

## Determination of H-Crosslinks in $\gamma$ -Irradiated Polybutadiene by $^{13}\text{C}$ -NMR

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### Summary

The solid-state  $^{13}\text{C}$  NMR spectra of a 99% cis-1,4-polybutadiene after  $\gamma$ -irradiation at 25°C showed a reduction in the intensity of the -CH= resonance at 130.1 ppm and the development of a broad resonance at 45.8 ppm due to H-crosslinks. The -CH<sub>2</sub>- signal comprises the original narrow resonance at 28.2 ppm due to -CH<sub>2</sub>- groups remote from crosslinks, and a broad resonance centred at 30.5 ppm attributable to -CH<sub>2</sub>- groups adjacent to crosslinks. There was an increase in the intensity of the -CH<sub>2</sub>- resonance at 33.6 ppm due to trans -CH<sub>2</sub>- groups resulting from radiation-induced isomerization. Quantitative determinations of (i) the decrease in -CH= and (ii) the increase in crosslinked carbon atoms both gave G values of about 14 after 3 MGy. The crosslinks are evidently located in clusters, since literature G(X) values derived from gel contents and swelling ratios range from 3 to 6. The high G(X) value from NMR is consistent with a chain reaction for the crosslinking process.

### Introduction

The advent of solid-state NMR, utilizing magic angle spinning, cross-polarization and high-power, dipolar-decoupling offers the opportunity to examine the molecular structure of insoluble, crosslinked polymers. High-energy irradiation, e.g. electron beams, x-rays or  $\gamma$ -rays, is an important method for introducing crosslinks into solid polymers, especially as the radiation can be absorbed throughout quite large samples, which may be opaque or non-absorbent to visible/UV light and impermeable to liquid reactants.

There has been considerable interest, but as yet little success, in the detection and measurement of crosslinking in irradiated polymers by NMR. Randall (1) observed an increase in the number of Y-branch points in the high-resolution, solution spectra of high-density polyethylene after  $\gamma$ -irradiation in the melt and in the solid state. He attributed their formation to the addition of main chain -CH- radicals to vinyl groups on chain ends, and deduced that this is the main mechanism of radiation-induced crosslinking in this polymer. O'Donnell and Whittaker (2) suggested that H-crosslinks may be present, but not observable, in solution spectra on account of the low segmental mobility around these carbon atoms. Therefore, they examined the solid-state  $^{13}\text{C}$  NMR spectra of two ethylene-propylene copolymer elastomers containing 28% and 46% of propylene. The line widths

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increased from 50 to 100 Hz after 10 MGy of  $\gamma$ -irradiation and subtraction of simulated and experimental spectra showed the development of a peak at 14.3 ppm due to chain-end methyl groups resulting from scission of the backbone chain, and a broad resonance in the range 39-47 ppm, which is the predicted region for H-crosslinks between chains. Quantitative measurements of the NMR intensities gave yields of scission and crosslinking in agreement with values obtained by measurement of soluble fractions at various doses beyond the gel dose and evaluation of the data by the Charlesby-Pinner method, with allowance for the initial molecular weight distributions of the polymers.

There have been a number of reports of the radiation-induced crosslinking of polybutadiene. Kuzminsky et al. (3) (1958) obtained values for the yields of crosslinking,  $G(X)$ , and loss of double bonds,  $G-(C=C)$ , from measurements of elastic modulus and by titration with IBr, respectively. A marked dependence of the  $G$  values on absorbed dose was observed.  $G-(C=C)$  decreased from 325 at low doses (0-0.2 MGy) to 5 after doses of 2-3 MGy, while  $G(X)$  increased from 2 at low doses to 10 at higher doses. Witt (4) (1959) reported  $G(X)$  values of 3.20, 3.79, and 3.87 from a Charlesby-Pinner analysis of the soluble fractions, and Miller et al. (5) (1963) obtained  $G(X) = 5.8$  from swelling and gel measurements.  $G(X) = 3.6$  (0- 0.7 MGy) was reported by Jankowskii and Kroh (6,7) (1965,1969). Kozlov et al. (8,9) (1969,1970) reported  $G(X) = 5.3$  and a yield for chain-scission  $G(S) = 0.52$  at 25°C. This contrasts with  $G(S) < 0.01$  for 7 polybutadienes of different structures obtained by Pearson et al. (10) (1975). Soluble fractions were analysed by Pearson et al. using Saito's equations, which were modified to allow for crosslinking by a chain reaction.  $G(X)$  varied from 3.1- 6.7, and for each polymer slightly less than half of the crosslinking was attributed to a chain reaction. The sensitivity of the double bonds to crosslinking was reported to decrease in the order 1,2-vinyl, 1,4-cis, 1,4-trans.

