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New Developments in the Field of Radiochemical Ageing of Aromatic Polymers

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1. Introduction

Polymers having an aromatic backbone polymers have a high mechanical strength and a high modulus. Their aromaticity increases their resistance for use in relatively severe conditions especially in aerospace and nuclear industry for which lifetime prediction is a key issue. For example, a challenge for nuclear plants is to extend lifetime from the initially planned 40 years duration to 50 or 60 years, which makes necessary to determine lifetime by a non-empirical method. Since polymers mechanical failure originates from chain scission or crosslinking of the backbone, the ideal method of lifetime prediction would first involve the elaboration of a kinetic model for chain scission and crosslinking. Then, the changes of molecular mass would be related to the changes of mechanical properties using the available laws of polymers physics. Lifetime would be then determined using a pertinent lifetime criterion. A noticeable difficulty comes here from the fact that oxidation, which plays a key major role in chain scission, is diffusion controlled and thus heterogeneously distributed in sample thickness. It is crucial, indeed, to determine experimentally and to predict this depth distribution of chain scission and crosslinking because it will play a key role on fracture properties.

This chapter will be henceforward devoted to the effect of aromaticity on radiostability, the effect on temperature on the chain scission/crosslinking competition, the diffusion limited oxidation (which will be illustrated by the effect of dose rate, atmosphere and sample thickness), then some concluding remarks on oxidative stability of aromatic polymers and the possible link with the absence of macromolecular mobility below T_g. We will start by some basics of radiochemistry which are necessary for the good understanding of this paper, and especially the quantitative treatment for crosslinking and chain scission.

2. Basics of radiochemical degradation

Let us first consider the reaction:

$$A + h\nu \rightarrow B$$

The radiochemical yield is defined as the number of B molecules that are generated per absorbed joule:

$$G' = \frac{n}{E'} = \frac{N}{N_{Av}} \cdot \frac{1}{E \times (1.6 \times 10^{-17})} = 10^{-7}.G \quad (1)$$

where:
- G' is the radiochemical yield expressed in mol J^{-1},
- n is the number of moles of B which is formed by the radiochemical reaction,
- E' is the amount of absorbed energy in J,
- E is the amount of absorbed energy in 100 eV,
- N is the number of B molecules,
- N_{Av} is the Avogadro's number,
- G is the yield in molecules per 100 eV absorbed.

Since the absorbed dose (denoted by δ and expressed in Gy) is defined as the amount of received energy (in J) per kilogram of polymer, the following equation can be derived:

$$\frac{n}{m} = 10^{-7}.G.\delta \quad (2)$$

So that:

$$r = \frac{dc}{dt} = 10^{-7}.G.I \quad (3)$$

r being the rate of a radiochemical event (in mol l^{-1} s^{-1}), I the dose rate in Gy s^{-1} and c the concentration of reacted or generated species (in mol kg^{-1} even if one often considers that it is the same than in mol l^{-1}).

2. Mathematical treatment for chain scission and crosslinking

Irradiation can provoke both chain scission and crosslinking, the relative proportion of these phenomena depending on many factors which will be presented in the following. The radical coupling may lead to trifunctionnal or tetrafunctionnal crosslinking noduli called respectively Y- and H-crosslinkings (Fig. 1):

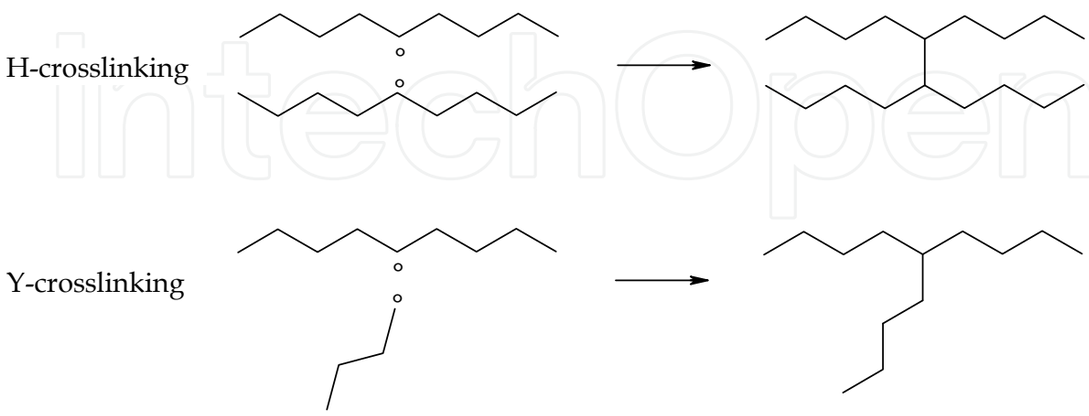


Fig. 1. Reaction of H- and Y- crosslinking.

The radiochemical yields for chain scissions G(s) and crosslinking G(x) in thick samples can be tentatively assessed using

- The Charlesby-Pinner's (Charlesby, 1960) from an analysis of the residual soluble fraction after beginning of sol-gel transition,
- Saito's equations (Saito, 1958) describing the average molar mass changes for soluble polymers before the sol-gel transition.

The corresponding mathematical treatment of these theories differs for Y- and H-crosslinking:

1. In the case of H- crosslinking mode:

$$\frac{1}{\overline{M}_N} - \frac{1}{\overline{M}_{N0}} = s - x = 10^{-7}.\left[G_H(s) - G_H(x)\right].\delta \tag{4}$$

$$\frac{1}{\overline{M}_W} - \frac{1}{\overline{M}_{W0}} = \frac{s}{2} - 2x = 10^{-7}.\left[\frac{G_H(s)}{2} - 2G_H(x)\right].\delta \tag{5}$$

$$w_S + w_S^{1/2} = \frac{G_H(s)}{2G_H(x)} + \frac{10^7}{\overline{M}_{W0}.G_H(x).\delta} \tag{6}$$

2. In the case of Y- crosslinking mode:

$$\frac{1}{\overline{M}_N} - \frac{1}{\overline{M}_{N0}} = s - x = 10^{-7}.\left[G_Y(s) - G_Y(x)\right].\delta \tag{7}$$

$$\frac{1}{\overline{M}_W} - \frac{1}{\overline{M}_{W0}} = \frac{s}{2} - x = 10^{-7}.\left[\frac{G_Y(s)}{2} - G_Y(x)\right].\delta \tag{8}$$

$$1 + 3w_S^{1/2} = \frac{2G_Y(s)}{G_Y(x)} + \frac{1.93 \times 10^7}{\overline{M}_{N0}.G_Y(x).\delta} \tag{9}$$

where:

- $w_S = 1 - w_I$ is the soluble fraction,
- $G_H(s)$, $G_H(x)$, $G_Y(s)$, and $G_Y(x)$ are the radiochemical yields expressed for 100 eV respectively for chain scissions and crosslinking for an H- and a Y- crosslinking mechanism,
- δ is the dose (Gy)
- M_{N0} and M_{W0} are respectively the initial number and weight average molar mass (kg mol^{-1}).

3. Effect of aromaticity on radiostability

The degradation of aromatic polymers was studied by many authors:

1. By monitoring mechanical properties (Sasuga et al., 1985, see Table 1):

These results give a first indication on the relative radiostability of aromatic polymers. Let us first mention that these lethal doses are considerably greater than those compiled by Wilski for polymer having an aliphatic backbone (Wilski, 1987). It can be attributed to the well-known stabilizing effect of aromatic groups which was first observed on methyl methacrylate-styrene copolymers (Alexander & Charlesby, 1954, Kellman et al., 1990,

Thominette et al., 1991). However, the results of these studies cannot be directly used in kinetic models for aromatic polymers.

