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RADIATION DEGRADATION OF ELASTOMERS

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ABSTRACT

The dependence on molecular structure of the effects of high energy radiation on a variety of elastomers has been examined by ^1H - and ^{13}C -NMR spectra in solution, swollen gel, and the solid state. Scission and crosslinking yields obtained for an ethylene-propylene copolymer by NMR were in agreement with values from soluble fraction analysis, showing that the NMR method was quantitative and that the radiation-induced scission and crosslinking events were randomly spatially distributed. High crosslinking yields in *cis*-1,4-polybutadiene indicated a kinetic chain reaction producing crosslinks in clusters. A variety of new chain ends from main-chain scission were observed in polyisobutylene, providing evidence on the validity of proposed radiolysis mechanisms. In chlorobutyl rubber, crosslinking occurred with very high yield by reaction of both $\text{C}-\text{Cl}$ and $\text{C}=\text{CH}_2$ groups in the chlorinated isoprene units, but decreased after quite low doses due to depletion of these groups.

INTRODUCTION

High energy radiation produces changes which may be beneficial or deleterious in the properties of polymeric materials [1–3]. The irradiation may result from unavoidable exposure to radiation environments or by using radiation in processing. The properties of diene elastomers are affected by relatively small doses of radiation due to the facile reaction of the $\text{C}=\text{C}$ bonds to form crosslinks. The absence of

C=C bonds in polyolefin rubbers, such as ethylene-propylene and polyisobutylene, reduces crosslinking. However, polyisobutylene undergoes main-chain scission with high yield, which is consistent with the behavior of vinyl polymers containing a quaternary carbon in the repeat unit [4].

Although the yields of crosslinking and scission in irradiated polymers can be derived from changes in molecular weight and soluble fraction with radiation dose, there is still much to learn about the chemistry of these processes. Knowledge of the chemical reactions initiated by irradiation should lead to a greater understanding of the factors which influence radiation sensitivity.

The availability of ^{13}C -NMR spectrometers with high magnetic fields, and the development of solid-state NMR with magic-angle spinning and cross-polarization, enables the detection, and measurement in suitable circumstances, of new molecular structures in irradiated polymers. Thus, the chemical products of main-chain scission, crosslinking, and elimination reactions can be identified, and the reactions involved in their formation can be proposed with greater certainty than previously.

In this paper we present a comparison of the behavior upon irradiation of an ethylene-propylene copolymer (a saturated alkane elastomer with methylene, methine, and methyl carbons), *cis*-1,4-polybutadiene (an unsaturated diene-containing hydrocarbon elastomer), polyisobutylene (containing methylene, methyl, and quaternary carbons), and chlorobutyl rubber (a copolymer of polyisobutylene with halogen-substituted isoprene). ^1H - and ^{13}C -NMR spectroscopy is utilized to determine the yields of new molecular structures, giving direct information on the radiation chemistry in contrast to measurements of molecular weight or solubility.

EXPERIMENTAL

Ethylene-propylene copolymer was obtained from Japan Synthetic Rubber. The composition was determined from ^{13}C -NMR spectra in solution in trichlorobenzene at 120°C using the assignments of Carman et al. [5] and Randall [6]. ^{13}C -NMR spectra of the irradiated samples were obtained in CDCl_3 in solution, swollen gel, or in the solid state with magic angle spinning and cross-polarization with a Bruker CXP300 spectrometer at 75 MHz.

High *cis*-1,4-polybutadiene was provided by Phillips Petroleum, and the structure was confirmed by ^{13}C NMR in solution in CDCl_3 . Polyisobutylene was obtained from Aldrich and chlorobutyl rubber from Australian Synthetic Rubber. Both polymers were purified by reprecipitation from chloroform into methanol and dried under vacuum at 30°C.

Samples of the polymers were evacuated for 24 hours and sealed in glass tubes, which were irradiated at ambient temperature with ^{60}Co gamma rays in an AECL Gammacell at the University of Queensland or in the pond facility of the Australian Nuclear Science and Technology Organization.

RESULTS AND DISCUSSION

Polyethylene

The effects of high-energy radiation on polyethylene (PE) have been studied more extensively than for any other polymer. Despite the apparent simplicity of

the molecular structure of PE, $(-\text{CH}_2-\text{CH}_2-)_n$, the details of the mechanism of radiolysis are uncertain and quantitative treatment is unreliable, mainly on account of the variation in the crystalline, amorphous, and interfacial components of the morphology, the complexity of chain ends, intrachain unsaturation, short and long branches, and molecular weight distribution.