Parkinson and Sears (11) (1967) used IR spectroscopy to obtain  $G-(cis-C=C) = 15$ ,  $G-(trans-C=C) = 11- 22$ , and  $G(cis \rightarrow trans) = 7$ .  $G-(1,2-vinyl-C=C)$  was dependent on the initial 1,2-vinyl content; values from 40 to 0.2 were reported. Golub (12) (1965) has reported  $G-(C=C) = 7.9$  and  $G(cis \rightarrow trans) = 7.2$  for  $\gamma$ -irradiated cis-polybutadiene (i.e.  $G-(cis-C=C) = 15.1$ ). He suggested that some of the double bonds are converted to cyclic structures.

Patterson and Koenig (13,14,15) have studied peroxide crosslinked polybutadiene by solid-state,  $^{13}C$  NMR. They observed a reduction in the  $-CH=$  resonance, formation of methyl groups, due to chain scission, and apparent crosslinking after treatment with dicumyl peroxide at 150°C, but no quantitative results were reported. Schilling et al. (16) have reported the solid-state NMR spectrum of crystalline, trans-1,4-polybutadiene.

In this paper we report the first observation of H-type crosslinks in irradiated polybutadiene by  $^{13}C$  solid-state NMR. The radiation chemical yields ( $G$  values) for crosslinking and for the decrease in double bond concentration have been determined. Furthermore, the spatial distribution of the crosslinks is deduced by comparison of the  $G$  values for crosslinking obtained by NMR with those measured previously by other methods.

## Experimental

A high cis-1,4-polybutadiene was provided by Olympic Tyre Co. (quantitative  $^{13}C$  NMR analysis gave 99.0% cis-1,4, 1.0% trans-1,4, negligible 1,2). The block polymer was cut into small pieces, evacuated for 48 hr at 25°C and sealed in glass ampoules. The samples were irradiated with  $^{60}Co$

$\gamma$ -rays at 6.0 kGy/hr at 30°C for doses up to 10 MGy (1MGy = 100Mrad). Post-irradiation treatment consisted of heating the samples to 150–250°C depending on the radiation dose. ESR studies of the irradiated polymers showed negligible radical concentrations before the ampoules were opened. Solid-state  $^{13}\text{C}$  NMR spectra were obtained with a Bruker CXP-300 spectrometer at 75.46 MHz. The crushed polymer samples were spun in boron nitride rotors at the magic angle at ca. 2.5 kHz; the Dixon sequence, TOSS (17), was used to remove the spinning sidebands of the more highly irradiated samples (doses > 4 MGy). Comparison with normal cross-polarization spectra indicated that distortion of relative peak intensities, by use of the TOSS sequence was negligible. Spectra were recorded with  $^1\text{H}$  dipolar-decoupling and  $^1\text{H}$ - $^{13}\text{C}$  cross-polarization (contact times of 0.1–25 ms), and recycle times of 3–5 s. Quantitative intensities were obtained by computer simulation of the overlapping spectral regions and from plots of  $\ln(\text{peak intensity})$  versus contact time. Spectral simulations were performed on a Bruker Aspect-3000 computer. A more detailed description of the quantitative analysis will be published (18). Chemical shifts were referenced to TMS via adamantane.

### Results and Discussion

Excellent solid-state  $^{13}\text{C}$  NMR spectra were obtained using cross-polarization from the high-cis-1,4-polybutadiene sample after low radiation doses, although not for unirradiated polymer. A radiation dose of 0.44 MGy introduced sufficient molecular rigidity through crosslinking to enable  $^1\text{H}$ - $^{13}\text{C}$  cross-polarization. Fig 1 shows a spectrum after 0.44 MGy. The line widths are very narrow for solid-state spectra (about 20 Hz), although broader than for the solution spectra of the unirradiated polymer (ca. 1 Hz). Quantitative peak intensities were obtained from the contact time experiments as described in the experimental section.