Polymer	$\delta_{50\%}$	$\delta_{20\%}$
Kapton 500	10	90
Upilex	35	60
Ultem	1.5	4
A-Films	15	25
A-Paper	20	30
PEEK non-cryst	20	50
PEEK cryst	8	30
U-polymer	0.5	2
Udel-Polysulphone	0.75	1
PES	0.5	0.75
Noryl (modified PPO)	0.75	1.5

Table 1. Dose for reducing strain at break to 50% and 20% of initial value for various aromatic polymers submitted to 5.10^3 Gy s^{-1} in air (sample thickness ~ 0.1-0.2 mm) (Sasuga et al., 1985).

2. By radical appearance measured by Electron Spin Resonance spectroscopy (Heiland et al., 1996, see Fig. 2):

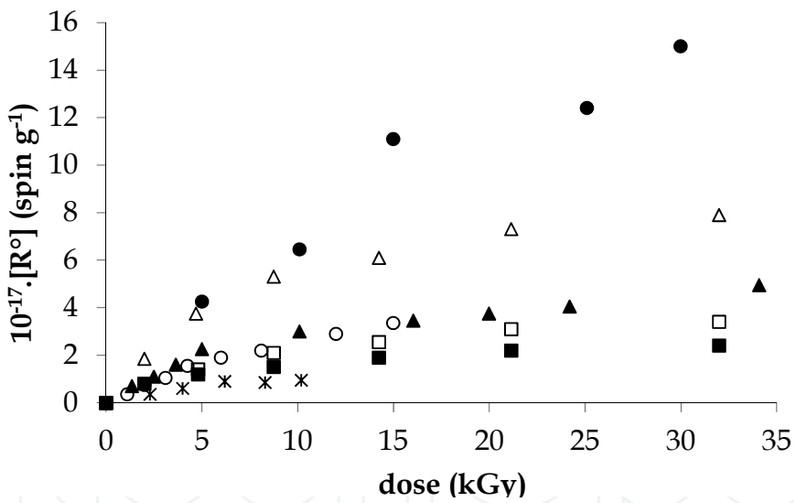


Fig. 2. Concentration in radicals versus dose measured in PPO (●), Kevlar (△), PSU (▲), PEPO (○), Ultem (□), Kapton (■), PEEK (∗) in aromatic polymers under 1 - 5 kGy h^{-1} dose rate at 77 K (Heiland et al., 1996).

Data presented in Fig. 2 permit the yield in radical build-up to be calculated according to the simplified scheme for radiochemical degradation in the absence of oxygen:

Initiation:	Polymer (PH) + hν → P°	r_i
Propagation:	P° + PH → PH + P°	k_P
β-scission:	P° → P° + s	k_R
Termination by coupling:	P° + P° → P–P + x	k_C
Termination by disproportionnation:	P° + P° → F + PH	k_D

Where F is a double bond.
The rate of radical formation is:

$$\frac{d[P^\circ]}{dt} = r_i - 2k_t[P^\circ]^2 \tag{10}$$

with:

$$k_t = k_C + k_D \tag{11}$$

Fig. 2 indicates the existence of an asymptote characterizing a steady-state at which the concentration in radicals is:

$$[P^\circ]_\infty = \sqrt{\frac{r_i}{2k_t}} \tag{12}$$

Eq. 10 gives:

$$\frac{d[P^\circ]}{\left(1+\frac{[P^\circ]}{[P^\circ]_\infty}\right)\cdot\left(1-\frac{[P^\circ]}{[P^\circ]_\infty}\right)} = \frac{r_i}{[P^\circ]_\infty}\cdot dt \tag{13}$$

Which is integrated in:

$$\ln\left(\frac{1+\frac{[P^\circ]}{[P^\circ]_\infty}}{1-\frac{[P^\circ]}{[P^\circ]_\infty}}\right) = \frac{2r_i}{[P^\circ]_\infty}\cdot t \tag{14}$$

At t ~ 0, [P°] ~ 0 so that:

$$\left(1+\frac{[P^\circ]}{[P^\circ]_\infty}\right)^2 = 1+\frac{2r_i}{[P^\circ]_\infty}\cdot t \tag{15}$$

thus:

$$G(P^\circ) = G_i = \left(\frac{d[P^\circ]}{dt}\right)_{t\to 0} \tag{16}$$

The corresponding yields for radical build-up are given in Table 2.
Let us first mention that Table 1 results correspond to degradation under air, meanwhile Table 2 results correspond to degradation in inert environment, the possible influence of oxygen being discussed in the following. However, it can be checked that the lethal dose (or dose to reach an arbitrarily chosen threshold for a mechanical property) varies oppositely with the estimated G(P°) values.

Polymer	G(P°)
PPO	1.35
Kevlar®	1.25
PSU	0.75
Bis-A-PEPO	0.55
Ultem	0.50
Kapton®	0.40
PEEK	0.25

Table 2. Yields for radical build-up for aromatic polymers irradiated under 1 - 5 kGy h^{-1} dose rate at 77 K.

- By gas yield emission:

Concerning the yield for total gas emission, it can be checked that there is no great difference between gamma, proton and electron-beam irradiation (Hegazy et al., 1992b, Hill & Hopewell, 1996) and that these values are considerably lower than those measured for aliphatic polymers such as PE or PP (Schnabel, 1978). An example is worth to be mentioned (Schnabel, 1978): aliphatic polysulfones have a gas emission yield equal to 39 (poly butene-1-sulfone) or 71 (poly hexene-1-sulfone) meanwhile PES or PSU gas emission yields are lower than 1, illustrating here the protective effect by aromatic rings. However, the relative proportion of each emitted gas can vary due to some differences in temperature rising under irradiation. As it will be seen below, this difference due to irradiation nature has a lower influence on the radio induced degradation of polymer than temperature, nature of environment atmosphere and oxygen gradient in sample thickness.

I (kGy h^{-1})	Gaz	Kapton	Upilex-R	Upilex-S	PEEK-c	PEEK-a	PES	U-PS	U-Polymer
10	**Total**	24.0	22.0	91.0	39.0	54.0	46.0	150.0	480.0
	H_2	3.2	0.4	7.5	-	14.0	7.1	39.0	72.0
	N_2	5.1	9.7	14.0	6.4	-	-	-	-
	CO	5.4	2.4	1.4	12.0	6.0	16.0	19.0	220.0
	CO_2	8.1	4.8	15.0	4.3	24.0	19.0	25.0	180.0
	CH_4	1.0	0.1	0.3	0.2	0.3	0.3	16.0	12.0
	SO_2	-	-	-	-	-	12.0	13.0	-
6120	**Total**	25.0	17.0	18.0	31.0	39.0	69.0	210.0	460.0
	H_2	4.9	1.3	2.4	10.0	12.0	19.0	62.0	80.0
	N_2	0.2	0.1	2.8	-	-	-		-
	CO	3.4	2.2	2.4	5.1	5.5	8.3	32.0	220.0
	CO_2	10.0	3.9	8.8	9.5	16.0	16.0	16.0	120.0
	CH_4	0.8	-	0.3	0.2	0.2	0.4	13.0	32.0
	SO_2	-	-	-	-	-	23.0	43.0	-

Table 3. 103.G(gas) for irradiation at 30°C 100 µm films vacuum (Hegazy et al., 1992a)

3. Let us turn to the radiation-induced crosslinking observed in PEEK and PSU.

Fig. 3 depicts the changes in thermal behavior which are induced by radio-ageing for a thick PEEK sheath under air (Richaud et al., 2010a). As it will be seen later, the observed behavior is comparable to the one obtained for an irradiation under vacuum. Virgin and degraded samples were characterized by DSC heating-cooling-heating cycle.