It has been established that crosslinking occurs with much higher yield than main-chain scission, but there is still controversy over the mechanism of crosslinking, i.e., the relative importance of H-links and Y-links and whether it is a radical or ionic process. Randall et al. [7] showed by ^{13}C NMR in solution that Y-linking occurs in linear polyethylene at low radiation doses. However, the Y-linking utilizes $\text{C}=\text{C}$ end groups on the polymer molecules and can be expected to be less important at higher doses.

Ethylene-Propylene (EP) Copolymers

Copolymers of ethylene and propylene, produced by Ziegler-Natta catalysis and containing 20–50% of propylene, are virtually completely amorphous due to disruption of packing in the solid state of sequences of units from either monomer. These copolymers have been shown to have the monomer units incorporated randomly in the polymer molecules, and this prevents crystallization.

Crosslinking would be expected from the ethylene units and both crosslinking and scission from the propylene units. Yields of scission and crosslinking have been determined by the conventional procedure of soluble fraction measurements. The values depend on assumptions about the mechanism of crosslinking (normally assumed to occur by H-linking) and that the crosslinks, and scissions, occur spatially at random in the sample.

The ^{13}C -NMR spectra of the unirradiated EP copolymer in solution was clearly resolved, and the resonances have been assigned [5, 6] to a variety of CH_3 , CH_2 , and CH peaks resulting from different comonomer sequences. Irradiation to high doses resulted in an increasing proportion of insoluble polymer gel above the gel dose, D_g . Good NMR spectra were obtained from the mixture of soluble polymer and swollen gel up to moderate radiation doses, as shown in Fig. 1, although the total intensity of the spectrum decreased with dose.

The peaks in the spectra broaden with dose, as shown in Fig. 1, and new peaks can be observed between 15 and 25 ppm, attributable to end groups formed by main-chain scission. Resonances due to crosslinked carbon atoms formed by H-linking would be expected to occur in the range of 40 to 45 ppm based on additivity rule calculations.

The methyl region of the spectrum between 10 and 25 ppm is shown expanded in Fig. 2(a) for a radiation dose of 0.5 MGy. The five small peaks which are identified have been attributed to CH_3 chain ends with different adjacent molecular structures. The areas of these peaks were found to increase with dose, and G values were calculated from the peak area versus dose relationships.

An expansion of the 40–45 ppm region of the ^{13}C -NMR spectrum is shown in Fig. 2(b) for a radiation dose of 0.135 MGy. A new peak attributed to a CH carbon in an H-type crosslink is evident at about 42.3 ppm. The area of this peak was not related to radiation dose and disappeared at higher doses. The molecular mobility will be reduced at crosslinks, and carbon atoms in H-crosslinks will have longer relaxation times and broadened peaks in the insoluble, but swollen, gel, leading to

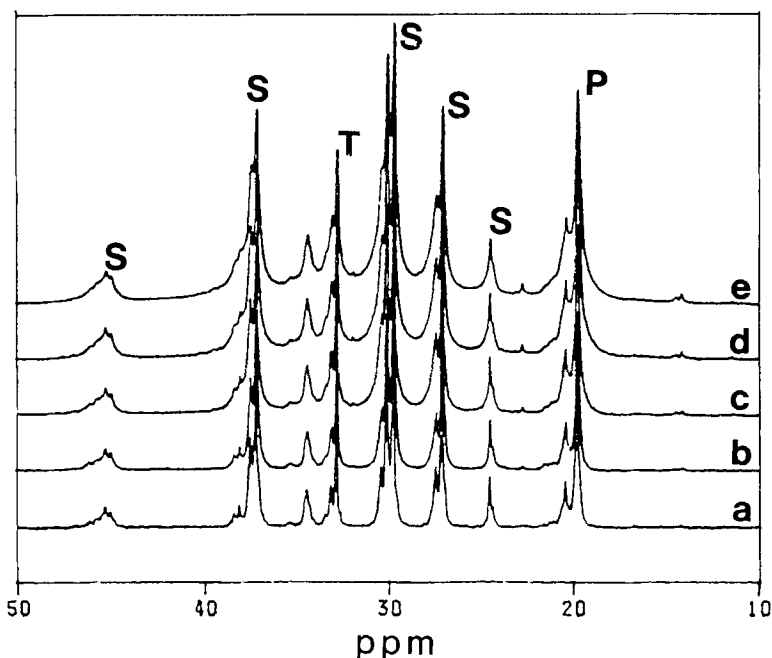


FIG. 1. ^{13}C -NMR spectra of ethylene-propylene (EP) copolymer (36%) obtained from solution/swollen gel after various radiation doses: (a) 0.02 MGy, (b) 0.2 MGy, (c) 0.5 MGy, (d) 1 MGy, (e) 2 MGy. $P = \text{CH}_3$, $S = \text{CH}_2$, $T = \text{CH}$ peaks.

lower efficiency for their measurement by the normal solution NMR procedure. Also, the crosslinks will be preferentially distributed in the highest molecular weight (gel) fraction of the irradiated polymer.

