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An investigation of γ-irradiated poly(methacrylonitrile) by electron spin resonance spectroscopy

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The radiation chemistry of poly(methacrylonitrile), which was γ-irradiated at different temperatures (−196°C, room temperature, 60°C, 100°C and 130°C) and with different radiation doses, has been studied by electron spin resonance (e.s.r.) spectroscopy. When γ-irradiated at −196°C, radical anions and neutral radicals were formed. Warming the sample from −53 to −3°C resulted in the conversion of the imide radical to the scission radical. The radical anions were found to decay in the temperature range from −196 to −100°C. On annealing the sample to 23°C, an e.s.r. spectrum similar to that obtained on γ-irradiation at room temperature was obtained. The $G(\mathrm{R}\cdot)$ values have been determined to be 2.2 on γ-irradiation at −196°C and 2.8 at room temperature. From photobleaching, microwave power saturation and annealing experiments, the major radical intermediates and their reactivities have been identified.

(Keywords: poly(methacrylonitrile); γ-radiation; e.s.r. spectroscopy)

INTRODUCTION

The study of radiation-induced degradation of polymers has been increasing in recent years[1-4]. From the earliest investigations of irradiated polymers, poly(methyl methacrylate), which is a typical degradation-type polymer, has been given a great deal of attention[5-12]. However, few studies have been conducted into the effects of high-energy radiation on poly(methacrylonitrile), which also is a degradation-type polymer, containing an α-methyl group in the main chain. Schlick and Kevan irradiated poly(methacrylonitrile) at room temperature using ^{60}Co γ-radiation with a dose of 100 kGy[13]. The electron spin resonance (e.s.r.) spectrum of the γ-irradiated poly(methacrylonitrile) showed that the resolution was so poor that any identification of the radicals was quite speculative. Schnabel and Klaumunzer irradiated poly(methacrylonitrile) in the absence of O_2 with heavy particle radiation, namely 275 MeV $^{20}_{10}\mathrm{Ne}^{7+}$ ions and 180 MeV $^{40}_{18}\mathrm{Ar}^{8+}$ ions, in which the 100 eV-yield (G value) of the main-chain scissions was found to decrease with increasing linear energy transfer[14]. The molecular weight changes of poly(methacrylonitrile) using ^{60}Co γ-irradiation have been investigated in the solution state by Yamaoka *et al.*[15] and in the solid state by Helbert *et al.*[16]. In a more recent work, the thermal degradation after γ-radiation of a poly(methacrylonitrile) sample has also been investigated[17].

The purpose of this present study is to elucidate the degradation behaviour of poly(methacrylonitrile) under γ-irradiation. In this investigation γ-irradiated poly(methacrylonitrile) has been examined at different temperatures through the application of e.s.r. spectroscopy. Photobleaching, microwave power saturation and annealing were used to identify the major radical intermediates and their reactivities.

EXPERIMENTAL

Materials

The synthesis and characterization of poly(methacrylonitrile) was reported previously[18]. The polymer has an $M_n = 2.5 \times 10^4$ and $M_w/M_n = 2.2$. The glass transition temperature (T_g) was measured by differential scanning calorimetry (d.s.c.) using a Perkin–Elmer DSC-7 instrument. The experiments were conducted under a flow of pure nitrogen using a heating rate of 20°C min^{-1}.

Sample preparation

The finely powdered poly(methacrylonitrile) was packed into quartz e.s.r. tubes and pumped under vacuum ($\sim$ 1 mPa) for at least 24 h prior to being sealed. These samples were irradiated at liquid nitrogen temperature (−196°C) or room temperature in a ^{60}Co AECL Gammacell 220 radiation unit. The high-temperature irradiation experiments (60, 100 and 130°C) were carried out in the pond facility of the Australian Nuclear Science and Technology Organisation at Lucas Heights, Sydney using ^{60}Co γ-irradiation. The radiation dose rates were determined by Frick dosimetry for the Gammacell 220 and by ceric dosimetry for the pond facility[19], and the values obtained

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were $\sim 2\,\mathrm{kGy\,h^{-1}}$ for both radiation facilities. After irradiation (whether at −196°C or other temperatures), the samples were transferred to a liquid nitrogen Dewar container, in the absence of light, and stored at −196°C.

E.s.r. analysis

The e.s.r. spectra were recorded on a Bruker ER-200D ESR X-Band spectrometer with a modulation value of 0.2 mT and a microwave power of 19.9 μW (40 dB), which is less than the saturation power for the radicals formed during radiolysis. A number of spectra were recorded at higher microwave powers in order to assist in the identification of the number and nature of the radical species present. The radical concentrations in the samples were determined through a comparison of the area under the absorption peak with that of a Varian standard (1% pitch in a potassium chloride matrix)[19].

The e.s.r. spectra were recorded principally at −196, −153 and 23°C. In annealing experiments, the spectrum was recorded first at the initial temperature of −153°C. The temperature was then increased, maintained at the desired annealing temperature for 10 min, cooled back to the initial temperature, left for a further 10 min to equilibrate and finally the e.s.r. spectrum was recorded. This procedure was adopted in order to avoid the need to make corrections for Boltzmann effects when spectra were compared. To remove the contribution of any anionic species to the e.s.r. signal at −196°C, photobleaching experiments were carried out. The photobleaching experiments were undertaken by using an Oriel 1000 W Hg/Xe lamp with cut-off filters ($\lambda \geqslant 600$ nm or $\lambda \geqslant 495$ nm) to selectively irradiate the polymer samples.

COMPUTATIONAL METHOD

Semiempirical quantum mechanical methods were used to analyse the electronic structure of the radicals formed on γ-irradiation of the polymer. The calculations were performed by MNDO (modified neglect of diatomic differential overlap)[20] and AM1 (Austin Model 1)[21] Hamiltonians based on the unrestricted Hartree–Fock (UHF) method, using software included in the MOPAC package version 6.00.

RESULTS AND DISCUSSION

E.s.r. spectra at −196 °C

Finely powdered poly(methacrylonitrile) was γ-irradiated at liquid nitrogen temperature, and the e.s.r. spectra produced, which were recorded at −196°C for the samples with different radiation doses, are shown in *Figure 1*. With an increase in the radiation dose, the signals become broad and ill-defined. A similar observation was reported for studies on polyacrylonitrile[22]. This could be attributed to the formation of an ill-defined broad singlet associated with formation of a polyimine or polyenyl radical. The relative concentration of this radical would be increased with an increase in the radiation dose. In addition, when the sample was irradiated with a dose of 10 kGy and the spectrum recorded with a magnetic field width of 70 mT, as shown in *Figure 2*, a doublet with a splitting constant of 50 mT was observed, which may be attributed to the proton radical[23].

