Irradiation effects on aromatic polymers: 1. Gas evolution by gamma irradiation

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The effects of gamma irradiation on 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), were investigated based on gas evolution. The radiation resistance in terms of gas evolution was in the following order: Upilex-R $\geqslant$ Kapton $>$ PEEK $>$ PES $>$ Upilex-S $\gg$ U-PS $>$ U-Polymer. The G values of total gases from these aromatic polymers were 1/100th to 1/1000th of the G values from aliphatic polymers. The major component gases were: H_2 and N_2 for polyimides; CO_2 and CO for PEEK; CO_2, CO and SO_2 for polysulphones; and CO and CO_2 for U-Polymer. The influence of crystallinity on the behaviour and yield of gas evolution was investigated in PEEK. Crystalline PEEK gave lower yield compared to amorphous PEEK. The radiolysis mechanism of gaseous products was discussed based on the structures of the aromatic polymers.

(Keywords: gamma irradiation; aromatic polymers; gas evolution; gas chromatography)

INTRODUCTION

Knowledge of the effects of ionizing radiation on aromatic polymers is important because these organic and heat-resistant materials are of interest for various applications in areas with a high radiation field, such as fusion reactors and space vehicles and satellites[1]. These aromatic polymers are sensitive to environmental hazards, especially ionizing radiation. The accumulated dose in the materials was estimated to be about 10 MGy for a satellite during a typical 30 years exposure[2], and 50 MGy for a fusion reactor.

The production of volatile products from aromatic materials upon irradiation induces undesirable results, which leads to premature failure due to mechanical degradation, thus limiting service life[3]. Although the degradation of mechanical and thermal properties of aromatic polymers by high-energy radiation has been investigated, showing that aromaticity generally promotes higher stability[4–9], no information on gas evolution has so far been reported, except for poly(ether sulphones)[10].

Polyimides such as Kapton and Vespel have been extensively studied and reported, with resistances to gamma and electron beams up to 100 MGy of irradiation[11]. PEEK offered excellent radiation resistance as well as thermal stability and superior resistance to common solvents, heat, abrasion and fatigue[12]. Consequently, PEEK is a good candidate for materials such as advanced composites and for insulating materials in the wires and cables in nuclear power plants[13–15]. Two aromatic polysulphones that are currently available commercially have been shown[10] to be resistant to ionizing radiation.

Because of the potential usefulness of these materials, a study has been carried out on the quantitative analysis of evolved gases by gamma irradiation under vacuum at room temperature. The effect of chemical structure and component unit linkages to the aromatic structure on the radiation resistance in terms of gas evolution was determined.

EXPERIMENTAL

Materials

The materials used in this study are films of polyimides (Kapton, Upilex-R and Upilex-S), poly(aryl ether ether ketone) (PEEK-a, non-crystalline; and PEEK-c, semi-crystalline), poly(aryl ether sulphone) (PES), bisphenol A type Udel poly(aryl sulphone) (U-PS) and poly(aryl ester) (U-Polymer). The chemical structures and suppliers of these aromatic polymers are shown in *Table 1.*

Irradiation and gas analysis

About 1 g of the film sample of thickness 100 μm was sealed in a glass ampoule after being evacuated to 10^{-3} Pa and then subjected to ^{60}Co gamma rays at a dose rate of 10 kGy h^{-1} at room temperature (30°C). The amount of gaseous products accumulated in the glass ampoule was obtained by measurement of pressure and volume of the ampoule. Then the gas components were analysed by two gas chromatographs (model 263-50, Hitachi Ltd) with different types of columns. The gases were introduced into a 1 cm^3 injection holder, then injected into the g.c. column with He carrier gas. A photoionization detector (p.i.d.) was used in g.c. and has the minimum detectable concentration of 1 ppm N_2. A molecular sieve 13X column was used for the analysis of light molecules such as H_2, CH_4, N_2 and CO, and a