Increasing radiation dose caused the widths of the NMR peaks to broaden and the total intensity (area) of the spectrum to decrease, although less than the decrease in soluble fraction, indicating that the structure of the swollen gel was being observed, but with decreasing efficiency.

The solution NMR method could not be used for doses above about 2 MGy due to the reduced signal-to-noise ratio. Solid-state NMR with magic angle spinning gave good spectra, although the linewidth was much greater than from solution or swollen gel. The solid-state ^{13}C -NMR spectrum of unirradiated EP is shown in Fig. 3(a) and should be compared with the solution spectra in Fig. 1. The solid-state spectrum could be simulated quantitatively, except for the methyl peak at 20 ppm, using the peak positions and intensities in Fig. 1(a) and a greater linewidth (50 Hz). The methyl peak is too small in the experimental solid-state spectrum, which can be explained by the greater mobility of the methyl group in the polymer structure compared with the other carbons giving incomplete cross-polarization with the normal contact times.

The ^{13}C solid-state NMR spectrum of irradiated EP copolymer after a dose of 10 MGy is shown in Fig. 3(b). There is a significant increase in linewidth. This spectrum was simulated quantitatively using the same chemical shift and intensity values for the peaks as in Fig. 3(a), but with a linewidth of 100 Hz. The simulated

and experimental spectra coincide, including the methyl peak, except for the small peak which has appeared at 16 ppm (CE) and the discrepancy at 40–45 ppm, which gives by difference a broad peak (X).

The radiation chemical yields of scission and crosslinking were calculated from the appropriate peak areas in the solid-state NMR spectra [8, 9]. These G values from NMR were in good agreement with values derived from measurements of the soluble fractions, s , using the Charlesby–Pinner equation [10] for $s + s^{1/2}$, versus $1/\text{dose}$, as shown in Table 1. This agreement indicates that the scission and crosslinking events must occur with a random spatial distribution, which is consistent with the completely amorphous morphology of the polymer and the absence of any chemical structure which would give rise to a kinetic chain reaction. The EP copolymer had a most-probable molecular weight distribution, which is also a requirement for the Charlesby–Pinner equation to apply.

Polybutadiene

Natural rubber (polyisoprene) and a variety of synthetic rubbers are polydienes, characterized (for the 1,4 structure) by a carbon-carbon backbone in which every fourth bond is $\text{C}=\text{C}$. The stereospecific structure, *cis*-polybutadiene, was chosen for this study because the ^{13}C -NMR spectrum is simple, comprising peaks of equal intensity at about 30 ppm due to CH_2- and at about 130 ppm due to $\text{CH}=\text{C}$, as shown in Fig. 4.

After low doses of radiation, the solution/swollen gel spectra show 1) a decrease in the intensity of the $\text{CH}=\text{C}$ peak relative to $-\text{CH}_2-$, 2) an increase in line-

