5.9; mol wt, 474.6. Found: C, 58.0; H, 9.1; N, 5.4; mol wt (bp in benzene), 470.

The infrared spectrum showed a characteristic ester band at 1735 cm^{-1} and additional bands at 1190, 1160, 1100, 1010, and 850 cm^{-1} all absent in the staring material: NMR ($CDCl_3$) δ 1.29 (s, CH_2), 2.32 (t, $J = 6$ Hz, α-CH_2), 3.69 (s, OCH_3), 4.50 (s, $HCNO_2$), and no COOH absorption at δ 10–11.

Acknowledgments. In addition to the acknowledgments in the footnotes, several others must be made. Thus, I thank Eleanor G. Applegate for her expert technical assistance. Dr. Raymond C. Ferguson of this laboratory contributed exploratory experiments which gave impetus to this work. Discussions with Dr. William H. Sharkey were a valuable stimulus. Special thanks are due Mr. Charles R. Ginnard for the GPC analyses, and I also thank Naomi E. Schlichter and Ellen Wallace for determining the infrared spectra. Dr. J. Lazar did the mass spectrum determinations, Dr. F. E. Weigert and Mr. Fred Davidson assisted with the ^{13}C NMR, and Mrs. Flora Youngken did the ebullioscopic molecular weight determinations.

References and Notes

(1) Contribution No. 2473; please include in reprint requests.

(2) For leading references see G. N. Patel and A. Keller, *J. Polym. Sci., Polym. Phys. Ed.*, **13,** 2275 (1975).

(3) D. J. Priest, *J. Polym. Sci., Part A-2,* **9,** 1777 (1971).

(4) A. Keller, E. Martuscelli, D. J. Priest, and Y. Udagawa, *J. Polym. Sci., Part A-2,* **9,** 1807 (1971).

(5) A. Keller and S. Sawada, *Makromol. Chem.*, **74,** 190 (1964).

(6) D. J. Blundell, A. Keller, and T. M. Connor, *J. Polym. Sci., Part A-2,* **5,** 991 (1967).

(7) R. P. Palmer and A. J. Cobbold, *Makromol. Chem.*, **74,** 174 (1964).

(8) A. Keller and Y. Udagawa, *J. Polym. Sci., Part A-2,* **9,** 1793 (1971).

(9) (a) A. Keller and Y. Udagawa, *J. Polym. Sci., Part A-2,* **8,** 19 (1970); (b) T. Williams, Y. Udagawa, A. Keller, and I. M. Ward, *ibid.*, **8,** 35 (1970).

(10) D. G. H. Ballard and J. V. Dawkins, *Eur. Polym. J.*, **9,** 211 (1973).

(11) These preliminary experiments were done by Dr. R. C. Ferguson of this laboratory.

(12) The polymers were commercial resins in the form of extruded pellets about 4 mm × 7 mm in size. They were obtained from the Plastic Products and Resins Department, E. I. du Pont de Nemours and Co., Wilmington, Delaware. Alathon polyethylene resin is a registered trademark of the Du Pont Co. Alathon 7040 polyethylene resin has $\overline{M}_w = 89\,000$, $\overline{M}_n = 25\,000$ (by GPC).

(13) Alathon 7050 polyethylene resin has $\overline{M}_w = 68\,000$, $\overline{M}_n = 11\,000$.

(14) R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry", Wiley, New York, N.Y., 1953, pp 418–419.

(15) Pellets were recrystallized from xylene (50 mL/g) without any special care to control cooling rate or optimize crystal growth. Boiling solutions were merely allowed to cool spontaneously to room termperature.

(16) Corrected for instrument broadening.

(17) Marlex 6009.

(18) Rigidex 2.

(19) Private communication from Mr. C. R. Ginnard of this laboratory.

(20) For our estimations, we used the value 1.00 for the ratio of the extinction coefficient of one COOH group to one NO_2 group. For known mixtures of decanoic acid and 1-nitrododecane, the ratio varied between 0.82 and 1.22 depending on whether the samples were run neat or in solution in dichloromethane or mineral oil. The average was 1.03 which for practical purposes we took to be unity. There is further uncertainty in this, however, because although the ratio was linear with different proportions run neat, they were significantly nonlinear in solution. Keller and Udagawa (ref 8) used the ratio 0.71.

(21) Nitrogen elemental analyses are not useful in determining the degree of nitration because the low levels dealt with are within the error limit of combustion analysis.

(22) Percent nitration can be calculated from the relationship 200/(COOH/NO_2 ratio) assuming only that there are two carboxyl groups per molecule.

(23) The solvent was acetone and the titrant was tetra(*n*-butyl)ammonium hydroxide. I thank Mr. Robert J. Berndt for the measurements.

(24) P. A. D. De Maine, M. M. De Maine, A. A. Briggs, and G. E. McAlonie, *J. Mol. Spectrosc.*, **4,** 398 (1960).

(25) H. Feuer and A. T. Nielsen, *J. Am. Chem. Soc.*, **84,** 688 (1962). After 2 weeks in refluxing hydrochloric acid, 2-nitrooctane was only 65% converted to 2-octanone.

(26) In the procedure of ref 10, 0.3 g of nitro acid was heated with concentrated sulfuric acid in a sealed tube at 70 °C for 20 h. In ref 9a, the treatment was with 0.2 g at 60 °C for 2 days.

(27) Keller and Udagawa (ref 9a) used activated charcoal in hot xylene solutions, but this failed in our hands. Ballard and Dawkins (ref 10) used hot concentrated nitric acid but in at least one such trial we had evidence for the reintroduction of nitro groups.

(28) "Organic Reactions", Vol. I, Wiley, New York, N.Y., 1942, p 155.

(29) M. G. Grundon, H. B. Henbest, and M. D. Scott, *J. Chem. Soc.*, 1855 (1963).

(30) Fisher Scientific Co., Fair Lawn, N.J.

(31) J. T. Baker Chemical Co., Phillipsburg, N.J.

An ESR Study of Oxidation in Uniaxially Deformed Polybutadiene and Polyisoprene

W. T. Mead, Roger S. Porter, and P. E. Reed*

Department of Materials, Queen Mary College, University of London,
London E1, England.

Received June 20, 1977

ABSTRACT: The possible reactions of polybutadiene and other diene rubbers, with oxygen during initial processing, low-temperature mechanical degradation, and subsequent handling, are reviewed. Radicals formed following tensile testing of polybutadiene and polyisoprene at 83 K in predominantly nitrogen atmospheres, but containing different amounts of oxygen, are examined using electron spin resonance (ESR) techniques. It is concluded that two or more radical species result from mechanical deformation at low temperature when oxygen is present. Radicals identifed are a peroxy radical and most probably an allyl radical arising from main chain rupture. Peroxy radicals are shown to arise mainly from combination of radical species with oxygen in the test environment, although a small proportion is attributed to oxygen incorporated into the rubber network during processing. The relative stability with increasing temperature of the peroxy to other radical species present is studied quantitatively.

I. Introduction

The effect of atmospheric oxygen on unsaturated rubbers at ambient temperature and above is pronounced and has been widely studied.[1,2] It is known that chain rupture mechanically induced by mastication produces radicals which are stabilized by reaction with oxygen.[3] For natural rubber this leads to a reduction in molecular weight into the processable range. More recently, the application of electron spin resonance (ESR) technique to monitor radical formation during mechanical deformation of diene rubbers in the glassy state, close to the liquefaction temperature of nitrogen, has also revealed oxygen-containing radicals.[4-8] The reactivity of oxygen with polymer radicals formed by mechanical degradation has been recently reviewed by Sohma and Sakaguchi,[9,10] while DeVries[11] has reviewed radical formation in rubbers. The presence of such oxygen-containing radicals is

0024-9297/78/2211-0056$01.00/0

both a nuisance and a source of interest to the study of the deformation of rubbers in the glassy state. It is a nuisance in that it confuses the spectrum of the expected primary allyl radical resulting from main chain scission, but it is interesting to an understanding of the role of oxidation in the mechanical deformation of glassy polymers.

