

THE PREPARATION, CHARACTERIZATION AND HYDROLYSIS OF
EPOXIDIZED NATURAL RUBBER

by

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**This thesis is dedicated to Hunter S. Thompson,
John Pilger and Alien Jorgensen: contemporary
heroes in a sordid and decadent world.**



ABSTRACT

The double bonds in NR can be partially epoxidized using peracids and mild experimental conditions. More forcing conditions result in hydrolysis and the ring-opening of epoxy groups. The epoxidation of NR latex concentrates using performic acid generated *in situ* from hydrogen peroxide and formic acid has been studied intensively; variability in the reaction is consistent with the presence of adventitious iron and the intervention of Fenton's Reagent.

The determination of epoxy groups in ENR by a range of analytical techniques has been examined and conflicting results in the literature have been resolved.

The fractionation of ENR by molecular mass and particle size in latices has yielded further evidence for epoxidation being a random chemical reaction. However, there is conflicting chemical evidence for a non-random process.

The acid-catalysed hydrolysis of ENR results in ring-opening and the preferential formation of tetrahydrofuran rings and/or ether crosslinks. The products of hydrolysis are determined by the concentration of epoxy groups and acid and the activity of counter-ions. Intermolecular ether bonds in ENR have been characterized. The formation of crosslinks can be monitored by ^{13}C -NMR spectroscopy *via* the concentration of pendant alcohol groups. Model studies have demonstrated that ring-expansion results in the exclusive formation of tetrahydrofuran rings. *Cis*- and *trans*-epoxy groups are formed during the uninhibited

autoxidation of NR and ENR in an apparent *trans:cis* ratio of 1.4:1.0. This result is consistent with the exclusive formation of epoxy groups by the addition of peroxy radicals to double bonds.

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ABBREVIATIONS

AA	Atomic absorption spectrometry
ASTM	American Society for Testing and Materials
BHT	2,4-di- <i>tert</i> -butyl-4-methylphenol
BR	Polybutadiene
CR	Polychloroprene rubber
CW	Continuous wave
C ₆ D ₆	Deuteriated benzene
CDCl ₃	Deuteriated chloroform
CHCl ₃	Chloroform
CH ₂ Cl ₂	Dichloromethane
CSA	10-Camphorsulphonic acid
DPNR	Deproteinized natural rubber
DSC	Differential scanning calorimetry
ENR	Epoxidized natural rubber
FT	Fourier transform
GC-MS	Gas liquid chromatography-Mass spectroscopy
GLC	Gas liquid chromatography
GPC	Gel permeation chromatography
HA	High-ammonia
HPLC	High pressure liquid chromatography
IIR	Butyl rubber
IR	Infrared spectroscopy
IRHD	International rubber hardness degrees
M _n	Number-average molecular mass
M _w	Weight-average molecular mass
M _z	z-average molecular mass
MCPBA	3-chloroperbenzoic acid
MEK	Methyl ethyl ketone
MRPRA	Malaysian Rubber Producers' Research Association
NBR	Acrylonitrile-butadiene rubber
NMR	Nuclear magnetic resonance
¹ H-NMR	Proton nuclear magnetic resonance spectroscopy
¹³ C-NMR	Carbon-13 nuclear magnetic resonance spectroscopy
nOe	Nuclear Overhauser enhancement

NR	Natural rubber
pphr	Parts per hundred rubber
ppm	Parts per million
rpm	Revolutions per minute
RRIM	Rubber Research Institute of Malaysia
RSS	Ribbed smoked sheet
SBS	Styrene-butadiene-styrene block copolymer
SFORD	Single frequency off-resonance decoupling
T_g	Glass transition temperature
TEAB	Tetraethyl ammonium bromide
THF	Tetrahydrofuran
TMS	Tetramethylsilane
TSA	4-Toluenesulphonic acid
T_1	Spin-lattice relaxation time
UV	Ultraviolet
v_r	Volume fraction of rubber in the swollen state
δ	Solubility parameter
δ	Chemical shift

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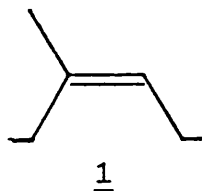
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CHAPTER 1

INTRODUCTION AND SUMMARY OF PREVIOUS WORK

1.1 The Chemical Modification of Natural Rubber

NR has been commercially available for over a century. The development of plastics in the 1920`s precipitated research into the chemical transformation of NR and resulted in the commercial production of derivatives such as chlorinated rubber and cyclized rubber¹. The development of the first synthetic elastomers during the second world war led to the onset of serious competition for NR and the start of an extensive programme to investigate the preparation and properties of chemically-modified NR. The chemical modification of NR has been reviewed²⁻⁶. The majority of transformation reactions are dependent upon the reactivity of the trisubstituted alkene group in the *cis*-1,4-isoprene repeat units that constitute NR, 1⁷.



The physical properties of NR make it a general purpose (and hence low price) elastomer. An improvement in certain physical properties such as gas permeability and oil resistance, would allow chemically modified NR to become competitive with highly priced speciality rubbers and the introduction of a higher

price⁴. This is an important economic consideration in view of recent trading prices for bulk NR.

The chemical modification of NR can be categorised according to the extent of transformation of polymer chains^{3,4,6} (Table 1.1). It has been estimated from the average price of reagents

Table 1.1

Classes of chemical modification

Type of reaction	Extent (mole%)	Effect on properties
Surface	<1	Basically unchanged bulk physical properties
Slight	<5	Chemical effects due to crosslinks, ageing etc
Intermediate	5-25	Modified elasticity; an improvement in certain physical properties
Extensive	25-100	Loss in elasticity; gross physical changes; new polymers

that the price of chemically-modified NR is increased by 10% for each mole% modification⁴. A sufficient improvement or change in the physical properties of NR must result to warrant the higher premium, characteristic of a speciality elastomer, necessary to make the material commercially viable. In addition, chemical transformation must be achieved either by the reaction of NR latices or during dry mixing processes; reactions in solution are not economically viable.

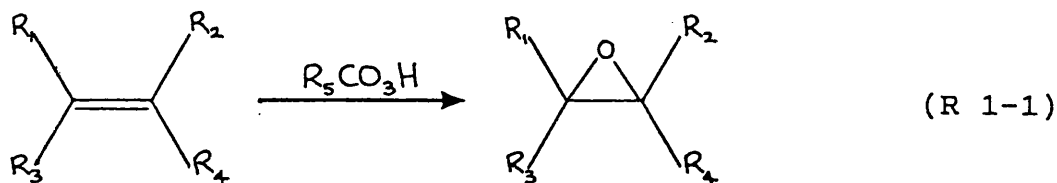
In the last 15 years, the partial epoxidation of the double

bonds in NR with peracids has received considerable attention⁸.

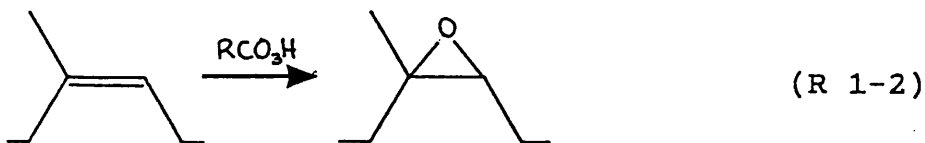
1.2 Epoxidized Natural Rubber

1.2.1 The Preparation of Epoxidized Natural Rubber

Prilezhaev⁹⁻¹¹ established that alkenes could be oxidised to epoxides using peracids in organic solvents (R 1-1). The



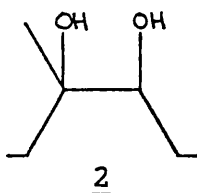
epoxidation of alkenes with peracids has been extensively reviewed¹²⁻²⁰. The reaction can be made quantitative and has been used to estimate the degree of unsaturation in polyisoprenes using perbenzoic acid^{21,22}. In principle, the epoxidation of NR in solution with peracids (R 1-2) should prepare partially-



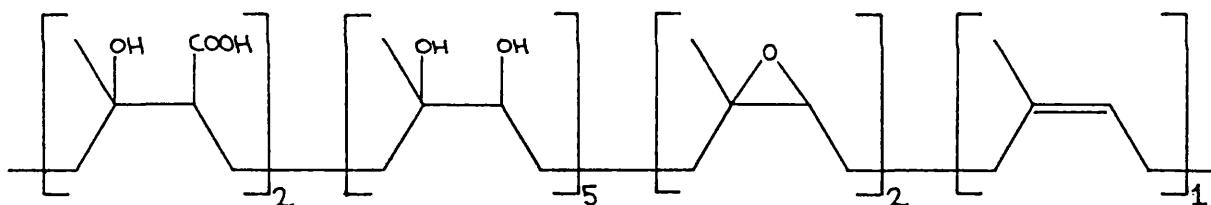
epoxidized NR in a quantitative yield.

An initial investigation of the reaction of NR with perbenzoic acid in CHCl_3 ²³ failed to prepare ENR. The oxidation of NR with hydrogen peroxide in glacial acetic acid and carbon tetrachloride yielded a highly degraded resin with an empirical formula of $\text{C}_{30}\text{H}_{48}\text{O}$ ²⁴. A similar reaction resulted in the preparation of low molecular mass (≈ 1000) resins with alcoholic properties and an elemental composition of $\text{C}_{59}\text{H}_{102}\text{O}_{16}$ ²⁵. The reaction of NR with

hydrogen peroxide in glacial acetic acid yielded a low molecular mass resin, $C_{50}H_{92}O_{16}$, which was claimed to contain oxygen solely in the form of hydroxyl groups and the formation of 1,2-diol units, 2, was assumed²⁶. The reaction of NR in solution with



peracetic acid, hydrogen peroxide in glacial acetic acid, or hydrogen peroxide and formic acid yielded thermoplastic powders which were shown by acetylation to be polyhydroxylated²⁷. Kambara and co-workers²⁸⁻³⁰ claimed that the epoxidation of NR in solution yielded products containing a variety of oxygenated functional groups (*Scheme 1-1*). The substitution of strongly



Oxygenated functional groups from the epoxidation of NR²⁸

Scheme 1-1

acidic reagents at high reaction temperatures with milder reagent systems resulted in the preparation of ENR without accompanying ring-opening reactions (Section 1.3.1). Under these conditions, NR can be epoxidized in solution cleanly and quantitatively using several peracids³¹⁻³⁷.

In 1962, Colclough demonstrated the facile epoxidation of BR and NR latices with perbenzoic acid³⁸. In the same year, the

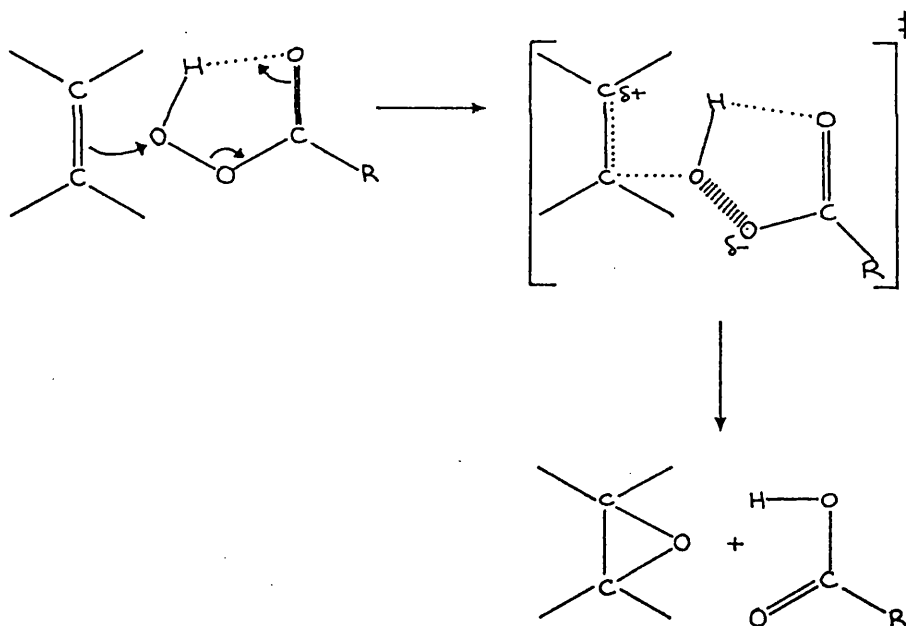
epoxidation of unsaturated-elastomer latices with peracetic acid in the presence of a sodium acetate buffer was patented³⁹. It was shown that high molecular mass polymers could be epoxidized in the latex state, despite evidence from earlier studies which indicated that the efficiency of epoxidation of unsaturated elastomers in solution depended upon the molecular mass of the substrate¹⁶. In mildly acidic regimes, the complete conversion of the double bonds in NR to epoxide rings yielded a rubber with a T_g of 0°C (*cf.* a T_g above 100°C for the thermoplastics formed from reactions in which ring-opening was prevalent^{30,40}) and the relatively low T_g suggested that partially-epoxidized NR would have useful physical properties⁴¹ (Section 1.3.1). This result stimulated extensive studies by Gelling and co-workers at MRPRA into the epoxidation of NR latex with preformed peracetic acid^{41,42} and subsequently, with performic acid generated *in situ* from hydrogen peroxide and formic acid^{6,43,44}. Both methods were shown to prepare partially-epoxidized NR (up to an epoxy-group content of 75 mole%) with no **observable** side reactions. Both economic and safety criteria favour the epoxidation of alkenes with peracids generated *in situ*. Consequently, the epoxidation of NR latex with hydrogen peroxide and formic acid has been commercially exploited to prepare two grades of rubber, ENR-25 and -50, containing 25 and 50 mole% epoxy groups respectively^{6,44-46}.

An assortment of methods to epoxidize NR latices have been studied by Burfield and co-workers^{47,48} including inorganic peracid salts, the oxidation of bromohydrins and hydrogen

peroxide-acetonitrile. Of all the methods tried, preformed peracetic acid was the only reagent which resulted in the efficient preparation of cleanly epoxidized NR⁴⁸. The reaction of NR latex with *t*-butyl hydroperoxide in the presence of sodium molybdate was found to yield heavily-crosslinked ENR⁴⁹.

1.2.2 Mechanism and Kinetics

The accepted mechanism⁵⁰ for the epoxidation of alkenes with peracids, proposed by Bartlett⁵¹ and elaborated by other workers^{52,53}, is a one-step process involving a non-ionic spiro transition state and oxygen transfer occurring by a concerted intermolecular process (*Scheme 1-2*). Molecular orbital studies by



The mechanism of alkene epoxidation with peracids

Scheme 1-2

Azman and co-workers indicated the formation of an unsymmetrical

transition state⁵⁴. Evidence for this mechanism was provided by the following observations⁵⁵:

(a) the reaction obeys second-order kinetics

(b) reaction takes place readily in non-polar solvents in which ion formation would be difficult

and, (c) the reaction is stereospecific⁵⁶ (i.e. *trans*-alkenes are oxidized to *trans*-epoxides).

Additional features of the reaction can be summarised^{12,13,20};

(a) electron donating groups increase the rate of epoxidation

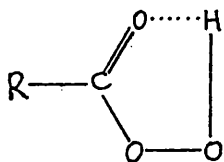
(b) experimental conditions are mild

(c) the reaction is efficient

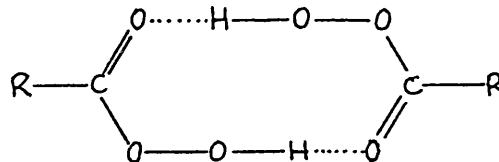
and, (d) the reaction is exothermic and possesses a large negative entropy of activation.

The kinetics of epoxidation of low molecular mass alkenes⁵² and unsaturated elastomers^{33,57,58} in solution have been widely studied. There are few corresponding studies on the epoxidation of elastomer latices with peracids. Burfield and co-workers found that the epoxidation of NR latex with peracetic acid was

quantitative and obeyed second-order kinetics up to an epoxy-group content of 15 mole%^{47,48}. A large negative entropy of activation, $\Delta S^\ddagger = -265 \text{ JK}^{-1}\text{mol}^{-1}$, and an activation energy of reaction, $E^\ddagger = 56.2 \text{ kJmol}^{-1}$ were calculated for the reaction^{47,48}. Poluektov and co-workers^{59,60} studied the reaction of peracetic acid with *cis*-1,4-polyisoprene, BR, and SBR latices and found that the reaction obeyed second-order kinetics with the rate independent of the surfactant⁵⁷, particle size distribution and stirring speed. The linearity of rate plots indicated that the peracid diffused through the surfactant monolayer at a much greater rate than that required for formation of the transition complex; the reaction was therefore considered to be homogeneous. The rate constant for the epoxidation of BR latex was found to be approximately 200 times smaller than the corresponding reaction in chloroform. This was attributed to restricted accessibility of the double bonds in latex particles and deactivation of the peracid by the loss of intramolecular hydrogen bonding⁶¹ (Scheme 1-3). Calculated values for E^\ddagger and ΔS^\ddagger of 67 kJmol^{-1} and



Intramolecular hydrogen bonding
bonding in organic solvents



Intermolecular hydrogen
bonding

Hydrogen bonding in peracids

Scheme 1-3

of 67 kJmol^{-1} and $-96 \text{ JK}^{-1}\text{mol}^{-1}$ respectively, for the epoxidation of synthetic *cis*-1,4-polyisoprene latex^{59,60} with peracetic acid

The relative rates of epoxidation of NR latex with preformed peracetic acid and performic acid, generated *in situ*, indicated that the formation of performic acid in the aqueous phase was the rate-controlling step in the latter reaction. The structure of products from the reaction of alkenes with formic acid and hydrogen peroxide are critically dependent upon the molecular mass of the substrate and the solubility of the epoxidized alkene. The hydrophobic nature of latex particles severely restricts the access of water and acid to rubber-bound epoxy-groups and this promotes epoxidation and retards hydrolysis⁶⁴.

1.2.3 The Characterization of Epoxidized Natural Rubber

1.2.3.1 The Measurement of Epoxy-Group Content

Several methods have been used to estimate the concentration of epoxy groups in partially-epoxidized NR^{65,66}. In early studies, the analysis of epoxides was based on volumetric methods using acidic reagents. The use of excess hydrochloric acid^{67,68} was replaced by a more rapid technique using hydrogen bromide in glacial acetic acid⁶⁹. The necessity to frequently restandardise this reagent and the production of poisonous fumes led to an improvement of the procedure in which hydrogen bromide is generated *in situ* from the reaction of perchloric acid with a bromide salt, TEAB⁷⁰. The estimation of epoxy-group content by both volumetric methods and DSC demonstrated that titrimetry yielded anomalously-low results for ENR above an epoxy-group

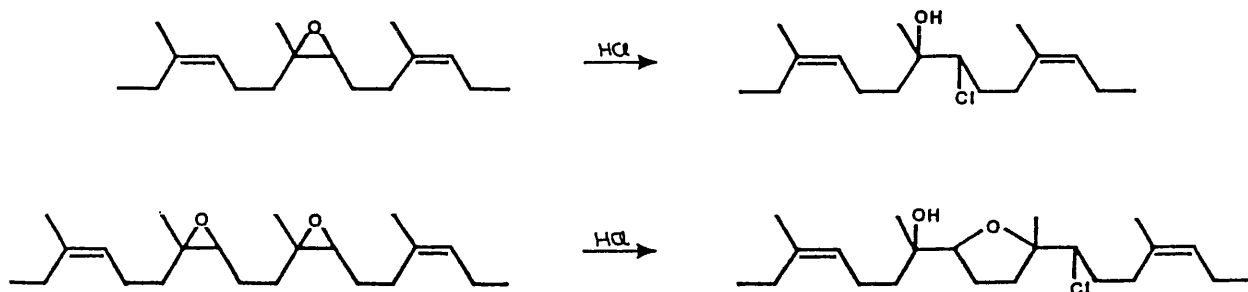
content of 10 mole%⁶⁵ (Table 1.2). This effect has been attributed

Table 1.2

The estimation of epoxy-group content in ENR by volumetric methods and DSC⁶⁵

----- Epoxy-group content (mole%) -----		
DSC	Volumetric methods	
	TEAB ⁷⁰	HCl ⁶⁷
10.0	8.7	9.9
17.0	14.0	15.5
25.0	19.6	20.5
27.5	22.7	23.5
34.5	24.5	24.5
44.0	27.0	27.0
47.0	27.5	26.0
50.0	27.0	26.0

to the preferential formation of tetrahydrofuran rings from the acid-catalysed hydrolysis of adjacent epoxidized units that is in competition with the hydrohalogenation of isolated epoxidized units (Scheme 1-5). The chemical degradation of ENR (i.e. hydrolysis with acids and subsequent cleavage of diols) has



Competition between the formation of tetrahydrofuran rings and halohydrins during the titration of ENR with acidic reagents⁶⁵

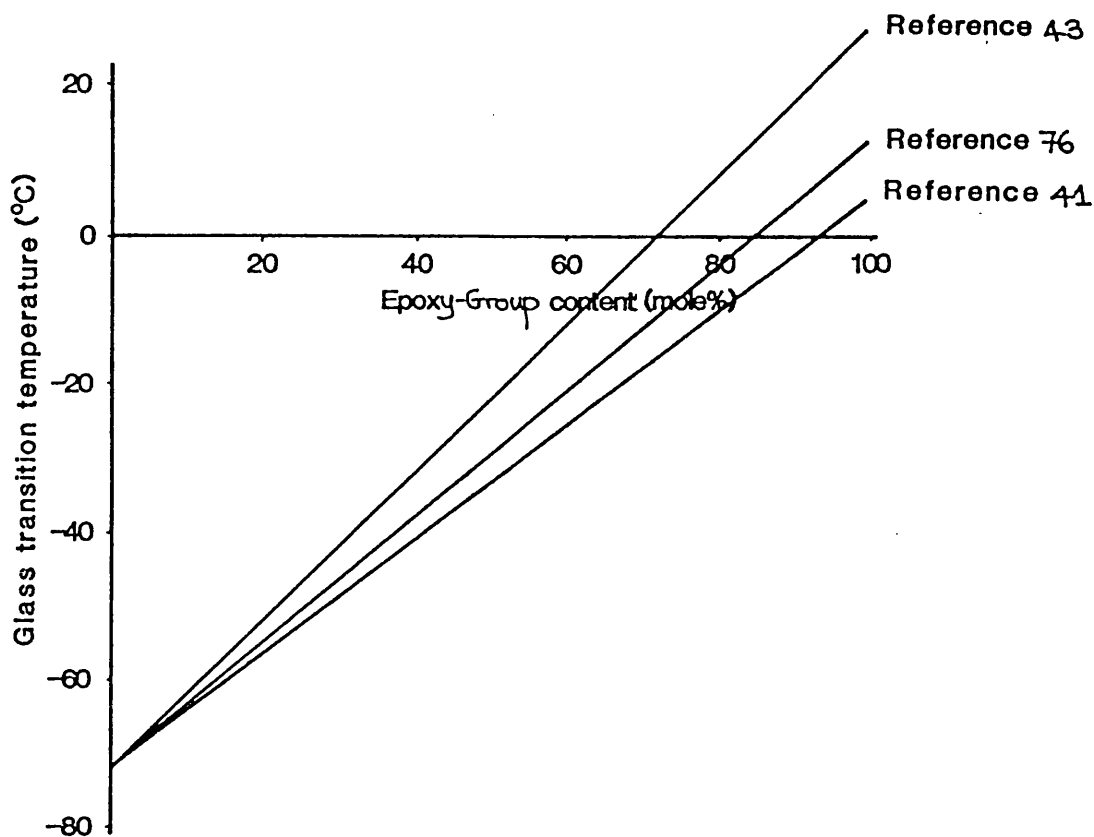
Scheme 1-5

been investigated as a method to determine epoxy-group content⁷¹.

Anomalously-low estimates were found (*cf.* spectroscopic methods) to an extent consistent with the preferential formation of tetrahydrofuran rings from adjacent epoxidized units (*Scheme 1-5*).

Elemental analysis for carbon or oxygen has been investigated as a method to analyse ENR^{38,65,66}. The technique assumes that the polymer is free of hydrolysis products and its accuracy is found to be limited by uncertainties in the oxygen content of the rubber *prior* to epoxidation. Burfield and co-workers have reported significant discrepancies between elemental analyses for carbon in samples of ENR between different laboratories⁶⁶. Many studies have demonstrated a linear dependence of T_g (measured by DSC) on epoxy-group content for ENR^{65,66,72,73}, with an approximate increase in T_g of 1°C for 1 mole% epoxy groups. The technique requires independent calibration by an absolute method (usually NMR spectroscopy) and has been claimed to be the most accurate method available, with an estimated precision of ± 0.25 mole%⁶⁶. However, the presence of other functional groups or residual solvent⁶⁵ can cause a disproportionate change in T_g ⁷⁴ and there are significant differences in the literature for the DSC calibration plot (*Figure 1.1*).

It has been suggested that density measurements are a relatively precise method to determine the concentration of epoxy groups in the absence of other functional groups due to a linear dependence of density on epoxy-group content. However, there are significant differences between results from different workers^{43,49}.

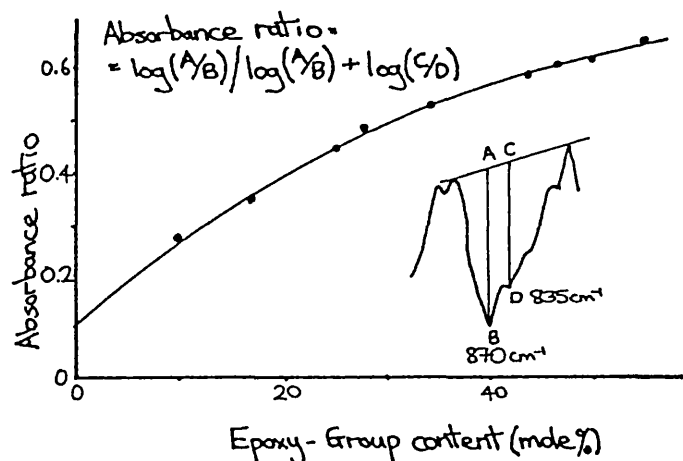


Calibration plots for the dependence of T_g on epoxy-group content

Figure 1.1

The methods discussed above are dependent on spectroscopic techniques to demonstrate that results are not distorted by the presence of other functional groups in the polymer. IR and NMR spectroscopies can be used both to measure epoxy-group content and monitor the presence of anomalous functional groups. Roux and co-workers reported characteristic infrared absorption bands for double bonds and epoxy groups at 835 and 870cm^{-1} respectively in epoxidized polyisoprenes³⁷. Davey and Loadman developed a

quantitative method to determine epoxy groups in ENR from solution or cast latex films⁶⁵ (Figure 1.2). Infrared measurements



The analysis of ENR by IR spectroscopy⁶⁵

Figure 1.2

are critically dependant on the stability of the higher and lower frequency shoulders and limited by the solubility of ENR (the preparation of ENR is usually accompanied by crosslinking) since crosslinked samples preclude the preparation of solutions and cannot be pressed into coherent films⁷⁴. Terlemezyan and co-workers showed that solvent combinations of MEK and CHCl_3 or MEK and chlorobenzene could be used to dissolve ENR and hence extended the application of IR analysis to highly-epoxidized samples which are insoluble in CDCl_3 ⁷⁵.

In the absence of secondary reaction products, $^1\text{H-NMR}$ spectra can be used to determine the concentration of epoxy groups from the relative peak area under the resonances at 2.68 and 5.12ppm that are attributable to epoxy and alkene methine protons respectively^{77,78} (Figure 3.2). The reproducibility of $^1\text{H-NMR}$ measurements was estimated to be ± 1.5 mole% for ENR in the range

of 20-75 mole%⁶⁶. Corresponding ^{13}C -NMR resonances can be used to determine the epoxy-group content of ENR^{78,79} (Figure 3.2) using quantitative acquisition parameters. The reproducibility of ^{13}C -NMR measurements was estimated to be ± 0.8 mole%⁶⁶.

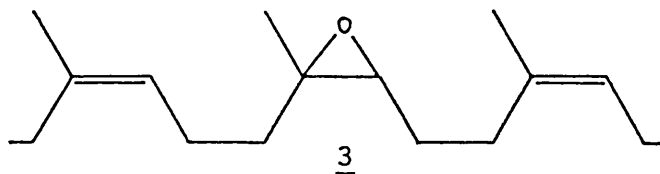
The solubility of ENR has been found to decrease with increasing epoxy-group content⁷⁸ and partial solubility is a problem in analytical work. Duch and Grant⁸⁰ showed that well-resolved ^{13}C -NMR spectra could be obtained from insoluble ENR samples, swollen in CDCl_3 .

1.2.3.2 The Microstructure of Epoxidized Natural Rubber

^1H and ^{13}C -NMR spectroscopies have been used to study both ENR^{48,65,78} and synthetic analogues^{77,79-82}. The assignment of resonances has been achieved using substituent effects⁸³, lanthanide-shift reagents⁷⁸ and spectral-editing techniques⁷⁸. Triad- and pentad-unit sequences have been invoked to explain the ^{13}C -NMR spectra of partially-epoxidized NR⁷⁸. The multiplicity of epoxy-ring carbon-resonances is consistent with diastereoisomeric pairs formed by adjacent epoxy units^{78,84} (Scheme 4-5).

NMR spectroscopy has been used to study the sequence of units in epoxidized polyisoprenes. Tutorskii and co-workers³³ used ^1H -NMR spectroscopy to investigate the microstructure of partially-epoxidized *cis*-1,4-polyisoprene and claimed that epoxidation claimed to be a non-random chemical reaction. This contrasts with ^{13}C -NMR studies of partially-epoxidized *trans*-1,4-polyisoprene occurred at alternate double bonds, 3. Epoxidation was therefore

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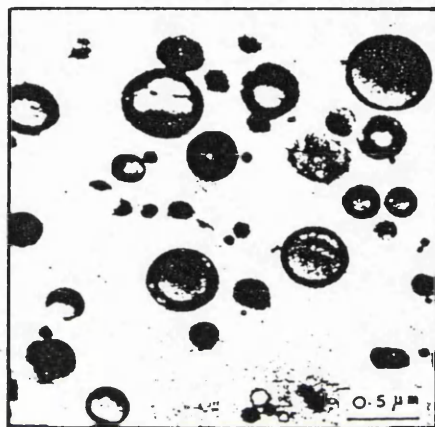


and trans-1,4-polybutadiene which indicated that epoxidation was a random chemical reaction^{81,82}. Accumulated evidence from DSC⁶⁵, volumetry with acidic reagents⁶⁵ (*Table 1.2*) and ¹³C-NMR studies⁷⁸ for ENR (in solution and latex media) indicates that epoxidation results in the random epoxidation of the available double bonds. However, electron micrographs of stained ENR latex particles were claimed to show marked chemical heterogeneity⁸⁵ (*Figure 1.3*).

1.2.4 The Physical Properties of Epoxidized Natural Rubber

Colclough³⁸ reported that fully-epoxidized NR had a comparatively low T_g (for ENR-98, $T_g = -2^\circ\text{C}$), showing that the highly-modified NR retained some rubbery properties. Peroxide-cured sheets of ENR-65 and -94 were found to have a tensile strength of approximately 15 MPa, similar to the tensile strength of a peroxide-cured sheet of NR³⁸. These results demonstrated a retention of elasticity in partially-epoxidized NR and suggested that these materials would have useful physical properties⁴¹. Subsequently, Gelling and co-workers have extensively investigated the physical properties of ENR^{6,8,41-44,76,86-91}.

Prior to 1979, the few reports on the physical properties of partially-epoxidized unsaturated elastomers gave conflicting results. Roux and co-workers³⁷ epoxidized synthetic *cis*-1,4-



Electron micrographs of stained ENR latex particles⁸⁵

Figure 1.3

polyisoprene in solution. At 10 mole% epoxy-group content, the vulcanized product had similar properties to NR; at 30 mole% epoxy-group content, the vulcanizate had a greatly decreased tensile strength and a significantly increased hardness (56%). Similarly, vulcanizates of ENR above an epoxy-group content of 20 mole% were found to show a distinct deterioration in tensile properties⁴⁸. Conversely, the epoxidation of NR and other unsaturated elastomers has been reported to improve wear, solvent resistance and to increase tensile strength in the vulcanizates⁹². Partially-epoxidized SBR was found to have

comparable tensile properties and swelling resistance to hydrocarbon oils, to vulcanized CR and NBR^{93,94}. The increase in hardness observed by Roux and co-workers³⁷ has been attributed to acid-catalysed hydrolysis and epoxy-group ring-opening during preparation to yield crosslinked products with abnormally high T_g s⁴¹.

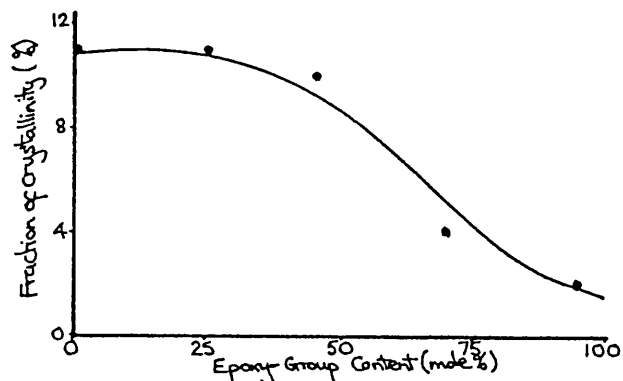
In the absence of hydrolysis, high tensile strength is retained by vulcanized ENR up to an epoxy-group content of 90 mole%⁴¹(*Table 1.3*). The high tensile strength of vulcanized NR is

Table 1.3

The physical properties of ENR vulcanizates⁴²

	NR	ENR-25	ENR-50	ENR-75
Tensile strength (MPa)	25.3	23.6	31.4	28.9
100% Modulus (MPa)	0.73	0.63	0.78	1.06
300% Modulus (MPa)	1.70	1.41	2.23	3.00
Elongation at break (%)	769	799	758	622
Hardness (IRHD)	35.5	34.5	37.0	37.0

partially attributable to strain crystallization⁹⁵. In general, the chemical modification of 1,4-polyisoprenes reduces crystallinity and hence tensile properties⁹⁶⁻¹⁰⁰. However, the retention of tensile strength, and the independence of tear strength on tear rate, suggested that strain crystallization may be retained in ENR. X-ray diffraction studies⁷⁶ demonstrated appreciable strain crystallinity in ENR up to an epoxy-group content of 50 mole% (*Figure 1.4*). The unique ability of highly-



Strain crystallization in partially-epoxidized NR

Figure 1.4

epoxidized NR to undergo strain crystallization has been attributed to the relatively small difference that epoxidation makes to the unit cell in NR (i.e. epoxidation is stereospecific⁵⁶ and the oxygen atom occupies a small volume), allowing the epoxidized units to be incorporated into strain crystals⁷⁶. The useful physical properties of ENR are largely derived from its ability to strain crystallize (*Figure 1.4*), accompanied by a progressive increase in T_g with epoxy-group content. Epoxidation improves the resistance of NR to hydrocarbon-based oils and solvents (*Table 1.4*) and ENR-50 has

Table 1.4

The swelling of rubbers in hydrocarbon oils

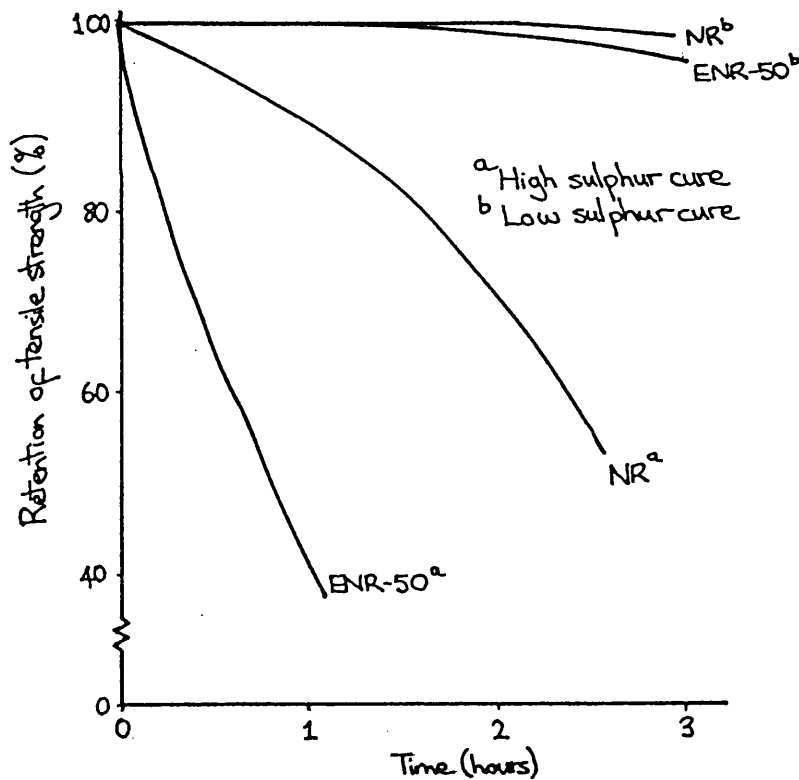
	Volume swelling (70 hours at 100°C, %)				
	NR	ENR-25	ENR-50	CR	NBR
ASTM No 1 oil	97	16	-2	3	-4
ASTM No 2 oil	141	86	13	33	6
ASTM No 3 oil	235	167	39	59	26

been proposed as a replacement for NBR in this application⁸⁶.

The gas permeability of NR is significantly reduced by epoxidation and ENR-50 has a gas permeability comparable to that of IIR and NBR^{48,86}.

A combination of improved wet-grip and rolling-resistance has been found for ENR-25 and these are desirable qualities in tyre applications⁸⁶.

ENR was expected to have superior ageing characteristics in NR due to the decrease in unsaturation. However, the vulcanization of ENR with a high sulphur content curing system was found to give a product of poor oxidizability, which hardened rapidly⁴¹ (Figure 1.5). Hardening during ageing was attributed to



The ageing of ENR vulcanizates in air at 100°C⁴¹

Figure 1.5

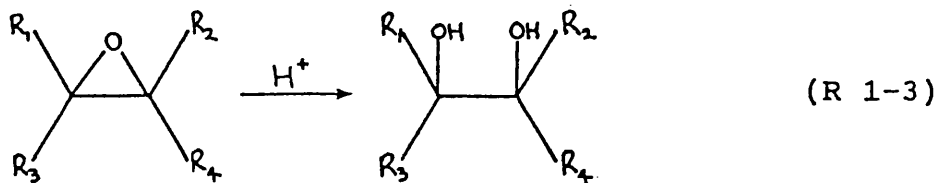
epoxy-group ring-opening by 'sulphur acids' produced by the

thermal decomposition of sulphides⁸⁹. Use of a more efficient curing system (i.e less sulphur), or the addition of sodium carbonate to cure formulations, removes the deleterious effects of ageing (*Figure 1.5*).

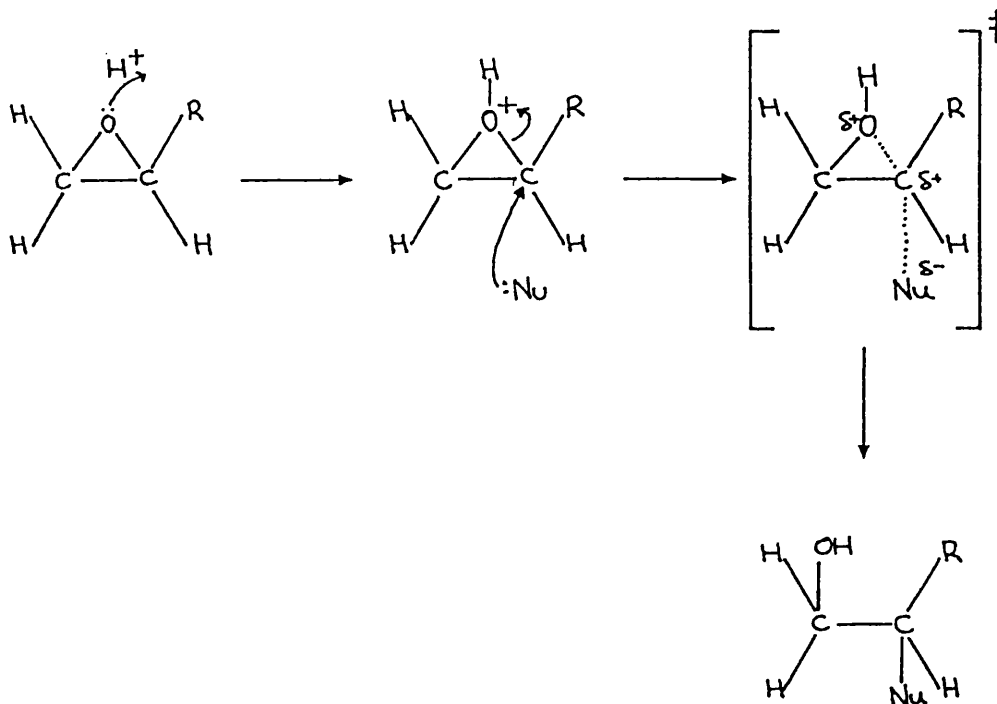
1.3 The Hydrolysis of Epoxides

The reactivity of oxiranes is due to ring strain and the basicity of the oxygen atom in the ring¹⁰¹. In acidic conditions, facile ring-opening occurs as a result of the initial protonation of oxygen. Although the mechanism is subject to debate^{102,103}, the addition of nucleophiles to epoxides is believed to proceed through a S_N2 transition state in which both partial bonds are longer than encountered in the majority of S_N2 reactions¹⁰⁴. The transition state possess considerable S_N1 character and hence this is known as the borderline S_N2 mechanism (*Scheme 1-6*). Nucleophilic attack occurs preferentially at the carbon centre most capable of stabilising the partial positive-charge generated in the transition state. Addition results at the more substituted carbon centre with inversion of configuration.

In the absence of competing counter-ions, the hydrolysis of simple oxiranes yields 1,2-diols (*R 1-3*). The rate of hydrolysis



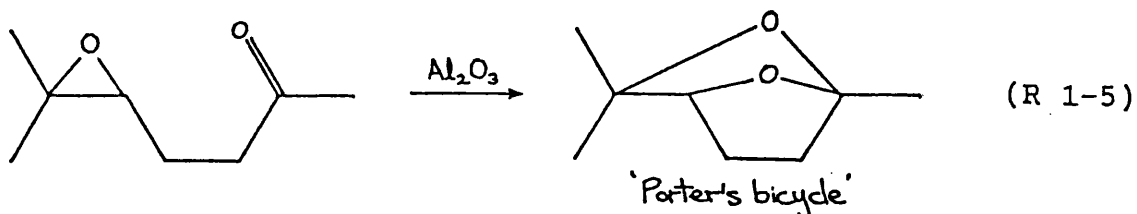
is considerably enhanced by acids. The acidic hydrolysis of trisubstituted epoxides can be complicated by skeletal carbon

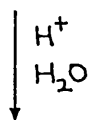
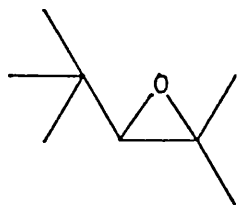


The mechanism of the addition of nucleophiles to epoxides¹⁰⁴

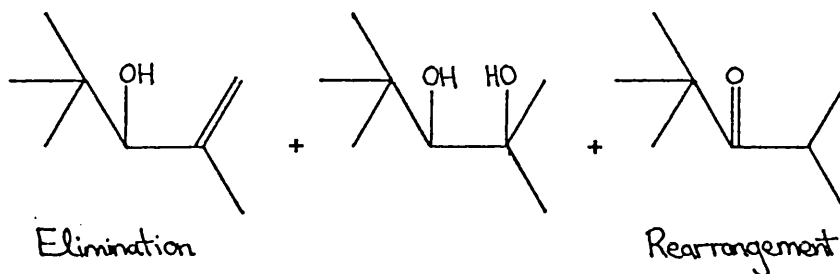
Scheme 1-6

rearrangements to yield unsaturated alcohols and ketones¹⁰⁵ (R 1-4). Neighbouring functional groups can lead to abnormal hydrolysis products; thus, whilst various workers reported the sole formation of 1,2-diols from epoxyalkenes¹⁰⁶⁻¹¹⁰, preferential **intramolecular** reactions yielding carbocyclic rings and cyclic ethers are well known^{109,111-151} (Scheme 1-7). Epoxyketones have been reported to undergo facile intramolecular cyclization in the presence of acidic catalysts¹⁵²⁻⁴ (R 1-5).

