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**"Radiation induced changes
in the structure of
cis-1,4-polybutadiene"**

S. G. Burnay
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September 1978

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"Radiation induced changes in the structure of cis-1,4-polybutadiene"

S. G. Burnay

Abstract

The processes occurring during electron irradiation of cis-polybutadiene have been investigated. The concentration of unsaturated bonds decays during irradiation with the formation of intermolecular crosslinks, intramolecular cyclic structures and polyene groups. The decay processes can be described by equations which approximate to first order kinetics. Rate constants for the decay processes have been estimated from the experimental data.

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AERE Harwell.

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1. Introduction

The behaviour of elastomeric materials under irradiation is very important to the nuclear industry because of their widespread use in seals in reactors and other equipment. Their use is often limited and always somewhat uncertain, partly because insufficient data on the changes in mechanical and electrical properties which occur during irradiation are not available and partly because there is no framework of understanding against which interpolation and extrapolation of data can confidently be made. The present work seeks to improve that understanding.

It is known that damage in organic materials comes principally through excitation of electrons in the molecules and that direct displacement of atoms by momentum transfer is less important. The consequence of this is that all radiation environments can be simulated by γ -ray or electron irradiation.

Polybutadiene is the simplest of the hydrocarbon elastomers having $(-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-)$ as its repeat unit. On polymerisation, three isomeric forms are possible in the long chain molecule; these are illustrated below.

CIS - 1,4

TRANS - 1,4

VINYL - 1,2

In this work, the radiation induced changes which occur in the structure of a high cis-1,4-polybutadiene have been examined over a wide range of absorbed dose after electron irradiation. The growth of conjugated polyene groups, changes in unsaturation and in cis, trans and vinyl group concentration have been studied by optical absorption techniques, while crosslink densities have been estimated from swelling experiments.

Optical absorption techniques have been used widely by other workers to investigate radiation effects in elastomers. In polybutadiene, radiation induced cis/trans isomerism⁽¹⁻⁴⁾ and loss in unsaturation⁽³⁻⁵⁾ have been studied previously using infrared spectroscopy. However, there appears

to be a considerable variation in the observed G values* dependent on the irradiation conditions. Ultraviolet spectroscopy has been used less widely than infrared but has been used to identify the formation of conjugated diene and triene groups in natural rubber⁽⁶⁾ and polybutadiene⁽⁷⁾.

2. Experimental

The material used in this investigation was a high cis-1,4-polybutadiene designated Buna CB10**, which was purified by a double precipitation in methanol from benzene solution. Any residual solvent was removed by evacuation for at least 5 hours. Sample films for ultraviolet spectroscopy (0.2-0.5 mm thick) were prepared by hot pressing between PTFE lined steel plates and by solution casting. Thinner films for infrared spectroscopy (~ 10 μ m thick) were prepared on KCl plates from dilute solution of the polymer in benzene.

Ultraviolet absorption spectra were obtained on a Unicam SP-700 spectrometer using an unirradiated sample in the reference beam. Infrared spectra were taken on a Hilger and Watts Infracan spectrometer with air as reference.

The irradiations were carried out at room temperature in a Van der Graaf accelerator using 475 keV electrons under a vacuum of $< 10^{-5}$ torr. Absorbed doses were calculated from the beam energy parameters, using the data of Makhlis⁽⁸⁾ on the stopping power of electrons in polybutadiene to correct for sample thickness effects.

Swelling experiments were carried out in benzene at 20°C; sample strips weighing 0.06-0.07 gm were used. The swollen weight of the sample was measured at intervals up to ~ 300 hours total immersion. After removal from the solvent, excess solvent was removed on filter paper and the sample weight recorded over several minutes. The weight at the time of removal from the solvent was then obtained by extrapolation back to zero time.

3. Results

3.1 Ultraviolet absorption

On irradiation a series of overlapping bands appears in the

*G values are defined as the number of molecular groups changed per 100 eV absorbed.

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ultraviolet absorption spectrum. The strongest of these bands first becomes detectable at an absorbed dose of $\sim 10^4$ rads. For doses less than $\sim 10^7$ rads, the dominant absorption occurs in two broad bands in the region 30,000 to 45,000 cm^{-1} , fig. 1, i.e. mainly in the near ultraviolet. At higher doses, further bands appear at the low energy end of the spectrum, extending into the visible region at doses $> 3 \times 10^7$ rads.