- In the case of virgin sample, melting endotherms for the first and the second heating ramps are very comparable (peak temperature and enthalpy). The crystallization from molten state is characterized by a sharp exotherm at c.a. 300°C.
- In the case of 30.7 MGy irradiated sample, melting endotherm for the second heating ramp and crystallization exotherm are shifted to the lower temperatures with a lower transition enthalpy.

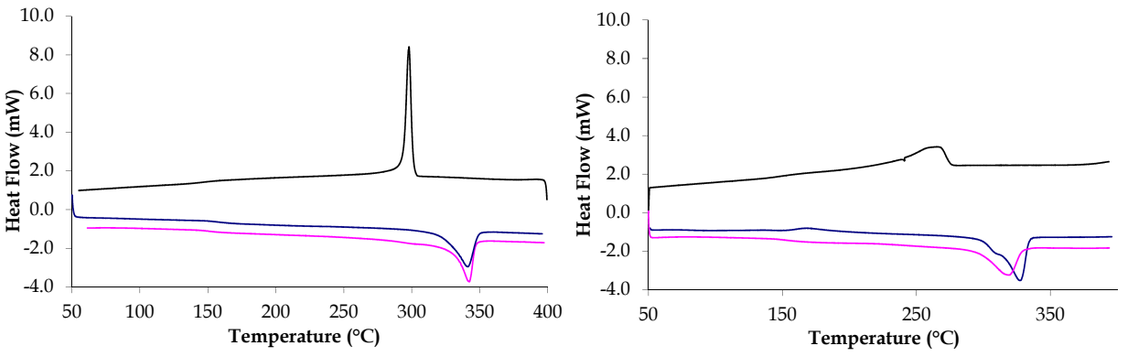


Fig. 3. Heating-cooling-heating cycle by DSC for non-irradiated (a) and 30.7 MGy irradiated PEEK sample.

During irradiation of semi-crystalline polymers, chain scission and crosslinking occur only in amorphous phase, the crystalline phase undergoes only small changes so that melting characteristics remain almost unchanged at the first heating scan. After a first melting however, the sample is homogenized, and the changes of molar mass, branching ratio or crosslink density resulting from irradiation affect melting and crystallization. Irradiation effects become then observable by DSC. Here, the decrease of crystallization temperature and enthalpy is explained by the occurrence of radiation-induced crosslinking (Sasuga, 1991). This latter disfavors crystallization because it lowers the transport rate of chain segments from the melt to growing crystals. As a consequence, the degree of crystallinity and the lamellae thickness are decreased that explains the observed decrease of melting point and melting enthalpy.

Comparable data were obtained by Hegazy (Hegazy et al., 1992c). T_g values from this study are reported (Fig. 4):

It is well known that for a linear polymer, T_g is an increasing function of molar mass. According to Fox and Flory (Fox & Flory, 1950):

$$T_g = T_{g0} - \frac{k_{FF}}{\overline{M}_N} \tag{17}$$

Where:
- T_{g0} is the T_g of a virtual infinite polymer (K).
- M_N is the number average molar mass (kg mol^{-1}).
- k_{FF} is a constant characteristic of the chain chemical structure (K kg mol^{-1}).

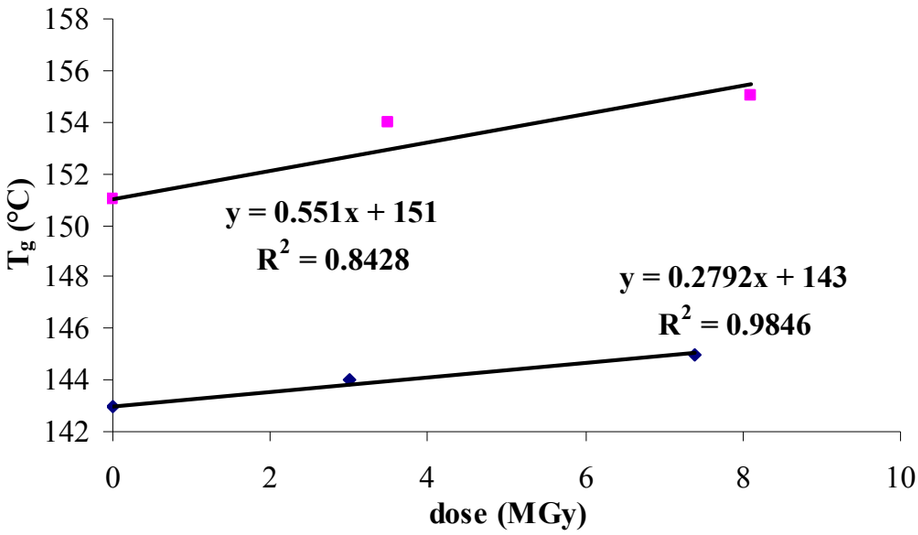


Fig. 4. T_g changes for PEEK amorphous (◆) and semi-crystalline (■) samples irradiated under vacuum.

For a network, T_g is an increasing function of crosslink density. According to Di Marzio (DiMarzio, 1964):

$$T_g = \frac{T_{gl}}{1 - k_{DM}.F.\nu_A} \tag{18}$$

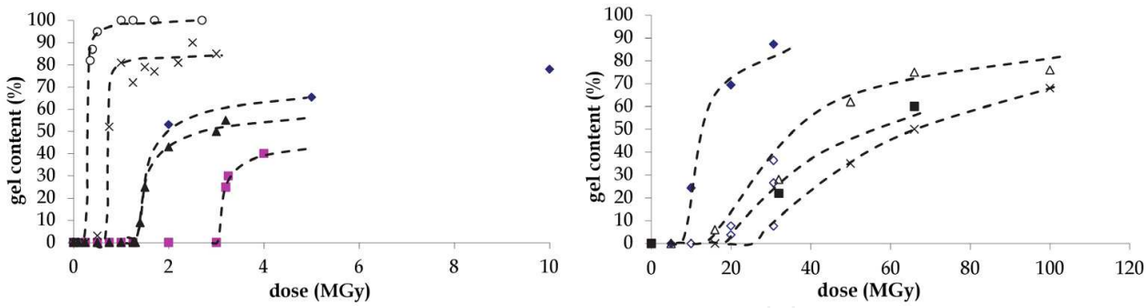
Where:
- T_{gl} is the T_g of a virtual linear polymer containing all the structural units of polymer except crosslinks (K).
- F is a flex parameter linked to chain stiffness (kg mol^{-1}).
- ν_A is the concentration in elastically active chains, which is calculated from crosslinks concentration (mol kg^{-1}).

Under vacuum, chain scission is generally negligible. Above gel point, it seems to us that T_g changes are given by combining Fox-Flory relationship and Saito's equation (assuming first that s << x):

$$\frac{dT_g}{d\delta} = \frac{dT_g}{dx} \cdot \frac{dx}{d\delta} = 10^{-7}.G(x).k_{FF} \tag{19}$$

One obtains:
- G(x) ~ 0.012 for amorphous PEEK,
- G(x) ~ 0.023 for semi-crystalline one.

It seemed to us interesting to compare radio-induced gelation for PEEK, PSU and PES (Fig. 5).



(a) (b)

Fig. 5. Gel formation for PSU at 210°C (○), 180°C (×), 100°C (▲), 60°C (◆), room temperature (■) from Murakami & Kudo, 2007, Richaud et al., 2011), and PEEK (■: 24 kGy h^{-1}, ◆,△,×: 60 MGy h^{-1} for 3 different initial crystalline microstructures) samples irradiated at several temperatures (Vaughan & Stevens, 1995 , Richaud, 2010a).