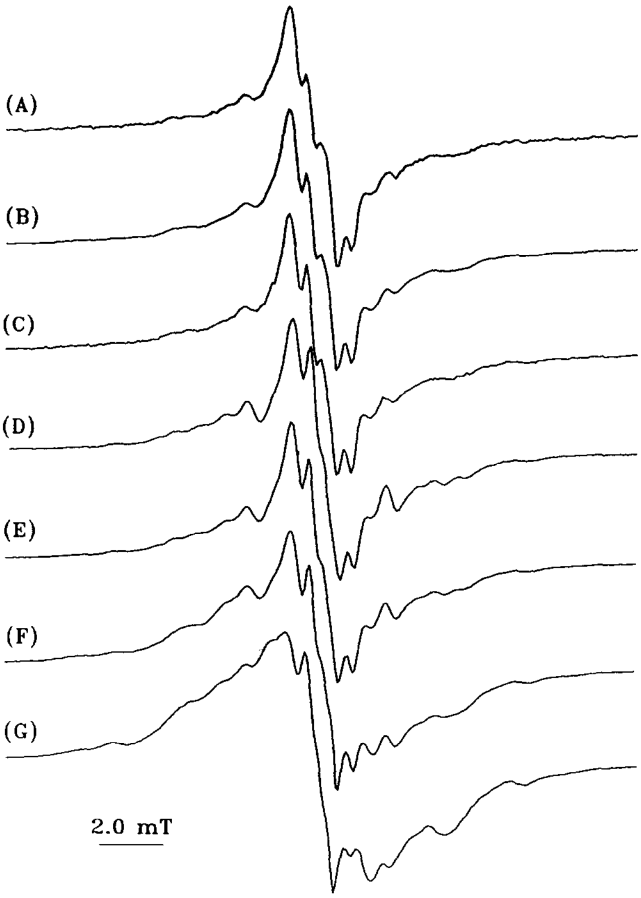


Figure 1 The e.s.r. spectra of poly(methacrylonitrile), γ-irradiated at −196°C with various radiation doses: (A) 1.6 kGy; (B) 4.8 kGy; (C) 7.1 kGy; (D) 10.7 kGy; (E) 16.6 kGy; (F) 31.8 kGy; (G) 43.3 kGy

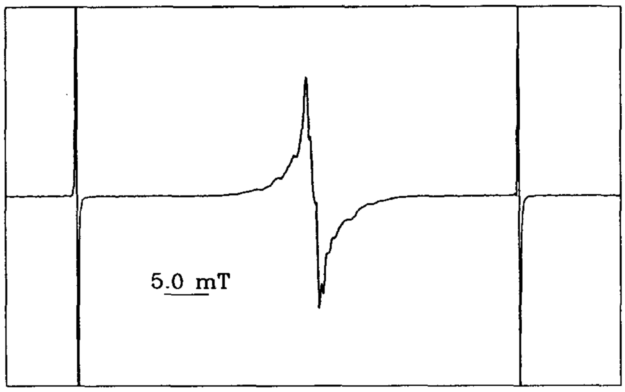


Figure 2 The e.s.r. spectra of poly(methacrylonitrile), γ-irradiated at −196°C with a radiation dose of 10 kGy; the recorded magnetic field width was 70 mT

It is evident that, in addition to the proton and polyimine or polyenyl radicals, other radicals are also present in the sample, which are associated with the hyperfine structure in the spectra. Photobleaching and annealing experiments were therefore carried out in order to assign these radicals.

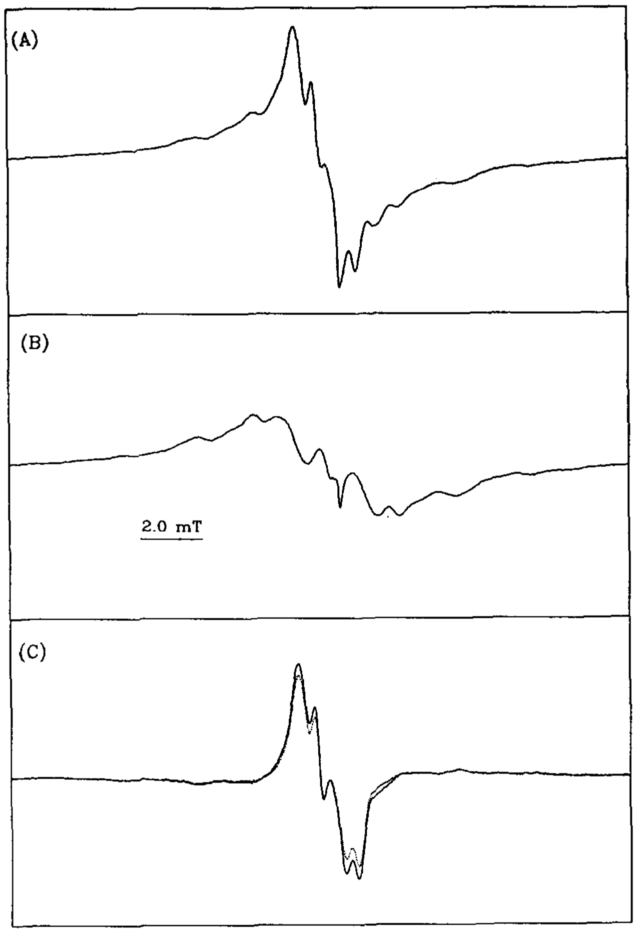


Figure 3 The e.s.r. signal changes for the photobleaching experiment using light of wavelengths greater than 495 nm: (A) before photobleaching, sample with a radiation dose of 10 kGy; (B) after photobleaching; (C) the lost signals during photobleaching, where the dotted line represents 2 min photobleaching time, and the solid line represents 10 min photobleaching time

Photobleaching experiments

The e.s.r. spectrum of γ-irradiated poly(methacrylonitrile) at −196°C was examined for the presence of radical anions, through exposure of the irradiated sample to high-intensity visible light. *Figure 3* shows the e.s.r. signal changes for the photobleaching experiment using light of wavelength longer than 495 nm. There was a loss of e.s.r. signal intensity in the central region, which can be attributed to the anionic radical species[22]. It is more interesting to note that the hyperfine structures in the spectra of the radicals which were lost provide some information related to the radiation chemistry of poly(methacrylonitrile).