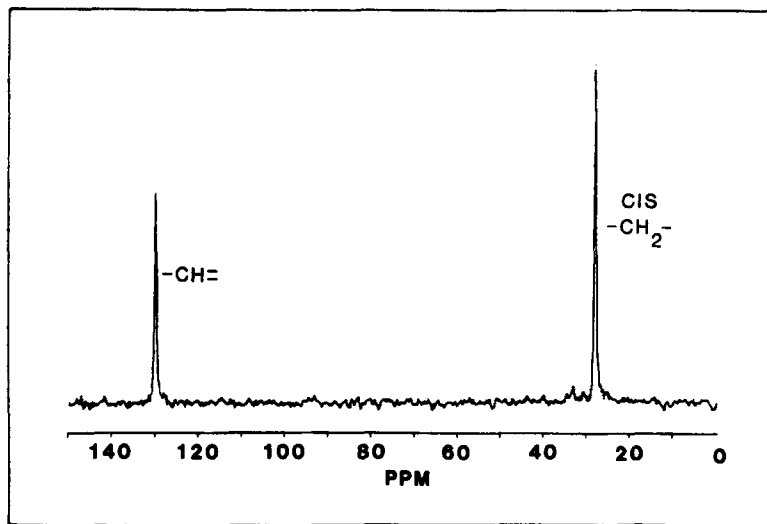


Figure 1. Solid-state  $^{13}\text{C}$  NMR spectrum, with cross-polarization (contact time = 1ms, recycle time = 5s), of 99% cis-1,4-polybutadiene after 0.44 MGy of  $\gamma$ -irradiation at 30°C.

The  $^{13}\text{C}$  NMR spectrum after 3 MGy is shown in Fig. 2. The main features of the spectrum, in comparison with Fig. 1, are (i) a decrease in intensity of the  $-\text{CH}=\text{}$  peak, indicating loss of double bonds, attributable to crosslinking reactions, (ii) development of a broad resonance centred at 45.8 ppm; this is the region where H-crosslinks would be expected to be seen, (iii) a small increase in intensity of the  $\text{trans}-\text{CH}_2-$  peak at 33.6 ppm; (iv) a new broad peak at 30.5 ppm appearing as a shoulder on the  $\text{cis}-\text{CH}_2-$  peak, (v) the total intensity of the  $-\text{CH}_2-$  peak is much larger than the  $-\text{CH}=\text{}$  peak. The chemical shift positions and identification of the main resonances and their line widths after 3 MGy are shown in Table 1.

A similar spectrum has been observed by Patterson and Koenig (13-15) in polybutadienes crosslinked with cumyl peroxide. An additional peak at 14.9 ppm was assigned to methyl groups at new chain ends formed by chain scission. There is no evidence for a similar signal in any of our irradiated samples, indicating that the yield of scission relative to crosslinking is negligible after irradiation.

The aliphatic region was analysed by computer simulation in order to obtain the relative numbers of carbon atoms in each of the structures 2-5 in Table 1. The simulation in Fig. 3 confirms the presence of the broad resonance (4) at 30.5 ppm, which seems likely to arise from a change in the chemical shift of  $-\text{CH}_2-$  groups that are adjacent to crosslinks.

The intensity of the crosslinked carbon resonance (2) at 45.8 ppm gave  $G(\text{crosslink}) = 14.1$ . A G value of 13.9 was obtained for the loss of  $-\text{C}=\text{C}-$  bonds after 3 MGy of  $\gamma$ -irradiation from the decrease in intensity of the  $-\text{CH}=\text{}$  resonance at 130.1 ppm, relative to the total aliphatic resonances in Fig. 2. These values are in close agreement, which would be expected since no other changes occur in the spectrum except for a small increase in the  $\text{trans}$  content.

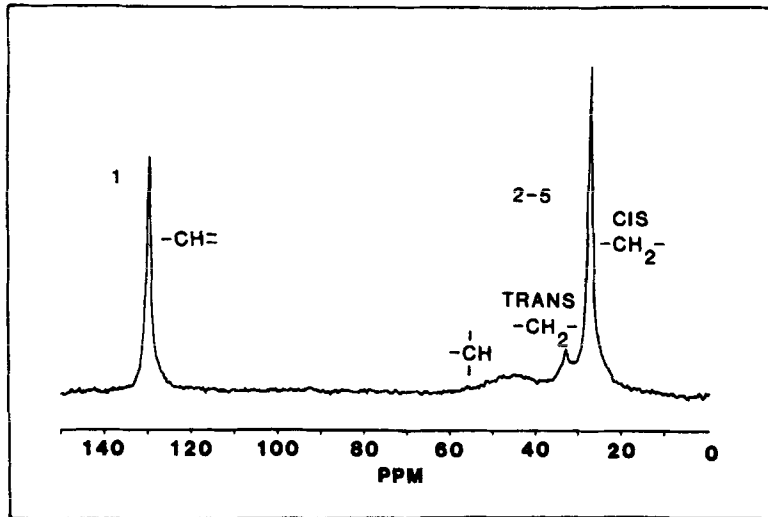


Figure 2. Solid-state  $^{13}\text{C}$  NMR spectrum, with cross-polarization (conditions as in Fig. 1), of 99%  $\text{cis}$ -1,4-polybutadiene after 3 MGy of  $\gamma$ -irradiation at  $30^\circ\text{C}$ .