From the above given mechanistic scheme where chain scission results from radical rearrangement and crosslinking results from radical coupling scheme, the following stationary rate expressions can be derived:

- Rate of chain scission:

$$\frac{ds}{dt} = \frac{k_R}{2} \cdot \left(\frac{r_i}{k_C + k_D} \right)^{1/2} \tag{20}$$

- Rate of crosslinking:

$$\frac{dx}{dt} = \frac{r_i}{2} \frac{k_C}{k_C + k_D} \tag{21}$$

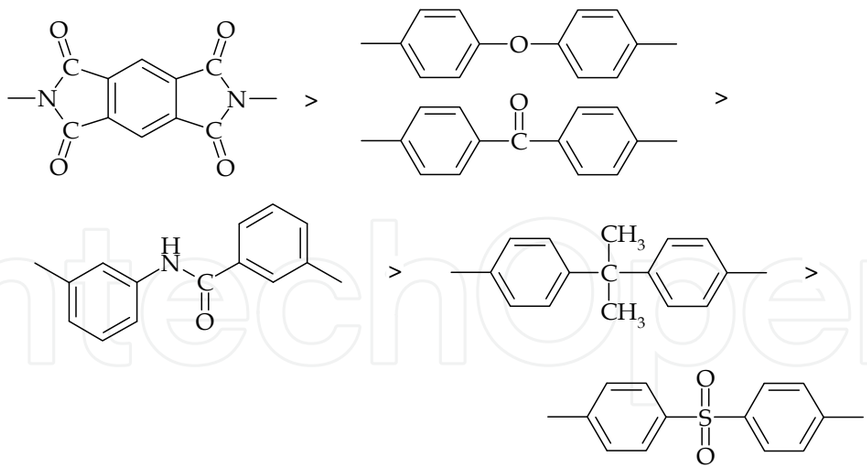
Assuming that disproporationation is negligible compared to coupling for polymers under study, it comes:

$$\frac{dx}{dt} = \frac{r_i}{2} \tag{22}$$

So that : $G_i = 2G(x)$ in the absence of oxygen.

It seems that this relationship disagrees with experimental results in the case of aromatic polymers which will be discussed next.

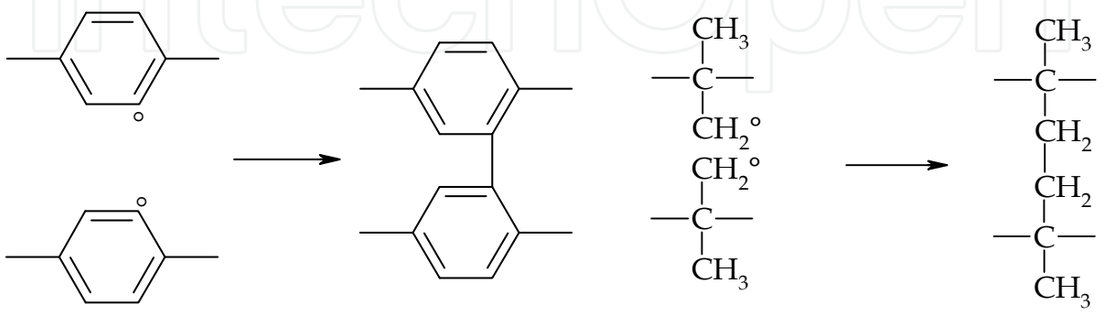
As a conclusion of this short review of experimental results, it is clear that aromatic polymers belong the family of relatively radiostable polymers because primary radiochemical events, presumably radiolytic chain scissions of C-H bonds, have a radiochemical yield less than 0.5, i.e. 5 to 50 times lower than for aliphatic polymers. Aromatic groups are actually able to dissipate a great part of the absorbed energy into reversible processes (fluorescence, phosphorescence...). Data militate in favour of the following ranking:



A comparison of the rate of gel content increase (Fig. 4) for samples irradiated at various temperatures and dose rates shows that gelation is more sudden in the case of PSU and more progressive in PEEK which means that radiation generated radicals would be more reactive for PSU than PEEK.

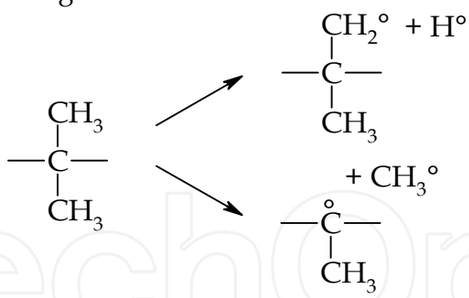
Data also show unambiguously:

- The protective effect of aromaticity: Kapton®, which is the most aromatic polymer, presents a very limited degradation, or even no significant degradation (Kang et al., 2008, Richaud et al, 2010b).
- The role of SO_2 moiety: experimental results for radiochemical yields values (Horie & Schnabel, 1984) shows that aliphatic polysulfones are among the less stable polymers with G(s) values on the order of 10. High yields of SO_2 emission are also observed indicating thus the probable existence of the weak (Li & Huang, 1999, Molnár et al., 2005) carbon-sulfone bond cleavage. It seems reasonable to suppose that such events occur also in PSU even though the yield is considerably lower owing to the well-known protective effect of aromatic nuclei illustrated for instance in studies on isobutylene-styrene.
- The role of isopopylidene group: gelation is undoubtedly due to the coupling of alkyl radicals. The difference in gelation rate would be explained by the nature of radicals: in PEEK, only aryl radicals can react meanwhile both aryl and primary methyl radical can react in PSU.



Theoretically, it seems that yields in gas emission G(gas) is half of yield radicals G(P°) as illustrated by proposal of degradation mechanisms below:

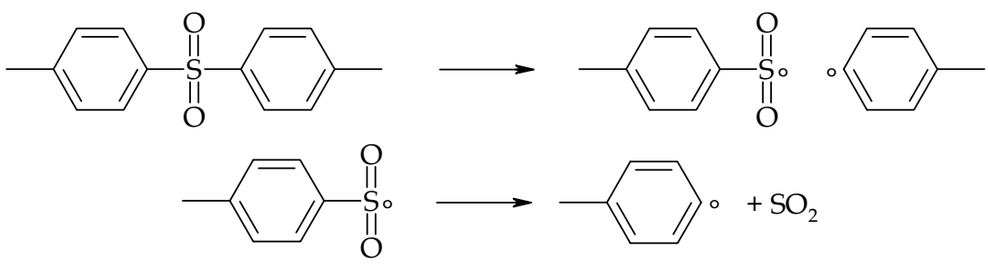
1. In isopropylidene containing materials:



Then radicals react by coupling to give a gaseous molecule:

$$H° + H° \rightarrow H_2$$
$$CH_3° + H° \rightarrow CH_4$$
$$CH_3° + CH_3° \rightarrow C_2H_6$$

2. In sulfone containing polymer:



Analogous mechanisms could lead to carbon monoxide formation from PEEK.
Data for Kapton®, PEEK and PSU (Table 1 and Table 2) seem also to show that:

$$G(P°) >> 2G(x) \text{ and } 2G(gas)$$

PEEK and PSU values gathered in this work are compared with those for polyethylene (Khelidj 2006), and those compiled for cyclohexane and benzene (Ferry, 2008) in Table 4:

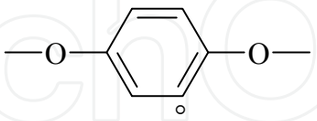
thickness	T (K)	dose rate	atmosphere	$\delta_{50\%}$ (MGy)	δ_{gel} (MGy)	G (gas)
100 µm	298	0.1 kGy s^{-1}	He	> 0.3		
	423			> 0.15		
	463			0.1		
	503			0.1		
50 µm	298	1.7 Gy s^{-1}	vacuum		3	0.025
	373				1.25	0.07
	453				0.5	0.17
	483				< 0.25	2

Table 4. Yields for radicals, gas emission, crosslinking and double bond formation (corresponding to disproportionnation process). *: $G(H_2)$ is expected to be close to G(gas), **: G(F) is expected to be negligible in aromatic polymers.

