Post-irradiation thermal degradation of poly(olefin sulphones)

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Post-irradiation thermal degradation of six poly(olefin sulphones) has been studied by measuring (1) the increases in volatile product yields upon isothermal annealing at various temperatures after irradiation at 0°C, and (2) the decay of trapped free radicals, produced by γ-irradiation at −196° and 20°C, with time at various temperatures. Above the ceiling temperature for each poly(olefin sulphone) rapid depolymerization occurred, generally yielding equal amounts of sulphur dioxide and olefin. The rates of radical decay also increased greatly in this temperature region.

INTRODUCTION

High energy irradiation of poly(olefin sulphones), e.g. γ-ray or electron beam, has been shown to result in main chain scission with $G(S) \approx 10$, followed by release of SO_2 and olefin, the yields depending on irradiation temperature and olefin structure[1,2].

Poly(olefin sulphones) are produced by a free radical chain reaction according to equation (1) and the polymer formed in the liquid-phase reaction has a 1:1 alternating composition:

$$CH_2{=}CHR + SO_2 \rightleftharpoons {-}CH_2{-}CHR{-}SO2{-} \qquad (1)$$

The copolymerization has a characteristic 'ceiling' temperature, T_c, above which the equilibrium lies increasingly to the left and depropagation predominates over propagation.

Degradation of poly(olefin sulphones) via the reverse reaction in equation (1), i.e. depropagation, subsequent to the production of free radical chain ends by radiation-induced random, main-chain scission, should lead to equal yields of SO_2 and the parent olefin, but this rarely occurs[2,3], the $G(SO_2)$/(olefin) ratio usually being >1. An investigation of the volatile radiolysis products from a variety of poly(olefin sulphones), has shown that both free radical and cationic intermediates are involved in the degradation[3,4]. Thus, cationic homopolymerization of product olefin is initiated by polymer carbonium ions and isomerization in the formation of olefin proceeds via a carbonium ion intermediate. Depropagation apparently occurs by both radical and cation pathways.

Poly(olefin sulphones) undergo facile thermal degradation, which is also attributed to the weak C–S bonds in the main chain, and may be related to the ceiling temperature. We have previously observed[2] that there is a synergistic relationship between thermal and radiation initiation of degradation in poly(olefin sulphones). This paper reports the results of a quantitative investigation of the effects of thermal treatment on the rates of formation of volatile products from six poly(olefin sulphones) with different olefin structures, subsequent to γ-irradiation at 0°C.

This work is also relevant to measurements of radiation degradation since polymers are frequently subjected to some post-irradiation heat treatment, even if this is only ambient temperature, which may significantly affect the yields of volatile products. For many polymers, post-irradiation heating is desirable to release trapped gases from the polymer matrix, but such treatment has serious consequences in poly(olefin sulphones).

We also report a related electron spin resonance (e.s.r.) study of the free radicals trapped in the polymers. The rates of decay and the temperature dependence have been measured. Above the ceiling temperature, rapid depolymerization proceeded from free radical and cation sites in the polymer. This was accompanied by increased termination rates of the radical–radical reactions, evidently due to greater mobility of the radical sites in this environment.

EXPERIMENTAL

Polymer preparation

Poly(propene sulphone), PPS; poly(isobutene sulphone), PIBS; poly(1-hexene sulphone), PHS; poly(4,4-dimethyl-1-pentene sulphone), PDMPS; poly(3-methyl-1-butene sulphone), PMBS and poly(2-butene sulphone), P2BS were prepared by free radical, bulk polymerization with tert-butyl hydroperoxide as initiator.

The sulphur dioxide and olefins were dried over molecular sieves and purified by distillation. The poly(olefin sulphones) were shown by ^1H n.m.r., ^{13}C n.m.r. and infra-red spectroscopy to have 1:1 alternating structures, which were confirmed by elemental microanalysis.

Powdered, dried samples (20–40 mg) of the polymers were evacuated at 20°C in thin-walled glass tubes for 50 h at $<10^{-2}$ Pa and sealed to form ampoules (40–50 mm length × 4–5 mm diameter). For e.s.r. experiments, 100 mg samples of PPS, PIBS and PMBS were packed into Spectrosil tubes and similarly evacuated.