Inspection of the spectra shows that the broad bands consist of several overlapping components. Ultraviolet absorption bands are generally Gaussian in shape, hence the spectra can be analysed in terms of a series of overlapping Gaussian bands. This has been carried out using the Dupont Curve Resolver to find a consistent set of Gaussian bands which remained at constant peak position and peak width, and which fitted the spectral variation with dose by changing the peak heights alone. An example of this breakdown of a spectrum into its constituent bands is shown in figure 1.

The dose dependences of these resolved bands were found to fall into five distinct groups, figure 2. From the grouping of the bands and the peak positions, the bands are considered to be due to the formation of polyene groups $-(\text{CH}=\text{CH})_n$, similar to those observed in irradiated polyethylene⁽⁹⁾. The resolved bands and their assignment to particular polyene groups are shown in Table I compared with data on polyethylene, natural rubber and previous work on polybutadiene. For polyene groups⁽⁹⁾,

$$\lambda^2 \propto n \quad \dots(1)$$

where λ is the wavelength of the band in the group. The three bands at 26500, 25400 and 24400 cm^{-1} have not been positively identified but on the basis of equation (1) are most likely due to polyenes with $n = 6, 7$ and 8 respectively.

In calculating the concentrations of polyene groups from the peak absorbances, the molar absorptivity* values of Fallgatter and Dole⁽¹⁰⁾

*The molar absorptivity E is defined by the expression,

$$\text{Absorbance} = \log_{10} \left(\frac{I_0}{I} \right) = Ebc$$

where b is sample thickness in cm, c is concentration of groups in moles.litre⁻¹.

have been used for the diene, triene and tetraene groups. Estimates of the absorptivity E of higher polyenes have been made by extrapolation from the $n = 2, 3, 4$ values. A linear dependence of absorptivity on the number of conjugated bonds has previously been observed for various series of low molecular weight polyenes⁽¹¹⁾. The values of E used are listed in Table II.

At low doses (< 1 Mrad), the concentrations of dienes and trienes (groups I and II) are approximately proportional to dose. The tetraene and pentaene concentrations (groups III and IV) more closely fit a $(\text{dose})^2$ dependence, while the higher polyenes in group V are approximately proportional to $(\text{dose})^3$. These dose dependences imply a one-hit process for diene and triene formation, whereas tetraene and pentaene groups would require a two-hit process, and the higher polyenes a three-hit process.

Initial G values have been estimated from the low dose part of linear plots of the polyene concentration versus dose. These values are summarised in Table III.

3.2 Infrared absorption

The main bands in the infrared absorption spectrum of polybutadiene have previously been categorised⁽¹²⁾. Peaks due to the *cis*-1,4-, *trans*-1,4 and vinyl-1,2- structures are well separated in the $600\text{--}1100\text{ cm}^{-1}$ region, figure 3, enabling quantitative measurements of the *cis*, *trans* and vinyl content to be made. The peak absorbance of the 967 cm^{-1} band due to *trans* groups requires a correction due to overlapping bands. The spectra in this region have been analysed by assuming Lorentzian band shapes and using the Dupont Curve Resolver to isolate the 967 cm^{-1} peak. The absorptivities quoted by Binder⁽¹³⁾ have not been used directly because of the difficulty in measuring the thickness of the films sufficiently accurately. However, the relative absorptivities have been used to calculate the relative amounts of *cis*, *trans* and vinyl; the concentrations have then been calculated on the assumption that the theoretical degree of unsaturation is present in the unirradiated polymer. The data of Parkinson and Sears⁽⁴⁾ on infrared spectra of various polybutadienes indicated that this is a reasonable assumption.

On irradiation there is a marked change in the cis/trans ratio and in the total degree of unsaturation, figure 4. As has been seen in the previous studies⁽¹⁻⁵⁾, there is a rapid decrease in cis concentration and the total degree of unsaturation. Trans concentration increases to a maximum at ~ 3 Mrad, then decreases steadily; vinyl concentration increases slightly to a maximum at ~ 1 Mrad, then decreases. Initial G values have been calculated from the low dose portion of the concentration curves. These values are summarised in Table IV.