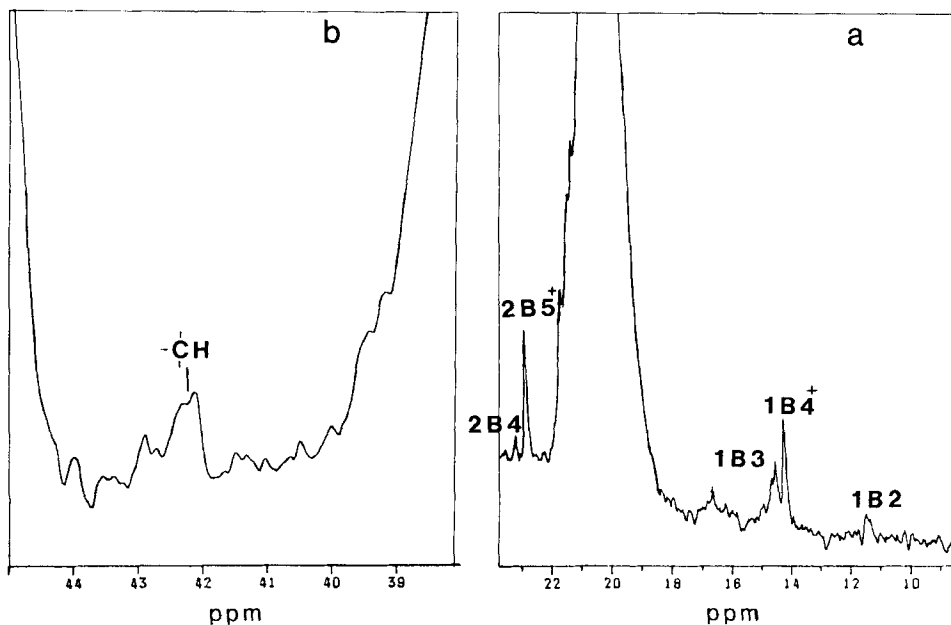


FIG. 2. ^{13}C -NMR spectrum of solution/swollen gel sample of irradiated EP copolymer: (a) CH_3 region, dose 0.5 MGy; (b) CH region, dose 0.135 MGy.

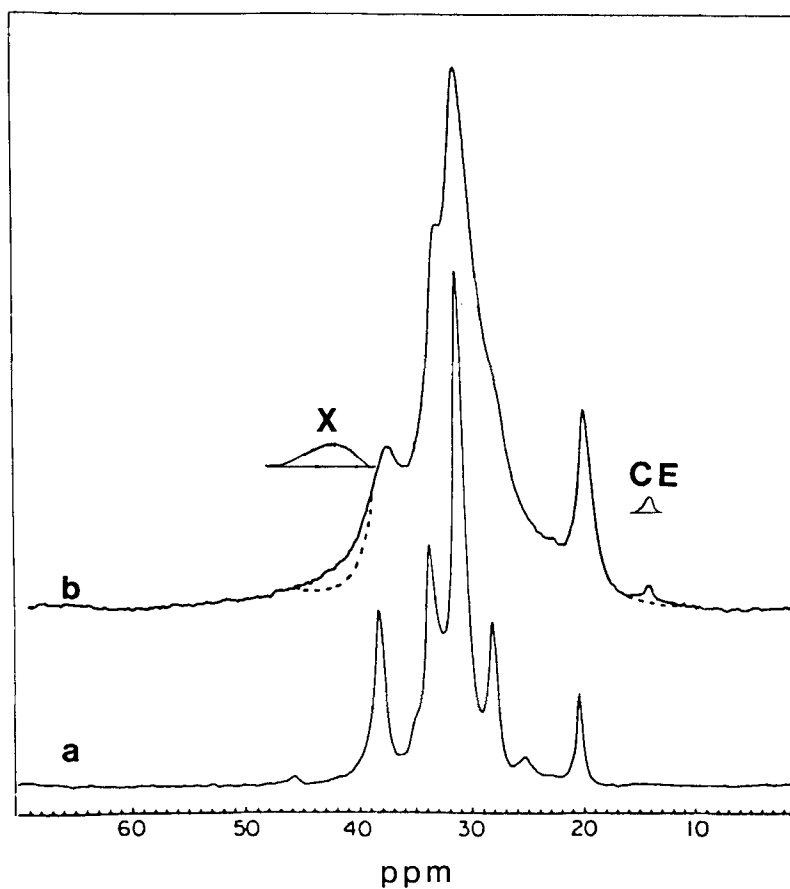


FIG. 3. Solid-state ^{13}C -NMR spectra of EP copolymer: (a) unirradiated, (b) dose 10 MGy. CE is the peak due to methyl groups on new chain ends, and X is a broad peak due to carbons in H-crosslinks.

TABLE 1. Radiation Chemical Yields of Scission and Crosslinking for Ethylene-Propylene (EP) Copolymer (36% P) at 25°C in vacuum

Method	$G(\text{S})$	$G(\text{X})$	$G(\text{S})/G(\text{X})$
Sol fraction	0.38	0.82	0.46
^{13}C -NMR solid	0.31	0.84	0.37
^{13}C -NMR solution/gel	0.37		