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Table 1 Radiolysis yields[a] from γ-irradiation of poly(olefin sulphones) at 0°C

Polymer	Ceiling temperature[b] (T_c/°C)	$G(SO_2)$	G(olefin)[c]
PPS	90	13.2	1.7
PHS	60	21.1	23.1
PMBS	36	31	3M1B = 3.6 2M1B = 0.25 2M2B = 2.3
P2BS	32–35	80.6	2-Butene = 40.4 1-Butene = 0.06
PDMPS	14	115	53
PIBS	5	80.0	40.2

[a] Yields measured with pre-analysis temperatures below the ceiling temperatures for the particular copolymers
[b] Ceiling temperatures from solution copolymerization – ref 12
[c] 3M1B = 3-methyl-1-butene, 2M1B = 2-methyl-1-butene, 2M2B = 2-methyl-2-butene

Irradiation details

The irradiations were carried out with a ^{60}Co Gammacell 220 irradiation unit, using Fricke dosimetry[6] with absorbed doses calculated from mass–energy absorption coefficients[7]. The ampoules were irradiated at 0°C (ice–water bath) to doses up to 100 kGy (1 Gy = 1 J/kg = 100 Rad). The samples for e.s.r. studies were irradiated at either 25°C (2.2 kGy) or −196°C (3.8 kGy), and stored at −196°C in the dark to minimize post-irradiation reactions.

Thermal treatment and analysis

The ampoules containing the irradiated polymers were placed in a special thermostatically-controlled oven attached to the injection system of a Hewlett–Packard Model 5730A gas chromatograph[8]. The samples were subjected to a chosen thermal treatment and then the volatile products analysed by crushing the ampoule in the carrier gas stream of the gas chromatograph. The temperature of the sample oven was varied from 3° to 150°C. In addition, the effluent gas from the T_c detector was collected and analysed by (1) ^1H n.m.r. spectroscopy, and (2) mass spectroscopy.

The e.s.r. spectra were obtained on a Varian V4502 spectrometer, using low power levels to avoid saturation effects. A Varian variable-temperature accessory was utilized for temperatures between −177°C and 110°C. The concentrations of radicals were obtained from the areas under the absorption curves calculated by double integration of the recorded spectra using a Hewlett–Packard 9185A programmable calculator as an analogue-to-digital interface to a PDP11/34 computer. The changes in concentration and species of the radicals were determined during warming of irradiated samples from −196° to +110°C.

RESULTS AND DISCUSSION

Volatile products

The major volatile products from the γ-irradiation of poly(olefin sulphones) are sulphur dioxide and olefin — the two original monomers — with G values which are large relative to the G values for gaseous products from hydrocarbon polymers, e.g. 10–200 compared with 0.5–2.0. The results of a detailed investigation of the volatile radiolysis products from poly(olefin sulphones) have been reported elsewhere[9]. The G values for sulphur dioxide and olefin production from irradiation at 0°C of the poly(olefin sulphones) used for the post-irradiation, thermal degradation studies reported in this paper are shown in *Table* 1.

For PPS, post-irradiation thermal degradation was investigated for three sets of conditions, (a) 20°–25°C, (b) 80°C and (c) above 100°C ($T_c \approx 90$°C).

There was no difference in the yields of volatile products after thermal treatments (a) and (b); however, a sample of PPS (9 kGy at 0°C) heated at 120°C for 15 min — treatment (c) — and then analysed showed an increase of 0.14 μmol mg^{-1} (10 000%) for propene and 0.16 μmol mg^{-1} (1500%) for sulphur dioxide over the yields obtained from (a) and (b). Quite clearly, substantial depolymerization had been induced by heating the irradiated polymer above its ceiling temperature, yielding approximately equal amounts of propene and sulphur dioxide.

Greatly increased depolymerization when the irradiated sample was heated above the ceiling temperature of the polymer was observed for all six poly(olefin sulphones). *Table* 2 shows the increases in yields of olefin and SO_2 after heating at selected temperatures (T_d) above the ceiling temperature for 10 min.

In the case of PIBS and P2BS, the absolute increase in SO_2 was approximately twice the absolute increase in olefin, whereas the copolymer has an alternating 1:1 structure. The other polymers degraded as expected to give equal amounts of sulphur dioxide and olefin. In the case of PMBS, isomerization of the olefin occurred during radiation-induced thermal depolymerization, but not to the same extent as during radiation degradation alone; thus we can compare the irradiation products at 0°C in *Table* 1 with the increases in yields shown in *Table* 2.