3.3 Swelling

Crosslink densities were obtained from equilibrium swelling data using the Flory-Rehner equation modified for doses beyond the gelation dose⁽⁸⁾.

$$[X] = \frac{\phi + \mu\phi^2 + \ln(1-\phi)}{\rho_p v_o (\phi - 2\phi/f)} \quad \dots(2)$$

where ϕ is the volume fraction of polymer; μ is the Huggins constant; ρ_p is the polymer density; v_o is the molar volume of swelling agent; f is the lattice functionality constant. In calculating $[X]$, the crosslinks have been assumed to be tetrafunctional. The value of the Huggins constant, $\mu = 0.314$, is that quoted by Makhlis⁽⁸⁾ for the polybutadiene/benzene system. The crosslink densities obtained from equation (2) are shown in figure 5 as a function of dose.

4. Discussion

The processes which are believed to be occurring during irradiation of polybutadiene can be summarised by the schematic diagram in figure 6. The mechanisms for an increase in trans and vinyl double bonds are cis/trans isomerism and chain scission respectively. All three types of double bond can then be converted to crosslinks, polyene groups or cyclic structures. The relative importance of these possible routes will be determined by the kinetics of the processes as discussed below.

4.1 Kinetics of decay of unsaturation

The decay of cis-1,4 double bonds can be described by first order kinetics, i.e. a semilog plot of concentration versus dose is approximately linear. However, a somewhat better fit to the experimental data is obtained using the following semi-empirical equation,

$$[\text{cis}] = (C_o - C_\infty) \exp(-k_c R) + C_\infty \quad \dots(3)$$

where R is the dose, k_c is the first order rate constant, C_o is the concentration at zero dose and C_∞ is the concentration at infinite dose. This is in contrast to the data of Parkinson and Sears⁽⁴⁾ who observed that the decay of cis-1,4 bonds in a high cis-polybutadiene approximated to zero order decay at low doses. However, the number of data points on which their observations were based were very limited. In polyethylene, changes in unsaturation generally follow first order kinetics⁽¹⁴⁾.

The observed variation of trans-1,4 double bonds with dose arises from the growth of trans bonds due to cis/trans isomerism and their subsequent decay. First order kinetics have previously been found to hold for the decay of trans bonds in a high trans-polybutadiene⁽⁴⁾. Assuming first order kinetics, the decay rate can be described by

$$\frac{d[\text{trans}]}{dR} = k_{ct}[\text{cis}] - k_t[\text{trans}] \quad \dots(4)$$

where k_{ct} and k_t are the rate constants for cis/trans isomerism and trans decay respectively. Integrating, the equation for trans concentration becomes

$$\begin{aligned} [\text{trans}] = & T_o \exp(-k_t R) + \frac{k_{ct} C_\infty}{k_t} [1 - \exp(-k_t R)] \\ & + \frac{k_{ct} (C_o - C_\infty)}{k_t - k_c} [\exp(-k_c R) - \exp(-k_t R)] \quad \dots(5) \end{aligned}$$

where T_o is the initial trans concentration. The best fit of the experimental data to this equation is given by the values indicated in Table V.

The observed increase in vinyl-1,2 double bonds at low doses indicates that there is some formation of vinyl groups occurring during irradiation. This is most likely due to chain scission producing terminal vinyl groups. Vinyl decay in a high vinyl-polybutadiene has previously been observed to follow first order kinetics⁽⁴⁾. On this basis, the decay rate can be described by

$$\frac{d[\text{vinyl}]}{dR} = k_{sc} [\text{chain}] - k_v [\text{vinyl}] \quad \dots(6)$$

where k_{sc} and k_v are the first order rate constants for chain scission and vinyl decay respectively. Although chain scission will tend to increase the number of chains, crosslinking will decrease the number. Since crosslinking is expected to be the dominant process in polybutadiene, the overall chain concentration will be expected to decrease as irradiation proceeds. If one assumes an equation for the chain concentration of the form,

$$[\text{chain}] = A_0 \exp(-k_{sc} R)$$

Then the vinyl concentration is given by,

$$[\text{vinyl}] = V_0 \exp(-k_v R) + \frac{k_{sc} A_0}{k_v - k_{sc}} [\exp(-k_{sc} R) - \exp(-k_v R)] \quad \dots(7)$$

where V_0 is the initial concentration of vinyl double bonds. The values of the constants giving the best fit of the data to equation (7) are also given in Table V.

The overall loss of unsaturation will be given by the following expression,

$$[\text{d.b. loss}] = (C_0 + T_0 + V_0) - ([\text{cis}] + [\text{trans}] + [\text{vinyl}]) \quad \dots(8)$$

Figure 4 shows the calculated variation of cis, trans and vinyl concentration and the total loss of unsaturation as given by equations (3), (5), (7) and (8) respectively. The calculated curves fit the experimental data well.