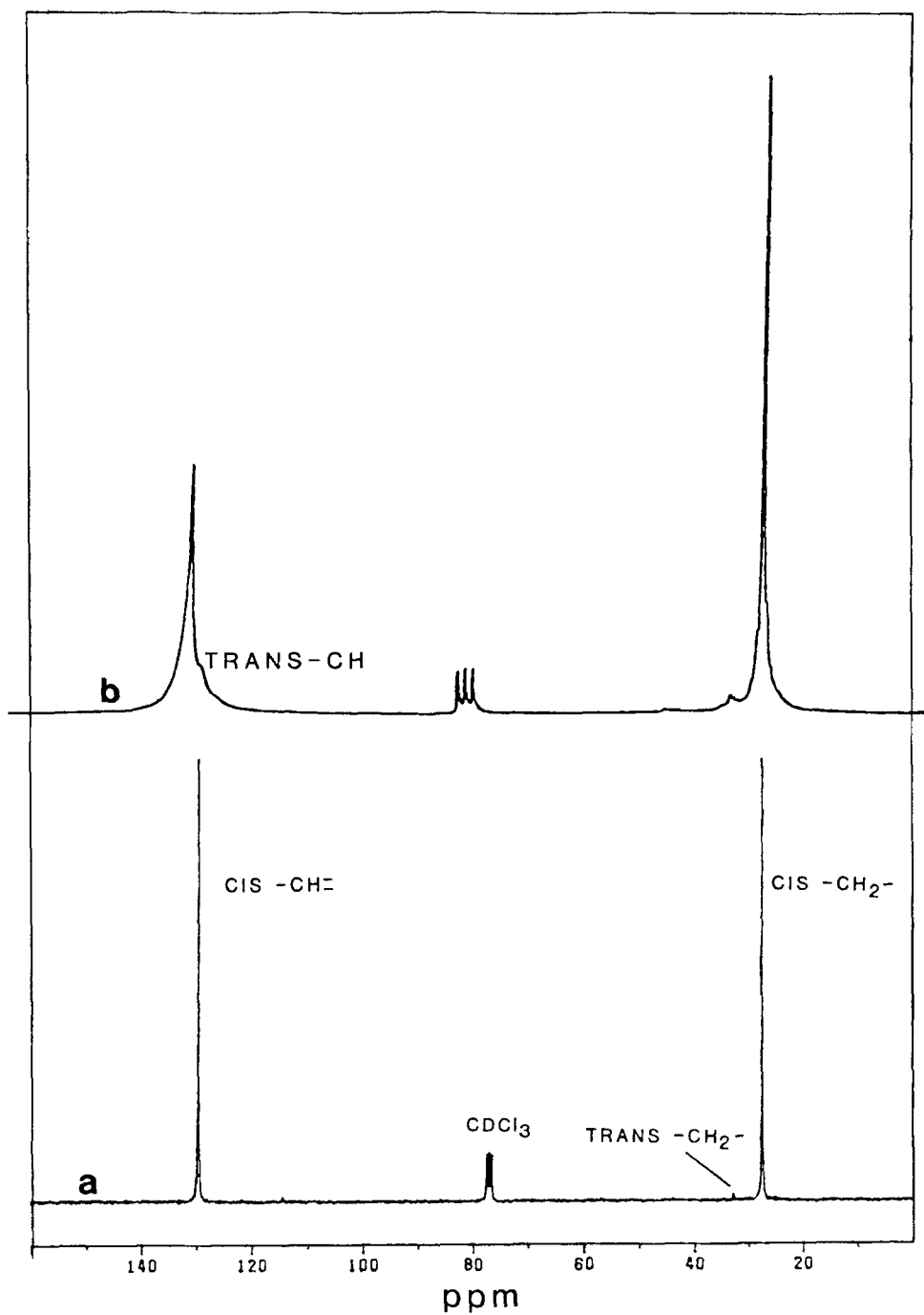


FIG. 4. ^{13}C -NMR spectra of *cis*-1,4-polybutadiene: (a) unirradiated (solution), (b) radiation dose 1.5 MGy (swollen gel).

width, and 3) an increase in the very small initial *trans* peaks. These spectra can only be obtained after very low doses due to the high yield of crosslinking. Solid-state ^{13}C -NMR spectra obtained after moderate and high doses showed much greater linewidths increasing with dose. The intensities of the $\text{CH}=\text{C}$ peak and of a new broad peak at about 35–55 ppm could be determined by simulation of the spectra and were used [11, 12] to calculate values for the rate of disappearance of $\text{C}=\text{C}$ double bonds, $G(-\text{d.b.})$, and formation of crosslinks, $G(\text{X})$. Some conversion of *cis* to *trans* could be identified from the simulation analysis of the spectrum after low doses, and also a peak at about 30 ppm attributable to CH_2 adjacent to crosslinks was identified. The values of $G(-\text{d.b.})$ over successive dose intervals are shown in Fig. 5.