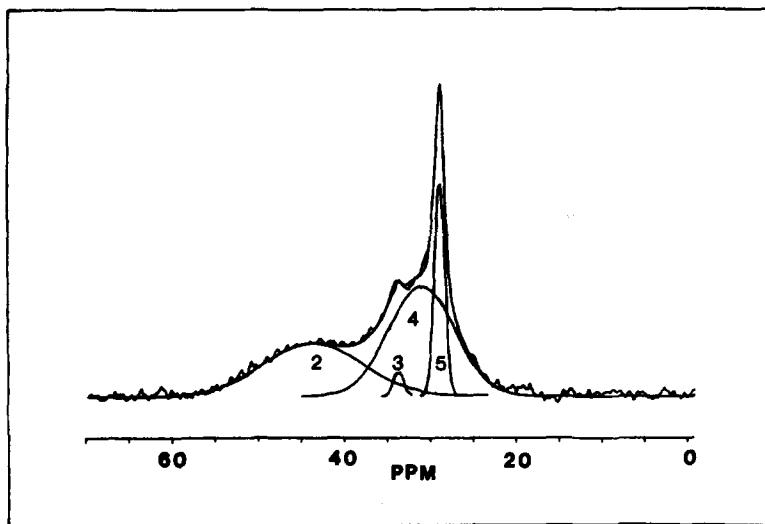


Figure 3. Computer simulation of the aliphatic region of solid-state  $^{13}\text{C}$  NMR spectrum of 99% cis-1,4-polybutadiene after 3 MGy of  $\gamma$ -irradiation at  $30^\circ\text{C}$ . Identification of the peaks is given in Table 1.

Table 1. Assignments to  $^{13}\text{C}$  NMR spectra of irradiated 99% cis-polybutadiene.

No.	Structure	(ppm)	linewidth(Hz)	Comments
1	-CH=	130.1	150	cis/trans structures unresolved
2	CH	45.8	1100	H-crosslinks
3	-CH <sub>2</sub> -	33.6	110	trans methylene
4	-CH <sub>2</sub> -	30.5	750	adjacent to crosslink
5	-CH <sub>2</sub> -	28.2	120	cis methylene

Table 2. Radiation yields from gamma radiolysis of 99% cis-polybutadiene.

	0-0.44 MGy	0-3 MGy
G-(C=C)	23.8	13.9
G(crosslink)	21.5	14.1

A similar analysis was made of the  $^{13}\text{C}$  NMR spectra after 0.44 MGy. The values of  $G-(\text{C}=\text{C})$  and  $G(\text{crosslink})$  were about 23.  $G$  values obtained in the present study are summarised in Table 2. Decreasing  $G-(\text{C}=\text{C})$  values with increasing dose were reported by Kuzminsky et al. (3) in 1958 and this appears to be the first confirmation of this early report. However, we find that  $G(X)$  also decreases with increasing dose, rather than increases.

Fig. 4 shows the solid-state  $^{13}\text{C}$  NMR spectrum after 10 MGy. All the line widths have increased compared to lower doses and the individual components of the spectrum are not easily resolved. The  $-\text{CH}=\text{C}-$  peak is greatly reduced after this large dose, therefore a high proportion of the  $-\text{C}=\text{C}-$  double bonds must be able to undergo reaction. The H-crosslinking peak is very large, indicating that crosslinking is not prevented in the highly crosslinked network.