The lost signals in the e.s.r. spectrum during photobleaching, shown as C in *Figure 3*, contain some hyperfine structure. When the photobleaching time was increased from 2 to 10 min, the change in the lost signal could be accounted for by a single broad peak without any hyperfine structure. Therefore, the signal lost on photobleaching from 2 to 10 min may be assigned to a polyimine or polyenyl radical anion, which is a little more photostable than the other radical anions. When the photobleaching time was increased further from 10 to 15 min, no change in the e.s.r. signal was observed. By using light of wavelength longer than 600 nm for the photobleaching experiments, the lost signal, shown as A in *Figure 4*, is similar to that obtained for photobleaching using light of wavelength greater than 495 nm.

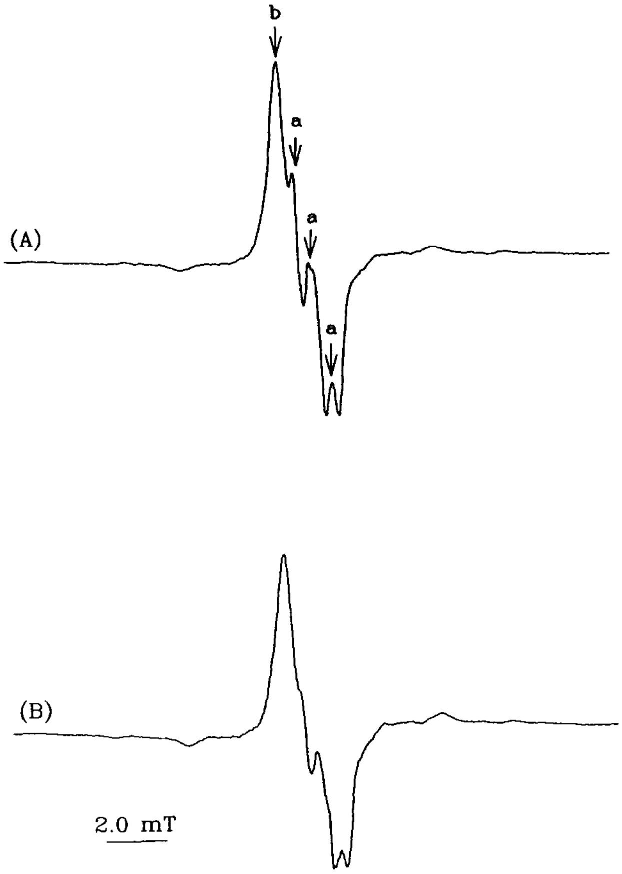


Figure 4 The lost signals for the photobleaching experiment using light of wavelength longer than 600 nm: (A) experiment recorded at a microwave power of 20 μW (40 dB); (B) experiment recorded at a microwave power of 200 μW (30 dB)

When the spectra were recorded with higher microwave power (200 μW, 30 dB), the relative intensity of the triplet of peaks (indicated by the arrow a in spectrum A) in *Figure 4*, which have a splitting constant of ∼ 0.6 mT, decreased in intensity when compared with the intensities of the other peaks, as shown in spectrum B in *Figure 4*. This implies that the paramagnetic relaxation rate of the radical anion corresponding to this triplet is much lower than that of the other radical anions present. This triplet of peaks may thus be attributed to a radical anion generated by a CN group capturing an electron with the spectral line split by the nitrogen atom. The g value for this radical anion was similar to that found for the broad polyimine or polyenyl radical anion. It is evident that another radical anion, characterized by a singlet, which has a g value of about 2.0028, is also present. This radical anion has been assigned to a 'physically trapped' electron (see *Figure 4*, arrow b in spectrum A), which is characterized by a sharp peak and is not saturated by increased microwave power. Previous workers who have studied irradiated poly(methyl methacrylate) and some organic solids, such as 2-methyltetrahydrofuran, have noted that there are physically trapped electrons in these systems which are observable at −196°C[24,25]. It has been suggested that the spin density of the physically trapped

Table 1 Ionization potentials (eV) for the isobutyronitrile and trimethylacetonitrile radical anions obtained by using MNDO and AM1 methods

Radical anion	MNDO	AM1
$(CH_3)_2CHCN$	−0.032	−0.655
$(CH_3)_3CCN$	0.146	0.232

electron at any one atom is less than that for an unpaired electron in a free radical and also that it is more delocalized than a radical. Since the electron is comparatively independent of molecular orbitals it can be regarded as an independent entity.

Thus from the above analysis, the radicals lost on photobleaching are mainly composed of a conjugated polyimine or polyenyl radical anion, a nitrile group radical anion and a 'physically trapped' electron.

It was reported that in the study of the radical anions formed on the γ-irradiation of the polyacrylonitrile system[22], under the same experimental conditions, the signal lost in the central region on photobleaching was small and less than that observed here for the poly(methacrylonitrile) sample. In polyacrylonitrile, the hyperfine structure due to splitting by the nitrogen atom of the radical anion was not observed. A theoretical study of the nature of the radical anions using semiempirical quantum mechanical methods has been carried out in an attempt to explain these experimental results.

Trimethylacetonitrile and isobutyronitrile have been used as model compounds to simulate the electronic structures of poly(methacrylonitrile) and polyacrylonitrile, respectively. The optimized geometrical parameters and electron charges for the radical anions of both compounds may be obtained by using semiempirical quantum mechanics calculations based on the AM1 and MNDO methods, respectively. The ionization potentials of the radical anions for the optimal geometrical structures have been calculated and are shown in *Table 1*. The calculations using both methods show that the radical anion of trimethylacetonitrile has a positive ionization potential, while that of isobutyronitrile has a negative potential, which clearly indicates that the radical anion for the poly(methacrylonitrile) model compound is more stable than that for the corresponding polyacrylonitrile compound. This calculation is consistent with the observation in the e.s.r. experiments that the radical anion is more stable in poly(methacrylonitrile) than it is in polyacrylonitrile.