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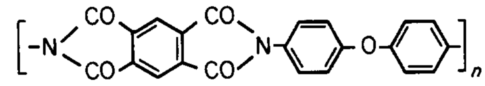
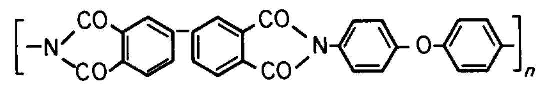
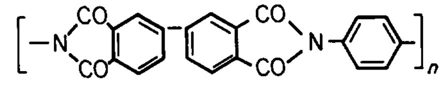
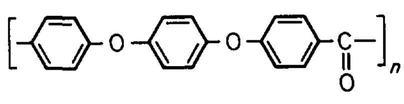
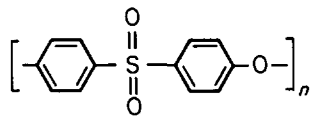
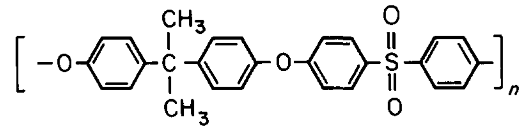
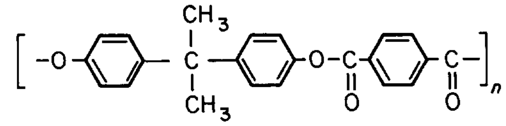
Table 1 Chemical structures and suppliers of aromatic polymers

Polymer	Supplier	Chemical structure
Kapton	Du Pont	
Upilex-R	UBE Industries Ltd	
Upilex-S	UBE Industries Ltd	
PEEK	Sumitomo Co. Ltd	
PES	ICI Co. Ltd	
U-PS	Toray Industries Inc.	
U-Polymer	Unitika Co. Ltd	

Porapack-S column for the analysis of the higher-molecular-weight gases, CO_2, C_2H_6, C_3H_8 and SO_2. The peak area of analysed gas in the g.c. spectrum was measured using an integrator (Hitachi Chromato-Integrator D-2500).

RESULTS AND DISCUSSION

Polyimides

The yields of evolved gases from polyimides (Kapton, Upilex-R, Upilex-S) by gamma irradiation under vacuum as a function of dose are shown in *Figures 1*, *2* and *3*, respectively. The component gases evolved are CO_2, CO, N_2, H_2 and CH_4. The total gas increases proportionally with dose in the initial stage, and the yield per dose tends to decrease at higher doses. The total gas of Upilex-R is almost the same as that of Kapton, but it saturates at higher doses above 8 MGy. All the component gases of Upilex-R tend to level off above 10 MGy. The total gas of Upilex-S is eight times higher than that of Kapton or Upilex-R. *Figure 3* shows also that there is a large difference between the total gas and the sum of detected component gases. Such a difference is not observed for Kapton and Upilex-R.

The presence of a biphenyl unit in the molecular structure of Upilex-R effectively depresses the gas evolution to high doses. The elimination of H_2 and CH_4 was significantly reduced by the presence of such a unit compared with those of Kapton. However, a small increase of CO and N_2 was observed. The phenyl ether units at the chain ends of Kapton and Upilex-R have a great effect in protecting the main chains against ionizing radiation. This is clear from the lack of such a unit in Upilex-S, resulting in a higher yield of gas evolution compared with that of Kapton and Upilex-R.

The G values of evolved gases from Kapton, Upilex-R and Upilex-S on gamma irradiation are listed in *Table 2*. For Kapton and Upilex-R, it seems that all the eliminated gases are detected, because of the small difference between the *G* value of total gas and the sum of the detected component values. However, in Upilex-S this is not the case and all eliminated gases were not detected; larger-molecular-weight gases should be evolved.

It can be reasonably assumed that N_2, CO and CO_2 are mainly eliminated from the imide groups at the chain ends, but H_2 is abstracted from the adjacent phenyl groups. The incorporation of biphenyl and phenyl ether units in the structure of polyimides greatly enhanced their radiation resistance.

Poly(aryl ether ether ketone)

PEEK is a crystalline polymer and the crystallinity depends on the heat treatment; the amorphous polymer of lower crystallinity (PEEK-a) is achieved by quench cooling from the melt, and the crystalline polymer (PEEK-c) by slow cooling from the molten state. The influence of crystalline domains and morphology of the polymer was also investigated based on the gas evolution on irradiation.

