THERMAL STUDIES OF BUTADIENE - ACRYLONITRILE COPOLYMERS

A thesis submitted to the University of Glasgow for the degree of Doctor of Philosophy in the Faculty of Science.

By

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I wish to express my gratitude to Professor Norman Grassie for suggesting the problem, and for his advice and supervision throughout this period of study.

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CHAPTER ONE

INTRODUCTION

1.1 General Introduction.

Macromolecular science defines the term 'degradation' such that it encompasses any process which causes a modification in the properties, either chemical or morpholigical, of the initial material. This degradative change may ensue from the action of a variety of agencies. Radiation in the ultra-violet and visible range of the spectrum, combining with aerobic oxidation, feature prominently in normal ageing processes of polymeric materials. Application of mechanical degradation or heat may cause failure of the desired mechanical properties, and chemical breakdown of the material respectively. Exposure to certain bacteria also has a detrimental effect on some polymers.

It is apparent then, that the need to retain favourable properties in polymers has caused much interest to be centred on the prevention, retardation, or control of the processes induced by degradation agencies.

However, polymer degradation has also been usefully employed, as in the production of graphitic fibres by heating polyacrylonitrile fibres to 1500°C in an inert atmosphere. In the future controlled degradation is also likely to play a large part in the disposal of plastic waste.

Earliest degradation studies were usually concerned with the determination of the structure of polymer molecules. One of the earliest examples of such investigations is the work of Williams[1] in 1860 which demonstrated that isoprene is produced in the heat treatment of natural rubber.

The growth and development in the technology of synthetic polymeric materials has caused a corresponding advance in the study of degradation processes. It was soon found that degradation could be retarded by the use of additives, but at first very little was known of the mode of action of these stabilisers. More recently modern physical and chemical methods have been applied to the problem and progress achieved may be measured by the vast literature of polymer degradation, and the number of books and monographs on the subject.

This thesis is concerned with an investigation into the thermal degradation of the butadiene-acrylonitrile copolymer system, which merits study for several reasons. Firstly, it is a constituent of the commercially important terpolymer system acrylonitrile-butadiene-styrene, more commonly refered to as ABS plastic. Secondly, by itself it constitutes another system growing in commercial standing - the nitrile rubbers. Thirdly, it is considered that the terpolymer system may be better understood by examination of the possible copolymer systems present, thus enabling a comparison of the behaviour of the monomer units in different environments to be made.

1.2 Degradation Reaction Types.

It is relevant to review the various reaction types occuring in the thermal degradation of polymers and copolymers, and to discuss in particular present knowledge of the thermal decomposition of acrylonitrile and butadiene homopolymers, copolymers, and related systems.

Polymer degradation processes may be classified as follows:

Reaction Type	Example
Random scission	Polyethylene
Depolymerisation	Poly(methyl methacrylate)
Side group rearrangement	Polyacrylonitrile
Side group elimination	Poly(vinyl acetate)
Crosslinking	Polyacrylates

Random Scission

On heating, the methylene chains of polyethylene break at random and the reaction is characterised by a rapid drop in molecular weight, with the formation of a complex mixture of hydrocarbons having a wide carbon number distribution.

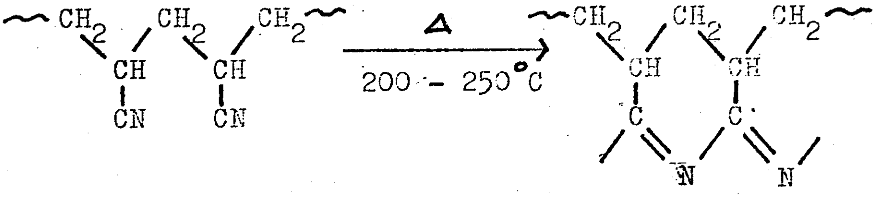
Depolymerisation

Depolymerisation is defined as the successive release of monomer units from a chain end in a depropagation reaction which is the reverse of chain polymerisation.

The thermal degradation of poly(methyl methacrylate) is probably the best example, quantitative yields of monomer being formed.

Side Group Rearrangement

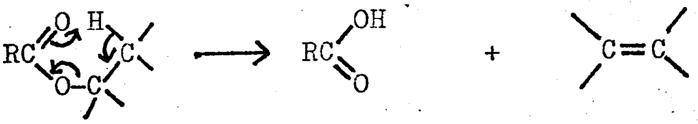
An important example of side group rearrangement is the formation of conjugated carbon-nitrogen sequences during heat treatment of polyacrylonitrile:



The degradation of polyacrylonitrile will be discussed later in greater detail.

Side Group Elimination

Side group elimination occurs commonly in ester type polymers. The reaction may be illustrated generally as follows:



Clearly the esters must incorporate hydrogen atoms on the β carbon of the alkyl group. Poly(vinyl acetate) degrades in this way to yield acetic acid and polyacetylene.

Crosslinking

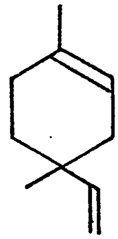
Crosslinking reactions are most often found when polymers are exposed to ultra-violet light or high energy radiation. These reactions are favoured by tertiary hydrogen atoms on the chain backbone, thus the polyacrylates and polystyrene are particularly susceptible.

1.3 The Thermal Degradation of Natural Rubber and Polyisoprene.

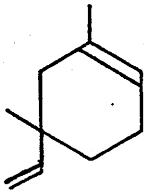
The nature and concentrations of products obtained by thermal degradation of natural rubber are very much influenced by the experimental method, and in particular the speed at which primary reaction products are removed from the reaction zone.

Up to 200°C in vacuum, natural rubber is stable over long periods, with no weight loss and no detectable structural changes.[2] Bolland and Orr[3] have reported little or no loss of unsaturation in the bulk rubber in the temperature range 200-270°C, although the rubber undergoes both scission and crosslinking. Above 300°C, breakdown becomes progressively more rapid, giving monomer and a mixture of dimers.

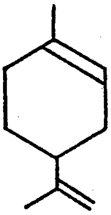
Although there are eighteen possible cyclic dimers of isoprene, only the four cyclohexene type dimers have been identified during pyrolysis of polyisoprene.[4,5] Their structures are:



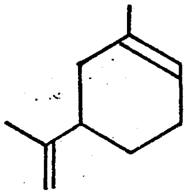
(1) 1,4 Dimethyl 4-vinyl cyclohexene.



(2) 1,5 Dimethyl 5-vinyl cyclohexene

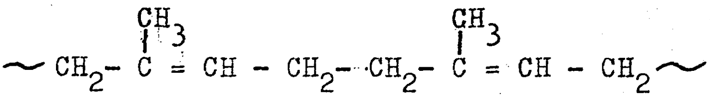


(3) 1 Methyl 4-isopropenyl cyclohexene (dipentene).

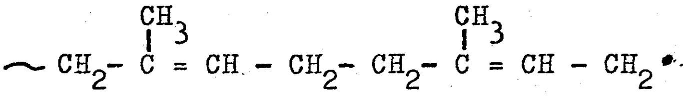


(4) 1 Methyl 5-isopropenyl cyclohexene (diprene).

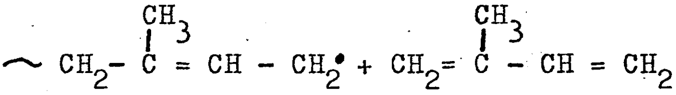
Bolland [3] suggests that the thermal degradation of polyisoprene occurs through chain scission at a carbon atom β to the double bond, and a reverse 1,4 polymerisation step to produce mainly isoprene:



$$\sim CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2\sim$$



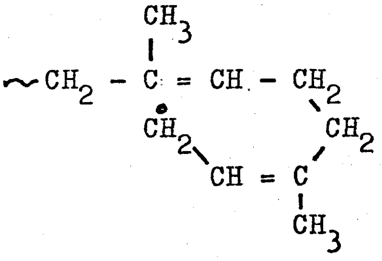
$$\sim CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2^{\bullet}$$

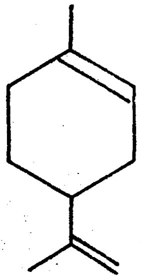


$$\sim CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2^{\bullet}+CH_2=\overset{CH_3}{\overset{|}{C}}-CH=CH_2$$

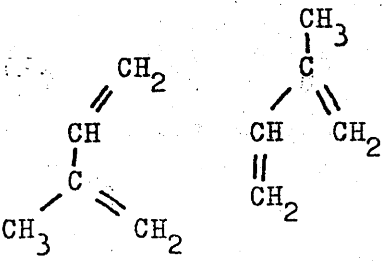
(Isoprene)

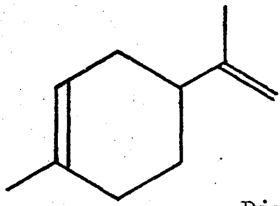
Dimer products are produced either by a reverse polymerisation step involving two monomer units, or by a recombination of the isoprene molecules producing dipentene from natural rubber:





Dipentene





Dipentene

Hackathorn[6] has recently used pyrolysis gas chromatography to investigate the dimeric products from several polyisoprenes in relation to polymer microstructure, and has come to the following conclusions:

1. Dipentene is produced from adjacent head-tail cis and/or trans 1-4 structures.
2. Dimethyl vinylcyclohexene is produced from a cis or trans 1-4 unit adjacent to a vinyl unit.
3. Diprene is produced from adjacent vinyl units.

1.4 The Thermal Degradation of Polybutadiene.

Wall[7] used pyrolysis and mass spectrometry to investigate polybutadiene, restricting his analysis to volatile products having a vapour pressure, at room temperature, of 1 m.m. or more. On complete degradation at 400°C, volatile products amount to 3% of the weight of the original polymer sample with butadiene monomer accounting for 1%, the remainder consisting of a mixture of hydrocarbons up to C_8.

Madorsky et al.[8] found that at temperatures between 350°C and 500°C the products of pyrolysis are (1) a solid residue; (2) a wax-like fraction, volatile at the temperature of pyrolysis, but not at room temperature; (3) a liquid fraction volatile at room temperature; and (4) a gaseous fraction, volatile at the temperature of liquid nitrogen (-196°C). Polybutadiene begins to break up at about 350°C and decomposition is almost complete at 477°C. The yields of fraction 3 (14%), and of fraction 4 (0.3% of volatiles), stay fairly constant for the major part of the pyrolysis reaction. The wax-like fraction 2, has an average molecular weight of 739, signifying that the average fragment in this fraction consists of about 13 to 14 monomer units. Mass spectrometric analysis of fraction 3 showed it to consist of a complex mixture of saturated and unsaturated hydrocarbons up to the C_6-C_8 region. Fraction 4 was found to consist chiefly of methane.

Straus and Madorsky[9] made a study of rates of thermal degradation of polybutadiene, and concluded that the reaction approximates to first order, with an activation energy of 62 K.cals. per mole.

Nagao and Hikita[10] pyrolysed samples of polybutadiene at temperatures between 400°C and 1100°C. The products obtained were hydrogen, methane, ethane, ethylene, acetylene, 1-3 butadiene, vinylcyclohexene(butadiene dimer) and others.

Gas chromatographic analysis was applied to the degradation of polybutadiene by Zulaica and Guchon[11]. A wide range of saturated and unsaturated hydrocarbons was identified, similar to that found by other workers.

Bolland and Orr[3] have shown that resonance stabilisation of alkyl radicals formed by scission of a carbon-carbon bond decreases the strength of that bond, from 81 K.cals. per mole, by 19 K.cals. per mole for each allylic radical formed, to 43 K.cals. per mole. Activation energies for the formation of dipentene (42 K.cals. per mole) and isoprene (52 K.cals. per mole), determined in the same temperature range (220-270°C), are of the same order of magnitude.

The overall degradation of polybutadiene and related polymers may be summarised as in figure 1. After random scission of the polymer backbone (eq. 1), experimental conditions now dictate the course of events. The most favoured next step is loss of one or two monomer unit fragments from chain ends (eq. 2), a step which is

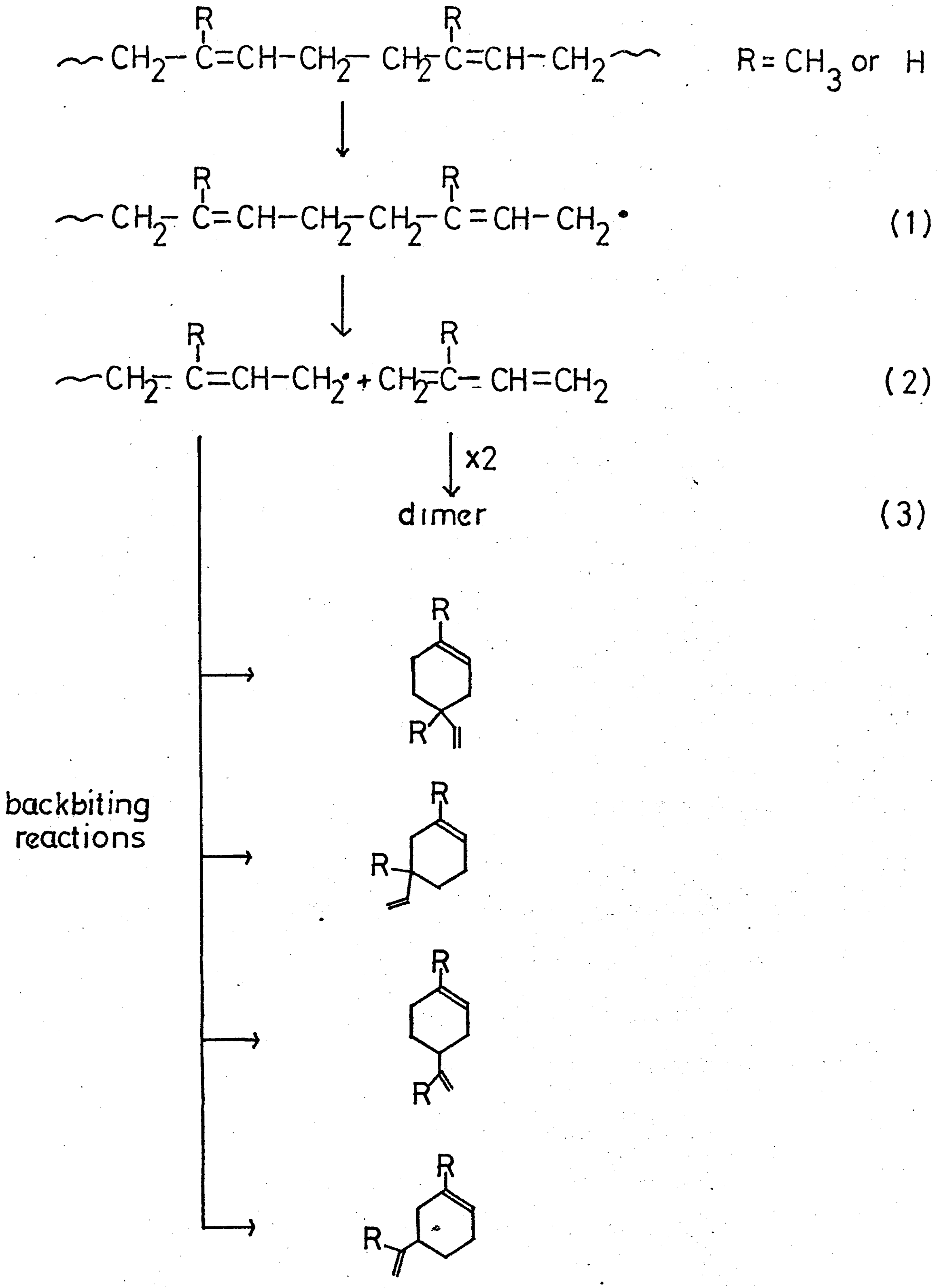
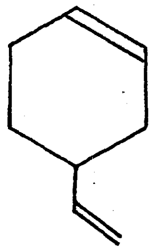