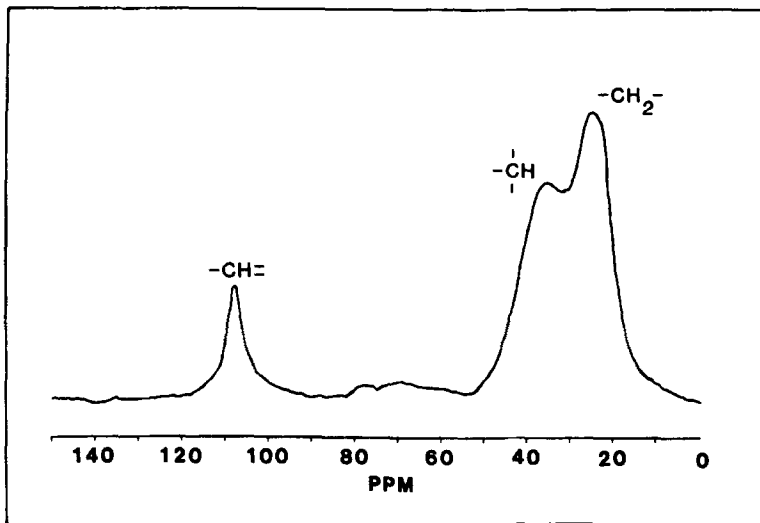
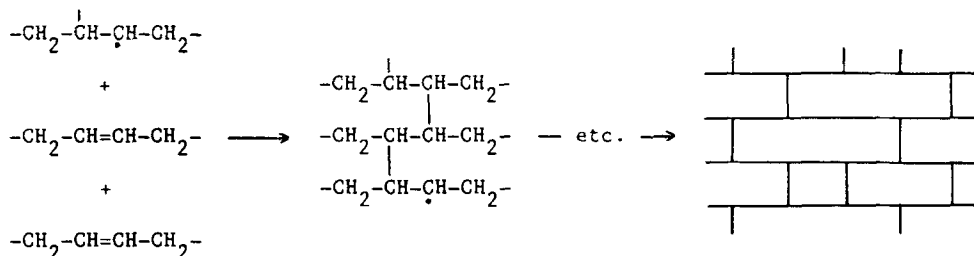


Figure 4. Solid-state  $^{13}\text{C}$  NMR spectrum, with cross-polarization and TOSS (conditions as in Fig. 1), of 99% cis-1,4-polybutadiene after 10 MGy of  $\gamma$ -irradiation at  $30^\circ\text{C}$ .

Parkinson and Sears (11) measured the decrease in double bonds in irradiated polybutadienes by IR spectroscopy. A  $G$  value for loss of cis double bonds of 15 (0-1 MGy) compares well with our values in Table 2. Golub (12) also reported a  $G$  value for loss of double bonds of 15.

The  $G$  value for crosslinking after 0.44 MGy obtained from analysis of the NMR spectra was 21.5, whereas literature  $G(X)$  values obtained from swelling, elastic modulus or sol fraction analysis after similar doses are of the order of 3-6. This apparent discrepancy arises because the usual methods for determining  $G(X)$  are sensitive only to isolated crosslinks, which are assumed to be randomly distributed throughout the polymer. The NMR method on the other hand determines the total crosslink yield, including clustered and intramolecular crosslinks. We suggest that the clustering of the crosslinks arises because of a chain reaction in the bulk polymer involving the double bonds, and giving rise to the following structure.



A similar reaction has been suggested to occur in the crosslinking of polybutadiene initiated by peroxides (19) to account for the large yields of crosslinks compared with the number of radicals formed by the decomposition of the initiator.

### Conclusions

1. H-crosslinks in  $\gamma$ -irradiated polybutadiene can be observed by solid-state  $^{13}\text{C}$  NMR as a broad resonance centred at 45.8 ppm. This definitive assignment supports our previous report (2) identifying crosslinks in the region of 39-47 ppm in  $\gamma$ -irradiated ethylene-propylene copolymer elastomers, based on subtraction of simulated and experimental, solid-state  $^{13}\text{C}$  NMR spectra.
2. The loss of backbone  $\text{-C=C-}$  double bonds can be observed quantitatively from the decrease in intensity of the  $\text{-CH=}$  resonance at 130.1 ppm.
3. G values for (i) loss of main-chain  $\text{-C=C-}$  double bonds from cis-1,4-polybutadiene and (ii) formation of crosslinks can be obtained from quantitative measurements of peak intensities. These two values, obtained independently, are in close agreement.
4.  $G(\text{-C=C-})$  and  $G(\text{crosslink})$  decrease with increasing radiation dose (average of 23 after 0.44 MGy and 14 after 3 MGy).
5. A broad resonance centred at 30.5 ppm develops with irradiation and is attributed to  $\text{-CH}_2\text{-}$  groups adjacent to crosslinks.
6. The G values for formation of H-crosslinks by  $\gamma$ -irradiation of 1,4-polybutadiene in the solid state obtained in this study by solid-state NMR are considerably higher than the values reported in the literature, based on swelling and soluble fraction measurements. This difference indicates that radiation-induced crosslinking occurs by a chain reaction, similar to that proposed for peroxide initiated crosslinking, so that clustering of crosslinks occurs. Main chain scission does not occur during irradiation, in contrast to crosslinking of polybutadiene by peroxide.

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