In general, the yields remained constant, irrespective of the post-irradiation thermal treatment until the ceiling temperature was reached. Above this temperature depolymerization is apparently initiated at free radical and cationic sites produced during the radiolysis. The role of these reactive intermediates in depolymerization and isomerization during the radiolysis of poly(olefin sulphones), and in PMBS in particular, has been discussed previously[3,4].

Table 2 Increases in yields of volatile degradation products after post-irradiation heating for 10 min at temperature T_d. Polymer samples irradiated to ≈100 kGy

Polymer	T_d (°C)	Increase SO_2 μmol mg^{-1}	Increase SO_2 %	Increase Olefin[a] μmol mg^{-1}	Increase Olefin[a] %
PPS	120	0.10	1000	0.10	7000
PHS	70	0.83	300	0.83	300
PMBS	50	0.035	80	3M1B = 0.024 2M1B = 0.0004 2M2B = 0.0096	1000 150 550
P2BS	50	0.130	110	2-Butene = 0.072 1-Butene = 0.002	210 180
PDMPS	34	0.071	40	0.071	95
PIBS	25	0.030	40	0.015	35

[a] See *Table 1*, footnote c

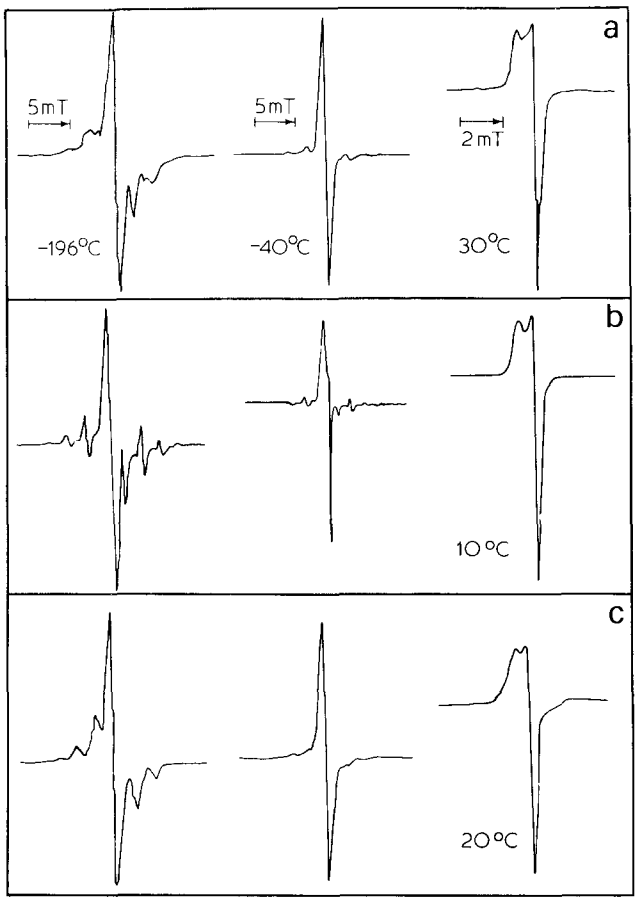


Figure 1 E.s.r. spectra of radicals produced by γ-irradiation of poly(olefin sulphones) at −196°C and on subsequent warming. Radiation doses 2–4 kGy. Temperatures of measurement as shown. (a) PPS; (b) PIBS; (c) PMBS

Free radicals

After PPS, PIBS and PMBS were irradiated at −196°C and 20°C, the trapped free radicals were examined by e.s.r. spectroscopy.

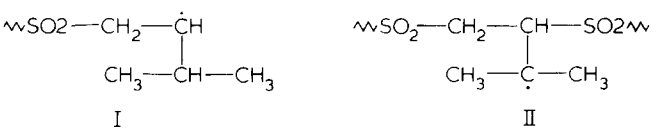
Poly(propene sulphone). After irradiation at −196°C, the spectrum (*Figure* 1*a*) consisted of (1) 7 or 9 lines with hyperfine splitting (*HFS*) of 2.3 mT attributed to an alkyl radical, and (2) a narrow, asymmetric singlet previously reported as a sulphonyl radical[10,11].