Figure 1 Degradation Pattern of Polybutadiene and Related Polymers.

energetically probable. Monomer produced at this stage may dimerise (eq. 3) or be released as monomer. At this stage, according to Hackathorn[6], for substituted polybutadienes the microstructure of the polymer determines the structure of the dimer produced by the backbiting reactions mentioned above. For polybutadiene, microstructure may influence the mechanism of dimer production, but only one dimer is possible - 4 vinyl cyclohexene:



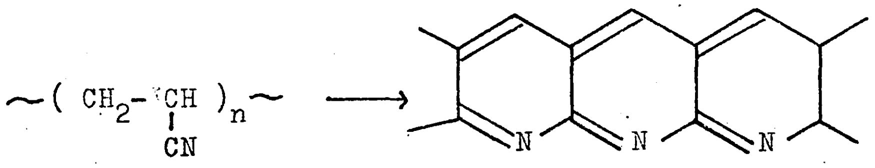
4-vinyl cyclohexene

1.5 The Thermal Degradation of Polyacrylonitrile and Related Polymers.

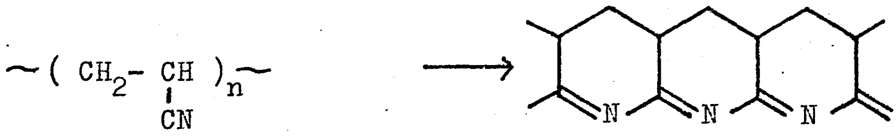
Since about 1950, acrylonitrile-rich copolymers known under trade names such as Orlon, Acrilan, and Courtelle, have become very important as commercial synthetic fibres. This has prompted many studies into the thermal degradation of polyacrylonitrile which have resulted in conflicting explanations of the thermal colouration and decomposition which results ultimately in a thermally stable residue.

The Colour Reaction

Colouration in polyacrylonitrile, studied mainly in the temperature range 150 - 200°C, was first reported by Houtz[12]. From spectral considerations, he advanced a totally aromatic structure for the coloured polymer:

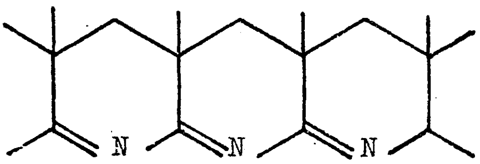


McCartney[13] Then proposed a structure consisting of partially hydrogenated rings:



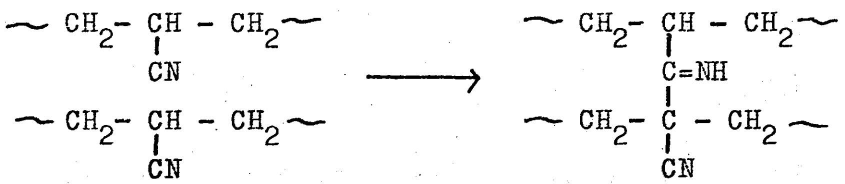
This structure was later supported by the work of Burlant and Parsons[14] and of Grassie and McNeill[15]. Further support came from La Combe[16], who, while working on the colouration in polyacrylonitrile due to the action of bases, concluded that the coloured structure was similar to those proposed in thermal treatments.

An investigation of thermal colouration in polymethacrylonitrile was carried out by Grassie and McNeill[15], who stated that initiation of the colour reaction was by trace quantities of methacrylic acid in methacrylonitrile. A structure was deduced from these studies analogous to those already proposed for coloured polyacrylonitrile:



It was suggested that this structure is formed in a non-radical chain process initiated at methacrylic acid units and propagated through adjacent nitrile units.

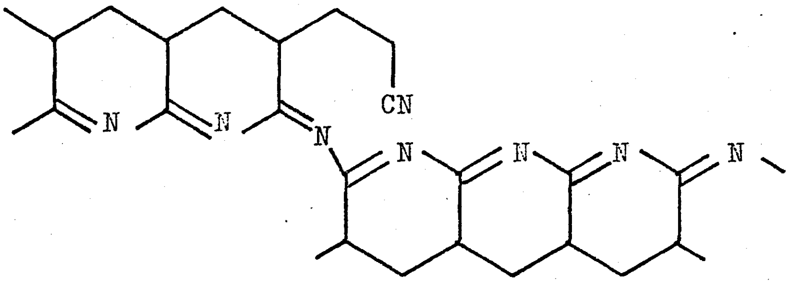
Shurz[17] believed that formation of azomethine crosslinks between neighbouring chains may take place during colouration, being favoured by the strong attraction exerted upon the active α hydrogens by nitrogen atoms:



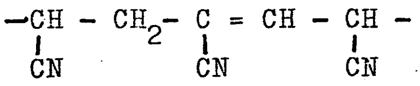
Grassie and McNeill[18] then noted that condensation of the type suggested by Schurz, occurring inter or intra molecularly, may occur in the purely thermally initiated reaction, but this alone could not explain colour formation; it would only be the initiation step of the chain process leading to napthyridene-type structures.

The investigation of colouration was continued by Grassie[19] who reported that initiation could be carried out by tertiary C-H groups. This was closely followed by the work of Grassie and Hay[20], which produced further evidence for the nitrile group polymerisation mechanism and the ability of tertiary C-H structures to initiate. It was in this paper that the theory of "propagation crosslinks" was put forward. That is, it appeared that linking up of nitrile groups could move from chain to chain:

from chain to chain:



In contrast to ring theories, a single bond conjugated with a nitrile group was suggested by Conley and Bieron[21] as a precursor to the polyacrylonitrile chromophore:

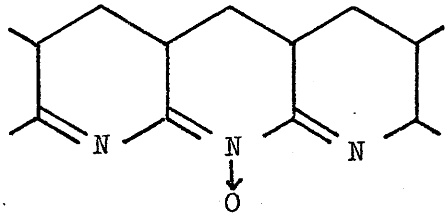


$$-\underset{\mathrm{CN}}{\mathrm{CH}} - \mathrm{CH_2} - \underset{\mathrm{CN}}{\mathrm{C}} = \mathrm{CH} - \underset{\mathrm{CN}}{\mathrm{CH}} -$$

This idea was later extended by Berlin[22] and by Fester[23] to the fully conjugated system:

$$- \mathrm{CH} = \underset{\mathrm{CN}}{\mathrm{C}} - \mathrm{CH} = \underset{\mathrm{CN}}{\mathrm{C}} - \mathrm{CH} = \underset{\mathrm{CN}}{\mathrm{C}} - \mathrm{CH} =$$

Confirmation that the species responsible for colouration in polyacrylonitrile was a conjugated C = N and not a conjugated C = C system, came from Peebles and his co-workers[24], as a result of an investigation using model compounds, and a chemical method for distinguishing between C = N and C = C in conjugated systems. They also illustrated that the Grassie-type structure of coloured polyacrylonitrile could be oxidised to the imine-nitrone copolymer:

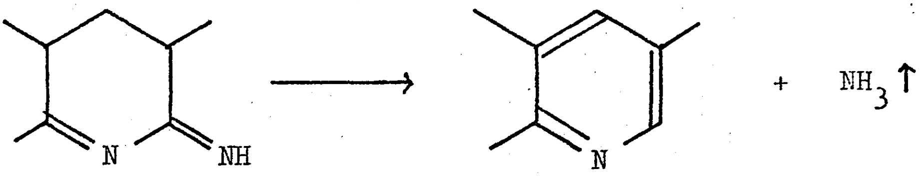


Products of Degradation

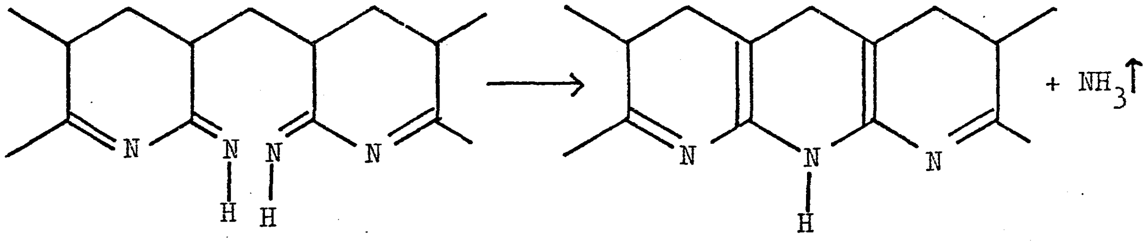
Many workers have studied the products of thermal degradation of polyacrylonitrile under differing conditions, and a good deal of dispute exists.

Straus and Madorsky[9] found hydrogen cyanide, acrylonitrile and vinylacetonitrile as the major degradation products, while Houtz[12] reported that pyrolysis at 400°C yields only a trace of hydrogen cyanide. However Nagao and co-workers[25] reported the evolution of a considerable amount of hydrogen cyanide when polyacrylonitrile is heated at temperatures from 200 - 350°C in an atmosphere of air or nitrogen.

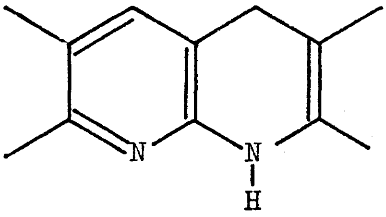
Burlant and Parsons[14] also found ammonia as one of the products, as did Hay[26] who suggested that ammonia formation might be exothermic and occur either by aromatisation of the propagating unit:



or by chance intervention of two propagating units:



Monahan[27] studied the degradation in vacuum over the temperature range 280 - 450°C, and identified five major products: cyanogen, hydrogen, hydrogen cyanide, acrylonitrile, acetonitrile, and vinyl acetonitrile. His results indicated the residue to have the following structure:



He also reported that ammonia is only produced when trace amounts of water are present, and he suggested the reaction:

$$H_2O + HCN \longrightarrow CO + NH_3\uparrow$$

In a recent study Grassie and McGuchan[28] found hydrogen cyanide and ammonia as the major gaseous products.

The Exotherm

In 1959 Kennedy and Fontana[29] reported a drastic and sudden change when polyacrylonitrile is heated to 265°C but no heat change was detected. The first indication that the reaction is strongly exothermic comes from Vosburgh[30] who found that on heating the acrylic fibre Orlon, an exothermic reaction takes place resulting in the formation of a black fireproof textile.

Thomson[31] then investigated the exotherm using Differential Thermal Analysis and reported a strong molecular weight dependence of the exotherm temperature, and a substantial weight loss accompanying the exotherm.

Hay[25] reported that the reaction is reduced by the insertion of inert comonomer units, such as styrene and methacrylonitrile and also that the process is associated with acrylonitrile units, since methacrylonitrile polymers and copolymers, although colouring, do not exhibit an exotherm. Hay relates the exotherm to ammonia production as mentioned previously.

On the other hand, Reich[32] has reviewed the many Differential Analysis studies on this subject and has suggested that the exotherm is caused by the nitrile group polymerisation process.

Turner and Johnston[33] have recently supported this suggestion, and further convincing evidence has resulted from a comprehensive investigation of the phenomenon by Grassie and McGuchan[28].

1.6 The Thermal Degradation of Copolymers.

Butadiene - Acrylonitrile Copolymers.

Straus and Madorsky[9] investigated the volatile products and rates of thermal degradation of a copolymer containing 31% by weight of acrylonitrile and 69% by weight of butadiene. The gaseous fraction was analysed by mass spectroscopy and the results were similar to those obtained by Madorsky et al[8] for polybutadiene, except that the wax-like fraction now had a molecular weight of about 400 compared with 740 for polybutadiene. It was noted that none of the products characteristic of polyacrylonitrile degradation could be detected during the pyrolysis of the copolymer. Degradation began at a lower temperature in the copolymer, but a larger percentage residue was obtained form it.

Butadiene - Styrene Copolymers.

A number of investigations have been carried out on the thermal degradation of butadiene - styrene copolymers. Wall[7] analysed the products from a copolymer with 23.5% styrene by weight and found that 3% of the polymer degraded to styrene.

Madorsky and co-workers[8] used their molecular still to investigate a copolymer consisting of 75% by weight of butadiene. The mass spectrometer was used to carry out analysis of the low molecular weight products. The yield of the fraction volatile at room temperature (fraction 3) was constant up to a temperature of 426°C. Analysis of this fraction showed that its composition closely resembled that of butadiene. The yield of butadiene amounted to 2% of the total volatilised part. The wax-like fraction had an average molecular weight of 712 corresponding to eight or nine butadiene units and three styrene units.

Straus and Madorsky[9] also studied this system with respect to rates of degradation and the copolymer was found to be less stable than the homopolymer.

Acrylonitrile - Styrene Copolymers.

Grassie and Bain[34] have studied the thermal degradation of copolymers of acrylonitrile-styrene, investigating changes in molecular weight, products of reaction, and chain scission. Changes in molecular weight which occur during the reaction indicate that the primary effect of the acrylonitrile units on stability is to cause an increased rate of chain scission, and an increasing proportion of dimer, trimer etc.