These results call for the following comments:

1. The effect of aromaticity on radiostability is confirmed.
2. The ratio G(P°)/G(gas) is surprisingly lower than 1 for cyclohexane, is fairly close to 2 for benzene and PE, but increases for PSU and PEEK.

A possible explanation is the existence of very stable radicals that would be detected by ESR but would contribute neither to gas emission nor to crosslinking (see later) as for example:



Let us also note that the absence of contribution to gas emission seems easily explainable because the probability for generating a short and volatile segments from such macroradicals is very low.

3. The ratio G(P°)/(G(x)+G(F)) is also clearly greater than 2 for PSU and particularly for PEEK meanwhile it is close to 1 in PE and in cyclohexane. The comparison with benzene suggests that this behaviour is due to the macromolecular structure of radicals preventing them to react by coupling to give crosslinking.

In fact, even if a negative concavity is observed in Fig. 1 and indicates the existence of a termination process even at 77 K, the relatively low value of G(x) indicates that segmental mobility would be reduced below T_g, which will be discussed in a first section dedicated to temperature effect and another one dealing with oxidizability.

4. Effect of temperature

Data in Table 5 confirm that lethal dose (here. the necessary dose to half the initial elongation at break) and gel dose vary oppositely with temperature meanwhile gas emission yield would increase.

thickness	T (K)	dose rate	atmosphere	δ_{50}% (MGy)	δ_{gel} (MGy)	G(gas)
100 µm	298	0.1 kGy s^{-1}	He	> 0.3	-	-
100 µm	423			> 0.15	-	-
100 µm	463			0.1	-	-
100 µm	503			0.1	-	-
50 µm	298	1.7 Gy s^{-1}	vacuum	-	3	0.025
50 µm	373			-	1.25	0.07
50 µm	453			-	0.5	0.17
50 µm	483			-	< 0.25	2

Table 5. Effect of temperature on lethal dose for PES (Sasuga & Hagiwara, 1987 and Murakami & Kudo, 2007).

As previously suggested, the only knowledge of changes in macroscopic (engineering) properties does not permit to ascribe the right cause of failure. Yields in chain scission and crosslinking permit to elucidate the degradation mechanism.

Let us first comment the T_g changes in PES (Li et al., 2006) presented in Fig. 6:

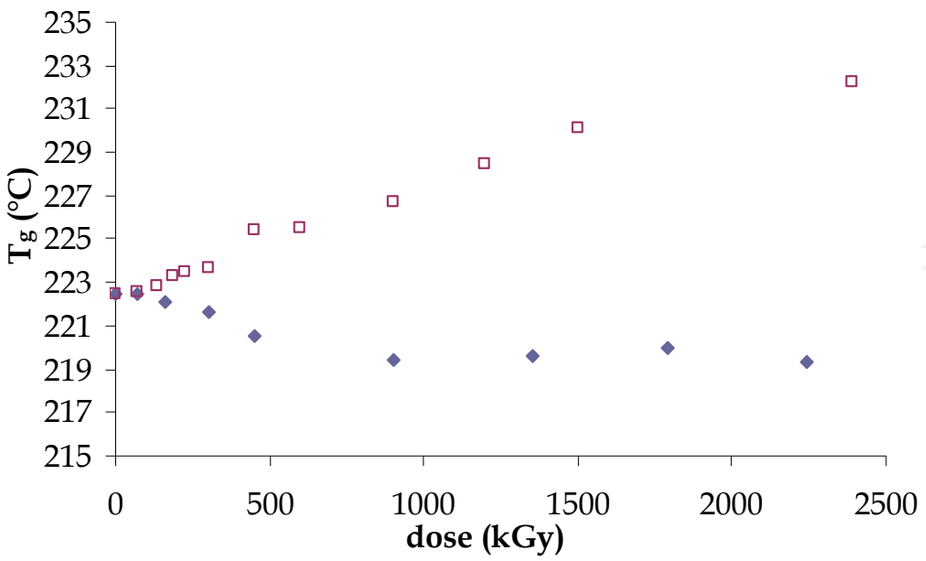


Fig. 6. Change in T_g for PES submitted to electron beam irradiation at room temperature (◆) or 230°C (□) (Li et al., 2006).

Before sol-gel transition, T_g changes are given by combining Fox-Flory law (Fox & Flory, 1950) with Saito's equation (Saito, 1958) irrespectively of H- or Y-crosslinking mode:

$$T_g - T_{g0} = -k_{FF}.\left(\frac{1}{\overline{M}_N} - \frac{1}{\overline{M}_{N0}}\right) = -10^{-7}.k_{FF}.[G(s) - G(x)].\delta \tag{23}$$

It turns into:

- for a pure crosslinking mechanism:

$$\frac{dT_g}{d\delta} = 10^{-7}.k_{FF}.G(x) \tag{24}$$

- for a pure chain scission mechanism:

$$\frac{dT_g}{d\delta} = -10^{-7}.k_{FF}.G(s) \tag{25}$$

Results presented in Fig. 5 indicate that crosslinking predominates above T_g, whereas chain scission predominates below T_g. Comparable exploitation can be done from other published results (Murakami & Kudo, 2007, Brown & O'Donnell, 1979):

All data converge towards the fact that G(x) increases with temperature. Despite some scattering, it also suggests that G(s)/G(x) decreases with temperature. According to Brown and O'Donnell (Brown & O'Donnell, 1979), it falls to 0 above T_g.

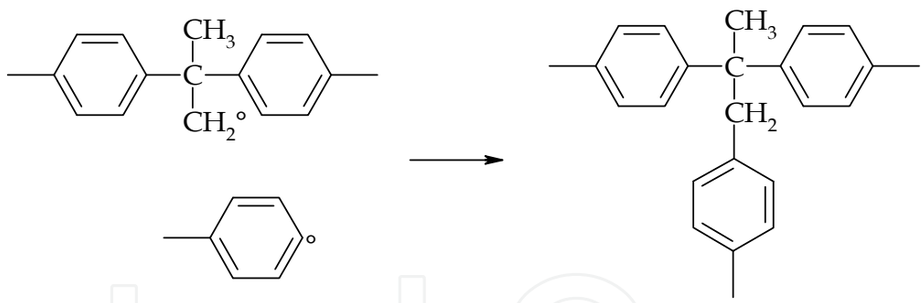
The results in Table 6 can be explained as follows: irradiation creates macroradicals. At low temperature, they react by an unimolecular process which generates a chain scission (possibly accompanied by gas emission). At high temperature, macromolecular mobility is sufficient to permit macroradicals to react by coupling to give a crosslinking. According to Zhen (Zhen, 2001) most polymers can only crosslink above their melting point.

dose rate	method	T (K)	$G_H(s)$	$G_Y(s)$	$G_H(x)$	$G_Y(x)$	G(s)/G(x)	thickness
8 Gy s^{-1}	Sol gel	308	0.03		0.04		0.75	3 mm
		353	0.05		0.05		1.00	3 mm
		398	0.3		0.2		1.50	3 mm
		493	0		0.67		0.00	3 mm
1.7 Gy s^{-1}	GPC	298	0.100	0.373	0.100	0.301	1.00	50 µm
		373	0.104	0.318	0.104	0.313	1.00	50 µm
		423	0.147	0.455	0.147	0.442	1.00	50 µm
		453	0.216	0.601	0.216	0.647	1.00	50 µm
1.7 Gy s^{-1}	Sol gel	298	0.067	0.065	0.104	0.147	0.64	50 µm
		373	0.170	0.138	0.245	0.312	0.69	50 µm
		453	0.075	0.268	0.170	0.575	0.44	50 µm

Table 6. Effect of temperature on radiochemical yields in chain scissions and crosslinking (envisaging the possibility of H- or Y- crosslinking mode) (Murakami & Kudo, 2007, Brown & O'Donnell, 1979).