Components (1) and (2) of the spectrum have *g* values differing by 0.003, which is larger than that found for carbon-centred radicals in different environments and may be attributed to radicals (1) and (2) being centred on different atoms, carbon and sulphur. Upon warming from −196°C, the concentration and identity of the radicals remained constant until −80°C, whereupon the central asymmetric peak began to grow while the alkyl radical decayed with the total radical concentration remaining constant as shown in *Figure* 2. Above 0°C the asymmetry of the signal increased, the radical concentration decreased and the width of the spectrum decreased. At 20°–25°C a spectrum was obtained which was identical to that produced by irradiation at 20°C. The radical concentration decayed slowly up to 90°–100°C. At any one temperature up to 90°C an equilibrium concentration was rapidly established (5–10 min), after which the spectra were stable for at least 2 h. Above 90°–100°C the concentration of radicals decayed to below the level of detection after ≈45 min. Above 20°C the shape of the spectra remained constant, i.e. the radical species did not change. The temperature dependence of the radical concentration during progressive warming from −196° to 110°C is shown in *Figure* 2. A value of *G* (radicals) = 2.2 ±0.5 was obtained after irradiation at −196°C.

Poly(isobutene sulphone). After irradiation at −196°C, the spectrum comprised (1) approximately 12 lines spread over ≈15 mT attributable to an alkyl radical, and (2) a small amount of a narrow asymmetric signal (*Figure* 1*b*). These are similar components to PPS, but the sulphonyl radical makes a smaller contribution. *G*(radicals) after irradiation at −196°C was 1.9 ±0.5.

Upon warming from −196°C, neither the radical species nor the concentration changed until −80°C. Between −80° and −40°C the radical concentration decreased to 0.8 of the initial value and the asymmetry increased. From −40°C to 0°C the spectrum was unchanged, but above 0°C the radicals began to decay (*Figure* 2). The spectrum disappeared completely after 20 min at 70°C.

Poly(3-methyl-1-butene sulphone). After irradiation at −196°C, *G*(radicals) = 1.8 ±0.5, and the spectrum consisted of components due to alkyl and sulphonyl radicals. The alkyl radical was a quintet with a *HFS* of ≈2.2 mT which may be attributed to either radical I or II by comparison with:



I II

the radicals produced by irradiation of poly(3-methyl-1-butene)[12]. The sulphonyl radical made only a small contribution to the spectrum at −196°C, but its presence was indicated by the inflection points (*Figure* 1*c*). The

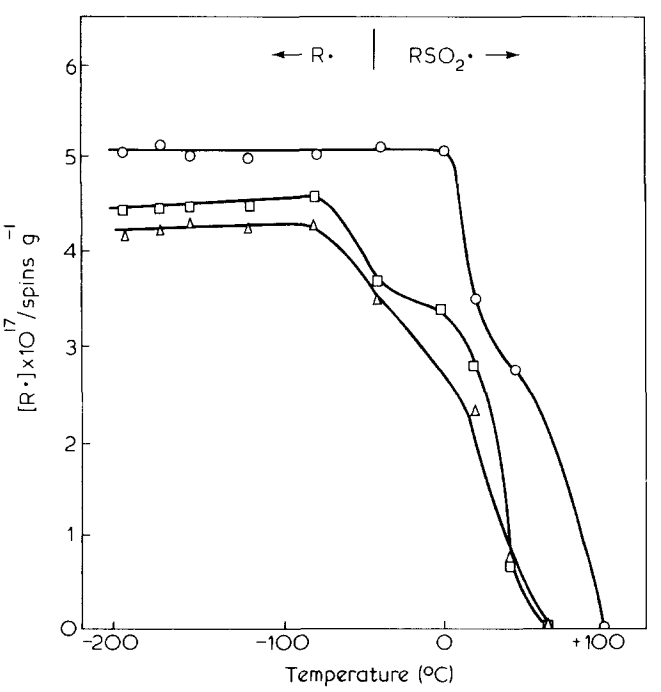


Figure 2 Radical decay with increasing temperature after γ-irradiation at −196°C. ○, PPS; □, PIBS; △, PMBS