Annealing experiments

The dependence of the e.s.r. signal on temperature was studied over the temperature range from −153 to 120°C for photobleached (λ > 600 nm light for 15 min) and unphotobleached samples which had been γ-irradiated at −196°C with a dose of 10 kGy. The e.s.r. spectra obtained at temperatures from −153°C to room temperature for the annealed samples are given in *Figures 5* and *6*. The e.s.r. spectra do not change substantially between −196 and −153°C. However, when the temperature was warmed from −153 to −103°C, we find some radical loss for the unphotobleached sample, but no significant change wa observed for the photobleached sample, as shown i *Figure 7*. The lost signal for the unphotobleached sampl in this temperature range was mainly attributed to th loss of the physically trapped electron and the radica anion located on the nitrile group. When the temperatur was increased further from −103 to −53°C, radicals wer lost in both the unphotobleached and the photobleache samples. More clearly defined hyperfine structures can b observed in the spectra recorded at −53°C. The los signal for the photobleached sample was mainl composed of a doublet, which has an intensity ratio o 1 : 1, with a splitting constant of 2.3 mT, as shown i *Figure 8*. This radical has been assigned to the imid

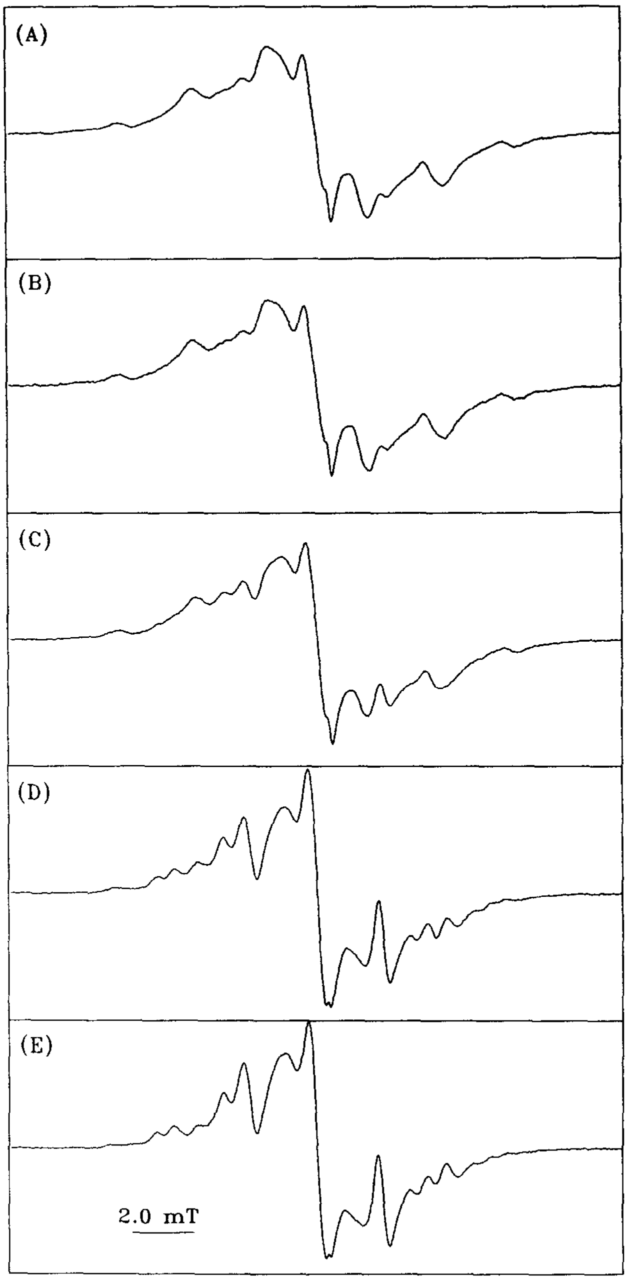


Figure 5 The effect of increasing temperature on the e.s.r. spectrum o poly(methacrylonitrile), γ-irradiated at −196°C to 10 kGy and the photobleached for 15 min using the light of wavelengths greater tha 600 nm: (A) −153°C; (B) −103°C; (C) −53°C; (D) −3°C; (E) 27°C. A spectra were recorded at a constant gain

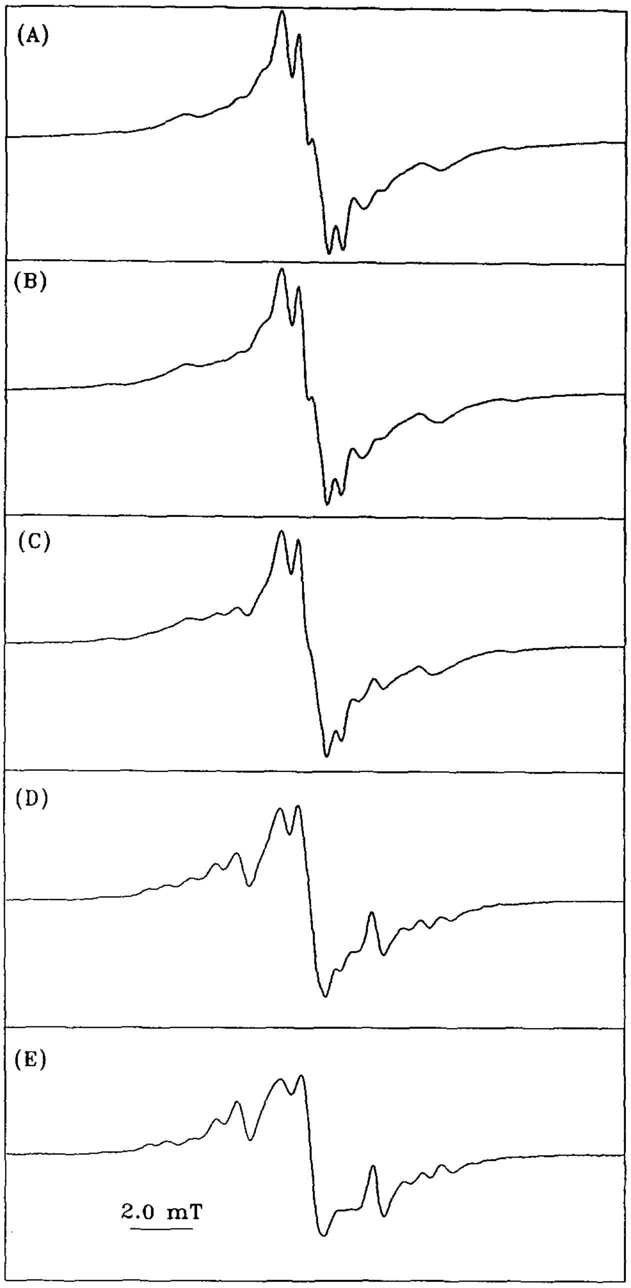
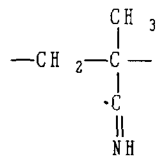