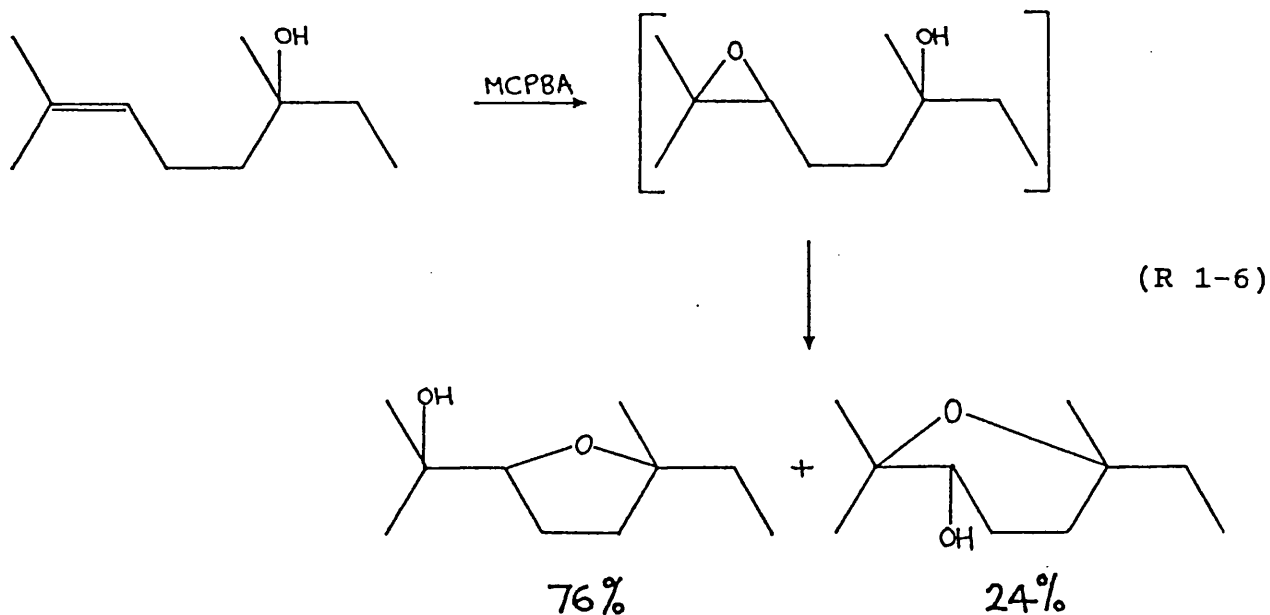




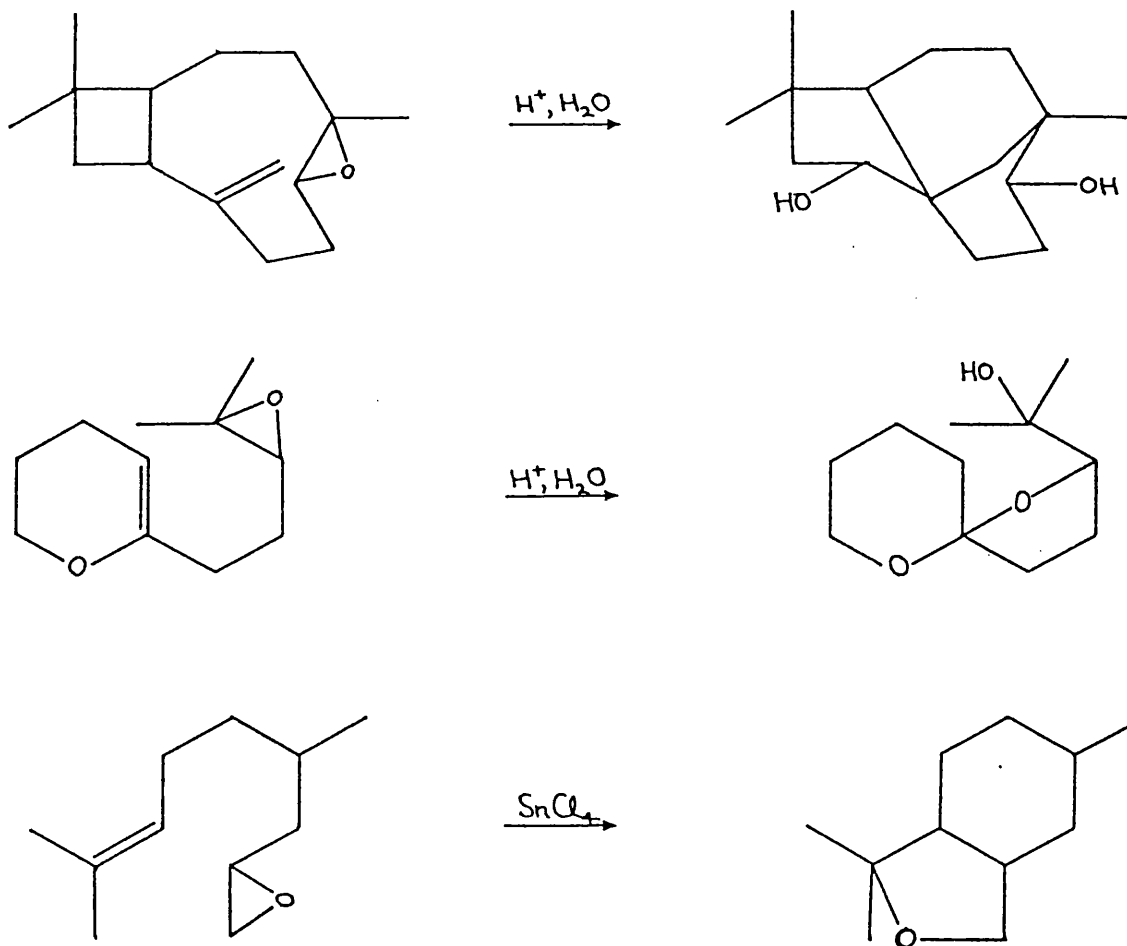
(R 1-4)



Epoxyalcohols¹⁵⁵⁻¹⁵⁷, epoxynitriles¹⁵⁸ and diepoxides^{159,160} behave in a corresponding manner. Gelling has demonstrated the predominant formation of five-membered rings from the cyclization of 3,7-dimethyl-6,7-epoxyoct-3-ol⁴² (R 1-6).



Coxon and co-workers illustrated a definite order of preference for the size of ring formed by the cyclization of

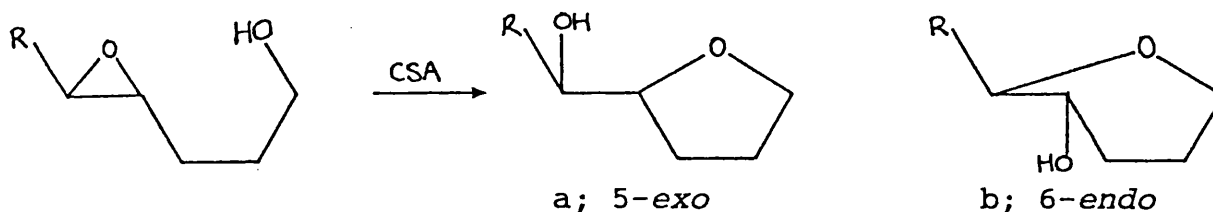


The intramolecular cyclization of epoxyalkenes

Scheme 1-7

epoxyalcohols: tetrahydrofuran > tetrahydropyran >> oxepan¹⁵⁵⁻¹⁵⁷
 and the same trend has been reported for epoxynitriles¹⁵⁸.
 Baldwin's rules for ring-closure¹⁶¹ correctly predict the size of
 the ether ring formed by the hydrolysis of epoxides in the
 majority of cases. However, alteration of the reaction
 conditions¹⁶²⁻¹⁷⁰ can promote the synthesis of disfavoured cyclic
 ethers. Nicolau and co-workers promoted 6-*endo* over 5-*exo* ring
 closure in epoxyalcohols by the addition of substituents with the
 ability to weaken the adjacent C-O bond and/or stabilise an

adjacent positive charge¹⁶⁴ (Scheme 1-8). The hydrolysis of



Substrate

Product ratio a:b

R = CH₂CH₂CO₂CH₃

100:0

R = CH=CH₂

0:100

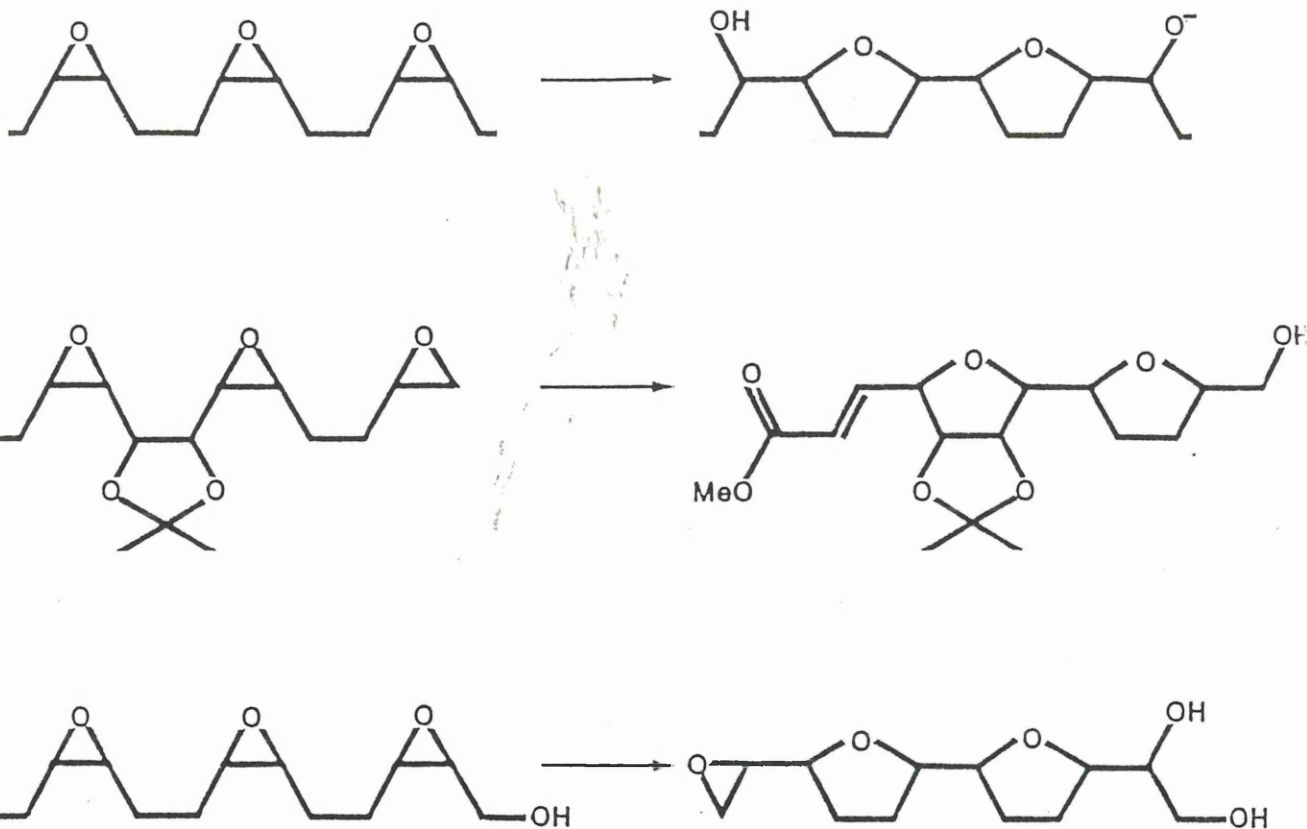
The formation of disfavoured cyclic ethers from the hydrolysis of epoxides

Scheme 1-8

triepoxides, derived from 1,5,9-triene precursors, is a 'cascade' reaction and results in the exclusive formation of tetrahydrofuran rings with terminal hydroxyl or epoxy groups¹⁷¹⁻¹⁸² (Scheme 1-9).

1.3.1 The Hydrolysis of Epoxidized Natural Rubber

Products from the acid-catalysed hydrolysis of ENR depend primarily on the acidity of the reaction and the epoxy-group content of the substrate. The preparation of ENR, in solution or latex, using peracids (preformed or generated *in situ*) yields predominantly ring-opened products unless the concentration of carboxylic acids is minimised^{16,42}. In early studies²⁴⁻³⁰, the oxidation of NR with hydrogen peroxide in acetic acid yielded resins of low molecular mass. Analogous synthetic methods are now used to directly hydroxylate double bonds^{55,183}. Milder reagent

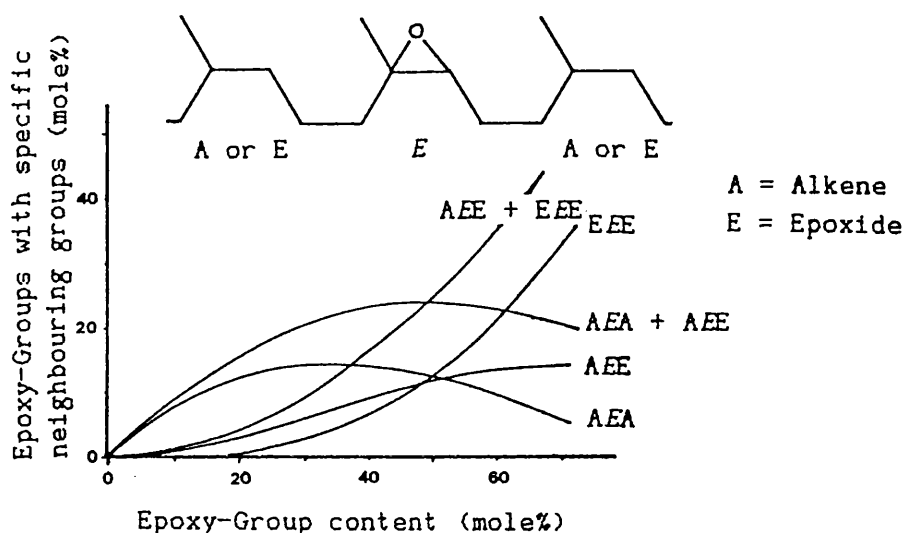


The hydrolysis of triepoxides

Scheme 1-9

systems have been used to prepare ENR up to an epoxy-group content of 100 mole%^{38,42,78}. The poor physical properties reported for vulcanized ENR above an epoxy-group content of 20 mole%^{37,48} resulted from the partial hydrolysis of epoxy groups (Section 1.2).

The epoxidation of NR has been shown to be a random chemical reaction^{65,78} (Section 1.2.3.2) and the progressive formation of adjacent epoxidized units occurs above an epoxy-group content of 10 mole%⁶⁵ (Figure 1.6). Sefton and Merrill reported the formation of tetrahydrofuran rings from the epoxidation of SBR with peracetic acid in the solid state¹⁸⁴. Polyepoxides, based on

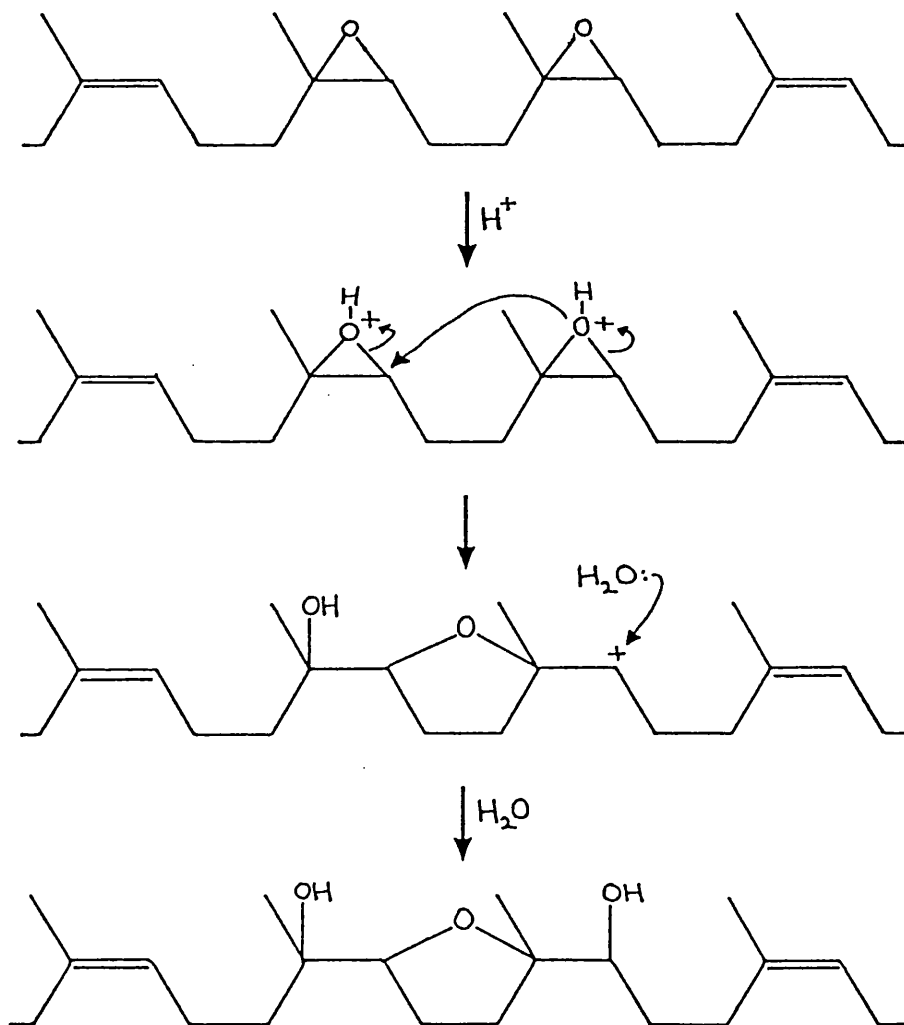


The probability of formation of adjacent epoxidized units in ENR⁶⁵

Figure 1.6

1,5,9-trienes, have been shown to yield tetrahydrofuran derivatives¹⁷¹⁻¹⁸² (Scheme 1-9). Vulcanized ENR-50 has been partially hydrolysed to yield a product with decreased tensile strength, resilience and increased hardness: the hydrolysis of ENR-100 yielded a hard thermoplastic powder (with a broad T_g commencing at 100°C) with physical properties similar to polystyrene⁴². This material was believed to contain a substantial concentration of tetrahydrofuran rings, based on ambiguous IR evidence^{40,42} (Section 4.3), and has been termed 'furanized' rubber. Gelling proposed that tetrahydrofuran rings are formed by the acid-catalysed hydrolysis of adjacent epoxidized units in an intramolecular 'zip-type' cascade reaction⁴² (Scheme 1-10).

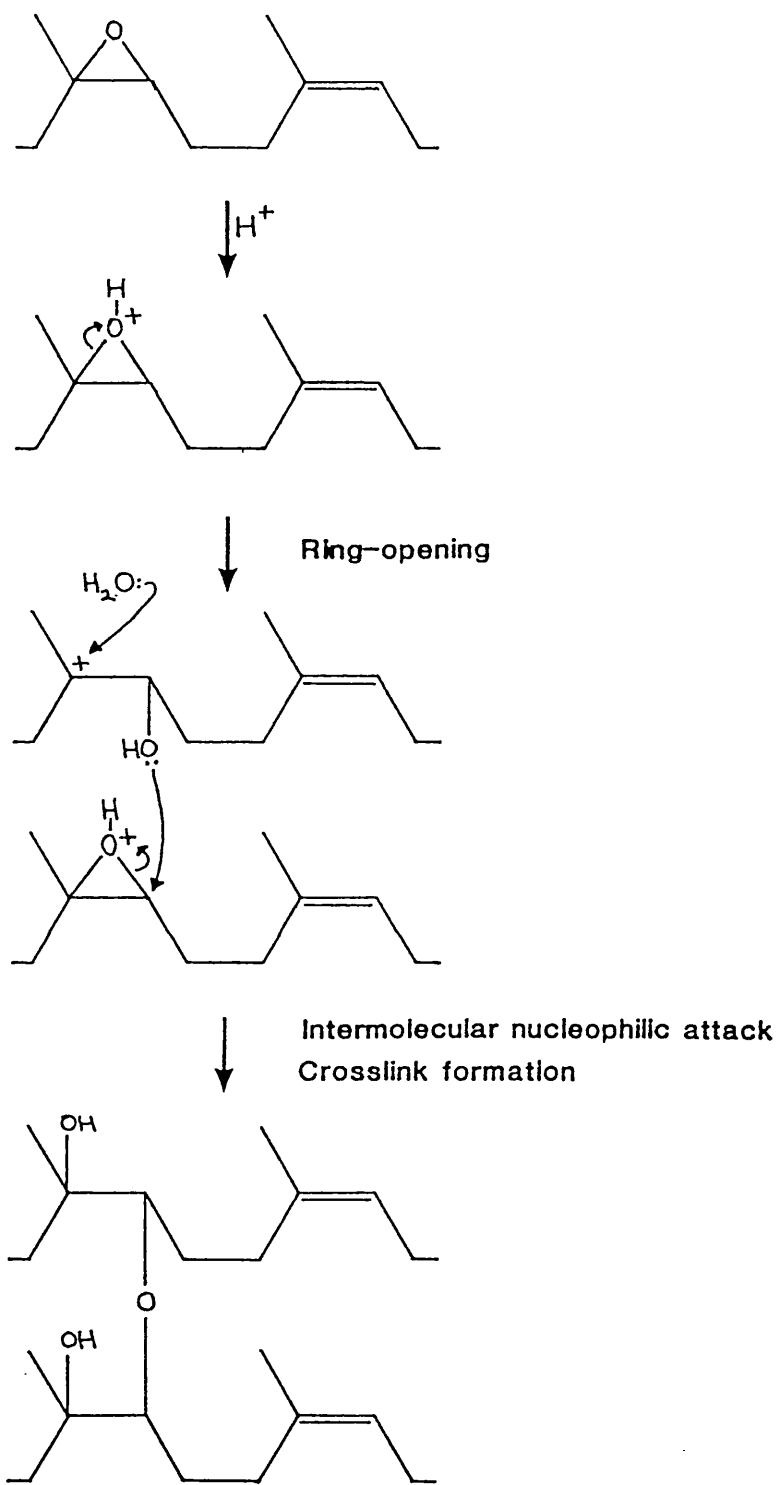
Bradbury and Perera observed that the solubility of ENR



The formation of tetrahydrofuran rings from the hydrolysis of adjacent epoxidized units

Scheme 1-10

decreased with increasing epoxy-group content⁷⁸. Other workers described the formation of gel in ENR³⁴ and epoxidized BR¹⁸⁵ on standing. This behaviour has been attributed to the formation of ether crosslinks by the intermolecular reaction of hydroxyl groups with epoxy groups^{40,93,185} (Scheme 1-11). Lee³⁴ proposed that ether crosslinks were formed by the condensation of trace amounts of hydrolytic reaction products with epoxy groups and



The formation of ether crosslinks from the acid-catalysed hydrolysis of ENR

Scheme 1-11

corresponding reactions have been observed from the hydrolysis of low molecular mass epoxides¹³. The hydrolysis of low molecular mass models for partially-epoxidized NR failed to yield acyclic ether compounds³⁴. More forcing reaction conditions resulted in the formation of a low molecular mass analogue for ether crosslinks between ENR chains⁸⁹(R 4-1).

Law⁴⁷ has shown that the hydrolysis of dialysed ENR latex with a strong base results in the formation of 2.

1.4 Objectives

The preceding discussion has demonstrated that mild reagent systems can be used to prepare partially-epoxidized NR in solution or in latex media. Nevertheless, the susceptibility of trisubstituted epoxides to be cleaved in acidic conditions can lead to the formation of ether crosslinks and/or tetrahydrofuran rings, and the hydrolysis of partially-epoxidized NR results in the formation of elastomers with impaired physical properties. The reaction of NR latex with performic acid generated *in situ* from hydrogen peroxide and formic acid has been commercially exploited to prepare two grades of rubber, ENR-25 and -50. Initial tonnage-scale batches of ENR were found to have a high gel content and an undesirably high viscosity^{45,46}, effects consistent with partial ring-opening during preparation and processing.

The primary objectives of this study are summarised below;

(a) to improve the efficiency of preparation of ENR from the reaction of NR latex with hydrogen peroxide and formic acid

(b) to investigate alternative methods of preparing ENR

(c) to establish the primary products from the acid-catalysed hydrolysis of ENR

(d) to determine the primary factors determining the extent of hydrolysis of ENR in acidic conditions

and, (e) to investigate conflicting results in the literature for the determination of epoxy groups in ENR.

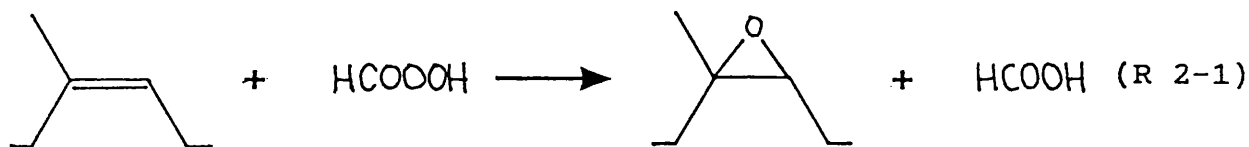
CHAPTER 2

THE PREPARATION OF EPOXIDIZED NATURAL RUBBER

The partial epoxidation of double bonds in *cis*-1,4-polyisoprenes can be achieved using a wide range of reagents (Section 1.2.1). Synthetic procedures based on the *in situ* formation of peracids are preferred on economic and safety criteria. The chemical modification of NR as dry rubber or in the latex state (*cf.* solution reactions) is preferred on economic grounds (Section 1.1); consequently, studies on the preparation of ENR were confined to methods applicable to NR latices.

2.1 The Preparation of Epoxidized Natural Rubber with Formic Acid and Hydrogen Peroxide

The double bonds in NR latices can be epoxidized using performic acid, generated *in situ* from hydrogen peroxide and formic acid^{8,44,186}(R 2-1). The reaction has been commercially



exploited to prepare two grades of rubber, ENR-25 and -50, containing 25 and 50 mole% epoxy groups respectively^{8,45}. A standard recipe for the preparation of ENR-50 from HA latex concentrates has been used in the laboratories of MRPRA for several years and results in the preparation of ENR-50 with

acceptable physical properties (Table 2.1). However, the recipe

Table 2.1

The preparation of ENR-50 latex using a standard preparative recipe

Reaction time (hours)	Molecular mass		Gel content (%w/w, THF)	Epoxy-group content (mole%) ^a
	10 ⁵ M _n	10 ⁶ M _z		
0 ^{b,c}	2.10	1.40	81	0
1	1.74	1.57	13	5
2	2.06	1.67	19	11
3	1.92	1.64	17	16
20	1.28	1.11	17	51
22	1.57	1.03	33	53
24	1.19	0.89	45	56

^a1H-NMR spectroscopy at 200MHz

^bReagent concentrations (M); Isoprene units (4.03), Formic acid (0.81), Hydrogen peroxide (3.16)

^cReaction temperature = 60°C

is inefficient and uses double the quantity of hydrogen peroxide necessary for the stoichiometric epoxidation of half of the available double bonds in NR. An economic assessment of ENR-50 production⁴⁹ showed that 41% of the total cost was due to the cost of hydrogen peroxide and formic acid. The cost of hydrogen peroxide alone constituted 30% of the total and therefore alternative approaches to the preparation of partially-epoxidized NR were investigated.

2.1.1 The Effect of Formic Acid Concentration

The rate-controlling step in the epoxidation of NR latices with hydrogen peroxide and formic acid is the rate of formation

of performic acid in the aqueous phase^{64,187} (*Scheme 1-4*). Therefore, one method of optimising the preparation of ENR-50 with an efficient usage of hydrogen peroxide is to simultaneously decrease the concentration of hydrogen peroxide and increase the concentration of formic acid. Under these conditions, the desired rate of epoxidation of NR latex may be attained, but complications may arise from the susceptibility of trisubstituted epoxy groups to acid-catalysed ring-opening reactions¹⁰⁴ (Chapter 4). Ng and Gan showed that the epoxidation of NR latices in the presence of concentrations of formic acid between 7.7 and 8.6M resulted in extensive ring-opening and *in situ* coagulation of the polymer^{40,63}. There is, however, an intermediate concentration range of formic acid (0.8-7.7M) for which studies had not been conducted prior to this work¹⁸⁸.

Initial studies on the epoxidation of NR latex in the presence of concentrations of formic acid above 0.8M were based on a recipe in which the concentration of formic acid was increased fourfold to 3.2M and the concentration of hydrogen peroxide halved. After 24 hours at 60°C, volumetric analysis indicated that the consumption of hydrogen peroxide (Section 2.5) corresponded to an epoxy-group content of 38 mole% for a quantitative conversion of hydrogen peroxide (*Table 2.2*). The high gel of the product precluded epoxy-group content estimation by ¹H-NMR spectroscopy. ¹³C-NMR spectroscopy of the product, swollen in CDCl₃ and using the methodology of Gemmer and Golub⁷⁹,

Table 2.2

The effect of the concentration of formic acid on the epoxidation of NR latex

Concentration of reagents (M)	Isoprene units (4.12) ^a Formic acid (0.81) Hydrogen peroxide (3.16)	Isoprene units (4.09) Formic acid (3.22) Hydrogen peroxide (1.58)
Apparent pH	3.8	2.4
Gel content (%w/w)	45	95
Hydrogen peroxide consumption (mole%) ^b	79	100
Epoxy-group content (mole%) ^b	56	38
Conversion efficiency (%) ^c	92	100

^aStandard recipe

^b24 hours reaction

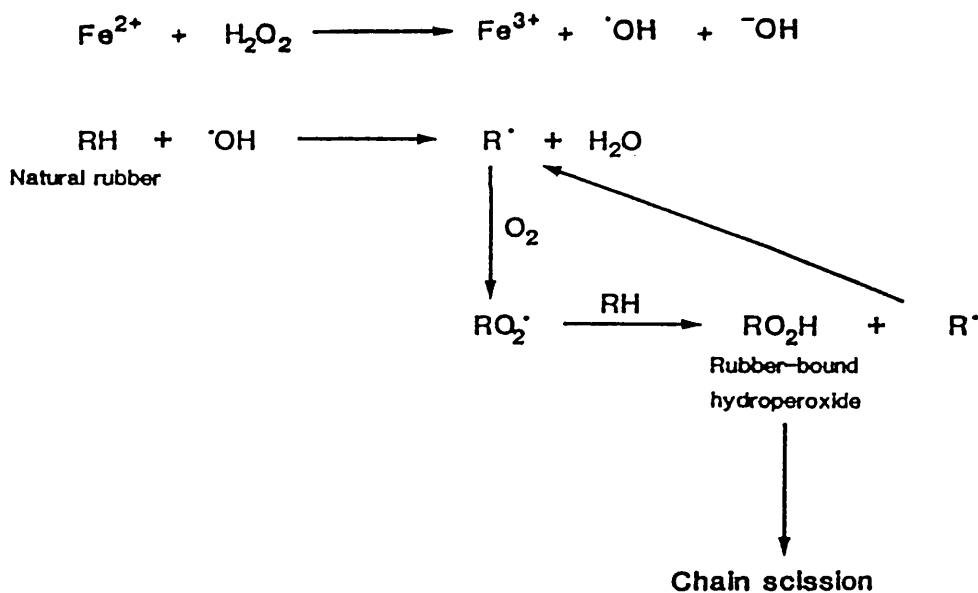
^cConversion efficiency = 100(Epoxy-group content of the polymer/Moles of hydrogen peroxide)

indicated an apparent epoxy-group content of 38 mole%[⊕] with no detectable resonances for tetrahydrofuran rings and other functional groups associated with acid-catalysed hydrolysis (Chapter 4). The results apparently indicated a quantitative conversion of hydrogen peroxide to epoxy groups; however, the high gel content in the product (95%w/w) indicated that sufficient crosslink formation occurred during epoxidation to form a tough material with an unacceptably high viscosity⁴⁵. Crosslinks could be formed during the epoxidation or by the

Footnote[⊕]

The methodology of Gemmer and Golub⁷⁹ is only semi-quantitative and results in an over-estimate of epoxy-group content (Section 3.3.2).

action of residual acid during work-up; the latter possibility was precluded by treatment of latex samples with excess base prior to coagulation of the polymer. The experiment was repeated with a sufficient increase in the concentration of hydrogen peroxide to form ENR-50 under quantitative conversion conditions. The reaction was prematurely stopped after 40 minutes due to the uncontrollable formation of foam in a highly exothermic reaction. The vigorous evolution of oxygen and steam from a reaction which reached 90-100°C, are effects consistent with the interference of iron(II) and the intervention of Fenton's Reagent in latex epoxidations¹⁸⁹ (Scheme 2-1 and Section 2.4). The rate of gas and



The intervention of Fenton's Reagent during latex epoxidations

Scheme 2-1

heat evolution were similar to that encountered for the preparation of ENR-50 under the standard experimental conditions

and in the presence of 100 ppm iron(II) (*Table 2.3*). The

Table 2.3

NR latex epoxidations with similar gas and heat evolution

Concentration of reagents (M)	Isoprene units (4.03) Formic acid (3.16) Hydrogen peroxide (2.01)	Isoprene units (4.16) ^a Formic acid (0.82) Hydrogen peroxide (3.19)
Apparent pH	2.5	6.8
Iron content (ppm)	5.4 ^b	100 ^c
Gel content (%w/w)	45	95

^aStandard recipe

^bTotal iron content by AA

^cIron (II) content

comparison suggests that the activity of Fenton's Reagent is significantly dependant upon reaction acidity.

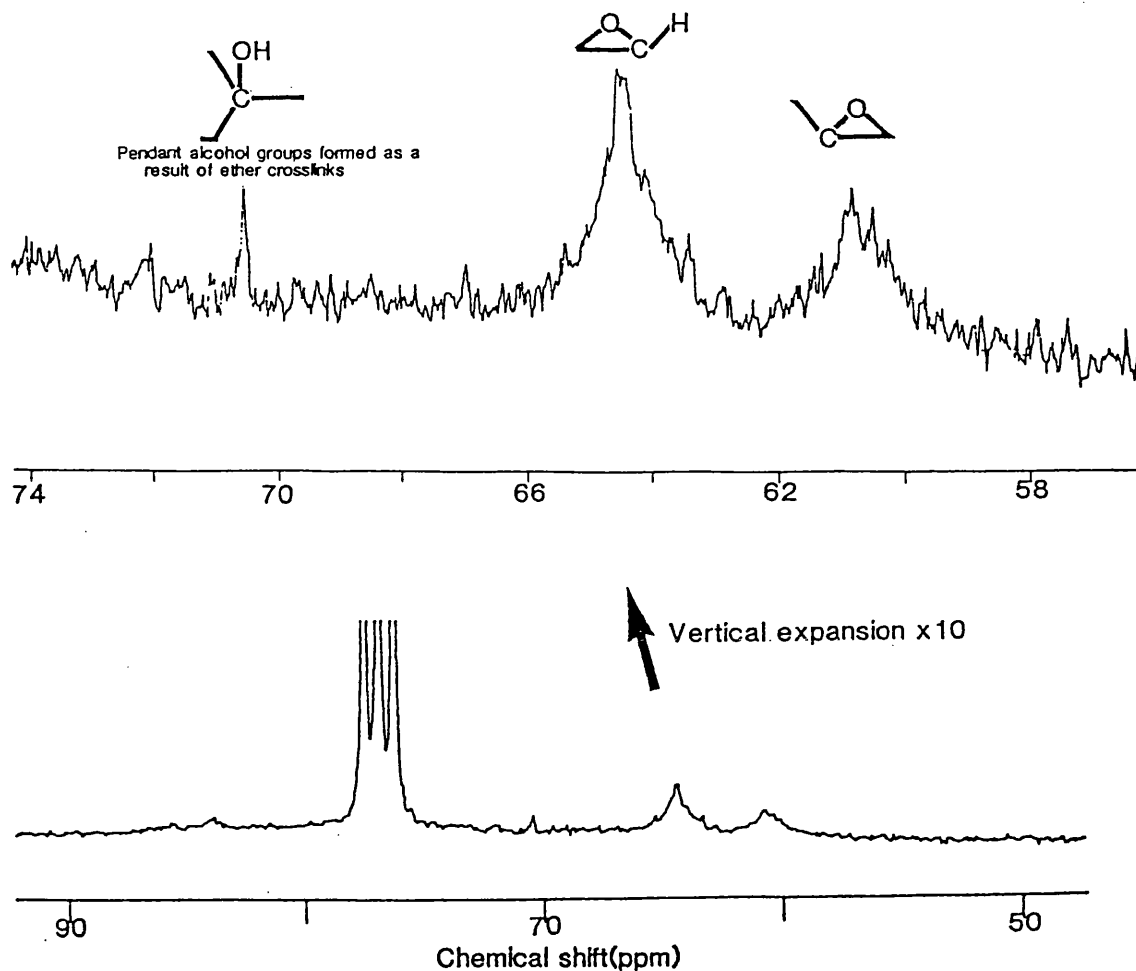
Subsequent studies used a single batch of HA latex concentrate with a total iron content (i.e. iron in all oxidation states, Section 2.4) of 5.9 ppm, corresponding to 2.7 ppm in an epoxidation reaction). A further attempt to prepare ENR-50 in the presence of 3.2M formic acid remained controllable, despite gas evolution in the initial stages and a maximum temperature of 83°C.

¹³C-NMR analysis of the product after 24 hours indicated an apparent epoxy-group content of 48 mole% and a conversion efficiency of 96%. A detailed examination of the ¹³C-NMR spectrum demonstrated that minor levels of *cis-trans* isomerization (characterized by resonances at 16 and 39-40ppm¹⁹⁰) and tetrahydrofuran rings (characterized by resonances at 83.8 and

86.2ppm, Section 4.3.2) were present in the product. Relative to analogous model reactions (Section 4.3.1), the extent of formation of tetrahydrofuran rings was minor for epoxy-group ring-opening in the presence of 4.3M formic acid. A significant peak at 70.5ppm (Figure 2.1) is attributable to a tertiary

^{13}C -NMR spectroscopy at 50 MHz

ENR-48
Minimum of 1.5% mole epoxy-group ring-opening



^{13}C -NMR resonances for ether crosslinks and epoxy groups

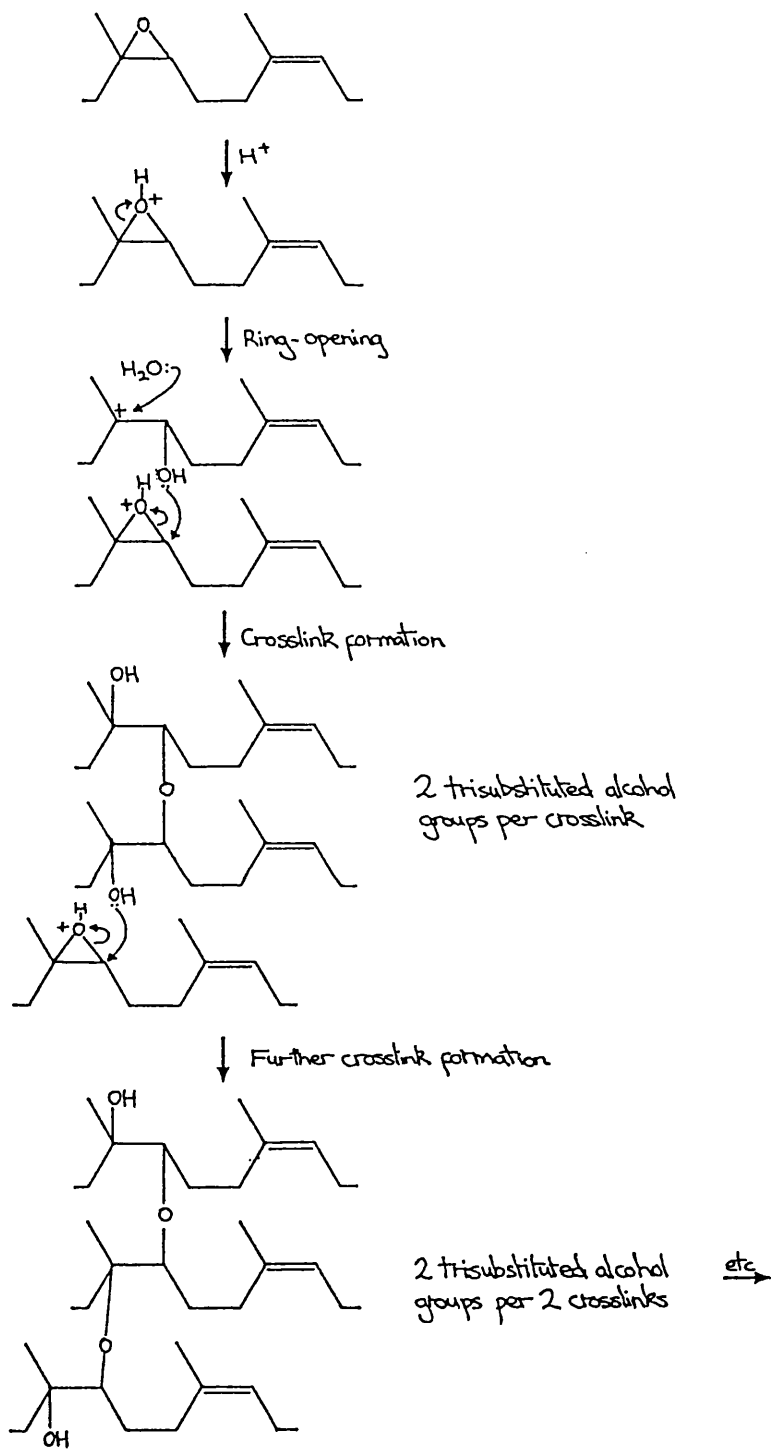
Figure 2.1

alcohol group (Section 4.4). In the absence of 2 and terminal alcohol groups arising from the formation of tetrahydrofuran rings (Section 4.3), tertiary alcohol groups can only result from the intermolecular formation of ether bonds (*Scheme 2-2*). The intensity of the resonance can be used to estimate the **minimum** extent of ether crosslinking, based on the premise that the formation of a single crosslink is accompanied by the formation of two tertiary alcohol groups (*Scheme 2-2*). The detection of functional groups at low concentrations by ^{13}C -NMR spectroscopy necessitated the use of nOe and the analytical technique is therefore only semi-quantitative (Section 3.3.2).

Using this scheme, ^{13}C -NMR analysis indicated that the product contained a minimum of 1.5 mole% ether crosslinks.

In summary, the epoxidation of NR latices at 60°C in the presence of 3.2M formic acid can be highly efficient, but results in the formation of ENR-50 with an unacceptably high gel content.

The effect of temperature was investigated as a potential method for limiting crosslink formation (*Table 2.4*). At 50°C, a significant decrease in foaming during the initial stages of reaction was accompanied by extensive gelation. After 24 hours, volumetric analysis indicated the total consumption of hydrogen peroxide; an apparent epoxy- group content of 37 mole% in the final product indicated that the reaction was inefficient (75%). ^{13}C -NMR analysis of the product showed trace amounts of both *cis-trans* isomerization and tetrahydrofuran rings and a minimum content of 0.5 mole% ether crosslinks was estimated from the relative intensity of the resonance at 70.5ppm.



The sequential formation of ether crosslinks

Scheme 2-2

Table 2.4

The epoxidation of NR latex in the presence of 3.2M formic acid^a

Time (hours)	Temperature (°C)	Molecular mass		Gel content (%w/w, THF)	Epoxy-group content (mole%) ^b
		10 ⁵ M _n	10 ⁶ M _z		
1	60	1.00	1.08	66	48 ^c
2		0.75	0.50	91	
4				98	
6				99	
24				99	
1	50	2.50	1.90	26	37 ^d
2		1.95	1.67	58	
4		0.95	0.80	90	
24				99	
1	40	2.20	2.00	34	42 ^e
2		2.45	1.80	49	
24				100	

^aReagent concentrations (M): Isoprene units (4.03), Formic acid (3.16), Hydrogen peroxide (2.01)

^b¹³C-NMR spectroscopy

^cConversion efficiency = 96%

^dConversion efficiency = 75%

^eConversion efficiency = 86%

At 40°C, complete gelation occurred after 20 hours (Table 2.4). After 24 hours, ENR-42 was formed at a conversion efficiency of 86%. ¹³C-NMR tetrahydrofuran rings; a small resonance at 70.5ppm demonstrated the presence of ether crosslinks at a concentration close to the detection limit (estimated to be 0.25-0.50 mole% for ¹³C-NMR spectroscopy at 50MHz) and the product was tough.

Overall, the epoxidation of NR latex in the presence of 3.2M formic acid results in the formation of ether crosslinks and tetrahydrofuran rings irrespective of temperature and this precludes the preparation of 'easy-processing' ENR-50⁴⁵.

A further series of experiments were conducted in the presence of 1.7M formic acid at 40-60°C to determine if crosslink formation could be limited under these conditions. Foam formation in these reactions was minimal and the rate of formation of gel was retarded (Table 2.5). ¹³C-NMR spectra of the final products

Table 2.5

The epoxidation of NR latex in the presence of 1.7M formic acid^a

Time (hours)	Temperature (°C)	Molecular mass		Gel content (%w/w, THF)	Epoxy-group content (mole%) ^b
		10 ⁵ M _n	10 ⁶ M _z		
1	60	1.65	1.69	19	12
3		1.65	1.70	26	25
5		1.40	1.33	62	30
6		1.60	1.28	57	32
24				97	40 ^c
1	50	2.40	1.43	24	5
3		2.55	1.49	21	15
5		2.40	1.43	40	21 ^d
24				95	41 ^d
1	40	2.20	1.82	34	3
2		2.20	1.75	26	8
5		2.20	1.76	36	14
24		1.55	1.10	74	33 ^e
1 ^f	60	1.75	1.57	13	5
2		2.05	1.67	19	11
3		1.90	1.64	17	16
20		1.30	1.10	17	51
24		1.20	0.89	43	56

^aReagent concentrations (M): Isoprene units (4.29), Formic acid (1.69), Hydrogen peroxide (2.14)

^b¹H- or ¹³C-NMR spectroscopy

^cConversion efficiency = 80%

^dConversion efficiency = 85%

^eConversion efficiency = 86%

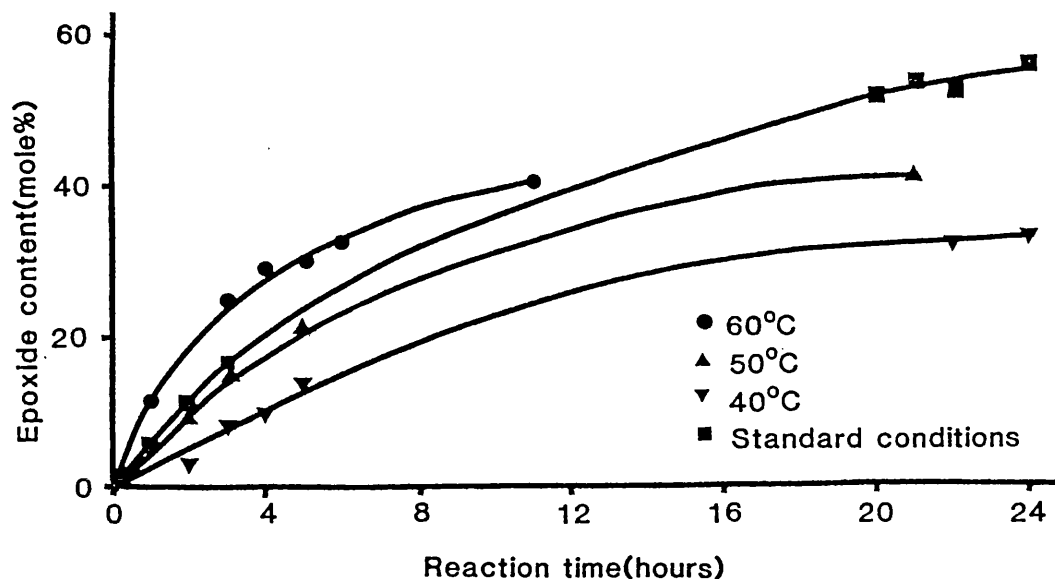
^fStandard reagent concentrations (M): Isoprene units (4.16), Formic acid (0.82), Hydrogen peroxide (3.19)

from each reaction did not contain the 70.5ppm resonance

characteristic of ether crosslinks, but only the final product from the reaction at 40°C could be described as not being tough. ¹H-NMR analysis of latex samples at intermediate reaction times was used to determine the rate of epoxidation in each reaction. A comparison of these results with the rate of epoxidation for NR latex using the standard experimental conditions (*Figure 2.2*) demonstrated that the rates of epoxidation at 40° and 50°C were inadequate (i.e. the standard recipe was established on the premise that the consequent rate of epoxidation was barely sufficient for an economically viable reaction). Furthermore, the high gel content in the final products from all epoxidations in the presence of 1.7M formic acid (*Table 2.5*) demonstrates that these experiments fail to meet the requirements for the preparation of 'easy-processing' ENR-50.

