

# High energy radiation effects on halogenated butyl rubbers

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The effect of high energy radiation on halogenated butyl rubbers was studied using electron spin resonance and nuclear magnetic resonance spectroscopies and gas chromatography. During high energy irradiation, most of the radicals were found to be generated on the halogenated isoprene units. A higher radiation yield for scission was observed in chlorinated butyl rubber than in brominated butyl rubber. This is due to the ready abstraction of hydrogen from the main chain by the chlorine radicals to give main-chain radicals which are known to contribute to scission in butyl rubbers. However, in both polymers, crosslinking predominates over scission up to a limiting dose.

(Keywords: radiation; butyl rubber; radicals)

## INTRODUCTION

Aliphatic halides, with the exception of fluorides, are among the organic compounds most sensitive to radiation<sup>1</sup>. In these compounds carbon–halogen bonds are weaker than both carbon–carbon and carbon–hydrogen bonds, and the main effect of radiation is to break the carbon–halogen bond to give an organic free radical and a halogen radical. The high electron affinity of the halogens permits electron attachment reactions leading to  $X^-$  (where X is a halogen atom), in addition to the more usual reactions for hydrocarbons. Further, halogen atoms show a marked diminution in reactivity in the series  $F > Cl \gg Br > I$ . For example, chlorine atoms can abstract hydrogen from organic molecules while bromine atoms do so less readily. Thus the initial radiolysis products from chloro compounds tend to include hydrogen chloride, whereas bromides give bromine as well as hydrogen bromide.

Irradiation of certain alkyl chlorides and bromides can bring about isomerism<sup>2,3</sup> in which the location of the halogen atom is changed, the carbon skeleton of the molecule remaining unaltered. For example, irradiation of n-butyl bromide gives high yields of the secondary isomer and irradiation of isobutyl chloride gives tertiary butyl chlorides. The isomerizations are attributed to free radical chain reactions.

Alkyl halides are used as crosslink promoters in various elastomers<sup>4</sup>. It has been proposed that the presence of alkyl halides enhances radical formation. One means of this enhancement is via the reaction of the very mobile X, formed during the primary process, with the polymer molecules. However, the observed enhancement of crosslinking by halides is not inconsistent with an ionic reaction mechanism.

Due to the above behaviour of low-molecular-weight alkyl halides when exposed to high energy radiation, it is interesting to see the behaviour of polymers which contain halogen atoms. For example, the exposure of poly(vinyl chloride) to high energy radiation causes dehydrochlorination and formation of conjugated structures<sup>5</sup>. Chlorination of polyethylene causes an increase in the radiation stability at <30% Cl content, but the stability decreases at >30% Cl content<sup>6</sup>.

Halogenated butyl rubbers and polychloroprene (chloroprene rubber) are the principal commercially available halogen-containing diene rubbers. While butyl rubber is known to undergo predominantly chain scission during exposure to high energy radiation, a drastically different response towards high energy radiation has been found for the halogenated butyl rubbers. Rapid gelation occurs in these polymers at low doses<sup>7</sup>. Wenwei *et al.*<sup>8</sup> compared the radiation effects on polyisobutylene and chlorinated polyisobutylene, but neither the method of obtaining chlorination of polyisobutylene nor the structure of the product was discussed by these authors. C–Cl bonds in chlorinated polyisobutylene were found to act both as radiation-sensitive groups and reactive species in the radiation process. No detailed study has been reported on the radiation-induced reactions in halogenated butyl rubber. The present study was carried out to obtain information regarding the changes in structure during exposure of halogenated butyl rubbers to high energy radiation and so to identify the mechanism of radiation degradation.

## EXPERIMENTAL

### *Materials and methods*

Halogenated butyl rubber samples were obtained through Australian Synthetic Rubber Co. All polymers were precipitated twice from chloroform with methanol,

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and dried in a vacuum oven at 30°C (until no trace of solvent could be detected in the nuclear magnetic resonance (n.m.r.) spectrum). Samples were sealed in glass tubes at  $10^{-5}$  torr and irradiated using a  $^{60}\text{Co}$  source with a dose rate of  $3.0 \text{ kGy h}^{-1}$ . After irradiation, samples were allowed to sit for a period of 1 week at room temperature before being exposed to air, to ensure all radicals would decay. It is shown below that the radicals produced during irradiations are unstable at room temperature.

#### Electron spin resonance (e.s.r.) spectroscopy

The e.s.r. spectra were obtained using a Bruker ER 200D X-Band spectrometer fitted with a variable temperature unit. The spectrometer microwave frequency was 9.26 GHz, which corresponds to a centre field at around 332.4 mT for carbon radicals, and a 250-G sweep width was used. A standard of pitch in KCl (Varian) was used as a reference for determination of the absolute radical concentration. Initial measurements were carried out at 77 K. Photobleaching experiments were performed at 77 K with a 1000 W Hg/Xe lamp (Oriel Corporation), using either 495 or 530 nm cutoff filters. The sample probe was then warmed up using a variable temperature unit to study the decay of the radicals. The spectral recording during annealing experiments was always performed at 110 K (leaving the sample for 10 min at each annealing temperature before cooling to 110 K). This was done to avoid errors in spectral subtractions which could otherwise arise from Boltzmann distribution effects.