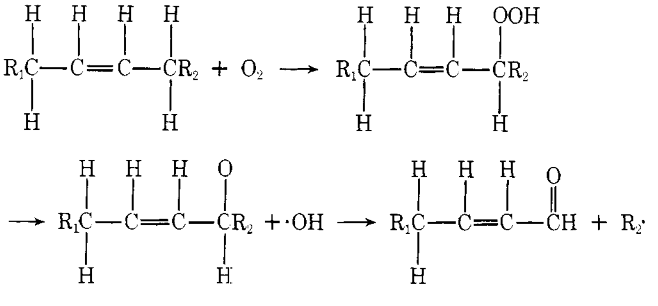
It has been found that ESR is a sensitive method for monitoring the oxidation of diene rubbers both during ageing and during mechanical deformation below the glass transition temperature when the radical species are stable. Concentrations of oxygenated radical species as low as $\sim 10^{-8}$ g mol (10^{16} spin/g) may be detected using ESR, and this compares very favorably with other techniques such as infrared,[12] weight gain, oxygen take-up methods, and cross-link density changes resulting from oxidation.[13]

ESR spectra observed after mechanically deforming polybutadiene,[5] natural rubber,[4] and polychloroprene[6] at low temperatures are normally composed from at least two radical species, that due to the allyl radical following main chain rupture and that due to oxidation reactions which appears as a peroxy radical. The oxygenated radicals can derive from several sources, and it is the purpose of this present paper to examine some of these sources and the stability of the oxygenated radicals formed.

There are three stages at which oxygen may be introduced into the rubber which subsequently gives rise to the oxygenated radicals. First the rubbers are compounded on an open mill and pressed into sheets. During these operations oxygen may be either conjugated into the rubber network as oxygen bridges or may be introduced simply in the form of dissolved air for later reaction. Oxygenated radicals may alternatively be formed during mechanical testing at the low temperature by reaction of the primary radicals formed with dissolved oxygen or oxygen in the test environment. Finally oxygenated radicals may be formed, or destroyed, following mechanical testing as the material is returned to ambient temperature. All these possibilities have been examined and ESR has been used to monitor the quantity, nature and stability of the oxygenated and other radicals throughout the rubbers history of manufacture, mechanical testing at low temperature, and subsequent warming.

II. Oxygenated Radicals in Rubbers

Many different reactions have been suggested to occur between oxygen and rubbers during processing. Some of the possible oxidative structural units resulting from these reactions are shown in Table I, although the reactions are not completely understood. A commonly proposed path involves the formation of hydroperoxides (ROOH) and their subsequent decomposition to give chain rupture, aldehydes, and ketones.[2,3,20–22] For 1,4-polybutadiene this path could proceed as follows.



$$R_1\overset{H}{\underset{H}{C}}-\overset{H}{C}=\overset{H}{C}-\overset{H}{\underset{H}{C}}R_2 + O_2 \longrightarrow R_1\overset{H}{\underset{H}{C}}-\overset{H}{C}=\overset{H}{C}-\overset{OOH}{\underset{H}{C}}R_2$$

$$\longrightarrow R_1\overset{H}{\underset{H}{C}}-\overset{H}{C}=\overset{H}{C}-\overset{O}{\underset{H}{C}}R_2 + \cdot OH \longrightarrow R_1\overset{H}{\underset{H}{C}}-\overset{H}{C}=\overset{H}{C}-\overset{O}{\overset{\|}{C}}H + R_2\cdot$$

A similar reaction at 1,2-vinyl units can lead to the oxidative structural unit listed as B in Table I. Hydroperoxides are readily reacted and brief heating at 403 K (130 °C) leads to their complete destruction.[12,22]

Competitive oxidation reactions during initial processing are those that result in cross-links rather than chain rupture and reduction in molecular weight. It has been stated[12] that oxidative cross-linking reactions depend on hydroperoxide decomposition and can result in peroxy, ether, or a hydrocarbon cross-link. An ether cross-link, suggested for zinc oxide cross-linked polychloroprene,[19] is shown as type F in Table I. Furthermore, peroxide groups may exist as inter- or intrachain bonding. Two possible types of intrachain peroxy bonding are shown as types D and E in Table I.

The network of the cross-linked rubbers is strained during tensile testing at low temperatures and molecular rupture occurs progressively as the strain is increased, giving rise to a monotonically increasing number of radicals.[4,5] It is reasonable to assume that molecular rupture occurs at the weakest link of the most highly strained network chain; the vulcanization technique used provides a cross-linked network with a wide range of network chain lengths. Possible radicals formed as a result of chain scission are given in Table I, while Table II lists the related bond energies. From a consideration of bond energy alone, it can be seen that rupture at a peroxy group, contained either in the backbone chain or as a cross-link, is the most favored rupture site. Rupture of the main chain between the α-methylene groups is also relatively easily accomplished. Rupture at the hydroperoxide group ($ROOH \rightarrow RO\cdot + \cdot OH$), although thermodynamically favorable, is unlikely to occur by mechanical deformation alone since it is a pendant group. Since it is unlikely that all network chains will neither necessarily contain a peroxide group nor be equally strained, it is considered that mechanical deformation is most likely to lead to the simultaneous formation primarily of $R_1O\cdot$ and $R_2CH\cdot$ radicals following homolytic cleavage of interchain peroxide links and carbon–carbon bonds β to the double bond. Kraus and Rollman[23] found an activation energy of 40 kcal mol^{-1} for mechanical reaction during the mastication of polybutadiene in the absence of air. This value, being significantly lower than the 60 kcal mol^{-1} for allyl radical formation and close to that for peroxide link rupture, suggests the predominant molecular rupture mode to be that of peroxy bond cleavage.

Whether the above alkoxy ($R_1O\cdot$) and allyl ($R_2CH_2\cdot$) radicals can be observed following tensile testing using ESR depends on their stability both during testing and subsequent warming. Some authors[26–28] suggest that the alkoxy radical is unstable and readily converts to the more stable peroxy radical ($R\dot{O}_2$) by the reaction.

$$R\dot{O} + ROOH \rightleftharpoons R\dot{O}_2 + ROH$$

Any allyl radicals of the form $R_2CH_2\cdot$ could also combine with dissolved oxygen, again leading to the formation of a peroxy radical.[29–33] Whether the latter reaction proceeds during low-temperature tensile testing (~90 K) is questionable. Less stable alkyl radicals are known to react with oxygen at 150–200 K. The more stable allyl radicals may thus only react with oxygen at higher temperatures nearer to the glass transition temperatures (T_g) of the rubbers. The activation energy of formation of peroxy radicals as a secondary reaction in glassy thermoplastics has been reported as about 6 kcal mol^{-1}.[34] It has been suggested[35] that processes at liquid nitrogen temperature requiring over 6 kcal mol^{-1} will not occur, which would suggest that peroxy radical formation during tensile testing at low temperature is only marginally possible. Ohnishi et al.[29,30] report that allyl radicals formed in polyethylene react with oxygen to form peroxy radicals at temperatures above 160 K; they also report that the allyl radical can be recovered by pumping on the specimens at 77 K. However, this appears to be the only reported reversible peroxide formation for an allyl radical. In careful studies on *cis*-polyisoprene and *cis*-polybutadiene, Carstensen observed a 25% maximum peroxy conversion from allyl radicals even by warming to T_g.[31,32]

Table I
Oxidative Structural Units and Possible Scission Products

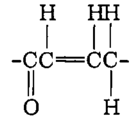
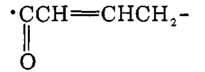
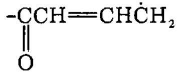
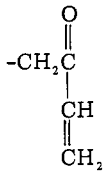
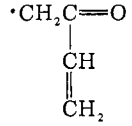
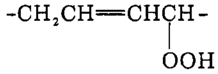
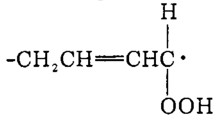
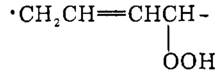
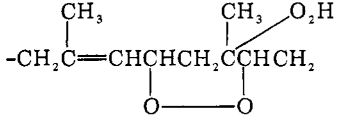
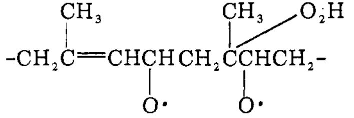
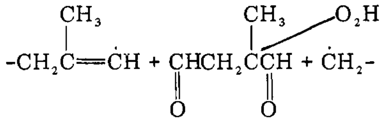
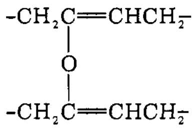
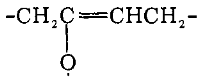
Type	Oxidative structural unit	Possible scission product	Ref
A	 $-\underset{O}{\overset{H}{C}}\overset{H}{C}=\overset{H}{C}\underset{H}{C}-$	 $\cdot\underset{O}{C}CH=CHCH_2-$ or  $-\underset{O}{C}CH=CH\dot{C}H_2$	14
B	 $-CH_2C(=O)CH=CH_2$	 $\cdot CH_2C(=O)CH=CH_2$	15, 16
C	 $-CH_2CH=CH\underset{OOH}{CH}-$	 $-CH_2CH=CH\underset{OOH}{\overset{H}{C}}\cdot$	17
		or  $\cdot CH_2CH=CH\underset{OOH}{CH}-$	18
D	$-CH_2CH=CHCH_2O_2CH_2$	$-CH_2CH=CHCH_2O\cdot$	19
E	 $-CH_2\overset{CH_3}{C}=CH\underset{O}{CH}CH_2\underset{O}{\overset{CH_3\;O_2H}{C}}HCH_2$	 $-CH_2\overset{CH_3}{C}=CH\underset{O\cdot}{CH}CH_2\underset{O\cdot}{\overset{CH_3\;O_2H}{C}}CHCH_2-$ or  $-CH_2\overset{CH_3}{C}=\dot{C}H+\underset{O}{C}HCH_2\overset{CH_3\;O_2H}{C}\underset{O}{C}H+\dot{C}H_2-$	12
F	 $-CH_2\underset{O}{C}=CHCH_2-$ $-CH_2C=CHCH_2-$	 $-CH_2\underset{O\cdot}{C}=CHCH_2-$	19