2.1.2 The Intervention of Fenton's Reagent

It is shown in Section 2.4 that adventitious iron(II) can have a significant effect upon the epoxidation of NR latex using hydrogen peroxide and formic acid. The primary effects observed are retardation of the rate of epoxidation (*Figure 2.2*) and enhanced oxidative degradation of the polymer (*Table 2.9*). It is proposed that the anomalous behaviour (i.e. gas evolution and a high exotherm) observed for latex epoxidations in the presence of formic acid above 0.8M results from the increased activity of Fenton's Reagent in high acidity regimes (Section 2.1.1). The pH dependence of the activity of Fenton's Reagent must therefore be



Relative rates for the epoxidation of NR latex

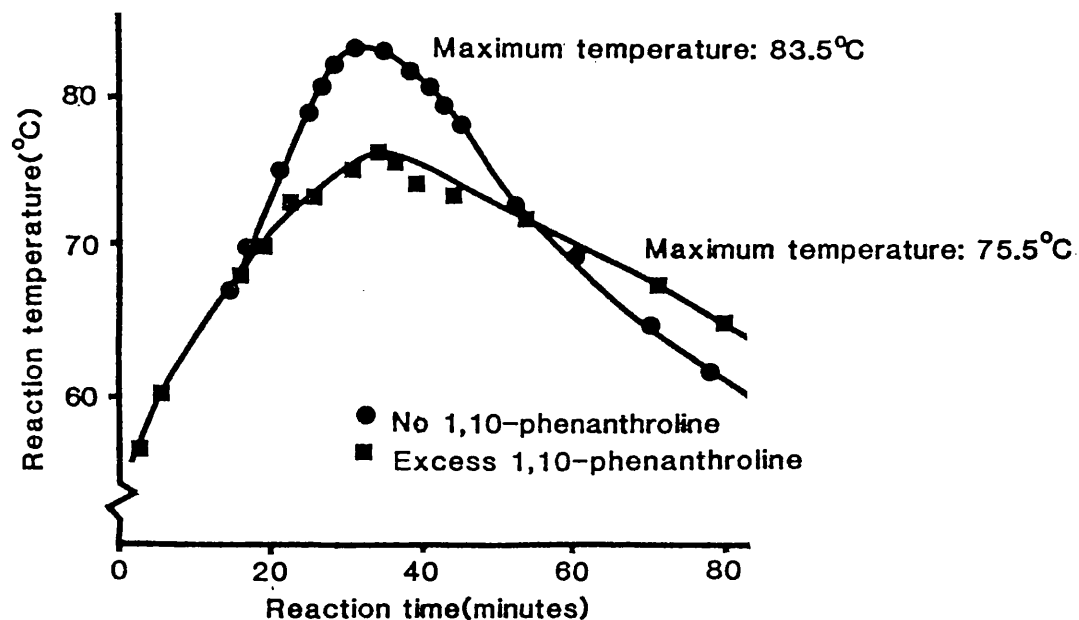
Figure 2.2

reconciled with the low concentration of **total** iron in the undoped latices used in these experiments, and the preponderance of iron(III) oxides in contaminated drums of latex (Section 2.4.4).

Experimental evidence for the presence of iron(II) in **undoped** latex epoxidations was provided by a study of the effect of added 1,10-phenanthroline. 1,10-Phenanthroline is a well known chelating agent for metal ions and was shown in control experiments to form a more stable complex with aqueous iron(II) than acetylacetone, 2,2'-bipyridine or ethylenediamine.

The attempted preparation of ENR-50 in the presence of 3.2M formic acid resulted in vigorous foaming in a highly exothermic reaction; in addition, *in situ* coagulation of the polymer after 60 minutes reaction occurred for a latex substrate containing a total iron content of 6.7 ppm. An identical reaction in the

presence of a molar excess of 1,10-phenanthroline led to a significant reduction in foaming and exothermicity (*Figure 2.3*)



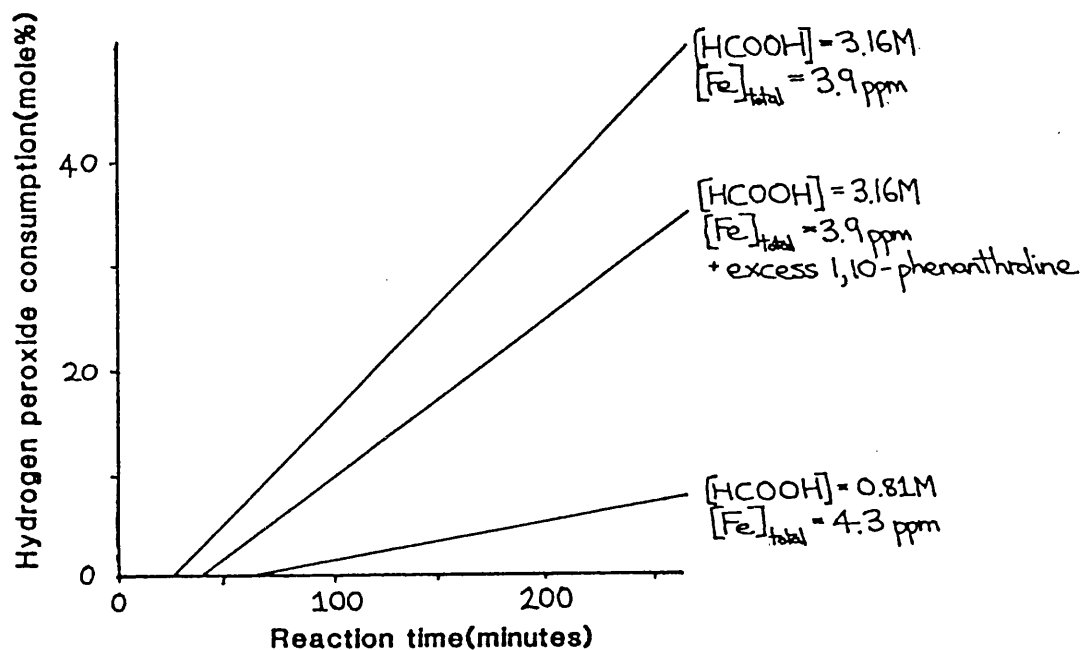
Epoxidation in the presence of 1,10-phenanthroline

Figure 2.3

and *in situ* coagulation of the polymer did not occur after several hours reaction. A less marked (but nevertheless evident) disparity in physical behaviour was observed from a corresponding pair of latex epoxidations in the presence of 1.7M formic acid.

The effect of doping latex epoxidations with 1,10-phenanthroline is consistent with retardation in the rate of decomposition of hydrogen peroxide resulting from the suppression of Fenton's Reagent by the chelation of iron(II). The suggested pH dependence for the rate of decomposition of hydrogen peroxide by Fenton's Reagent was investigated in controls (in which water was substituted for HA latex) for the preparation of ENR-50 latex. The volumetric estimation of hydrogen peroxide (Section

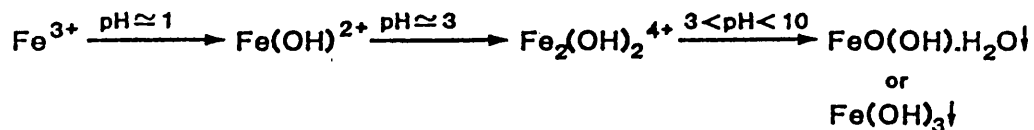
2.5) for reactions in the presence of 0.8M and 3.2M formic acid and a total iron content of 4 ppm clearly demonstrated the dependence of the activity of Fenton's Reagent on acidity (*Figure 2.4*). The rate of decomposition of hydrogen peroxide was



Control reactions for the pH dependence of Fenton's Reagent

Figure 2.4

increased by an order of magnitude for a fourfold increase in the concentration of formic acid. The reduced activity of Fenton's Reagent in more basic regimes is believed to result from the hydrolysis of iron(III) ions^{191,192} (*Scheme 2-3*). The formation of



The hydrolysis of iron(III) ions

Scheme 2-3

insoluble iron(III) oxides above a pH of 3 reduces the concentration of iron available for the generation of iron(II). The addition of a molar excess of 1,10-phenanthroline suppressed heat evolution, but failed to suppress fully the decomposition of hydrogen peroxide. It is suggested that incomplete suppression could result from two factors;

(a) the acid¹⁹³- and metal ion⁴⁴-catalyzed decomposition of performic acid

and, (b) the inability of the iron(II)-phenanthroline chelate fully to suppress the reaction of iron(II) with hydrogen peroxide.

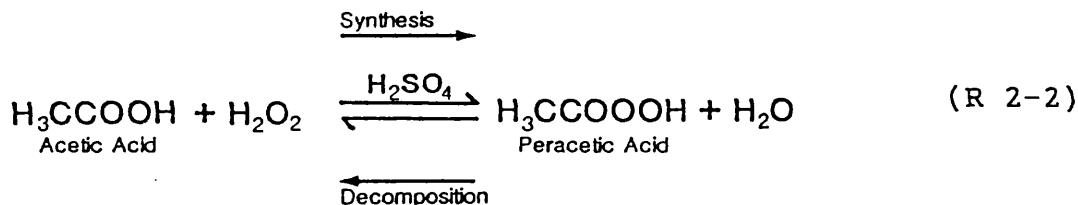
2.2 The Preparation of Epoxidized Natural Rubber with Preformed Peracetic Acid

The reaction of *cis*-1,4-polyisoprene latices with peracetic acid has been extensively studied^{42,48,59,66,76}. Epoxidation up to an epoxy-group content of 75 mole% can be achieved without accompanying ring-opening reactions; however, the acid-catalysed hydrolysis of epoxy groups can occur for reactions in which the temperature is not controlled or the concentration of peracetic acid is high⁴². The rate of epoxidation has been shown to follow second order kinetics up to an epoxy-group content of 15 mole%^{48,59}. Campbell has shown that the kinetics of epoxidation of NR latices with performic acid are dependent upon the two

phase nature of colloids⁶⁴, but this aspect of the corresponding peracetic reaction has not received attention.

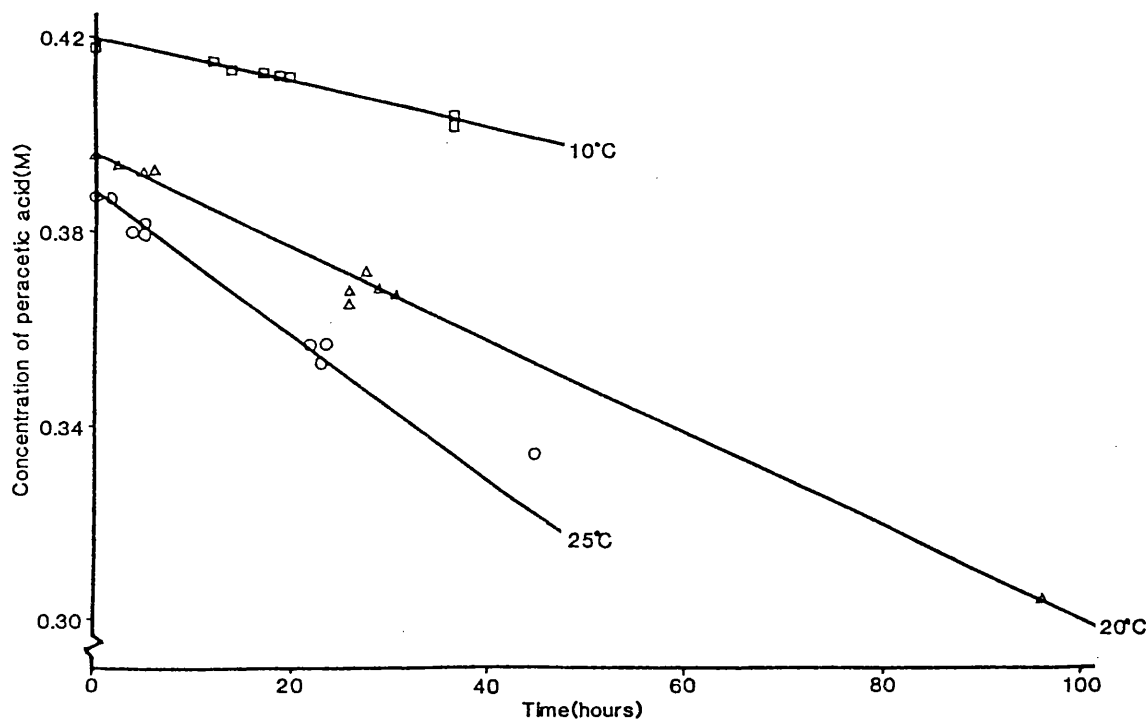
2.2.1 The Estimation and Decomposition of Peracetic Acid

Redistilled peracetic acid was supplied at an apparent concentration of 38-40% and was free of sulphuric acid. Aliphatic peracids react rapidly with iodide ions¹⁹⁴ and iodometry indicated an apparent concentration of 51%w/v for the reagent. The high estimate for peracid concentration resulted from the slow titration of hydrogen peroxide, an impurity commonly found in peracetic acid due to the method of preparation¹⁹⁵ and to the decomposition of peracetic acid (R 2-2).



Greenspan and MacKellar showed that the accurate assay of peracids could be achieved using a double titration¹⁹⁶; cerium(IV) sulphate at 5°-10°C was used to measure the concentration of hydrogen peroxide followed by iodometric estimation of the peracid. The double titration method yielded reproducible results (±1%) and showed that the peracetic acid reagent consisted of a mixture of 3.7%w/v hydrogen peroxide and 32.5%w/v peracetic acid. Hydrogen peroxide constituted 20 mole% of the reagent, accounting for the anomalous assay provided by iodometry alone.

The thermal dissociation of peracetic acid has been monitored⁶² (Figure 2.5) and it was shown that the reactions of



The decomposition of peracetic acid⁶²

Figure 2.5

peracetic acid should be studied at temperatures below 10°C to minimise dissociation. Burfield and co-workers claimed that the rate of decomposition of peracetic acid could be slowed to 2-3% per month at -20°C⁴⁸.

2.2.2 The Epoxidation of Natural Rubber Latex with Peracetic Acid

The observed lack of epoxy-group ring-opening during the epoxidation of NR latex with peracetic acid⁴² was confirmed by a

comparison of gel formation in latex epoxidations using preformed peracetic acid or performic acid, generated *in situ* from hydrogen peroxide and formic acid (Table 2.6). Epoxidation in the presence of acetic acid led to an initial loss in gel content of 15%w/w

Table 2.6

Gel formation during the epoxidation of NR latices with performic or peracetic acid

Reaction time (hours)	Epoxy-group content (mole%) ^a	Gel content (%w/w, THF)
0 ^b	0.0	60
1	26.0	43
2	31.0	47
4	34.0	49
6	36.0	43
0 ^c	0.0	81
1	5.0	13
2	11.0	19
20	51.0	17
22	53.0	33
24	56.0	43

^a¹H-NMR spectroscopy at 200MHz

^bInitial concentration of peracetic acid = 0.227M

^cReagent concentrations (M); Formic acid (0.334), Hydrogen peroxide (2.01)

and little change thereafter. In the presence of formic acid, a large reduction in gel content (58%w/w) in the initial stages of reaction was followed by a progressive increase in gel content. A significant reduction in the gel content of NR in the presence of carboxylic acids is believed to result from the disruption of a hydrogen-bonded network in the gel fraction (Section 4.2.1). Beyond the initial stages of reaction, these results are consistent with the relative dissociation constants of acetic

acid ($pK_a = 4.75$, $K_a = 1.76 \times 10^{-6}$) and formic acid ($pK_a = 3.75$, $K_a = 1.77 \times 10^{-4}$) and the dependence of ring-opening reactions on the acidity of the reaction conditions (Chapter 4). ^1H - and ^{13}C -NMR analysis of latex samples from the epoxidation of NR with redistilled peracetic acid indicated that ether crosslinks and tetrahydrofuran rings are not generally formed in the presence of acetic acid.

The preparation of ENR-50 latex using preformed peracetic acid is not considered economically viable owing to the high cost of the reagent⁴⁹. Nevertheless, this reaction was studied in order to prepare ENR samples free of ring-opened products (Section 3.4) and to investigate the kinetics of the reaction. In three experiments, the quantitative conversion of hydrogen peroxide to rubber-bound epoxy groups would have resulted in the preparation of ENR-32, -32 and -42. In previous studies, the conversion efficiency (Section 2.1.1) for hydrogen peroxide to epoxy groups has been claimed to be quantitative^{41,76} or more than 90%^{44,48}; the decomposition of peracid during the the course of reaction was attributed to adventitious transition metal ions⁴⁴. Burfield and co-workers claimed that the efficiency of epoxidation progressively decreased with increasing epoxy-group content⁴⁸. Conversion efficiencies of 89, 86 and 92% respectively were found for the final products from the experiments in this study.

Several workers have calculated second-order rate constants for the epoxidation of *cis*-1,4-polyisoprene latices with peracetic acid (Table 2.7). The epoxy-group content of intermediate samples from the epoxidations was measured by ^1H -NMR

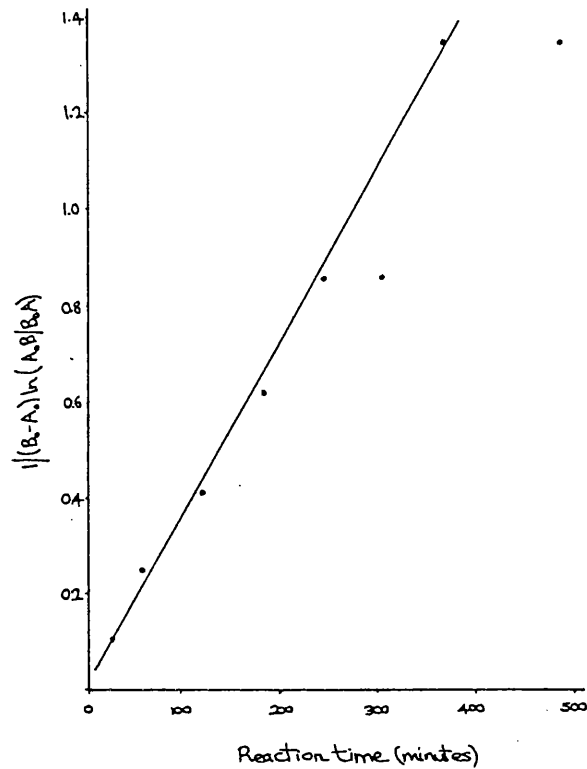
Table 2.7

Second order rate constants for the epoxidation of *cis*-1,4-polyisoprene latices with peracetic acid

Latex	Temperature (°C)	Rate constant 10^3k (l mol ⁻¹ min ⁻¹)
Natural rubber ⁴⁸	16.5	6.30
Natural rubber ¹⁹⁷	10.0	4.50
Natural rubber ⁴⁹	10.0 ^a	5.27
Synthetic polyisoprene ¹⁹⁷	10.0	5.00
Synthetic polyisoprene ⁵⁹	10.0	4.50

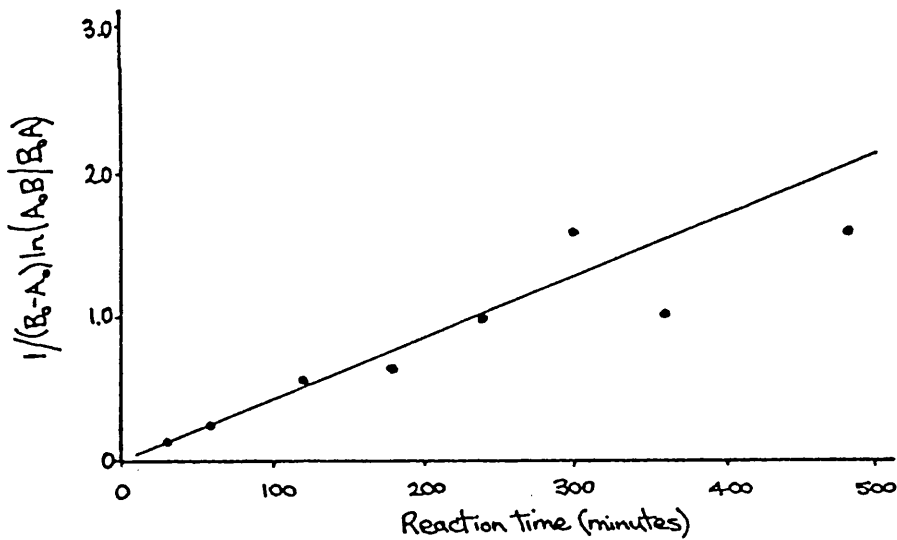
^aAssumed

spectroscopy (Section 3.3.1) and used to evaluate rate constants and used to evaluate rate constants for a reaction obeying second-order kinetics. Assuming a constant conversion efficiency for hydrogen peroxide to epoxy groups throughout the course of epoxidations, rate constants of 3.70×10^{-3} at 6.5°C and 5.30×10^{-3} l mol⁻¹ min⁻¹ at 7.5°C are observed (*Figures 2.6 and 2.7*). Within experimental error, the results indicated some deviation from second-order behaviour beyond an epoxy-group content of 20 mole%. An Arrhenius plot demonstrated that the rate constants found are consistent with previous results (*Figure 2.8*). The measurement of epoxy-group content in intermediate samples from latex epoxidations is an inaccurate method of following reaction kinetics without simultaneous measurement of the consumption of hydrogen peroxide. Accurate kinetic studies, using iodometry and autotitrimetry⁶², demonstrated that the epoxidation of *cis*-1,4-polyisoprene latices with peracetic acid in the temperature range of -5° to 15°C followed second-order behaviour up to an epoxy-group content of 10 mole%. Deviations from second-order behaviour



Second-order kinetic plot for latex epoxidation at 6.5°C

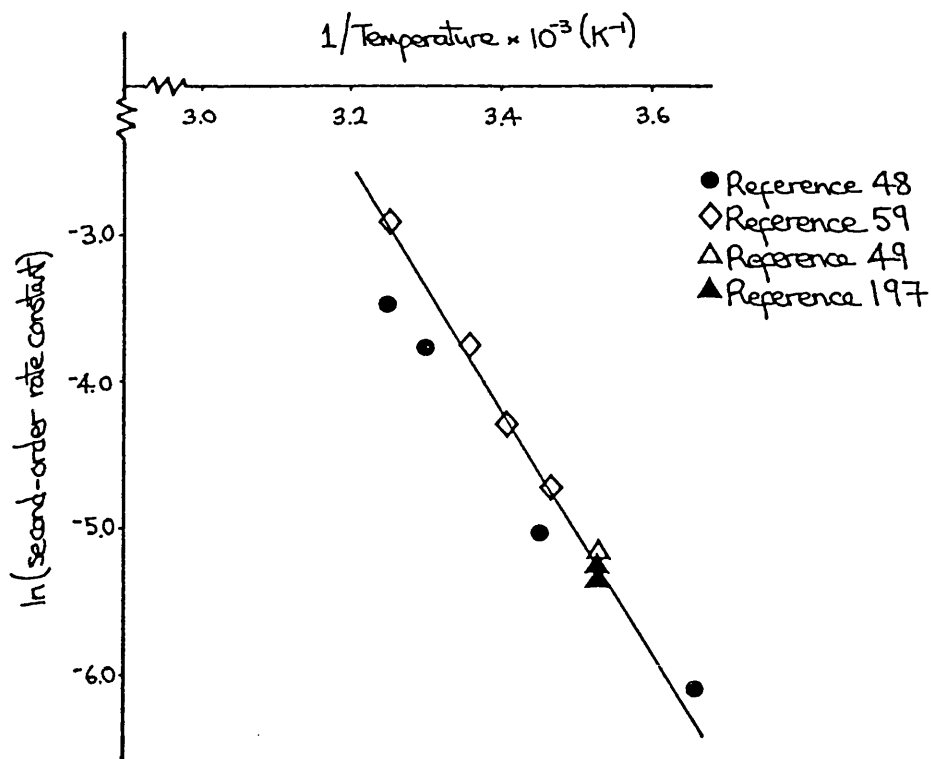
Figure 2.6



Second-order kinetic plot for latex epoxidation at 7.5°C

Figure 2.7

were shown to be associated with the strong dependence of the rate constant upon changes in the partition coefficient for



Arrhenius plot for the epoxidation of *cis*-1,4-polyisoprene latices with peracetic acid

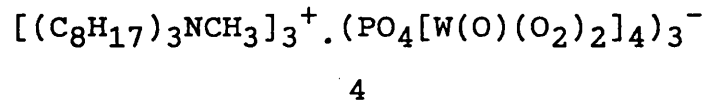
Figure 2.8

peracetic acid between the aqueous and hydrocarbon phases of latices. Model studies indicated that the partition coefficient increases by an order of magnitude as the epoxy-group content of the polymer is increased from 0 to 50 mole%⁶².

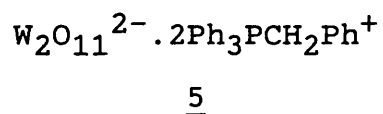
2.3 The Catalytic Epoxidation of Natural Rubber

There have been extensive studies on the epoxidation of alkenes using an oxidizing agent and an organometallic catalyst¹⁹⁸⁻²¹⁸. The majority of the catalysts are insoluble in one of the two phases that comprise latices and are therefore of little use in the epoxidation of NR latices. The failure of

hydrogen peroxide in the presence of sodium tungstate to epoxidize NR latices was attributed to the inefficient transfer of water-soluble active intermediates into latex particles⁴⁸. Jian and Hay²¹⁷ showed that SBS in 1,2-dichloroethane can be epoxidized using hydrogen peroxide and an organotungstate salt, 4. Prandi and co-workers reported the efficient epoxidation of



alkenes using hydrogen peroxide and a quaternary phosphonium pertungstate salt, 5²¹⁰. The catalyst was reported to be soluble



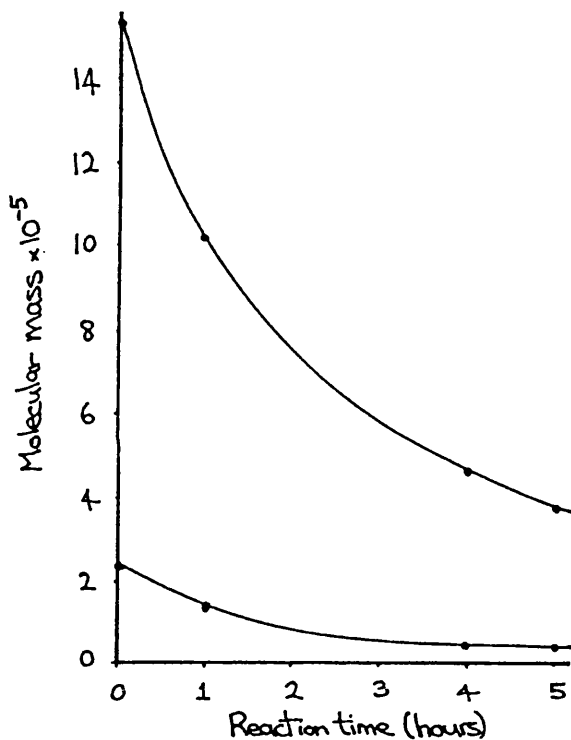
in both aqueous conditions and polar organic solvents and was therefore investigated for its potential use in the epoxidation of NR latices with hydrogen peroxide.

Above an apparent pH of 5.5, the addition of 5 to NR latices resulted in coagulation of the polymer. In acidic regimes, the latex was stable and volumetric estimation (Section 2.5) demonstrated that 38 mole% of the hydrogen peroxide was consumed after 5 hours' reaction. Intermediate samples were shown to have a minimal epoxy-group content by IR analysis⁶⁵. GPC analysis of intermediate samples demonstrated that the primary effect of 5 and hydrogen peroxide on NR latices was to promote chain scission (*Table 2.8 and Figure 2.9*). A linear correlation between the molecular mass distribution of the polymer and reaction time

Table 2.8

The effect of 5 and hydrogen peroxide on the molecular mass of NR

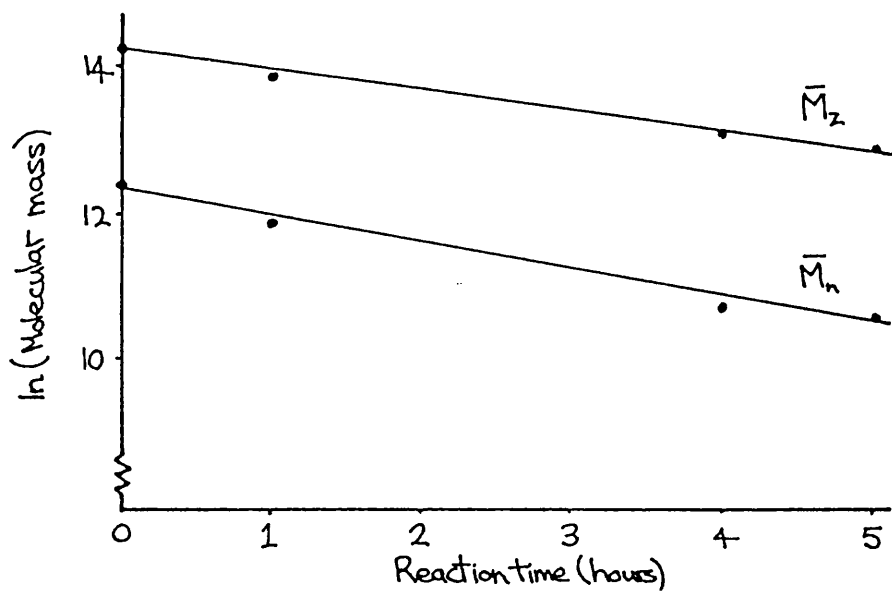
Reaction time (hours)	Molecular mass		Gel content (%w/w, THF)
	$10^5 M_n$	$10^6 M_z$	
0	2.30	1.52	60
1.0	1.40	1.02	14
4.0	0.45	0.46	4
5.0	0.40	0.37	2
6.25	0.70	0.77	13



The oxidation of NR during the catalytic epoxidation of NR latex

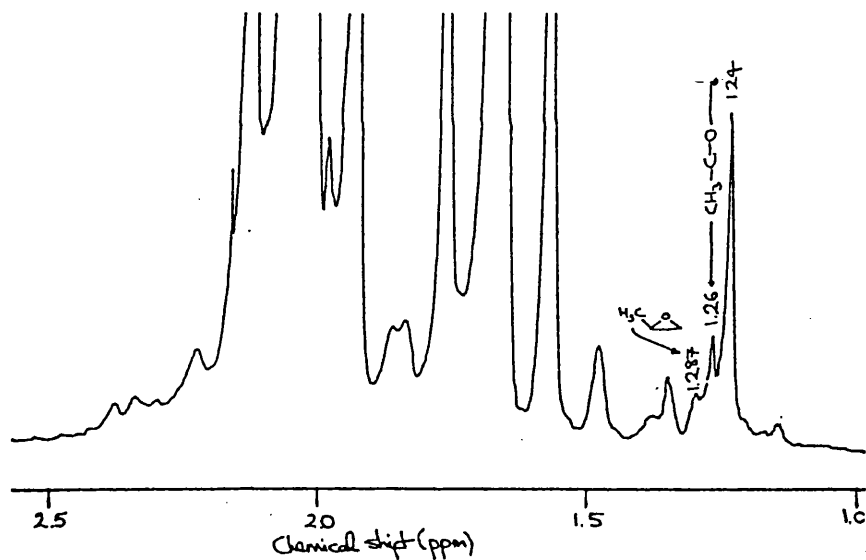
Figure 2.9

was observed (Figure 2.10). $^1\text{H-NMR}$ analysis of intermediate samples (Figure 2.11) showed new resonances at 1.260 and 1.287ppm, attributable to the methyl groups in *trans*- and *cis*-epoxidized units respectively and consistent with the chemistry



The linear relationship between oxidative scission and reaction time

Figure 2.10



$^1\text{H-NMR}$ spectrum of 'catalytically' epoxidized NR

Figure 2.11

of autoxidation (Section 3.6). A novel resonance of significant intensity at 1.24ppm is consistent with $\text{H}_3\text{C-C-O}$, but remains

unassigned at this time.

In summary, the reaction of 5 and hydrogen peroxide with NR latex does not result in the stereospecific epoxidation of double bonds, but promotes oxidative scission by an unknown mechanism.

Gelling has claimed that the treatment of NR latices with *t*-butyl hydroperoxide in the presence of sodium molybdate results in the preparation of heavily-crosslinked ENR⁴⁹.

2.4 The Effect of Adventitious Iron upon the Epoxidation of Natural Rubber Latex

In the laboratories of MRPRA, ENR-50 is routinely prepared from HA latex concentrate using a standard recipe, but significant differences in the rate of epoxidation and the epoxy-group content of the product were observed in several cases. The source of variability was found to be associated with the substrate latex rather than acid-catalysed hydrolytic reactions accompanying epoxidation¹⁸⁶ and any chemical species which varied significantly in concentration between individual batches of latex was scrutinised. NR latex concentrates of Malaysian origin are subject to strict quality control²¹⁹ and it is improbable that any chemical species which has a deleterious effect upon the physical properties of latices is not monitored prior to shipment. However, rupture of the lining in drums of latex during handling and transportation results in a considerable variation in the iron content of HA latex concentrate. Iron contents of 2-250 ppm have been recorded about a mean value of 50

ppm²²⁰ (cf. the iron content of fresh latex concentrates which varies within the range of 0.5-5.0 ppm⁴⁹).

The primary iron(III) species present in a contaminated drum of latex will be rust, which is chemically passive, and therefore iron(II) was examined as the potential source of variability. The effect of iron(II) on the epoxidation of NR latices was investigated by enhancement of the concentration of iron(II) in HA latex concentrate from a single drum. The total iron content of the latex was measured using AA and found to be 4.8 ppm. The standard AA procedure for the assay of iron content in NR²²¹ is based on the conversion of all iron present to iron(III) chloride and therefore the absolute concentration of iron in different oxidation states (commonly 0, +2 and +3) is not determined. The concentration of total iron in an epoxidation using standard reaction conditions and this latex as substrate was calculated at 2.2 ppm (calculation based on total reaction volume) and therefore assumed to be negligible. Iron(II) ammonium sulphate was used as a dopant to examine the effect of iron(II) on latex epoxidations in the range of 0-100 ppm (equivalent to 0-214 ppm in an undoped latex concentrate).

The standard preparation of ENR-50 latex is usually well behaved with the minimal formation of foam. As the concentration of iron(II) was increased, several effects were observed; foam formation, steam evolution, a decrease in the acidity of the latex serum and *in situ* coagulation of the polymer (Table 2.9). **At iron(II) concentrations beyond 50 ppm, rapid coagulation of the polymer can result in the formation of a thick film which**

Table 2.9

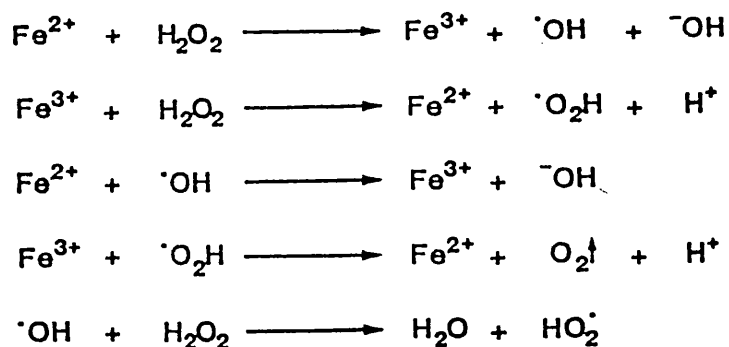
The physical behaviour of epoxidations in the presence of iron(II)

Iron(II) concentration (ppm)	Physical effects
0	Minimal foam formation A stable latex after 24 hours reaction at 60°C Apparent final pH = 3.8
10	Minimal foam formation <i>In situ</i> coagulation after 18-22 hours Apparent final pH = 4.0
50	Considerable foam formation Steam generation <i>In situ</i> coagulation after 5½ hours Apparent final pH = 4.4
50 ^a	Vigorous gas evolution Maximum reaction temperature = 75°C Final serum pH = 1.9
100	Uncontrollable foaming at the start of reaction Copious steam generation Maximum reaction temperature = 98°C <i>In situ</i> coagulation after 85 minutes Final serum pH = 6.8

^aControl reaction in which distilled water was substituted for latex

overlays the serum and prevents the escape of steam and oxygen. The resultant build up in pressure makes this reaction potentially hazardous.

Vigorous gas evolution and an increase in basicity are effects consistent with the reaction of iron(II) with hydrogen peroxide, a combination known as Fenton's Reagent. This considerably enhances the otherwise mild oxidizing power of hydrogen peroxide via the facile generation of hydroxyl radicals^{222,223} in a free-radical chain mechanism²²⁴⁻²²⁶ (Scheme 2-4). A catalytic cycle can



Free-radical generation of hydroxyl radicals

Scheme 2-4

be established which results in the regeneration of iron(II) and the catalytic decomposition of hydrogen peroxide to yield oxygen, hydroxide ions and hydroxyl radicals. Foaming in the initial stages of reaction is consistent with the evolution of oxygen and the apparent decrease in reaction acidity is consistent with the generation of hydroxide ions. Fenton's Reagent leads to the consumption of hydrogen peroxide and would therefore result in an enhanced depletion of the reagent due to competition between iron(II) and epoxidation processes. The measurement of residual hydrogen peroxide during epoxidations can be used to define a conversion efficiency by relating the consumption of hydrogen peroxide to the epoxy-group content of the polymer. It can be shown that conversion efficiencies are lowered as the iron(II) content is increased (*Table 2.10*). An increase in the concentration of iron(II) from 0 to 10 ppm results in a loss in conversion efficiency of 23 mole% over 24 hours, demonstrating the significant effect of Fenton's Reagent during latex epoxidations. At higher concentrations of iron(II), *in situ*

The consumption of hydrogen peroxide as a function of iron(II) content

Iron(II) concentration (ppm)	Residual hydrogen peroxide (mole%)	Conversion efficiency ^a Hydrogen peroxide → ENR (%)
0	21 ^b	92
10	9	69
50	48 ^c	69 ^d
50 ^e	76 ^f	
100 ^g		

^aConversion efficiency = 100(Epoxy-group content/Moles of hydrogen peroxide consumed)

^b24 hours reaction

^c24 hours reaction; *in situ* coagulation occurred after 5½ hours

^dAssumed

^eControl reaction

^fAfter 5½ hours

^gUncontrollable foaming precluded sampling

coagulation of the polymer complicates the interpretation of results, but a control reaction at an iron(II) concentration of 49 ppm (in which distilled water was substituted for HA latex) resulted in the consumption of 24 mole% hydrogen peroxide in 5½ hours.

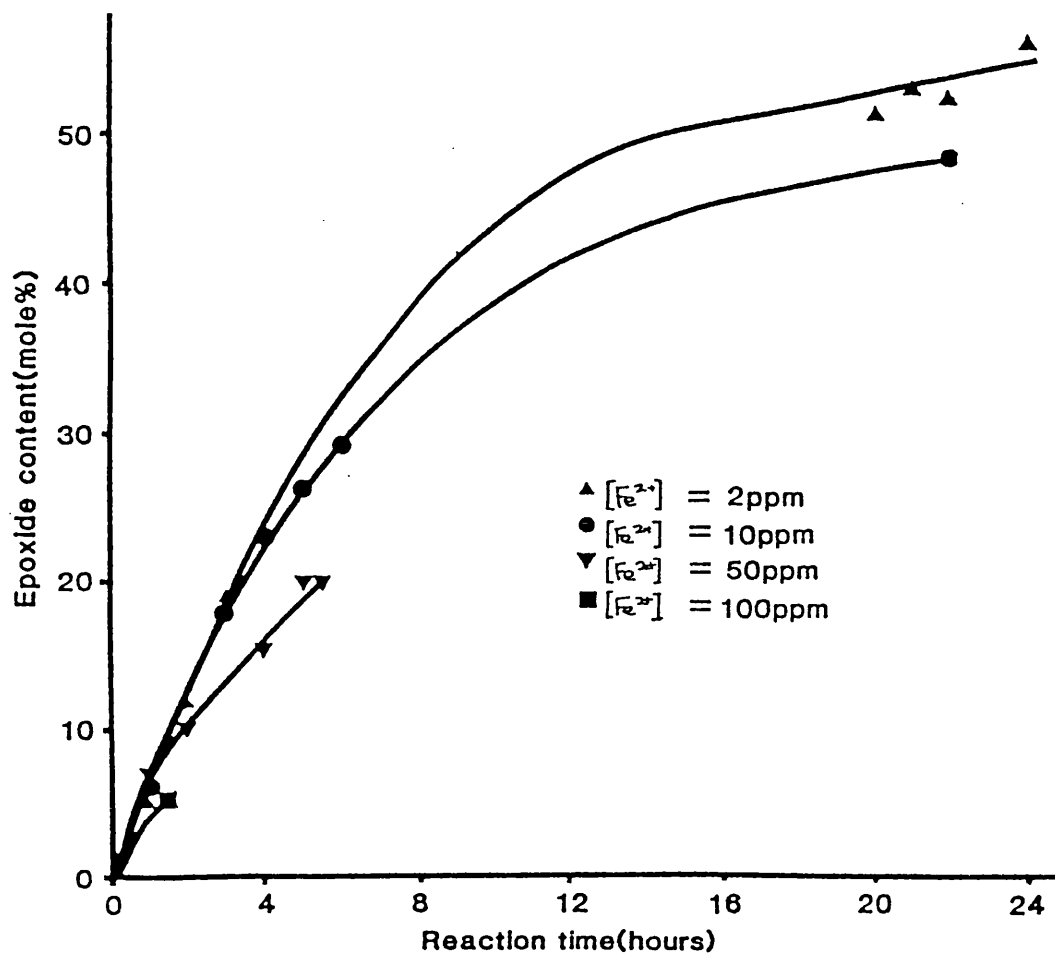
2.4.1 Fenton's Reagent and the Rate of Epoxidation of Natural Rubber Latex

The rate-controlling step in the epoxidation of NR latices using hydrogen peroxide and formic acid is the formation of performic acid in the aqueous phase^{64,187}. The reaction can be considered as pseudo first-order for hydrogen peroxide because formic acid is regenerated when the peracid reacts with the

double bonds in NR (*Scheme 1-4*). Iron(II) promotes the catalytic decomposition of hydrogen peroxide and its presence therefore results in enhanced depletion of hydrogen peroxide; furthermore, the generation of hydroxide ions will lead to the consumption of formic acid. Campbell has shown that formate ions do not promote the formation of peracid from hydrogen peroxide¹⁹³ and therefore Fenton's Reagent should retard the rate of NR latex epoxidation. The relative reaction rates for the catalytic decomposition of hydrogen peroxide and formation of performic acid should determine the maximum epoxy-group content of the polymer (in practice, the use of a large molar excess of hydrogen peroxide in the recipe for epoxidation precludes the possibility that Fenton's Reagent would prevent the ultimate formation of ENR-50). The epoxy-group content of latex samples was measured using ¹H-NMR spectroscopy (Section 3.3.1) and basic coagulation conditions were used to prevent the hydrolysis of epoxy groups. *Figure 2.12* illustrates that a progressive retardation in the rate of epoxidation occurred as the concentration of iron(II) was increased, an effect consistent with interference in the epoxidation chemistry by Fenton's Reagent.