Hydrogen cyanide was found to be only a minor product of degradation and ammonia was not identified. Liquid products identified were styrene, acrylonitrile, toluene and benzene. The fraction of products volatile at the temperature of degradation, but involatile at ambient temperatures was analysed by gas chromatography - mass spectrometry. Four dimers and four trimers were identified. Three types of chain scission were discernable, namely, at weak links which are associated with styrene units, normal scission in styrene segments of the chain, and scission associated with the acrylonitrile units.

1.7 The Function of Unsaturation During the Pyrolysis of Butadiene Polymers.

The work described in this thesis includes an investigation into the function of pendant vinyl groups during heat treatment of polybutadiene and butadiene - acrylonitrile copolymers. The study was prompted by the observation of a rapid disappearance of unsaturation in the polymer on heating at 390°C. It is therefore pertinent to review the literature which may concern this phenomenon.

Sotnikova[35] has investigated the vulcanisation by heat alone of the following polybutadiene rubbers:

SKB (Na catalysed);	SKV (K catalysed)
SKBM (Li catalysed);	SKD (stereoregular)

The samples were vulcanised at 160 - 230°C, and the mole percentage of vinyl groups (N) in the rubber was correlated with the apparent activation energy (Ea) of crosslink formation. The results are:

Rubber	N	Ea
SKB	65	18
SKV	50	15
SKBM	43	22
SKD	6	26

An increase in activation energy with decreasing vinyl group concentration is noted. Analysis of the kinetic curves showed that thermal vulcanisation appears to be a second order reaction. The extent of vulcanisation was determined by a swelling method. A recent Czechoslovakian patent[36] discusses a method of vulcanising polymers containing vinyl side groups. They are processed by heating at 190 - 205°C in absence of vulcanisation agents, since the necessary interbonding is provided by the unsaturated groups.

Zakharov[37] has shown that butadiene - nitrile rubbers readily undergo thermal vulcanisation and that the rate and extent of the process increases in proportion to the nitrile groups in the polymer. Further experiments have indicated that the nitrile groups take part in the crosslinking reaction, and a mechanism has been suggested which involves elimination of a hydrogen atom from the carbon atom in the α - position with respect to the nitrile group, thereafter a mechanism similar to that accepted for the colouration reaction in heated polyacrylonitrile suggested by Grassie[14], is considered feasible. By means of infra-red spectroscopy and measurement of electrical conductance at higher temperatures, Zakharov[38] has produced evidence which he considers substantiates his theory concerning the nitrile groups.

The opposite view is found in the literature[39], where it states that the reactivity of such polymers, with respect to the thermal vulcanisation is dependent on the double bond content of the rubber.

CHAPTER TWO

EXPERIMENTAL TECHNIQUES

2.1 Copolymer Preparation and Microstructure.

1 - 3 Butadiene (Air Products Inc.) was obtained pure and free from inhibitor by repeated distillation under vacuum immediately before use, the first and last 10% being discarded at each distillation.

Acrylonitrile (Hopkin and Williams Ltd.) was purified by washing with 10% w/v NaOH solution to remove inhibitor, washing with distilled water to remove all traces of NaOH, drying over calcium hydride, and twice distilling under vacuum, the first and last 10% being discarded.

The initiator 2.2' - azobisisobutyronitrile was purified by recrystallisation from methanol.

Few studies have been published about the kinetics of the radical copolymerisation of butadiene and acrylonitrile, and the reactivity ratios reported are not in good aggreement[46-52]. Also, the experiments have been carried out over a limited range of monomer feed composition . In the present work, a series of copolymers was prepared and the feed and composition data used to calculate a new set of reactivity ratios.

The chosen volumes of monomers were distilled under vacuum into dilatometers containing 1% w/v of initiator. It was found that butadiene monomer distilled at a convenient rate into a reservoir at liquid nitrogen temperature (-196°C) if the monomer temperature was kept in the region of -30°C. Polymerisations were carried out in bulk at 60°C to approximately 5% conversion. The dilatometer contents were then poured directly into excess Analar methanol causing the polymer to precipitate as a rubbery mass. The polymer was then freed of unreacted monomer by repeated soaking and pressing in methanol, followed by drying at 60°C under vacuum for five days to remove the methanol. The polymers were stored in the dark under nitrogen at -18°C.

Ten polymers covering the entire composition range were prepared and copolymer compositions were determined from elemental analysis data using a Perkin - Elmer 240 Elemental Analyser. Copolymer molecular weights were determined in toluene, using a Mechrolab 501 High Speed Membrane Osmometer, but no data could be obtained for those polymers with less than 66% butadiene content due to the onset of insolubility. The appropriate data for the polymers is shown in table 1.

Nuclear Magnetic Resonance data were obtained for the polymers from 20% w/v solutions in deuterochloroform run at 25°C on a Perkin - Elmer R10 60 Mc/s spectrometer with integrator.

Mole % butadiene		Elemental Analysis				$\overline{Mn}$
Polymer	Feed	%C	%H	%N	Total	
100	100	88.68	11.02	———	99.70	18,000
89	92.8	86.76	10.51	2.76	100.03	17,500
80	85.9	84.77	10.14	5.17	100.08	20,000
75	80.0	83.69	9.88	6.49	100.06	21,700
66	68.3	81.76	9.19	8.81	98.76	27,000
52	34.1	78.81	8.61	12.84	99.90	———
41	11.5	76.39	7.96	15.50	99.95	———
33	6.4	74.37	7.61	17.70	99.68	———
30	4.5	73.88	7.39	18.35	99.62	———
25	2.0	73.18	7.14	19.86	100.13	———

Table 1. Polymerisation data for the polymers.

Column	Conditions	Use
10' 1/4" diameter 30 - 60 mesh silica gel.	Isothermal at 70°C for 6 minutes, then programmed at 5°C/min.	General gas column.
20' as above.	Isothermal at room temperature.	Permanent gases.

Table 2. GLC conditions and columns.

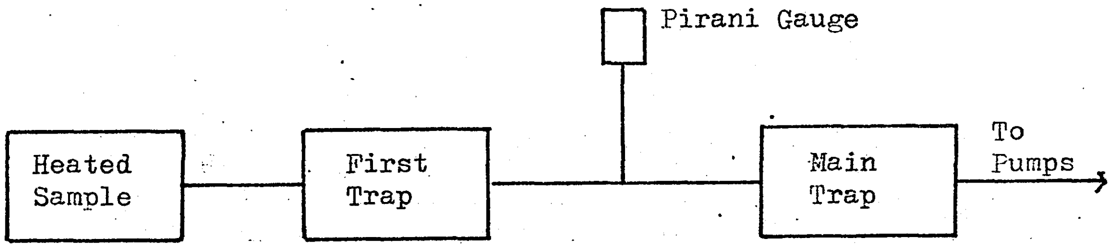
Infra-red spectra were measured using a Perkin - Elmer 275 Double Beam Grating Spectrometer, and a Unicam SP800 Spectrophotometer was used for the measurement of U.V. visible spectra.

2.2 Thermal Analysis Methods.

Thermal Volatilisation Analysis (TVA)

The technique of Thermal Volatilisation Analysis was first described by McNeill[40], and since that time many papers have been published discussing studies of polymer degradation or characterisation in which the technique has been employed[41-53]. Recent modifications to the technique have greatly increased the amount of information obtainable from TVA, by permitting differential condensation of the volatile products of degradation[51].

In the basic TVA system, a Pirani gauge is attached to a vacuum line system at a convenient point between the heated sample and the cold trap (-196°C). The products which leave the hot zone pass through the system and produce a response on the Pirani gauge. If an additional trap, at some temperature between ambient and that of the main trap, is placed before the Pirani gauge, as shown:



then the gauge will now respond only to substances sufficiently volatile to pass through the trap. By varying the first trap temperature in a series of experiments, a considerable amount of information about the nature of the products may be obtained. The system used in this work is an improved version which provides this information from one experiment by having several traps at different temperatures, each followed by a Pirani gauge and recording all the TVA curves simultaneously on the same chart (DCTVA). Such an arrangement is illustrated for a four line system in figure 2. The apparatus is constructed in such a way that the products can be routed through one or other half system. This retains the facility in the earlier TVA apparatus for collecting separately products corresponding to different stages of degradation. In normal use all four lines are open, and the four initial traps (6,7,8,9 figure 2) are at different temperatures, 0°, -45°, -75°, -100°C. A Pirani gauge is also situated beyond the main trap (15, figure 2) to monitor the system for the passage of gases non-condensible in a liquid nitrogen trap in the evacuated apparatus.

The information obtained by applying the technique of DCTVA to the butadiene - acrylonitrile copolymer system is discussed later.

Differential Thermal Analysis (DTA)

The instrument used was a Du Pont 900 Thermoanalyser with standard DTA cell which operates up to 500°C. DTA, like other dynamic methods of thermal analysis is sensitive to the experimental variables such as sample size, heating rate etc. Throughout this work 10 mg. samples of copolymer contained in 4 m.m. diameter glass tubes were run against a 10 mg. glass-bead reference also in a 4 m.m. diameter tube.

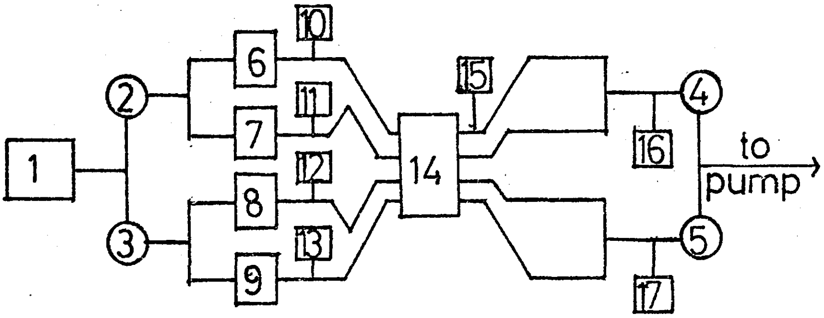


Figure 2. Four line differential condensation TVA system.
1= heated sample; 2,3,4,5,=stopcocks; 6,7,8,9,= initial cold traps; 10,11,12,13,=Pirani gauge heads; 14= main cold trap; 15 =exhaust Pirani gauge head; 16, 17,= product collection points.

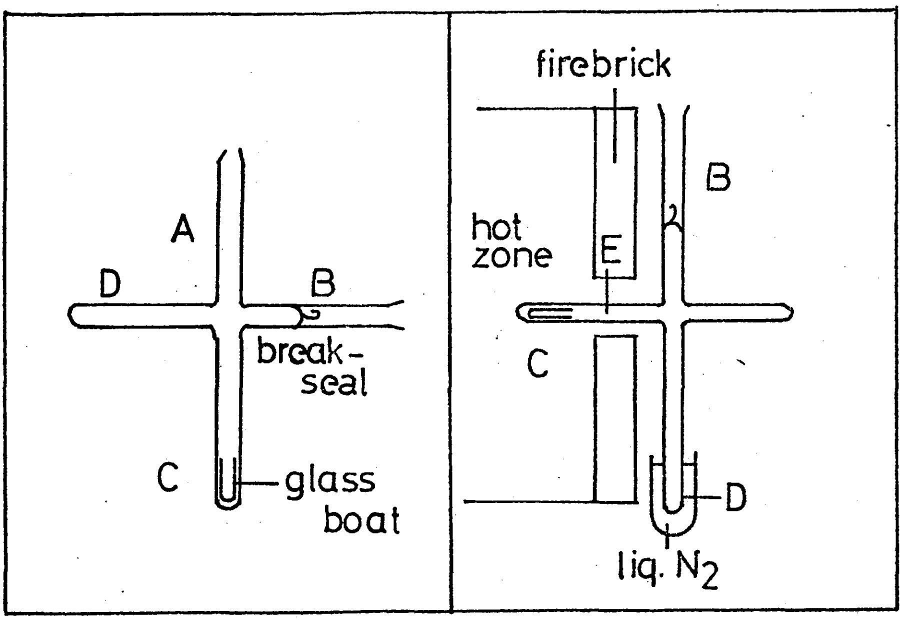


Figure 3. The sealed tube technique.

In the DTA experiment, the difference in temperature between the polymer and the inert (ΔT) is plotted against sample temperature (T) on an X-Y recorder. This technique proved to be of little value for the butadiene - acrylonitrile system, since the molten polymers had a tendency to creep up the sides of the glass sample tubes causing erratic response.

Differential Scanning Calorimetry (DSC)

The Du Pont 900 also carries a standard DSC cell which operates up to 500°C. The advantage of DSC over DTA is that the actual heat change in the sample is plotted against the sample temperature, and the fact that the sample is contained in a shallow aluminium pan eleminates any creep problems during temperature programming. Throughout this work 35 mg, samples of polymer were used. No inert reference is necessary in DSC.

Thermal Gravimetric Analysis (TGA)

Thermogravimetric analysis experiments were done using the Du Pont 950 Thermobalance, a modular attachment to the 900 unit described above. In TGA the weight of the sample is plotted against sample temperature. It should be noted that the DSC and TGA thermograms do not give equivalent information; thus some degradation reactions may give small, poorly defined transitions in the DSC. DSC can also show melting and glass transitions which would not be observed by TGA. In the present work 10 mg, samples were degraded in platinum pans under a nitrogen flow of 80 ml/minute at a heating rate of 10.2°/minute.

2.3. Degradation Apparatus.

The system used to study the degradation of the butadiene-acrylonitrile copolymers in vacuum is termed the sealed tube technique and the apparatus illustrated in figure 3. Approximately 100 mg. samples of polymer are placed in limb C in a small glass boat, the tube is then evacuated and sealed off at A. Limb C is then placed in an oven at the required temperature, while limb D is immersed in liquid nitrogen. Degradation products leaving the hot zone condense either on the part of the tube passing through the furnace firebrick E or in limb D, depending on their volatility. This technique allows degradation tubes to be stored at sub-zero temperature until required. The break-seal in the degradation tube allows products to be transferred with ease into pressure measuring devices, infra-red gas cells, etc. Chain fragments and residue are obtained by cutting the tube in the appropriate places. The oven used was a Catterson-Smith G31LX Electric Furnace contrilled by an S.K. Instruments Series 9 Skil Controller, which maintained the temperature to within ±1° of that required. At intervals the oven temperature was monitored by a thermocouple sealed into a tube similar to the one containing the polymer sample. The thermocouple output was fed into a potentiometer or a Beckman Servoscribe recorder.

In the past, degradation systems which are not continuously pumped have been criticised on the grounds that diffusion of products from the hot zone is inhibited by the increase in pressure in the system which would then encourage secondary reactions to occur. In the present instance only trace amounts of non-condensible materials are produced.