Let us now discuss of the possibility of Y- and H-crosslinking.

- At 150°C, Hill (Hill et al., 1998) unambiguously showed that PSU crosslinks in Y-mode. A comparable analysis was performed by Li (Li et al., 2006). A proposal of mechanism is shown below:



- Kudo (Murakami & Kudo, 2007) proposed a Y-mechanism also. However, by reexaminating his results using the above equations, his conclusion is questioned.
- Richaud (Richaud et al., 2011) proposed a H- crosslinking mechanism at 60°C, basing on the observation that if isopropopylidene groups are generated, the →C–CH_2° group is considerably more reactive than aryl one and should react by coupling to give →C–CH_2-CH_2-C← crosslinking bridges corresponding more to a H- crosslinking mechanism.

As a conclusion, it seems that elevating the temperature promotes the crosslinking. However, the nature of this latter and presumably the role of temperature remain unclear.

5. Effect of atmosphere and sample thickness

Results in Fig. 7 (Sasuga & Hagiwara, 1987) clearly show that oxygen accelerates the degradation of aromatic polymers.

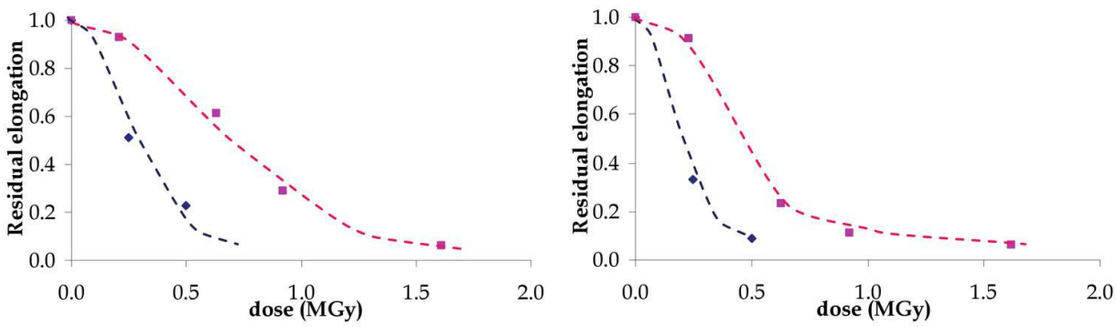


Fig. 7. Residual elongation as a function of dose for PSU (a) and PES (b) submitted to g-rays under air (■) or 0.7 MPa oxygen (◆).

The nature of the responsible process is suggested in a study on the degradation of PET films monitored by T_g measurements (Burillo et al., 2007): a strong T_g decrease is observed in air at the beginning and is certainly due to chain scission whereas a moderate T_g decrease is observed for irradiation under vacuum. As proposed by Sasuga (Sasuga, 1988), polymer radio-degraded under anaerobic conditions would undergo mainly crosslinking meanwhile they would undergo chain scissions when they are degraded under aerobic (oxidative) conditions.
The effect of atmosphere nature and the effect of thickness have the same origin linked to oxygen diffusion: thick samples present a diffusion limited oxidation (DLO), i.e. that their surface undergoes an oxidative degradation leading to chain scission meanwhile bulk undergoes an anaerobic radio-ageing generating radicals reacting only by coupling.
This effect was quantified by comparing the degradation of thin and thick samples by means of GPC (for molar mass assessment and subsequently chain scission and crosslinking yields assessment) and T_g (Richaud et al., 2011). T_g decreases for both 2 mm and 200 µm thick samples, but more significantly for thin films (Fig. 8) which is not surprising since T_g decreases with chain scissions and increases with crosslinking.

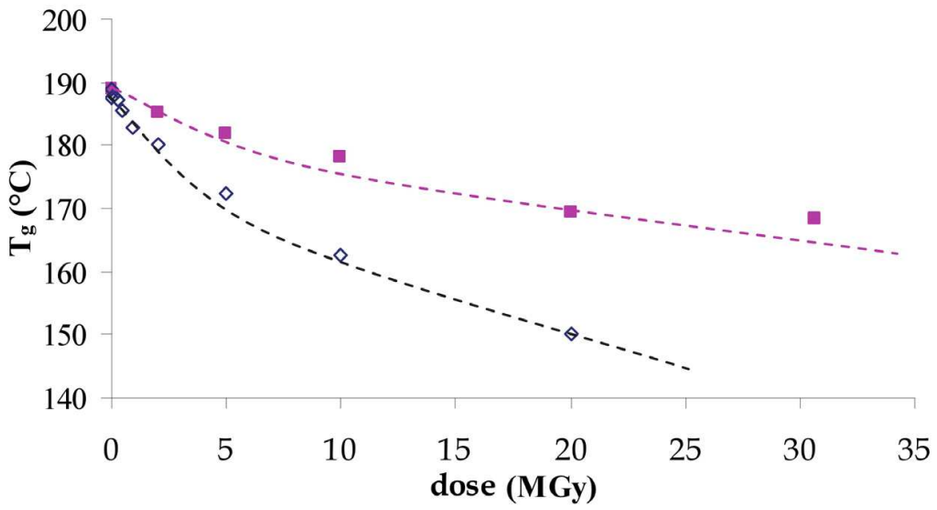


Fig. 8. T_g changes with dose for thin films (◆) or thick samples (■).

1. Case of thin films

Thin films undergo certainly a "pure" random chain scissions process. A graphical estimation (Fig. 5) gave for the thin samples (using $k_{FF} \sim 220$ K kg mol^{-1} for PSU):

$$\frac{dT_g}{d\delta} \sim \frac{T_g(0\ MGy) - T_g(5.0\ MGy)}{5.0 \times 10^6} = 3.2 \times 10^{-6}\ K\ Gy^{-1}$$

from which one obtains G(s) ~ 0.15

2. Case of thick samples

Here, the simultaneous crosslinking compensates partially chain scissions consequences on T_g changes. For ideal networks having no dangling chains, the effect of crosslinking on T_g obeys the DiMarzio's law (DiMarzio,1964 – equation (18)) with:

- $T_{gl} \sim 473$ K
- $F_{PSU} = 0.1105$ kg mol^{-1}
- k_{DM} is the DiMarzio's constant: k_{DM} is close to 1
- ν is the elastically active chains concentration. For ideal tetrafunctional networks:

$$\nu = 2.x \tag{26}$$

x being the concentration of crosslinks events. Supposing that DiMarzio's equation can be applied for non-ideal networks, Eq. 23 turns into the Fox-Loshaek (Fox & Loshaek, 1955) equation for low conversion of the crosslinking process:

$$T_g = T_{gl} + k_{FL}.x \tag{27}$$

with the Fox-Loshaek constant k_{FL} being equal to:

$$k_{FL} = 2.T_{gl}.F.k_{DM} \tag{28}$$

so that: $k_{FL} \sim 104$ K mol kg^{-1}

Finally, the global changes of T_g would be given by:

$$\frac{dT_g}{d\delta} = \left(\frac{\partial T_g}{\partial s}\right).\frac{ds}{d\delta} + \left(\frac{\partial T_g}{\partial x}\right).\frac{dx}{d\delta} \tag{29}$$

so that:

$$\frac{dT_g}{d\delta} = 10^{-7}\left(k_{FL}.G(x) - k_{FF}.G(s)\right)$$

Using G(s) ~ 0.15, one can simulate the experimental T_g decrease:

$$\frac{dT_g}{d\delta} = 15.6 \times 10^{-7}\ K\ Gy^{-1}$$

with G(x) ~ 0.15.