#### Gel permeation chromatography (g.p.c.) (sol fraction determination)

A sample (30–60 mg) of irradiated halogenated butyl rubber was accurately weighed into a 10 ml volumetric flask and approximately 9 ml of tetrahydrofuran (THF) added. The flask was agitated for 24 h to completely extract the soluble polymer. The flask was made up to the mark with solvent and agitated for at least a further 4 h. Phase separation occurred on standing, with the gel rising to the top. An aliquot of the soluble phase was taken by a syringe and filtered through a Millex-SR  $0.5 \mu\text{m}$  Millipore filter. A constant volume, typically  $80 \mu\text{l}$ , was injected into the chromatograph. The amount of soluble polymer in the aliquot was determined using a Waters Liquid Chromatograph fitted with a Waters  $10^5$  microstyragel column and a differential refractive index detector. Waters HPLC grade THF was used as eluent at a flow rate of  $1.0 \text{ ml min}^{-1}$ . Multiple determinations were made on each sample. The same syringe and injection volume were used in calibration of the detector response for all samples. The area of the chromatogram was converted to a concentration of soluble polymer by comparison with a calibration plot of peak area versus polymer concentration, established by injecting solutions of known concentrations of the unirradiated polymer. The soluble fraction could then be calculated by taking the ratio of the soluble polymer to the total amount of polymer weighed into the flask.

#### N.m.r. spectroscopy

High resolution  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. spectra of the unirradiated polymers were obtained in  $\text{CDCl}_3$  with a Jeol GX 400 spectrometer operating at 100 MHz for

carbon. For  $^1\text{H}$  n.m.r., free induction decay (FID) was accumulated in 8000 data points, with a spectral width of 4400 Hz, and a 7.0 ms ( $90^\circ$ ) pulse with a recycle time of 4 s. For  $^{13}\text{C}$  n.m.r., FID was accumulated in 32 000 data points, with spectral width of 22 000 Hz, and a 9.1 ms ( $90^\circ$ ) pulse with a recycle time of 10 s with gated decoupling. DEPT (distortionless enhancement by polarization transfer) spectra<sup>9</sup> were used to assign the  $^{13}\text{C}$  n.m.r. spectra. The yields of the new structures and the polymer compositions were determined by integration of the n.m.r. spectra.

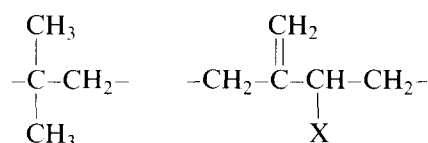
Solid-state  $^{13}\text{C}$  n.m.r. spectra were obtained with a Bruker CXP300 spectrometer at 75 MHz. The polymers were powdered in a cryoscopic grinder, packed into  $\text{ZrO}_2$  rotors with Kel-f caps and spun at the magic angle at 3 kHz.  $^{13}\text{C}$  n.m.r. spectra were obtained in the solid state from the one pulse experiment (dipolar decoupling) which consisted of a single  $90^\circ$  radio frequency pulse (duration  $5 \mu\text{s}$ ) and a recycle time of 5 s with high power proton decoupling during the data acquisition.

#### Gas chromatography (g.c.)

Polymer samples were irradiated at 303 K in sealed glass ampoules. These ampoules were broken inside a modified g.c. injection port block heater at  $60^\circ\text{C}$  in a stream of high purity nitrogen which carried the volatile products through the column, as explained in detail by Bowmer<sup>10</sup>. The gaseous products were analysed using a flame ionization detector and a thermal conductivity detector in a temperature programmable Hewlett Packard Gas Chromatograph 5730 fitted with a Chromosorb 102 80/100 column (column initial temperature,  $80^\circ\text{C}$ ; initial time, 16 min; heating rate,  $16^\circ\text{C min}^{-1}$ ; final temperature,  $200^\circ\text{C}$ ; injector temperature,  $80^\circ\text{C}$ ). The volatile product peaks were identified and calibrated using pure gases under the same conditions.

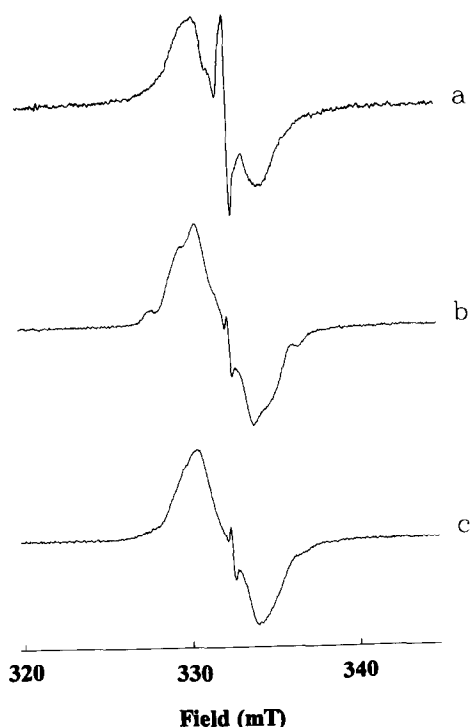
## RESULTS AND DISCUSSION

The structure of the halogenated butyl rubbers was determined from the  $^{13}\text{C}$  n.m.r. spectra, which have been assigned previously by Chu *et al.*<sup>11</sup>. Accordingly, the structures were predominantly isobutylene with 1.85 ( $\pm 0.5$ )% (from n.m.r.) halogenated isoprene units, which are of exo structure:



#### Radical intermediates

The e.s.r. spectra of polyisobutylene, chloro- and bromobutyl rubber samples irradiated and measured at 77 K are shown in Figure 1. While the spectrum of bromobutyl rubber is similar to those of polyisobutylene and butyl rubber reported previously<sup>12</sup>, the spectrum of chlorobutyl rubber was different. The spectra of polyisobutylene, butyl rubber and bromobutyl rubber were broad singlets while the chlorobutyl rubber spectrum did show some fine structure. Spectra were recorded using different microwave powers at 77 and 110 K to obtain



**Figure 1** E.s.r. spectra (measured at 77 K) of (a) polyisobutylene, (b) chlorobutyl rubber and (c) bromobutyl rubber irradiated at 77 K

power plots and a power of 40 dB was selected for the present study.

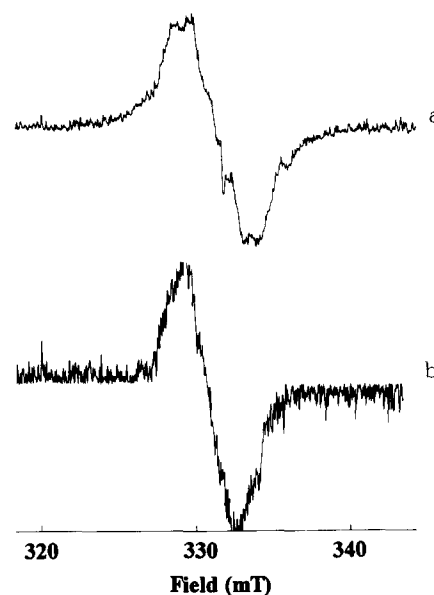
Both the halogenated butyl rubber samples irradiated at 77 K lose about 66% of the radicals during photobleaching at wavelengths in the range 490–900 nm. This is much higher than the drop observed in polychloroprene<sup>13</sup>, which was 20%. This is due to the labile allylic C–X bond in halogenated butyl rubber. The photobleaching experiments indicated the presence of ionic radicals in the irradiated samples (R1 in *Table 1*). The spectrum of the photobleachable radicals and the residual spectrum after photobleaching of chlorobutyl rubber are shown in *Figure 2*. The spectrum of the radical ions which are photobleached is a broad singlet.

**Table 1** Radicals generated during high energy irradiation of chlorobutyl rubber

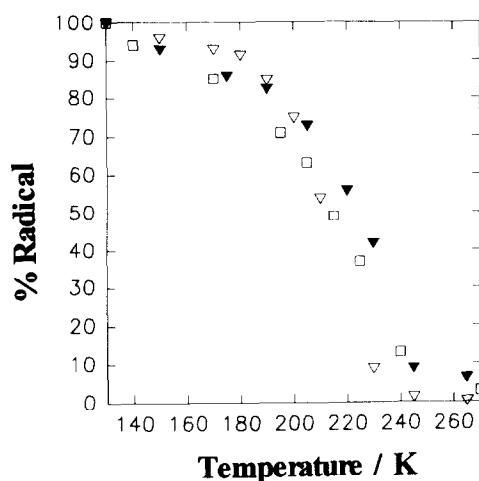
Symbol	Structure	Percentage	G(R)
R1	$\begin{array}{c} \text{CH}_2 \\    \\ -\text{CH}_2-\text{C}-\text{CH}-\text{CH}_2- \\ + \\ \text{Cl}^- \end{array}$	66	2.8
R2	$\begin{array}{c} \cdot\text{CH}_2 \\   \\ -\text{CH}_2-\text{C}-\text{CH}_2- \\   \\ \text{CH}_3 \end{array}$	16	0.7
R3	$-\dot{\text{C}}\text{H}-$	20	0.9
R4	$\begin{array}{c} \text{CH}_2 \\    \\ -\dot{\text{C}}\text{H}-\text{C}-\text{CH}-\text{CH}_2- \\   \\ \text{Cl} \end{array}$	10	0.4
R5	$\begin{array}{c} \text{CH}_2 \\    \\ -\text{CH}_2-\text{C}-\dot{\text{C}}\text{H}-\text{CH}_2- \end{array}$		