2.4. Product Analysis.

The materials produced during the thermal breakdown of the polymers were identified and measured using the techniques and instrumentation outlined below.

2.5. Product Separation.

Gases non-condensible at -196°C were removed from degradation tubes by attaching the tube to a vacuum line system and surrounding limb D (figure 3) with liquid nitrogen. The break-seal was then broken and the gases were pumped into a collection vessel by means of a Topler pump.

Products volatile at 20°C. were then obtained by surrounding limb D with a water bath maintained at 20°C., allowing adequate time for equilibration, and distilling the volatiles into a reservoir at liquid nitrogen temperature. The usual procedure was to remove the permanent gases firstly into an infra-red gas cell, and then, a spectrum having been run, they were collected into a glass sample vessel suitable for use in MS or GLC analysis. The gases volatile at 20°C. received similar treatment after firstly being distilled into a constant-volume manometer for pressure measurements. The gas sample containers were normally fitted with break-seals to enable the gases to be withdrawn at a later date for further examination thus avoiding the possibility of leaks or of the contents being absorbed on tap grease.

2.6. Qualitative Analysis of Degradation Products.

Infra-red Spectra Measurement.

The infra-red spectra of gaseous products were recorded by transferring the gases into a gas cell of path-length 10 cms. An identical evacuated cell was placed in the reference beam of the spectrometer.

The spectra of chain fragments were measured by smearing a thin film of the material between two NaCl plates, using a clean salt plate in the reference beam.

KBr discs (100 mgs.) containing 3 mgs. of smaple were used to record the infra-red spectra of polymer residues, In this case a KBr reference disc was used.

Gas-Liquid Chromatography (GLC)

GLC data were obtained using a Microtek GC 2000R Research Gas Chromatograph fitted with a temperature programmer and flame ionisation detector. The permanent gases produced during degradations were analysed using a modified Gallenkamp chromatograph equiped with a thermal conductivity detector. The columns and conditions employed are given in table 2. Gases were introduced into the chromatograph using the apparatus shown schematically in Figure 4. The apparatus was first evacuated and the tap T_1 closed. The gases volatile at 20°C were distilled into the cold finger from a degradation tube or from a sample vessel. Tap T_2 was then closed and the liquid nitrogen removed. Upon achieving equilibrium the pressure was made up to atmospheric with nitrogen gas, and in this way samples could be withdrawn via the septum using a gas syringe and injected into the chromatograph.

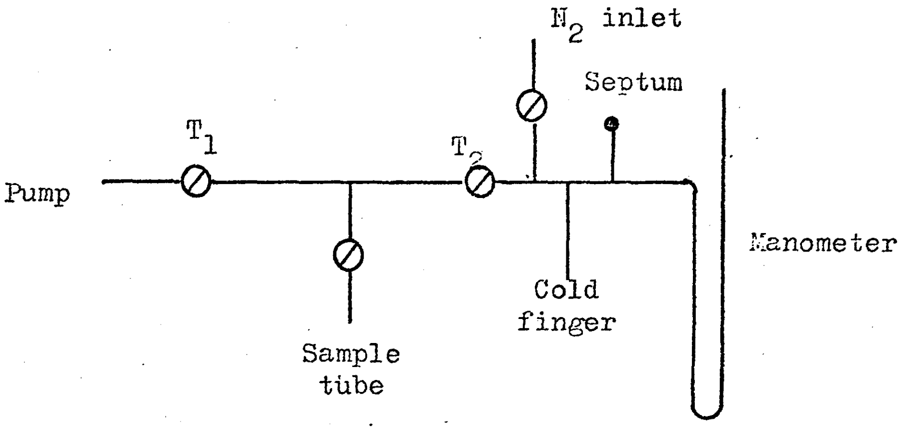


Figure 4. Apparatus for the introduction of gases into the GLC.

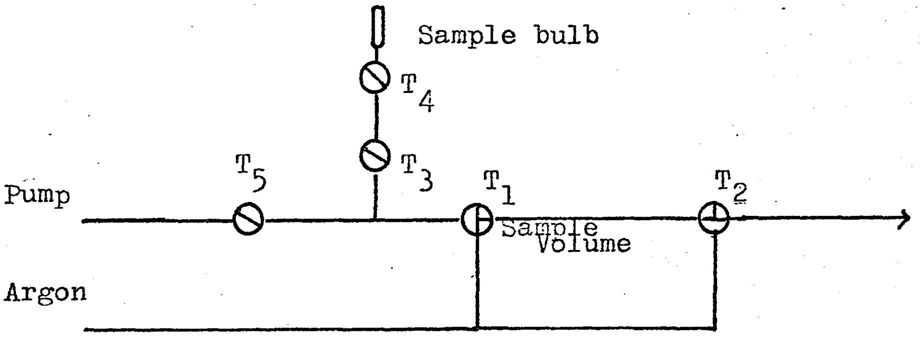


Figure 5. Apparatus for the introduction of non-condensible gases into the GLC.

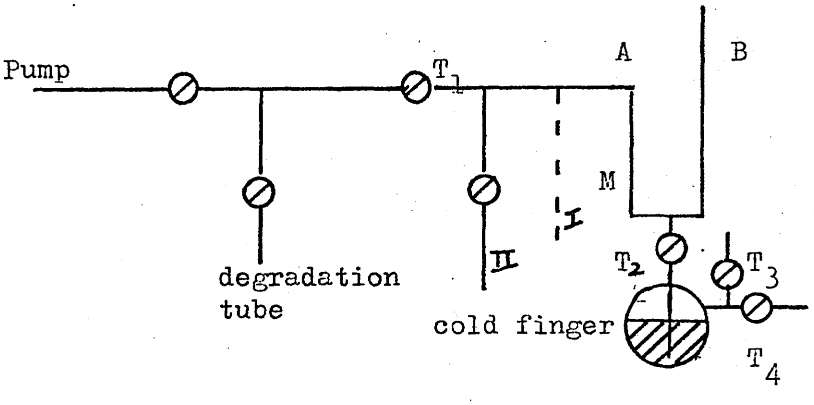


Figure 6. Constant volume manometer.

Since the permanent gases are non-condensable at -196°C., the above technique could not be applied to this fraction, so the system shown schematically in Figure 5 was used for injecting samples into the Gallenkamp chromatograph. The sample bulb containing the permanent gas fraction was attached to the socket with taps T_3 and T_5 open and taps T_1 and T_2 set in such a way as to allow the carrier gas argon, to pass through the system by-passing the sample volume. To fill the sample volume, tap T_5 was closed and T_4 and T_3 opened. The sample was introduced by closing T_3 and reversing the positions of T_1 and T_2 so that the carrier now flushed the sample into the GLC column.

Mass Spectrometry (MS)

Mass spectra were obtained for gaseous materials using an A.E.I. M.S. 12 Mass Spectrometer.

U.V. - Visible Spectrometry

A Unicam SP 800 Spectrophotometer was used for measurements in this region.

Molecular Weight Measurements

A 301A Vapour Pressure Osmometer (Mechrolab Inc.) was used to measure the molecular weight of chain fragments.

2.7. Quantitative Analysis of Degradation Products

Several techniques were employed to measure quantitatively the products of degradation. The polymer residue weights were obtained by weighing the glass-boat empty, and after the reaction was complete. The amounts of chain fragment material produced were determined by washing the sample out of the tube sections with Analar chloroform, and removing the solvent under vacuum to constant weight.

Pressure Measurement

The pressures of gaseous materials produced during degradation were of the order of several centimetres, and were recorded using a constant volume manometer (CVM).

The constant volume manometer is shown schematically in Figure 6. Before any reading was taken, the mercury level had to be adjusted to the constant volume mark M. on the left hand limb A of the manometer. The pressure is given by the difference in height of the mercury columns in limbs A and B.

In order to record the pressure of a given sample, the manometer was first evacuated with all the mercury contained in the reservoir. The mercury was then brought into limbs A and B by opening tap T_2 and controlling the pressure above the mercury in the reservoir by adjustment of taps T_3 and T_4. Tap T_2 was then closed and the sample of gas distilled into the cold finger (II) immersed in liquid nitrogen. Tap T_1 was then closed and the liquid nitrogen replaced by a water bath at 20°C. When equilibrium was obtained the mercury level in A was adjusted to the mark M, and the pressure recorded.

The constant volume of the manometer must be known in order to measure absolute quantities of gas. This was measured by admitting a little nitrogen into the constant volume. A series of pressure versus volume difference readings was then taken, the internal diameter of A being measured before assembly.

Let Vo = constant volume of the manometer.

V = volume of nitrogen sample.

ΔV is defined such that $V = Vo + \Delta V$.

pV = a constant, where p = pressure of gas.

Therefore $p\,(Vo + \Delta V) = \text{constant}$.

Therefore $\Delta V = \text{constant}\,(1/p) - Vo$.

Let r = internal radius of limb A.

Let Δh be the height ofthe mercury in A below the mark M.

Then, $\Delta V = \pi r^2 . \Delta h$

Therfore, $\pi r^2 . \Delta h = \text{constant}(1/p) - Vo$.

i.e. $$\Delta h = \frac{\text{constant}(1/p)}{\pi r^2} - \frac{Vo}{\pi r^2}$$

This is in the form of a straight line, so that a plot of Δh versus $1/p$ will have a gradient of $(\text{constant}/\pi r^2)$. From the gradient, Vo may be found since $Vo = (\text{constant}/p_{h=o})$.

Known pressures of pure samples of the product gases of interest were measured using the constant volume manometer, and infra-red spectra obtained over a wide pressure range. The optical density of the appropriate characteristic peaks was then plotted against the pressure of the pure gas so that these calibration curves could be used to determine the composition of the gaseous products of polymer breakdown.

2.8. Low Temperature Investigation

Studies of the reaction in which pendant vinyl groups in the polymers disappear on heat treatment were carried out in the temperature range 200 - 250°C, using the following techniques.

Vinyl Group Studies

During heat treatment of the polymer at low temperatures insolubility occurs rapidly and the resulting products cannot easily be prepared for the recording of infra-red spectra. It was found convenient to follow the disappearance of vinyl groups by casting films of the untreated polymers between two standard 13 m.m. salt plates. The solutions were made up in Analar chloroform to concentrations of the order of 0.05 gms./ml. Reproducibility of the characteristic vinyl and trans peaks in the 900 - 1000cm^{-1} region of the infra-red, was found to be at its best if the film thickness was such that with a baseline at about 80% transmittance, the trans peak (962cm^{-1}) had a transmittance value near 40%. The quantity of polymer solution necessary to produce this condition was about 0.3mls. The salt plates carrying the polymer film were placed in glass tubes approximately 9 inches long which were then evacuated and sealed off. After heat treatment the infra-red spectrum was recorded by removing the salt plates from the glass tube and inserting them directly into a standard holder for the spectrometer. When the spectrum had been determined the salt plates, now held firmly together by crosslinked polymer, could be separated by immersion in chloroform for one hour.

Nitrile Group Studies

In order to determine whether or not the nitrile groups or other unsaturation in the polymer were undergoing any reaction at the same time as the pendant vinyl groups, a different system was used. This system permitted repeated scanning of the infra-red spectrum of a sample while it was being heated. The apparatus is shown in figure 8. A research and Industrial Instruments J. 2 cell-heater was used together with sample-holder fitted with retaining screws and designed to carry a thermocouple for temperature control. It was found that air could be effectively excluded over short periods from the sample film by/

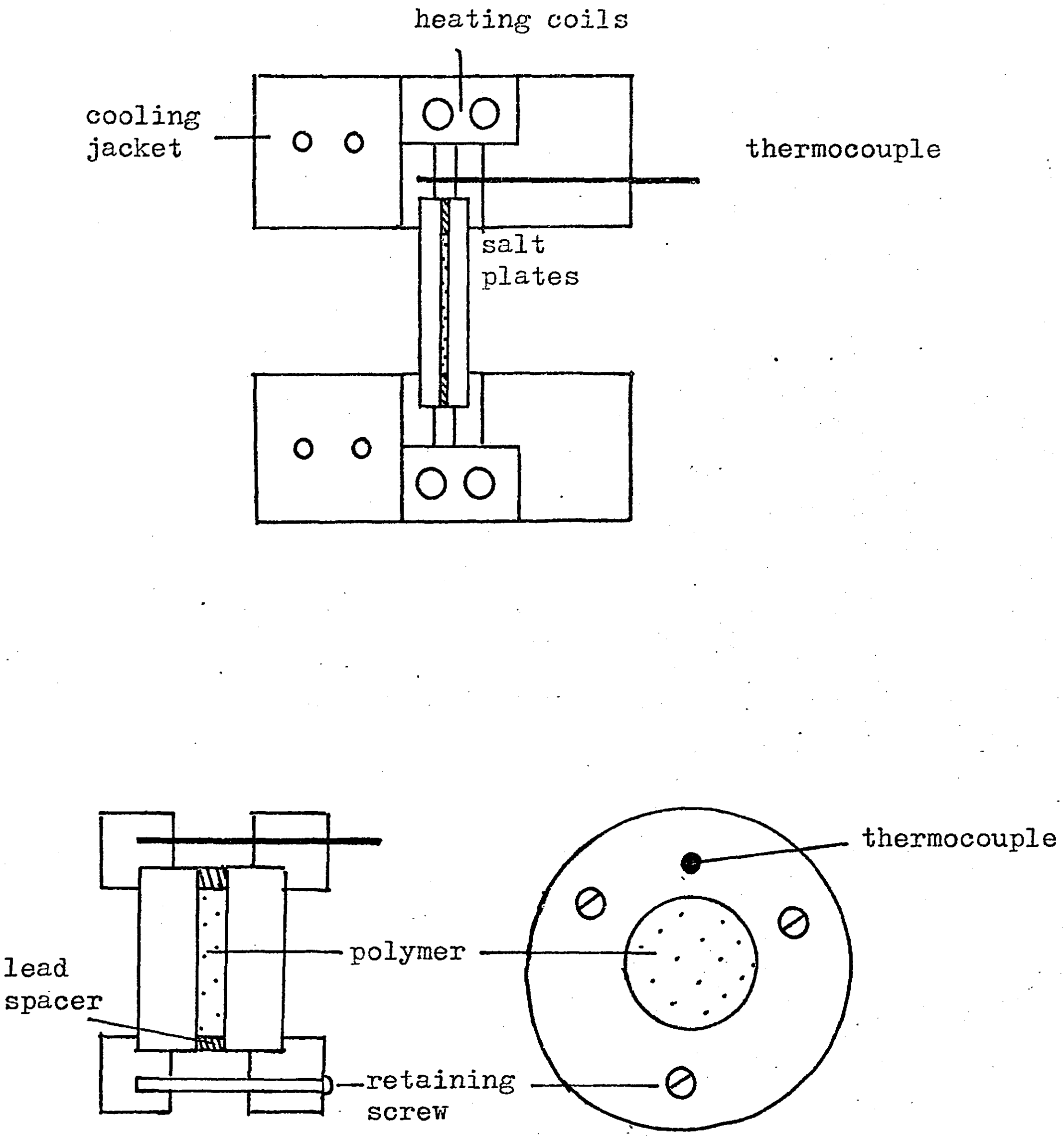


Figure 8. Apparatus for the investigation of nitrile group function at low temperatures.

by use of a lead spacer 0.007" in thickness. This arrangement was not used for the general vinyl reaction investigation due to the inaccuracy of temperature control, and the inability to achieve total exclusion of air over long periods.