Figure 6 The effect of increasing temperature on the e.s.r. spectrum of poly(methacrylonitrile), γ-irradiated at −196°C to 10 kGy: (A) −153°C; (B) −103°C; (C) −53°C; (D) −3°C; (E) 27°C. All spectra were recorded at a constant gain

radical I:



$$-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle \overset{\cdot}{C}{=}NH}{C}}- \qquad (I)$$

In previous studies on γ-irradiated polyacrylonitrile[26], it was noted that hydrogen atoms added to the nitrile group, thus forming an imide radical $-\cdot C{=}NH$, which may be observed between −173 and −93°C, but at higher temperatures this radical became unstable and was quenched. In this present work, it was found that the imide radical I in poly(methacrylonitrile) was formed at −196°C on γ-irradiation by the addition of hydrogen atoms to the nitrile groups.

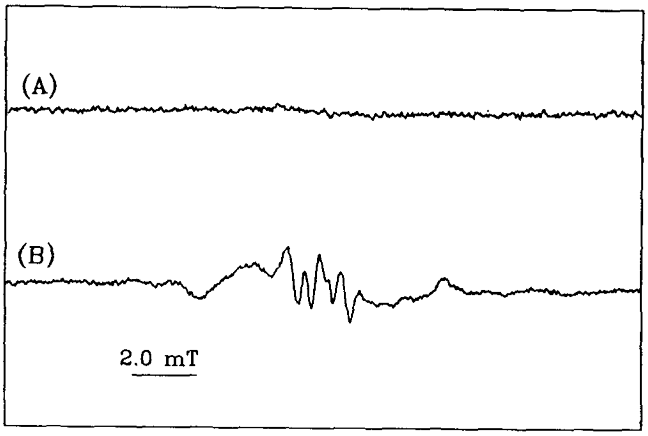


Figure 7 The lost signals after warming from −150 to −103°C for: (A) photobleached samples; (B) unphotobleached samples

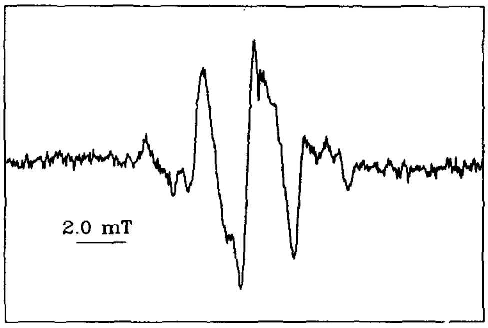


Figure 8 The lost signal for a photobleached sample on warming from −103 to −53°C

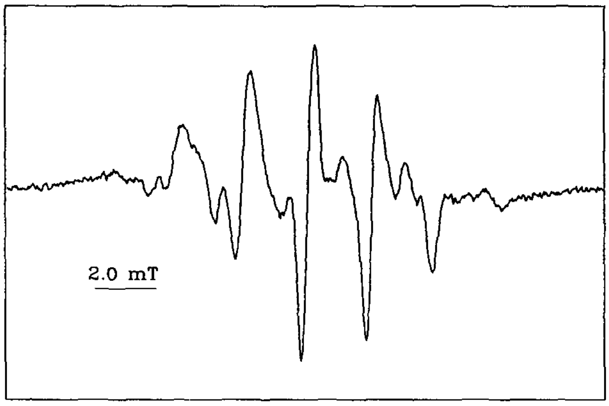
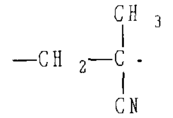


Figure 9 The signal changes for poly(methacrylonitrile), γ-irradiated at −196°C followed by photobleaching, and then warmed and annealed from −53 to −3°C. The spectrum was obtained by subtracting the spectrum at −3°C from that at −53°C

When the photobleached sample was warmed from −103 to 53°C, the decay of the imide radical could be observed as the loss of a double with a splitting constant of 2.3 mT, due to splitting by the proton attached to the nitrogen atom.

On further increasing the temperature to −3°C, the spectrum exhibited some more clearly defined hyperfine structure when compared with the spectra recorded at lower temperatures. This component of the spectrum was obtained by subtracting the spectrum measured at −3°C from that at −53°C and is given in *Figure 9*.

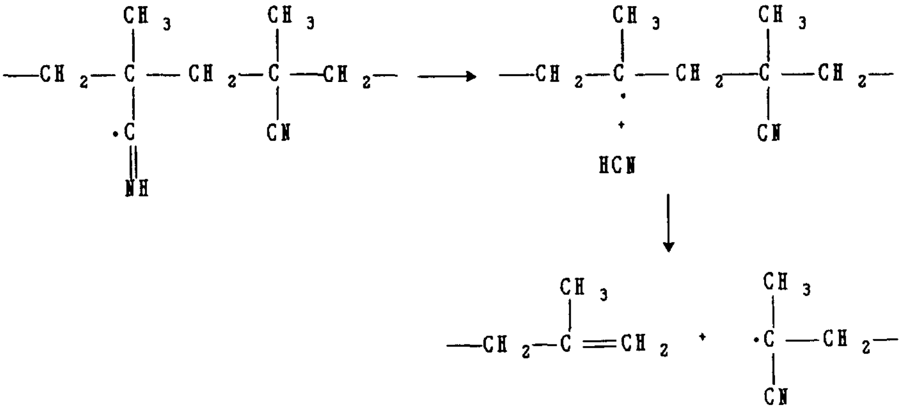
The features of the spectrum in *Figure 9* appear similar to those observed in the spectra of poly(methyl methacrylate) which has been γ-irradiated at room temperature; this has a 5 + 4 line-shape, with the latter assigned to the scission or propagating radical of poly(methyl methacrylate)[27]. However, the 5 + 4 line-shape in *Figure 9* is inverted compared with that of the propagating radical of poly(methyl methacrylate). The scission or propagating radicals for poly(methyl methacrylate) and poly(methacrylonitrile) have a similar structure. In previous work on a study of the free-radical polymerization of methacrylonitrile[28], it was reported that the methacrylonitrile propagating radical was characterized by a 5 + 4 line-shape. Therefore, the 5 + 4 line spectrum in *Figure 9* may be assigned to a main chain scission radical (II):