The main features of Fig. 5 are the high values of $G(-\text{d.b.})$ and the rapid decrease in $G(-\text{d.b.})$ with dose. The G values for crosslinking were similar to the values of $G(-\text{d.b.})$. The large initial values of $G(-\text{d.b.})$ and $G(\text{crosslink})$ can only be explained by a kinetic chain reaction which could occur if adjacent $\text{C}=\text{C}$ bonds were involved in the reaction sequence of one active intermediate species. Such a kinetic chain reaction would lead to the formation of a cluster of crosslinks.

The rapid decrease in $G(-\text{d.b.})$ and $G(\text{crosslink})$ with dose would be due to the depletion of $\text{C}=\text{C}$ bonds in sufficiently close proximity to one another to maintain the kinetic chain reaction. This clustering of crosslinks would also explain the much higher $G(\text{crosslink})$ values obtained by NMR [11, 12] than by the traditional gel fraction analysis using the Charlesby-Pinner equation, which assumes a spatially random distribution of crosslinks. These results for *cis*-polybutadiene are in marked contrast to the result for EP copolymers, although both systems are amorphous.

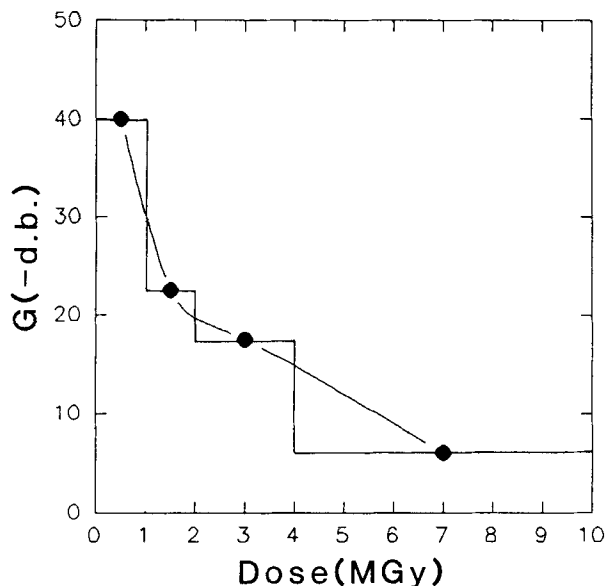


FIG. 5. Dose dependence of the rate of consumption of $\text{C}=\text{C}$ double bonds during the irradiation of *cis*-1,4-polybutadiene obtained from solid-state ^{13}C -NMR spectra.

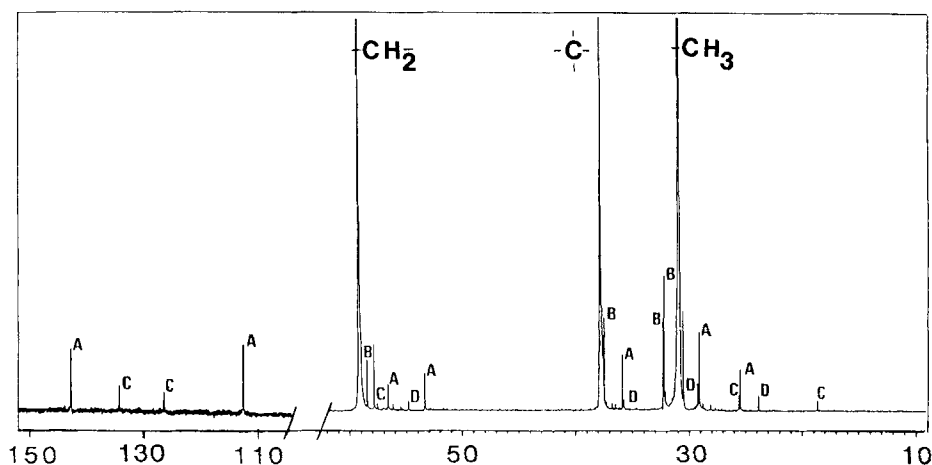


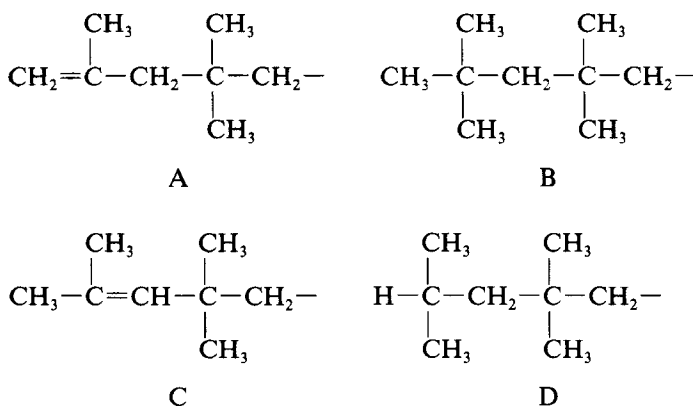
FIG. 6. ^{13}C -NMR spectrum of polyisobutylene after irradiation showing peaks due to new chain end structures A-D. Radiation dose 0.9 MGy.