The decay of the radical concentration during annealing of the irradiated chloro- and bromobutyl rubber samples is shown in *Figure 3*. For comparison, the radical decay of polyisobutylene is also given in the same figure. A small drop initially is followed by a sharp drop at around the glass transition temperature, similar to that found for other rubbery materials. The spectra of the annealed radicals in chlorobutyl rubber are shown in *Figure 4*. The component of spectrum 4a that disappears in the range 110–215 K is a triplet, corresponding to the triplet observed previously in polyisobutylene and butyl rubber<sup>12,14</sup>. This is assigned to the radical R2 (*Table 1*) generated by hydrogen abstraction from the methyl group in the isobutylene units. The spectrum 4b, for annealing radicals between 215 and 240 K, is a doublet corresponding to the doublet in polyisobutylene, which is assigned to the radical R3 (*Table 1*) generated by hydrogen abstraction from the methylene groups of the isobutylene units. The spectrum 4c, which remains at 254 K, is a 6–7 line spectrum with hyperfine splitting of 1.3 mT. The difference between the spectra of chlorobutyl rubber and polyisobutylene, both irradiated and measured at 77 K, is also a 6–7 line spectrum with similar hyperfine splitting, as shown in *Figure 4d*. Both of these spectra (4c and 4d) are similar to the spectral component (subspectrum) observed<sup>12</sup> in butyl rubber at 230 K. This was assigned to the allyl radicals R4/R5 (*Table 1*) generated from the isoprene unit. In chlorobutyl rubber this spectrum would be due to the allyl radical generated by hydrogen abstraction at a methylene carbon  $\alpha$  to the exo-methylene group, or by chlorine abstraction. This radical consists of three  $\alpha$ -protons and two  $\beta$ -protons with similar splitting, which gives rise to a six-line spectrum, as was observed.

The radiation yields of radicals (*G* values) at 77 K are 4.3, 3.7 and 2.3 for chlorobutyl rubber, bromobutyl rubber and polyisobutylene, respectively. It was observed that the radiation yield of radicals for halogenated butyl rubbers is nearly double that for polyisobutylene, indicating that most of the initial



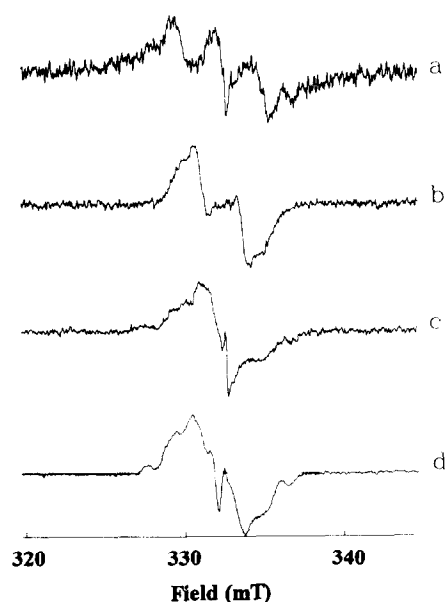
**Figure 2** E.s.r. spectra of chlorobutyl rubber: (a) photobleachable radical ion, (b) residual spectrum after photobleaching at 77 K



**Figure 3** Changes in the concentration of radicals during warming up of butyl ( $\nabla$ ), chlorobutyl ( $\blacktriangledown$ ) and bromobutyl ( $\square$ ) rubbers irradiated at 77 K

activity during exposure to high energy radiation is centred in the halogenated isoprene units. *Table 1* summarizes the radical components produced in the chlorobutyl rubber, confirming this observation. The radical concentrations were calculated using the data in *Figure 3*. This gives the fractional drop in the radical concentration at various temperature regions where a particular radical was observed to decay. The total yield of isobutylene centred radicals (R2 and R3) is 1.1 compared with 3.2 for radicals centred on chlorinated isoprene units (R1 and R4/R5). This is due to the labile C–Cl bond. During annealing of the bromobutyl rubber sample, no decay of radicals which are characterized by a two- or three-line spectrum was observed. Hence the subspectra of the annealed radicals were broad singlets without any hyperfine structure.

The e.s.r. study therefore indicates that the major transient intermediate formed during the exposure of



**Figure 4** E.s.r. spectra of chlorobutyl rubber (a) between 110 and 215 K, (b) between 215 and 240 K and (c) at 245 K; (d) e.s.r. spectral difference between chlorobutyl rubber and polyisobutylene measured at 77 K

chlorobutyl rubber to high energy radiation is the radical ion generated by C–Cl bond cleavage. This is expected, due to the lower bond energy of the C–Cl bond. It also indicates that more than 75% of the radicals generated in the primary process are on the halogenated isoprene unit, which constitutes only 2% of the total. By contrast, in butyl rubber<sup>12</sup> only 9% of the radicals generated were centred on the isoprene unit.

#### Gaseous products

The gas chromatograms of irradiated rubbers clearly show the methane and isobutylene peaks. Small peaks due to ethylene, ethane, propene and propane are also identified. Higher molecular weight fractions, which have not been identified, are formed during irradiation of bromobutyl rubber. One other prominent observation from these chromatograms is the proportion of isobutylene/methane in the samples. The calculated radiation yield values are given in *Table 2* and compared with values for polyisobutylene.

The data in *Table 2* indicate that the radiation yields of hydrogen, methane and isobutylene for halogenated butyl rubber are very small compared with those for polyisobutylene. This result confirms that most of the primary activity in the halogenated rubber is on the isoprene unit, involving the abstraction of halogen from the polymer.