2.4.2 Fenton's Reagent and the Oxidation of Natural Rubber

The primary application of Fenton's Reagent in synthetic chemistry lies in the facile generation of hydroxyl radicals, a powerful oxidizing agent which is capable of abstracting hydrogen atoms from most organic substrates (*R 2-3*). Fenton's Reagent has



The rate of epoxidation as a function of iron(II) content

Figure 2.12

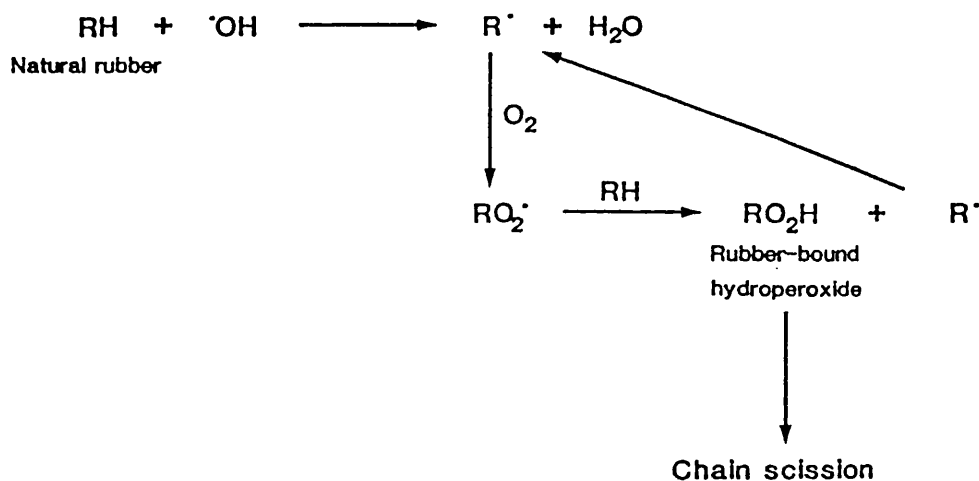
therefore been used to oxygenate many organic compounds^{225,226}. Iron(II) is also known to catalyse the decomposition of alkyl



hydroperoxides via a catalytic cycle similar to that generated by Fenton's Reagent²²². The autoxidation of NR is propagated by the abstraction of allylic hydrogen atoms and initiated by the decomposition of rubber-bound hydroperoxide groups^{227,228}.

Although the mechanism for the oxidative scission of NR chains is

unclear²²⁹, Fenton's Reagent can enhance the rate of autoxidation (Scheme 2-5) due to three factors;



Enhanced oxidation of NR with hydroxyl radicals

Scheme 2-5

- (a) the increased availability of oxygen arising from the catalytic decomposition of hydrogen peroxide
- (b) an increase in propagation rate due to the facile abstraction of allylic hydrogen atoms from NR by hydroxyl radicals
- and, (c) an increase in the overall rate of autoxidation due to iron(II)-catalysed decomposition of rubber-bound hydroperoxide groups.

Trace-metal catalysis in the autoxidation of alkenes^{230,231} and polyisoprenes has been studied. Mayo and co-workers reported the catalytic effect of transition metal ions on the autoxidation of polyisoprenes in solution²³² and Bevilacqua attributed the

rate of aerobic oxidation in NR latices to adventitious metal-ion catalysts^{233,234}. It is probable that a patented method to depolymerize NR latices with hydrogen peroxide²³⁵ operates through the catalytic effect of adventitious iron(II) and other transition metal ions.

The tacky nature of ENR which coagulated *in situ* from latex epoxidations in the presence of 10-100 ppm iron(II) is indicative of enhanced oxidative scission and this was confirmed by molecular mass and gel content data (*Table 2.11*). Iron(II) concentrations above 10 ppm promote autoxidation and eliminate the gel content of the polymer; above 50 ppm, highly depolymerized products ('liquid rubbers'²³⁶) are formed and Fenton's Reagent may therefore be promoted as a chemical method to depolymerize polyisoprene latices²³⁵.

2.4.3 Fenton's Reagent and the Destabilization of Latices

Experimental results indicated a rough relationship between the concentration of iron(II) and *in situ* coagulation of the polymer (*Table 2.9*) and the most plausible explanation for this behaviour is based on chemical degradation of the surfactant. Texofor A60 is a mixture of two polyethers and derives surface activity from the combination of a lipophilic aliphatic alkane and a hydrophilic polyether component in each molecule (*Scheme 2-6*). Alkanes are resistant to Fenton's Reagent^{225,237}, whereas aliphatic ethers readily undergo fragmentation to yield aldehydes and alcohols^{225,238,239}

Table 2.11

The effect of Fenton's Reagent on the oxidation of NR

Reaction time (hours)	Molecular mass		Gel content (%w/w, THF)
	$10^5 M_n$	$10^6 M_z$	
1 ^a	1.70	1.85	20
2	1.75	1.62	18
5	1.85	1.78	26
24	1.80	1.54	61
1 ^b	2.50	2.02	31
3	2.80	1.97	33
5	2.40	2.31	30
22 ^c	1.40	2.05	15
1 ^d	1.85	1.65	11
2	1.85	1.64	9
5	0.70	1.03	0
5½ ^c	0.45	1.44	0
1½ ^e	0.45	0.69	4

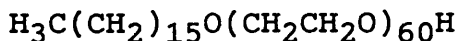
^aIron(II) content = 2 ppm

^bIron(II) content = 10 ppm

^c*In situ* coagulation of the polymer

^dIron(II) content = 50 ppm

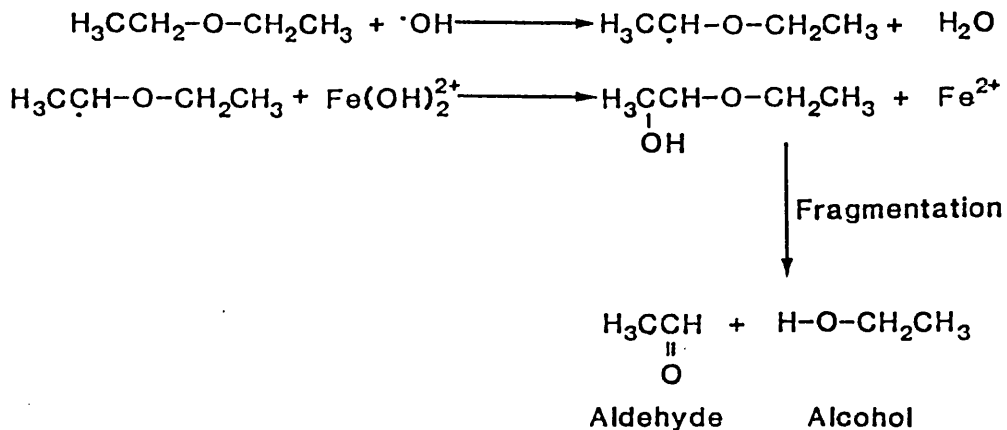
^eIron(II) content = 100 ppm



The composition of Texofor A60

Scheme 2-6

(Scheme 2-7). Chemical degradation of the surfactant was investigated through a control reaction for epoxidation in which distilled water was substituted for HA latex and the mixture for HA latex and the mixture doped with iron(II) to a concentration of 49 ppm. After 5½ hours (the time at which *in situ* coagulation occurred in the corresponding latex epoxidation), organic species



The fragmentation of aliphatic ethers with hydroxyl radicals

Scheme 2-7

in the reaction were extracted with ether and isolated to yield a waxy material. The extract did not contain Texofor A60 since it was shown that the surfactant is insoluble in ether. $^1\text{H-NMR}$ analysis of the extract showed a multiplicity of $\text{CH}_2\text{-O(H)}$ resonances between 3.65-3.69ppm (*cf.* a major resonance at 3.65ppm in Texofor A60) and several resonances between 8-10ppm in the chemical shift region characteristic of aldehydes.

The spectroscopic evidence is consistent with fragmentation of the surfactant by hydroxyl radicals, and *in situ* coagulation of polymer can plausibly be attributed to degradation of the surfactant.

2.4.4 Iron(II) Content in Drums of Latex Concentrate

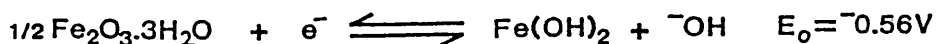
The potential of Fenton's Reagent to exert a significant effect upon the epoxidation of NR latices has been demonstrated. Determination of the concentration of iron(II) in the

adventitious iron content of latex from drums is therefore important. The standard method for the assay of iron in NR is non-specific²²¹ and in the absence of more specific data, one can only speculate upon the relative concentrations of iron(II) and iron(III) in latex concentrates. The main source of iron in latex concentrates is contamination from the inner surfaces of steel drums and probably consists of iron(III) oxides (i.e. rust). Aqueous solutions of iron(II) are susceptible to superficial oxidation by oxygen which is particularly favoured in basic regimes²⁴⁰ (*Scheme 2-8*). Neutral and acidic solutions of iron(II)

Acidic conditions:



Basic conditions:



Redox reactions for iron(II)/(III)

Scheme 2-8

oxidize less rapidly due to the formation of hydroxo complexes. The basicity of ammoniated latex concentrates would be anticipated to promote the oxidation of any iron(II) present; however, iron(II) can be generated from the reaction of iron(III) with hydrogen peroxide (*Scheme 2-4*).

2.5 The Estimation of Hydrogen Peroxide in Latex Media

The use of acidified cerium(IV) sulphate with ferroin as

indicator to assay hydrogen peroxide is a standard analytical procedure²⁴¹ and has been used to monitor the consumption of hydrogen peroxide during latex epoxidations. At room temperature, the titration has a transient colour change at the end-point and reversion is believed to result from the slow titration of performic acid. Cerium(IV) sulphate solution can be used to titrate 0.1% hydrogen peroxide in 30% peracetic acid at 0-10°C without interference from the peracid^{194,196}. Hydroperoxides are sufficiently reactive to be titrated at 0-10°C, whereas diacyl and dialkyl peroxides are passive.

Volumetric analysis of samples from a latex epoxidation demonstrated that analyses at 4-5°C and 20°C gave the same end-point if the initial colour change at 20°C was taken. Reversion occurred within 20 seconds at 20°C, whilst the end-point at 4-5°C was stable.

CHAPTER 3

THE CHARACTERIZATION OF EPOXY GROUPS IN 1,4-POLYISOPRENES

3.1 Introduction

Gelling and co-workers have shown that the physical properties of ENR are systematically changed with increasing epoxy-group content. These changes arise principally from the dependence of T_g , polarity and extent of strain crystallization on the concentration of epoxy groups^{76,87,186}. Methods to determine epoxy groups in partially-epoxidized *cis*-1,4-polyisoprenes have therefore received considerable attention^{65,66,75,242}. Many different techniques have been applied to the estimation of epoxy groups, ranging in complexity from volumetric techniques²⁴³ and density measurements⁶⁶ to ¹³C-NMR spectroscopy⁷⁹. The techniques can be conveniently grouped into two types; absolute methods which can determine epoxy groups in the absence of additional information and secondary methods which require calibration via an absolute technique. Only IR, ¹H- and ¹³C-NMR spectroscopies can be considered as absolute techniques due to the tendency of epoxy groups in ENR to ring-open in acidic conditions to yield ether crosslinks, tetrahydrofuran rings and other functional groups¹⁸⁸ (Chapter 4). Hydrolysis products can be observed by IR⁴⁰, but cannot be accurately quantified without recourse to NMR spectroscopy¹⁸⁴. Tetrahydrofuran rings have a disproportionate effect on T_g and therefore distort the estimation of epoxy groups

by DSC⁷⁴.

In the absence of other modifying groups, the estimation of epoxy groups in *cis*-1,4-polyisoprenes should be easy using the available techniques. However, a review of the literature reveals inconsistencies in the procedures, especially with respect to calibration data for DSC. A measure of the discrepancies observed between different techniques is illustrated in *Table 3.1* for

Table 3.1

The estimation of epoxy groups in sundry samples of ENR

Epoxy-group content (mole%)		
IR ^a	DSC ^b	¹ H-NMR ^c
4	5	5
6	7	6
10	10	14
13	14	15
17	16	18
19	15	23
24	18	26
25	24	29
37	37	48
40	37	48
47	44	51
48	46	53
50	46	56

a ± 0.5 mole%⁷⁵

b ± 0.25 mole%⁶⁶

c ¹H-NMR spectroscopy at 200MHz; ± 1.5 mole%⁶⁶

sundry samples prepared in our laboratories. Some effort has therefore been made to produce reliable and reproducible methods to estimate epoxy groups in ENR.

The chapter closes with a section on the characterization of epoxy groups formed during the autoxidation of *cis*-1,4-

polyisoprenes. The formation of both *cis*- and *trans*-epoxy groups during autoxidation has important implications for the ageing of NR.

3.2 The Estimation of Epoxy Groups by Volumetric Methods

Initial studies on the measurement of epoxy groups in ENR were based on the application of titrimetry to low molecular mass trisubstituted epoxides. The direct titration of epoxides with hydrogen bromide in glacial acetic acid^{69,244} was attempted, based on the applicability of the method to ENR^{35,245}. This approach was abandoned owing to the instability of the reagent and the frequent need for restandardisation. An improved procedure which generates hydrogen bromide *in situ*⁷⁰, was found to accurately determine the concentration of cyclohexene oxide in solution, provided that the correct end-point colour of the indicator, Crystal Violet, was used²⁴⁶. A series of titrations indicated that accurate assays were ensured by a colour change of grey to green at the end-point (*Table 3.2*). The procedure was not extended to ENR owing to the poor solubility of many samples and the availability of less tedious spectroscopic techniques. Subsequent studies⁶⁵ unambiguously demonstrated the limited scope of volumetric methods, based on acidic reagents, to analyse ENR. Above an epoxy group content of 10 mole%, there are sufficient epoxy groups to result in the formation of adjacent epoxidized units and the consequent promotion of preferential ring-expansion reactions in the presence of acidic

Table 3.2

The volumetric estimation of epoxy groups

Indicator colour change	Apparent quantity of cyclohexene oxide (moles x 10 ⁴) ^{a-c}
Blue to Grey	9.73
Grey to Green	9.77
Green to Yellow	9.88

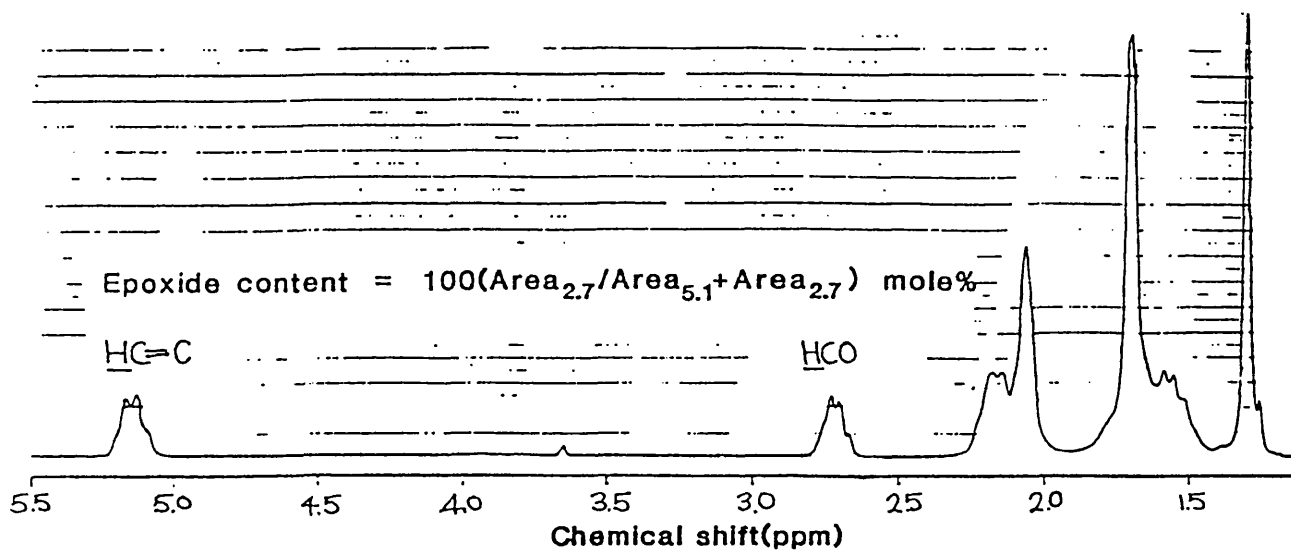
^a99% by GLC
^bActual quantity = 9.770x10⁻⁴ moles (by mass)
^cMean results from several titrations (±0.02x10⁻⁴ moles)

reagents (*Scheme 1-5*).

3.3 The Estimation of Epoxy Groups by NMR Spectroscopy

3.3.1 ¹H-NMR Spectroscopy

The estimation of epoxy groups by ¹H-NMR spectroscopy is based upon the relative areas under the resonances at 2.68 and 5.12ppm attributable to the epoxy (HC-O) and alkene (HC=C) methine protons in partially epoxidized NR⁷⁷ (*Figure 3.1*). This method is claimed to be accurate to ±1.5 mole% over the range of 20-75 mole%⁶⁶. Quantitative ¹H- NMR acquisition parameters were determined by the initial measurement of the 90° pulse width (8μs) and the subsequent determination of T₁ for each resonance using an inversion recovery experiment²⁴⁷. Typical relaxation rates for ENR-50 are collated in *Table 3.3* and the most inefficient relaxation occurs for the alkene methine proton at T₁ = 1.3 seconds. Relaxation rates were found to be relatively independent of epoxy-group content. A standard set of NMR



The estimation of epoxy groups by $^1\text{H-NMR}$ spectroscopy

Figure 3.1

Table 3.3

Typical spin-lattice relaxation rates for ENR-50^a

$^1\text{H-NMR}$ resonance	Chemical shift (ppm)	T_1 (seconds)
$\text{H}_3\text{C-CO}$	1.287	0.988
$\text{H}_3\text{C-C=}$	1.67	1.002
$-\text{CH}_2-$	2.0-2.3	0.849
HC-O	2.68	1.220
HC-C=	5.12	1.294

^aFor 1%w/v solutions of sol fractions in CDCl_3

acquisition parameters was compiled, based primarily on the criterion that the minimum delay-time between pulses for the recovery of 99% magnetization can be calculated for any desired pulse angle (Eq 3.1).

The application of $^1\text{H-NMR}$ spectroscopy at 200MHz, using quantitative acquisition parameters, to various samples of ENR gave the results collated in Table 3.1. The divergence between

$$M_0 - M_z = M_z(1 - \cos\theta)\exp(-t/T_1)$$

$M_0 - M_z$ = residual magnetization
 θ = pulse angle
 t = delay-time between pulses
 T_1 = spin-lattice relaxation time

Then, for the recovery of 99% magnetization;

$$0.01 = (1 - \cos\theta)\exp(-t/T_1)$$

(Eq 3.1)

assays by IR/DSC and ^1H -NMR spectroscopy respectively, generally increases with a progressive increase in epoxy-group content and this effect will be discussed further (Section 3.4).

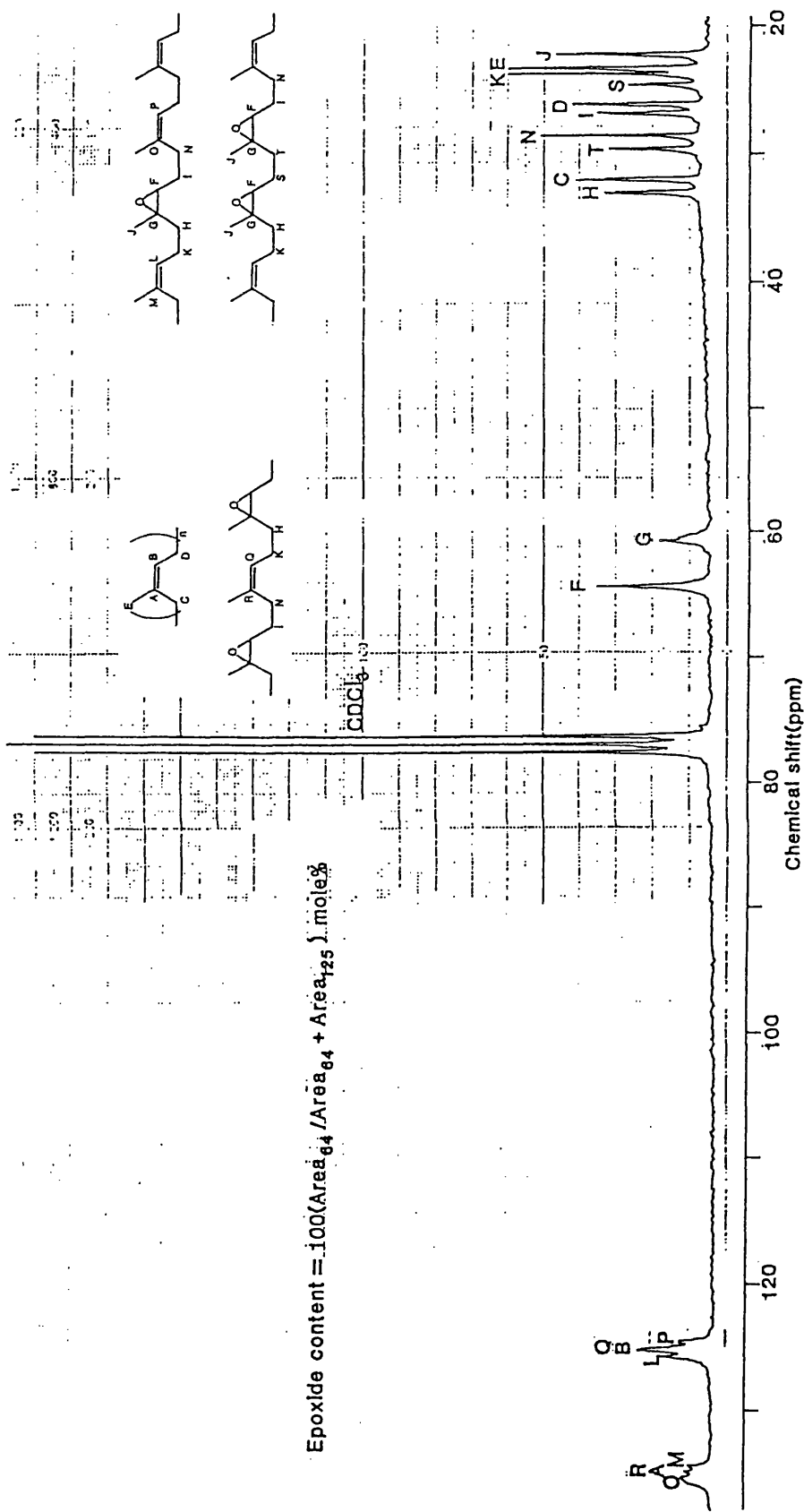
3.3.2 ^{13}C -NMR Spectroscopy

^{13}C -NMR spectroscopy is not routinely used for determining epoxy group-content in partially epoxidized *cis*-1,4-polyisoprenes, due to the prolonged time required to acquire spectra with an acceptable signal-to-noise ratio under quantitative acquisition conditions. ^{13}C -NMR spectra can be made quantitative if two criteria are satisfied;

- (a) the delay-time between pulses must be sufficient to allow full recovery of magnetization. The latter is ensured by the determination of T_1 rates and the calculation of appropriate acquisition parameters (Eq 3.1).
- (b) the enhancement of ^{13}C -NMR peak intensities arising from continuous broadband-decoupling and the consequent nOe must be suppressed. nOe can theoretically enhance ^{13}C -NMR peak

intensities by a factor of three. nOes can be suppressed by the use of inverse-gated decoupling which eliminates both nOe and C-H scalar coupling²⁴⁸.

The need to satisfy both criteria means that the acquisition of quantitative ¹³C-NMR spectra is impracticable; ¹³C-T₁ rates can be highly inefficient, especially for quaternary carbons, and nOe suppression can reduce peak intensities by 67%. It is not therefore surprising that previous studies have used simplifying assumptions in order to acquire 'quantitative' ¹³C-NMR data in a practicable time. Gemmer and Golub considered the use of paramagnetic relaxation-reagents to shorten T₁ rates²⁴⁷, but advised against their use in the absence of inverse-gated decoupling⁷⁹. The cluster of resonances attributed to alkene (=CH) and epoxide (OCH) carbons (at chemical shifts in the region of 125 and 64ppm respectively) were claimed to possess both full nOe and efficient T₁ rates, and in these circumstances quantitative data can be acquired using a short delay-time between pulses and continuous broadband-decoupling⁷⁹. The determination of epoxy-group content is then based upon the relative peak areas under the resonance clusters attributed to =CH and OCH resonances (*Figure 3.2*), in a manner akin to that used for ¹H-NMR spectra. This approach has been universally adopted^{63,65,66,72,78,242} in the absence of available values for T₁ and nOe. ¹³C-T₁ and nOe values for the resonances of interest in ENR-50 were determined using standard NMR experiments (*Table 3.4, Figure 3.2*). The results indicate that whilst all the



Epoxy-group estimation by ^{13}C -NMR spectroscopy

Figure 3.2

Table 3.4

T_1 and nOe values for alkene, epoxy and methylene resonances in ENR-50

Resonance ^a	Assignment	T_1 ^b (seconds)	nOe
F	CH(E) ^c	0.905	1.73
B,Q ^d	CH(A) ^e	0.635	1.43
H	CH ₂ (E)	0.565	1.47
I	CH ₂ (E)	0.480	1.70
K	CH ₂ (A)	^f	1.94
N	CH ₂ (A)	0.460	1.99
S	CH ₂ (E)	0.235	1.99
T	CH ₂ (E)	0.575	1.99

^aAssignments illustrated in *Figure 3.2*

^b ± 0.005 seconds

^c(E) = epoxidized unit

^dOverlapping resonances

^e(A) = alkene unit

^fAnomalous result

resonances of interest have T_1 rates of less than 1 second, the variation in nOe will result in the inaccurate determination of epoxy-group content if continuous broadband-decoupling is employed during spectral acquisition.

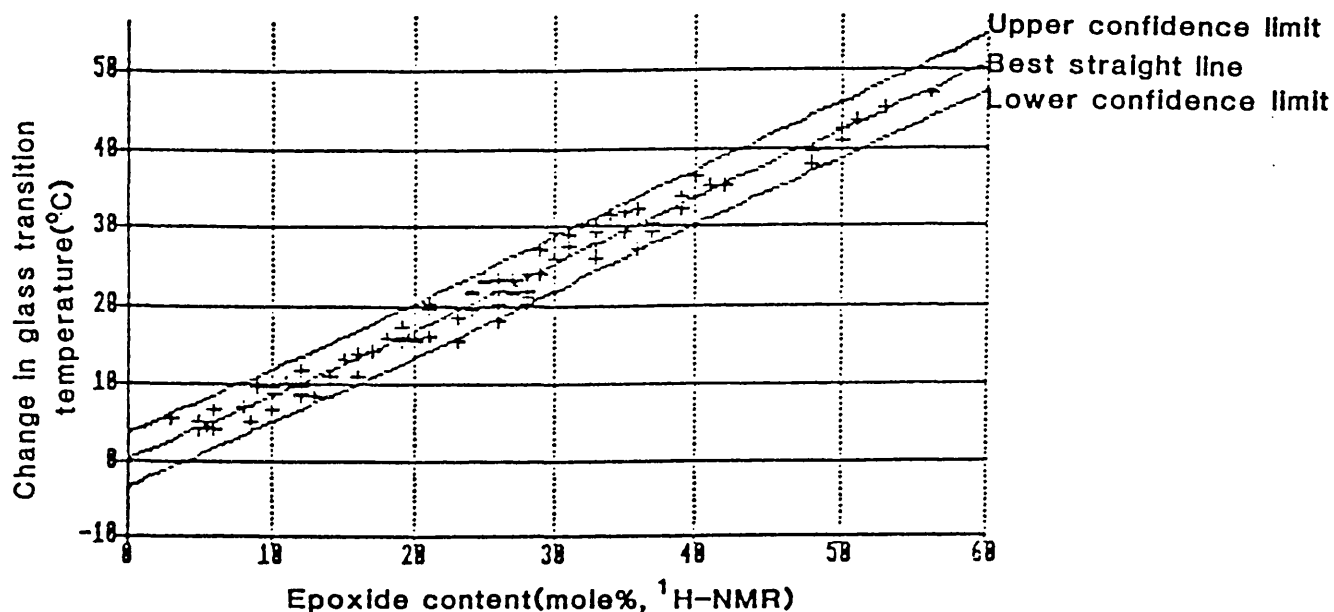
In extended acquisitions, the epoxy-group content of a sample of 'ENR-50' was determined using ^{13}C -NMR spectroscopy with the two alternative modes of broadband decoupling (together with a sufficient delay-time between pulses to facilitate the recovery of 99% magnetization). Under fully quantitative acquisition conditions, the epoxy-group content was found to be 56.5 mole% (*cf.* 56.0 mole% by 1H -NMR spectroscopy); the use of continuous broadband decoupling led to an estimate of 59.3 mole%. nOe suppression must therefore be employed if ^{13}C -NMR spectroscopy is to be employed as a quantitative procedure. A further experiment in which inverse-gated decoupling was used in conjunction with a

short delay-time between pulses led to an epoxy-group content estimation of 60.6 mole%, indicating that a sufficiently long recycle time is also necessary to ensure quantitative results.

3.4 The Estimation of Epoxy Groups by DSC

The application of DSC to the measurement of epoxy groups is usually based on calibration plots derived from the use of $^1\text{H-NMR}$ spectroscopy for absolute measurements. Published calibration plots for DSC vary widely and therefore this method of determining epoxy groups was studied in detail. $^1\text{H-NMR}$ spectroscopy at 200MHz was used to measure the epoxy-group content of samples from fourteen NR latex epoxidations using performic or peracetic acid. The results have been correlated with measurements of T_g using DSC under standard experimental conditions⁶⁵. Approximately one hundred samples were screened for functional groups arising from epoxy ring-expansion by $^1\text{H-NMR}$ spectroscopy (Section 4.3.2) and furanized samples were discarded from the study. The results of this study are summarised in *Table 3.5* and have been analysed statistically. In all cases, a linear correlation between T_g and epoxy-group content is obtained for sets of samples derived from individual preparations (*Table 3.5*). The linearity of each plot permits the calculation of a 'DSC calibration factor' from the gradient. Values of the DSC calibration factor are found to vary within the range of 0.75-0.92K $\text{mole}\%^{-1}$, with the absolute value apparently dependent upon the experimental conditions of each individual preparation. On

this basis, DSC may be considered unsuitable for the estimation of epoxy groups in sundry samples of ENR. **However**, a full linear regression treatment (by Dr J.F. Smith) of the data from all fourteen epoxidations yields a single linear correlation (Figure 3.3) with a gradient of 0.84 ± 0.01 and a correlation coefficient of



Linear regression analysis for DSC measurements

Figure 3.3

0.987. The statistically-derived DSC calibration factor for epoxy-group content determination is therefore $0.84 \pm 0.01 \text{K mole}^{-1}$, similar to published values of 0.81⁷² and 0.85^{66,76}. The regression analysis suggests that the major source of error in the results lies in the irreproducibility of T_g measurements. Within 95% confidence limits, the analysis indicates an uncertainty of 4°C in T_g determination; this result corresponds to experimentally-observed variations in T_g values for a NR calibration standard (207-211K).

Table 3.5

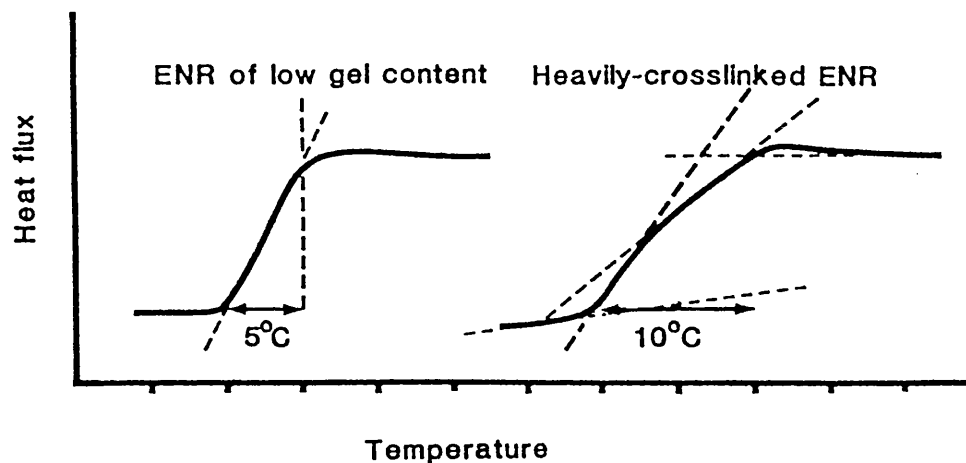
The correlation of T_g with epoxy-group content in ENR

Epoxy-group content (mole%) ^a	T_g (K)	DSC calibration factor (K mole% ⁻¹)	Correlation coefficient
6, 12, 16, 20, 23 28, 26	212, 216.5, 219, 224 226.5, 228.5, 230	0.81	0.991
8, 13, 20, 21, 24 26, 24, 27, 26	215.5, 217, 224, 228 230, 232, 230.5, 232 231.5	0.91	0.988
9, 26, 31, 35, 34 39, 36	218, 229, 237.5, 240.5 240.5, 242.5, 241	0.89	0.994
8, 5, 12, 19, 24 28, 50	213, 217, 225.5, 227.5 229, 249	0.84	0.994
5.5, 10, 19, 27 30, 48	212.5, 216.5, 224 229.5, 234, 247.5	0.82	0.999
5, 10, 17, 27, 42	212.5, 217, 223, 231 244	0.81	0.999
6, 18, 23, 26, 29 48	213.5, 223, 222.5 231, 245	0.75	0.999
12, 25, 29, 30, 32 40	220.5, 232, 235.5, 238 239, 245	0.89	0.997
3, 8, 10, 14, 33, 33	215, 216.5, 218.5 220.5, 239.5, 239	0.92	0.988
5, 9, 15, 21, 41	214, 219, 222.5, 229.5 244.5	0.84	0.997
5, 11, 16, 51, 53 56	213.5, 219.5, 223 252.5, 254, 256	0.83	0.999
12, 19, 25, 28, 31 33, 35, 36, 37, 37	219, 224, 231.5, 232.5 236, 234.5, 238, 235.5 238, 239	0.84	0.985
12, 21, 27, 33, 37 39	218, 225, 230.5, 236.5 238.5, 241	0.87	0.996
8.5, 12, 19, 24, 28, 50	213, 217, 224.5, 227.5 230, 250.5	0.87	0.997

^a 1 H-NMR spectroscopy at 200MHz

Four sets of workers have evaluated the DSC calibration factor using $^1\text{H-NMR}$ spectroscopy as an absolute technique^{65,66,72,73} and a range of instruments varying in sensitivity from 60⁷² and 90MHz⁶⁵ CW to 100⁶⁶ and 200MHz⁷³ FT spectrometers. Similar values for the DSC calibration factor have been derived by three research groups (0.81, 0.84 and 0.85K mole^{-1})^{66,72,73} and are more consistent than values ranging between 0.77-1.00K mole^{-1} obtained in the laboratories of MRPRA^{41,43,65,186}. The latter results are anomalous and indicate significant unreliability in the $^1\text{H-NMR}$ spectroscopic measurements used for calibration purposes. The discrepancies in epoxy-group content determined using IR or DSC and $^1\text{H-NMR}$ spectroscopy (*Table 3.1*) become explicable when it is noted that both the IR and DSC techniques were calibrated against unreliable $^1\text{H-NMR}$ measurements⁶⁵.

Davey and Loadman showed that the presence of ring-opened products in ENR was indicated in DSC traces by a broadened transition with a width of more than 10K⁶⁵. A careful examination of DSC traces for ENR samples with a high gel content, but no tetrahydrofuran rings (by $^1\text{H-NMR}$ spectroscopy), indicates that heavily-gelled samples also give rise to broadened transitions. Considerable curvature in the T_g transition leads to difficulties in the accurate derivation of T_g (*Figure 3.4*) and DSC cannot be recommended for the measurement of epoxy groups in such samples.



DSC traces for heavily-gelled ENR

Figure 3.4

3.5 The Microstructure of Epoxidized Natural Rubber

The microstructure of partially-epoxidized *cis*-1,4-polyisoprenes has been examined by several groups in order to determine whether the reaction of *cis*-1,4-polyisoprenes with peracids leads to random or non-random epoxidation of the available double bonds in polymer chains. Tutorskii and co-workers claimed that the reaction of 1,4-polyisoprenes with perbenzoic acid in solution led to non-random epoxidation of double bonds³³. This claim was based on the preponderance of ¹H-NMR resonances attributable to isolated epoxidized units between alkene segments. Burfield and co-workers claimed that the presence of a single T_g in ENR, prepared in solution or from NR latex, was indicative of a random copolymer composition⁴⁸. Davey and Loadman showed that the epoxidation of NR (prepared in solution or from latex) is a random process, based on the correspondence of experimental ¹³C-NMR peak intensities with theoretical values derived from a statistical analysis for random

copolymer composition⁶⁵. Furthermore, the shortfall in acidic volumetric determinations for ENR with an epoxy-group content above 10 mole% corresponded to the theoretical extent of tetrahydrofuran ring formation arising from adjacent epoxidized units in randomly epoxidized polymer chains⁶⁵ (*Scheme 1-5*). Bradbury and Perera analysed ¹³C-NMR spectra of ENR by the relative intensity of methylene carbon resonances and confirmed the random nature of the reaction of NR with peracids⁷⁸. However, the use of continuous broadband-decoupling in the ¹³C-NMR studies cited leads to some uncertainty in the conclusion owing to differences in nOe for the calibration resonances employed (*Section 3.3.2, Table 3.4*).

The random nature of epoxidation was also indicated by GC-MS analysis of fragments prepared by the ozonolysis of ENR²⁴⁹.

A lack of time precluded an investigation of polymer composition by ¹³C-NMR spectroscopy under quantitative acquisition conditions (*Section 3.3.2*). However, fractionation studies have provided additional evidence for random epoxidation. 'ENR-50' latex was separated by centrifuge creaming (by Dr D.S. Campbell) into several fractions differing in average particle size (*Table 3.6*). The estimation of epoxy groups by ¹H-NMR spectroscopy demonstrated that all the fractions had an epoxy-group content of 42±1 mole% (*Table 3.6*).

'ENR-50' was separated into several fractions, differing in molecular mass, using a fractional precipitation technique based on the methanolic precipitation of ENR-50 swollen in toluene (*Section 4.2*). Variability in the epoxy-group content of

Table 3.6

Epoxy-group content as a function of latex particle size

Fraction	Average particle diameter (μ)	Epoxy-group content (mole%) ^a
A	0.86	43
B	0.87	42
C	2.43	41
D	3.37	42
Whole latex	1.96	42

^a¹H-NMR spectroscopy at 400MHz

individual fractions was suggested by DSC measurements (*Table 3.7*). However, ¹H-NMR spectroscopy indicated that the epoxy-

Table 3.7

The epoxy-group content of molecular mass fractions from ENR-48

Fraction	Epoxy-group content (mole%)	
	DSC	¹ H-NMR
Whole polymer	47	48
Gel fraction	46	
Total sol fraction	33	48
Sol fraction 1	46	48
Sol fraction 2	43	48
Sol fraction 3	44	48
Sol fraction 4	46	48
Sol fraction 5	48	48

group content of all the fractions was 48 mole% (*Table 3.7*). The anomalous DSC results are attributed to the plasticization of sol fractions by traces of residual solvent⁶⁵.

The fractionation of ENR samples by molecular mass and latex particle size, and the invariance of epoxy-group content to these factors, provides further evidence for the homogeneity of the

reaction between *cis*-1,4-polyisoprene latices and peracids.

However, there is chemical evidence for the non-random epoxidation of double bonds from the hydrolysis of ENR-4 and ENR-10 with perchloric acid (Section 4.4). The spectroscopic evidence is consistent with the formation of tetrahydrofuran rings from ENR substrates which essentially contain only isolated epoxidized units if the distribution of epoxidized units were random. These results are anomalous and cannot be explained at present.

3.6 The Formation of Epoxy Groups during the Autoxidation of Natural Rubber and Epoxidized Natural Rubber

The epoxidation of *cis*-1,4-polyisoprene chains does not necessarily arise from the reaction of double bonds with peracids and can occur through the action of a range of alternative reagents²⁵⁰. For example, epoxy groups have been proposed as the primary modification arising during the uninhibited autoxidation of *cis*-1,4-polyisoprenes²⁵¹. ¹H- and ¹³C-NMR spectroscopic evidence has demonstrated the presence of epoxy groups in heavily-oxidized polybutadienes and polyisoprenes^{77,252,253}.

3.6.1 The Characterization of Epoxy Groups in *Syn*-Epoxidized Natural Rubber, *Gutta Percha* and Isomerized Natural Rubber

The formation of epoxy groups during autoxidation was investigated by the spectroscopic analysis of NR that had been oxidized to specific levels of oxygen uptake (1-10%w/w). Thin

films of purified DPNR were thermally autoxidized (prepared by Drs A.R. Arnold and S. Cook) as part of a programme to characterize the ageing behaviour of NR.

Diagnostic NMR resonances for trisubstituted *cis*-epoxy groups were assigned by the stereospecific *syn*-epoxidation of NR with performic acid¹⁸⁰. Corresponding *trans*-epoxy group resonances were assigned by the *syn*-epoxidation of *gutta percha* with MCPBA. Diagnostic ¹H- and ¹³C-NMR resonances for trisubstituted *cis*- and *trans*-epoxy groups are collated in Table 3.8. Chemical shifts for

Table 3.8

Characteristic NMR resonances for epoxy groups in 1,4-polyisoprenes

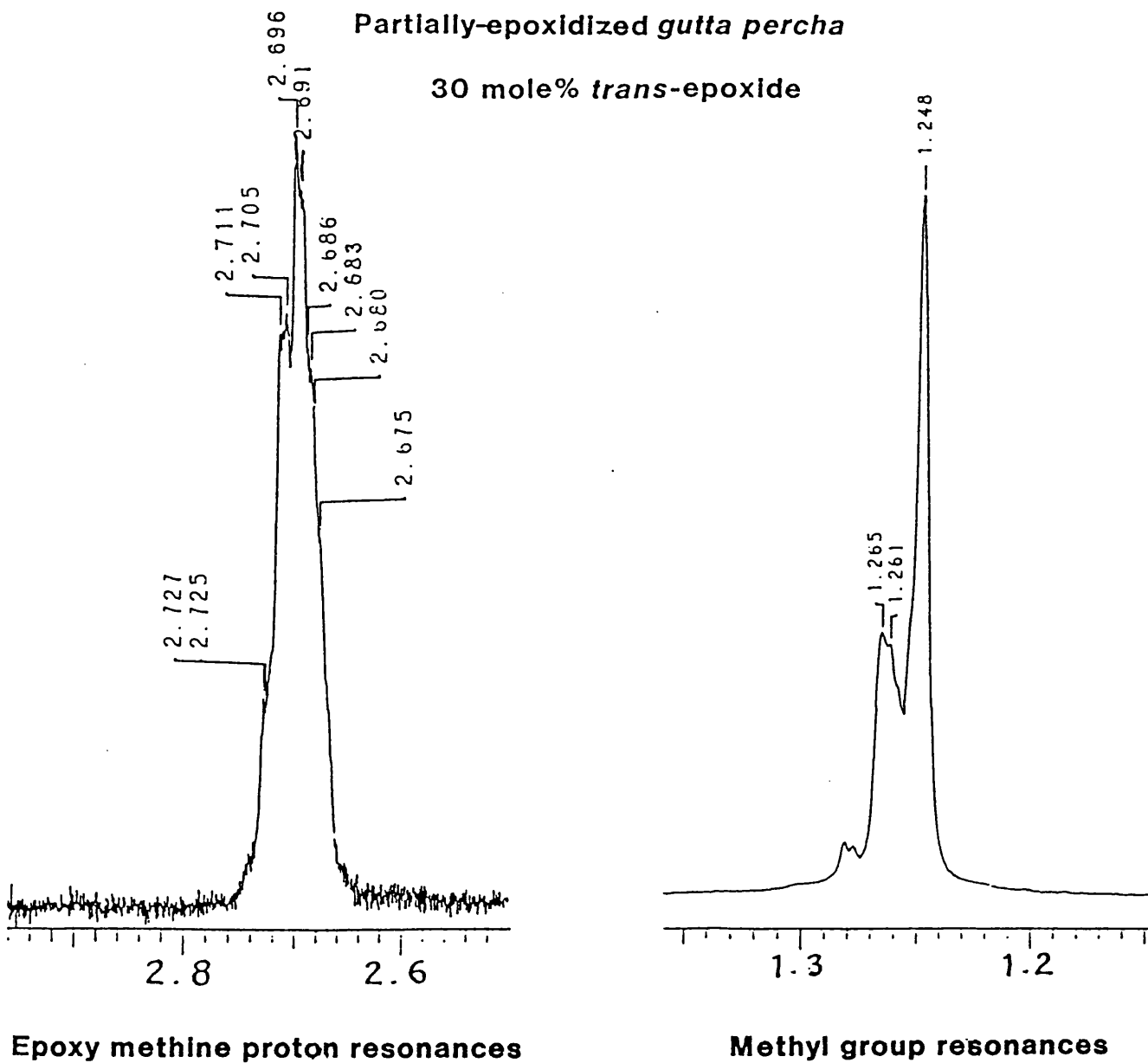
Modification	Characteristic resonances (ppm, CDCl ₃)	
	¹ H-NMR	¹³ C-NMR
<i>Cis</i> -epoxy groups in NR	1.285 (H ₃ C-CO, s) 2.680 (O C H, t) ^b	60.82 (CO) ^a 64.53 (HCO)
<i>Trans</i> -epoxy groups in <i>gutta percha</i>	1.260 (H ₃ C-O, s) ^c 2.70 (O C H, t)	60.26 and 60.65(CO) 63.21 (HCO)

^aAt higher levels of epoxy-group content, additional quaternary carbons are observed at 60.37, 60.56 and 60.90ppm

^bdistorted triplet; in C₆D₆, a doublet of doublets

^cAt higher levels of epoxy group content, the single resonance at 1.260ppm is superseded by resonances at 1.240, 1.248 and 1.256ppm

the characteristic resonances are generally consistent with previous studies^{65,78,82,190,254,255}. The sensitivity of ¹H-NMR spectroscopy to changes in unit distribution in partially epoxidized *gutta percha* results in the observation of multiple HCO and H₃C-CO resonances (Figure 3.5). This effect was not



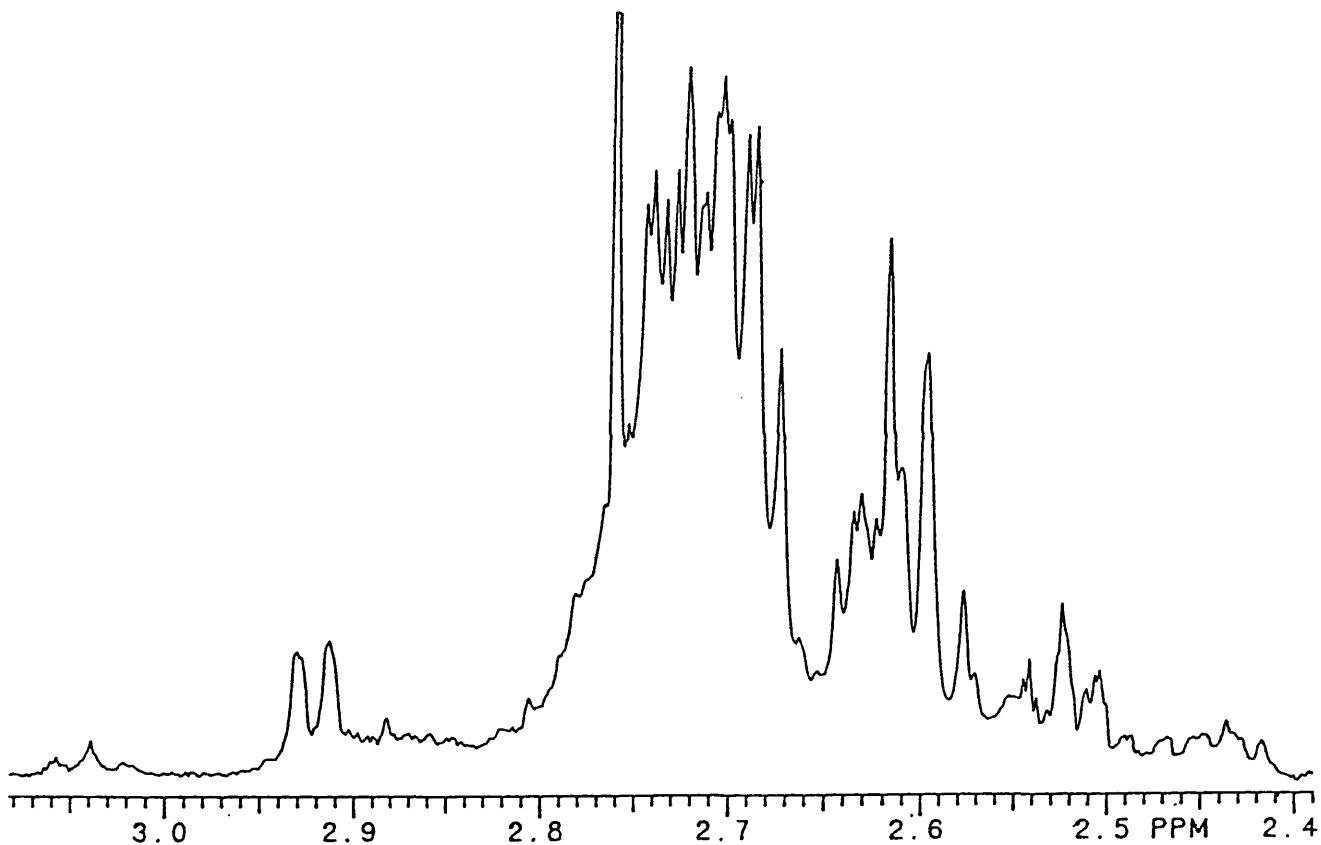
$^1\text{H-NMR}$ spectrum of partially-epoxidized *Gutta-Percha*

Figure 3.5

observed by Hayashi and co-workers⁸² owing to the poor spectral resolution attainable at 60MHz.