Table II
Thermodynamic Strength of Some Chemical Bonds

Bond	Bond energy, kcal mol^{-1}	Ref
$-CC\overset{\downarrow}{-}CC-$	80	19
$=CC\overset{\downarrow}{-}CC=$	60	23
-C-O-	79	19
RO-OH	42	24, 25
RO-OR	37	
R-OOH	70	
ROO-H	90	

Several authors report that free radicals formed in glassy polymers, including diene rubbers, by mechanical deformation or irradiation, decay at or close to the glass transition temperature.[4-11,31,32,49,52] Mechanisms for the decay of radicals involving oxygen and the decay of peroxy radicals have been discussed by Loy.[36] He suggest the following possible reactions.

$$R\cdot + O_2 \rightarrow R\dot{O}_2$$

$$R\dot{O}_2 + R'H \rightleftharpoons ROOH + R'\cdot$$

$$R'\cdot + R'\cdot \rightarrow R'R' \text{ or } R'\cdot + O_2 \rightarrow R'\dot{O}_2$$

Further intermediate stages have also been suggested, for example,[37]

$$2R\dot{O}_2 \rightarrow 2R\dot{O} + O_2$$

$$R\dot{O} + ROOH \rightarrow R\dot{O}_2 + ROH$$

The first stage of this latter reaction is interesting. In a series of tests carried out in this laboratory, samples of gas evolved from the deformed polybutadiene as it was warmed to its T_g were analyzed quantitatively by mass spectrometry. An increase in oxygen content was detected in some tests as the rubber approached its T_g. However, the technique adopted for the quantitative analysis was to calibrate the mass spectometer with known mixtures of gases and study the relative peak heights of the constituents in the mass spectrograph. This technique is not precise, and the observed oxygen increase is considered as interesting but open to some doubt.

It can be seen that there are many opportunities for oxygen to react with the rubbers during their history of preparation, tensile testing, and subsequent warming, giving rise to the oxygenated radicals observed by ESR.

III. Experimental Section.

Rubbers used for the experiments were: (a) synthetic *cis*-polyisoprene, Shell, 96% cis, containing no stabilizer or oil; (b) synthetic polybutadiene, Shell Cariflex BR1202, 94% cis; (c) Intene 55NF, International Synthetic Rubber Co., 40% cis, 50% trans, and 10% 1,2-vinyl units; (d) high vinylpolybutadiene, greater than 50% 1,2-vinyl units and specially prepared at the National College of Rubber Technology, London.

The T_g's for the cross-linked materials (a) to (d) were assessed using a Du Pont differential thermal analyzer and found to be 213, 188, 203, and 220 K, respectively. The cross-linking agent used with all the rubbers was dicumyl peroxide. The rubber was mixed with dicumyl peroxide on an open laboratory mill, using 0.1 pph dicumyl peroxide for the polybutadiene and 0.5 pph with polyisoprene. The mill rolls were unheated but mastication naturally caused heating of the rubbers during mixing. After mixing the rubbers were pressed into 2-mm thick sheets and cross-linked at 180 °C in a press. No provision existed for controlling the environment during milling and pressing. Tensile test specimens were stamped from the prepared sheets and tested in a low-temperature cabinet attached to an Instron testing machine.[5,38] The atmosphere within the test chamber could be modified by purging and sweeping continuously during testing with gas from a cylinder. Commercial grades of nitrogen and oxygen-free nitrogen were used for this purpose. The test environment temperature was maintained at approximately 83 K. All specimens were oriented by 100% at room temperature prior to testing to ensure a ductile mode of deformation at the low temperature and hence a high radical concentration.[5] The particular ductile mode obtaining during the tensile tests was crazing, which meant that the environment was able to diffuse easily to all parts of the specimen through the crazes and hence contact any radicals formed within the body of the specimen.

Following tensile testing to rupture, a section of the deformed specimen was removed, placed in a Spectrosil tube, and transferred to the ESR cavity precooled to 123 K. The entire specimen removal and transfer to the ESR was carried out at, or close to, a temperature of 83 K to avoid radical decay. The Varian E.9X-band spectrometer used was fitted with a variable temperature controller capable of operating in the range 93–563 K. Microwave power of 0.2 mW was used, which avoided power saturation and spectra distortion. A modulation frequency of 100 kHz was used with an amplitude of 6.3 G. Radical concentrations and g values were evaluated using diphenylpicrylhydrazl (DPPH). The first derivative ESR spectra were integrated to obtain absorption spectra and doubly integrated to determine the total radical concentrations.[39] The method of determining the relative quantity of peroxy to other radicals present will be described in section 6.

To examine the effect of relaxation on warming on the radicals produced, one experiment was carried out in which the specimen was deformed and then held at constant strain while ESR measurements were taken, using a specially designed insitu-tensile testing apparatus.[40]

A Phillips UV irradiation lamp was used to irradiate samples either in evacuated tubes or in the presence of liquid nitrogen which was not oxygen free. The tubes were transferred to the ESR cavity at regular intervals until a clearly identifiable spectrum was obtained.

IV. ESR Spectra for Polybutadiene

Figure 1a shows a typical first derivative ESR spectrum obtained from dicumyl peroxide cross-linked *cis*-polybutadiene after uniaxial deformation in the glassy state in a commercially pure nitrogen atmosphere. It is seen to be a five-line asymmetric spectrum. The line at lowest field has a g value of 2.033. The remaining four lines on the high-field side of the spectrum are observed to have equal splittings of 12 G approximately.

Figure 1b shows the spectrum of a peroxy radical. The double peak in this instance arises from g-value anisotropy and not from nuclear hyperfine splitting. Spectral subtraction of the peroxy radical spectrum (Figure 1b) from the spectrum obtained from polybutadiene (Figure 1a) yields the spectrum shown in Figure 1c. The result is a symmetric four-line spectrum of 50 G overall width. The typical spectrum for polybutadiene deformed in the presence of oxygen is considered to arise from a combination of that due to a peroxy radical and that due to a polymer radical species. The peroxy radical produces the low-field line at $g = 2.033$ and gives rise to the asymmetry in the spectrum. The four-line polymer radical species could be due to three equal protons, since the intensity ratio of the four-line spectrum is approximately 1:3:3:1.

Figure 2b shows the ESR spectrum recorded at 123 K obtained by tensile testing polybutadiene in an oxygen-free nitrogen atmosphere. The peroxy content is much reduced, as can be seen by comparing the relative magnitudes of the line at $g = 2.033$ in Figures 1a and 2b. The spectrum shown in Figure 2b is a nearly symmetrical quartet or perhaps sextet, although the residual peroxy radical continues to distort the spectrum making it difficult to resolve the polymer radical species definitively. By comparison with the subtracted spectrum shown in Figure 1c, the quartet seems the more likely candidate in the case of polybutadiene.

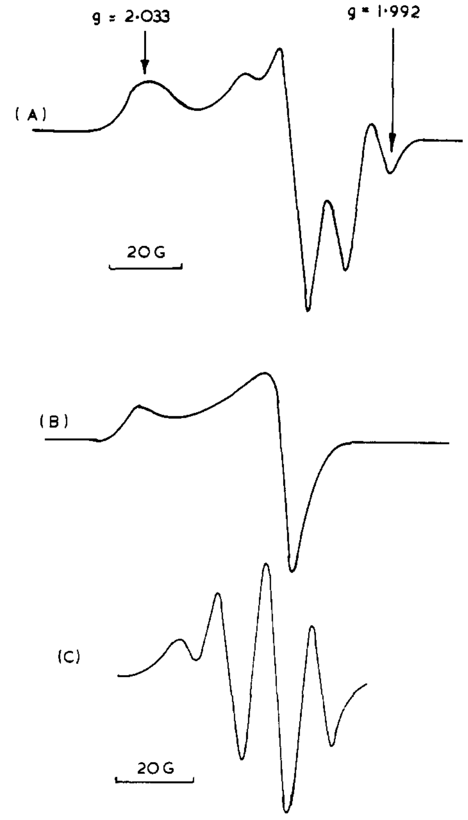


Figure 1. First-derivative ESR spectrum: (a) from *cis*-polybutadiene following tensile testing in commercial purity nitrogen gas at 83 K (spectrum recorded at 123 K); (b) for a peroxy radical; (c) as for (a) above, but after spectral subtraction of the peroxy radical spectrum.