Polyisobutylene

Polyisobutylene is a fully saturated hydrocarbon polymer which is used as an elastomer for specialized applications (usually with a small amount of isoprene as a comonomer to enable crosslinking). Main-chain scission should be the dominant effect of irradiation due to the quaternary carbon in the backbone of the polymer molecule and the T_g value of about -75°C , and this has been observed. $G(\text{scission})$ has been reported to be temperature dependent with a value of about 3.5 at 25°C from viscosity measurements [13]. Various mechanisms have been proposed to account for the scission, and a number of new chain ends and main-chain structures postulated. Interpretation of the ESR spectra of irradiated polyisobutylene [14, 15] has provided the main evidence for free radical intermediates which could be involved in these reaction mechanisms.

NMR spectroscopy offers the possibility of observing and measuring the concentrations of new structures in the irradiated polymers. The ^{13}C -NMR spectrum of polyisobutylene obtained in solution is very simple, comprising three peaks of equal intensity due to $-\text{CH}_3$, $-\text{CH}_2-$, and $>\text{C}<$. Solution spectra can be readily obtained after all radiation doses since there is little or no crosslinking. A variety of new peaks with narrow linewidths, which consequently are well resolved and have measurable heights, were observed in the NMR spectra, as shown in Fig. 6.

These peaks have been assigned to new chain-end structures A-D by comparison with predicted chemical shifts calculated by additivity rules [16, 17]. Some of the structures previously postulated by various researchers were not observed, and the corresponding reactions apparently do not occur. The yields of new chain ends have been determined from quantitative evaluation of the ^{13}C -NMR spectra of irradiated polyisobutylene, and the $G(\text{scission})$ value derived at 25°C is in good agreement with values calculated from molecular weight measurements.



Chlorobutyl Rubber

Reaction of chlorine with the isoprene units (about 1–2 mol%) in butyl rubber (a random copolymer with isobutylene) results in complete monochlorination, but also isomerization to the structure containing $>\text{C}=\text{CH}_2$ and $>\text{CH}-\text{Cl}$ substituents. Both of these substituents should be highly sensitive to radiation, and the radiation chemistry of chlorobutyl rubber was investigated by NMR for comparison with polyisobutylene.

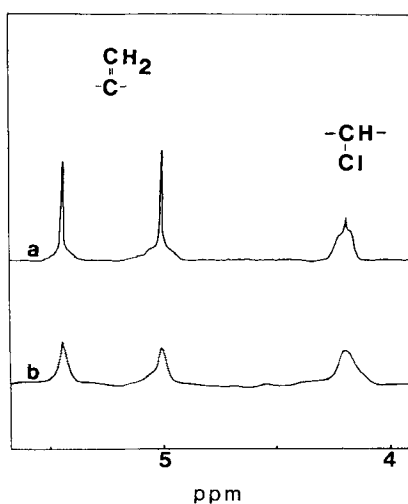
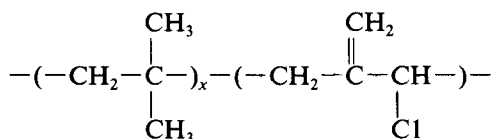


FIG. 7. ^1H -NMR spectrum (isoprene region) of chlorobutyl rubber: (a) unirradiated, (b) radiation dose 0.02 MGy.