In other words, effect of sample thickness is explained by the effect of oxygen diffusion (which will be developed in the next section): irradiation generates radicals. In the absence of oxygen (i.e. for the core a bulk sample), these later react together by coupling which gives a crosslinking phenomenon. When oxygen is present (which is the case for thin samples or

the superficial layer of a bulk sample), it orientates the degradation towards an oxidative mechanism with the formation of peroxy radicals POO°, and POOH of which decomposition induces chain scissions.

6. Effect of dose rate

This effect is illustrated by some results by Tavlet (Tavlet, 1997) presented in Fig. 9:

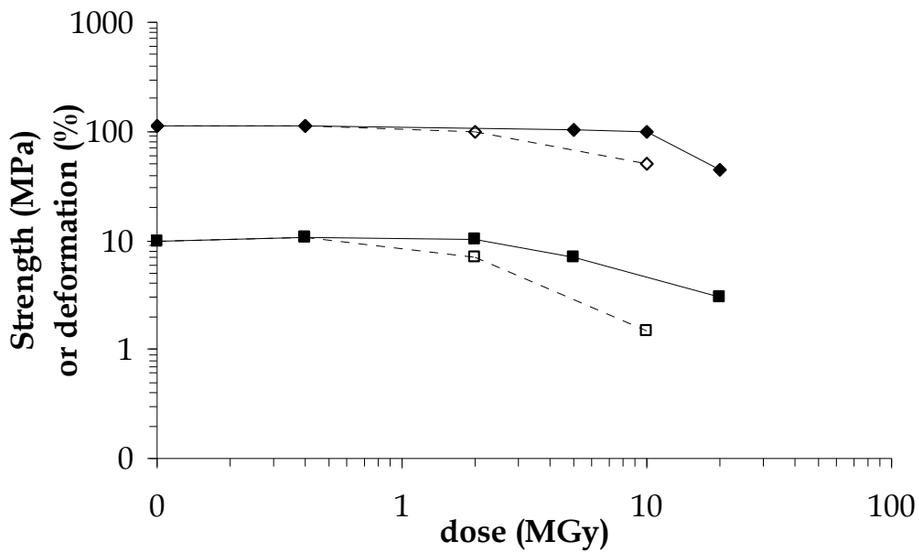


Fig. 9. Radiation degradation in an epoxy resin on strain (■,□), stress (◆,◇). Open symbols correspond to long term (low dose rate) ageing (Tavlet, 1997).

There are two effects to be distinguished:
- An increase in temperature involved by enhancing the dose rate,
- A physical and chemical effect linked to Diffusion Limited Oxidation, which will be described below.

From a simplified theory of diffusion controlled oxidation (Audouin et al, 1994), a rough estimation of oxygen consumption rate r_{OX} in films or superficial layers of thick samples can be done:

$$r_{OX} = \frac{D_{O2}.[O_2]_S}{TOL^2} \tag{30}$$

where:
- TOL is the thickness of oxidized layer (m),
- D_{O2} is the oxygen diffusion coefficient in polymer amorphous phase ($m^2\ s^{-1}$),
- $[O_2]_S$ is the equilibrium concentration under atmospheric pressure given by Henry's law:

$$[O_2] = s_{O2} \times P_{O2} \tag{31}$$

s_{O2} being the solubility coefficient of oxygen in polymer amorphous phase.
r_{OX} can be expressed from a simplified mechanistic scheme for radio-thermal oxidation:

$PH + h\nu \rightarrow P^\circ + \frac{1}{2} H_2$	r_i
$P^\circ + O_2 \rightarrow P^\circ$	k_2
$POO^\circ + PH \rightarrow POOH + P^\circ$	k_3
$POO^\circ + POO^\circ \rightarrow$ inact. prod. $+ O_2$	k_6

k_i being the rate constants (expressed in l mol^{-1} s^{-1}).
The oxidation rate for oxygen consumption can be expressed as:

$$r_{OX} = -\frac{d[O_2]}{dt} = - k_2.[P^\circ][O_2] + k_6.[POO^\circ]^2 \quad (32)$$

Using the classical steady-state assumption:

$$k_2.[P^\circ][O_2] = r_i + k_3.[POO^\circ].[PH] \quad (33)$$

$$r_i = 2k_6.[POO^\circ]^2 \quad (34)$$

it comes:

$$r_{OX} = \frac{r_i}{2} + k_3 \cdot \sqrt{\frac{r_i}{2k_6}} \cdot [PH] \quad (35)$$

knowing that: $r_{OX} = 10^{-7}.G(P^\circ).I$
I denoting the dose rate. Consequently, if:

- I is very high

$$\Rightarrow \quad r_{OX} \approx \frac{r_i}{2} \quad (36)$$

$$\Rightarrow \quad r_{OX} \propto I \quad (37)$$

$$\Rightarrow \quad TOL \propto I^{-1/2}$$

- I is moderate

$$\Rightarrow \quad r_{OX} \approx k_3 \cdot \sqrt{\frac{r_i}{2k_6}} \cdot [PH] \quad (38)$$

$$\Rightarrow \quad r_{OX} \propto I^{1/2} \quad (39)$$

$$\Rightarrow \quad TOL \propto I^{-1/4} \quad (40)$$

It is thus demonstrated that radiothermal oxidation is characterized by a skin-core structure: superficial layers are oxidized meanwhile bulk not. Results by Tavlet (Tavlet, 1997) are thus explained as follows: for irradiation performed under a relatively elevated dose rate, only a very thin polymer layer is degraded and time for drop of elongation at break is longer than for irradiation performed under a moderate dose rate. This reasoning is confirmed by the comparison of a bulk sample (4 mm) for which no dose rate effect is observed undoubtedly because the thickness of degraded superficial layer is negligible compared to the total thickness of bulk material. Examples of Oxidized layers measured for radiochemical degradation of aromatic polymers (Richaud et al., 2010a) are presented in Fig. 10 and confirm the existence of a Diffusion Limited Oxidation.

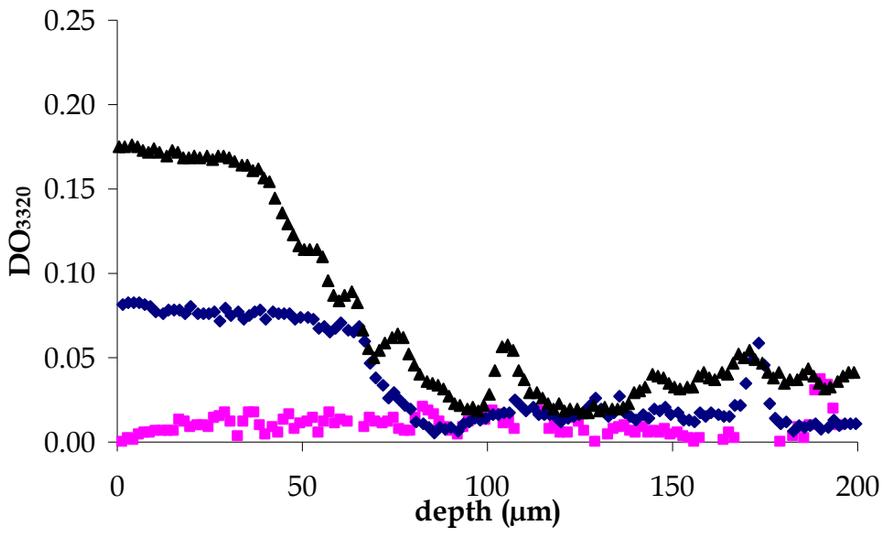


Fig. 10. Oxidation profiles in PEEK sheaths submitted to 10 MGy (■), 20 MGy (◆), 30.7 MGy (▲) γ-rays exposure (Richaud et al., 2010a).