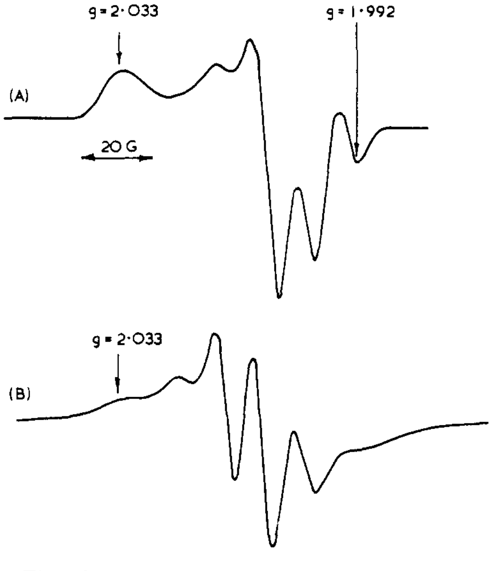


Figure 2. First-derivative ESR spectra recorded at 123 K for polybutadiene following tensile testing: (a) tensile tested in commercial purity nitrogen; (b) tensile tested in oxygen-free nitrogen.

Spectra obtained from similarly deformed high trans (Intene 55NF) and high vinylpolybutadiene in oxygen-free nitrogen also gave similar symmetrical quartet structures with

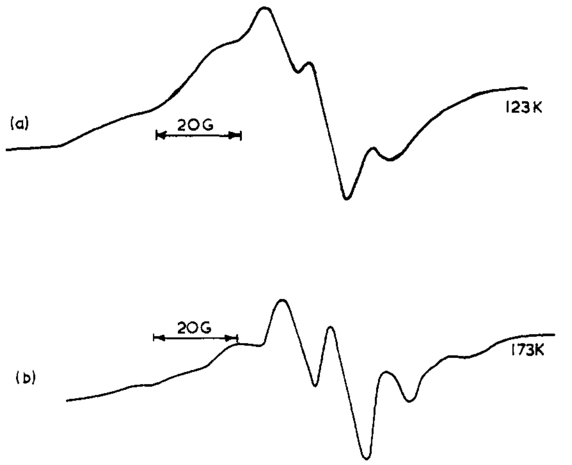


Figure 3. First-derivative ESR spectra from peroxide cross-linked *cis*-polybutadiene after UV irradiation at 77 K in partial vacuum (10^{-4} mm Hg). Spectra recorded at specimen temperatures of (a) 123 K, (b) 173 K.

12 G splitting and an intensity distribution of approximately 1:3:3:1. The four-line spectrum of the polymer radical species therefore appears to be independent of chain conformation. It is assigned to a allylic radical species and possibly the result of main-chain scission between the α-methylene groups. Three factors which support the scission of the carbon–carbon covalent bond of the main chain follow:

(a) Scission is most likely to occur at the energetically most favorable position, i.e., the weakest bond in the main chain. (b) The allyl radical formed by main-chain scission between the α-methylene groups is the only one whose spectrum will be independent of chain conformation. (c) Zhurkov et al.[41] have studied the skeletal vibrations of oriented stressed polypropylene by infrared spectroscopy. A shift in the C–C vibrational frequency was observed which was attributed to straining of the C–C bonds in the main chain.

Carstensen[31] showed, from theoretical considerations, that a symmetrical spectra with 12 G splitting could only occur with the allyl radical species $-CH_2CH{=}CH\dot{C}H_2 \leftrightarrow -CH_2\dot{C}HCH{=}CH_2$. Such a radical species should give rise to a symmetrical six-line spectrum, although an allyl radical species of the form $-CH{=}CH\dot{C}H_2$ would only produce a four-line spectrum. since only a quartet spectrum is observed from deformation of high-trans and vinylpolybutadiene, particularly in the presence of oxygen, assignment of the spectra to main-chain scission radicals must be regarded as tentative, although strongly favored.

A six-line spectrum was observed by Carstensen after UV irradiation of uncross-linked polybutadiene. Hence UV irradiation was also applied to the rubbers used in the present work in order to compare the spectra produced by irradiation and mechanical degradation. Specimens used for irradiation were placed in spectrosil tubes which were then evacuated prior to irradiation. Radicals thus formed were produced in vacuo, which was not possible in the case of the mechanical tests.

Figure 3 shows ESR spectra obtained from cross-linked *cis*-polybutadiene following UV irradiation at 77 K in partial vacuum (10^{-4} mm Hg). Irradiation of the Cariflex BR1202 sample in partial vacuum produces a quartet spectrum with hyperfine splitting of ~12 G. However, the overall width of the spectrum is ~100 G which suggests either the presence of additional lines or that some peroxy radical is again present. The slight asymmetry of the spectrum is thought to be due to the peroxy radical. In contrast to spectra obtained from tensile tested specimens, the spectra obtained following UV irradiation are not well resolved at comparable temperature (123 K). This may be due to different radicals being formed in the two different circumstances or reflect the different conformation of the same allyl species; in the tensile tests the molecules are preferentially oriented. Line narrowing is observed as the specimen is warmed through 173 K and the spectrum is then indistinguishable from that obtained by mechanical degradation of the polymer.

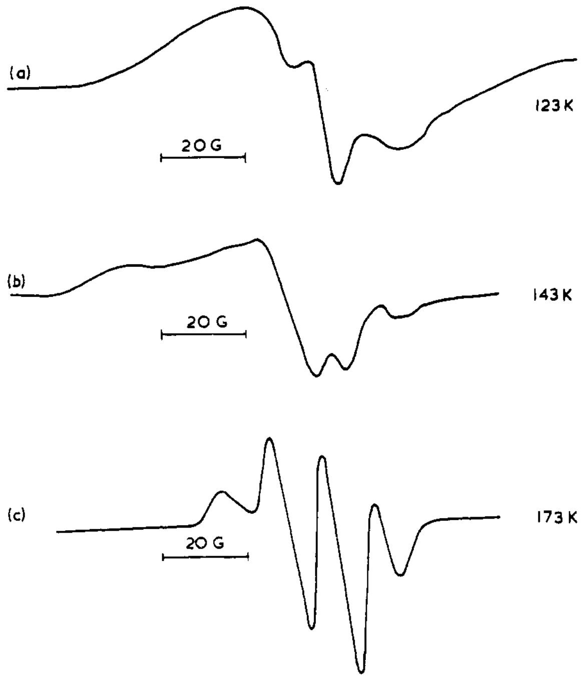


Figure 4. First-derivative ESR spectra from peroxide cross-linked *cis*-polybutadiene after UV irradiation at 77 K for specimens in commercial purity liquid nitrogen. Spectra recorded at specimen temperatures of: (a) 123 K, (b) 143 K, and (c) 173 K.

Figure 4 shows ESR spectra obtained from *cis*-polybutadiene UV irradiated in commercial purity liquid nitrogen. The spectrum at 143 K shows a high peroxy radical content, which changes to the symmetrical quartet when the specimen is heated to 173 K. The radicals obtained by irradiation in liquid nitrogen are thus very similar to those obtained by mechanical degradation at low temperature in commercial purity nitrogen gas.

A possible explanation of the line narrowing which occurs as the specimen is warmed above 173 K is that the polymer radicals are formed in pairs following main-chain scission, and heating causes the chain ends to move apart. This would reduce dipolar interaction between the radicals and therefore one source of line broadening. The oriented chains of the tensile tested specimens would be more prone to such radical separation on warming than the unoriented UV irradiated samples. The small differences between the ESR spectra obtained by UV irradiation and tensile testing may be due to the different chain conformations in the two cases. However, the possibility of the two different radical species being produced by the two methods cannot be completely excluded.

V. ESR Spectra for Polyisoprene

Typical first-derivative ESR spectra for dicumyl peroxide cross-linked *cis*-polyisoprene following tensile deformation at 83 K in commercial purity nitrogen environment and oxygen force nitrogen are shown in Figure 5. Figure 5a is a broad asymmetric signal which is predominantly due to a peroxy radical. For the peroxy radical spectrum, $g_\perp$ and $g_\parallel$ correspond to a maximum and zero points on the first derivative curve, respectively,[42] and the average g value (g_{av}) is $g_{av} \sim \frac{1}{3}(g_{\parallel} + 2g_{\perp}) = 2.015$, while $\Delta g = (g_{\parallel} - g_{\perp}) = 0.03$.