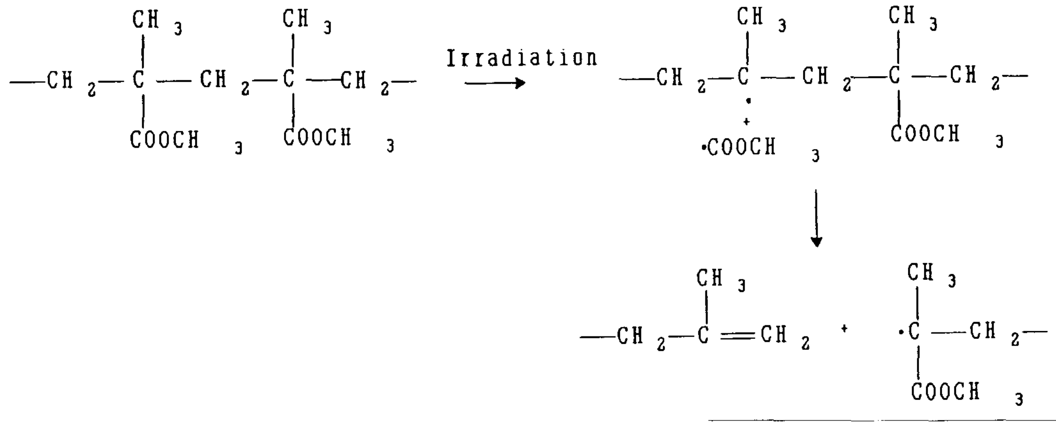
$$-CH_2-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}\cdot$$

(II)

We suggest that on annealing the photobleached sample in the temperature region from −53 to −3°C the main chain scission radical is formed from the imide radical. A major product of the radiolysis of polyacrylonitrile is HCN[29], and we expect that this is also the case for poly(methacrylonitrile). Thus, the following mechanism is suggested to explain the formation of the main chain scission radical from the imide radical:



The formation of a scission radical in poly(methyl methacrylate) which was γ-irradiated at −196°C has been observed when the sample is warmed to temperatures above −93°C[4]. It has been proposed by David *et al.* that the main chain scission radical of γ-irradiated poly(methyl methacrylate) is generated by the following reaction[30]:



However, it has also been suggested by Ichikawa and Yoshida[4] that the scission radical can be formed from the side chain $-COCCH_2\cdot$ radical. They also suggested that the volatile products may be formed either via a non-radical excited state reaction or by decomposition of the side-chain radical. However, the mechanism proposed by these workers does not account for the range and yields of the observed volatile and radical products as well as does the mechanism proposed by David *et al.*[30].

During the annealing experiments, the radical decay for the unphotobleached sample was more complicated than that observed for the photobleached sample, because there is additional signal loss from radical anion decay. However, when two samples, one unphotobleached and the other photobleached, were warmed to room temperature (23°C), the features of the two spectra were quite similar, as shown by the spectra E in both *Figures 5* and *6*. This suggests that the same neutral radical species are present in these two samples.

On further increasing the temperature from room temperature, the radical intensity continuously decreased for both samples, until at 100°C the e.s.r. signal for both samples consisted of only a broad singlet in the central region. When the temperature was increased to 120°C, which is higher than the glass transition temperature (T_g) for poly(methacrylonitrile) (108°C), the major part of the central broad singlet was also lost.

Room temperature, 60°C, 100°C and 130°C irradiation

The e.s.r. spectrum which results after irradiation with a dose of 10 kGy at room temperature is given in *Figure 10* (curve A). The features of this spectrum mirror very

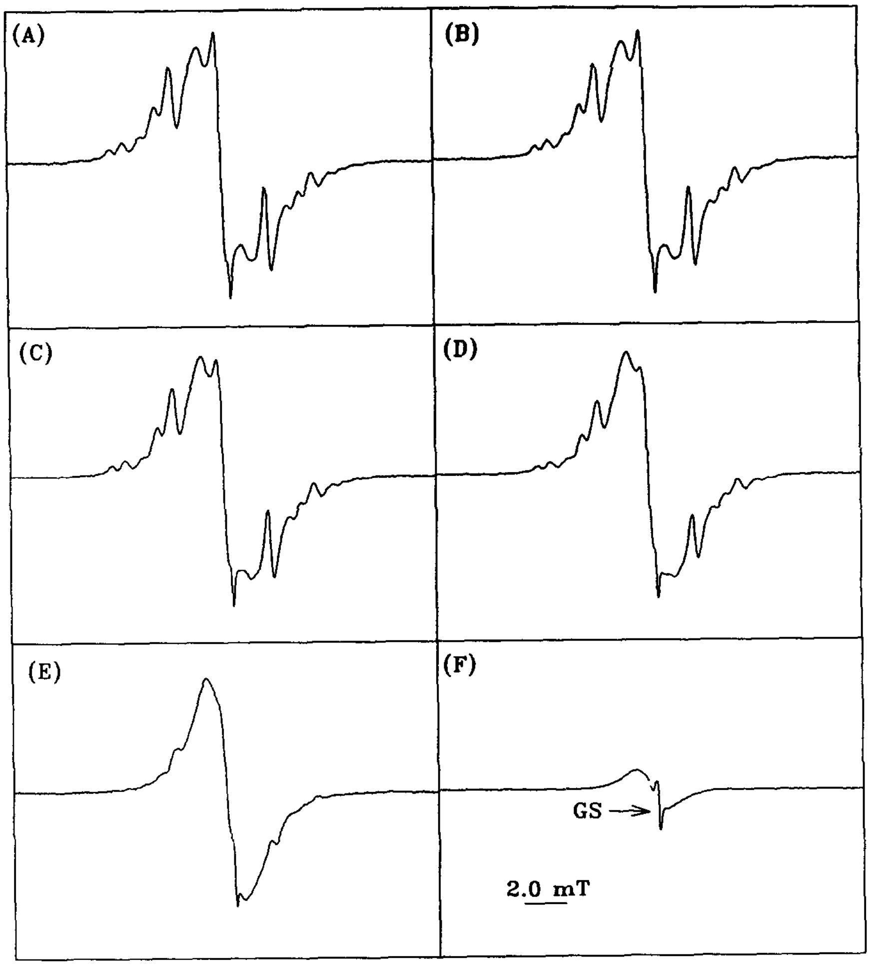


Figure 10 The effects of increasing temperature on the e.s.r. spectrum of poly(methacrylonitrile), γ-irradiated at room temperature with a dose of 10 kGy: (A) 21°C; (B) 40°C; (C) 60°C; (D) 80°C; (E) 100°C; (F) 120°C. All spectra were recorded at a constant gain

closely those observed in the spectra of poly(methacrylonitrile) irradiated at −196°C and annealed to room temperature (see *Figures 5* and *6*, spectra E in both cases). This suggests that the same radical processes occur in both samples.