7. On the radio-induced oxidizability of aromatic polymers

It seemed to us interesting to compare the k_3^2/k_6 ratio estimated from radiodegradation of aromatic polymers with polypropylene or polyethylene ones. Let us recall that k_3^2/k_6 describes the oxidizability of a polymer irrespectively of the oxidation mode (i.e. photo, thermo- or radio-induced). k_3^2/k_6 can be calculated from Eq. (32) using:

- [PH] = ρ/M, ρ being the polymer density and M the molar mass of repetitive unit,
- $r_i = 10^{-7}.G(P°).I$ from Heiland's results (Table 2),
- r_{OX} from TOL measured for example in FTIR mapping mode (Eq (30)).

One can use with a good approximation the values of oxygen permeation of BisPhenol A Polycarbonate values for in PEEK and PSU (Van Krevelen & Te Nijenhuis, 2009) at 60°C :

- $D_{O2} = 8.1\times10^{-8}$ m² s^{-1}
- $s_{O2} = 4\times10^{-8}$ mol l^{-1} Pa^{-1}

For samples exposed under 1.5 bar oxygen, TOL were found close to:

- 100 µm in PSU (Richaud et al., 2011),
- 70 µm in PEEK (Fig. 10).

	TOL (m)	r_{OX} (mol l^{-1} s^{-1})	G_i (mol/100 eV)	r_i (mol l^{-1} s^{-1})	[PH] (mol l^{-1})	BDE (kJ mol^{-1})	k_3^2/k_6 (l mol^{-1} s^{-1})	k_3 (l mol^{-1} s^{-1})	k_6 (l mol^{-1} s^{-1})
PEEK	1.00E-04	5.2E-06	0.25	1.7E-07	12.9	460	1.8E-06	1.0E-04	5.6E-03
PSU	7.00E-05	1.1E-05	0.75	5.0E-07	5.6	410	1.3E-05	9.5E-03	6.8E+00

Table 7. Kinetic parameters of PEEK and PSU estimated from DLO theory.

so that one can calculate (Table 6):

- $k_3^2/k_6 = 1.3\times10^{-5}$ l mol^{-1} s^{-1} for PSU
- $k_3^2/k_6 = 1.8\times10^{-6}$ l mol^{-1} s^{-1} for PEEK

These orders of magnitude are surprisingly on comparable or higher than values reported in PP (Richaud et al., 2006) and PE (Khelidj, 2006). k_3 can be conveniently estimated from the paper by Korcek (Korcek et al., 1972) using the relations:

$\log k_3^{s\text{-}POO°} = 16.4 - 0.2\times BDE(C\text{-}H)$ at 30°C

$\log k_3^{t\text{-}POO^\circ} = 15.4 - 0.2 \times BDE(C\text{-}H)$ at 30°C
$E_3^{s\text{-}POO^\circ} = 0.55.(BDE(C\text{-}H) - 65)$
$E_3^{t\text{-}POO^\circ} = 0.55.(BDE(C\text{-}H) - 62.5)$
s-POO° and t-POO° representing respectively secondary and tertiary peroxy radicals. Given the difference in Bond Dissociation Energies for C-H (denoted by BDE(C-H)) in benzene (Davico et al., 1995) or in $-CH_3$ (Korcek et al., 1972), it is clear that:

$$k_3(PEEK) < k_3(PSU) < k_3(PE) < k_3(PP)$$

Thus, it suggests that (Table 7):

$$k_6(PEEK, PSU) << k_6(PE, PP)$$

From a chemical point of view, the reactivity of aryl or primary peroxy radicals is not low enough to justify such values (Table 6). A possible explanation is that the termination between two POO° radicals is a process involving two rare species. The mobility of segments favouring the coupling could thus control the kinetics of the reaction. The low order of magnitude below T_g could be hence justified. Aromatic polymers could be interesting substrate for studying the Waite's theory:

$$-\frac{dC}{dt} = 4\pi N_A r_0 D\left(1 + \frac{r_0}{\sqrt{\pi D t}}\right)C^2 \quad (41)$$

where:
- r_0 is the cage radius, which corresponds to the maximal distance permitting the reaction: It would be on the order of $r_0 \sim$ 1-10 nm (Emanuel & Buchachenko, 1990),
- D is the diffusion coefficient of radical species. On the order of $D \sim 10^{-22} - 10^{-20}$ m^2 s^{-1} (Emanuel & Buchachenko, 1990),
- N_A is Avogadro's number.

According to this theory, kinetic constant depends on the diffusivity of a radical and in other words of macromolecular mobility.

8. Conclusions

A comparison of yields for gas emission, gel dose or critical dose for reaching an unacceptable level of mechanical properties shows that aromatic polymers radiochemical behaviour can be first explained by their aromatic character which is doubly favourable:
- Yield for radical formation is very low compared with aliphatic polymers, because aromatic groups are able to dissipate a great part of the absorbed energy into reversible processes (fluorescence, phosphorescence...).
- In the case of radio-oxidation, the propagation rate constant of hydrogen abstraction by peroxy radicals (k_3) is a decreasing function of the C-H bond dissociation energy, that takes a high value for aromatic hydrogen.

These positive effects are partially counterbalanced by the relatively low termination rate linked to the low segmental mobility in glassy state. It is noteworthy that P° + P° termination (which leads to crosslink when oxygen is lacking) is more efficient than expected because P° radicals can diffuse independently of segmental mobility by the valence migration process ($P_1^\circ + P_2H \rightarrow P_1H + P_2^\circ$).
This chapter also illustrates the effect of dose rate, thickness and oxygen concentration in polymers layers, which are linked by the theory of Diffusion Limited Oxidation: chain

scissions predominate in aerobic degradation (i.e. thin sample, and low dose rate) and crosslinking in case of anaerobic degradation (thick sample, high dose rate). The effect of temperature can be considered as not partially understood.

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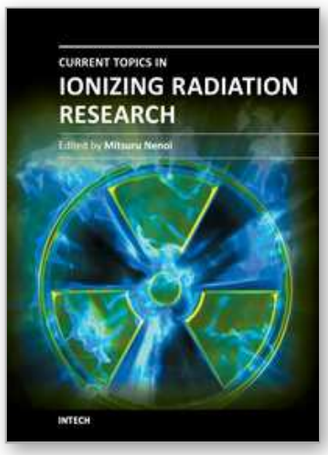
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Since the discovery of X rays by Roentgen in 1895, the ionizing radiation has been extensively utilized in a variety of medical and industrial applications. However people have shortly recognized its harmful aspects through inadvertent uses. Subsequently people experienced nuclear power plant accidents in Chernobyl and Fukushima, which taught us that the risk of ionizing radiation is closely and seriously involved in the modern society. In this circumstance, it becomes increasingly important that more scientists, engineers and students get familiar with ionizing radiation research regardless of the research field they are working. Based on this idea, the book "Current Topics in Ionizing Radiation Research" was designed to overview the recent achievements in ionizing radiation research including biological effects, medical uses and principles of radiation measurement.

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