In a previous section it was shown that some oxidation mechanisms lead to oxy radicals (RO·) while others lead to the formation of peroxy radicals ($\text{R}\dot{\text{O}}_2$). It would be convenient if ESR could be used to distinguish between these oxygenated radicals and hence help to distinguish between the possible mechanisms operating. It has been stated[43] that the oxy and peroxy radicals can be distinguished by their average g values, that for peroxy radicals being in the range 2.014–2.019 and that for oxy radicals less than 2.01. Whether oxy radicals have been observed by ESR is disputed in the literature. Broad singlets with $g \simeq 2.003$ have been attributed to alkoxy radicals.[44,45] The majority of references, while not excluding the possibility of oxy radicals, consider it unlikely that oxy radicals have been observed due to their reactivity to form peroxy radicals.[28,46–48] It therefore appears that ESR cannot unequivocably distinguish between the types of possible oxygenated radicals and mechanisms discussed in the previous section.

In contrast to the spectrum obtained following tensile testing in commercial purity nitrogen, testing in oxygen-free nitrogen produces a symmetrical spectrum, as shown in Figure 5b. The latter spectrum has possibly six lines, although the continued presence of some peroxy radicals giving the line at $g = 2.033$ is a complicating feature. Spectral subtraction of the peroxy-radical spectrum, suitably scaled, from Figure 5b yields Figure 5c. Figure 5c is seen to be a symmetrical, probably six-line spectrum with 12 G splitting and is thought to be that arising from the primary polymer radical species.

Carstensen[32] has shown that two different allyl radicals should theoretically form by main-chain scission of the polyisoprene chain at the weakest C–C bond,

$$\text{-CH}_2\text{C(CH}_3\text{)=CH}\dot{\text{C}}\text{H}_2$$

and

$$\text{-CH}_2\text{CH=C(CH}_3\text{)}\dot{\text{C}}\text{H}_2$$

The first of this pair should give an eight-line spectrum while the second should give rise to a six-line spectrum. Hence the resultant spectrum should be a superposition of both. The spectrum shown in Figure 5b, and more particularly Figure 5c, is similar to that reported by Carstensen[32] from UV irradiated uncross-linked polyisoprene. However, only six lines are observed in the spectrum produced by tensile testing, whereas Carstensen detected eight following UV irradiatin, of which the outermost lines were very weak in intensity. Spectra obtained by UV irradiation of cross-linked polyisoprene in the presence of oxygen show a poorly resolved broad singlet of total width 110 G at 103 K.

It is considered that the radicals resulting from both UV irradiation and tensile testing of *cis*-polyisoprene at approximately liquid nitrogen temperatures are similar and are tentatively assigned to primary radicals produced by main-chain scission at the weakest bond, as was the conclusion reached in the case of polybutadiene. However, the primary radicals produced at the low temperature are different for the two rubbers because of the different molecular structures. Differences between the observed and theoretically derived spectra may be due to different conformations of the chains or possibly to different radical species produced in the presence of oxygen. Hence the ESR spectrum obtained by mechanically deforming polyisoprene is tentatively assigned to an allylic radical species because of the 12 G splitting and symmetry of the spectra when the peroxy content is subtracted.

VI. Factors Affecting Peroxy-Radical Concentration

A number of tests have been performed to establish which experimental parameters affect the peroxy content in the spectrum recorded at 123 K following tensile testing at 83 K. The following treatments produced no observable change in the peroxy–other radical concentration: (i) evaculating the specimens for 1 day to a pressue of less than 10^{-5} Torr at room temperature to remove air absorbed during processing before tensile testing; (ii) soaking the rubbers in oxygen for 12 h at room temperature prior to testing in commercial purity nitrogen at 83 K; soaking the polybutadiene specimens for 2 weeks in oxygen caused them to become brittle; (iii) after tensile testing in commercial purity nitrogen and transferring the specimens to the Spectrosil tubes, the tubes were evacuated prior to the ESR spectra being recorded at temperatures in the range 123 to 173 K; (iv) heating the rubbers to 373 K in air prior to tensile testing; and (v) the form of the spectrum was found to be independent of strain and sample strain rate.

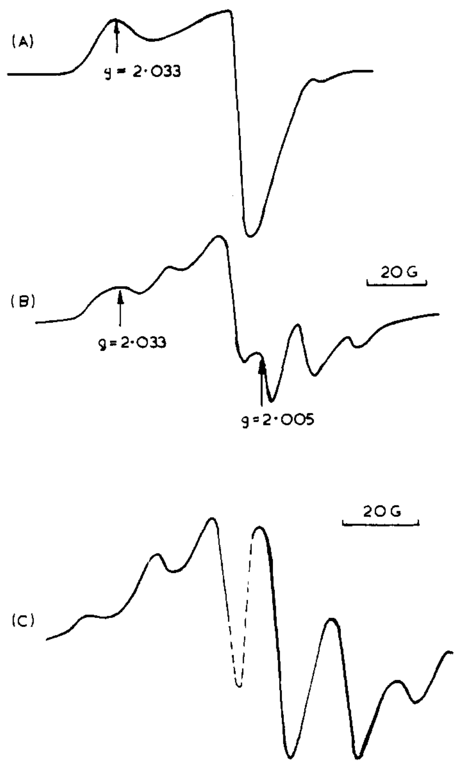


Figure 5. First-derivative ESR spectra from *cis*-polyisoprene following tensile testing at 83 K: (a) tensile tested in commercial purity nitrogen; (b) tensile tested in oxygen-free nitrogen; (c) as for (b) above, but after spectral subtraction of the peroxy-radical spectrum.

The following treatments produced significant changes in the ratio of peroxy–other radical species: (i) performing the tensile tests in an oxygen-free nitrogen atmosphere instead of commercial purity nitrogen significantly reduced the proportion of peroxy content for both rubbers tested; (ii) heating the samples to 393 K in oxygen-free nitrogen for 15 min prior to tensile testing in oxygen-free nitrogen reduced the peroxy-radical content; (iii) raising the temperature of the sample while repeatedly recording ESR spectra following tensile testing in commerical purity nitrogen resulted in a rapid decline in the peroxy-radical portion as the temperature approached the glass-transition temperature of the rubber; (iv) deforming the samples in commercial purity nitrogen near the liquefaction temperature of oxygen increased the relative peroxy radical content; and (v) stressing the rubbers for several days in air prior to low-temperature tensile testing increased the resultant peroxy content.

The effects on the spectra from *cis*-polyisoprene specimens following the heat treatment at various elevated temperatures for 15 min in an oxygen-free nitrogen atmosphere prior to

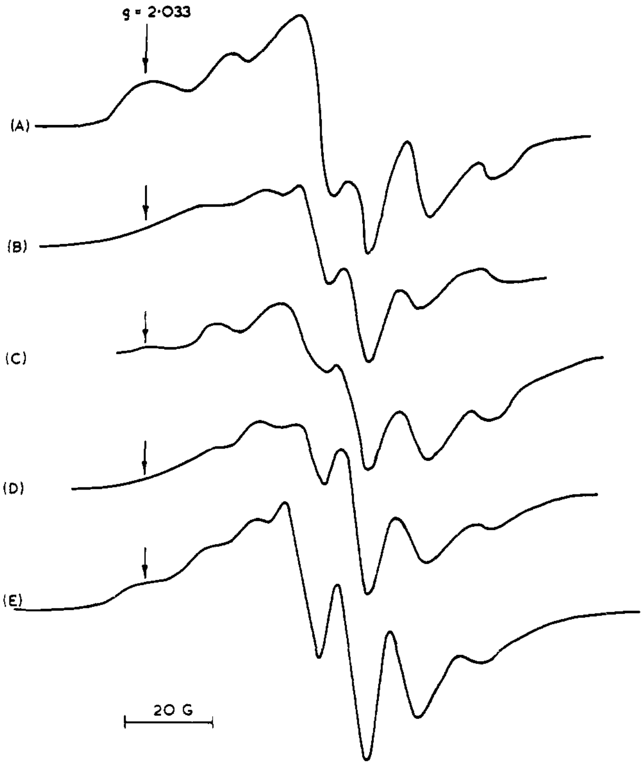


Figure 6. Effect of heat treatment on the peroxy-radical content in the ESR spectrum from *cis*-polyisoprene following tensile testing in oxygen-free nitrogen at 83 K: (a) no heat treatment; (b) heated for 15 min at 90 °C, (c) 120 °C, (d) 150 °C, and (e) 160 °C.