The Use of Radical Inhibitors.

When studies were being made using free-radical inhibitors, the inhibitor was added to the polymer solution in the required concentration and the technique already outlined for the general investigation of vinyl group function was used, except that the volume of the tube was kept as small as possible to minimise any possible vapourisation of the inhibitor. A 9" glass rod attached to the small glass tube prior to sealing off facilitated removal from the oven.

CHAPTER THREE

Reactivity Ratios, Sequence Distribution, Microstructure.

3.1. Reactivity Ratios.

The composition of the copolymer obtained from a given monomer mixture is defined by the Copolymer Composition Equation[54-58],

$$\frac{d(M_1)}{d(M_2)} = \frac{M_1}{M_2} \cdot \left[\frac{r_1(M_1) + (M_2)}{r_2(M_2) + (M_1)}\right]$$

in which M_1/M_2 and dM_1/dM_2 are the molar ratios of the monomers in the mixture and copolymer respectively, and r_1, r_2 are the reactivity ratios, which are the ratios of the rate constant for a given radical adding to its own monomer, to that for its adding the other monomer. Thus $r_1 > 1$ means that radical $M_1\bullet$ prefers to add M_1; $r_1 < 1$ means that it prefers to add to M_2.

The data in Table 4 demonstrate that the literature values of reactivity ratios of the acrylonitrile - butadiene system are not in good agreement. The feed and composition data provided by the polymerisations carried out in this work have therefore been used to calculate a new set of ratios for this system.

Figure 9 shows the experimental relationship obtained between monomer mixture and copolymer composition. Copolymer composition was obtained by analysis of nitrogen content. At conversions below 5%, this graph may be taken as approximating to the instantaneous composition of copolymer plotted against the corresponding mole fraction of monomer in the feed at that time, and as such can yield some prelinimary information on the relative reactivities of the monomers. The diagonal illustrates the ideal case when $r_1=r_2=1$. Consider the right-hand side of the graph where a small amount of butadiene present creates a rapid drop in the percentage of acrylonitrile incorporated into the copolymer. At the other end a small amount of acrylonitrile added does not have quite so drastic an effect. Thus the reactivity ratio for butadiene is greater than that for acrylonitrile. At the point of intersection of the curve with the diagonal, polymerisation proceeds without a change in the composition of feed or polymer. This is known as azeotropic copolymerisation, and the azeotrope conposition is seen to be about 36 mole% acrylonitrile, 64 mole% butadiene.

Fineman and Ross Calculations

Reactivity ratios for the system have been calculated according to the method of Fineman and Ross[66].

Consider the copolymer equation:

$$\frac{d(M_1)}{d(M_2)} = \frac{M_1}{M_2}\left[\frac{r_1(M_1) + (M_2)}{r_2(M_2) + (M_1)}\right] \qquad (5)$$

$$= \frac{m_1}{m_2} \quad \text{at low conversions} \qquad (6)$$

Let $\frac{m_1}{m_2} = N_1$ and $(M_1)/(M_2) = X_1$ (7)

then the Copolymer Equation becomes:

$$X_1/N_1 \cdot (N_1 - 1) = r_1 X_1^2/N_1 - r_2^2 \qquad (8)$$

$$(N_1 - 1)/X_1 = r_1 - r_2 N_1/X_1^2 \qquad (9)$$

Therefore a plot of $-N_1/X_1^2$ against $(N_1 - 1)/X_1$ will be a straight line with gradient = r_2 and intercept r_1. Table 5 gives the appropriate data for the butadiene-acrylonitrile system with M_1 = butadiene; M_2 = acrylonitrile. Table 5 also shows the data required for equation (9) written in terms of monomer 2:

$$(N_2 - 1)/X_2 = r_2 - r_1 N_2/X_2^2 \qquad (10)$$

By reversing the situation in this way a more accurate value for r_1 can be obtained. Thus, by plotting $-N_2/X_2^2$ against $N_2 - 1/X_2$, r_1 is given by the gradient, and r_2 by the intercept. This approach was considered necessary since the form of equation (9) makes it difficult to plot all the data on the one graph, as can be seen from the column headed N_1/X_1^2 in table 4. Figure 10 shows the plot of $-N_1/X_1^2$ against $(N_1 - 1)/X_1$ giving a value of $r_{\text{acrylonitrile}} = 0.07$. The intercept here shows that $r_{\text{butadiene}}$ (r_1) is approximately equal to 0.5. From figure 11, $r_{\text{butadiene}} = 0.5$.

$r_{acrylonitrile}$	$r_{butadiene}$	Temperature(°C)	Conditions	Ref.
0.18	0.03	5	Emulsion oil phase	59
0.28	0.02	5	Emulsion water phase	59
0.35	0.0	50	Bulk	60
0.35	0.05	50	Emulsion	61
0.46	0.0	50	"	62
0.33	0.25	60	"	63
0.1	0.06	40	Radiation graftimg	64
0.3	0.02	40	"	64
0.58	0.067	—	Solution	65

Table 4. Reactivity ratios from literature.

% butadiene		$\frac{N_2-1}{X_2}$	$\frac{N_1-1}{X_1}$	$\frac{N_2}{X_2^2}$	$\frac{N_1}{X_1^2}$
Feed	Polymer				
92.8	89	-11	0.55	20	0.049
85.9	80	-4.6	0.49	9.3	0.11
80.0	75	-2.7	0.50	5.3	0.19
68.3	66	-.10	0.42	2.4	0.42
34.1	52	-0.041	0.19	0.25	4.1
11.5	41	-0.053	-2.3	0.025	42
6.4	33	-0.069	-7.5	0.0098	110
4.5	30	-0.061	-12	0.0052	200
2.0	25	-0.041	-33	0.0012	800

Table 5. Data for the Fineman and Ross plots.

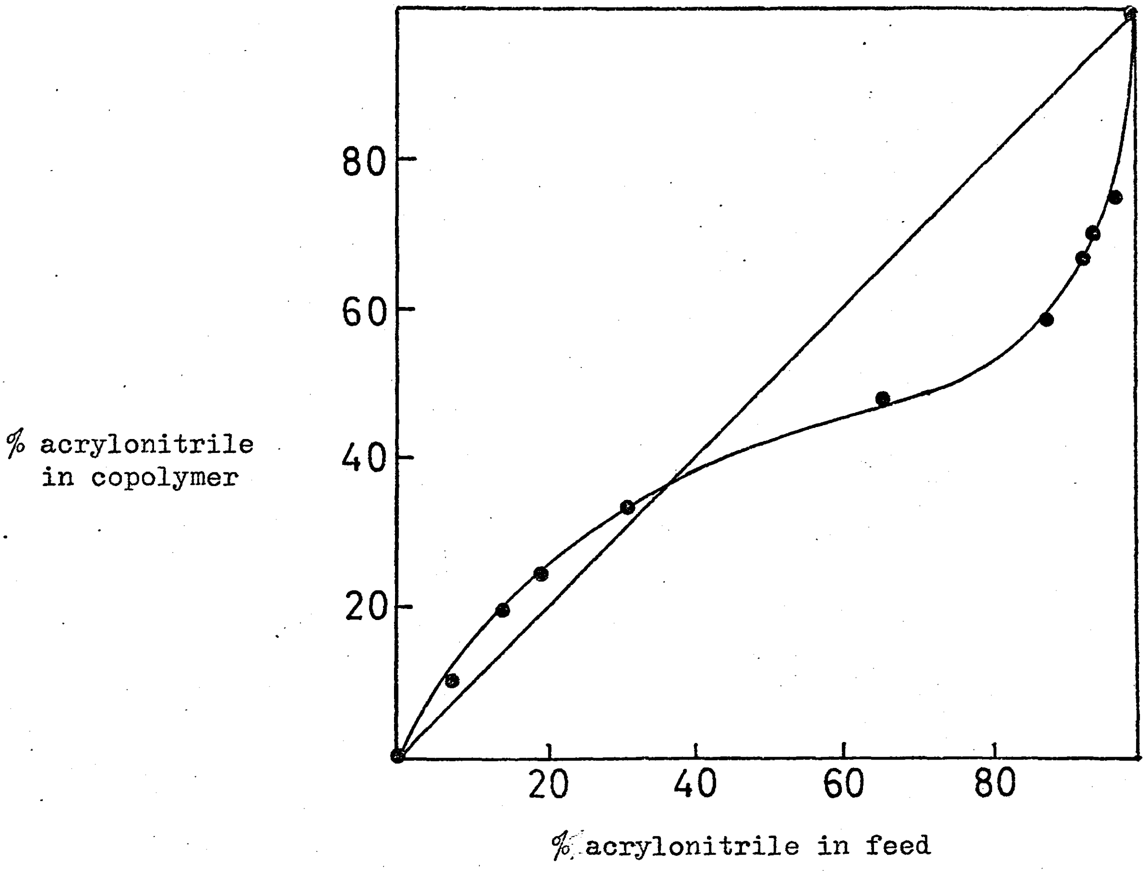


Figure 9. Feed composition versus copolymer composition.

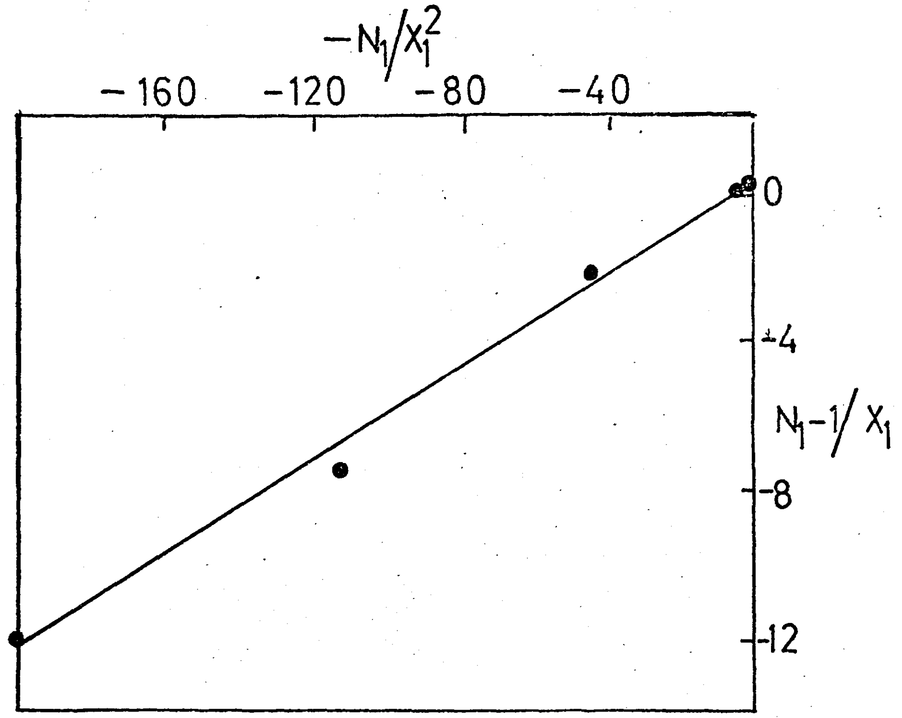


Figure 10. Fineman and Ross plot for $r_{acrylonitrile}$.

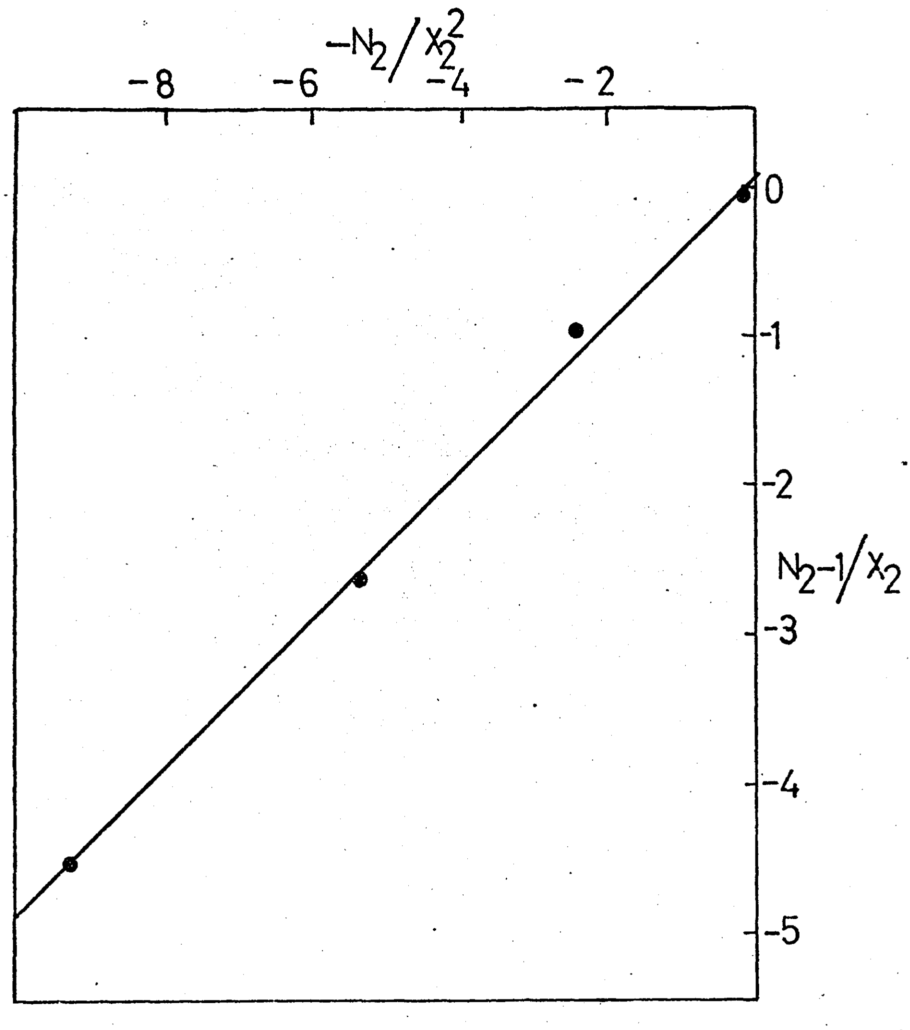


Figure 11. Fineman and Ross plot for $r_{butadiene}$.