Mixtures of *cis*- and *trans*-epoxy groups in 1,4-polyisoprenes were examined by the *syn*-epoxidation of partially isomerized NR²⁵⁶ with performic acid. These experiments were necessary in order to avoid complications arising from additional overlapping resonances observed in ¹H-NMR spectra of autoxidized NR (Figure 3.6)²⁵⁷ and to validate the analytical protocol used subsequently

Autoxidized NR 5.0%w/w oxygen uptake

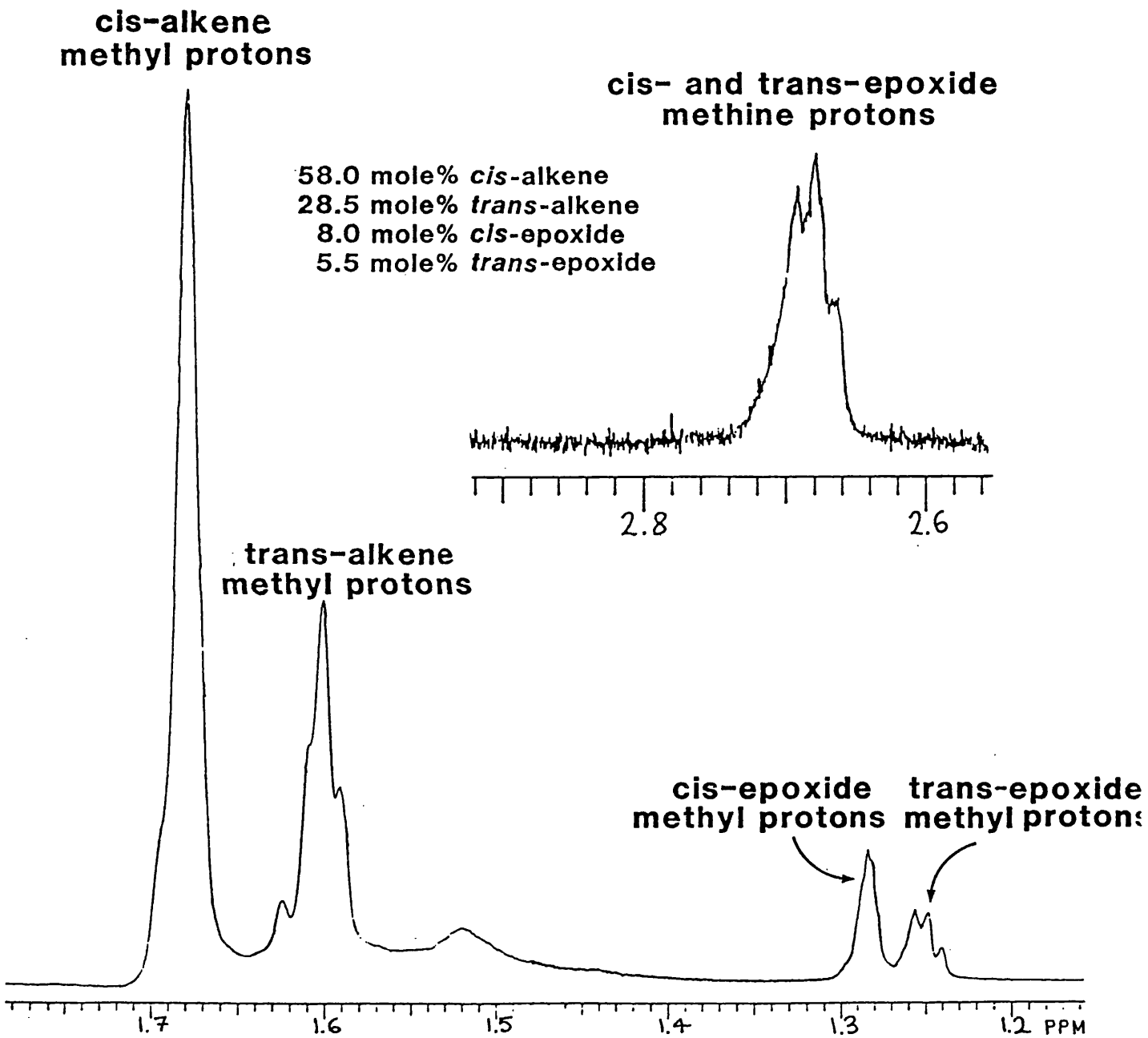


¹H-NMR spectrum in the region of chemical shift characteristic of epoxy methine protons in autoxidized NR

Figure 3.6

to analyse autoxidized NR. Trace- and weigh analysis of ¹H-NMR peak areas for the methyl resonances at 1.240/1.248/1.256 and

1.258ppm (*trans*- and *cis*-epoxy groups respectively) and the overlapping methine resonances at 2.70 and 2.68ppm (Figure 3.7)



¹H-NMR spectrum of epoxidized isomerized NR

Figure 3.7

yields an average ratio of 3.05:1.00 for protons in methyl and methine resonances. This result is close to the theoretical ratio for resonances arising solely from the two isomeric structures. Inclusion of the diagnostic *cis*- and *trans*-alkene methyl resonances (at 1.678 and 1.601ppm respectively, *Figure 3.7*) into the trace-and-weigh analysis permits complete elucidation of the composition of samples taken from the solution epoxidation of partially-isomerized NR[Ⓢ] (*Table 3.9*). The relative rates of epoxidation for *cis*- and *trans*-alkene units can then be

Table 3.9

The *syn*-epoxidation of partially-isomerized NR

Reaction time (hours)	Modification level (mole%) ^a			
	<i>Cis</i> -alkene	<i>Trans</i> -alkene	<i>Cis</i> -Epoxide	<i>Trans</i> -Epoxide
0	43.0	57.0	0.0	0.0
1	38.0	53.0	5.0	4.0
2	35.0	50.0	8.0	7.0
4	30.5	46.0	12.5	11.0
6	27.5	43.0	15.5	14.0
22	19.0	35.0	24.0	22.0

^a¹H-NMR spectroscopy at 400MHz

calculated and it was found that the epoxidation of *cis*-alkene units was 50% faster than the *trans*-alkene units. This result is consistent with analogous kinetic studies on low-molecular-mass

Footnote[Ⓢ]

The relative rates of *syn*-epoxidation of *cis*- and *trans*-alkene units in isomerized NR with MCPBA or performic acid is dependent upon the reaction medium. In solution, the epoxidation of *cis*-alkene units is 50% faster than the corresponding *trans*-alkene units; in a latex medium, the rate of epoxidation is the same for both isomeric alkenes²⁵⁶.

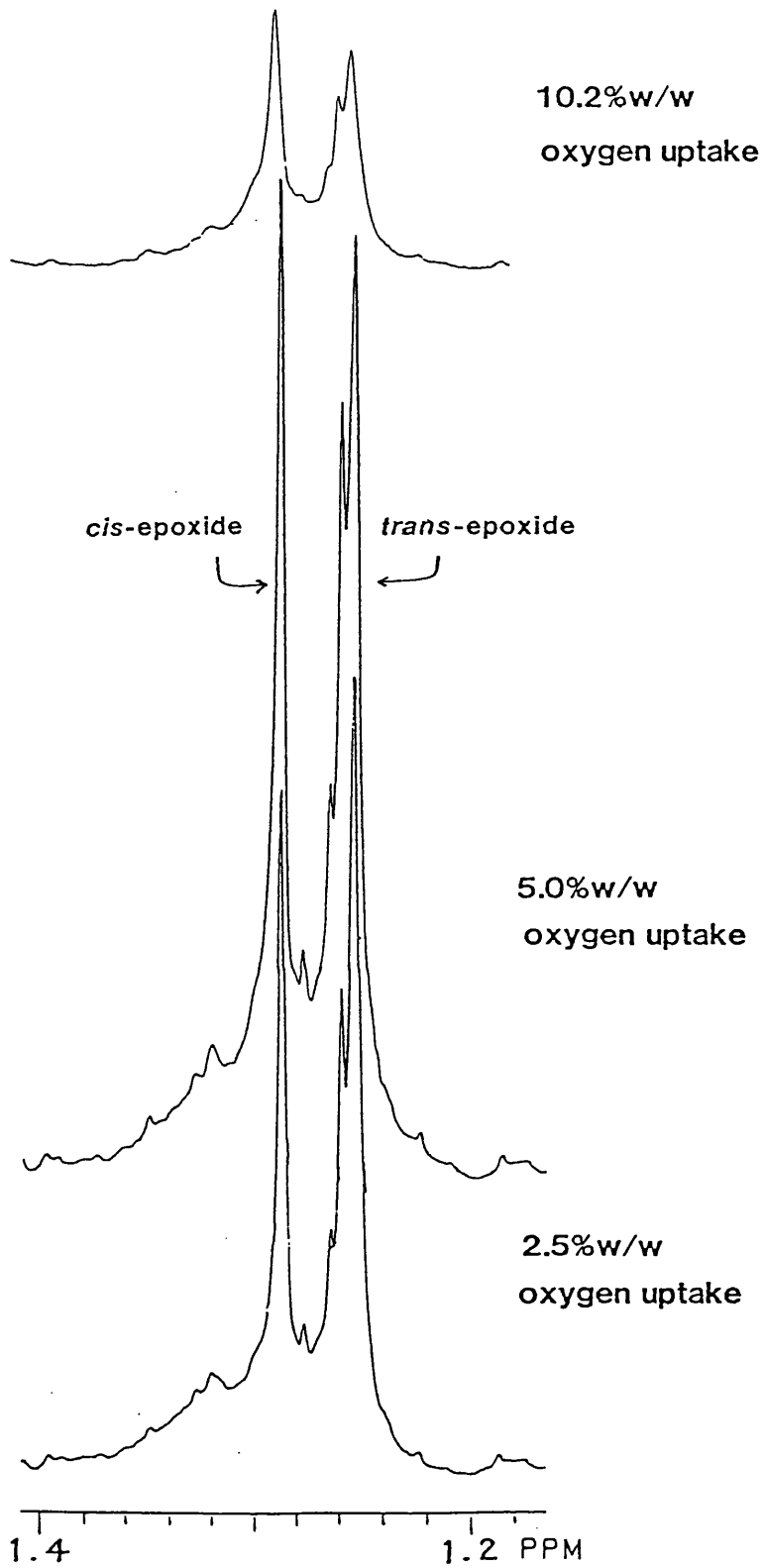
trisubstituted alkenes^{56,258} and justifies the use of the ¹H-NMR methyl group resonances to estimate the concentration of *cis*- and *trans*-epoxy groups in modified 1,4-polyisoprenes.

3.6.2 The Characterization of Epoxy Groups in Autoxidized Natural Rubber

The chemical shift region in which tertiary epoxy methine protons resonate has been examined in ¹H-NMR spectra of autoxidized NR (*Figure 3.6*) and several additional functional groups develop during autoxidation which resonate in the same region²⁵⁷. This portion of ¹H-NMR spectra cannot therefore be used for the unambiguous identification of epoxy groups. These problems are absent in the region of chemical shift characteristic of epoxy methyl groups and the spectra are consistent with the predominant presence of *cis*- and *trans*-epoxy group resonances[Ⓢ](*Figure 3.8*). The inspection of spectra acquired from samples of autoxidized NR with 2.5, 5.0 and 10.2%w/w oxygen uptake indicates that the relative size of the methyl group resonances does not change with total oxygen uptake (*Figure 3.8*). Trace-and-weigh analysis of the manually deconvoluted resonances yields constant ratio of 1.4±0.1:1.0 for *trans*:*cis*-epoxy groups.

Footnote[Ⓢ]

There are several constituents in unpurified *cis*-1,4-polyisoprenes which have characteristic resonances at 1.260ppm²⁵⁰ which can therefore distort the *cis*:*trans*-epoxy-group ratio obtained by this procedure. Furthermore, the presence of minor resonances in the envelope of signals attributed solely to *cis*- and *trans*-epoxidized units cannot be fully discounted.

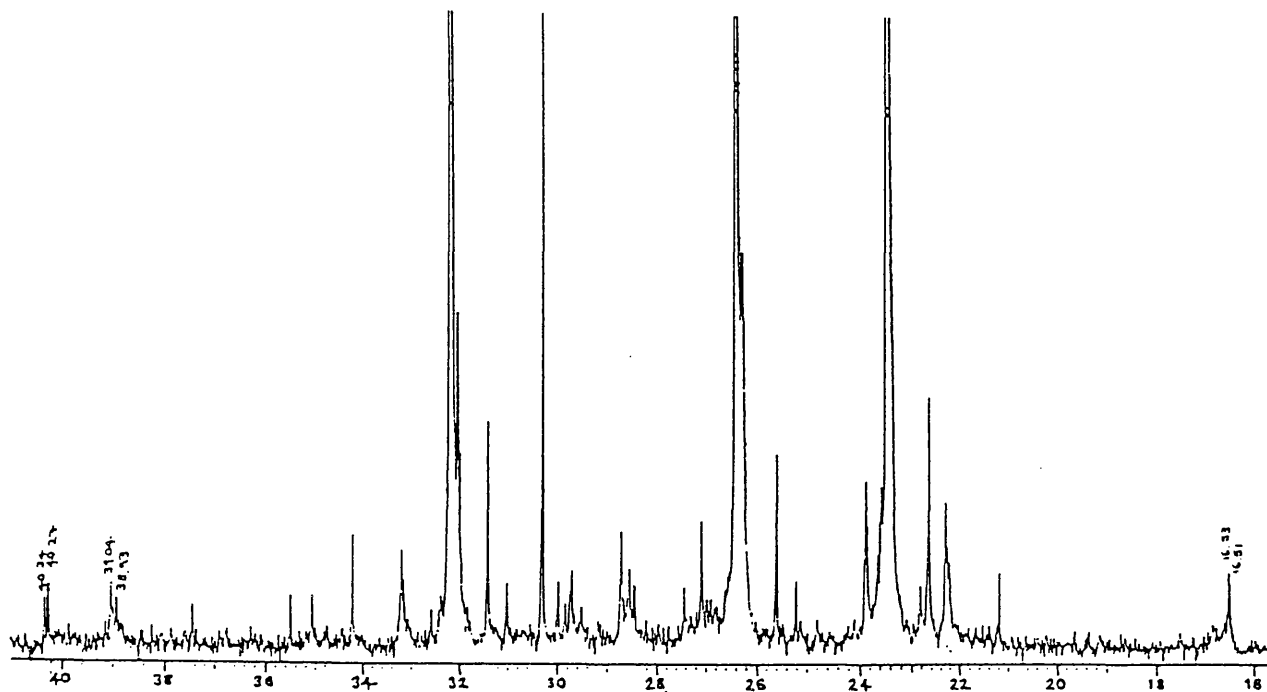


$^1\text{H-NMR}$ spectrum of epoxy methyl protons in autoxidized NR

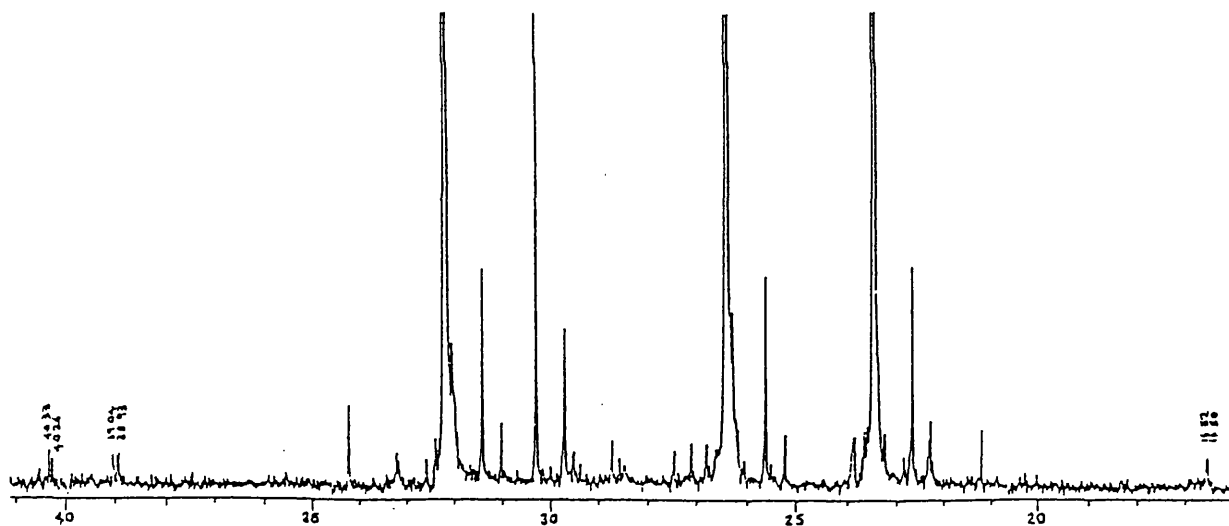
Figure 3.8

This result is consistent with the relative rate of formation of *trans*- and *cis*-epoxides during the autoxidation of low-molecular-mass trisubstituted alkenes²⁵⁹.

The formation of epoxy groups during autoxidation can be unambiguously demonstrated by ¹³C-NMR spectroscopy. Samples of autoxidized NR containing 3.2 and 10.2%w/w oxygen were analysed using ¹³C-NMR spectroscopy and diagnostic chemical shift regions are illustrated (*Figures 3.9 and 3.10*). Resonances at 16.51 and 16.53ppm (*Figure 3.10*) are consistent with methyl groups in *trans*-epoxidized units (16.70ppm in partially epoxidized *gutta percha*⁸²). Resonances at 38.93, 39.04, 40.27 and 40.43ppm (*Figure 3.10*) are attributable to methylene carbons in *trans*-epoxy groups (38.87 and 39.80ppm in partially epoxidized *gutta percha*⁸²). The resonances at 40.27 and 40.34ppm are suggested to be attributable to methylene carbons in *trans*-epoxidized units adjacent to *cis*-alkene units. Six major resonances are observed in the chemical shift region characteristic of epoxy ring carbon atoms (*Figure 3.10*); additional resonances at 62.97 and 63.77ppm in heavily autoxidized samples remain unassigned. The resonances at 64.53 and 60.83ppm are attributable to the quaternary and tertiary carbon atoms in *cis*-epoxidized units (64.53 and 60.82ppm in ENR⁷⁸), whilst the resonances at 63.31 and 60.71ppm are attributable to the corresponding carbon atoms in *trans*-epoxidized units. The remaining resonances at 61.20 and 62.58ppm are tentatively assigned to a further epoxidized unit, which may also give rise to the broad doublet at 2.92ppm in ¹H-NMR spectra of autoxidized NR (*Figure 3.6*).



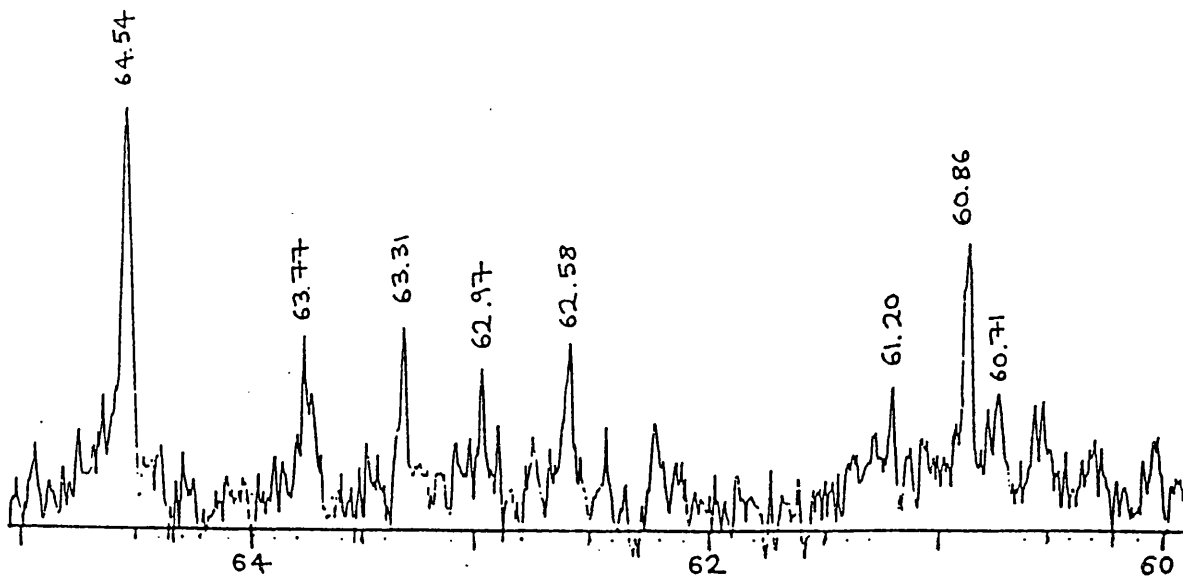
Autoxidized NR 10.2%w/w oxygen uptake



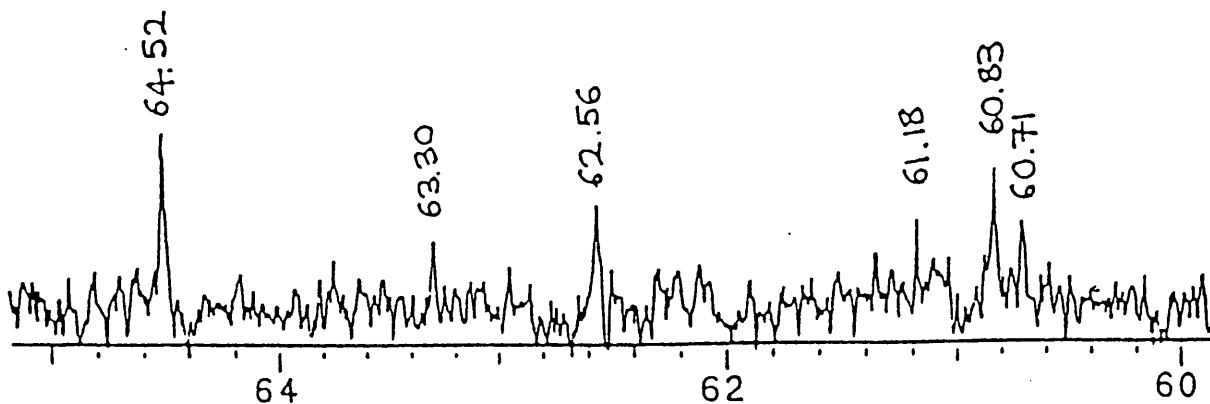
Autoxidized NR 3.2%w/w oxygen uptake

^{13}C -NMR spectrum of methyl and methylene carbons in autoxidized NR

Figure 3.9



Autoxidized NR 10.2%w/w oxygen uptake



Autoxidized NR 3.2%w/w oxygen uptake

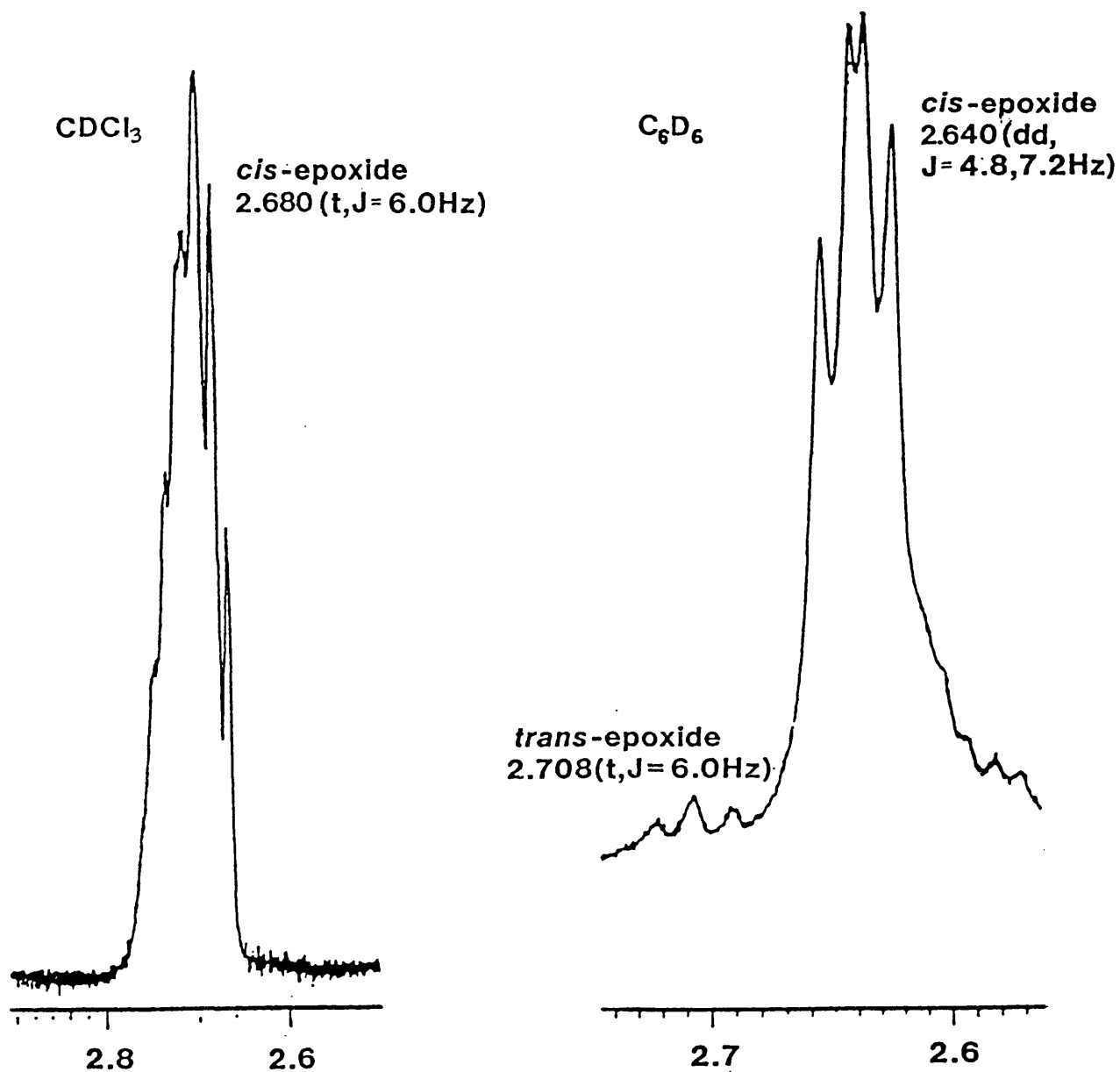
^{13}C -NMR spectrum of epoxy ring carbons in autoxidized NR

Figure 3.10

3.6.3 The Autoxidation of Epoxidized Natural Rubber

The autoxidation of ENR has not been directly studied. However, ^1H -NMR spectroscopy has been used to demonstrate the

presence of *trans*-epoxidized units in ENR. The multiplicity of the epoxy methine proton resonance in ENR-40 is consistent with a complex multiplet and inconsistent with a simple triplet or doublet of doublets (Figure 3.11). The use of C_6D_6 as the NMR

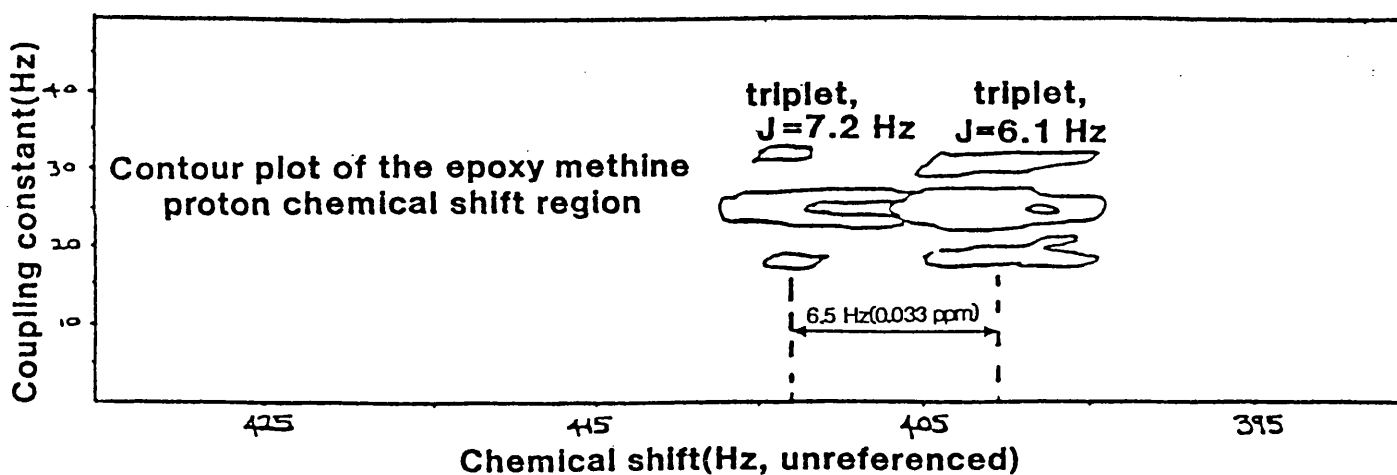


¹H-NMR spectrum of epoxy methine protons in ENR-40

Figure 3.11

solvent results in the deconvolution of two overlapping resonances attributable to *cis*- and *trans*-epoxy isomers (Figure 3.11); increased spectral resolution has also been observed for proton resonances in partially-isomerized NR when C₆D₆ is used as the NMR solvent³⁴.

More modern NMR techniques have been used to identify convoluted epoxy group resonances in ENR. Homonuclear 2D J-resolved spectroscopy²⁶⁰, an experiment in which multiplets are 'broadband-decoupled' and isolated according to their chemical shift, was applied to ENR-40. The spectral detail illustrated in Figure 3.12 indicates the presence of two distinct triplets at



2D J-resolved NMR spectrum of ENR-40

Figure 3.12

2.68ppm (major) and 2.71ppm (minor resonance from the contour plot), at chemical shifts consistent with *cis*- and *trans*-epoxidized units respectively.

3.6.4 Epoxy Groups in Autoxidized Natural Rubber and Epoxidized Natural Rubber

NMR spectroscopy demonstrates that both trisubstituted *cis*- and *trans*-epoxy groups are formed during the autoxidation of NR. ENR is prepared by the stereospecific *syn*-epoxidation of NR latex with performic acid¹⁸⁶. The presence of *trans*-epoxidized units in ENR is therefore believed to result from autoxidation of the polymer; Terlemezyan and co-workers showed that the autoxidation of ENR resulted in an increase in the concentration of epoxy groups²⁶¹.

The analysis of ¹H-NMR spectra from autoxidized NR suggests that epoxy groups are formed in a constant ratio of 1.4:1.0 in favour of the *trans*-isomer, a result consistent with autoxidation studies on low molecular mass trisubstituted alkenes²⁵⁹.

The attempted quantitative estimation of corresponding ¹³C-NMR spectra involving the epoxy-ring carbons (*Figure 3.11*), yields a ratio of approximately 0.5:1.0 in favour of the *cis*-epoxy isomer. The result is similar to that derivable from previous ¹³C-NMR studies⁷⁷ and illustrates the inherent danger in the use of ¹³C-NMR spectroscopy to quantitatively characterise samples in which standard acquisition parameters (i.e. no nOe suppression and a rapid recycle-time) have been employed (Section 3.3.2).

The autoxidation of non-conjugated alkenes was classically believed to result in the predominant formation of hydroperoxides²⁶², but subsequent studies on low molecular mass alkenes demonstrated that mixtures of isomeric epoxy groups were

major autoxidation products²⁶³⁻²⁶⁵ (Table 3.10). It has been

Table 3.10

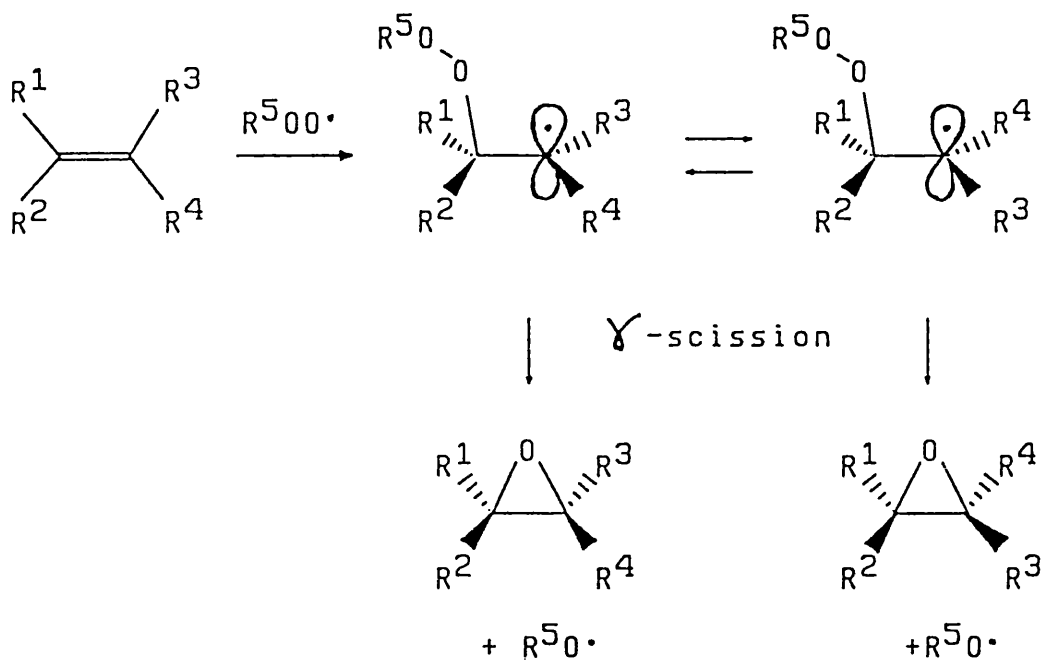
Isomeric epoxides formed during the autoxidation of alkenes

Alkene	Yield(%) ^a	<i>Trans:Cis</i> -epoxide ratio
<i>cis</i> -but-2-ene ²⁶⁴	48	1.5:1.0
<i>trans</i> -but-2-ene ²⁶⁴	39	3.3:1.0
<i>cis</i> -oct-2-ene ²⁶⁵	37	1.6:1.0
<i>trans</i> -oct-2-ene ²⁶⁵	37	5.2:1.0
<i>cis</i> -oct-3-ene ²⁶⁵	28	1.8:1.0
<i>trans</i> -oct-3-ene ²⁶⁵	22	10.0:1.0
<i>cis</i> -oct-4-ene ²⁶⁵	26	1.6:1.0
<i>trans</i> -oct-4-ene ²⁶⁵	27	8.0:1.0
<i>cis</i> -1,4-polybutadiene ^{252,253}	30-50	2.0:1.0 ^b
<i>cis</i> -1,4-polyisoprene ⁷⁷	/	0.5:1.0 ^b

^ayield based on reacted alkene

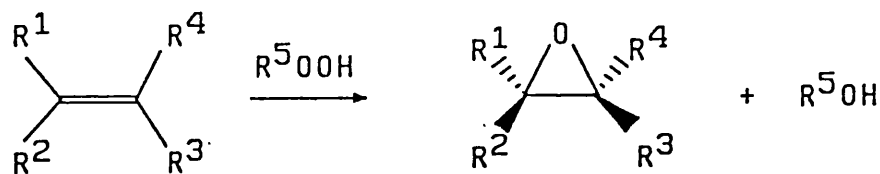
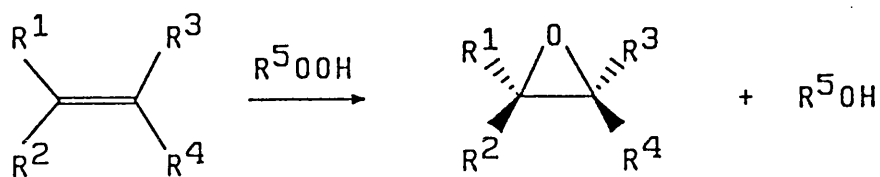
^bestimated from ¹³C-NMR peak areas for tertiary carbons in epoxy groups

proposed that the ratio of isomeric epoxy groups formed during autoxidation is dependent upon the relative rates of the addition of peroxy radicals to double bonds (*Scheme 3-1*) and the epoxidation of double bonds with hydroperoxides²⁵⁹ (*Scheme 3-2*). Results for low molecular mass trisubstituted alkenes suggest that the latter route is insignificant in NR and the *trans:cis*-epoxy group ratio in autoxidized NR should therefore be approximately 1.5:1.0²⁵⁹. The results yield an isomeric epoxy group ratio which is therefore consistent with peroxy radical addition being the principle pathway operating during autoxidation. An important inference of this finding is that an alkoxy radical is generated for each epoxy group formed (*Scheme 3-1*). Alkoxy radicals have been implicated as chain carriers in NR autoxidation²⁶³ and therefore epoxidation results in chain



The addition of peroxy radicals to double bonds

Scheme 3-1



The direct epoxidation of double bonds with hydroperoxides

Scheme 3-2

transfer. More importantly, the β -scission of alkoxy radicals has been proposed as the cause of chain scission during the autoxidation of NR²⁶⁶.

CHAPTER 4

THE HYDROLYSIS OF EPOXIDIZED NATURAL RUBBER

4.1 Introduction

ENR can be prepared from the reaction of NR latices with performic acid, generated *in situ* from hydrogen peroxide and formic acid^{44,186}. The procedure has been commercially exploited by RRIM to prepare two grades of rubber, ENR-25 and -50⁴⁵. Initial tonnage batches of ENR-50 were found to have a high gel content and viscosity⁴⁵, arising from the acid-catalysed ring-opening of epoxy groups and the formation of tetrahydrofuran rings (*Scheme 1-10*) and/or intermolecular ether crosslinks (*Scheme 1-11*). ENR-50 with a Mooney viscosity between 60 and 80 is desirable for optimum processing characteristics⁴⁹, whereas ENR-50 with a value of 140 was produced during the early stages of commercial production⁴⁶. The toughened rubbers required extended mixing times and suffered from a poor dispersion of filler in mixes^{46,72}. The deleterious effect of acid-catalysed hydrolysis on the physical properties of ENR-50 merited serious attention and the hydrolysis of ENR was investigated in detail.

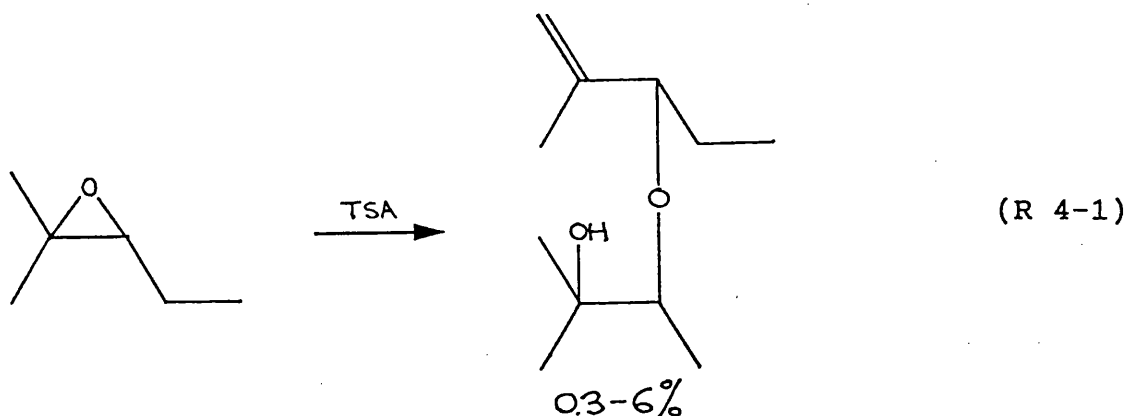
Footnote[Ⓢ]

Subsequent development of the commercial procedure has resulted in the preparation of 'easy processing' grades of ENR with substantially reduced gel content and Mooney viscosity⁴⁵.

4.2 The Formation of Crosslinks during the Preparation of Epoxidized Natural Rubber

The reaction of unsaturated polymers with peracids has been extensively studied²⁴². Epoxidation is generally accompanied by a decrease in solubility as the gel content of the polymer is increased⁴² and highly-epoxidized polyisoprenes are frequently insoluble^{38,63,72,78,267}. The degree of crosslinking in partially-epoxidized polydienes is determined by the epoxy-group content⁴² and the acidity of the reaction medium. Udipi showed that the partial replacement of formic acid with acetic acid in the epoxidation of SBS copolymers significantly reduced gel content⁹⁴.

It has generally been assumed that the increase in gel content during the epoxidation of polydienes results from the formation of intermolecular ether bonds⁸⁸ (*Scheme 1-11*). Gelling and Morrison isolated a low molecular mass analogue for an ether crosslink from the hydrolysis of 2-methyl-2,3-epoxypentane with a strong acid in the absence of a solvent⁸⁹ (*R 4-1*). The



characterization of a pendant trisubstituted alcohol in

crosslinked ENR by ^{13}C -NMR spectroscopy is consistent with the formation of ether crosslinks¹⁸⁸ (*Scheme 2-2*, Section 2.1.1). Many studies have claimed that the reaction of NR with peracids is not accompanied by hydrolysis products unless the reaction medium is strongly acidic^{40,182,262} (Section 2.1.1). Lee and Porter showed that the concentration of crosslinks in uncured ENR is very low and claimed that the crosslinks were more loosely associated than covalent bonding²⁶⁹. Differences in the susceptibility of ENR to form crosslinks according to whether epoxidation is performed in solution or latex media were claimed to demonstrate that the formation of crosslinks during latex epoxidation occurred *via* ring-opening and the nucleophilic addition of non-rubbers⁷⁸.

The insertion of crosslinks in high molecular mass elastomers leads to the production of an insoluble three-dimensional network which is difficult to analyse by traditional spectroscopic methods. However, the formation of crosslinks does not necessarily result in insolubility; molecular mass, chain-branching and chain-conformation are also determinant factors.