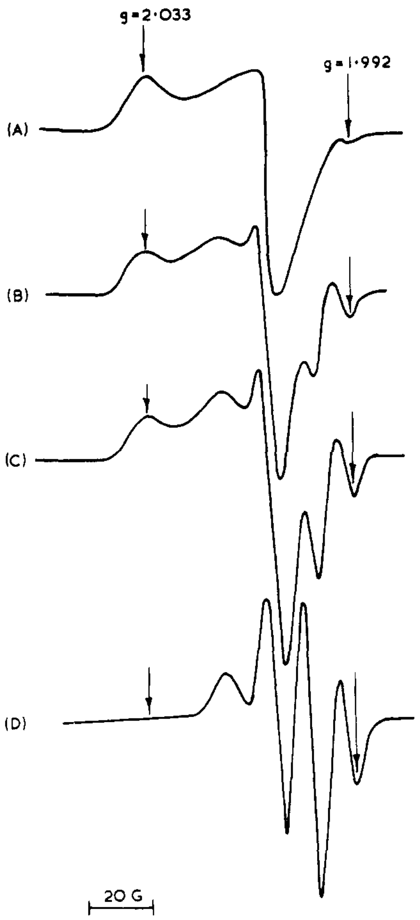


Figure 7. First-derivative ESR spectra for *cis*-polyisoprene following tensile testing at 83 K in commercial purity nitrogen, recorded for specimen temperatures at: (a) 123 K, (b) 193 K, (c) 203 K, and (d) 213 K.

tensile testing at 83 K in a similar atmosphere are shown in Figure 6. The line at g = 2.033, due to peroxy radicals, is clearly present when no heat treatment is applied. Heating for 15 min at 90 °C prior to testing results in a significant reduction in *the peroxide radical content and a possible six-line spectrum* of approximately equal 14 G splitting begins to emerge. There is still evidence of line broadening of the six-line spectrum. Heating at 120 °C for 15 min prior to tensile testing results in a more clearly defined six-line symmetrical spectrum on which is superimposed a small peroxy-radical content giving rise to the line at g = 2.033. An additional complication with the heat-treated specimens is that the ESR spectra may result from a single radical species in different configurations due to the magnetic environment. The heat-treatment technique does not therefore unambiguously show the existence of the hydroperoxide-radical species.

It is clear from the above listed tests that the majority of the peroxy-radical content arises from reaction with oxygen in the test environment and that only when oxygen is rigorously excluded can the peroxy content be reduced. The residual peroxy radical following testing in oxygen-free nitrogen can possibly be attributed to the oxygen dissolved into the rubber during processing. Excess oxygen dissolved in the rubber initially does not apparently increase the peroxy content beyond a certain level obtained with a small quantity of oxygen. A proportion of the peroxy radical content is not attributable to atmospheric oxygen reaction, since it can only be removed by heat treatment of the rubbers to 393 K in oxygen-free nitrogen. This proportion is believed to be associated with hydroperoxide groups formed during initial processing which are readily reacted at about 400 K. Failure to remove such radicals by performing the heat treatment in air is no doubt due to the recombination with oxygen on subsequent cooling.

The peroxide radicals observed in the spectra of samples tested in commercial purity nitrogen are therefore attributed to two sources. First the reaction of allyl radicals with any oxygen in the test environment; this forms the major source of peroxy radical formation and is greatly assisted when crazing occurs, permitting the environment to diffuse easily through the specimen. A second, and more minor, source is the hydroperoxide radicals formed during initial processing of the rubbers.

VII. Stability of the Peroxy Radical with Increasing Temperature

Figure 7 shows the variation in the ESR spectrum obtained from a *cis*-polyisoprene sample, following tensile testing at 83 K, as the sample temperature is raised from 123 K to just below its glass-transition temperature (T_{G}). $\delta(\lambda)$. Figure 8 shows similar data for *cis*-polybutadiene, which has a lower glass-transition temperature. The environment used for the tensile tests was commercial purity nitrogen, which gave rise to the large peroxy radical content in the spectra. Both Figures 7 and 8 show that the peroxy-radical content decreases with increasing temperature and that the peroxy radical decays more rapidly than the other radical species with increasing temperature. At temperatures just below the respective T_{g} of the two rubbers, the peroxy radical has apparently completely decayed.

Figure 7 shows that as the temperature increases, the asymmetric spectrum given by *cis*-polyisoprene changes to a four-line spectrum just below T_{g}. This spectrum is identical with that obtained from polybutadiene at an equivalent temperature (Figure 8b). This four-line spectrum persists as the samples are recooled to 123 K without the reappearance

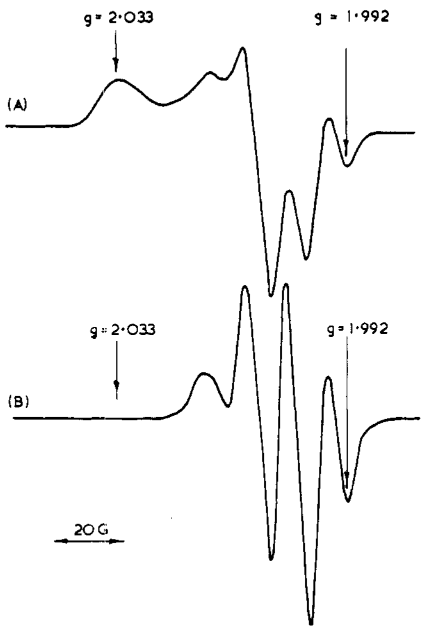


Figure 8. First-derivative ESR spectra for *cis*-polybutadiene following tensile testing at 83 K in commercial purity nitrogen, recorded for specimen temperatures at: (a) 123 K, (b) 173 K.

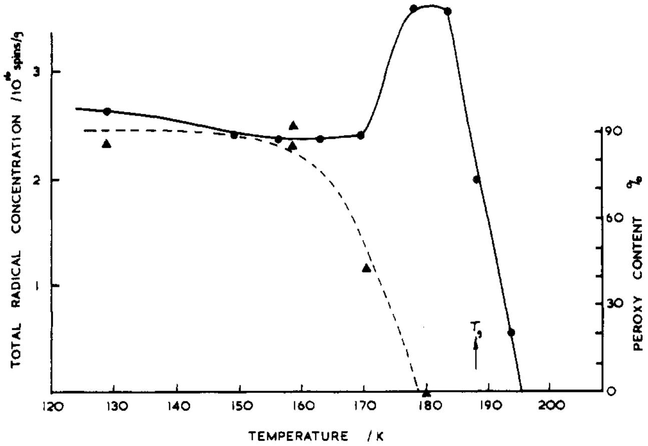


Figure 9. Variation of total radical concentration and peroxy-radical content (dotted) with temperature for *cis*-polybutadiene following tensile testing at 83 K in commercial purity nitrogen. Relaxation on warming unrestrained.

of the peroxy radical or the addition of further lines. It therefore appears that the radical species present just below T_g is identical for both rubbers. Since it has been argued in the previous section that a six-line spectrum probably exists initially at 123 K in the case of polyisoprene, it would appear that the polymer radical species in this case possibly changes as the sample is warmed toward T_g and the peroxy radical decays. No suggestion of similar changes is observed in the case of polybutadiene.

Attempts have been made to quantify the relative amounts of peroxy to other radical species present throughout the temperature range studied. The analytical technique adopted was to double integrate the first derivative curve to determine the total concentration of all radical species present. To obtain the absolute radical concentration, the area (A_T) derived by double integration was compared with that obtained by double integration of the singlet from a DPPH sample of quoted radical concentration. A typical first-derivative spectrum for a peroxy radical (Figure 1b) was taken and similarly double integrated to obtain a reference area (A_P). In order to progress further, it is necessary to assume that the line at $g = 2.033$ in any first-derivative spectra can be solely attributed to the peroxy radical. A scale fraction (α) was determined by comparing the peak heights at $g = 2.033$ with that in the peroxy reference spectrum. The proportion of the total radical concentration which could be assigned to peroxy radicals is then quoted as the ratio $\alpha A_P/A_T$.

This method of double integration and spectra subtraction is known to be inaccurate and the values so determined are only presented as a rough assessment of the ratio of peroxy-radical content to the other radical species present.

Figures 9 and 10 show the variation of the total radical concentration with temperature for polybutadiene and polyisoprene, respectively. Also shown on Figures 9 and 10 is the peroxy content of the total radical concentration. Figures 9 and 10 show that the total radical concentration varies little as the temperature is raised from 83 K to approximately 50 K below the T_g of the elastomer concerned. The peroxy radicals disappear at temperatures near T_g and approximately 20 K below the total decay point of all other radicals, showing that the peroxy radical is less stable than the allyl radical present at that temperature. The remaining radicals decay rapidly as the T_g is approached, with all sign of the allyl radicals disappearing at or just above the T_g of the rubber.