The very rapid loss in unsaturation indicated by the initial G values in Table IV and the rate constants in Table V is similar to that observed by Kuzminsky et al⁽⁵⁾ for polybutadiene γ -irradiated under vacuum without anti-oxidants. Other work on polybutadiene⁽¹⁻⁴⁾ yield considerably lower G values and rate constants; however Kuzminsky's observations of a massive decrease in G values (~ 150 times)

on irradiation in air indicate that G values are strongly dependent on the sample environment making comparison with other authors' work difficult.

4.2 Kinetics of crosslink formation

Since the decay of unsaturation approximates to first order kinetics, and assuming that part of this loss is due to the formation of crosslinks between molecules, the rate of crosslink formation will be given by

$$\frac{d[X]}{dR} = k_{cx}[cis] + k_{tx}[trans] + k_{vx}[vinyl] \quad \dots(9)$$

where k_{cx} , k_{tx} and k_{vx} are the rate constants for the formation of crosslinks from cis, trans and vinyl double bonds respectively. Using the equations for double bond concentrations and integrating, the crosslink density can be described by,

$$\begin{aligned} [X] = & A_1[1 - \exp(-k_c R)] + A_2[1 - \exp(-k_t R)] \\ & + A_3[1 - \exp(-k_v R)] + A_4[1 - \exp(-k_{sc} R)] \\ & + A_5 R. \end{aligned} \quad \dots(10)$$

where A_1 , A_2 , A_3 , A_4 and A_5 are constants related to the rate constants and the initial concentrations of cis, trans and vinyl groups.* The values of the rate constants k_{cx} , k_{tx} and k_{vx} giving the best fit to the experimental data are shown in Table VI; the curve described by equation (10) is also shown in figure 5. As expected, crosslink formation is dominated by the vinyl groups, approximately 50% of vinyl decay being accounted for. In comparison, crosslinking accounts for ~ 23% of trans decay and only ~ 1.5% of cis decay, whereas cis/trans isomerism accounts for ~ 10%.

4.3 Kinetics of polyene formation

Part of the decay of unsaturation observed in the infrared spectrum can also be considered to arise from the formation of polyene groups. It has been assumed that diene and triene groups are formed by the production of double bonds in the vicinity of existing cis, trans and vinyl double bonds to form conjugated

*See Appendix.

polyene groups. It has also been assumed that the inclusion of an existing double bond into a conjugated group will effectively remove that bond from the measured concentration of isolated double bonds.

The rate equations for diene and triene growth will have the same form as the rate equation for crosslink formation; therefore, diene and triene concentrations will be described by equations similar to equation (10). However, it is found that the values of the rate constants obtained from the curve fitting are such that, to a good approximation, both diene and triene concentrations can be described by an equation of the form,

$$[\text{diene}] = B_1[1 - \exp(-k_c R)] + B_2 R. \quad \dots(11)$$

Tetraene and pentaene groups are assumed to form from dienes and trienes respectively; consequently the observed concentrations of dienes and trienes will be less than the total concentration formed. In calculating the values of the rate constants to fit the experimental data, the sum of diene and tetraene concentration and triene and pentaene concentration have been used to allow for this. The best values of the rate constants are given in Table VII ; the curves in figure 7(a) illustrate the fit to the experimental data. The growth of dienes and trienes is dominated by the cis component; the values of the rate constants for the trans and vinyl components are only approximate since quite large changes in the k values hardly affect the fit to the data.

The rate equation for tetraene formation will have the form,

$$\frac{d[\text{tetraene}]}{dR} = k_4 [\text{diene}]$$

where k_4 is the rate constant for tetraene formation from diene groups. This will give an expression for tetraene formation of the form

$$[\text{tetraene}] = C_1[1 - \exp(-k_c R)] + C_2 R + C_3 R^2. \quad \dots(12)$$

Pentaene growth will be described by a similar equation. The best values of the rate constants for tetraene and pentaene formation to fit the experimental data are given in Table VII; the best fit curves are shown in Fig. 7(b).

As can be seen from the values of the rate constants for polyene formation relative to those for loss in unsaturation, polyene formation accounts for only a very small proportion of the overall change in double bond concentration.