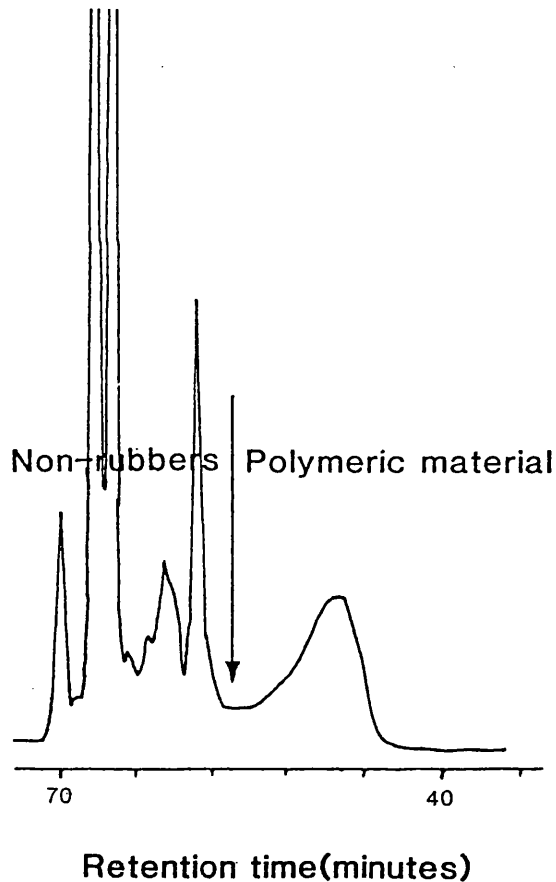
Initial experiments on the structure of crosslinks in ENR were concentrated on the isolation and characterization of ether bonds in the **sol** fraction of ENR. ENR-48 was prepared by the epoxidation of NR latex using hydrogen peroxide and formic acid⁴⁴, and the sol fraction was extracted with toluene. The sol was fractionally precipitated into several molecular mass fractions by the stepped addition of methanol to the rubber dissolved in toluene²⁷⁰ (*Table 4.1*). The methanol-soluble residue was shown by GPC to contain both low molecular mass compounds and

Table 4.1

The fractional precipitation of ENR-48

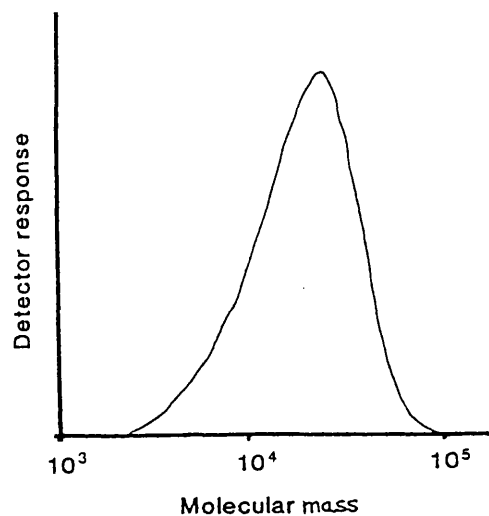
Fraction	Solution composition (%v/v of methanol)	Fraction of total sol (%w/w)	Molecular mass	
			$10^5 M_n$	$10^6 M_z$
1	58	63	1.30	1.05
2	63	12	1.00	0.35
3	68	9	0.60	0.18
4	73	5	0.30	0.09
5	77	4	0.30	0.13
6	Residue (100)	5	0.15	0.03

a polymeric fraction (*Figures 4.1 and 4.2*). ^{13}C -NMR spectroscopy



GPC trace for the low molecular mass fraction of ENR-48

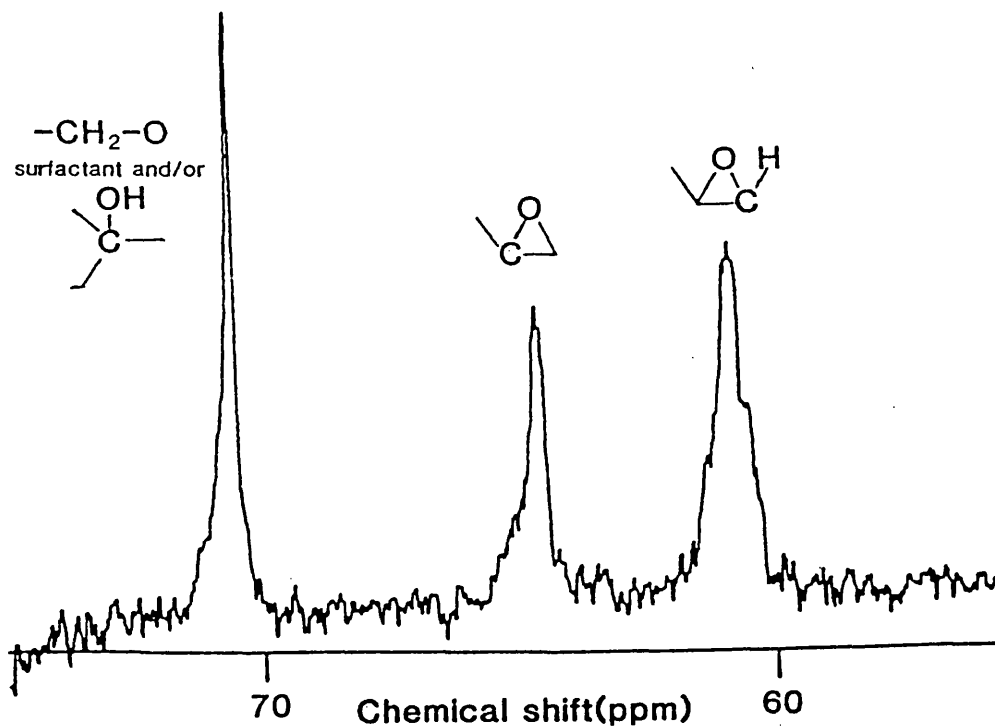
Figure 4.1



Molecular mass distribution for the polymeric fraction

Figure 4.2

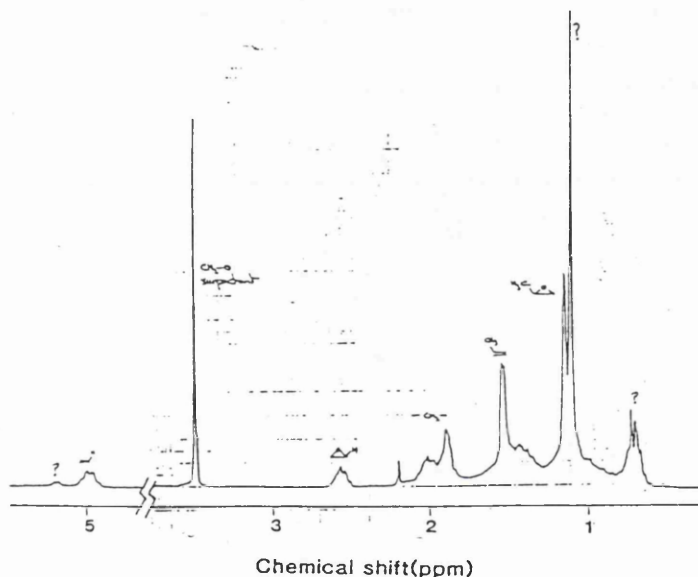
of the residue showed a resonance at 70.6ppm (*Figure 4.3*) which



^{13}C -NMR resonances for alcohol and epoxy group resonances

Figure 4.3

have been attributed to pendant alcohol groups in crosslinked ENR¹⁸⁸ (Section 2.1.1) or polyether chain carbons, CH₂-O, in the surfactant. Trace-and-weigh analysis of the spectrum indicated apparent[⊕] epoxy and alcohol group contents of 41 and 28 mole% respectively. ¹H-NMR analysis demonstrated that the residue contained a mixture of ENR-48, surfactant and other non-rubbers (Figure 4.4). GPC on a semi-preparative scale was used to divide



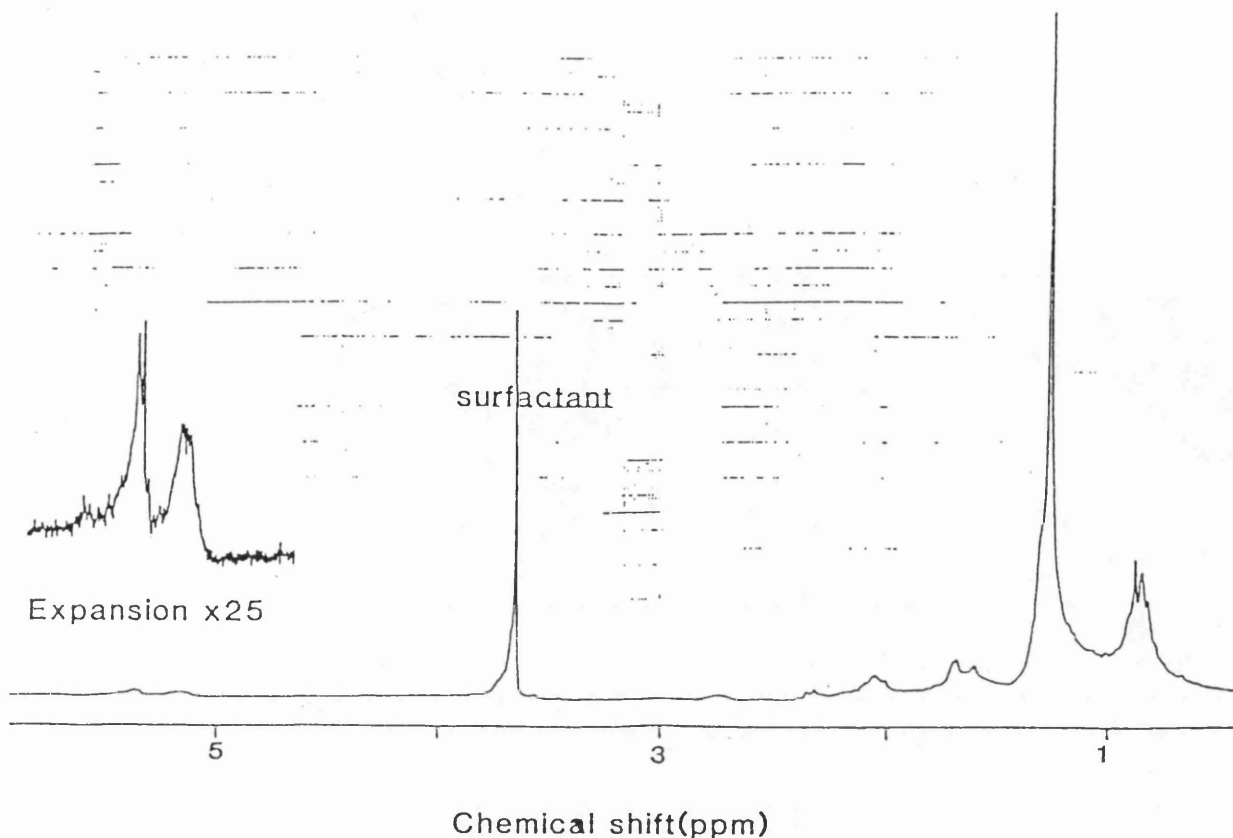
¹H-NMR spectrum of the low molecular mass fraction

Figure 4.4

the residue into four fractions. ¹H-NMR spectroscopy of the lowest molecular mass fraction indicated the presence of non-

Footnote[⊕]

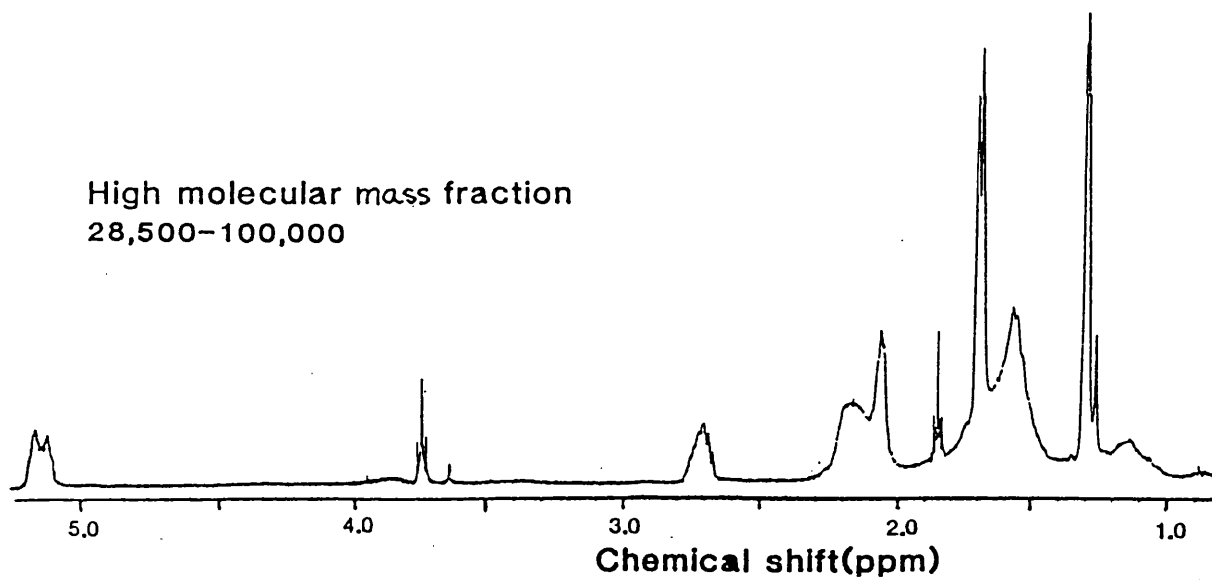
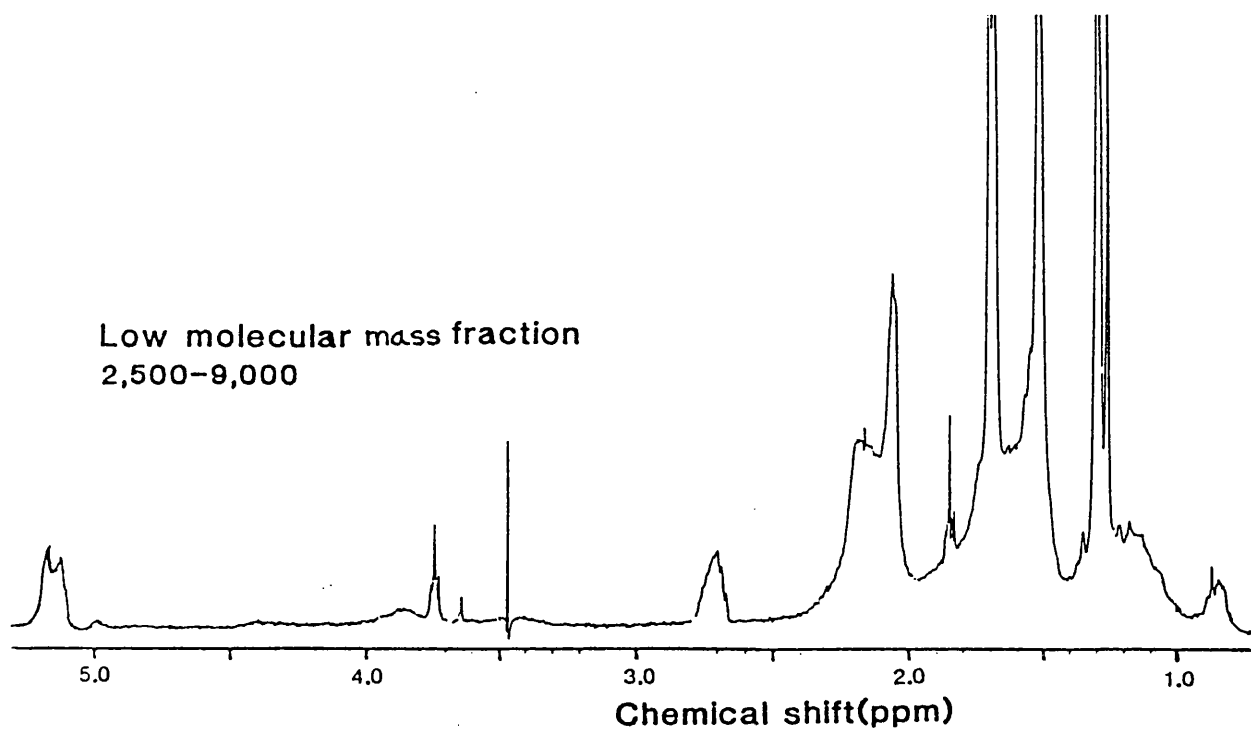
¹³C-NMR spectra from swollen samples of crosslinked ENR were acquired using continuous broadband-decoupling, in order to detect the low concentration of pendant alcohol groups. The method can therefore only be used for semi-quantitative analyses (Section 2.1.1).



$^1\text{H-NMR}$ spectrum of the non-rubbers

Figure 4.5

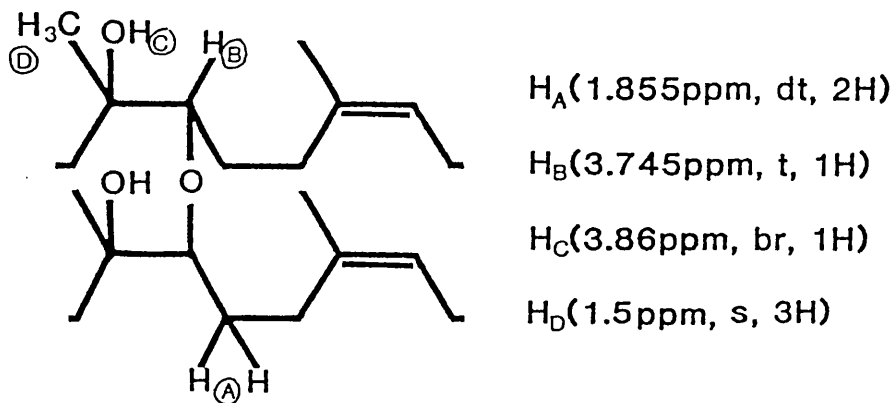
rubbers and all the anomalous resonances not normally associated with ENR (*Figure 4.5*). The three polymeric fractions were examined by $^1\text{H-NMR}$ spectroscopy and found to have spectra consistent with ENR, but with additional resonances; a broad peak at 3.86ppm, a triplet at 3.75ppm and a multiplet at 1.86ppm (*Figure 4.6*). The novel resonances integrated to a ratio of 1:1:2 and are consistent with an acyclic ether-diol fragment (*Scheme 4-1*). Inclusion of these resonances into the quantification scheme for epoxy groups showed that all three polymeric fractions had an ether content of 2 mole% and an epoxy-group content of 46 mole%. The $^1\text{H-NMR}$ spectroscopic evidence demonstrates the presence of



^1H -NMR spectra of polymer fractions

Figure 4.6

ether bonds in low molecular mass fractions of ENR and these bonds will contribute to the formation of gel from higher



The structure of an acyclic ether-diol fragment

Scheme 4-1

molecular mass molecules.

4.2.1 The Gel Fraction in Natural Rubber and Epoxidized Natural Rubber

The degree of crosslinking in NR can be evaluated by stress-strain measurements on strips of dry rubber or equilibrium volume swelling measurements²⁷¹. Unfortunately, neither of these methods could be applied to ENR. The formation of cracks in latex films precluded the application of stress-strain measurements²⁷², and the dependence of the Flory-Huggins interaction parameter for ENR upon both epoxy-group content and degree of swelling²⁷³⁻²⁷⁵ limits the utility of swelling measurements. Therefore, the only practicable method to follow crosslinking in ENR was by the

measurement of gel content in solvents.

The rate of dissolution of a polymer in a solvent is initially determined by diffusion of the liquid into the polymer and is thereafter dependent upon the thermodynamics of mixing of polymer and solvent^{276,277}. **In the absence of a specific interaction,** solubilization occurs for polymers and liquids with similar solubility parameters, δ . The considerable time required for high molecular mass chains to disentangle and dissolve in solvents has resulted in much conflicting results on the size of the gel fraction from different grades of NR. Hallensleben and co-workers²⁷⁸ found that RSS fully dissolved in cyclohexane over several weeks, whereas Bloomfield cited RSS grades as being typical of NR containing a gross gel fraction²⁷⁹ and other workers measured the gel content in RSS grades at 70-80%w/w^{280,281}. The dissolution of pale crepe in a range of solvents was shown not to follow ideal thermodynamic behaviour with a large variation in apparent gel content²⁸². Under the same experimental conditions, a blend of cured pale crepe with gel-free synthetic *cis*-1,4-polyisoprene had a constant gel content (Table 4.2). Prolonged extraction times significantly reduced the gel content to 10%w/w. The addition of 10% ethanol to cyclohexane reduced the gel content of pale crepe from 46 to 15%w/w²⁸² and similar results were achieved using chloroform containing ethanol or hexane containing acetic acid²⁸³.

Baker showed that the gel fraction in BR latices was solubilized by the addition of acetic acid or water to rubber solvents²⁸⁴. The reduction in the apparent gel content of NR in

Table 4.2

The apparent gel content of pale crepe²⁸²

Solvent ^a	Solubility parameter δ (MPa ^{1/2}) ^b	Apparent gel content (%w/w)	
		Pale crepe	Polyisoprene blend ^c
Cyclohexane	16.7	46	26
Cyclohexane ^d	16.7	15	
Carbon tetrachloride	17.6	29	24
Toluene	18.2	18	24
Chloroform	18.7	22	25
THF	19.3	16	22
Cyclohexane/ Ethanol (90/10%v/v)			15

^aExtraction conditions: 48 hours at room temperature

^b $\delta = 16.5$ MPa^{1/2} for NR²⁷⁶

^cCured pale crepe (25%w/w) and synthetic *cis*-1,4-polyisoprene (75%w/w)

^dExtraction conditions: 48 hours at 45°C or 15 days at room temperature

the presence of acids or alcohols has been attributed to the disruption of a hydrogen-bonded component in the gel fraction^{279,284}. A significant decrease of 30-60% in the gel content of NR latex concentrates, found immediately after the addition of formic acid and hydrogen peroxide, is believed to result from the disruption of such a hydrogen-bonded network²⁶⁶(Section 2.2.2).

The insoluble fraction of NR is proposed to consist of two components, microgel and macrogel²⁸⁵. Freshly-tapped field latex was almost fully soluble in toluene or THF²⁸⁶ whereas Bloomfield found a considerable gel content (21-71%w/w in light petroleum) in such latices²⁷⁹. Subsequent studies demonstrated that the rubber in fresh field-latices contained microgel, flocculent sub-micron sized particles that are suspended in rubber solvents and

which varied in amount according to the clone²⁸⁷ and age of the latex²⁸⁸. Ammoniation and storage leads to an increase in gel content and the production of macrogel²⁷⁹, a highly swollen gelatinous phase. The coagulation of fresh latices results in the formation of macrogel, which is therefore believed to consist of aggregates of microgel with proteins and entangled polymer chains²⁸². Drying, storage and processing is believed to result in the formation of additional crosslinks through storage hardening and free-radical reactions²⁸⁶.

Although the gel content of NR is known to vary widely between grades of NR²⁸⁶, there remains considerable confusion about the proportions of microgel and macrogel in NR (*Table 4.3*).

Table 4.3

Microgel and macrogel in RSS grades of NR

Sample	Gel content ^a (%w/w)	
	Microgel	Macrogel
RSS-1 ^b	9	49
RSS-3 ^c	0	0
RSS-1 ^d		5-15
RSS-1 ^e		0
RSS ^f	5	73
RSS ^g	0	73/16

^a+1%w/w

^bCentrifugation and membrane filtration using THF²⁸⁹

^cDissolution over several weeks in cyclohexane²⁷⁸

^dFresh RSS grade in benzene (25 samples)²⁸⁷

^eOld RSS grade in benzene (25 samples)²⁸⁷

^fCentrifugation and membrane filtration in benzene²⁸⁰

^gCentrifugation and membrane filtration in benzene; optimised filtration yielded the lower value of 16%²⁸¹

In the laboratories of MRPRA, THF is used as solvent for the

measurement of gel content in NR, *prior* to GPC analysis of the sol fraction. THF was initially selected due to its ability to dissolve a wide range of elastomers²⁹⁰ and the applicability of refractive index detection to monitor solutions of NR in THF by GPC²⁹¹. In the absence of antioxidant, polyisoprenes dissolved in THF degrade rapidly during GPC analysis²⁹². The use of THF as a solvent for polyisoprenes has been criticised because of its facile formation of peroxides with the consequent promotion of oxidative degradations^{286,293}. In the presence of an antioxidant, solutions of NR in THF have been found to plug GPC columns^{291,293}. Blockages are dissolved by elution with chloroform²⁹³ or the addition of a thiol²⁹¹, and these results indicate that blockages rise from the presence of hydrogen-bonded microgel in rubber 'solutions'. At MRPRA, ultracentrifugation is used to remove microgel from solutions of NR²⁹⁴; the preferential use of membrane filtration by other workers is based on the potential of ultracentrifugation to remove sol molecules of high molecular mass in addition to microgel²⁸⁰.

To summarise, THF is not an ideal solvent for NR and the standard MRPRA procedure for the determination of gel content does not measure the real gel content of NR.

Extension of the use of THF to the determination of gel content in ENR samples is further complicated by the dependence of the thermodynamics of mixing on the epoxy-group content of the polymer. Gelling and co-workers demonstrated that there is a linear correlation between δ and epoxy-group content over the modification range of 0-75 mole%²⁷⁵. Despite the limitations of

the procedure, the gel content in samples of ENR was measured using THF. Derived values for the gel content do not measure the true gel content of ENR, but have been found to be useful for comparative analyses and the establishment of trends for solubility.

Lee and Porter observed that ENR samples which were initially soluble, developed an insoluble component on standing²⁶⁹; other workers found that highly-epoxidized polyenes, prepared in solution, would not redissolve after drying²⁵⁹. Sol fractions from highly-epoxidized NR were found to redissolve fully after drying and storage. Occasionally, samples were prepared which developed a gel fraction after drying; ¹H-NMR spectroscopy demonstrated that these samples contained additional oxygenated groups arising from the hydrolysis of epoxy groups.

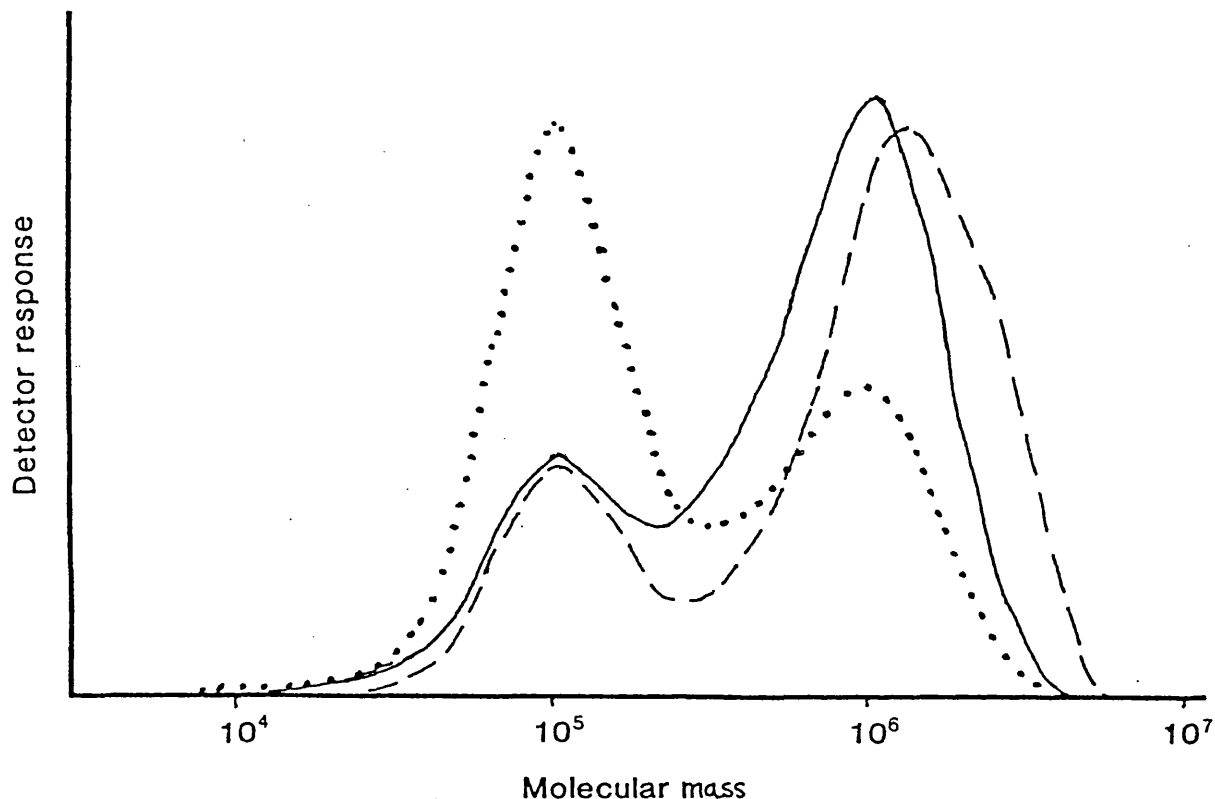
4.2.2 The Formation of Crosslinks during the Epoxidation of Natural Rubber and Synthetic *Cis*-1,4-Polyisoprene

The insolubility of highly-epoxidized SBS was attributed to the crosslinking of high molecular mass chains during drying which arose from the presence of residual acid after precipitation of the polymer²⁶⁷. We have found strong evidence for the formation of crosslinks **during** the epoxidation of *cis*-1,4-polyisoprenes²⁷². Maxprene IR-900, a fully soluble synthetic *cis*-1,4-polyisoprene latex, was epoxidized using performic acid and did not form an insoluble component until an epoxy-group content of 49 mole% was reached. GPC analysis of the

sol fraction from intermediate samples indicated the presence of a peak attributable to high molecular mass molecules (*Figure 4.7*). Progressive depletion of the high molecular mass shoulder was concurrent with gelation and is consistent with the formation of ether crosslinks. At longer reaction times, epoxy-group ring-opening is favoured with the progressive increase in the concentration of epoxy groups. The lack of change in the lower molecular mass peak in the bimodal distribution is indicative of the prevalence of higher molecular mass molecules to form crosslinks (*Figure 4.7*). This result is consistent with statistical predictions based on a random distribution of crosslinks from the random introduction of epoxy groups along the polymer chains.

The interpretation of GPC data for partially-epoxidized polyisoprenes must be treated with caution due to the dependence of elution behaviour on epoxy-group content. Consequently, the difference in hydrodynamic constants for NR and ENR-50 ($k = 1.09 \times 10^{-4}$ and $\alpha = 0.79$ for NR²⁹¹; $k = 4.85 \times 10^{-4}$ and $\alpha = 0.82$ for ENR-50²⁹⁵) has a significant effect upon derived molecular mass distributions (*Figure 4.8*). The molecular mass distributions presented for epoxidized Maxprene IR-900 (*Figure 4.7*) were derived from use of the hydrodynamic constants for NR. Use of the corresponding hydrodynamic constants for ENR-50 indicates that the high molecular mass shoulder in the 34 mole% epoxidized polyisoprene is more pronounced than is apparent in *Figure 4.7*, and the formation of crosslinks more extensive than indicated above.

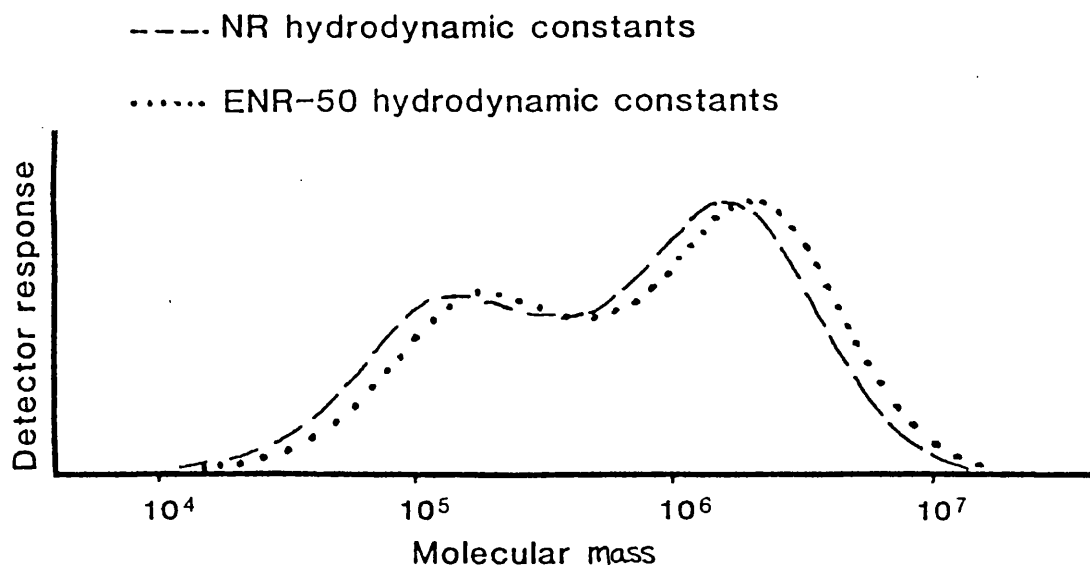
— 0.25 hours reaction; 1 mole% epoxide, 0% gel content
 - - - 12.50 hours reaction; 34 mole% epoxide, 0% gel content
 23.75 hours reaction; 49 mole% epoxide, 68% gel content



Molecular mass parameters for partially-epoxidized Maxprene IR-900

Figure 4.7

The extent of hydrolysis and the structures of the secondary products arising from epoxy-group ring-opening has been assumed to be primarily determined by the concentration of acids. The importance of the concentration of formic acid that is used during the epoxidation of NR latices has been discussed¹⁸⁸ (Section 2.1.1). The dependence of crosslinking on the epoxy-group content of the polymer was examined by the comparison of two latex epoxidations in which the only difference was the initial concentration of hydrogen peroxide (Table 4.4).



Molecular mass parameters derived using the hydrodynamic constants for NR and ENR-50

Figure 4.8

Maxprene IR-900 latex was epoxidized using hydrogen peroxide and formic acid. The onset of gelation was twice as rapid in the reaction containing a higher initial concentration of hydrogen peroxide (*Table 4.4*) in a manner consistent with general results for the relative gel content of ENR-25 and -50⁴². The extent of crosslinking was roughly assessed by equilibrium-swelling measurements (*Table 4.4*). Volume-fraction measurements (3-5%) for samples prepared in the presence of the higher concentration of hydrogen peroxide were an order of magnitude higher than those of corresponding samples from the alternative reaction (0.5-0.6%). These results are consistent with a partial dependence of the extent of crosslinking upon the epoxy-group content of the polyisoprene. In a further series of experiments, fully-soluble samples of partially-epoxidized Maxprene IR-900 were exposed to

Table 4.4

The formation of crosslinks in partially-epoxidized Maxprene
IR-900

Reaction time (hours)	Epoxy-group content (mole%) ^a	Gel content (%w/w, THF) ^b	Volume fraction of rubber in swollen state, v_r (%) ^c
0 ^d	0	0	
0.25	1.0	0	
2.50	9.0	0	
5.25	18.0	0	
7.33	23.0	0	
12.50	34.0	0	
23.75	49.0	68	2.8
26.50	51.0	76	3.8
28.75	53.0	78	3.9
30.50	54.0	82	5.0
96.00	65.0	95	e
=====			
0 ^f	0	0	
0.25	0.5	0	
1.25	1.5	0	
3.00	3.0	0	
5.50	7.0	0	
22.25	21.0	0	
25.00	23.0	0	
46.25	28.0	37	0.6
49.00	29.0	28	0.5
52.50	29.0	30	0.5

^aTheoretical values based on a conversion efficiency of 90%¹⁹³

^bSamples coagulated in methanol containing ammonia or pretreated with sodium hydroxide(2M) before coagulation in methanol

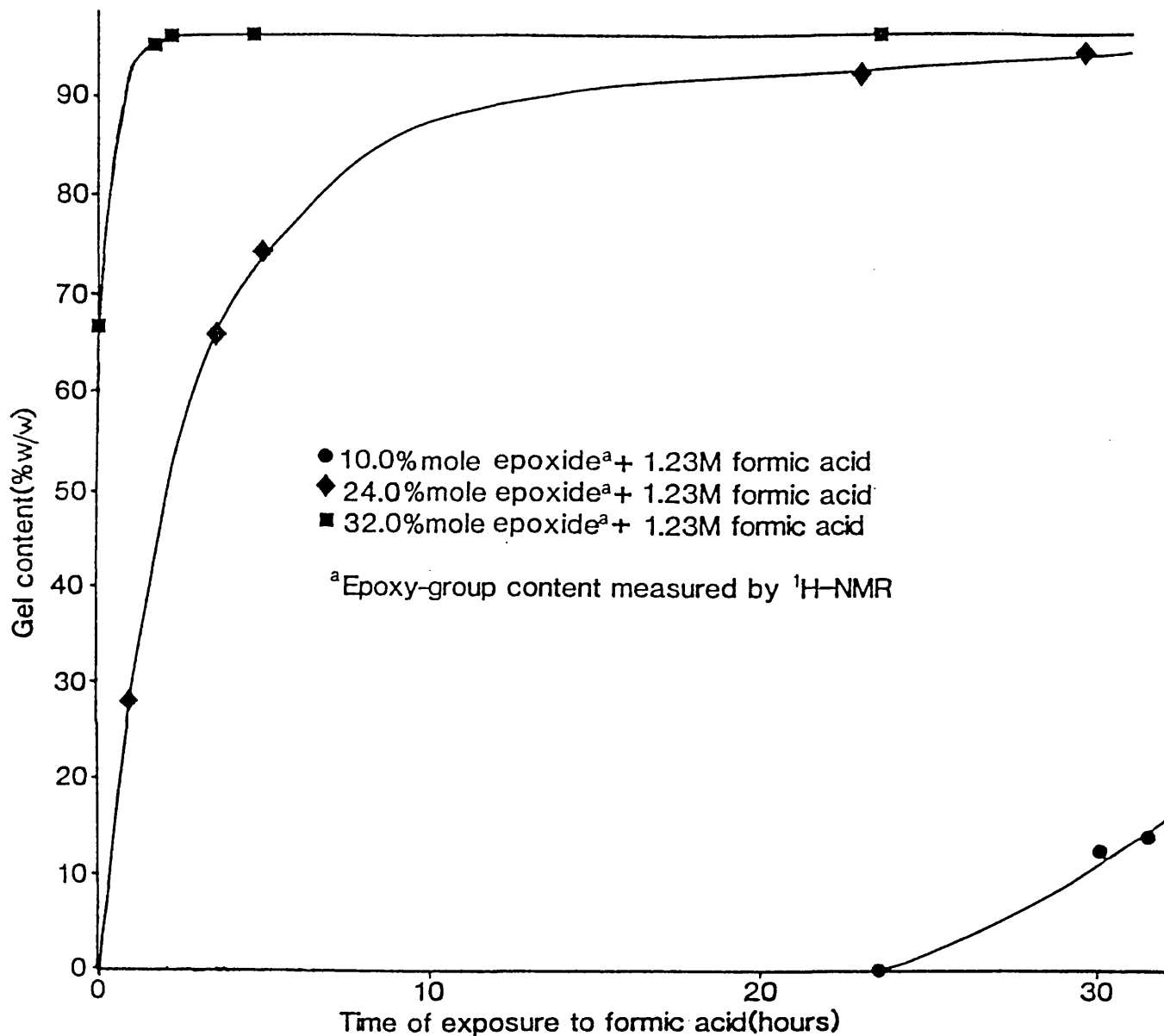
^cAverage values

^dReaction conditions: [Formic acid]₀ = 2.00M, [Hydrogen peroxide]₀ = 6.02M, 35°C

^eGel dispersed into small discrete particles

^fReaction conditions: [Formic acid]₀ = 1.92M, [Hydrogen peroxide]₀ = 2.85M, 35°C

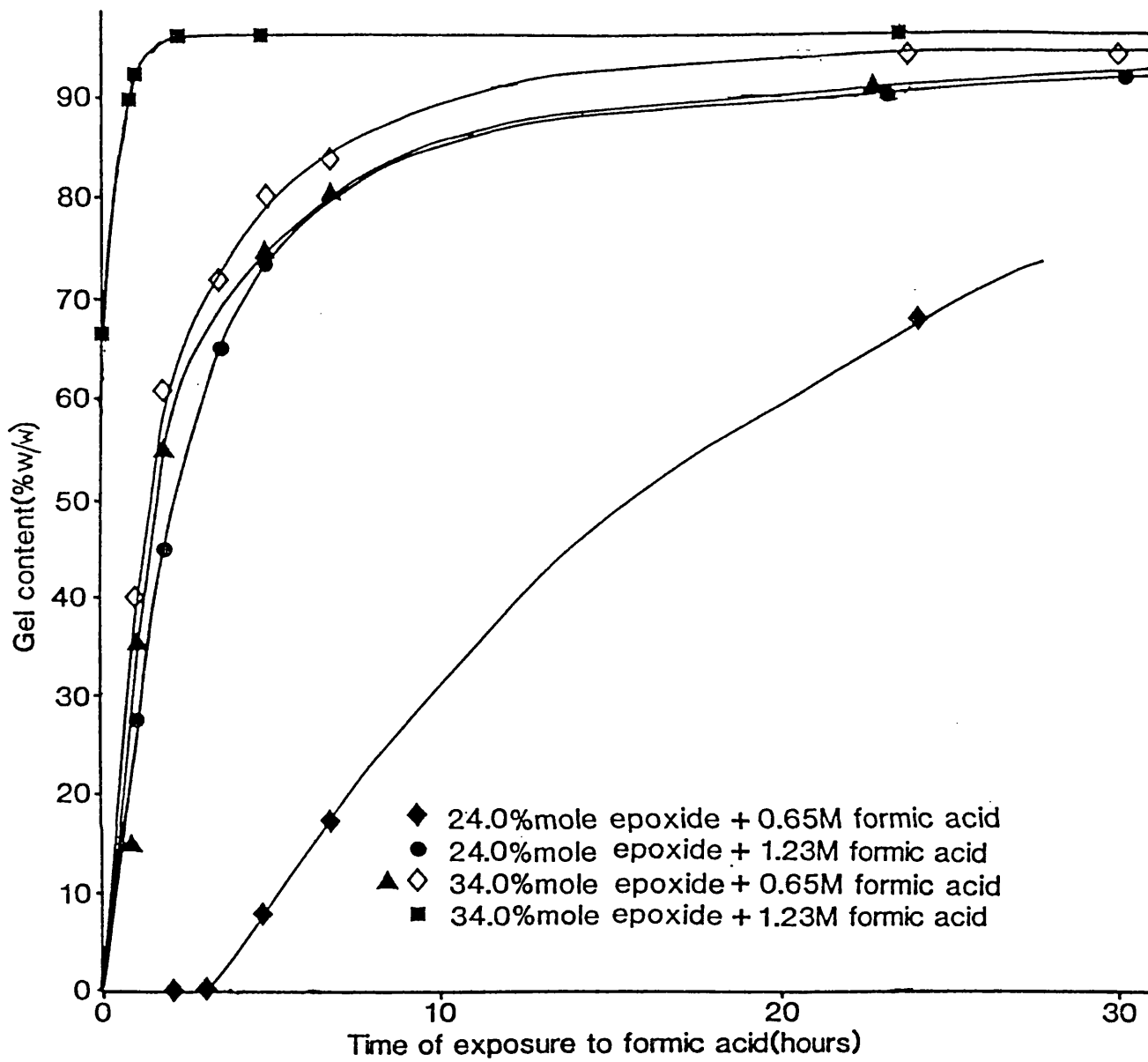
formic acid at 60°C. Gel content was monitored as a function of reaction time and the results are illustrated in *Figures 4.9 and 4.10*. A three-fold increase in epoxy-group content resulted in a far greater increase in the rate of gelation (*Figure 4.9*), consistent with the rate of ring-opening being partially



Gel content as a function of epoxy-group content

Figure 4.9

dependent upon epoxy-group content. The lack of a simple dependence between the two parameters is believed to arise from the increasing solubility of formic acid in latex particles as the oxygen content of the rubber is increased. The relative



The dependence of gel content on the concentration of epoxy groups and acid

Figure 4.10

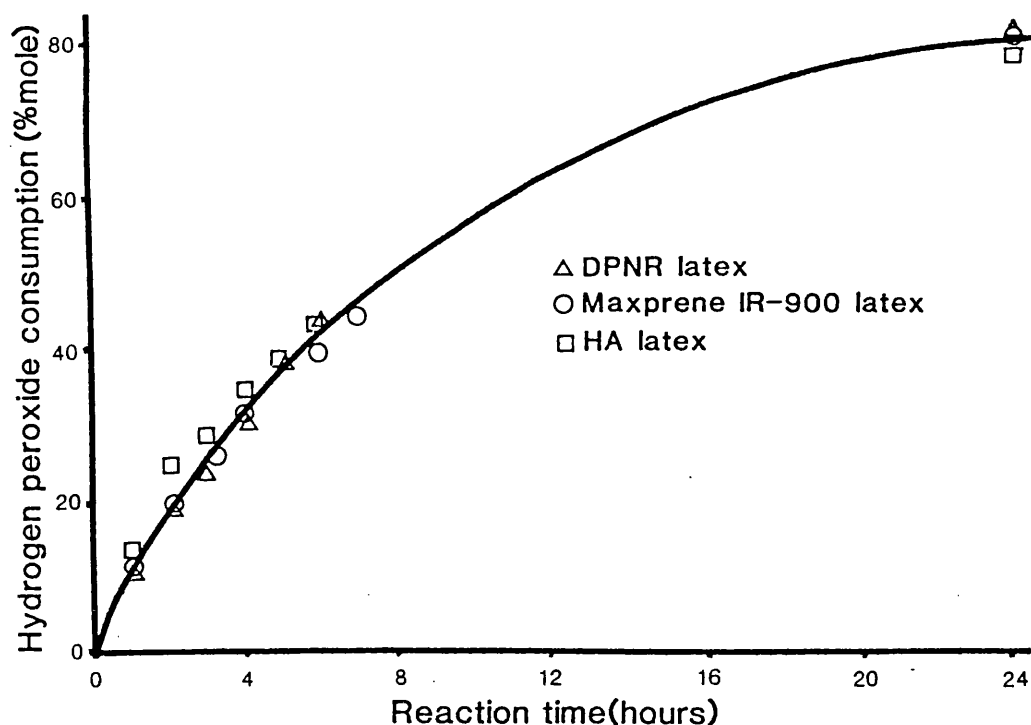
importance of epoxy-group content and concentration of formic acid to the rate of crosslinking is illustrated in *Figure 4.10*. Under these conditions, the epoxy-group content of the polymer is

more important than the concentration of acid[Ⓢ] in controlling the rate of crosslinking.