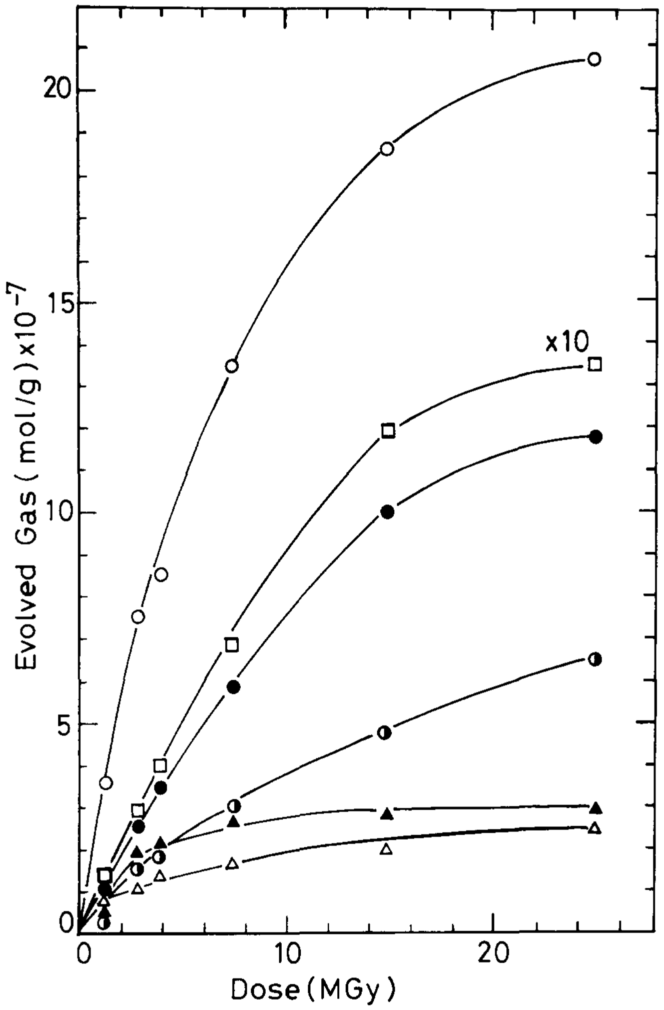


Figure 1 Yield of evolved gases vs. dose for Kapton by gamma irradiation: (○) total gas, (△) H_2, (□) CH_4, (◑) CO, (●) CO_2 and (▲) N_2

The yields of evolved gases from PEEK-a and PEEK-c as a function of dose are shown in *Figures 4* and *5*, respectively. The component gases are CO_2, CO, H_2 and CH_4. The total gas increases initially with dose and it tends to level off at higher doses.

The *G* values of evolved gases for PEEK-a and PEEK-c are listed in *Table 3*. The *G* value of CO_2 for PEEK-a is about three times larger than that of PEEK-c and decreases as the dose increases for both polymers. In contrast, the *G* value of CO for PEEK-a is about half of that for PEEK-c and no marked changes with dose are observed. The *G* value of H_2 for PEEK-a is about twice as high as that of PEEK-c.

It can be assumed that CO and CO_2 are eliminated from ketone and other groups of the PEEK structure and H_2 is abstracted from the phenyl rings.

Radiation effects should be affected not only by chemical structure but also by morphology, such as higher-order structure and the presence of crystallites, because the chain conformation and molecular motion may have a large influence on the reactivity of the active species produced by irradiation. A difference in gas evolution behaviour for both polymers is due to morphology. The chains in the amorphous region, where the molecules are more mobile than in the crystalline region, may result in enhancing the evolution of CO, CO_2 and H_2 by damage in the ketone group. It was reported that the gas evolution is higher from amorphous polymers than from crystalline ones[16].

The change in tensile properties of PEEK on electron beam irradiation[17] showed that the radiation resistance of PEEK-a, based on the change in elongation at break, is higher than that of PEEK-c. The authors insist that the higher probability of crosslinking in the amorphous region would compensate degradation by disintegration of ether and ketone linkages.

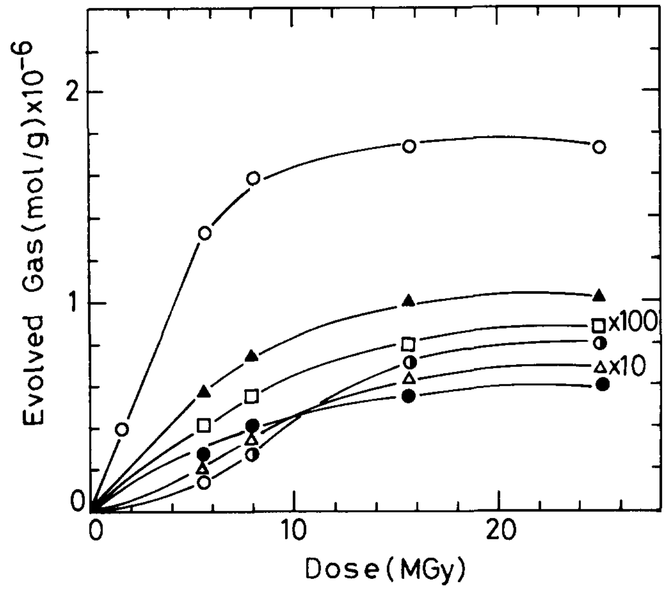


Figure 2 Yield of evolved gases vs. dose for Upilex-R by gamma irradiation: symbols are the same as in *Figure 1*