#### Sol fraction

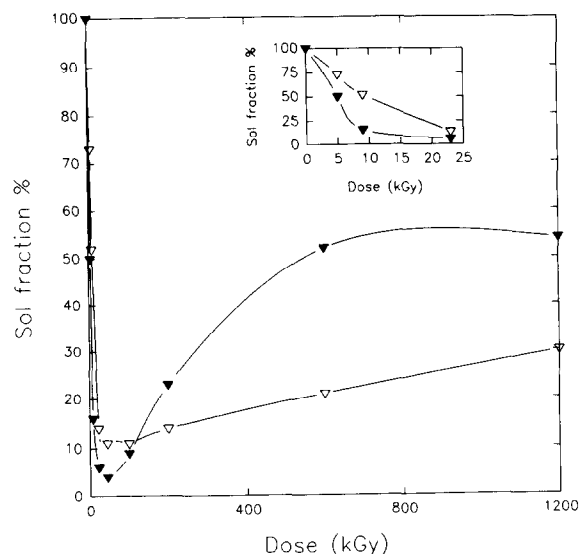
When polymers are subjected to ionizing radiation, crosslinking and main-chain scission are among the chemical effects observed. The process ultimately causes formation of an insoluble gel if crosslinking predominates over scission (that is,  $G(S) < 4G(X)$ ). In polyisobutylene, scission was found to predominate, therefore the polymer remains soluble. For the halogenated butyl rubbers, a gel is formed at very low doses as shown in *Figure 5*. The rate of gel formation is higher in bromobutyl rubber. This may be due to the increased radiation activity in the brominated isoprene unit compared with the chlorinated isoprene unit as a result of the lower C–Br bond energy. After a limiting dose, the sol fraction starts to increase again, as shown in *Figure 5*, and reaches a plateau. At doses lower than this limiting dose, crosslinking predominates and a gel is formed. Above this limiting dose the crosslinking yield is reduced to a value lower than that for scission, and the crosslinked network begins to break down. This increases the sol fraction. The limiting dose occurs when a critical proportion of the crosslinking sites has been consumed. In both polymers this limiting dose is around 50–100 kGy.

The sol fraction data ( $S$ ) were analysed using the Charlesby–Pinner equation<sup>15</sup>:

$$S + S^{1/2} = G(S)/2G(X) + 4.80 \times 10^4 / G(X) M n_0 R \quad (1)$$

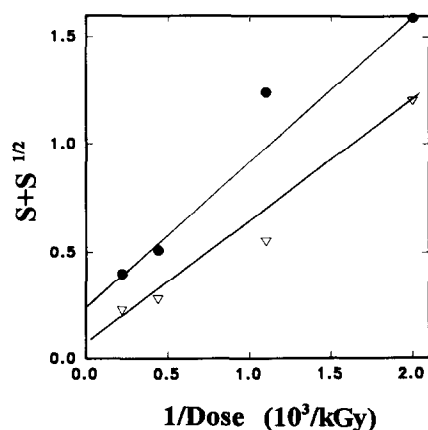
**Table 2** Radiation yields for gases produced in halogenated butyl rubber at 303 K

Rubber	Hydrogen	Methane	Isobutylene
Polyisobutylene	$1.68 \pm 0.05$	$0.67 \pm 0.01$	$0.62 \pm 0.01$
Chlorobutyl rubber	$0.22 \pm 0.01$	$0.09 \pm 0.002$	$0.03 \pm 0.002$
Bromobutyl rubber	$0.21 \pm 0.01$	$0.07 \pm 0.01$	$0.03 \pm 0.002$



**Figure 5** Sol fraction versus dose for chlorobutyl (V) and bromobutyl (▼) rubbers

where  $Mn_0$  is the initial number average molecular weight of the polymer and the dose  $R$  is in kGy. From the plot of  $S + S^{1/2}$  versus  $1/R$  shown in Figure 6,  $G(X)$  can be calculated from the slope and  $G(S)$  can be calculated from the intercept. The values are given in Table 3. These values are for doses ranging from 50 to 450 kGy. It is known that polyisobutylene undergoes predominantly scission and that the  $G(X)$  values are negligible compared with  $G(S)$ . The crosslinking in halogenated butyl rubber is through the halogenated isoprene unit, therefore the  $G(X)$  and  $G(S)$  values are a function of the residual isoprene content in the polymer. The straight-line plot of  $S + S^{1/2}$  versus  $1/R$  in the radiation dose range 50–450 kGy gives average values of the radiation yields which are given in Table 3. The calculated values indicate that  $G(X)$  is similar for both halogenated polymers in this region, while  $G(S)$  for the chlorinated butyl rubber is four times that of the brominated rubber. It is known<sup>1</sup> that chlorine atoms can abstract hydrogen from organic molecules more readily than bromine atoms. Therefore, the chlorine atoms that are produced by the initial C–Cl bond scission may abstract a hydrogen from an isobutylene unit giving either of the polymer radicals



**Figure 6** Charlesby-Pinner plot for chlorobutyl (●) and bromobutyl (▼) rubbers

**Table 3** Radiation yields for halogenated butyl rubber

Rubber	$G(X)$	$G(S)$
Polyisobutylene	0.0	$3.7 \pm 0.1$
Chlorobutyl rubber	$3.62 \pm 0.1$	$1.71 \pm 0.05$
Bromobutyl rubber	$3.70 \pm 0.1$	$0.44 \pm 0.06$

R2 and R3. Both these radicals are known<sup>12,14</sup> to initiate chain scission. This explains why these radicals were observed in the e.s.r. spectra of irradiated chlorobutyl rubber but not bromobutyl rubber.