VIII. Anomalous Radical Decay in Polybutadiene and Polyisoprene

Both Figures 9 and 10 show an increase in the total concentration as the T_g of the material is approached. This anomalous maximum in the radical concentration is only observed when the polymers are produced by mechanical deformation, either in tensile testing or by grinding the polymers.[5,49] The increase in radical concentration as T_g is approached does not occur when the radicals are produced by UV irradiation. Both previous references considered the increase in radical concentration to be a real effect, the first attributing it to the formation of new radicals as a result of mechanically stored energy release[5] and the second suggesting that the environment, particularly oxygen and earthing the specimen, affected the radical decay characteristics near T_g.[49] Since the increase in the total radical concentration occurs simultaneously with the decline in the peroxy-radical content, the extra radicals formed must be only polymer radicals.

Initially the specimens used for radical determination purposes were unrestrained and the increase in radical concentration was thought to be due to longitudinal contraction, resulting in more material being drawn into the cavity. Although this contraction might result in some increase in the radical content, it cannot explain the fourfold increase observed in the case of polyisoprene (Figure 10). The availability of alternative equipment allowed the tests to be performed in oxygen-free nitrogen and the radical decay to be observed in specimens held at constant extension while the temperature was varied. Figure 11 shows the variation with temperature of total radical concentration for *cis*-polybutadiene specimens held at constant extension when tested in oxygen-free nitrogen. The increase in total radical concentration just below T_g is absent in contrast to Figure 9, and the total radical concentration following testing in oxygen-free nitrogen is much lower than when testing in commercial purity nitrogen, as has also been previously reported by Sohma.[41] Hence the increase in radical concentration just below T_g may be related to the presence of oxygen in the test environment, or, alternatively, may be associated with nonuniform relaxation of the deformed network on warming, this network straining being absent in the case of the UV irradiated samples. Further testing shows that if the tensile tests are carried out in oxygen-free nitrogen and relaxation is not restrained, the rise in radical concentration near T_g, although still present, is much reduced. It

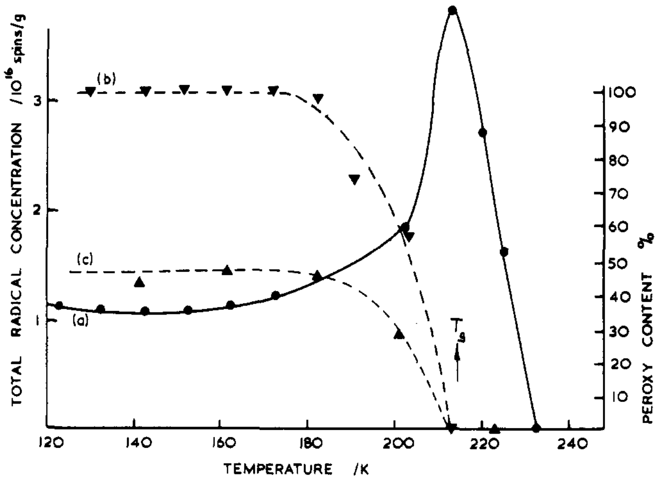


Figure 10. Variation of total radical concentration and peroxy-radical content with temperature for *cis*-polyisoprene following tensile testing at 83 K: (a) total radical concentration following tensile testing in commercial purity nitrogen; (b) peroxy-radical content followiing tensile testing in commercial purity nitrogen, (c) peroxy-radical content following tensile testing in oxygen-free nitrogen. Relaxation on warming unrestrained.

therefore, appears that both the presence of oxygen in the test environment on warming and the relaxation of strain or energy release on the network in unrestrained mechanically deformed samples are contributory factors to the increase in radical concentration near T_g in mechanically deformed samples. From the data obtained, it appears that the presence of oxygen is the major contribution to the process. Uncharacteristically it results in an increase in the allyl-radical content, since the peroxy radicals decay rapidly in this region.

A further possible explanation for the radical concentration increase concerns the mechanical scission of chains in loaded polymeric solids.[49,50] Johnson and Klinkenberg[51] step strained Nylon 6 fibres between 206–273 and 273–290 K. The tests showed the same result of stepwise increase of radical concentration with temperature as in the stepwise increase of strain tests. Increasing the temperature of the test produced stress relaxation and an increase in radical concentration. The stepwise temperature increase produced a proportional number of radicals, over the complete temperature range, whereas in the studies presented here the radical concentration rapidly increased at 50 K below T_g.

Sohma and Sakaguchi[9,10,52] have recently discussed the anomalous decay of polymer radicals in polypropylene produced by mechanical friction, ball milling, and sawing in liquid nitrogen. Decay curves similar to Figures 9 and 10 were observed but in these cases a more enhanced anomaly was observed than with a ground sample. Sohma and Sakaguchi confirmed the effect of the excess electric charge on the anomalous phenomenon by using electron scavengers which resulted in no anomalous increase being observed during the decay. According to Sakaguchi and Sohma the excess electric charge produced by friction, or triboelectricity, and the presence of oxygen molecules was necessary for the anomalous radical concentration behavior in the decay of the mechanoradicals of polypropylene. Similar experiments to those of Sohma et al. are required in order to establish if a similar mechanism can account for the anomalous decay in uniaxially deformed polybutadiene and polyisoprene. Recently Pillar and Ulbert[53] have observed an anomalous radical increase with temperature and in the presence of oxygen of radicals produced by vibrational grinding of poly(ethylene glycol methacrylate). Their explanation for the anomalous decay appears to be different from that of Sohma et al., since Pillar and Ulbert believe that the formation and gradual decomposition of polymer tetroxide is also the cause of the anomalous radical increase with temperature.

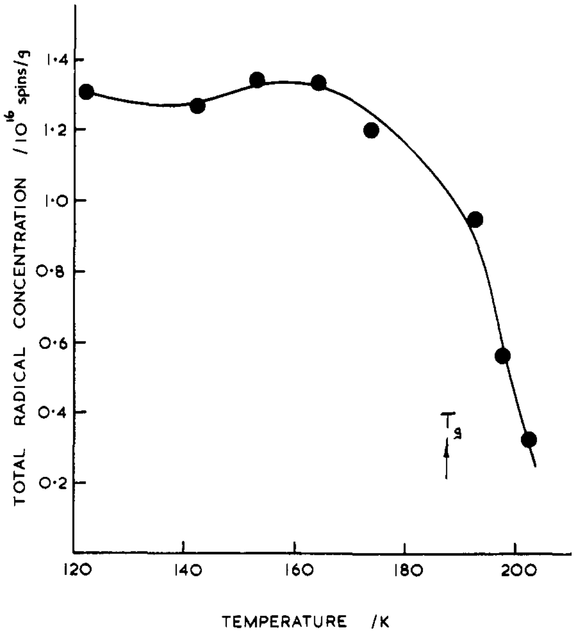


Figure 11. Variation of total radical concentration for *cis*-polybutadiene following tensile testing at 83 K in oxygen-free nitrogen. Relaxation on warming restrained.

It is therefore apparent that a simple explanation of the anomalous effect is not possible for the rubbers tested in the present work or other polymeric materials.

IX. Conclusion

The ESR spectra obtained from diene rubbers following mechanical deformation at cryogenic temperatures in a commercial purity nitrogen atmosphere are composite spectra arising from two or more radicals. The two radicals are thought to be an allyl radical resulting from main-chain rupture and a peroxy radical.

The majority of the peroxy radicals observed in the composite spectra are formed as a result of oxygen in the test environment reacting with the allyl radicals formed shortly after chain rupture occurs. However, it appears that a small proportion of the peroxy radicals arise from oxygen incorporated into the rubber network during the processing stage before mechanical testing commences. Only if oxygen is rigorously excluded at all stages of processing and testing is the true spectrum of the primary allyl radical observed following mechanical degradation, showing that the chain rupture site is at the weakest bond, between the α-methylene groups. Oxygenated radical species incorporated during processing can be removed by heat treatment, provided the heat treatment is carried out in an oxygen-free atmosphere.

The radical stability vs. temperature tests have shown that the peroxy radical decays at a temperature approximately 20 K lower than the allyl radical, which in turn decays rapidly in the vicinity of the T_g of the rubber.

It appears that the anomalous increase in radical concentration near T_g, particularly noticeable in the case of mechanically deformed polymers, possibly arises from stored energy release on warming assisted by the presence of oxygen, oxygen being the major contributor to the process. However, the anomalous effect appears to be complex and other factors may contribute to it.

It is generally concluded that the ESR technique offers a sensitive method of observing the oxidation of polybutadiene and other diene rubbers.