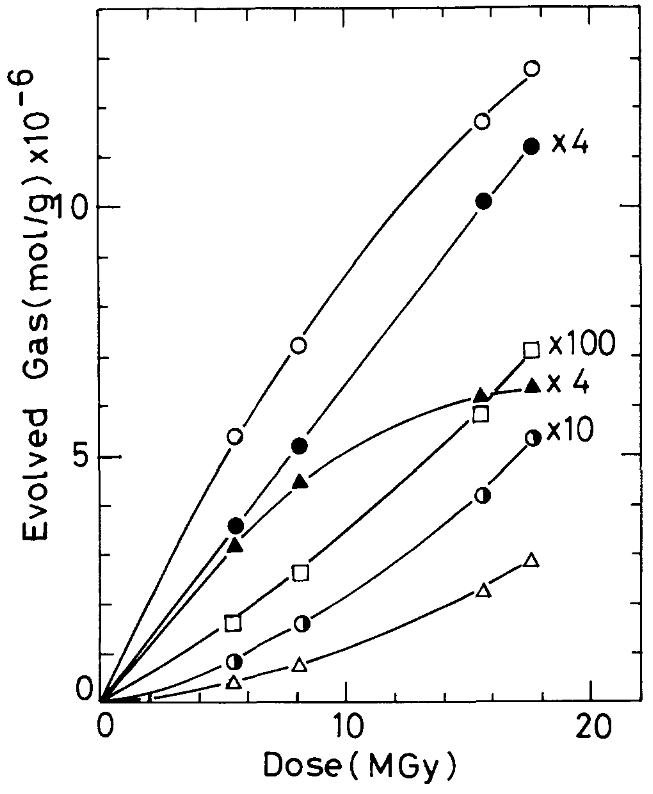


Figure 3 Yield of evolved gases vs. dose for Upilex-S by gamma irradiation: symbols are the same as in *Figure 1*

Table 2 *G* values of evolved gases from polyimides by gamma irradiation under vacuum

Polymer	Dose (MGy)	*G* value (10^{-4}) of component gas					
		Total	H_2	N_2	CO	CO_2	CH_4
Kapton	E[a]	24	3.2	5.1	5.4	8.1	0.96
	2.9	25	3.3	5.4	5.1	8.6	0.95
	7.4	18	2.1	3.6	3.9	7.4	0.89
	25.0	9.8	0.9	1.1	2.5	4.6	0.52
Upilex-R	E[a]	22	0.39	9.7	2.4	4.8	0.09
	5.7	21	0.38	9.8	2.5	5.2	0.08
	15.6	13	0.39	6.2	3.2	3.3	0.05
	25.0	8.9	0.26	3.5	3.0	2.1	0.03
Upilex-S	E[a]	91	7.5	14	1.4	15	0.29
	5.7	85	6.0	14	1.6	16	0.29
	8.1	80	8.4	13	1.8	15	0.30
	17.6	68	11	8.8	3.0	15	0.38

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

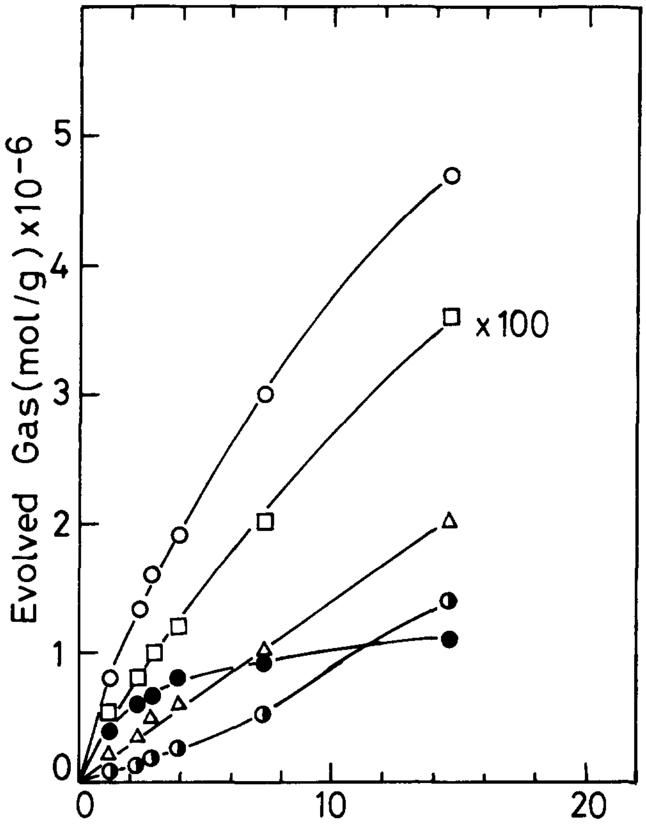


Figure 4 Yield of evolved gases vs. dose for PEEK-a by gamma irradiation: symbols are the same as in *Figure 1*

Polysulphones

Figures 6 and *7* show the yields of gas evolution vs. dose for PES and U-PS, respectively. Gas evolution of U-PS is almost three times higher than that of PES. The component gases from both polymers are CO_2, H_2, SO_2 and CO; the minor gas is CH_4.