The sol fraction plots can be used to calculate the gel doses, which are 38 and 29 kGy for chlorinated butyl rubber and brominated butyl rubber, respectively. The  $G(S)/G(X)$  values were used to calculate the maximum gel fractions ( $W_g$ ) from the equation<sup>16</sup>:

$$W_g = \{1 - G(S)/G(X) + [1 + 2G(S)/G(X)]^{1/2}\}/2 \quad (2)$$

These values were found to be 96 and 99%, respectively, for chlorobutyl rubber and bromobutyl rubber. The experimental values were found to be 90 and 97%, respectively. The slightly lower experimental values are due to the limited number of crosslinking points in these two polymers.

#### Structural changes

The proton n.m.r. spectra of the unirradiated halogenated butyl rubbers have been assigned before<sup>14</sup>. The two peaks assigned to the two olefinic (exo-methylene group) hydrogens and the peak assigned to the  $-\text{CHX}-$  group were used in both polymers to follow the changes in the proportion of halogenated isoprene groups in the samples with irradiation dose. Since both these protons (exo-methylene protons and  $-\text{CH-X}-$  protons) are in the same unit, a change in one changes the chemical shift of the other. Therefore, it is not possible to study the different reaction rates of the two groups. Since the initial concentrations are low, no new peaks could be observed at low radiation doses. Due to the limited solubility of the samples, only the samples irradiated to 10 kGy could be used to obtain  $^1\text{H}$  n.m.r. spectra acceptable for the quantification of peak area. The proportions of residual isoprene units based upon the calculation using both groups agree and are shown in Table 4. A plot of the residual isoprene content with radiation dose is given in Figure 7. The radiation yields for loss of isoprene units calculated from these data are 450 for chlorobutyl rubber and 525 for bromobutyl rubber. There is a considerable decrease in the yield for loss of double bonds with increasing dose. At doses of 250–500 kGy the values could be much smaller, but unfortunately they cannot be estimated at these doses because the resolution of the  $^1\text{H}$  n.m.r. spectra is not sufficient to allow quantification.

$^{13}\text{C}$  n.m.r. spectra of unirradiated and irradiated chlorobutyl rubber are shown in Figure 8. The irradiation dose for the sample shown in Figure 8b was 1.2 MGy, and at this dose it has a sol fraction of 31%. The sample irradiated to 0.6 MGy gave a  $^{13}\text{C}$  n.m.r. spectrum with broad resonances, because the crosslink density is high at this dose. Doses less than 0.6 MGy were not sufficient to show any new peaks in the  $^{13}\text{C}$  n.m.r. spectra. The spectra of unirradiated rubber has been assigned before<sup>11</sup>. The peaks marked X are those observed in irradiated butyl rubber which have been

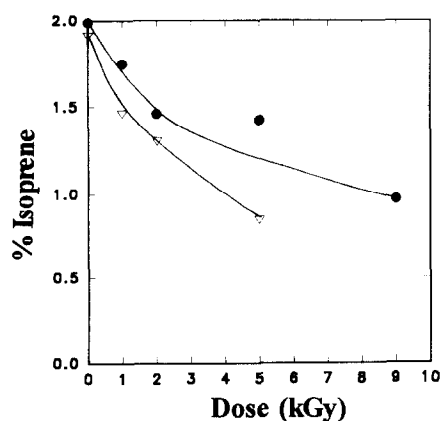
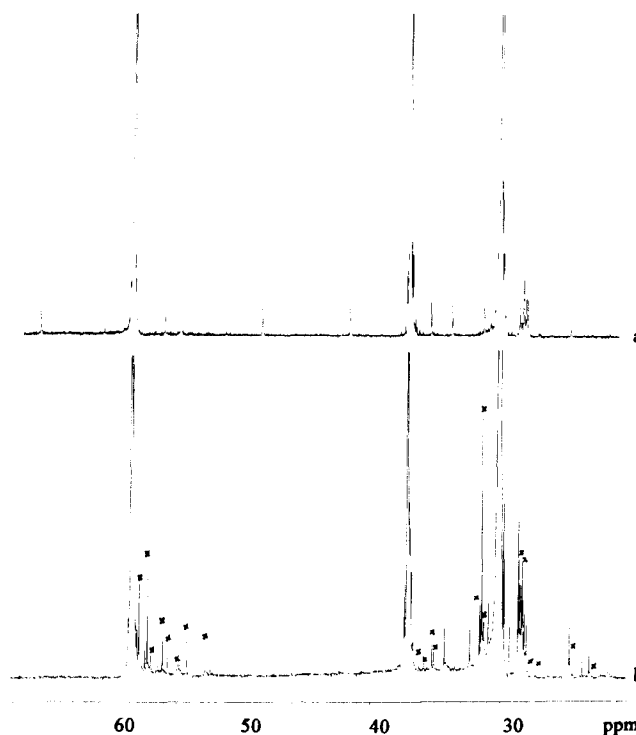
**Table 4** Proportion of isoprene units in halogenated butyl rubber with irradiation as measured by proton n.m.r.