The formation of some polyene groups in the polybutadiene chain can be explained fairly simply. Abstraction of a hydrogen molecule from the $-\text{CH}_2-\text{CH}_2-$ group between two double bonds will form a triene group.

The ease with which this process can occur in polybutadiene is illustrated by the high G value for triene formation relative to that for the other polyenes. A similar hydrogen abstraction alongside a triene group will yield a pentaene group. The formation of diene and tetraene groups is rather more difficult to explain. A diene group could be formed by hydrogen abstraction combined with migration of a double bond,

but this is unlikely in view of the observations of Golub⁽³⁾ on deuterated polybutadiene which indicates that double bond migration is infrequent. Further information is required on the intermediate stages leading to polyene formation before specific mechanisms can be put forward.

4.4 Cyclisation

On examination of the rate constants for crosslinking and polyene formation, it is observed that there is a considerable discrepancy between the sum of the k values for the observed decay processes and the overall decay rate, as indicated in Table VIII. This discrepancy is generally considered to be due to the formation of cyclic structures^(1,2); such structures have been observed in the infrared spectrum of irradiated polyethylene⁽¹⁴⁾. However, as these groups absorb in the $900-1050 \text{ cm}^{-1}$ region, it would appear that their formation in polybutadiene is obscured by the rapid changes in the olefin bands which also absorb in the same region of the spectrum.

An estimate of the number of double bonds which are lost by cyclisation processes can be made as follows:

$$\begin{aligned} \text{loss from cyclisation} &= \text{overall loss} \\ &- \text{loss due to crosslinking and polyene formation.} \end{aligned}$$

This can be compared with the concentration of cyclic structures estimated from the kinetics, which will have the same form as equation (10). The rate constants for cyclisation from cis, trans and vinyl groups are designated k_{cc} , k_{tc} and k_{vc} respectively, where

$$k_{cc} = k_c - (k_{cx} + k_{2c} + k_{3c} + k_{ct})$$

$$k_{tc} = k_t - (k_{tx} + k_{2t} + k_{3t})$$

$$k_{vc} = k_v - (k_{vx} + k_{2v} + k_{3v})$$

The two estimates of cyclisation from unsaturation losses and from the kinetics are compared in fig. 8. Both give the same order of magnitude of concentration and similar dose dependences.

From the values of the rate constants, it can be seen that cyclisation processes are by far the most important of the decay processes, accounting for ~ 88% of cis decay, ~ 77% of trans decay and ~ 50% of vinyl decay.

5. Conclusions

The reactions which occur on irradiation of a high cis-1,4-polybutadiene can be summarised by figure 6. The growth of crosslinking and polyene groups and the loss of unsaturation can be described by first order kinetics; rate constants for each reaction have been estimated. The kinetics of growth of cyclic structures has been inferred from the difference between the total loss of unsaturation and that part of the loss due to formation of crosslinks and polyenes. The magnitudes of the rate constants indicate that cyclisation and crosslinking are the dominant processes occurring during irradiation. Relative to crosslinking and cyclisation, polyene formation is a minor process. For this high cis-polybutadiene, polyene formation arises almost exclusively from cis double bonds; the very small initial concentrations of trans and vinyl groups preclude the measurement of rate

constants for polyene formation from these groups.

The mechanisms suggested for polyene formation indicate that one molecule of hydrogen should be ejected per polyene group formed. Cross-linking and cyclisation however are not likely to produce hydrogen provided double bonds are consumed in the processes. Gas evolution should therefore closely follow polyene formation. G values for hydrogen evolution quoted in the literature (3,4) indicate a rate of gas evolution higher than can be explained by polyene formation alone. However, since the rate at which structural changes occur appears to be strongly dependent on the sample environment, measurements of gas evolution for the samples studied in this work would be instructive.

So far, cyclic structures have not been directly observed in polybutadiene since the infrared absorption bands due to such structures are obscured by the bands due to trans and vinyl double bonds, which lie at similar wavelengths. Hydrogenation of a sample after irradiation would remove or greatly reduce the trans and vinyl bonds enabling the weaker cyclic bands to become visible.

It is not yet known whether the structural changes occurring in polybutadiene are via ionic or free-radical reactions. There is some indication that free radicals are the dominant intermediate state in cyclisation⁽³⁾ and polyene formation⁽⁹⁾. Free radicals could be studied at low temperatures using ESR and ultraviolet spectroscopy.