The *G* values of evolved gases from PES and U-PS on gamma irradiation are listed in *Table 4*. The *G* values of gas evolution for PES and U-PS are higher than those for polyimides and PEEK, showing that their radiation resistance is about one order lower than that of polyimides and PEEK.

Comparing the chemical structures of PES and U-PS, the latter contains isopropylidene unit linkages, which may result in increasing the total yield of eliminated gases. The main significant change in the component gases due to the presence of isopropylidene unit linkages in U-PS is the increment of H_2 and CH_4 evolution by five and 100 times, respectively, compared with those of PES.

Irradiation of both polysulphones produced CO_2, CO and SO_2 as the major volatile products. Therefore, C–S main-chain scission is a principal step in the radiolysis, followed by scission of the adjacent C–S bond, liberating SO_2 from the phenylene sulphonyl radical as described by Brown and O'Donnell[18]. The mechanism is consistent with the preferred scission of C–S bonds and the liberation of SO_2 in gamma-irradiated polysulphones.

The production of H_2 from both PES and U-PS is very different; for PES, via C–H scission in the aromatic rings; and for U-PS, via decomposition of isopropylidene units.

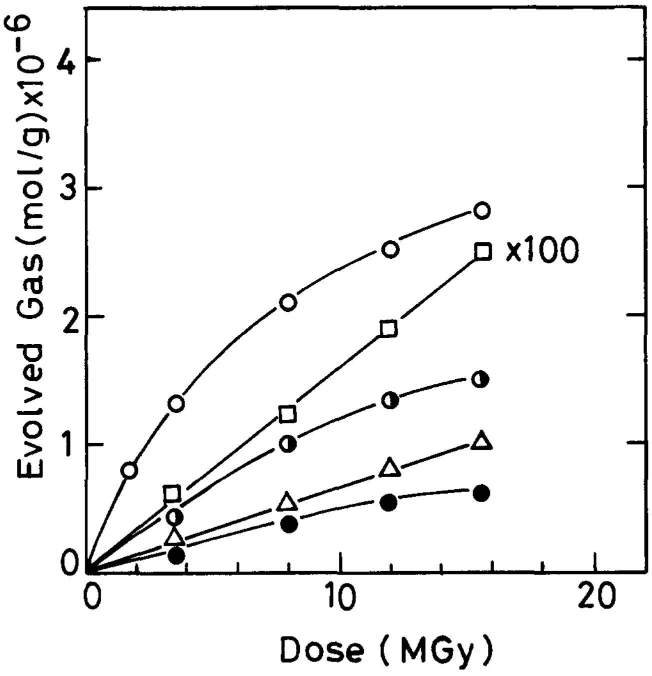


Figure 5 Yield of evolved gases vs. dose for PEEK-c by gamma irradiation: symbols are the same as in *Figure 1*

Table 3 *G* values of evolved gases from PEEK by gamma irradiation under vacuum

Pllymer	Dose (MGy)	*G* value (10^{-4}) of component gas				
		Total	H_2	CO	CO_2	CH_4
PEEK-a	E[a]	54	14	6.0	24	0.31
	2.9	48	14	5.8	22	0.30
	7.4	35	12	6.5	12	0.20
	14.7	28	12	6.7	7.1	0.23
	25.0	21	9.3	6.6	4.6	0.16
PEEK-c	E[a]	39	6.4	12	4.3	0.15
	3.5	33	7.5	12	6.0	0.18
	8.1	25	6.3	12	5.5	0.14
	15.5	20	6.2	9.9	3.5	0.15