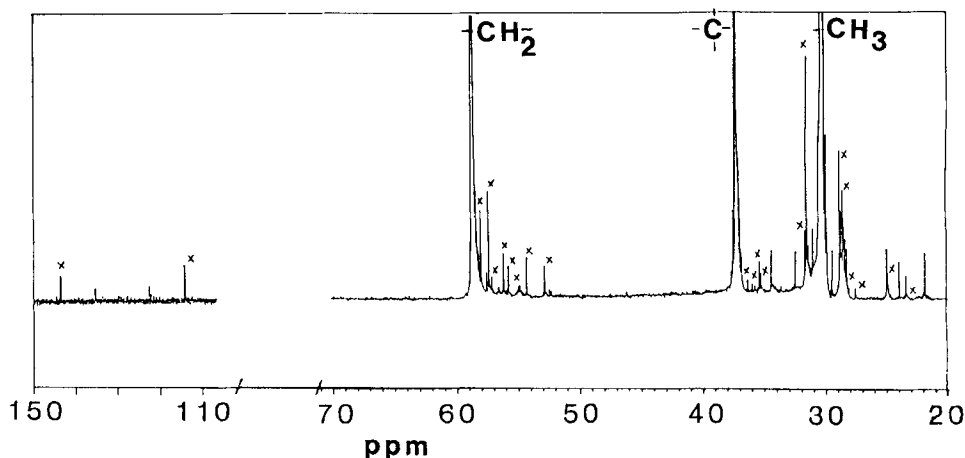


FIG. 8. ^{13}C -NMR spectrum of irradiated chlorobutyl rubber: radiation dose 1.2 MGy. x = new chain end structures due to scission of isobutylene sequences.

The $>\text{C}=\text{CH}_2$ and $>\text{CH}-\text{Cl}$ structures are clearly observed in the ^1H -NMR spectra of the polymer in solution, as shown in Fig. 7(a). Irradiation of chlorobutyl rubber caused increases in linewidth and reductions in the intensities of these peaks in the NMR spectrum (Fig. 7b). The concentrations of these two radiation-sensitive groups could be measured from the ^1H -NMR spectra and were found to be greatly reduced after low radiation doses.

The ^{13}C -NMR spectrum of an irradiated sample of chlorobutyl rubber is shown in Fig. 8. The major peaks are due to the three different types of carbons in polyisobutylene. New peaks previously observed and assigned in irradiated polyisobutylene are marked with an x . Additional peaks are observed and are attributed to new structures arising from reactions involving the chlorinated isoprene units. The low concentration of chlorinated isoprene units in the polymer greatly sensitizes the radiation degradation. Crosslinking predominates over scission in this copolymer, in contrast to polyisobutylene, and the soluble fraction decreases rapidly above a low gel dose. However, the sensitizer units are consumed, and after higher doses the soluble fraction increases.

CONCLUSIONS

The effects of high-energy radiation on elastomers is very dependent on their molecular structure. Sensitization by $\text{C}=\text{C}$ bonds and $>\text{CH}-\text{Cl}$ groups has been observed. A strong dependence on radiation dose can be attributed to the exhaustion of sensitizer structures.

NMR spectroscopy for solutions, swollen gels, and solid polymers has been shown to be a valuable technique for observing, and determining quantitatively, the yields of new molecular structures including chain ends and crosslinks formed by irradiation of polymers.

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REFERENCES

- [1] A. Charlesby, *Atomic Radiation and Polymers*, Pergamon, Oxford, 1960.
- [2] A. Chapiro, *Radiation Chemistry of Polymeric Systems*, Wiley-Interscience, New York, 1962.
- [3] M. Dole (Ed.), *The Radiation Chemistry of Macromolecules*, Academic Press, New York, 1973.
- [4] A. A. Miller, E. J. Lawton, and J. S. Balwit, *J. Polym. Sci.*, **15**, 503 (1954).
- [5] C. J. Carman, R. A. Harrington, and C. E. Wilkes, *Macromolecules*, **10**, 536 (1977).
- [6] J. C. Randall, *Ibid.*, **11**, 33 (1978).
- [7] J. C. Randall, F. J. Zoepfl, and J. Silverman, *Makromol. Chem., Rapid Commun.*, **4**, 149 (1983).
- [8] J. H. O'Donnell and A. K. Whittaker, *Br. Polym. J.*, **17**, 51 (1985).
- [9] J. H. O'Donnell and A. K. Whittaker, *Polymer*, **33**, 62 (1992).
- [10] A. Charlesby and S. H. Pinner, *Proc. R. Soc. London, Ser. A*, **249**, 367 (1959).
- [11] P. F. Barron, J. H. O'Donnell, and A. K. Whittaker, *Polym. Bull.*, **14**, 339 (1985).
- [12] J. H. O'Donnell and A. K. Whittaker, *J. Polym. Sci., Part A: Polym. Chem.*, **30**, 185 (1992).
- [13] K. Wundrich, *Eur. Polym. J.*, **10**, 341 (1974).
- [14] B. Ranby and P. Carstensen, *Adv. Chem. Ser.* **66**, 256 (1967).
- [15] Y. Hori and H. Kashiwabara, *J. Polym. Sci., Polym. Phys. Ed.*, **19**, 1141 (1981).
- [16] D. M. Grant and E. G. Paul, *J. Am. Chem. Soc.*, **86**, 2984 (1964).
- [17] L. P. Lindeman and J. Q. Adams, *Anal. Chem.*, **43**, 1245 (1971).