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TABLE I

Assignment of ultraviolet absorption bands
to polyene groups $-(CH=CH)_n-$

Group	Peak position (cm^{-1})	Polyene group	Previously measured peak positions in		
			polyethylene (9)	natural rubber (6)	polybutadiene (7)
I	44800 42900* 40900	Diene (n=2)	43700 42400 40800	- 40800	40000 to 42500
II	38600 37600 36000 35700* 34700 34100	Triene (n=3)	37900 36400 34700	34500	34500 to 38500
III	33400 32000* 30800	Tetraene (n=4)	32500	-	-
IV	30400 29200* 27900	Pentaene (n=5)	29400	-	-
V	26500 25400 24400	Higher polyenes (see text)	-	-	-

* Dominant band

TABLE II

Absorptivity E of polyene bands

n	E (litre.mol ⁻¹ .cm ⁻¹)
2	25000 (a)
3	41800 (a)
4	58900 (a)
5	76000 (b)

(a) Ref. 10

(b) Estimated value

TABLE III

Initial G values for
polyene formation

n	G
2	0.37
3	0.95
4	0.028
5	0.0033
6	0.0018*
7	0.0013*
8	0.0004*
Total polyene	1.60

*Rough estimates

TABLE IV

Initial G values for changes in cis, trans
and vinyl concentrations, and total unsaturation

G(cis)	G(trans)	G(vinyl)	G(unsat.)
-7530	+830	+120	-6300

TABLE V

Best values of the constants describing
the decay of cis, trans and vinyl double bonds

	cis	trans	vinyl
Rate constants (Mrad ⁻¹)	$k_c = 0.426$	$k_t = 0.109$ $k_{ct} = 4.4 \times 10^{-2}$	$k_v = 0.128$ $k_{sc} = 4.08$
Concentration constants (mole.gm ⁻¹)	$C_o = 1.7 \times 10^{-2}$ $C_c = 7.3 \times 10^{-4}$	$T_o = 3.6 \times 10^{-4}$	$V_o = 1.6 \times 10^{-4}$ $A_o = 7.3 \times 10^{-5}$

TABLE VI

Rate constants for crosslink formations from
cis, trans and vinyl groups

k_{cx}	k_{tx}	k_{vx}
6.0×10^{-3}	2.55×10^{-2}	$6.22 \times 10^{-2} \text{ (Mrad}^{-1}\text{)}$
$\pm 0.3 \times 10^{-3}$	$\pm 0.3 \times 10^{-2}$	$\pm 0.5 \times 10^{-2}$

TABLE VII

Rate constants for polyene formation

Diene	Triene	Tetraene	Pentaene
$k_{2c} = 2.65 \times 10^{-5}$	$k_{3c} = 5.0 \times 10^{-5}$		
$k_{2t} = <5 \times 10^{-7}$	$k_{3t} = <5 \times 10^{-7}$	$k_4 = 1.8 \times 10^{-2}$	$k_5 = 4.3 \times 10^{-3}$
$k_{2v} = <5 \times 10^{-7}$	$k_{3v} = <5 \times 10^{-7}$		

TABLE VIII

Estimate of the rate constants
for cyclisation. (Mrad⁻¹)

	Sum of k values for decay processes	Overall k values for decay	Difference (= k values for cyclisation)
cis	0.050	0.426	0.376
trans	0.025	0.109	0.084
vinyl	0.062	0.128	0.066

Fig. 1

Ultraviolet absorption spectrum of polybutadiene film irradiated to 0.5 Mrad. (-----) Gaussian bands making up the spectrum.

Fig. 2

Variation of peak absorbance with dose for the Gaussian bands which make up the ultraviolet absorption spectrum. (Assignment of these groups of bands to polyene structures is shown in Table I).

Fig. 3

Infrared absorption spectrum of polybutadiene. (——) unirradiated; (----) irradiated to 1.2 Mrad.

Fig. 4

Concentration of double bonds in irradiated polybutadiene.
(——) cis-1,4 concentration from equation (3).
(----) trans-1,4 concentration from equation (5).
(....) vinyl-1,2 concentration from equation (7).
(-.-.-) total unsaturation from equation (8).

Fig. 5

Crosslink density in irradiated polybutadiene, from swelling experiments. (——) computed curve from equation (10).

Fig. 6

Summary of processes occurring in irradiated polybutadiene.