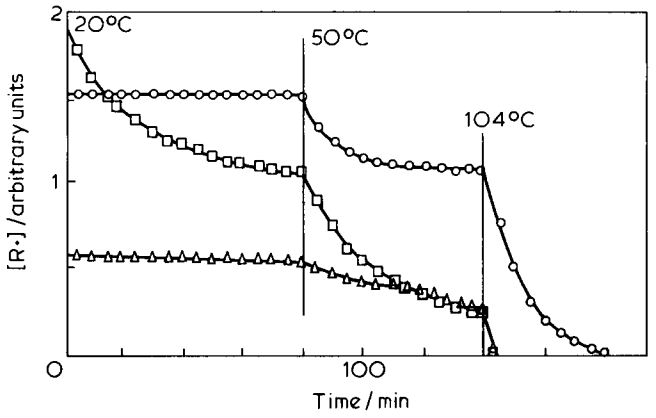


Figure 3 Isothermal radical decay during stepwise increase in temperature of irradiated poly(olefin sulphones). ○, PPS; □, PIBS; △, PMBS

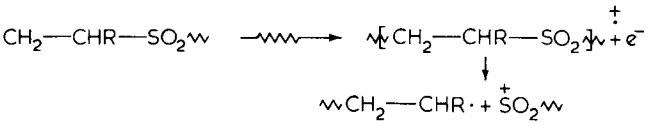
spectrum was unchanged from −196° to −80°C, but at higher temperatures the asymmetric signal began to dominate the spectrum, while the total radical concentration decreased. The decrease continued steadily (*Figure* 2) to 20°C, where the spectrum was found to be identical with that obtained after irradiation at 20°C. Above 0°C there was no significant change in the spectral shape until the radicals disappeared at high temperatures.

Figure 3 shows the time dependence of the radical decay for the three copolymers at three different temperatures. The radical concentrations are seen to decay to an equilibrium value at each temperature, until a critical temperature is reached, above which the radical concentrations drop rapidly to zero. For all the polymer samples, the changes observed upon warming were irreversible. The spectrum at 20°C, upon cooling to −196°C exhibited only the expected changes due to (a) redistribution of energy level populations, according to Boltzmann statistics, and (b) restriction of the radical mobility due to the lowering of thermal energies.

The isothermal decay rates were measured by warming to the desired temperature and recording the spectrum every 5 min. The 20–25 min spectrum was used for the temperature plots in *Figure* 2. At temperatures up to −40°C the spectra were stable for up to 45 min, while between −40° and 20°C the decay with time at any given temperature was small, i.e. 10–20% after 30 min.

Free radicals and thermal degradation

The e.s.r. study has shown that alkyl radicals are the predominant radical species trapped in the irradiated poly(olefin sulphones) at −196°C, and that they undergo transformation to sulphonyl radicals on warming. This may occur by addition of SO_2 or by loss of olefin. We believe that irradiation causes primary scission of C–S bonds; this would be expected to produce alkyl and sulphonyl radicals in comparable numbers, but was not observed in the e.s.r. spectrum at −196°C. The predominance of alkyl radicals is in accord with our hypothesis that decomposition of the parent, polymer cation radical occurs to form a cation and an alkyl radical[4]:



On warming, some depropagation can be expected and the equilibrium reaction $R\cdot + SO_2 = RSO_2\cdot$ favours the formation of sulphonyl radicals. This equilibrium has been observed in the reactions of irradiated polyolefins with SO_2[10].

The termination steps that lead to the loss of radical sites require more detailed study. However, the present work has clearly shown that the radical termination rate, via radical–radical reactions, increases at the same time as the rapid depolymerization commences, i.e. in the vicinity of T_c. The increased mobility of the radical sites by migration along the polymer chain (leaving an unzipped polymer chain) may explain the increased termination rate.

CONCLUSIONS

For most polymers, e.g. polyethylene, post-irradiation heating has been found necessary to extract the volatile products from the polymer matrix[7], but with poly(olefin sulphones) there is apparently sufficient disruption of the polymer structure to allow adequate release of volatile products at low temperatures. Heating of irradiated poly(olefin sulphones) above their characteristic ceiling temperatures initiates rapid depolymerization at free radical and probably also cationic sites present in the irradiated polymer.

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