The values $r_{butadiene} = 0.5$, $r_{acrylonitrile} = 0.07$ agree favourably with data recently published concerning the dimethyl formamide solution copolymerisation of butadiene and acrylonitrile[65].

3.2. Sequence Distribution

Copolymerisation of monomers can lead to a variety of copolymers differing in composition and in the arrangement of monomer units. The monomer units may be randomly distributed, may tend to alternate, or may tend to cluster in blocks of like units.

It is considered that knowledge of such distribution may shed some light on the possible mechanisms in operation during polymer degradation, and to this end sequence distribution calculations were carried out on the nine copolymers prepared. The method used is that due to Harwood[67] which is outlined as follows.

The method is based on the Run Number R, which is defined as the average number of monomer sequences (runs) occurring in a copolymer per 100 monomer units. Consider for example the portion of a copolymer chain shown:

-A-A-A-B-A-B-A-A-B-A-B-A-A-A-B-B-A-B-B-B-

The chain contains 20 monomer units arranged in 12 alternating runs or sequences, the run number is therefore 60.

By elementary stoichiometric and statistical considerations, several relationships between R and the sequence distributions in the copolymer can be obtained:

% A-B linkages = R/2

% B-A " = R/2

% (A-B + B-A) = R

% B-B = %B-R/2

% A-A = %A-R/2

where %A and %B refer to the molar percentages of monomer units in the copolymer. Also:

$$\langle A \rangle = \%A/(R/2)$$
$$\langle B \rangle = \%B/(R/2)$$

where $\langle\ \rangle$ indicates the number average length of the given sequence type. Furthermore,

$$P_{BA} = (R/2)/\%B = R/(2\%B)$$
$$P_{AB} = R/(2\%A)$$
$$P_{BB} = (\%B-R/2)/\%B$$
$$P_{AA} = (\%A-R/2)/\%A$$

where P_{BA} is the probability that a given B unit has an A unit on the right.

The probability that a given B unit has A units on both sides is the product of the separate probabilities, so that:

$$P_{ABA} = R^2/(2\%B)^2$$
$$P_{BBB} = \frac{(\%B-R/2)^2}{\%B^2}$$

$$P_{BBA} + P_{ABB} = \frac{R(\%B-R/2)}{\%B^2}$$

In essence these probabilities are the fractions of B units which are centred in the three possible triadic sequences ABA, ABB, BBB. Similar calculations can be made for A centred triads.

It can be shown that for a given system,

$$R = \frac{200}{2 + r_a(A_f/B_f) + r_b(B_f/A_f)}$$

where r_a and r_b are reactivity ratios, and A_f, B_f are the mole fractions of A and B in the feed.

Table 6 shows the run numbers and number average sequence lengths calculated using the feed and composition data of table 1, and the reactivity ratios determined as described previously.

% butadiene in polymer	Run no. (R)	$\langle B \rangle$	$\langle A \rangle$
25	36.76	1.36	4.08
30	56.96	1.05	2.46
33	65.33	1.01	2.05
41	76.62	1.07	1.54
52	82.65	1.19	1.23
66	62.16	2.12	1.09
75	47.42	3.16	1.05
80	37.30	4.29	1.07
89	21.99	8.09	1.00

$\langle B \rangle$ = The number average sequence length of butadiene units.

$\langle A \rangle$ = The number average sequence length of acrylonitrile units.

Table 6. Run numbers and number average sequence lengths.

% butadiene in polymer	R_{random}	$R_{experimental}$
25	37	37
30	42	57
33	44	65
41	49	77
52	50	83
66	45	62
75	37	47
80	32	37
89	21	22

Table 7. Random and experimental run numbers.

Some copolymerisation processes can be expected to produce copolymers having monomer units distributed randomly along polymer chains, and it can be shown that run numbers for such polymers are given by the following expression:

$$R_{\text{random}} = \%A.\%B/50$$

In general, if $R_{\text{experimental}} > R_{\text{random}}$, the monomer units tend to alternate in the copolymers, whereas if $R_{\text{experimental}} < R_{\text{random}}$, the monomer units tend to cluster in blocks of like units. Table 7 shows the calculated run numbers for random polymers compared with the experimental run numbers. Figure 12 shows that the maximum run number occurs at about 50% butadiene content, and it can be seen that these polymers tend to deviate from randomness between the limits 25% - 90% butadiene content. In other words, between these limits there is a tendency towards alternation. Below 25% butadiene content there may be a slight tendency to blocking ($R_{\text{experimental}} < R_{\text{random}}$), however not enough data is available in this region to make any firm conclusions.

Considering number average sequence length (NASL) (figure 13), the first point to note is that a NASL cannot fall below 1, since one comonomer molecule present in a complete chain would still be one unit in length. The fact that both curves tend to a NASL of 1 at an early stage (50/50 mark) illustrates the tendency towards alternation since for a totally alternant copolymer the NASL for each monomer is 1. For pure randomness in this region the NASL for each monomer should be about 2.

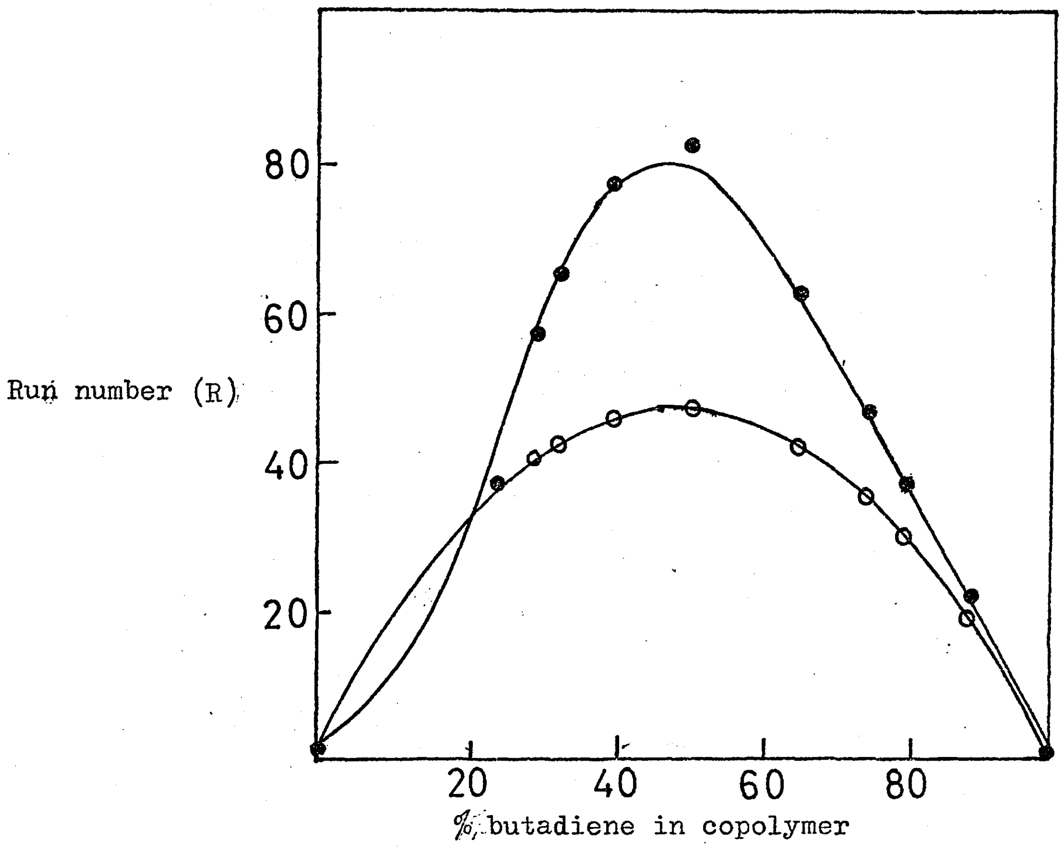


Figure 12. Random (o) and experimental (●) run numbers.

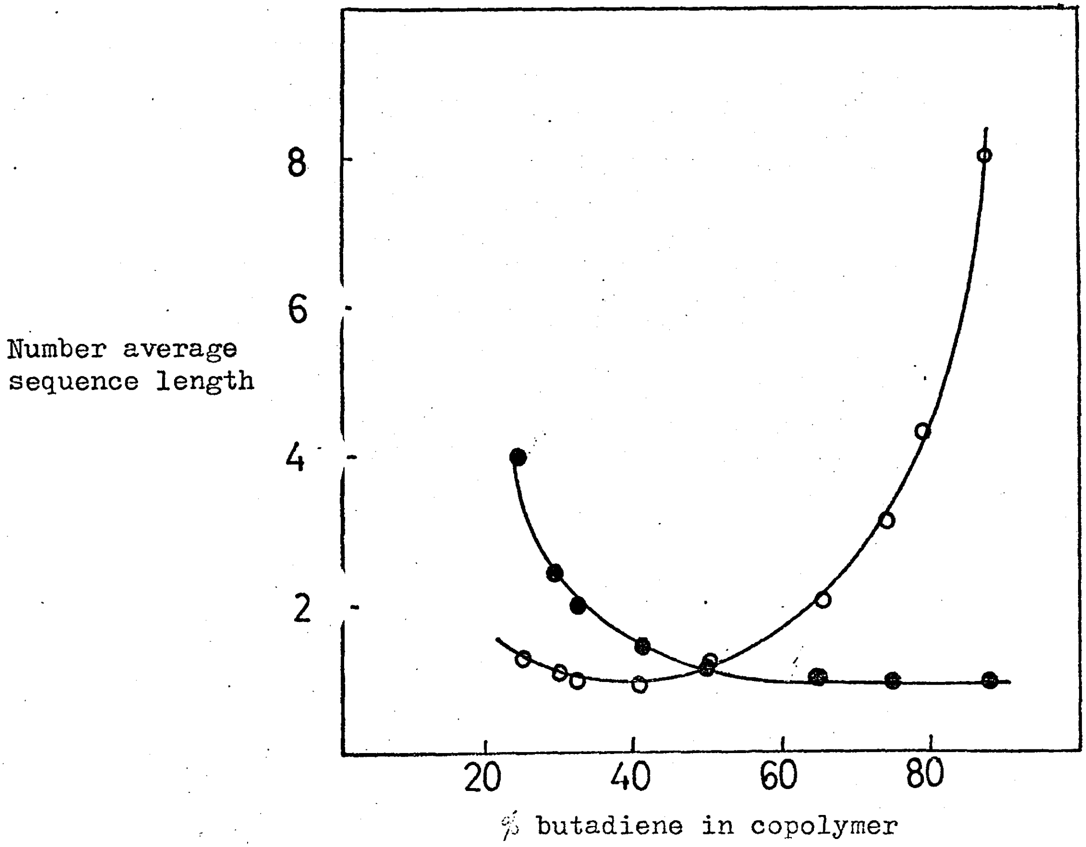


Figure 13. Number average sequence lengths of butadiene(o) and acrylonitrile(●

Table 8 shows the distributions of monomer unit sequences in the copolymers as calculated by the Harwood method, and the data is presented graphically for ease of analysis in figures 14-20.

In figure 14 P_{BA} is the fraction of butadiene units which have acrylonitrile units to the right, and the trend is as expected, that is, a general decrease in P_{BA} with increasing butadiene content. The maximum in P_{BA} and the minimum in P_{BB} at about 33% butadiene content, illustrates the previously mentioned tendency to blocking at this end of the scale. P_{BB} is the fraction of butadiene units which have a butadiene unit to the right, and therefore $P_{BA} + P_{BB}$ should be equal to 1. This is seen to be true from the data of table 8. Similar considerations apply to P_{AB} and P_{AA} (figure 15), except that in this case no maximum or minimum occurs. The reason for this is that if there is a tendency to block at low butadiene content, this will have a noticeable effect on the values of P_{BA}, P_{BB} etc., since these are fractions of the total amount of butadiene present, however in the case of P_{AB}, P_{AA} etc., the blocking effect would not be noticeable since the overall content of acrylonitrile is so much greater than that of butadiene.

P_{ABA} (figure 16) is the fraction of butadiene flanked by acrylonitrile units, while P_{BBB} is the fraction of butadiene flanked by butadiene units. P_{BAB} and P_{AAA} (figure 17) are the corresponding fractions for acrylonitrile units.

$(P_{BBA} + P_{ABB})$ gives the fraction of butadiene having a butadiene unit on one side and an acrylonitrile unit on the other, and this value is shown plotted against butadiene content in figure 18. The graph is seen to oscillate and this can be explained by considering

% butadiene in polymer	P_{BA}	P_{AB}	P_{AA}	P_{BB}	P_{BAB}	P_{ABA}
25	0.74	0.25	0.75	0.26	0.06	0.54
30	0.95	0.41	0.59	0.05	0.17	0.90
33	0.99	0.49	0.51	0.01	0.24	0.98
41	0.93	0.65	0.35	0.07	0.42	0.87
52	0.84	0.81	0.19	0.16	0.66	0.71
66	0.47	0.91	0.09	0.53	0.84	0.22
75	0.32	0.95	0.05	0.68	0.90	0.10
80	0.23	0.93	0.07	0.77	0.87	0.05
89	0.12	1.00	0.00	0.88	1.00	0.02

	P_{AAA}	P_{BBB}	$P_{AAB}+P_{BAA}$	$P_{ABA}+P_{ABB}$	$P_{BB} \cdot P_{BA}$
25	0.57	0.07	0.37	0.39	0.19
30	0.35	0.00	0.48	0.10	0.05
33	0.26	0.00	0.50	0.02	0.01
41	0.12	0.00	0.46	0.12	0.06
52	0.04	0.02	0.31	0.26	0.13
66	0.01	0.28	0.16	0.50	0.25
75	0.00	0.47	0.10	0.43	0.22
80	0.00	0.59	0.13	0.36	0.18
89	0.00	0.77	0.00	0.22	0.11

P_{BA} = The fraction of butadiene units with an acrylonitrile unit to the right.