Fig. 7

Variation of polyene concentration with dose.
(a) (——) triene growth from equation (11).
(----) diene growth from equation (11).
(b) (——) tetraene growth from equation (12).
(----) pentaene growth from equation (12).

Fig. 8

Estimate of the growth of cyclic structures:

- (a) from k values,
- (b) from unsaturation losses.

Appendix

Rate equations for crosslinking, polyene formation.

$$\begin{aligned}
 [\text{cis}] &= (C_o - C_\infty) \exp(-k_c R) + C_\infty \\
 [\text{trans}] &= T_o \exp(-k_t R) + \frac{k_{ct} C_\infty}{k_t} [1 - \exp(-k_t R)] \\
 &\quad + \frac{k_{ct} (C_o - C_\infty)}{k_t - k_c} [\exp(-k_c R) - \exp(-k_t R)] \\
 [\text{vinyl}] &= V_o \exp(-k_v R) + \frac{k_{sc}^A o}{k_v - k_{sc}} [\exp(-k_{sc} R) - \exp(-k_v R)] \\
 [X] &= \left[\frac{k_{cx} (C_o - C_\infty)}{k_c} + \frac{k_{tx} k_{ct} (C_o - C_\infty)}{k_c (k_t - k_c)} \right] [1 - \exp(-k_c R)] \\
 &\quad + \frac{k_{tx}}{k_t} \left[T_o - \frac{k_{ct} C_\infty}{k_t} - \frac{k_{ct} (C_o - C_\infty)}{k_t - k_c} \right] [1 - \exp(-k_t R)] \\
 &\quad + \frac{k_{vx}}{k_v} \left[V_o - \frac{k_{sc}^A o}{k_v - k_{sc}} \right] [1 - \exp(-k_v R)] \\
 &\quad + \frac{k_{vx}^A o}{k_v - k_{sc}} [1 - \exp(-k_{sc} R)] + \left[k_{cx} + \frac{k_{tx} k_{ct}}{k_t} \right] C_\infty R
 \end{aligned}$$

For [diene], replace k_{cx} , k_{tx} , k_{vx} by k_{2c} , k_{2t} , k_{2v} .

For [triene], replace k_{cx} , k_{tx} , k_{vx} by k_{3c} , k_{3t} , k_{3v} .

$$\begin{aligned}
 [\text{tetraene}] &= k_4 \left\{ \left[\frac{k_{2c} (C_o - C_\infty)}{k_c} + \frac{k_{2t} T_o}{k_t} + \frac{k_{2v} V_o}{k_v} - \frac{k_{2t} k_{ct} C_\infty}{k_t} \right. \right. \\
 &\quad \left. \left. + \frac{k_{2t} k_{ct} (C_o - C_\infty)}{k_c k_t} + \frac{k_{2v}^A o}{k_v} \right] \cdot R + \frac{C_\infty}{2} \left(k_{2c} + \frac{k_{2t} k_{ct}}{k_t} \right) R^2 \right. \\
 &\quad \left. + \frac{(C_o - C_\infty)}{k_c^2} \left[k_{2c} + \frac{k_{2t} k_{ct}}{k_t - k_c} \right] [1 - \exp(-k_c R)] \right. \\
 &\quad \left. + \frac{k_{2t}}{k_t^2} \left[T_o - \frac{k_{ct} C_\infty}{k_t} - \frac{k_{ct} (C_o - C_\infty)}{k_t - k_c} \right] [1 - \exp(-k_t R)] \right\}
 \end{aligned}$$

$$\begin{aligned}
& + \frac{k_{2v}}{k_v} \left[v_o - \frac{k_{sc} A_o}{k_v - k_{sc}} \right] [1 - \exp(-k_v R)] \\
& + \frac{k_{2v} A_o}{k_{sc} (k_v - k_{sc})} [1 - \exp(-k_{sc} R)] \}
\end{aligned}$$

For [pentaene], replace k_4 by k_5

replace k_{2c} , k_{2t} , k_{2v} by k_{3c} , k_{3t} , k_{3v} .

AERE - R 9231 Fig. 1

AERE - R 9231 Fig. 2

AERE - R 9231 Fig. 3

AERE - R 9231 Fig. 4

AERE - R 9231 Fig. 5

AERE - R 9231 Fig. 6

AERE - R 9231 Fig. 7a

AERE - R 9231 Fig. 7b

AERE - R 9231 Fig. 8