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

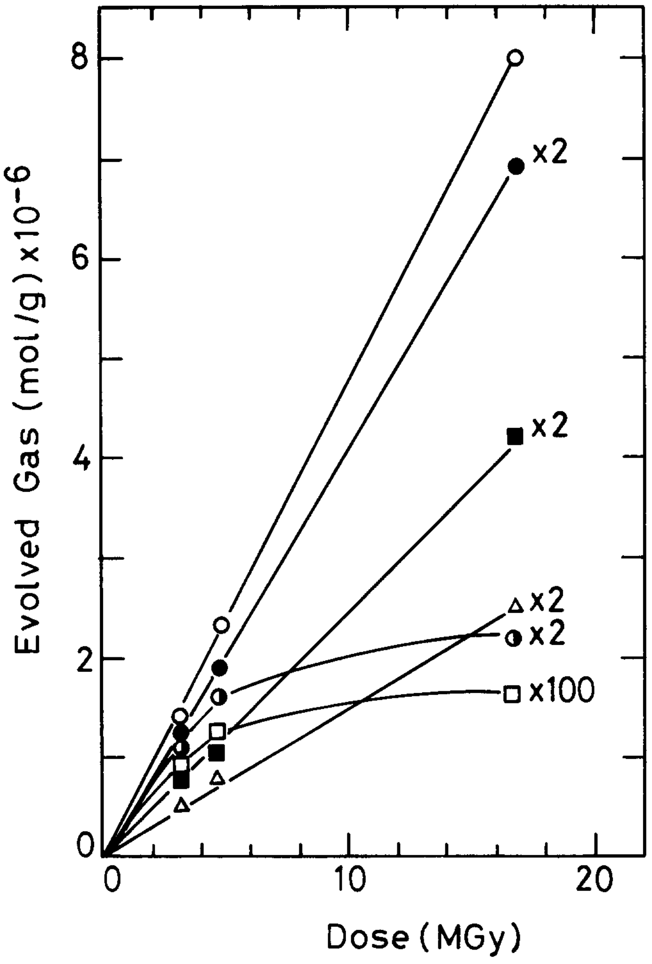


Figure 6 Yield of evolved gases vs. dose for PES by gamma irradiation: symbols are the same as in *Figure 1*, except (■) SO_2

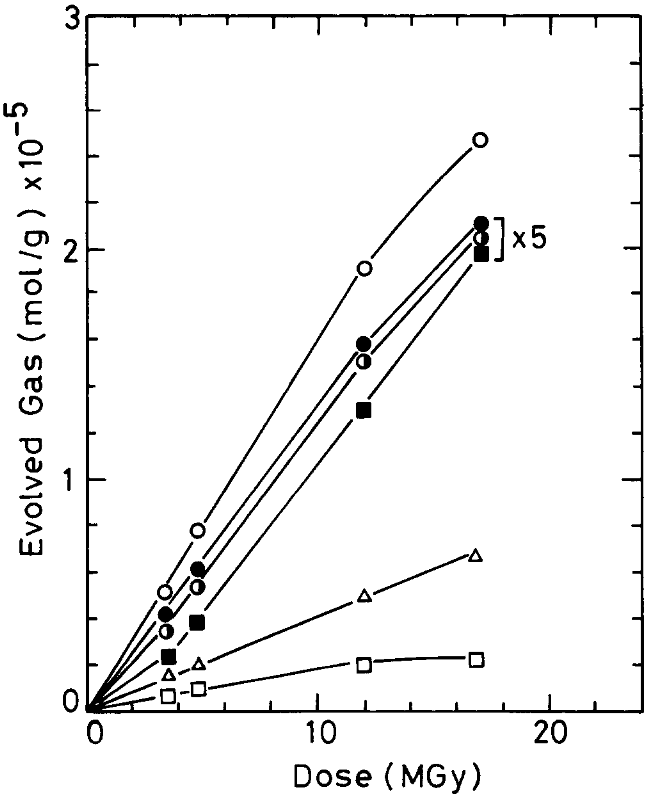


Figure 7 Yield of evolved gases vs. dose for U-PS by gamma irradiation: symbols are the same as in *Figure 6*

Elimination of the methyl radical by C–CH_3 scission from the isopropylidene group of U-PS, followed by hydrogen abstraction to form methane, might be expected to be an important process, since this is the only aliphatic part of this polymer.

Scission in the phenyl rings of the molecular structure of PES probably occurred, resulting in the evolution of CO and CO_2. The elimination of these two gases from U-PS presumably occurred by scission in its isopropylidene unit linkages. But the mechanism of CO and CO_2 elimination from polysulphones is not clear.

Results suggest that the radiation resistance of PES is higher than that of U-PS because of its high aromatic content and also the lack of aliphatic groups in its structure. Comparing the gas evolution between polysulphones and Kapton, one finds that its yield from PES and U-PS is almost four and 12 times, respectively, higher than that of Kapton.