References and Notes

(1) L. Bateman, Ed., "The Chemistry and Physics of Rubber-Like Substances", MacLaren and Sons, London, 1963.
(2) F. R. Mayo, *Rubber Chem. Technol.*, **41**, 271 (1968).
(3) M. Pike and W. F. Watson, *J. Polym. Sci.*, **9**, 229 (1952).
(4) R. Natarajan and P. E. Reed, *J. Polym. Sci. Part A-2*, **10**, 585 (1972).
(5) W. T. Mead and P. E. Reed, *Polym. Eng. Sci.*, **14**, 22 (1974).
(6) B. Reeve, Ph.D. Thesis, University of London, 1972.
(7) W. T. Mead and P. E. Reed, *Bull. Am. Phys. Soc.*, **CJ11**, 299 (1976).
(8) P. E. Reed, International Yield and Fracture Conference, March 1976, Cambridge, England.
(9) J. Sohma and M. Sakaguchi, *Adv. Polym. Sci.*, **20**, 109 (1976).
(10) J. Sohma and M. Sakaguchi, "Degradation and Stabilisation of Polymers", G. Geuskens, Ed., Wiley, New York, N.Y., 1975, Chapter 8.
(11) K. L. DeVries, *Rubber Chem. Technol.*, **48**, 445 (1975).
(12) M. L. Kaplan and P. G. Kelleher, *J. Polym. Sci., Part A-1*, **8**, 3163 (1970).
(13) J. N. Short, V. Thornton, and G. Kraus, *Rubber Plast. Age*, **38**, 880 (1957).
(14) G. Miller, V. Larson, and G. O. Pritchard, *J. Polym. Sci.*, **61**, 475 (1962).
(15) B. Bailey, E. Duck, and J. M. Locke, *J. Inst. Rubber Ind.*, **1**, 2577 (1967).
(16) J. O. Cole and J. E. Field, *Ind. Eng. Chem.*, **39**, 174 (1947).
(17) N. Grassie, "The Chemistry of High Polymer Degradation Processes", Butterworths, London, 1956.
(18) S. L. Madorsky, "Thermal Degradation of Organic Polymers", Interscience, New York, N.Y., 1964.
(19) A. Tager, "Physical Chemistry of Polymers", Mir. Publishers, Moscow, 1970.
(20) W. F. Watson, *Rubber Chem. Technol.*, **33**, 80 (1960).
(21) W. F. Watson in "Chemical Reactions of Polymers", E. M. Fetters, Ed., Interscience, New York, N.Y., 1964, p 1085.
(22) A. Casale, R. S. Porter, and J. F. Johnson, *Rubber Chem. Technol.*, **44**, 534 (1971).
(23) G. Kraus and K. W. Rollman, *J. Appl. Polym. Sci.*, **8**, 2585 (1964).
(24) S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).
(25) L. Batt and S. W. Benson, *J. Chem. Phys.*, **36**, 895 (1962).
(26) K. U. Ingold and J. R. Morton, *J. Am. Chem. Soc.*, **86**, 3400 (1964).
(27) M. C. R. Symons, *Adv. Phys. Org. Chem.*, **1**, 284 (1963).
(28) F. Mayo, private communication.
(29) S. I. Ohnishi, S. I. Sugimoto, and I. Nitta, *J. Polym. Sci., Part A-1*, 605 (1963).
(30) S. I. Ohnishi, S. I. Sugimoto, and I. Nitta, *J. Chem. Phys.*, **37**, 1283 (1962).
(31) P. Carstensen, *Makromol. Chem.*, **142**, 131 (1971).
(32) P. Carstensen, *Makromol. Chem.*, **135**, 219 (1970).
(33) P. Yu Butyagin, V. G. Drozdovskii, D. R. Razgon, and I. V. Kolbanev, *Sov. Phys.-Solid State* (*Engl. Transl.*), **7**, 757 (1965).
(34) Yu D. Tsvetkov, I. N. Molin, and V. V. Voevodskii, *Vysokomol. Soedin.*, **1**, 1805 (1959).
(35) P. Yu Butyagin, A. M. Dubinskaya, and V. A. Radtsig, *Russ. Chem. Rev.* (*Engl. Transl.*), **38**, 290 (1969).
(36) B. R. Loy, *J. Phys. Chem.*, **65**, 58 (1961).
(37) H. W. Melville and S. Richards, *J. Chem. Soc.*, 944 (1954).
(38) P. E. Reed, *J. Mater. Sci.*, **1**, 91 (1966).
(39) C. P. Poole, "Electron Spin Resonance", Interscience, New York, N.Y., 1967.
(40) W. T. Mead and P. E. Reed, to be published.
(41) S. N. Zhurkov, V. A. Zakrevskii, V. E. Korsukov, and V. S. Kuksenko, *Sov. Phys.-Solid State* (*Engl. Transl.*), **13**, 1680 (1972).
(42) P. Ayscough, "Electron Spin Resonance in Chemistry", Methuen, 1969, Chapter 3.
(43) M. Bersohn and J. R. Thomas, *J. Am. Chem. Soc.*, **86**, 959 (1964).
(44) L. H. Piette and W. C. Landgraf, *J. Chem. Phys.*, **33**, 1107 (1960).
(45) Y. A. Ershov, Y. V. Gak, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 778 (1967).
(46) J. C. W. Chien and M. Ross, *J. Am. Chem. Soc.*, **89** 571 (1967).
(47) J. T. Martin and R. G. W. Norrish, *Proc. R. Soc. London, Ser. A*, **220**, 322 (1953).
(48) P. J. Sullivan and W. S. Koski, *J. Am. Chem. Soc.*, **85**, 384 (1963).
(49) J. Sohma, T. Kawashima, S. Shimada, H. Kashiwabara, and M. Sakaguchi, "ESR Applications to Polymer Research", P.-O. Kinell, B. Ranby, and V. Runnstrom-Reio, Ed., Wily, New York, N.Y., 1972.
(50) H. H. Kausch and K. L. DeVries, *Int. J. Fract.*, **11**, 5 (1975).
(51) U. J. Johnson and D. Klinkenberg, *Kolloid Z. Z. Polym.*, **251**, 843 (1973).
(52) M. Sakaguchi and J. Sohma, *Polym. J.*, **7**, 490 (1975).
(53) J. Pillar and K. Ulbert, *Polymer*, **16**, 730 (1975).

Coenzyme Models. 10. Rapid Oxidation of NADH by a Flavin Immobilized in Cationic Polyelectrolytes

Seiji Shinkai, Shinji Yamada, and Toyoki Kunitake* [1]

Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Fukuoka 812, Japan.

Received June 8, 1977

ABSTRACT: The title flavin rapidly oxidizes NADH, the observed enhancement being of 460–4650-fold compared with 3-methyltetra-*O*-acetylriboflavin. Analysis of the kinetic data at 30 °C established that the reaction proceeds according to the Michaelis–Menten kinetics at low ionic strength ($\mu = 0.02$: $K_m =$ ca. 10^{-5} M, $k_{\text{cat.}} = 0.06$–$0.37\ \text{s}^{-1}$) and according to the simple second-order kinetics at high ionic strength ($\mu = 0.3$), the largest rate difference being 342-fold. On the other hand, the oxidation of 1-benzyl-1,4-dihydronicotinamide, a NADH model compound, was not accelerated by the use of the title flavin. It is concluded, therefore, that the formation of the polymeric flavin–NADH complexes due to the electrostatic interaction is responsible for the marked rate enhancement. This is the first example that the oxidation of NADH is facilitated in the nonenzymatic system.

Of many flavin coenzyme dependent reactions, the oxidation–reduction reaction couple between NADH (reduced form of nicotinamide–adenine dinucleotide) and flavoprotein is of special interest.[2,3] Although the reaction occurs in nonenzymatic systems, NADH by itself acts as a less reactive reducing agent for flavins than simple NADH model compounds such as 1-alkyl-1,4-dihydronicotinamide.[2,3] It is clear, therefore, that the environment of enzymes (e.g., FMN oxidoreductase) is performing the role of catalyst.

We recently found that rates and equilibrium constants for the addition of cyanide and sulfite ions to poly[1-(4-vinylbenzyl)nicotinamide chloride] (cationic polyelectrolyte) are markedly enhanced in comparison to the monomeric analogue.[4,5] Since the association constant can be correlated with the reactivity of NAD^+ (and analogues),[6] it is suggested that the nicotinamide group in cationic polyelectrolytes would serve as an excellent oxidizing agent, especially for the oxidation of anionic species. With the expectation to develop efficient oxidizing agents for flavin-mediated reaction systems, we synthesized the following flavin-containing polymers and assessed the oxidation of NADH(polyanion) and the model compound, 1-benzyl-1,4-dihydronicotinamide (BzlNicH) (eq 1). We found that the oxidation of NADH is remarkedly accelerated by the use of a flavin immobilized in cationic polyelectrolytes and that the reaction proceeds according to the Michaelis–Menten kinetics. To our knowledge this is the first

0024-9297/78/2211-0065$01.00/0