Bradbury and Perera suggested that the gel content of ENR prepared from latex was increased by the formation of crosslinks from the reaction of ring-opened epoxy groups with non-rubbers⁷⁸. A close examination of this study revealed that the observed difference in gelation between latex and solution epoxidations probably resulted from the high concentration of formic acid in the latex reaction (3.45M compared to a maximum concentration of 0.12M for carboxylic acid in the solution epoxidations)⁷⁸. Nevertheless, the role of non-rubbers in the epoxidation of NR latex was investigated by the epoxidation of Maxprene IR-900, HA and DPNR latices with performic acid under identical experimental conditions. The volumetric estimation of residual hydrogen peroxide (Section 2.5) was used to demonstrate that there was no significant difference in the rate of epoxidation between the latices (*Figure 4.11*). The formation of crosslinks was monitored by gel content measurements (*Figure 4.12*). Initial samples from the epoxidation of HA and DPNR latex showed a significant loss in gel content arising from the disruption of hydrogen-bonded material in the gel phase. Subsequent samples showed a slow increase in gel content over the initial 5-7 hours of reaction (corresponding to a maximum epoxy-group content of 30-40 mole%). A significant increase in the gel content of partially-

Footnote[Ⓢ]

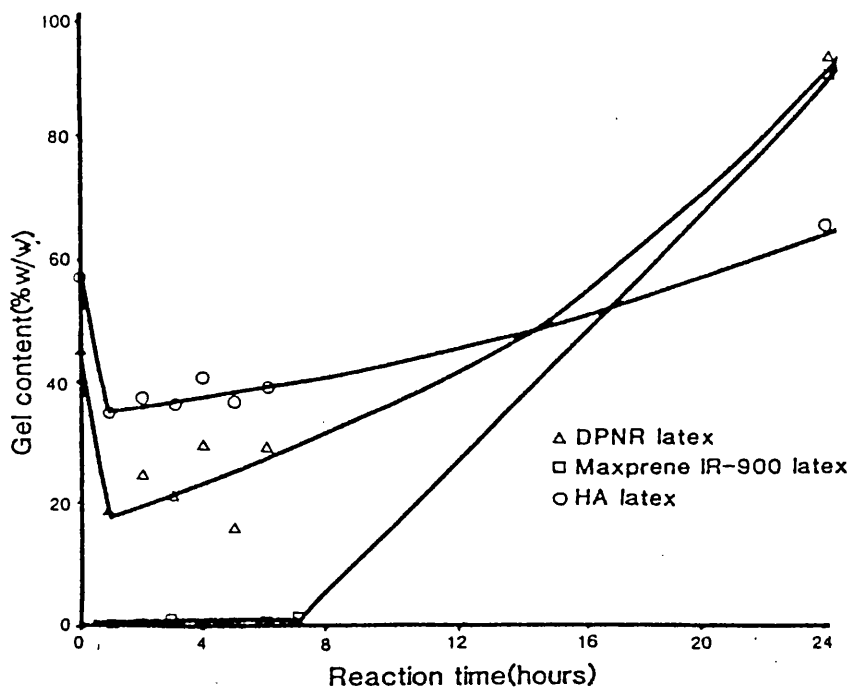
The reliability of these experiments was confirmed by duplicate runs.



The consumption of hydrogen peroxide during the epoxidation of *cis*-1,4-polyisoprene latices

Figure 4.11

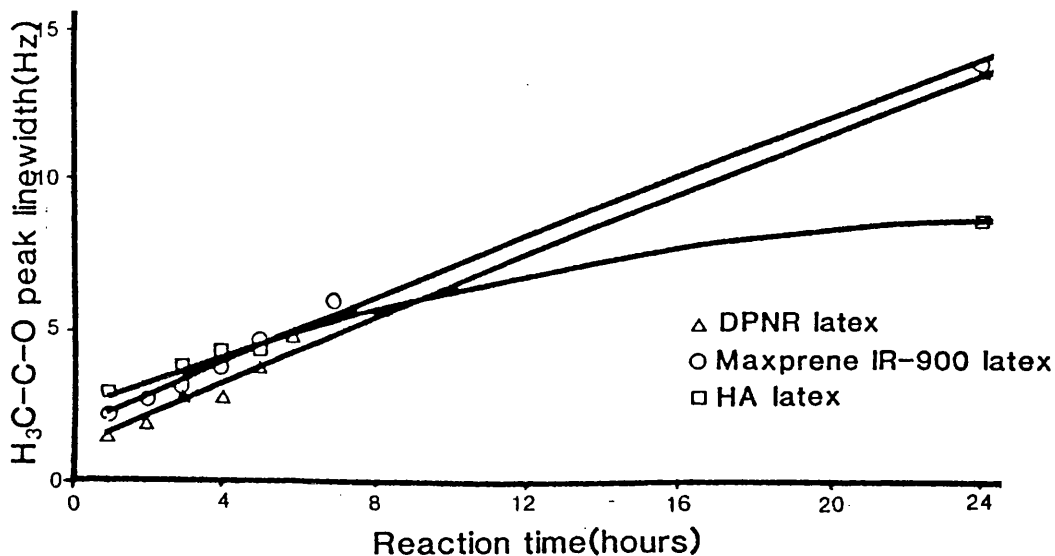
epoxidized DPNR latex was observed at an epoxy-group content of 50-60 mole%. The synthetic latex remained fully soluble up to an epoxy-group content of 36 mole% and thereafter gelled rapidly. The formation of gel in the latter stages of reaction is consistent with the dependence of crosslink formation on the concentration of epoxy groups. DPNR latex²⁹⁶ is thoroughly washed after enzymic deproteinization²⁹⁷ and is therefore left with a very low concentration of non-rubbers; the disparate gelation behaviour of partially-epoxidized HA latex (*Figure 4.12*) suggests this latex contains non-rubbers which **inhibit** the formation of crosslinks. Complementary evidence was provided by ¹H-NMR analysis of samples from each epoxidation. The breadth of NMR



The formation of gel during the epoxidation of *cis*-1,4-polyisoprene latices

Figure 4.12

peaks is primarily dependant upon molecular mobility; a linear correlation between the half-height linewidth²⁹⁸ of ¹H-NMR resonances and epoxy-group content in partially-epoxidized NR²⁵⁶ is consistent with a progressive decrease in chain mobility (the correlation is analogous to the linear dependence of T_g on epoxy-group content, Section 3.4). In the comparative epoxidations, the half-height linewidth of the epoxy-methine resonance was monitored as a function of reaction time (*Figure 4.13*) and the results complemented those yielded by gel-content measurements. A significant retardation of the rate of resonance broadening after 5 hours reaction' in the epoxidation of HA latex is consistent with a reduced rate of crosslink formation.



$^1\text{H-NMR}$ monitoring of crosslinking during the epoxidation of *cis*-1,4-polyisoprene latices

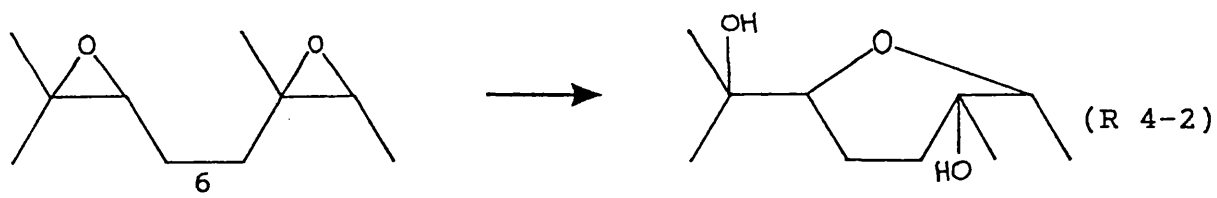
Figure 4.13

To summarise, both the gel content and $^1\text{H-NMR}$ measurements demonstrate that the non-rubbers in NR latex concentrates inhibit the formation of crosslinks during epoxidation. The mechanism of inhibition is not currently understood.

4.3 The Formation of Tetrahydrofuran Rings

The tendency of epoxide rings to cleave in the presence of acids or bases is well established²⁵⁰. Trisubstituted epoxides are particularly sensitive to ring-opening in the presence of acids¹⁰⁴ and therefore partially-epoxidized NR in the presence of formic acid is prone to hydrolysis. The attempted preparation of fully-epoxidized NR using peracetic acid resulted in the formation of a brittle plastic with a broad T_g commencing at 100°C ⁴². Gelling proposed that this material resulted from epoxy-

group ring-opening and subsequent intramolecular reaction between adjacent epoxy groups along polymer chains in a zip-type cascade⁴² (Scheme 1-10, Section 2.1.1). This process has been termed furanization and is believed to result in the formation of (five-membered) tetrahydrofuran rings in preference to (six-membered) tetrahydropyran rings. The probable size of the ether ring was based on the application of Baldwin's rules for ring closure¹⁶¹ and by analogy with corresponding reactions for model compounds of low molecular mass⁴² (Section 1.3). Experimental evidence for the size of ether rings in furanized NR is scant and Orszulik has published conflicting evidence for the preferential formation of tetrahydropyrans from the hydrolysis of a model for ENR with adjacent epoxy groups²⁹⁹ (6, R 4-2).



4.3.1 Model Studies

Evidence for the size of the ether rings in furanized NR is based upon ambiguous IR evidence relating to low molecular mass cyclic ethers^{40,42,184}. The complete insolubility of furanized rubber prepared from polyisoprene chains of high molecular mass is indicative of the presence of ether crosslinks and has precluded analysis by most analytical techniques. Consequently, Perera and co-workers resorted to the furanization of liquid rubber ($M_n =$

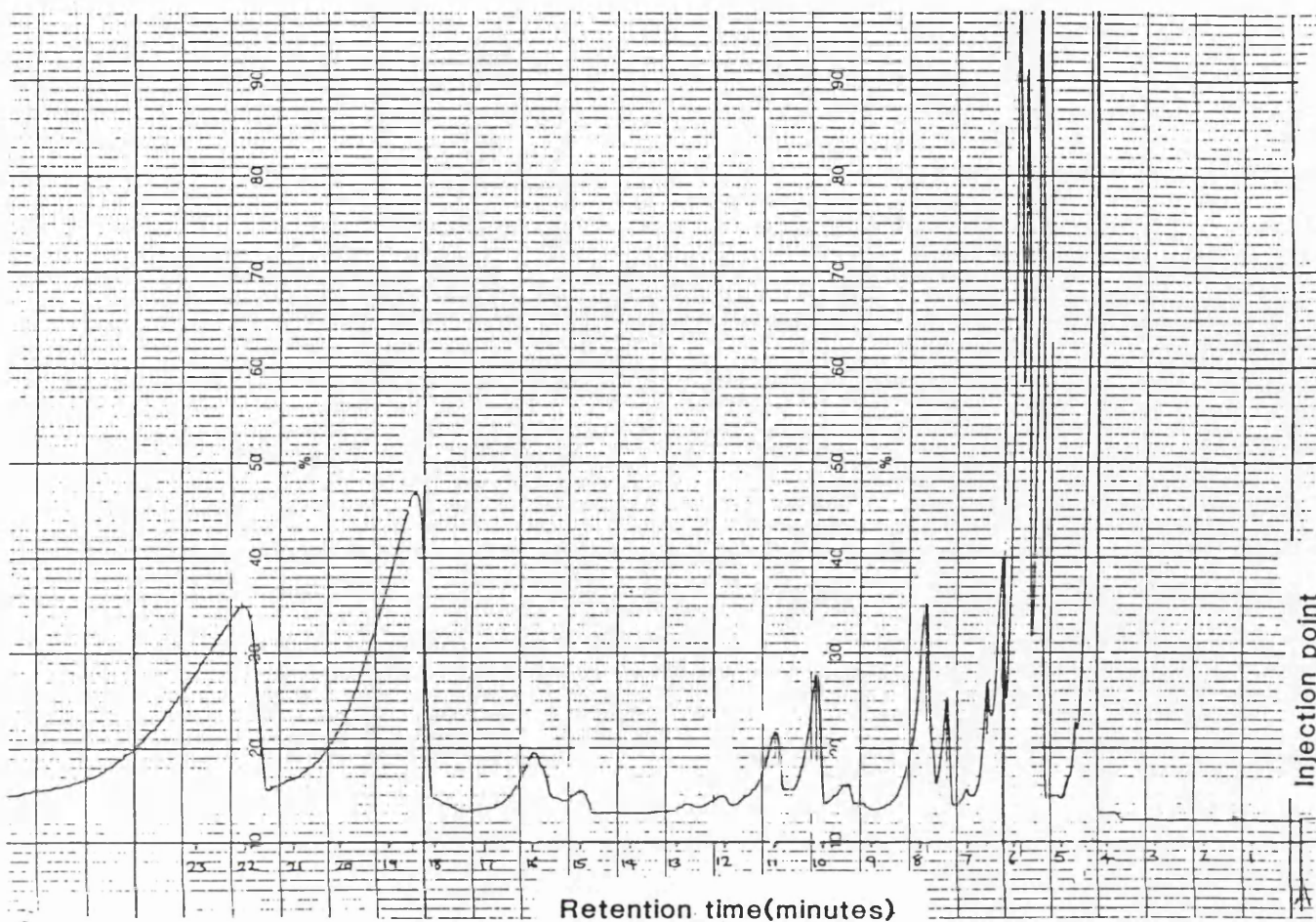
4500) in order to prepare a soluble material for analysis by NMR spectroscopy³⁰⁰.

Initial studies on furanization were based on 2,2-dimethyl-3-[(3-methyl-3-oxiranylpentyl]-oxirane, 6, a model for adjacent epoxidized units in partially-epoxidized NR. Orszulik claimed that the acid-catalysed hydrolysis of 6 led to the preferential formation of tetrahydropyran rings²⁹⁹(R 4-2). The reaction has been promoted as a convenient method to prepare tetrahydropyrans from 1,5-dienes²⁹⁹, despite overwhelming evidence for the formation of tetrahydrofuran rings from the acid- or base-catalysed hydrolysis of polyepoxides, based on 1,5-dienes or 1,5,9-triene skeletons^{159,160,171-182}(*Scheme 1-9*).

The hydrolysis of 6 with 0.01M sulphuric acid under similar conditions to those used by Orszulik gave a complex mixture of products (*Figure 4.14*). HPLC analysis, using a peak area integrator, demonstrated that two major products accounted for 54% of the hydrolysate[Ⓞ]. The parent 1,5-diene, an impurity in the starting material, was eluted at the solvent front and unreacted 6 was eluted at a retention time of 5.4 minutes. The complex mixture of products is consistent with the hydrolysis of an analogous 1,2,5,6-diepoxy¹⁷⁷(7, *Figure 4.15*). A further experiment with 0.03M sulphuric acid yielded the same products in different proportions with the two primary products accounting

Footnote[Ⓞ]

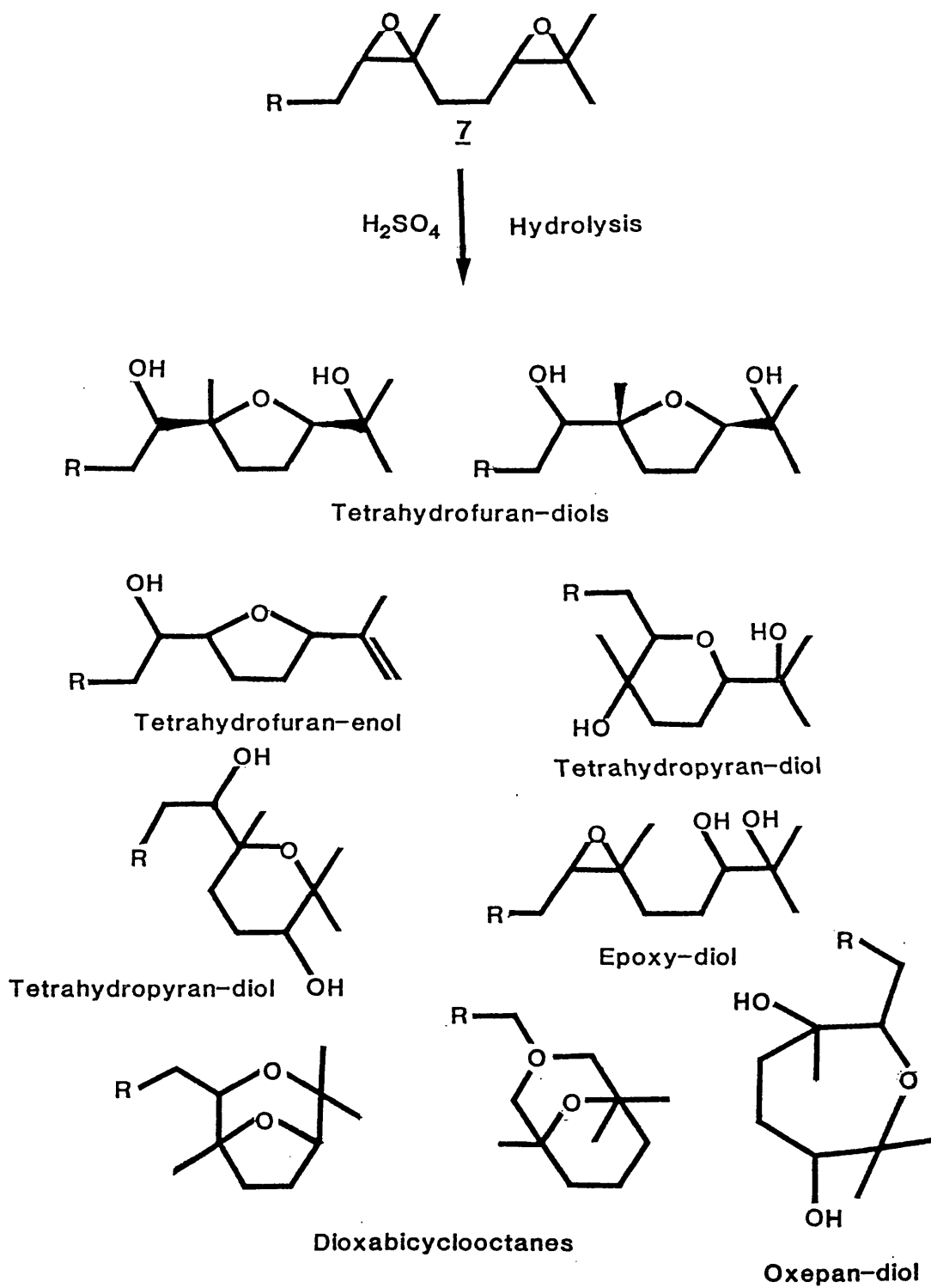
The yields quoted are not quantitative in the absence of known values for HPLC response factors (i.e. peak area as a function of concentration), but can be used for comparisons with similar HPLC analyses.



HPLC trace for the hydrolysis of 6 with dilute sulphuric acid

Figure 4.14

for 43% of the hydrolysate (*Table 4.5*). The relative concentrations of sulphuric acid in the two experiments (*Scheme 4-2*) suggests that hydrolysis in the presence of the higher concentration of acid leads to a lower yield of the primary products (43% compared to 54%), a higher yield of less polar products (47% compared to 21%) and an increase in unreacted 6 (15% compared to 8%, *Table 4.5*). This result is apparently anomalous, but is consistent with the effect of residual acid



Products from the hydrolysis of 7²⁹⁴

Figure 4.15

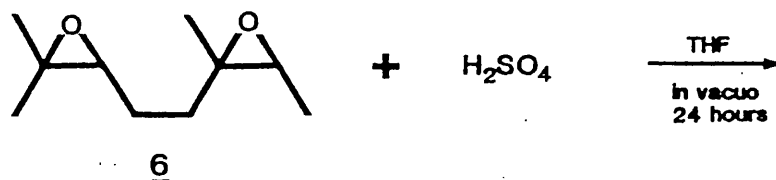
Table 4.5

HPLC analyses for the hydrolysis of 6 with dilute sulphuric acid

Retention time (minutes)	Concentration of sulphuric acid (M)	
	0.01 ^a	0.03 ^b
4.0-5.0	Solvent front	
5.4	8	15
5.7	6	10
5.9	10	14
6.2	3	2
6.6	2	1
7.5	1	<1
7.9	5	4
9.4	<1	<1
9.9	2	2
10.2	3	2
11.0	3	2
15.0	<1	2
16.0	3	2
18.5	33	25
22.0	21	19

^a[6]₀ = 0.05M, reaction worked up in the presence of sulphuric acid

^b[6]₀ = 0.05M, reaction worked up after neutralization



Reaction conditions

(1)	0.05M	0.01M
(2)	0.05M	0.03M

Experimental conditions for the hydrolysis of 6 with dilute sulphuric acid

Scheme 4-2

during work-up procedures. Such procedures in the absence of

neutralization result in a high concentration of acid during the isolation of products and accelerated hydrolysis. The corresponding effect in NR latex epoxidation is well established with ring-opening during epoxidation being of minor importance relative to the deleterious effect of residual acid during processing^{45,186}.

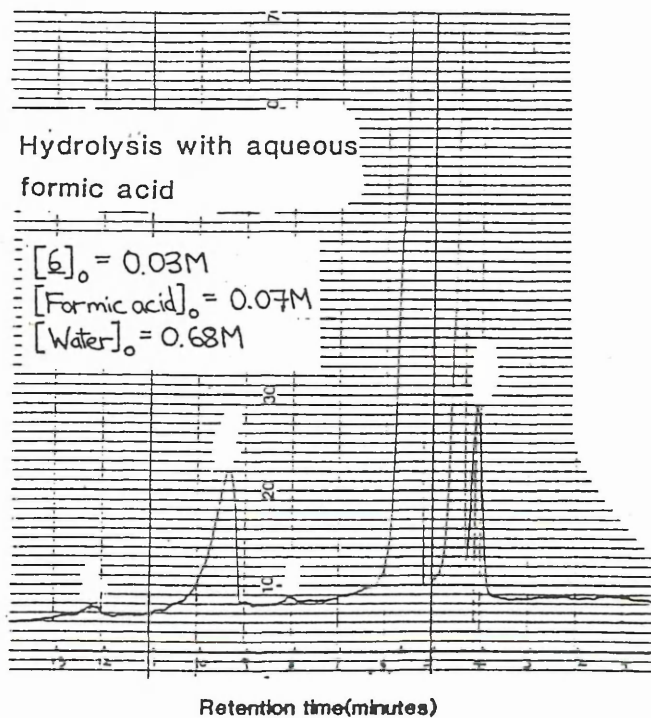
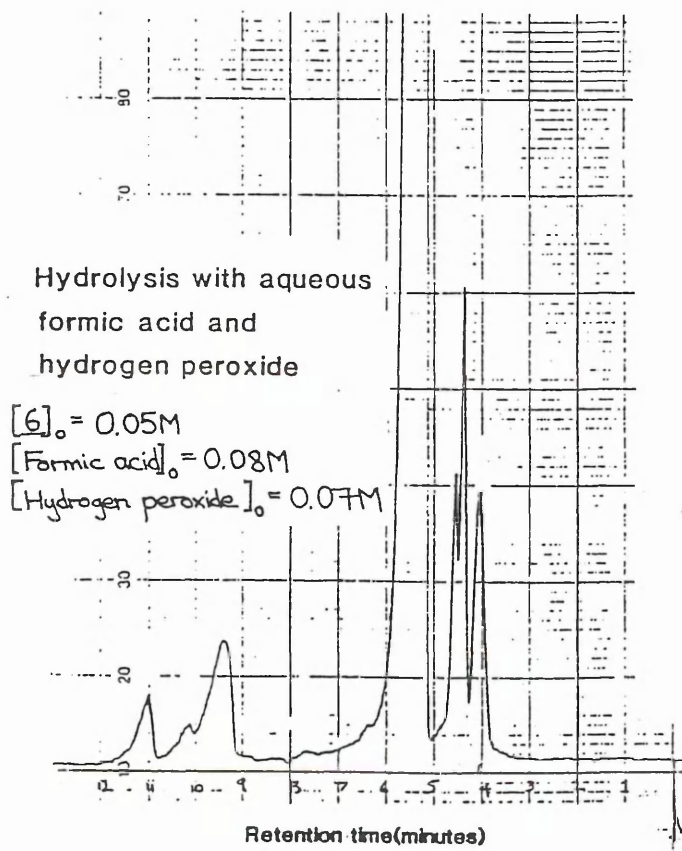
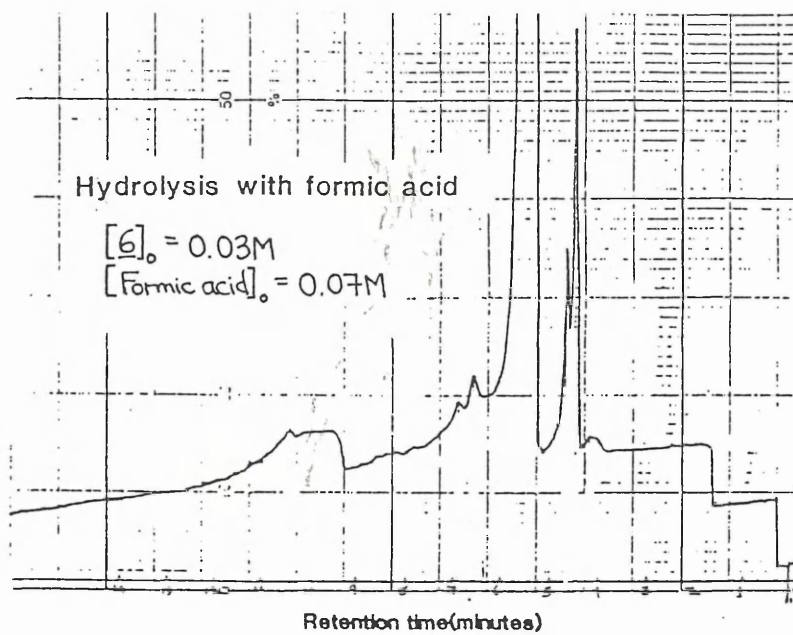
The hydrolysis of 6 with a variety of acids yielded hydrolysates with compositions consistent with the determination of product structures by the absolute concentrations of the acid and 6 (Figures 4.14 and 4.16, Tables 4.5 and 4.6).

Table 4.6

HPLC analyses for the hydrolysis of 6 with formic acid or CSA

Retention time (minutes)	Formic acid		10-Camphorsulphonic acid			
	0.07M ^a	0.08M ^b	0.01M ^c	0.01M ^d	0.1M	0.1M
	Product yield (area%, HPLC)					
4.0-5.0	Solvent front					
5.4-5.7	89	86	97	94	49	49
5.9	0	0	0	0	0	0
6.2	0	0	0	0	0	2
6.6	0	0	0	0	0	0
7.5	0	0	1	1	8	9
7.9	<1	<1	1	3	15	18
9.4	10	9	<1	1	8	7
9.9-10.2	0	2	<1	1	11	11
11.0	0	3	0	0	<1	<1
15.0	0	0	0	0	(1	<1
16.0	0	0	0	0	(1	<1
18.5	0	0	0	0	4	3
22.0	0	0	0	0	2	1

- ^a[6]₀ = 0.03M, aqueous formic acid
^b[6]₀ = 0.05M, formic acid and hydrogen peroxide (0.07M)
^c[6]₀ = 0.06M, 25°C
^d[6]₀ = 0.06M, 50°C
^e[6]₀ = 0.06M, 25°C
^f[6]₀ = 0.06M, 50°C



HPLC traces for the hydrolysis of 6 with formic acid

Figure 4.16

Use of CSA demonstrated the expected effect of increasing acid concentration (i.e. the formation of more polar products and increased consumption of 6).

A comparison of the hydrolysis of 6 with formic acid in aqueous or nominally anhydrous conditions (*Figure 4.16, Table 4.6*) indicates that water has a significant effect upon the structure of products. ¹H-NMR analysis of hydrolysate fractions, obtained by the reaction of 6 with formic acid or CSA in nominally anhydrous conditions, yielded little evidence for the presence of alcohols. The results are therefore consistent with analogous studies in which ring-cleavage resulted in the formation of cyclic ether-diols in aqueous conditions, or bicyclooctanes in anhydrous conditions¹⁷⁷ (*Figure 4.15*). The ability of the acid to provide effective counter-ions has an effect upon the structure of hydrolysis products. ¹H-NMR analysis of fractions from the hydrolysis of 6 with formic acid indicated the formation of several formates, whereas hydrogen sulphates were not detected in hydrolysates products from the use of sulphuric acid. This observation is consistent with the expected counter-ion activity of formic acid and sulphuric acid.

The hydrolysis of 6 with aqueous formic acid was compared with a similar experiment using aqueous formic acid and hydrogen peroxide (in a model reaction simulating conditions for the epoxidation of NR latex); HPLC analysis demonstrated that hydrogen peroxide promoted the formation of more polar products (*Table 4.6 and Figure 4.16*).

These results demonstrate that many factors determine the

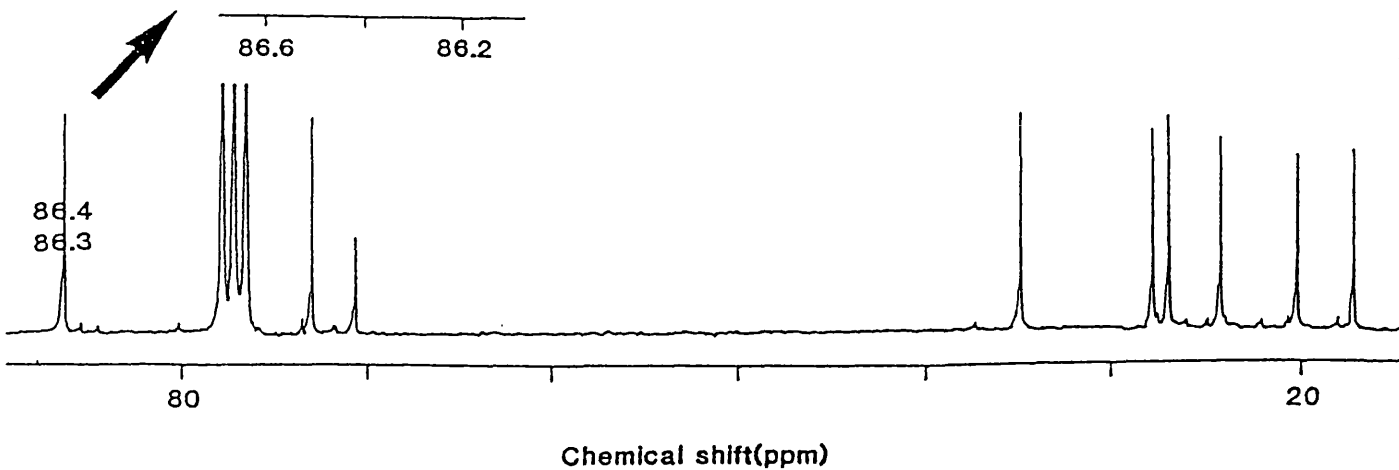
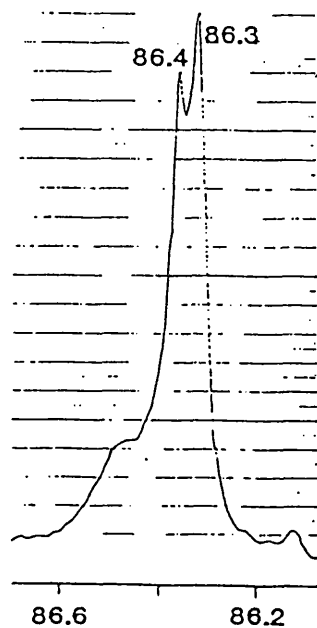
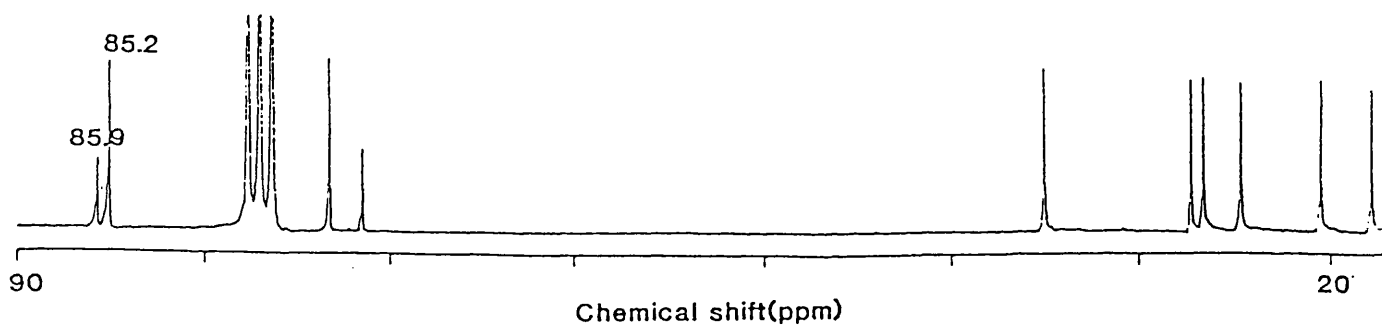
products arising from the hydrolysis of 6 and are in marked contrast to studies on the hydrolysis of ENR in which it has been assumed that only the acidity dictates product composition^{40,42,44,63,184}.

A complete characterization of hydrolysis products was not attempted and attention was concentrated on analysis of the two major products and the identification of cyclic ether-diols. HPLC on a semi-preparative scale was used to fractionate a hydrolysate. ¹H-NMR analysis of the fractions demonstrated that the two major hydrolysis products were cleanly separated; they were subsequently isolated as colourless oils. The ¹³C-NMR spectra of the two primary products were consistent with cyclic ether-diol structures (*Figure 4.17*); however, unambiguous elucidation of the ring size was not straightforward.

Theoretically, five-, six- or seven-membered cyclic ethers could be prepared from the acid-catalysed hydrolysis of 6 (*Figure 4.18*) based on two criteria;

(a) Baldwin's rules for ring closure favour *exo*-ring closures in general and five- or six-*exo* over seven-*exo* ring closures in particular¹⁶¹

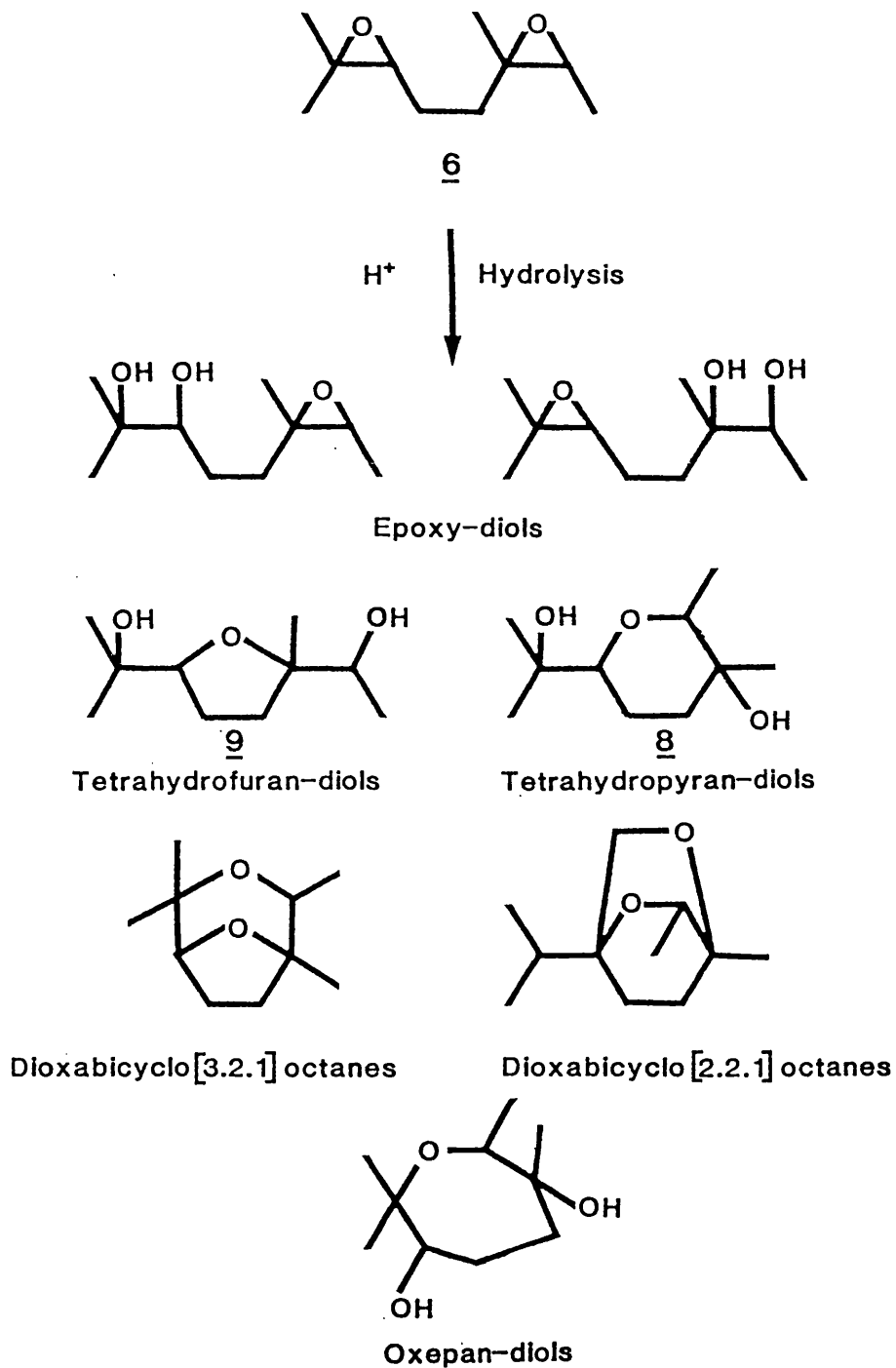
and, (b) The initial direction of ring-opening; The product of zip-type cascade reactions for polyepoxides is determined by the position of the initial epoxide ring activated towards ring-opening relative to adjacent epoxy groups, and the direction in which ring-expansion



^{13}C -NMR spectra of tetrahydrofuran-diols from the hydrolysis of 6

Figure 4.17

occurs.



The formation of cyclic ethers from the hydrolysis of **6**

Figure 4.18

Assignment of the cyclic ether present in furanized NR to tetrahydrofuran rings^{40,42} has been based on an IR absorption at 1065cm^{-1} , in comparison with a C-O-C stretching frequency for tetrahydrofuran at 1076cm^{-1} (and a corresponding absorption at 1100cm^{-1} in tetrahydropyran) and an absorption at 1067cm^{-1} ascribed to tetrahydrofuran rings in the SBS analogue of furanized NR¹⁸⁴. FT-IR analysis of the two major hydrolysis products from 6 indicated the presence of a series of absorptions between 1000 and 1100cm^{-1} (Table 4.7) which could plausibly be

Table 4.7

Analytical data for the major hydrolysis products

HPLC retention time (minutes)	18.5	22.0
FT-IR absorptions (cm^{-1})	992.3, 1029.4, 1069.0, 1106.1, 1181.6	1002.4, 1046.9, 1066.8, 1107.1, 1144.9
^{13}C -NMR resonances (ppm)	17.3, 20.3, 24.3, 27.0, 27.8, 35.0, 70.7, 73.0, 86.3, 86.4 ^a	17.9, 20.6, 24.8, 26.7, 27.4, 35.0, 71.6, 73.3, 85.2, 85.9 ^a

^aMinor component

interpreted as being consistent with either five- or six-membered rings. ^1H -NMR spectra of the two fractions did not permit discrimination between five- or six-membered rings since the multiplicity of resonances for both the anticipated tetrahydrofuran- and tetrahydropyran-diol is identical. Subtle differences in the ^1H -NMR chemical shifts of corresponding resonances could not be used to discriminate between five- or six-membered rings because of the lack of reference data for

comparable tetrahydrofurans and tetrahydropyrans. Fortunately, ^{13}C -NMR spectroscopy can be used to provide unambiguous evidence for ring size. Inspection of the structure of the cyclic ether-diols which could be formed from the hydrolysis of 6 (Figure 4.18) indicates that the tetrahydropyran-diol, 8, is unique in having two trisubstituted alcohol groups (cf. the tetrahydrofuran- and oxepan-diols which have one trisubstituted and one secondary alcohol group). Consequently, ^{13}C -NMR spectral editing techniques³⁰¹ (i.e. experiments which can distinguish between carbon nuclei according to the number of directly attached hydrogens) permits discrimination between 8 and the alternative structures. A primitive method of spectral editing, SFORD, was applied to the two major products from the hydrolysis of 6 and yielded, in both cases, a singlet and doublet for the two C-OH resonances between 70 and 74ppm (Table 4.7). Both fractions therefore contained a secondary and trisubstituted alcohol group, structural fragments inconsistent with the formation of 8.

Coxon and co-workers studied the acid-catalysed hydrolysis of epoxyalcohols and demonstrated the preferential formation of cyclic ethers in the ring order: tetrahydrofuran > tetrahydropyran >> oxepan¹⁵⁵⁻¹⁵⁷. The formation of oxepan rings is highly disfavoured and the hydrolysis of 6 with dilute sulphuric acid must therefore result in the primary formation of tetrahydrofuran-diols, 9.

The results of Orszulik are anomalous and should be treated with caution; for example, the observation of C-OH resonances at

76.0 and 77.1ppm would be obscured by the C-D triplet in the NMR solvent, CDCl_3 ²⁹⁹.

A careful examination of the ^{13}C -NMR spectra acquired for the two tetrahydrofuran-diol fractions shows additional resonances in the chemical shift region characteristic of C-O ring carbons in cyclic ethers (80-90ppm) which are consistent with the presence of two compounds in each fraction (*Table 4.5 and Figure 4.17*). Each fraction is therefore likely to contain a pair of isomeric tetrahydrofuran-diols, with separation into two resolved peaks by HPLC suggested to be a function of the extent of intramolecular hydrogen bonding in each isomer.

In principle, ^{13}C -NMR spectroscopy can be used to assign acyclic alcohols and cyclic ethers by diagnostic chemical shifts between 70-77ppm and 80-90ppm respectively. However, a search for minor quantities of tetrahydropyran- and oxepan-diols in hydrolysates was limited by the minor amount of each fraction isolated by semi-preparative HPLC. Both ^1H - and ^{13}C -NMR spectroscopies was used to analyse a fraction containing the mixture of compounds eluted between 14.5 and 16.5 minutes (and prepared by the hydrolysis of 6 with aqueous sulphuric acid, *Table 4.5*). An extended ^{13}C -NMR acquisition demonstrated the presence of several alcohols and a complete absence of cyclic ethers in the fraction. The result suggests that the formation of tetrahydropyran- and oxepan-diols is negligible under the conditions of hydrolysis. However, the formation of less polar six- or seven-membered cyclic ethers (i.e. bicyclic heterocycles, *Figure 4.17*) cannot be discounted.

4.3.2 The Furanization of Natural Rubber Latex

The concurrent formation of ether crosslinks with tetrahydrofuran rings results in the complete insolubility of furanized NR prepared from high molecular mass chains. Consequently, a spectroscopic analysis of furanized NR was based on the hydrolysis of ENR prepared from liquid rubbers; under these conditions, furanized NR was prepared as a viscous liquid which was soluble in polar solvents³⁰⁰.