On warming the room temperature irradiated sample, the radical concentration gradually decreased (*Figure 10*). When the temperature was raised to 100°C, the hyperfine structure in the e.s.r. spectrum was eliminated. The species remaining at 100°C was characterized by an undefined broad central singlet. The major part of this singlet disappears as the temperature is further raised to 120°C, which is higher than the glass transition temperature (T_g) for poly(methacrylonitrile) (108°C). It is suggested that the stable radicals which are responsible for this singlet are the conjugated polyimine or polyenyl radicals. Therefore, only when the sample is warmed to the T_g does the segmental motion of the macromolecule chain induce these stable radicals to quench.

The signal lost during warming the room temperature irradiated sample from room temperature to 100°C is shown in *Figure 11*. The 5 major lines in the spectrum have a hyperfine splitting of 2.22 mT. In addition to these 5-lines, there are another series of 4-lines interspaced between the 5-lines. These make up the so called '5 + 4 lines' (arrow a in *Figure 11*) of the propagation radical and are similar to those observed in other γ-irradiated polymers with quaternary carbon atoms in the main chain such as poly(methyl methacrylate)[27]. This lineshape therefore may be assigned to the poly(methacrylonitrile) main-chain scission radical (*Figure 12*, A), which has also been observed in the e.s.r. spectrum as the propagation radical in the polymerization of methacrylonitrile monomer[28].

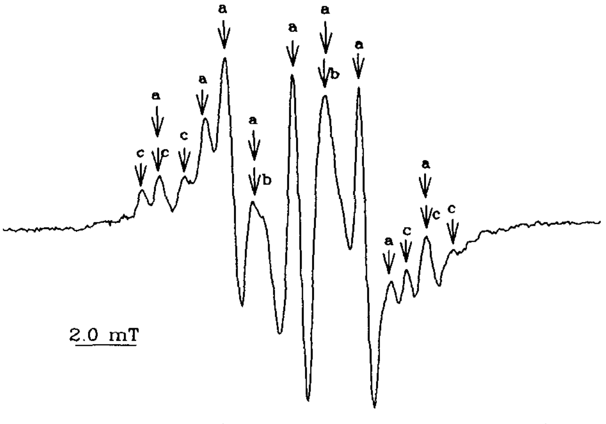


Figure 11 The lost signal for room temperature γ-irradiated poly(methacrylonitrile) (with a dose of 10 kGy) on warming from room temperature to 100°C

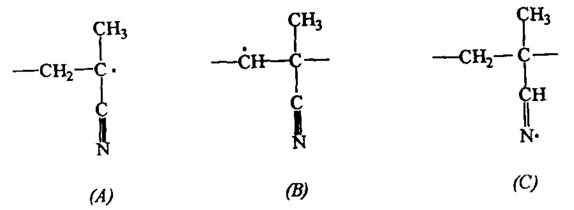


Figure 12 Some radical species present in γ-irradiated poly(methacrylonitrile)

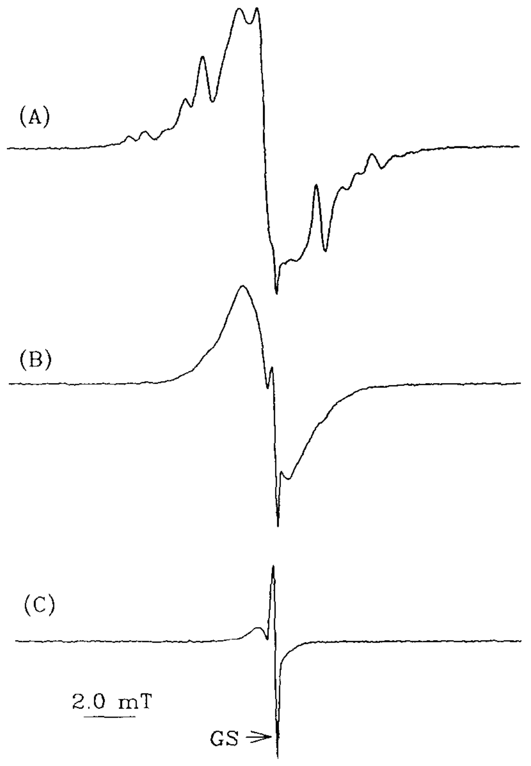


Figure 13 The e.s.r. spectra resulting after a dose of 10 kGy at different temperatures: (A) 60°C; (B) 100°C; (C) 130°C

A doublet in the spectrum (arrow b in *Figure 11*) with a hyperfine splitting of ~2.3 mT may be attributed to the radical B shown in *Figure 12*[22]. Previous workers have reported the observation of radicals in the form RCH=N·, which was generated in nitrile compounds at room temperature on exposure to high-energy electrons[31–33]. From *Figure 11*, we also can observe this radical (*Figure 12*, C), which has a doublet splitting of 8.8 mT due to the proton and a nitrogen triplet splitting of 0.7 mT (arrow c in *Figure 11*).