Brown and O'Donnell[18] studied the volatile product yields and limiting viscosity of irradiated PES and U-PS, and found that PES has higher radiation stability than U-PS. Our results are in good agreement with their results.

U-Polymer

The yield of gas evolution from U-Polymer as a function of dose is shown in *Figure 8*. The major component gases are CO, CO_2 and H_2, and the minor gases are CH_4 and C_2H_6. The total gas and each component gas show the same behaviour. They initially increase with dose and then tend to level off at higher doses.

The *G* values of evolved gases are shown in *Table 5*. The *G* values of CO and CO_2 are approximately three times that of H_2 and the value is higher by one order than those of U-PS. The gas evolution of U-Polymer is about 25 times higher than that of Kapton.

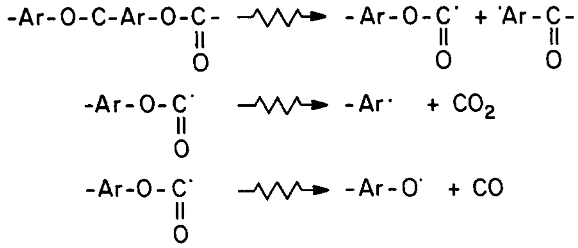
Results of gas evolution from U-Polymer suggest that main-chain scission occurred in the aryl ester linkages, because of the very high *G* values of CO and CO_2 compared with other component gases. H_2 elimination occurred by abstraction from aromatic rings and isopropylidene unit linkages. Main-chain scission in the isopropylidene aromatic linkages probably occurred and, subsequently, CH_4 and C_2H_6 were liberated. The radiolysis mechanism of U-Polymer may be presumed

Table 4 *G* values of evolved gases from polysulphones by gamma irradiation under vacuum

Polymer	Dose (MGy)	*G* value (10^{-3}) of component gas Total	H_2	SO_2	CO	CO_2	CH_4	C_3H_8
PES	E[a]	4.6	0.71	1.2	1.6	1.9	0.03	–
	3.3	4.8	0.72	1.0	1.5	1.7	0.03	–
	4.8	4.6	0.73	1.0	1.6	1.8	0.03	–
	16.9	4.6	0.74	1.1	0.6	2.0	0.01	–
U-PS	E[a]	15	3.9	1.3	1.9	2.5	1.6	–
	3.3	14	5.2	1.3	2.1	2.3	1.5	0.17
	4.8	16	3.9	1.5	2.2	2.4	1.4	0.16
	16.9	14	3.7	2.3	2.3	2.4	1.1	0.11

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

to be as follows:

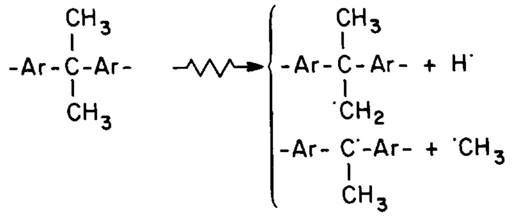


$$\text{-Ar-O-}\underset{\underset{O}{\|}}{C}\text{-Ar-O-}\underset{\underset{O}{\|}}{C}\text{-} \rightsquigarrow \text{-Ar-O-}\underset{\underset{O}{\|}}{C}{}^{\cdot} + {}^{\cdot}\text{Ar-}\underset{\underset{O}{\|}}{C}\text{-} \quad (1)$$

$$\text{-Ar-O-}\underset{\underset{O}{\|}}{C}{}^{\cdot} \rightsquigarrow \text{-Ar}^{\cdot} + CO_2 \quad (2)$$

$$\text{-Ar-O-}\underset{\underset{O}{\|}}{C}{}^{\cdot} \rightsquigarrow \text{-Ar-O}^{\cdot} + CO \quad (3)$$

Elimination of H_2, CH_4 and C_2H_6 may also occur by the following mechanism:



$$\text{-Ar-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\text{-Ar-} \rightsquigarrow \begin{cases} \text{-Ar-}\overset{\overset{CH_3}{|}}{\underset{\underset{{}^{\cdot}CH_2}{|}}{C}}\text{-Ar-} + H^{\cdot} & (4) \\ \text{-Ar-}\underset{\underset{CH_3}{|}}{C^{\cdot}}\text{-Ar-} + {}^{\cdot}CH_3 & (5) \end{cases}$$

The reactive species formed by equations (4) and (5) may recombine, resulting in elimination of H_2, CH_4 and C_2H_6 as follows:

$$H^{\bullet} + H^{\bullet} \rightarrow H_2 \quad (6)$$

$$^{\bullet}CH_3 + H^{\bullet} \rightarrow CH_4 \quad (7)$$

$$^{\bullet}CH_3 + {}^{\bullet}CH_3 \rightarrow C_2H_6 \quad (8)$$

The probability of the reaction in equation (7) is higher than that in equation (8), because of the higher G value of CH_4 compared with C_2H_6.