During the course of these studies, samples from the epoxidation of NR latex in the presence of a high concentration of formic acid (by D.S. Campbell) were analysed in our laboratories (*Table 4.8*). The high gel content and poorly-

Table 4.8

The analysis of furanized NR

Reaction time (hours)	Gel content (%w/w, CH ₂ Cl ₂)	Epoxy-group content (mole%)	
		¹ H-NMR ^a	DSC ^b
51.5	79	68	66
54.0	77	68	66
71.0	88	c	78
74.0	92	c	81

^a90MHz CW-NMR

^bUsing a calibration factor of 1.00K mole⁻¹

^cPoorly-resolved spectra

resolved ¹H-NMR spectra obtained from later samples are consistent with the partial hydrolysis of epoxy groups. The significant increase in T_g for later samples and the consequent inflation in apparent epoxy-group content is consistent with the

formation of tetrahydrofuran rings⁷⁴(Section 3.1). The poor ¹H-NMR spectral resolution observed from heavily-gelled samples, swollen in CDCl₃, was improved by the analysis of sol fractions. ¹H-NMR resonances observed at 2.7 and 3.9ppm are attributable to methine protons in epoxy groups (Section 3.3.1) and tetrahydrofuran rings³⁰⁰. The comparative analysis of whole samples and sol fractions by ¹H-NMR spectroscopy demonstrated that the formation of gel did not result in chemical heterogeneity (Table 4.9). These results are consistent with a

Table 4.9

The analysis of furanized NR by ¹H- and ¹³C-NMR spectroscopies

Reaction time (hours)		Modification level ^a (mole%)		
		¹ H-NMR (sol)	¹ H-NMR (whole)	¹³ C-NMR (whole)
51.5	Epoxide	65	66	67 _b
	Furan	5	4	
54.0	Epoxide	72 _b	73 _b	65
	Furan			7
71.0	Epoxide	57	57	55
	Furan	15	21	25
74.0	Epoxide	53	52	50 ^c
	Furan	24	23	28

^a¹H-NMR spectroscopy at 200MHz and ¹³C-NMR spectroscopy at 50MHz; trace-and-weigh analysis

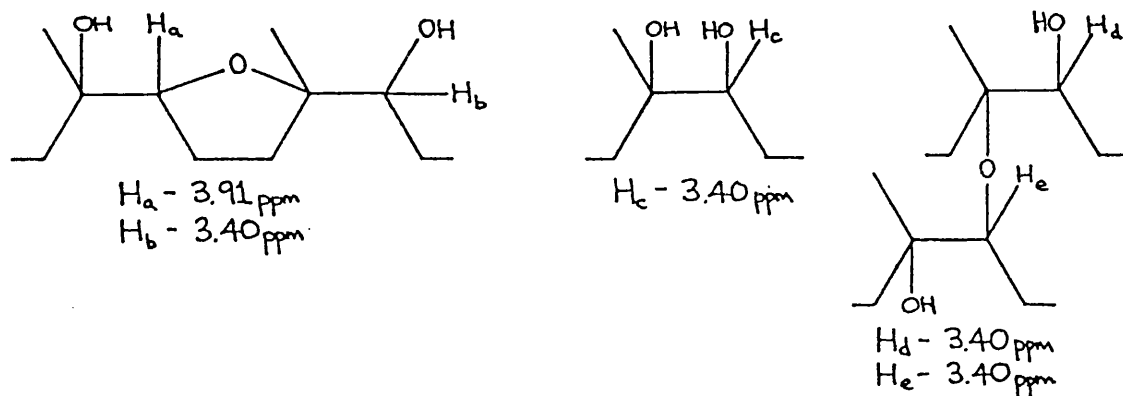
^bObserved at an unquantifiable concentration

^cDiscrete particles precluded the observation of a stable ²H-NMR lock signal

random crosslinking reaction in which intermolecular ether bonds are preferentially formed between chains of higher molecular mass. ¹³C-NMR analyses were based upon the method of Gemmer and

Golub⁷⁹ and are therefore semi-quantitative (Section 3.3.2).

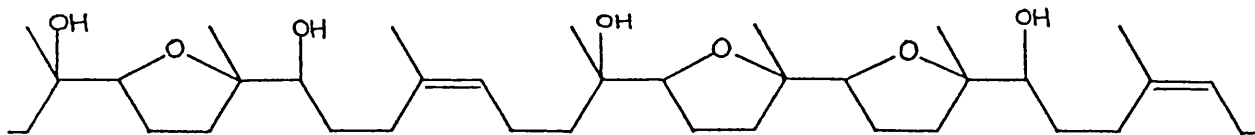
Characteristic ¹³C-NMR resonances at 83.8 and 86.2ppm are attributable to C-O ring carbons in tetrahydrofuran rings (*cf.* 83.8 and 85.9ppm in furanized liquid rubbers³⁰⁰). An additional ¹H-NMR resonance at 3.40ppm in furanized liquid rubber was suggested to arise from protons associated with alcohol groups³⁰⁰ (Scheme 4-3). The lack of a corresponding resonance in



Characteristic NMR resonances for ring-opened products³⁰⁰

Scheme 4-3

furanized NR prepared in these studies is indicative of the lack of pendant alcohol groups, and confirmed by the lack of ¹³C-NMR resonances between 70 and 75ppm in the region of chemical shift characteristic of C-OH in alcohols (Section 4.3.2). The concentration of alcohol groups arising from epoxy-group ring-opening is dependent upon the relative rate of formation of **isolated** tetrahydrofuran rings to **adjacent** tetrahydrofuran rings along chains (Scheme 4-4); consequently, the epoxy-group content of the polyisoprene (*prior* to ring-opening) determines the content of alcohol groups. In this particular case, the statistics of random epoxidation⁶⁵ predict that 70-80 mole% epoxy



2 alcohol groups for each tetrahydrofuran ring

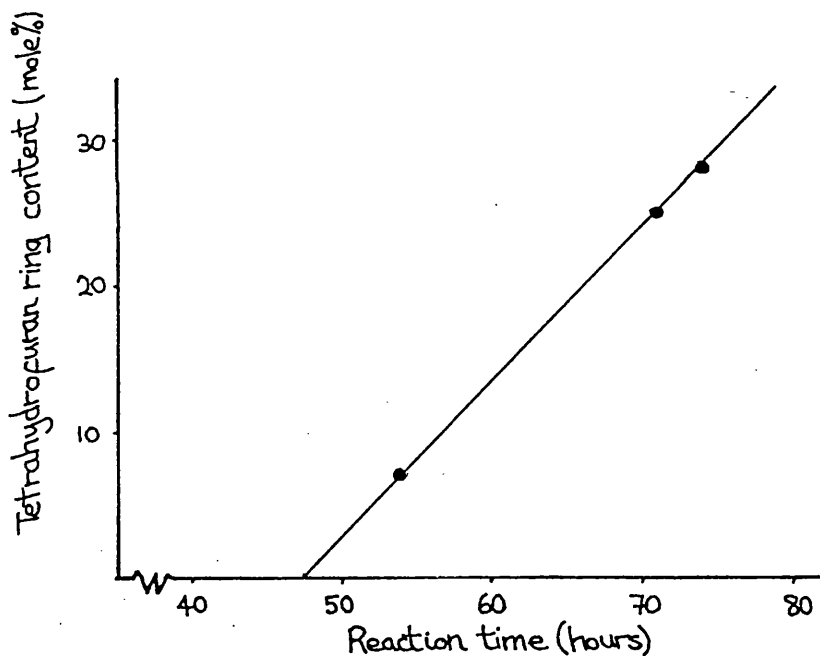
1 alcohol group for each tetrahydrofuran ring

The formation of isolated and adjacent tetrahydrofuran rings

Scheme 4-4

groups would result in the predominant formation of sequences of adjacent tetrahydrofuran rings and a minor concentration of terminal alcohol groups.

^{13}C -NMR analysis of the whole samples indicated a linear dependence of the rate of furanization on reaction time (Figure 4.19). Perera and co-workers monitored the furanization of



The rate of furanization of NR latex

Figure 4.19

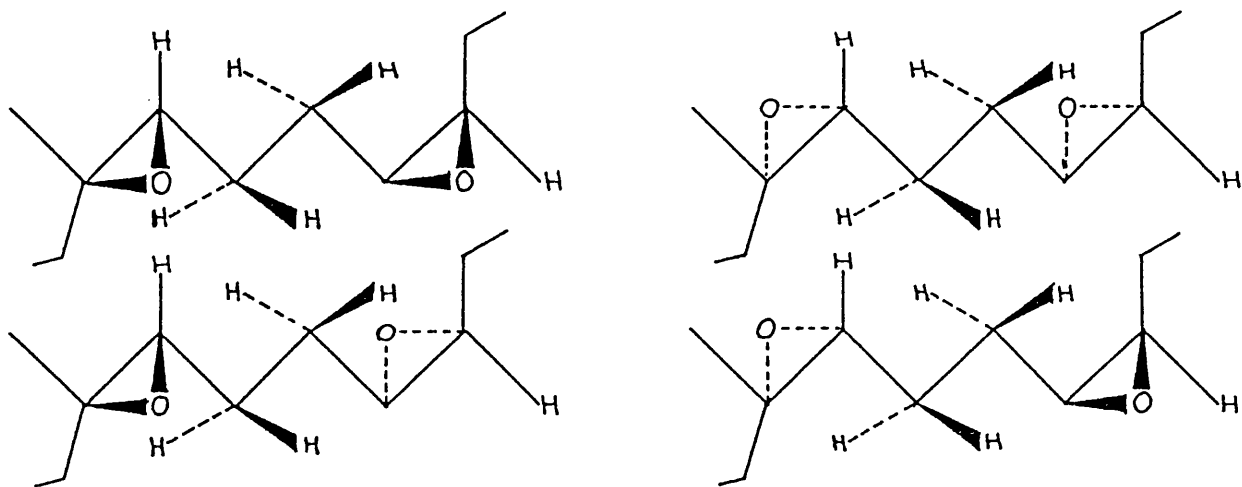
liquid rubber by ^1H -NMR spectroscopy and found that the rate of epoxidation was greater than the rate of furanization; ring-

expansion was therefore catalysed by the addition of orthophosphoric acid³⁰⁰. The same conclusion can be drawn from this study as furanization was not observed until the epoxy-group content of the polymer exceeded 60 mole%. Furanization results from a concerted cascade reaction (Section 1.3) and would therefore be expected to be rapid. The sluggishness of the reaction may be attributed to a number of factors;

- (a) the low solubility of formic acid in the hydrocarbon medium of latex particles⁶⁴
 - (b) the decrease in segmental mobility of polyisoprene chains as a function of increasing epoxy-group content and the introduction of tetrahydrofuran rings
 - (c) the stereochemistry of adjacent epoxidized units⁷⁸ (*Scheme 4.5*)
- and, (d) steric hindrance arising from chain entanglements and crosslinks.

4.4 The Formation of Alcohols

It has been shown that the acid-catalysed hydrolysis of low molecular mass models for adjacent epoxidized units in ENR results in a complex mixture of products (Section 4.3.1). Product composition is determined by the concentration of acid and epoxy



Stereochemical arrangements for adjacent epoxidized units in ENR

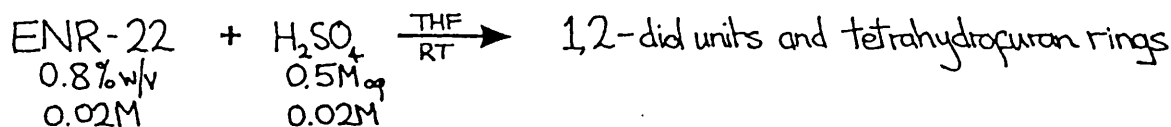
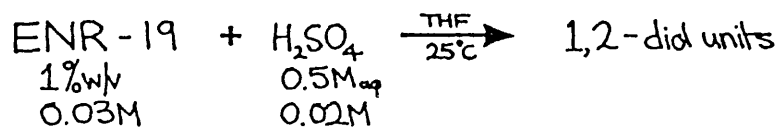
Scheme 4-5

groups and the efficiency of the acid or water to provide counter-ions. There is overwhelming published evidence that demonstrates that the hydrolysis of ENR latices results in the preferential formation of tetrahydrofuran rings by an intramolecular cascade reaction (*Scheme 1-10*) and/or ether crosslinks by a corresponding intermolecular reaction (*Scheme 1-11*). In the presence of abnormally high concentrations of formic acid (6.5- 9.2M), the epoxidation of NR latices was found to result in the formation of pendant formate groups (up to 5 mole%)⁹⁴ and there is some ¹H-NMR evidence for carbocation cyclization and the formation of carbocyclic rings during furanization³⁰⁰. During the course of these studies, experimental conditions were found which promote the formation of alternative hydrolysis products from ENR and these are described in this section.

The hydrolyses of ENR-4 and ENR-10 in solution with perchloric acid gave tacky products of low molecular mass. $^1\text{H-NMR}$ analyses indicated that a total loss of epoxy groups was accompanied by partial *cis-trans* isomerization of double bonds (1 mole% from ENR-4 and 5 mole% from ENR-10), two resonances at 1.06 and 1.10ppm and broad resonances between 3 and 4ppm. The latter resonances are observed in furanized NR³⁰⁰ (Section 4.3.2) and attributable to protons in tetrahydrofuran rings. A resonance at 1.10ppm has been attributed to the methyl group associated with the formation of diol units, HO-CH_2 , from ENR³⁴ and $^{13}\text{C-NMR}$ resonances at 70.5 and 75.0ppm are in the region of chemical shift characteristic of C-O carbons in alcohols. $^1\text{H-}$ and $^{13}\text{C-NMR}$ spectroscopic data for the product are therefore consistent with the formation of 2. The formation of tetrahydrofuran rings from the hydrolysis of ENR-4 or ENR-10 is anomalous because ring-expansion requires intramolecular reaction between adjacent epoxidized units (*Scheme 1-10*) and random epoxidation (Section 3.5) dictates the complete absence of adjacent epoxidized units in ENR-4 and a maximum of 1 mole% adjacent units in ENR-10⁶⁵. **These results offer chemical evidence for non-random epoxidation of the available double bonds in NR and cannot be explained at this time.**

The hydrolysis of ENR-19 in solution with dilute sulphuric acid was found to result in a complete loss of epoxy groups; $^1\text{H-NMR}$ analysis of the soluble product indicated that the disappearance of resonances attributable to epoxy groups coincided with the appearance of a new resonance at 1.10ppm,

attributable to methyl groups in 2³⁴. ¹³C-NMR resonances at 72.2 and 74.8ppm in the region of chemical shift characteristic of C-OH resonances are consistent (via SFORD) with the secondary and trisubstituted alcohol functional groups in 2[Ⓢ]. The hydrolysis of ENR-22 in solution was claimed to result in the exclusive formation of 2⁷⁷; however, the progressive formation of gel and the simultaneous appearance of new resonances at 1.10 and a broad resonance at 3.5ppm indicates of the formation of both 2 and tetrahydrofuran rings. A comparison of the conditions used in the two reactions (Scheme 4-6) suggests that the minor increase in



The hydrolysis of ENR-19 and -22 in solution

Scheme 4-6

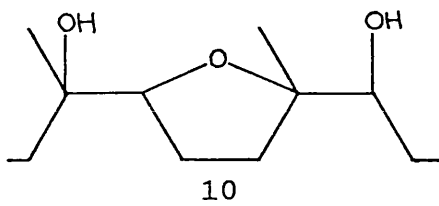
epoxy-group content from 19 to 22 mole% tilted the hydrolysis in favour of the formation of tetrahydrofuran rings. This observation is consistent with the fine balance between different factors determining the structure of hydrolysis products.

The hydrolysis of ENR-23 latex with sulphuric acid gave an

Footnote[Ⓢ]

The observation of ¹³C-NMR resonances at 72.4 and 74.3ppm in furanized liquid rubber is consistent with the presence of 1,2-diols³⁰⁰; Gan and Ng wrongly attributed resonances at 82.4 and 84.1ppm for C-O ring carbons in tetrahydrofuran rings to 2⁶³.

insoluble crosslinked material. $^1\text{H-NMR}$ spectra of the product, swollen in CDCl_3 , were poorly-resolved; $^{13}\text{C-NMR}$ analysis demonstrated a complete loss of epoxy groups and the appearance of broad resonances between 80 and 85ppm and sharp resonances at 70.5 and 75.0ppm. The C-O ring carbons in tetrahydrofuran rings in furanized NR resonate at 83.8 and 85.9ppm³⁰⁰ and the resonances at 70.5 and 75.0ppm are consistent with the formation of tetrahydrofuran-diols, 10.



The preferential formation of ether crosslinks and/or tetrahydrofuran rings with a variable concentration of pendant alcohol groups from the hydrolysis of ENR results from the inefficiency of counter-ions to reach and react with carbocation sites in the hydrocarbon medium of latex particles. In exceptional circumstances (i.e. a low concentration of acid and adjacent epoxidized units in the polymer), it has been shown that sufficient water can penetrate latex particles to promote the formation of tetrahydrofuran-diols. In solution reactions, counter-ions from the acid or water can freely react with carbocations on polymer chains, promoting the formation of 1,2-diols and/or tetrahydrofuran-diols.

CHAPTER 5

CONCLUSIONS

5.1 The Preparation of Epoxidized Natural Rubber

Recipes for the efficient epoxidation of NR latex with performic acid generated *in situ* from hydrogen peroxide and formic acid have been investigated. Increasing the concentration of formic acid results in extensive gelation of the polymer due to the ring-opening of epoxy groups and the formation of ether crosslinks. A semi-quantitative technique, based on ^{13}C -NMR spectroscopy, has been developed which can be used to estimate the extent of formation of ether crosslinks during epoxidation.

The epoxidation of NR latex with preformed peracetic acid was found to yield ENR without the accompanying formation of ether crosslinks or tetrahydrofuran rings. The reaction was shown to follow second-order kinetic behaviour up to an epoxy-group content of 20 mole%.

The vigorous evolution of gases and enhanced exothermicity in latex epoxidations using hydrogen peroxide and formic acid is found to arise from the reaction of adventitious iron(II) ions with hydrogen peroxide. This combination is known as Fenton's Reagent and results in the generation of hydroxyl radicals. The intervention of Fenton's Reagent during epoxidations results in retardation of the rate of epoxidation and enhanced oxidative scission of the polymer. The activity of Fenton's reagent has

been demonstrated to be significantly dependent upon the acidity of the reaction medium. This effect is consistent with the progressive formation of insoluble iron(III) oxides above a pH of 3. Chelating agents for iron(II) can be used to partially suppress the intervention of Fenton's Reagent.

The epoxidation of NR latices is believed to result in the random placement of epoxidized units along the polymer chains. Further evidence for this hypothesis has been provided by the invariance of epoxy-group content in ENR fractionated by molecular mass and latex particle size. However, the formation of tetrahydrofuran rings during the hydrolysis of ENR-4 and -10 is not consistent with random epoxidation.

5.2 The Characterization of Epoxidized Natural Rubber

The estimation of epoxy groups in partially-epoxidized *cis*-1,4-polyisoprenes should be easy using the available techniques; inconsistencies in the results derived from the use of some of these methods have been investigated. Criteria for the accurate determination of epoxy-group content by ^1H - and ^{13}C -NMR spectroscopies have been developed and simplistic assumptions used to acquire 'quantitative' ^{13}C -NMR data have been shown to yield inflated values for epoxy-group content.

The linear dependence of T_g (measured by DSC) on epoxy-group content has been examined; statistical analysis of the results indicates that a calibration factor of 0.84kmole^{-1} should be used. Anomalies in the literature for the the DSC calibration

factor are attributable to the use of unreliable ^1H -NMR measurements for calibration of the technique. DSC is not recommended as a method to measure the concentration of epoxy groups in heavily-gelled samples of ENR.

Autoxidation of NR has been shown to result in the formation of both *cis*- and *trans*-epoxy groups, whereas epoxidation with peracids gives solely *cis*-epoxy groups. ^1H -NMR spectroscopy has been used to show that these groups are formed during autoxidation in an apparent ratio of 1.4:1.0 *trans*:*cis*. This ratio is consistent with the addition of peroxy radicals to double bonds being the principle pathway for the formation of epoxy groups during autoxidation.

2D J-resolved NMR spectroscopy has been used to demonstrate that *trans*-epoxy groups are found in ENR and indicates that similar ageing processes operate in both NR and ENR.

5.3 The Hydrolysis of Epoxidized Natural Rubber

The sensitivity of trisubstituted epoxy groups to ring-opening in the presence of acids is believed to result in the formation of tetrahydrofuran rings and/or ether crosslinks from the epoxidation of NR in the presence of strong acids. However, experimental evidence for the presence of either of these structures in furanized NR was scant before the present investigation.

The acid-catalysed hydrolysis of a low-molecular-mass model for adjacent epoxidized units in ENR resulted in the formation of

four isomeric tetrahydrofuran-diols. The formation of tetrahydropyran derivatives was discounted by the analysis of hydrolysate fractions using ^1H - and ^{13}C -NMR spectroscopies. The formation of ether bonds between polymer chains was demonstrated by ^1H -NMR analysis of low-molecular-mass fractions of ENR-50.

It has been shown that crosslinks are formed **during** the epoxidation of *cis*-1,4-polyisoprene latices with performic acid. The analysis of fully-soluble samples of partially-epoxidized *cis*-1,4-polyisoprene by GPC demonstrated that high molecular mass chains are preferentially involved in the formation of crosslinks, in a manner consistent with a random chemical process. The concentration of formic acid and the epoxy-group content of the polymer have been shown to influence the rate of formation of ether crosslinks. The epoxidation of DPNR, Maxprene IR-900 and HA latices with performic acid under identical experimental conditions has demonstrated that the non-rubbers in NR latex inhibit the formation of crosslinks.

Furanized rubber has been characterized by ^1H - and ^{13}C -NMR spectroscopies. The concentration of pendant alcohol groups formed as a result of furanization is ultimately dependant upon the epoxy-group content of the modified polyisoprene. The rate of furanization has been shown to be slower than the rate of epoxidation of NR latices.

It has been shown that the acid-catalysed hydrolysis of ENR results in the predominant formation of tetrahydrofuran rings and/or ether crosslinks. Some *cis-trans* isomerization of double bonds often accompanies the primary hydrolysis products. The

hydrolysis of ENR with a low epoxy-group content (< 25 mole%) can result in the formation of 1,2-diol units and tetrahydrofuran-diols.

CHAPTER 6

EXPERIMENTAL

6.1 Instrumentation

Nuclear Magnetic Resonance Spectroscopy

^1H -CW-NMR data for ENR samples, swollen or dissolved in CDCl_3 , were collected at 90MHz using a Perkin-Elmer R32 NMR spectrometer operating at a probe temperature of 35°C with a sweep time of 80 seconds⁶⁵.

^1H - and ^{13}C -FT-NMR spectra were acquired for ENR samples at Larmor frequencies of 200 and 50MHz respectively using a Varian XL-200 NMR spectrometer. Spectral data were collected for 1-2%w/v solutions of sol fractions in CDCl_3 . Quantitative ^1H -NMR data were collected at a probe temperature of 25°C, a pulse angle of 23° and a delay-time between pulses of 5 seconds.

^{13}C -NMR spectra for the estimation of epoxy groups were acquired at a probe temperature of 35°C, a pulse angle of 23°, a delay-time between pulses of 2 seconds and inverse-gated broadband-decoupling. Spin-lattice relaxation rates were determined using the inversion-recovery technique²⁴⁷. $T_{1\rho}$ for ^{13}C -NMR resonances were determined by difference spectroscopy³⁰².

^1H - and ^{13}C -FT-NMR spectra were acquired at Larmor frequencies of 400 and 100MHz respectively, using a Varian VXR-400 spectrometer and 1%w/v solutions of sol fractions in CDCl_3 .

Typically, 32-128 transients were acquired for ^1H -NMR spectra at a probe temperature of 25°C using quadrature detection, double precision electronics and a spectral width of 5600Hz. The acquisition of quantitative data was ensured by the use of a pulse angle of 23° and a delay-time between pulses of 4.3 seconds; 32K data points were used with zero-filling to 64K prior to Fourier transformation.

^{13}C -NMR spectra were acquired at a probe temperature of 30°C with continuous broadband-decoupling, a pulse angle of 23° , an acquisition time of 0.54 seconds and a delay-time between pulses of 2.5 seconds. Several thousand transients were acquired in overnight experiments. The acquisition of ^{13}C -NMR spectra from samples in 10mm tubes were run in the absence of spinning to prevent the formation of spectral artefacts²⁵⁶.

The homonuclear 2D J-resolved spectrum of ENR-40 was acquired using the pulse sequence of Ernst and co-workers³⁰³ at a Larmor frequency of 200MHz using a Varian XL-200 NMR spectrometer. Acquisition conditions were based on a pulse angle of 90° , a spectral width in the first dimension of 1000Hz and 50Hz in the second, 8 pulses and 512 incremental interferograms. After Fourier transformation, the data were rotated and symmetrized.

Chemical shifts, δ , are quoted in ppm from TMS as internal reference at 80.00.

Infrared Spectroscopy

Infrared spectra from ENR samples were obtained for cast

films from CHCl_3 on potassium bromide plates or as dried latex films on silver(I) chloride plates using a Perkin-Elmer 377 spectrophotometer⁶⁵.

Differential Scanning Calorimetry

The glass transition temperature of ENR samples was measured using standard experimental conditions and a Perkin-Elmer DSC-2 calorimeter⁶⁵.

Atomic Absorption Spectrophotometry

Determinations of total iron content in rubber samples were made with a Varian Techtron 1200 spectrophotometer after digestion with concentrated hydrochloric acid to convert all the iron present to iron(III) chloride²²¹.

Gel Permeation Chromatography

The molecular mass distributions of the sol fractions of rubbers were determined using gel permeation chromatography, after removal of the macrogel using THF and ultracentrifugation for 60 minutes at 35000 rpm to remove microgel. The sol fractions were analysed using 0.02%w/v solutions in THF containing 0.005% BHT as an antioxidant and retention time marker. Rubber solutions were analysed at a flow rate of 0.5mlmin^{-1} through mixed-bed Micrel columns (2x50cm, Polymer Laboratories) in series with UV

detection at 215-220nm²⁹⁴. Molecular mass distributions for NR were calculated from the hydrodynamic constants determined by Subramaniam²⁹¹. Corresponding data for ENR-50 were derived using the hydrodynamic constants determined by Edwards²⁹⁵.

High Pressure Liquid Chromatography

Product mixtures from the hydrolysis of 2,2-dimethyl-3-[(3-methyl-3-oxiranyl)pentyl]oxirane were separated into several fractions by high pressure liquid chromatography with refractive index detection. A mobile phase of diethyl ether containing methanol (1%v/v) was used to reduce retention times and the tailing of peaks with a stationary phase of silica (5 μ m). HPLC on an analytical scale used 1-3 μ l injections at a flow rate of 1.2mlmin⁻¹ on a 10cm x 4.5mm column. On a preparative scale, 20 μ l injections were used at a flow rate of 2.0mlmin⁻¹ onto two columns (10cm x 4.5mm and 25.0cm x 7.0mm) in series.

Gas Liquid Chromatography

The purity of 2,2-dimethyl-3-[(3-methyl-3-oxiranyl)pentyl]oxirane was measured by gas liquid chromatography using a Perkin-Elmer F17 instrument. A Pye 4 column (3m) packed with a mobile phase of 3% OV101, a non-polar silicone oil, and a stationary phase of Diatomite CLQ was used with nitrogen as the carrier gas and an oven temperature of 80°C.

6.2 The Preparation and Hydrolysis of Modified Natural Rubbers

6.2.1 The Epoxidation of HA Latex using Hydrogen Peroxide and Formic Acid

Texofor A60 (108g, 5%w/v, 3pphr, ABM Chemicals) was stirred into HA latex (300g, 60%w/w drc, 2.65 moles isoprene units) over 30 minutes at 60°C in a thermostatted oil bath. Formic acid (20ml, 98%, 0.52 moles, BDH), diluted with distilled water (100ml), was added dropwise followed by the rapid addition of hydrogen peroxide (115ml, 50%w/w, 2.03 moles, Interlox). The reaction was sampled periodically; latex aliquots (2ml) were coagulated in methylated spirits (20ml) containing a molar excess of sodium hydroxide (2M). The coagula were leached in distilled water and dried *in vacuo* at 50°C.

6.2.2 The Epoxidation of HA Latex in the Presence of Formic Acid above a Concentration of 0.8M

These reactions were carried out as described in section 6.2.1 except for the use of the minimum quantity of hydrogen peroxide (75ml, 50%w/w, 1.32 moles) necessary to produce ENR-50 and the desired quantity of formic acid (40-80ml, 98%, 1.04-2.08 moles). For reactions in which the latex coagulated *in situ*, the polymer was leached in distilled water containing a molar excess of sodium hydroxide before washing and drying.

6.2.3 The Epoxidation of HA Latex in the Presence of 1,10-Phenanthroline

In an otherwise typical latex epoxidation (Section 6.2.1) with an adventitious total iron content of 3.9 ppm, 1,10-phenanthroline (0.014g, 98%, 7.4×10^{-5} moles, 21 ppm) was added to the water used to dilute the formic acid.

6.2.4 The Epoxidation of HA Latex in the Presence of Iron(II)

In otherwise typical latex epoxidations (Section 6.2.1), specific concentrations of iron(II) ranging between 5 and 100 ppm were added, using hydrated iron(II) ammonium sulphate (98%) dissolved in the diluted formic acid. For reactions in which the latex coagulated *in situ*, the polymer was leached in distilled water containing a molar excess of sodium hydroxide before washing and drying. **At iron(II) concentrations above 50 ppm, these reactions become highly exothermic; vigorous foam formation and *in situ* coagulation of the polymer result in uncontrollable and hazardous reactions.**

6.2.5 Control Reaction for the Epoxidation of HA Latex in the Presence of Iron(II)

In an otherwise standard reaction (Section 6.2.1), distilled water was substituted for the latex concentrate and hydrated iron(II) ammonium sulphate (0.2342g, 98%, 5.85×10^{-4}

moles) was dissolved in the reaction mixture to yield a concentration of iron(II) of 49 ppm. After 5½ hours (i.e. the time at which *in situ* coagulation of the polymer occurred in the corresponding latex epoxidation), the reaction was sampled and assayed for hydrogen peroxide (Section 6.4.5). The bulk of the reaction was treated with sodium hydroxide (4M) until a red-brown solid was precipitated. After standing overnight, the precipitate was filtered off and the filtrate was extracted with diethyl ether (2 x 500ml, dried with sodium wire). The extract was dried with anhydrous magnesium sulphate, filtered and dried by rotary evaporation to yield a beige waxy product.

6.2.6 Control Reactions for the Dependence of the Activity of Fenton's Reagent upon Acidity

Control reactions were designed to assess the extent of decomposition of hydrogen peroxide arising from the intervention of Fenton's Reagent during latex epoxidations. Distilled water was doped to the desired concentration of iron(II) with hydrated iron(II) ammonium sulphate in experiments which simulated the epoxidation of HA latex (Sections 6.2.1 and 6.2.2) with distilled water substituted for the latex concentrate.

6.2.7 The Epoxidation of HA Latex with Peracetic Acid

Texofor A60 (72.0g, 5%w/v, 3pphr), diluted to 300ml with distilled water, was stirred into HA latex (200g, 60%w/w drc,

1.76 moles isoprene units). A salt-ice bath was used to maintain the temperature between 5-10°C. Peracetic acid (157ml, 32.5%w/v, 0.76 moles, redistilled, Interlox) was added over 5 minutes with rapid stirring. The reaction was periodically sampled; aliquots (2ml) were coagulated in methylated spirits (50ml) containing a molar excess of sodium hydroxide (5ml, M, 5.0×10^{-3} moles), leached in water and dried *in vacuo* at 50°C.

6.2.8 The Catalytic Epoxidation of Natural Rubber Latex

Initial experiments indicated that addition of the tungstate salt, $W_2O_{11}^{2-} \cdot 2Ph_3PCH_2Ph^+$, to HA latex stabilized with Texofor A60, at measured pH values above 5.5 led to thickening of the latex and *in situ* coagulation.

HA latex (100g, 60%w/w drc, 0.88 moles isoprene units) was stabilized with Texofor A60 (36g, 5%w/v, 3 pphr) with stirring over 30 minutes at 60°C. The total volume of the reaction mixture was made up to 200ml with distilled water before the addition of sufficient formic acid (98%) to take the measured pH of the reaction to 5.5. The tungstate salt, $W_2O_{11}^{2-} \cdot 2Ph_3PCH_2Ph^+$ (7.0g, ≈90%, 5.0×10^{-3} moles) was added to the latex with stirring followed by hydrogen peroxide (25ml, 50%w/w, 0.44 moles). The reaction mixture was sampled periodically; latex aliquots (2ml) were coagulated in methylated spirits (20ml) containing excess sodium hydroxide (2ml, M, 0.002 moles) and further aliquots (1ml) were cast onto silver chloride plates for the estimation of epoxy groups by IR analysis. After 5 hours' reaction, a latex aliquot

(10ml) was assayed for hydrogen peroxide (Section 6.4.5).

6.2.9 The Epoxidation of Partially-Isomerized Natural Rubber

Partially-isomerized NR latex²⁵⁶ (50g, 37%w/w drc, 32.5 mole% *trans*-alkene content, 0.273 moles isoprene units) was stabilized with Texofor FN30 (2.22g, 25%w/v, 3 pphr) by stirring together for 30 minutes in a thermostatted oil bath at 60°C. Formic acid (2.0ml, 90%w/w, 0.470 moles) was diluted with distilled water (25ml) and slowly added to the stirred latex, followed by the rapid addition of hydrogen peroxide (10ml, 50%w/w, 0.173 moles). Over 24 hours, the reaction was periodically sampled. Latex aliquots (2ml) were coagulated in methylated spirits (10ml) containing a molar excess of sodium hydroxide (2M), leached in distilled water (50ml) and dried *in vacuo* at 50°C.

6.2.10 The Autoxidation of Natural Rubber

HA latex was deproteinized by enzyme digestion²⁹⁶ *prior* to oxygen uptake experiments. Typically, the sol fraction of DPNR was isolated by several extractions at 3%w/v in CH₂Cl₂ (AR, BDH). Extractions were conducted at room temperature under nitrogen and in the absence of light. The solution fraction was carefully separated from swollen gel at 24 hour intervals. After several days, a daily extraction yielded little further sol material. The solvent from successive fractions was partially removed by rotary

evaporation and the partially-dried sols were combined in CH_2Cl_2 before drying by rotary evaporation. The combined sol fraction was dissolved in toluene (AR, BDH) and purified further by coagulation with methanol. The polymer was dried *in vacuo* at 40°C and stored in a freezer under nitrogen. The purified NR was deposited in clean test tubes using 3%w/v solutions in toluene (AR). Uniform thin films were prepared by initial rotary evaporation to remove the bulk of solvent, followed by slow rotary evaporation of residual solvent from tubes held in a horizontal position. The last traces of solvent were removed at high vacuum (10^{-2} mbar). After three evaporation cycles, uniform films of $\approx 0.1\text{mm}$ thickness and containing $\approx 0.4\text{g}$ of rubber were deposited. Oxygen uptake studies were carried out in a home-built apparatus and monitored by volume change using a manometer. Typically, 2%w/w oxygen uptake was achieved after 8 hours at 70°C and 10%w/w after 16 hours at the same temperature.

6.3 The Epoxidation and Hydrolysis of 1,4-Polyisoprenes

6.3.1 The Epoxidation of *Cis*-1,4-Polyisoprene Latices

DPNR latex (226g, 53%w/w drc, 1.75 moles isoprene units) was stabilized by the addition of Texofor A60 (72g, 5%w/v, 3pphr) with stirring over 30 minutes at 60°C . Formic acid (14ml, 90%, 0.33 moles) diluted with distilled water (38ml) was added dropwise followed by the rapid addition of hydrogen peroxide (78ml, 50%w/w, 1.35 moles). The reaction was sampled periodically

with a latex aliquot (2ml) coagulated in methanol (20ml) containing excess sodium hydroxide (2ml, M, 0.02 moles). The coagula were leached in water and dried *in vacuo* at 50°C. A further aliquot (2ml) was assayed for hydrogen peroxide (Section 6.4.5).

Maxprene IR-900 latex (191g, 63%w/w drc, 1.76 moles isoprene units, Seitetsu Kagaku Co) was stabilized by the addition of Texofor A60 (72g, 5%w/w, 3 pphr) with stirring over 30 minutes at 60°C. Formic acid (14ml, 90%, 0.33 moles) diluted with distilled water (38ml) was added dropwise followed by the rapid addition of hydrogen peroxide (78ml, 50%w/w, 1.35 moles). The reaction was sampled as described for the epoxidation of DPNR latex.

HA latex (203g, 59%w/w drc, 1.76 moles isoprene units) was stabilized by the addition of Texofor A60 (72g, 5%w/v, 3 pphr) with stirring over 30 minutes at 60°C. Formic acid (14ml, 90%, 0.33 moles) diluted with distilled water (38ml) was added dropwise followed by the rapid addition of hydrogen peroxide (78ml, 50%w/w, 1.35 moles). The reaction was sampled as described above.

6.3.2 The Epoxidation of *Gutta Percha*

Gutta Percha (3.75g, recrystallized, 0.055 moles isoprene units, MRPRA) was dissolved in 1,4-dioxan (25ml, AR, Aldrich) at 60°C to yield a transparent yellow viscous solution. MCPBA (2.80g, 85%, 0.014 moles, BDH) dissolved in 1,4-dioxan (25ml) was added at 60°C and the mixture was stirred for 48 hours. Aliquots

(2ml) were removed at regular intervals, coagulated in methanol (20ml) containing sodium hydroxide (1ml, 2M, 0.002 moles), leached in distilled water and finally dried *in vacuo* at 50°C. Dried products were opaque white and rubbery.

6.3.3 The Epoxidation of Maxprene IR-900 Latex

A stabilized batch of latex was prepared by the addition of Texofor FN30 (44ml, 20%w/v, 3pphr) to Maxprene IR-900 latex (500g, 63%w/w drc, 4.62 moles isoprene units) with stirring. To stabilized Maxprene IR-900 latex (60g, 56%w/w drc, 0.49 moles isoprene units) in a water bath at 35°C, formic acid (5ml, 90%, 0.12 moles), diluted with distilled water (21ml), was added dropwise followed by the rapid addition of hydrogen peroxide (12.5g, 50%w/w, 0.22 moles). The reaction was sampled periodically; latex aliquots (5ml) were coagulated in methanol (50ml) containing excess sodium hydroxide (2M). The coagula were leached in water and dried *in vacuo* at 50°C.

In a further reaction, formic acid (5ml, 90%, 0.12 moles) diluted with distilled water (9ml) and hydrogen peroxide (25g, 50%w/w, 0.44 moles) were added dropwise to stabilized Maxprene IR-900 latex (60g, 56%w/w drc, 0.49 moles isoprene units) in a water bath at 35°C. The reaction was periodically sampled as described above.

6.3.4 The Treatment of Partially-Epoxidized Maxprene IR-900 Latices to Formic Acid⁶²

The epoxidation of stabilized Maxprene IR-900 latex was based on initial dilution to the desired drc followed by cooling to 0°C in a cryocool circulating bath and the dropwise addition of the desired quantity of peracetic acid (38%w/w, redistilled) over several minutes. The concentration of peracid was monitored using iodometry and a Radiometer autotitration system⁶⁴. After complete consumption of the peracid, the desired quantity of formic acid (90%) was added to the partially-epoxidized latex and heated at 60°C for 30-40 hours. The reactions were periodically sampled; latex aliquots (2ml) were coagulated in methanol (20ml) containing ammonia (10%v/v). The coagula were leached in water and dried *in vacuo* at 50°C.

6.4 The Characterization of Reactions of Natural Rubber Latices

6.4.1 The Preparation of Sol Fractions

Samples of NR or ENR were adequately separated by swelling at 0.5-1.0%w/v in CDCl₃ for 24-48 hours at 5°C in the refrigerator. The sol fractions were separated by filtration through two layers of lens tissue followed by the evaporation of solvent using a stream of nitrogen and drying *in vacuo* at 50°C.

6.4.2 The Fractionation of ENR-48 by Molecular Mass

The sol fraction of ENR-48 (8.4g) was diced and dissolved slowly in toluene (1000ml, AR) by stirring overnight in a water bath at 40°C. The polymer was fractionally precipitated to a cloud point (observed as turbidity in the solution) by the dropwise addition of methanol (AR) to the stirred solution. After maturing for 2 hours at 40°C, the precipitated polymer was redissolved at 45°C and left to reprecipitate under equilibrium conditions at room temperature. The cloudy solution was siphoned to yield a resinous precipitate and a clear solution. The solution was fractionated further at 40°C until five fractions had been collected. Each fraction was partially-dried by rotary evaporation and taken to dryness *in vacuo*. The mother liquor was dried to yield a final fraction.

6.4.3 The Determination of Gel Content using Tetrahydrofuran²⁹⁵

Degassed THF (8.0ml, redistilled) containing BHT (0.005%) was added to an accurately weighed sample of rubber (≈ 0.030 g) in a 10ml volumetric flask. After standing at room temperature in the absence of light for approximately 65 hours, the mixture was agitated and made up to volume. Discrete pieces of macrogel were removed by filtration through lens tissue and the microgel was isolated by ultracentrifugation (60 minutes at 30000 rpm). After decantation, a weighed aliquot of the supernatant (3.0ml) was dried on the bench and dried at 100°C for 5 minutes. After

cooling, the sample was reweighed and the weight fraction of sol calculated.

6.4.4 Equilibrium Volume Swelling Measurements

Accurately weighed samples of rubber (0.040-0.080g) were immersed in decane (2ml, 99%, Aldrich) and allowed to swell for 68 hours in a water bath at 25°C. The swollen rubbers were filtered through lens tissue, weighed, dried *in vacuo* at 50°C and subsequently reweighed to calculate the volume fraction of rubber in the swollen state, v_r^{304} .

6.4.5 The Estimation of Hydrogen Peroxide

The concentration of hydrogen peroxide in samples from latex epoxidations was measured volumetrically. Latex aliquots (5ml) were made up to 100ml with distilled water and cooled to 4-5°C in an ice bath. Aliquots (10ml) of the diluted latex were titrated against acidified cerium(IV) sulphate (0.05M, 'Convolve', BDH) using ferroin as indicator.

6.4.6 The Estimation of Peracetic Acid

Peracetic acid (1.0ml, redistilled) was made up to 100ml in a volumetric flask. Excess potassium iodide (0.15g, 9.04×10^{-4} moles) was added to aliquots (10ml) of the diluted acid and titrated against sodium thiosulphate solution¹⁸⁸ (0.09988M, 'AVS',

BDH). Further aliquots (10ml) were cooled to 5-10°C in an ice bath, acidified with dilute sulphuric acid (2 drops, 2M) and manually titrated against cerium(IV) sulphate solution (0.05M, Convol) using ferroin as indicator. Excess potassium iodide (0.15g, 9.04×10^{-4} moles) was subsequently added and the liberated iodine was titrated against sodium thiosulphate solution¹⁹⁶.

6.4.7. The Estimation of Epoxy-Group Content by Volumetric Methods

A solution of hydrogen bromide ($\approx 0.1M$) in glacial acetic acid was prepared from a concentrated stock solution and standardized against sodium carbonate using Crystal Violet (0.1%) as indicator⁶⁹.

A solution of perchloric acid ($\approx 0.1M$) in glacial acetic acid was prepared in the presence of excess acetic anhydride and stored in a Karl Fischer burette. The solution was standardized against potassium hydrogen phthalate using Crystal Violet (0.1%) as indicator⁷⁰. To cyclohexene oxide (0.1ml, 99%, Aldrich) in acetone (10ml, AR, BDH), TEAB (1.2M) in glacial acetic acid (10ml) was added and titrated against perchloric acid (0.107M) using Crystal Violet (0.1%) as indicator⁷⁰.

6.5 Model Reactions

6.5.1 The Preparation of a Quaternary Phosphonium Pertungstate Salt

$W_2O_{11}^{2-} \cdot 2Ph_3PCH_2Ph^+$ was prepared using the method of Prandi and co-workers²¹⁰. Tungstic acid (15.0g, 99%, 0.081 moles, Aldrich) was dissolved with stirring in hydrogen peroxide (60ml, 30%w/w, 0.58 moles) at 40°C. After cooling, benzyltriphenylphosphonium chloride (23.4g, 99%, 0.060 moles, Aldrich) was added dropwise as a slurry in distilled water (150ml) over 30 minutes with the temperature maintained between 0-5°C using a salt-ice bath. The white precipitate was stirred for a further 15 minutes at 0°C, filtered under pressure, washed with ice-water (3 x 20ml) and dried in vacuo in a dessicator. The product was a white powder (34.35g, 91%) with a melting point of 142-143°C (decomp) (cf. 150°C ,decomp,²¹⁰).

6.5.2 The Preparation of 2,2-dimethyl-3-[(3-methyl-3-oxiranyl)pentyl]oxirane

The diepoxide was prepared by Dr S.T. Orszulik by the epoxidation of 2,6-dimethylocta-2,6-diene³⁰⁵ with MCPBA²⁹⁹. GLC and HPLC analysis of the distillate indicated that the product contained two components in equal proportions consistent with diastereoisomers²⁹⁹. GLC analysis indicated a yield of 94% with unreacted 1,5-diene accounting for the remaining 6%.

6.5.3 The Acid-Catalysed Hydrolysis of

2,2-dimethyl-3-[(3-methyl-3-oxiranyl)pentyl]oxirane

The hydrolysis of the diepoxide was investigated under a range of experimental conditions using sulphuric acid, formic acid or CSA. In a typical experiment, dilute sulphuric acid (1.4ml, 0.5M, 7.50×10^{-4} moles) was added to the diepoxide (0.208g, 94%, 1.15×10^{-3} moles) in THF (40ml, distilled) and the reaction stirred at room temperature in the absence of light. After 24 hours, a molar excess of sodium hydroxide (2.4ml, M, 2.40×10^{-3} moles) was added and the majority of solvent was removed by evaporation using a stream of nitrogen. The mixture was extracted with CHCl_3 (3 x 25ml, AR, BDH) and the organic fraction was dried with anhydrous magnesium sulphate. Rotary evaporation yielded a pale yellow oily liquid.

For hydrolyses in anhydrous conditions, THF was freshly distilled from lithium aluminium hydride and reaction mixtures transferred to Carius vials which were degassed in freeze-evacuate-thaw cycles (3x) *prior* to sealing *in vacuo* at high vacuum (10^{-3} mbar). The vials were left in a thermostatted water bath at 25°C or an oil bath at 50°C. After 24 hours, the reactions were worked up using the standard procedure to yield pale yellow liquid products.

The effect of hydrogen peroxide on the hydrolysis of epoxy compounds with formic acid was investigated in a reaction which simulated the conditions used for the epoxidation of NR latices with performic acid. Formic acid (0.13ml, 98%, 3.38×10^{-3} moles),

diluted with distilled water (0.5ml), and hydrogen peroxide (0.17ml, 50%w/w, 3.00×10^{-3} moles) were added to the diepoxide (0.202g, 94%, 1.11×10^{-3} moles) in THF (40ml, distilled). After 24 hours reaction at room temperature in the absence of light, the reaction was worked up using the standard procedure.

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