Dose (kGy)	Proton/10 000 protons		Isoprene content ( $\pm 0.1$ mol%)
	CH <sub>2</sub> =	-CH(X)-	
Chlorobutyl rubber			
0	49.6	23.6	1.99
10	44.0	19.6	1.75
20	36.9	18.6	1.47
50	41.1	17.8	1.42
90	24.3	14.4	0.97
Bromobutyl rubber			
0	48.1	23.9	1.91
10	35.1	18.3	1.46
20	32.3	17.8	1.42
50	22.1	10.5	0.84

assigned<sup>13</sup> to different unsaturated and saturated end groups. In addition to these peaks, there are new peaks at 135.8, 123.0, 72.8, 58.5, 35.3, 33.3, 32.0, 30.4 and 24.7 ppm. These new peaks can be assigned to the structures shown in Table 5, based on literature data<sup>17,18</sup> for model compounds. One of the structures is an end group containing a chlorine atom, the other is an unsaturated group on the main chain.

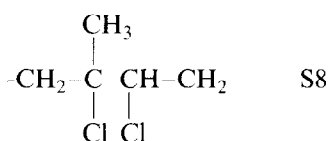
The <sup>13</sup>C n.m.r. spectra of unirradiated and irradiated bromobutyl rubber are shown in Figure 9. In contrast to chlorobutyl rubber, the bromobutyl rubber sample irradiated to 0.6 MGy gave a spectrum with sharper peaks and better resolution, because this sample had a higher soluble fraction than the corresponding chlorobutyl rubber sample. At 0.6 MGy all the peaks due to brominated isoprene units (which have been assigned before<sup>11</sup>) have disappeared, and new peaks appear. Among the new peaks, those with mark X were also present in irradiated butyl rubber and were assigned<sup>12</sup> to chain end structures. The additional five new peaks appearing at 135.8, 123.0, 34.9, 33.5 and 24.7 ppm can be assigned to an unsaturated structure similar to that formed in chlorobutyl rubber. There was no indication of a bromine-terminated structure corresponding to the one observed in the irradiated chlorobutyl rubber. This is due to the low yield for chain scission in bromobutyl rubber.

No peaks due to crosslinks could be observed in the solution-state <sup>13</sup>C n.m.r. spectra of the irradiated samples of either of the rubbers. A dipolar decoupled solid-state <sup>13</sup>C n.m.r. experiment was carried out on the

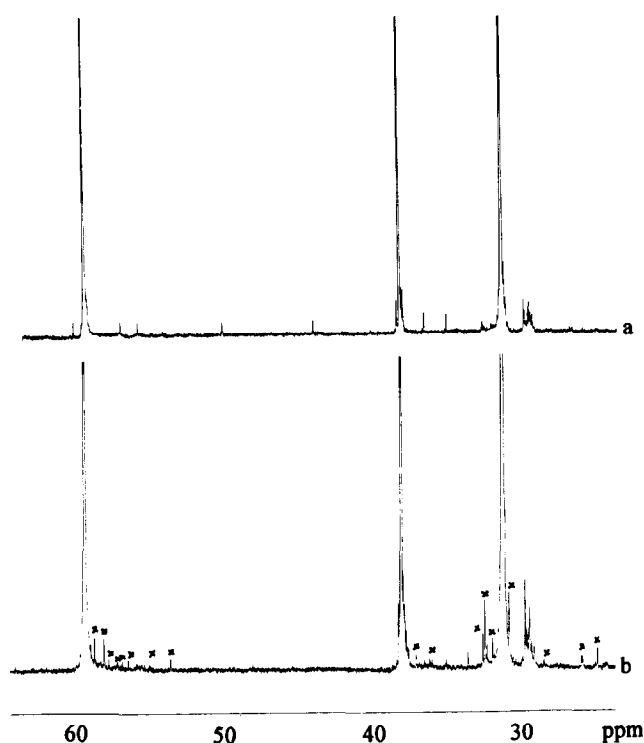
**Figure 7** Change in % isoprene with dose in chlorobutyl (●) and bromobutyl (▽) rubbers**Figure 8** <sup>13</sup>C n.m.r. spectra of chlorobutyl rubber (a) unirradiated and (b) irradiated to 1.2 MGy

chlorobutyl rubber irradiated to 0.6 MGy, and is shown in Figure 10. The peaks at 32, 38.6 and 60.0 ppm are due to the carbons of the isobutylene unit. Because the peaks are broad, the small peaks in the solution-state spectra are not resolved. There are two new resonances appearing at 77 and 84 ppm. The peak at 77 ppm can be assigned to the -C-Cl structure, on the basis of the observations for chlorinated natural rubber by Makani *et al.*<sup>18</sup>. The peak at 84 ppm is likely to be due to the -C-Cl<sub>2</sub> group, since it falls within the chemical shift region expected for this group<sup>18-20</sup> (85-95 ppm).