P_{AB} = " " " acrylonitrile " " a butadiene " " ".
P_{AA} = " " " " " " an acrylonitrile " " ".
P_{BB} = " " " butadiene " " a butadiene " " ".

P_{BAB} = " " " acrylonitrile units flanked by butadiene units.
P_{ABA} = " " " butadiene " " " acrylonitrile " .
P_{AAA} = " " " acrylonitrile " " " " " .
P_{BBB} = " " " butadiene " " " butadiene " .
Similarily for P_{AAB}, P_{BAA}, P_{BBA}, and P_{ABB}.

Table 8. Data for the sequence distribution analysis.

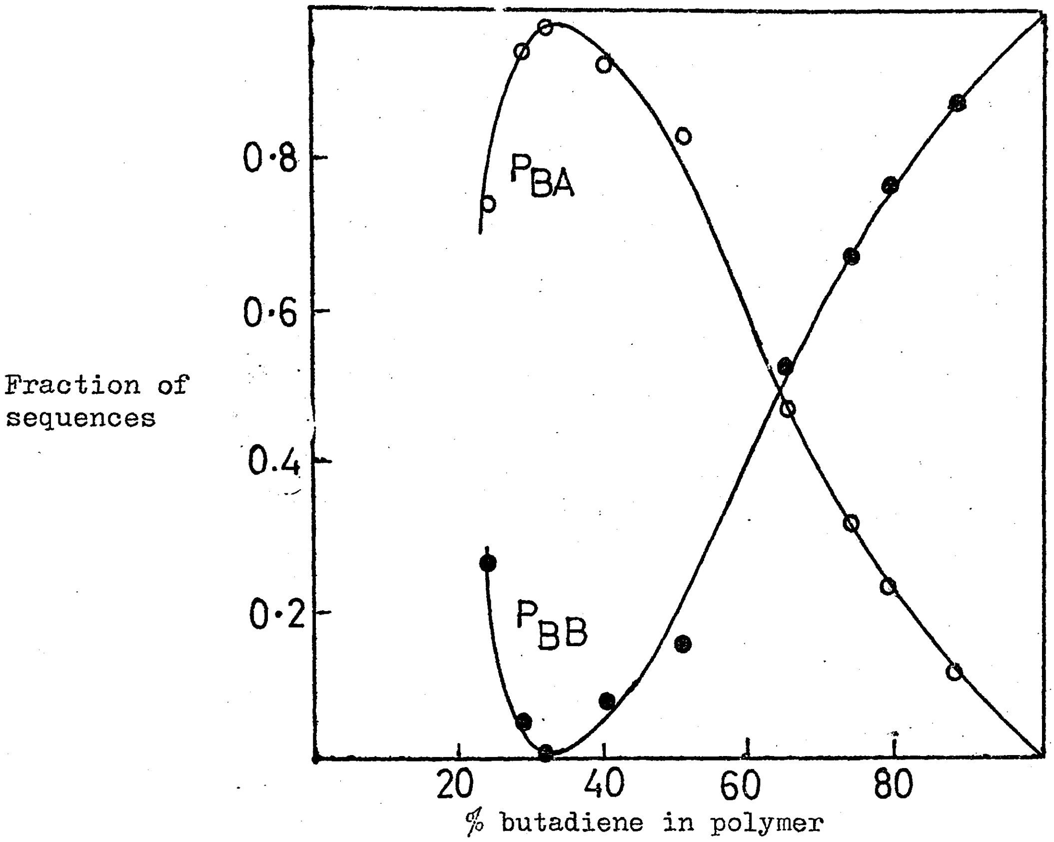


Figure 14. Fractions of BA units present (O) and fractions of BB units present (●). See text.

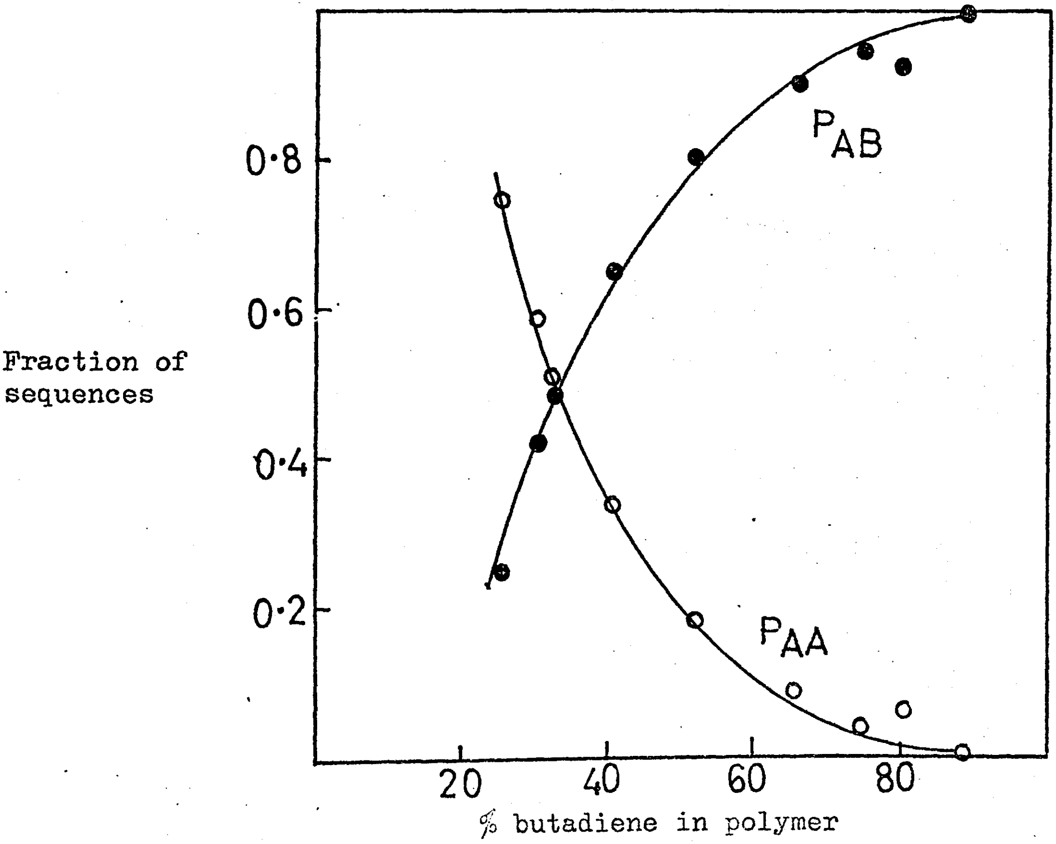


Figure15. Fractions of AA (O) and AB (●) units present. See text.

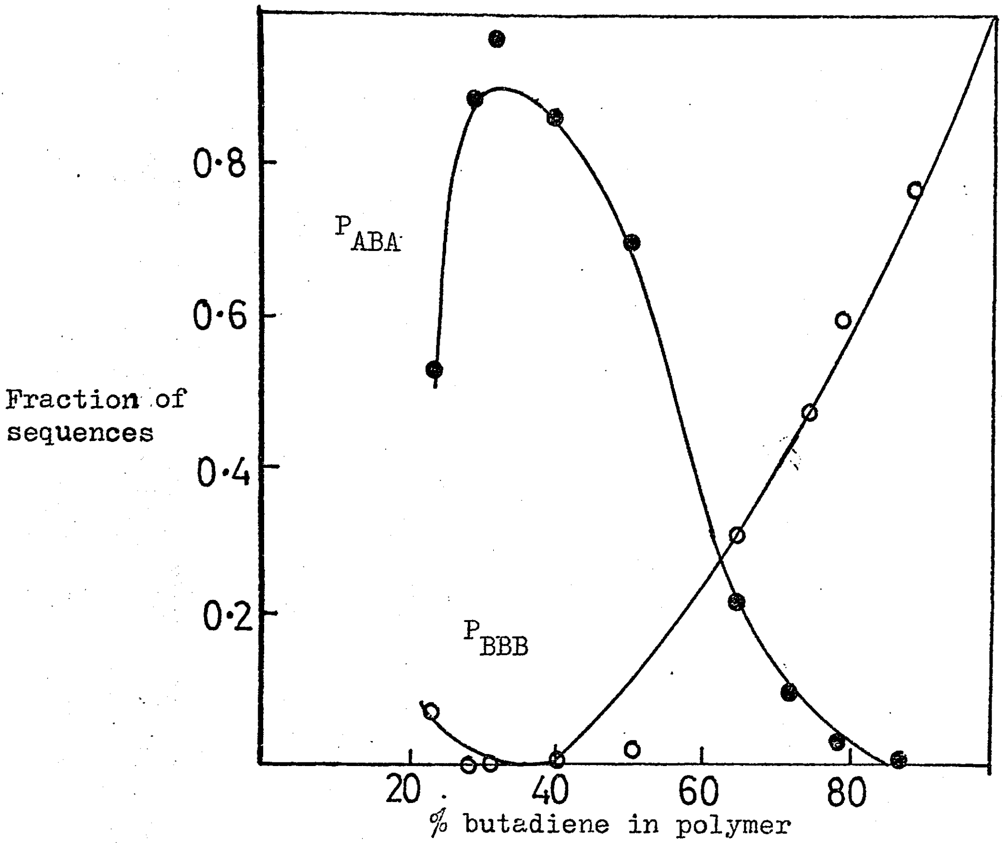


Figure 16. Fractions of ABA (O) and BBB(●) units present. See text.

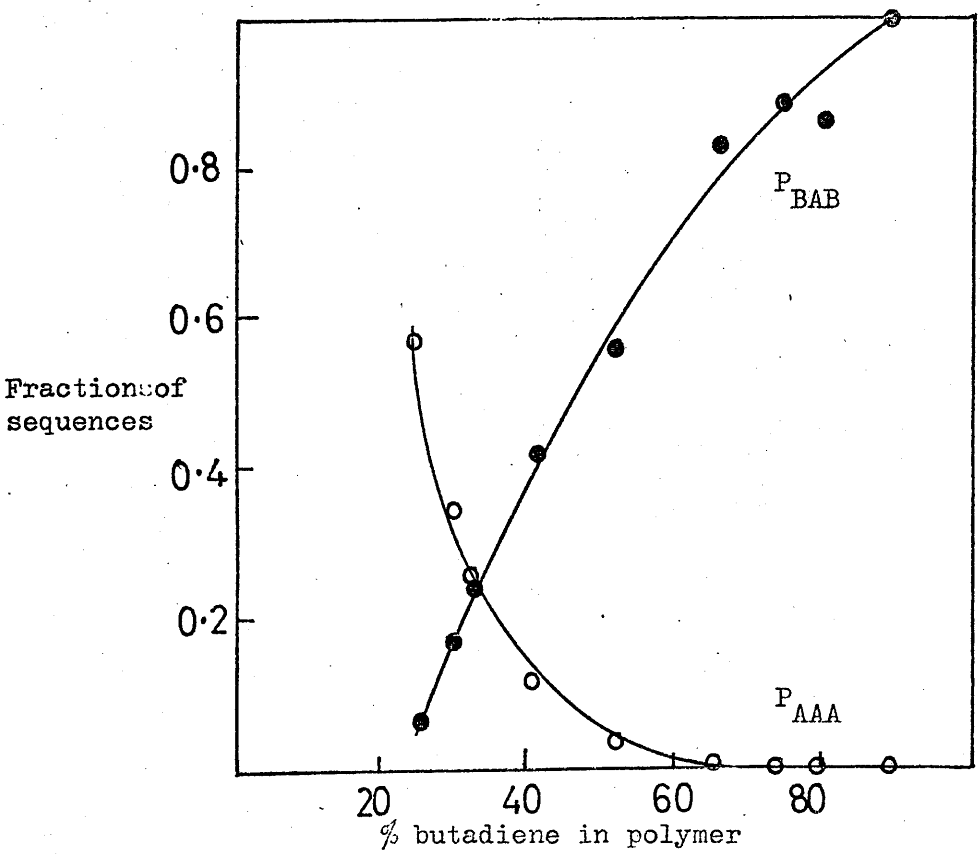


Figure 17. Fractions of AAA (O) and BAB (●) units present. See text.

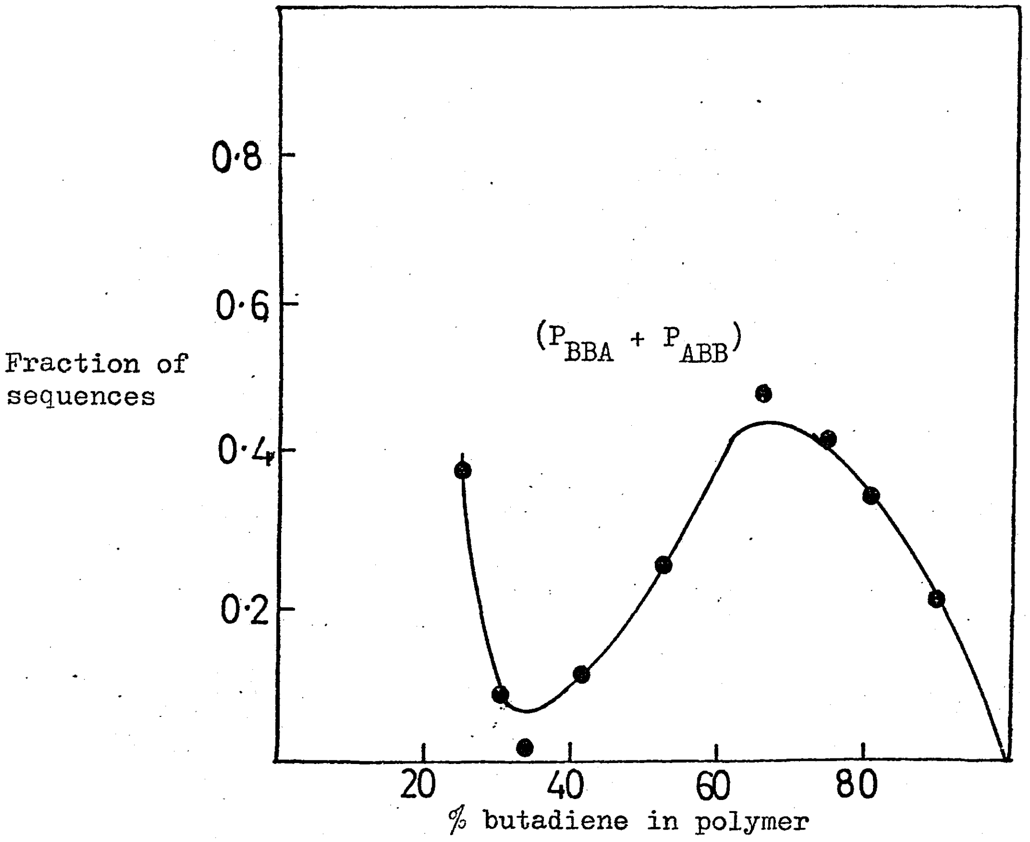


Figure 18. Fraction of BBA plus ABB units present. See text.