The e.s.r. spectra resulting after a radiation dose of 10 kGy at 60°C, 100°C and 130°C, respectively, are shown in *Figure 13*. With the increase in the radiation temperature, the radical concentrations are decreased, as shown in *Table 2*. In addition, the hyperfine structure in the spectra also gradually disappeared when the γ-irradiation temperature was increased. This can be explained by the formation of the conjugated polyimine

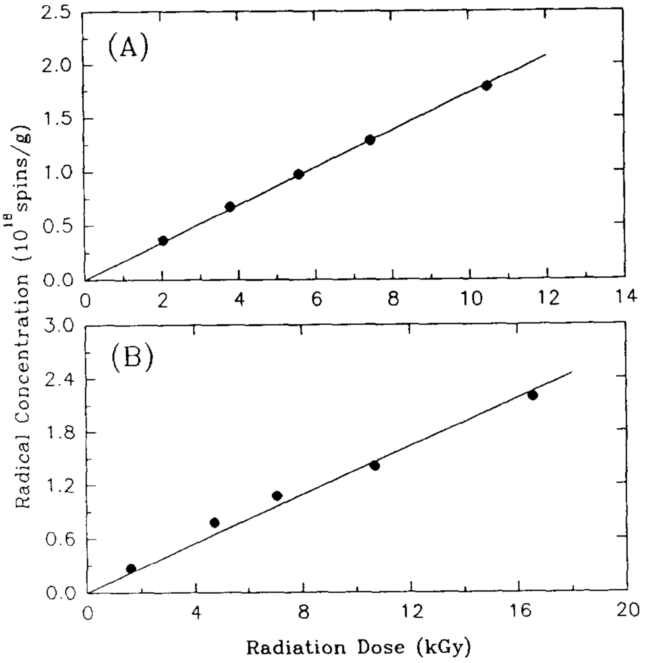


Figure 14 The radical concentration determined by e.s.r. spectroscopy *versus* absorbed dose for poly(methacrylonitrile) γ-irradiated at: (A) room temperature; (B) −196°C

or polyenyl radical (broad singlet), which is a more stable radical than the other radicals with hyperfine structure. Raising the γ-irradiation temperature will induce the radical concentration ratio of the polyimine (or polyenyl) radical to the other radicals to be increased. When the γ-irradiation temperature was increased to 100°C, only the conjugated polyimine (or polyenyl) radical signal could be observed (a broad singlet). On further increasing the radiation temperature to 130°C, which is higher than the T_g (108°C), no significant radical signal could be observed in the sample after radiolysis.

G(*R*·) *value*

The 100 eV-yield of radicals, *G*(R·), may be calculated from the plot of the radical concentratio (spins g^{-1}) *versus* absorbed dose (kGy), as shown i *Figure 14*. From this figure we calculated the *G*(R· value for γ-irradiated poly(methacrylonitrile) to be 2.2 ± 0.2 at −196°C and 2.8 ± 0.1 at room temperature. Th value at room temperature is larger than that at −196°C which suggests that the increased molecular mobility o the sample at the higher temperature allows th formation of stable radical intermediates before radica recombination of the primary radical species within th 'cage' can take place. A similar situation has bee observed in studies of the polyacrylonitrile system[22].

Temperature decay curve of radicals

Figure 15 shows the changes in the radical concentra tions with the annealing temperature for unphoto bleached and photobleached poly(methacrylonitril

Table 2 Radical concentration (spins g^{-1}) for γ-irradiated poly(methacrylonitrile) at different temperatures after a radiation dose of 10 kGy

Radiation temperature	Room temperature	60°C	100°C	130°
Radical concentration	1.7×10^{18}	8.8×10^{17}	5.8×10^{16}	~0.

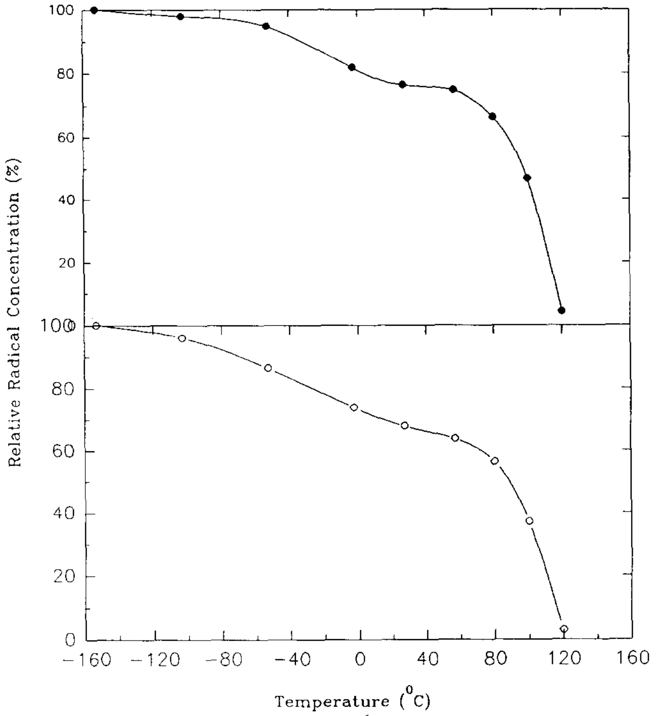


Figure 15 Quantitative loss of radical signal, as poly(methacrylonitrile), γ-irradiated at −196°C to a dose of 10 kGy, was raised in temperature from −153 to 120°C: (●) unphotobleached sample; (○) photobleached sample

which had been γ-irradiated at −196°C. The relative rate of radical decay for the unphotobleached sample is faster than that of the photobleached sample because the radical anions in the latter have been removed prior to annealing the sample. From the figure, we find that there are obviously two stages for the radical decay of the photobleached sample. The decay from −53 to 23°C may be attributed primarily to the decay of the imide radical, and the decay from 50 to 130°C may be attributed primarily to the decay of the radicals A, B and C in *Figure 12* and the conjugated polyimine or polyenyl radical.

CONCLUSIONS

The G values for radical formation on γ-irradiation of poly(methacrylonitrile), $G(\mathrm{R}\cdot)$, have been determined to be 2.2 at −196°C and 2.8 at room temperature.

The radical anions formed in the samples which have been γ-irradiated at −196°C have been assigned and their e.s.r. spectra have been identified. On annealing a sample which was γ-irradiated at −196°C, an e.s.r. spectrum, similar to that obtained on γ-irradiation at room temperature, was observed at −23°C.

The radicals observed by e.s.r. are primarily the result of main chain scission, hydrogen atom addition and abstraction. The thermal decays for these different radical intermediates depend on the experimental temperature. The conversion from the imide radical to the scission radical has been observed when poly(methacrylonitrile) which had been γ-irradiated at −196°C was warmed from −53 to −3°C.

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