The -C-Cl group may be formed by hydrochlorination of the exo-methylene group to yield the structure

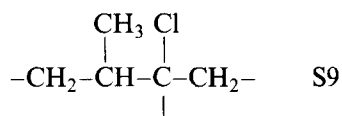
**Table 5** Chemical shift assignments in the <sup>13</sup>C n.m.r. spectrum of irradiated chlorobutyl rubber

Symbol	Structure	Carbon no.	Chemical shift (ppm)
S6	$  \begin{array}{c}  {}^1\text{CH}_3 \quad \text{CH}_3 \\    \quad   \\  \text{Cl} - \text{C}^2 - \text{CH}_2^3 - \text{C}^4 - \\    \quad   \\  \text{CH}_3 \quad \text{CH}_3  \end{array}  $	1	32.0
		2	72.8
		3	58.5
		4	35.3
S7	$  \begin{array}{c}  {}^3\text{CH}_3 \\    \\  \text{CH}_3 - \text{C}^2 = \text{CH}^4 - \text{CH}_2^5 - \text{CH}_2 - \\    \quad   \\  \text{CH}_3 \quad \text{CH}_2  \end{array}  $	1	33.3
		2	135.8
		3	24.7
		4	123.0
		5	30.4

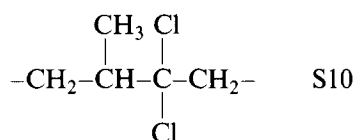


**Figure 9**  $^{13}\text{C}$  n.m.r. spectra of bromobutyl rubber (a) unirradiated (b) irradiated to 0.6 MGy

or by the reaction of an allylic radical to form a crosslink, e.g.



The  $-\text{CCl}_2-$  structure may be formed by the reaction of a  $\text{Cl}^\cdot$  with the allylic radical to yield the structure

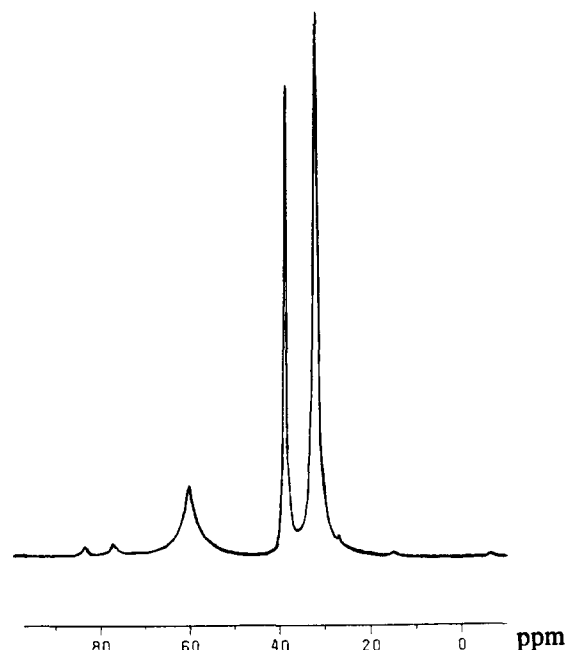


The corresponding unsaturated structures of S9 and S10 (structures containing the exo-methylene group) were not considered here, due to the large  $G(-\text{db})$  value, which indicates double bond saturation.

The resonance intensities of the solution-state  $^{13}\text{C}$  n.m.r. spectra and dipolar decoupled/magic angle spinning solid-state spectra were used to calculate the number of different structural units per 10 000 carbon atoms, and the radiation yields for the different structural groups. The values are given in Table 6. The

**Table 6**  $G$  values of different structural units formed in irradiated chlorobutyl rubber

Symbol	Dose (MGy)	Units/10 000 carbons	$G$ values
S6	1.2	5.2	0.29
S8/S9	0.6	246	28.6
S10	0.6	159	18.3



**Figure 10** Dipolar decoupled/magic angle spinning  $^{13}\text{C}$  n.m.r. spectra of chlorobutyl rubber irradiated to 0.6 MGy

large yields obtained for the formation of  $-\text{C}-\text{Cl}$  groups correlate well with the high yields for the loss of unsaturation in the system.

## CONCLUSIONS

Both the halogenated butyl rubbers show evidence for formation of radical anions during exposure to high energy radiation. The yield of radical anion in halogenated butyl rubber is much higher than in polychloroprene. This is due to the labile allylic  $\text{C}-\text{X}$  bond in the halogenated butyl rubber.

Nearly 75% of the radicals formed in halogenated butyl rubber are centred on the halogenated isoprene units, even though only 2% of these units are present in the polymer. This observation is confirmed by the lower yields for hydrogen, methane and isobutylene in halogenated butyl rubber compared with polyisobutylene.

The radiation yield for scission in chlorinated butyl rubber is higher than for brominated butyl rubber, since the chlorine atoms that are formed during cleavage of  $\text{C}-\text{Cl}$  bonds abstract hydrogen more readily than do bromine atoms. Therefore the radicals on the isobutylene units, which undergo chain scission, are formed readily in chlorinated butyl rubber.

In both halogenated rubbers, crosslinking predominates over scission up to a limiting dose of about 50–100 kGy. Above this dose, chain scission predominates and the soluble fraction increases. The gel doses for the polymers are very small (30–40 kGy).

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