Table 5 G values of evolved gases from U-Polymer by gamma irradiation under vacuum

Dose (MGy)	G value (10^{-2}) of component gas					
	Total	H_2	CO	CO_2	CH_4	C_2H_6
E[a]	4.8	0.72	2.2	1.8	0.12	–
1.9	4.5	0.61	2.0	1.8	0.09	0.04
5.5	4.2	0.56	1.8	1.6	0.10	0.04
11.1	3.4	0.53	1.7	1.0	0.08	0.02
17.2	2.9	0.52	1.4	0.80	0.07	0.02

[a] G value obtained by extrapolation to zero dose

CONCLUSIONS

Based on the gas evolution and the G values obtained by extrapolation to zero dose (*Tables 2–6*), it can be concluded that the radiation resistance of these aromatic polymers is in the following order: Upilex-R $\geqslant$ Kapton > PEEK-c > PEEK-a > PES > Upilex-S $\gg$ U-PS > U-Polymer. The yield of gas evolution from these aromatic polymers is low compared to that of aliphatic polymers[16,19,20]. The aryl imide and aryl ether ketone unit linkages in polyimides and PEEK structures possess a high protective effect against gamma irradiation. But aryl sulphone, isopropylidene aryl sulphone and aryl ester unit linkages are sensitive to radiation, and main-chain scission is the predominant radiation mechanism in these polymers. The dependence of the volatile product yield on molecular structure can be a very sensitive probe of radiation resistance and the protective effect of polymer chains.

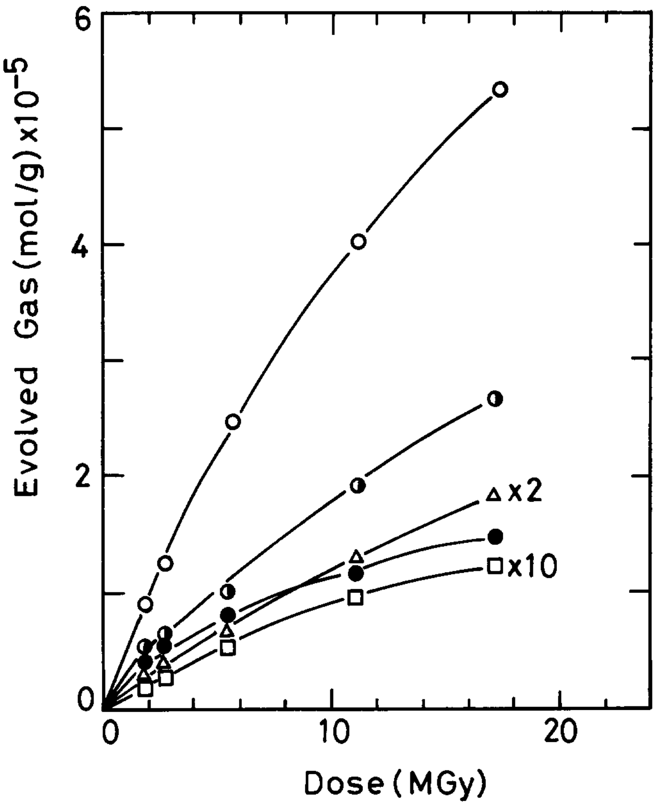


Figure 8 Yield of evolved gases vs. dose for U-Polymer by gamma irradiation: symbols are the same as in *Figure 1*

Table 6 Yield of evolved gases from atomatic polymers by gamma irradiation under vacuum. Dose range: 4–25 MGy

Component gas	Yield (mol g^{-1} MGy^{-1} × 10^{-7})							
	Kapton	Upilex-R	PEEK-c	PEEK-a	PES	Upilex-S	U-PS	U-Polymer
Total	1.8	1.8	2.2	3.5	5.0	7.0	15	45
H_2	0.21	0.05	0.71	1.3	0.84	2.1	3.8	6.4
CH_4	0.09	0.01	0.02	0.03	0.01	0.05	0.84	1.1
CO	0.39	0.29	1.2	1.3	0.62	1.0	2.8	20
CO_2	0.81	0.50	0.42	0.81	2.1	1.8	2.5	15
N_2	0.32	0.90	–	–	–	1.0	–	–
SO_2	–	–	–	–	1.3	–	2.6	–

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