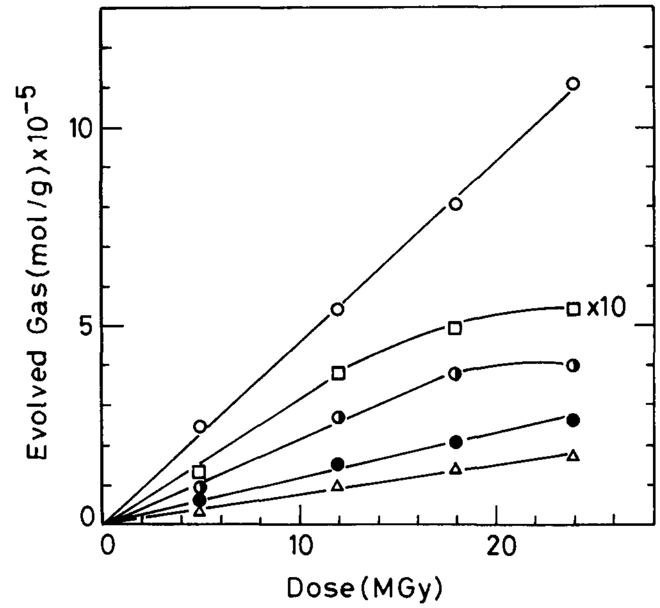


Figure 9 Yield of evolved gases vs. dose for U-Polymer on e.b. irradiation: (○) total gas, (△) H_2, (□) CH_4 (observed value × 10), (◑) CO and (●) CO_2

The G values for evolved gases are shown in *Table 2*. The G value for total gas and the component products is almost constant with dose. The $G(CO)$ is approximately two times that of $G(CO_2)$ and three times that of $G(H_2)$. The gas evolution for U-Polymer is 2.5 times that from U-PS and is higher by more than one order of magnitude compared with that of PES.

The aromatic ester unit linkages of the molecular structure of U-Polymer possessed high radiation sensitivity compared to the linkages in polyimides and PEEK. This produced a higher amount of gas evolution compared to the other aromatic polymers investigated. The gas evolution from U-Polymer is about 25 times higher than that of polyimides. The same result was found for the gamma irradiation of U-Polymer[5]. No very significant changes are observed in the G values for evolved gases for e.b. and gamma irradiation of U-Polymer. Because of the high radiation sensitivity of U-Polymer structure, the temperature rise during e.b. irradiation has no significant effect on the gas evolution compared with gamma irradiation.

It can reasonably be assumed that, based on the high G value for CO_2 and CO, main-chain scission in the aromatic ester unit linkages is the predominant degradation process. Chain scission has also occurred in the isopropylidene aryl linkages, resulting in the elimination of H_2 and CH_4 with a high G value compared with other aromatic polymers. The radiolysis mechanism of U-Polymer seems to be the same for e.b. and gamma irradiation and was discussed in detail in our previous paper[5].

CONCLUSIONS

Based on the gas evolution and the G values obtained by extrapolation to zero dose for aromatic polymers on e.b. irradiation (*Tables 1* and *2*), it can be concluded that their radiation resistance is in the order: Upilex-R $\simeq$ Upilex-S > Kapton > PEEK-c > PEEK-a > PES $\gg$ U-PS > U-Polymer. A similar order of resistance to gamma irradiation was found to be: Upilex-R $\simeq$ Kapton > PEEK-c > PEEK-a > Upilex-S $\gg$ PES > U-PS > U-Polymer. The large difference in ranking order of radiation resistance for Upilex-S is not yet understood, and further work is required to establish the reasons. The yield of gas evolution from aromatic polymers is about 1/100 to 1/1000 of that from aliphatic polymers[9–11]. The behaviour of gas evolution and the composition of the gases evolved from aromatic polymers are the same for both e.b. and gamma irradiation. Some differences were found in the G value for some component gases when comparing e.b. and gamma irradiation. This was attributed primarily to the temperature rise caused by the high dose rate for e.b. irradiation. The biphenyl imide, tetracarboxylic acid anhydride imide and aryl ether ketone unit linkages showed a high protective effect against both e.b. and gamma irradiations. But aryl sulphone, isopropylidene aryl sulphone and aryl ester structures are sensitive to radiation. The polyimides and PEEK showed high radiation resistance, which is of practical importance.

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