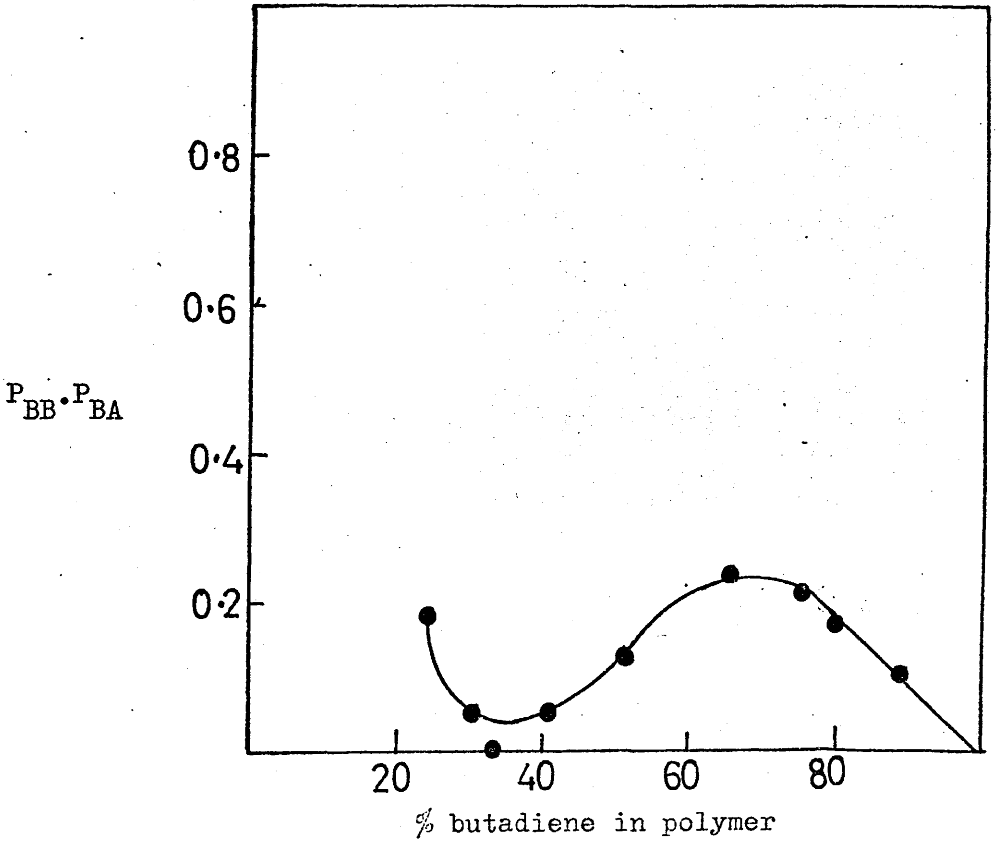


Figure 19. Variation in $P_{BB}.P_{BA}$ with butadiene content.

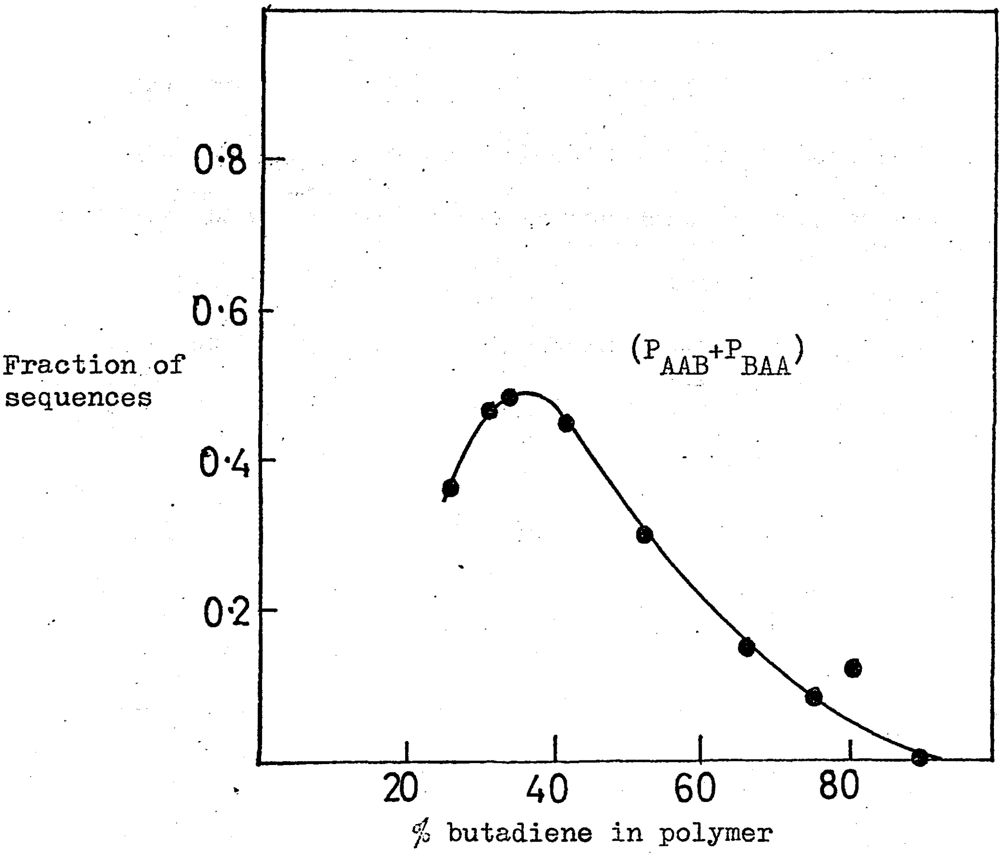


Figure 20. Fraction of AAB plus BAA units present. See text.

the terms that constitute $(P_{BBA} + P_{ABB})$. Thus,

$$(P_{BBA} + P_{ABB})$$

$$= (P_{BB} \cdot P_{BA} + P_{AB} \cdot P_{BB}) ,$$

Now a plot of $P_{BB} \cdot P_{BA}$ is shown in figure 19. This is in itself seen to oscillate by virtue of the trends in the components P_{BB} and P_{BA}, hence the variations in the plot of $(P_{BBA} + P_{ABB})$. A similar treatment can be applied to $(P_{AAB} + P_{BAA})$ (figure 20).

It is clear that this kind of sequence distribution data might be extremely valuable when taken in conjunction with experimental data on the production of degradation products, especially when the mechanisms operating are believed to involve pairs or triads of monomer units, as in cyclisation reactions.

3.3 Polymer Microstructure

Butadiene units may become incorporated in homopolymer or copolymer in three configurations, viz., trans 1-4, cis 1-4, and 1-2 (vinyl), as illustrated in figure 21. The relative concentrations of these three structures in a given polymer are dependent upon the experimental conditions and type of polymerisation catalyst used, and will have a profound effect on the physical and chemical properties of the polymer. Knowledge of the polymer microstructure is therefore desirable before embarking on a programme of research relating to butadiene containing polymers.

In this work the techniques of IR and NMR have been used to provide the necessary data.

Infra-Red Microstructure Analysis

Figure 22 shows the infra-red spectra of polybutadiene and of a copolymer containing 89% butadiene and 11% acrylonitrile. Table 9

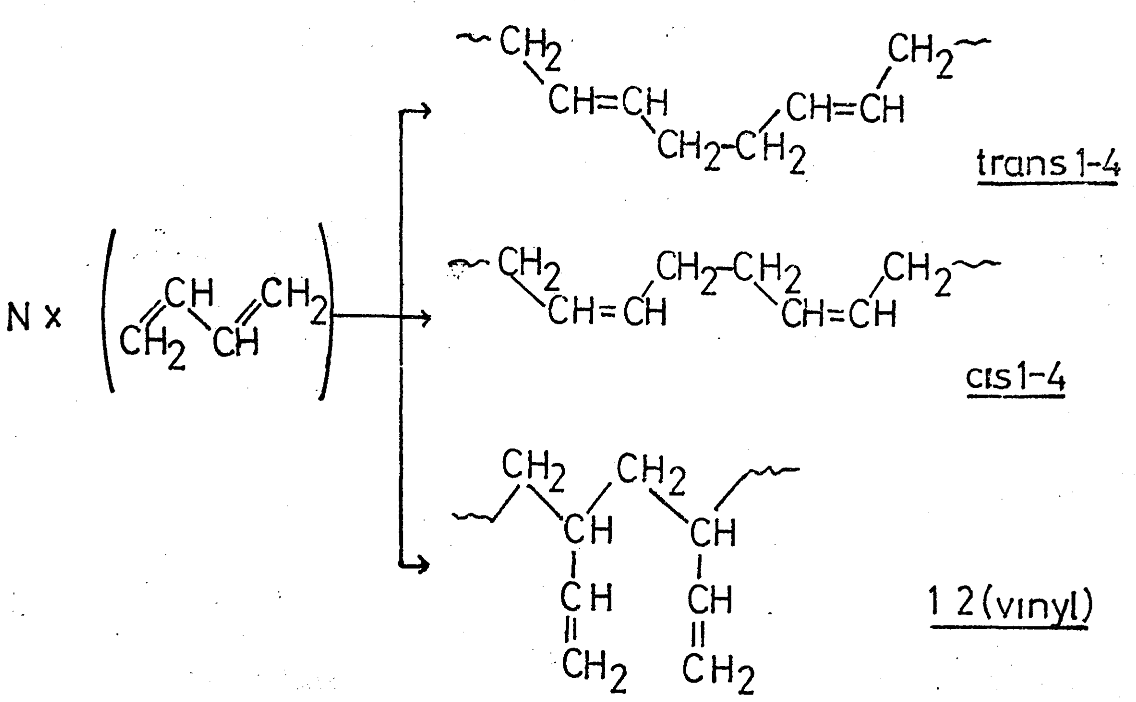


Figure 21. The three possible double bond structures in polybutadiene.

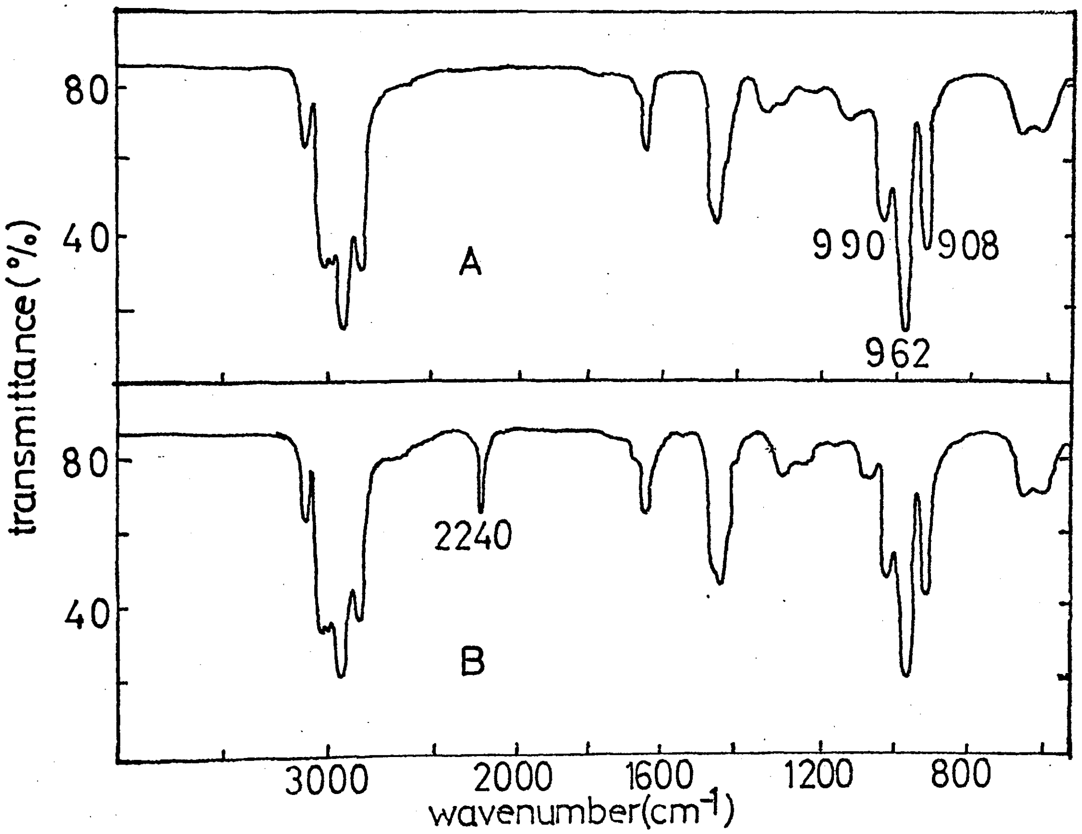


Figure 22. I.R. spectra of polybutadiene (A) and an 89% butadiene copolymer(B).

gives a full peak assignment assembled with reference to published data[68-76].

Several methods for determining unsaturation distribution in polybutadienes have been published. Hampton[68] determined trans 1-4 , 1-2 (vinyl) and cis 1-4 at 962, 908, and700 cm^{-1} respectively. Binder[72] determined trans 1-4 and 1-2 (vinyl) addition at the same frequencies, but cis 1-4 at 680 cm^{-1}. Richardson[77] determined trans 1-4 and 1-2 (vinyl) addition, calculating the cis 1-4 content by difference.

The development of Ziegler-Natta type catalyst systems in recent years has made available polybutadienes with almost any unsaturation distribution required. Making use of such polymers, Silas and his co-workers[71] have studied the absorption of cis 1-4 addition in the 800 - 625 cm^{-1} region and have developed a method for determining unsaturation distribution using high cis 1-4, trans 1-4, and 1-2 vinyl polymers as the only calibration standards. The method however, is a complex one, and in this work an approach has been devised which makes use of the molar absorptivities of the Silas calibration standards to find the 1-4 trans and 1-2(vinyl) contents, the 1-4 cis contents being determined by difference.

The bands at 962 and 908 cm^{-1} used in the methods cited above for measuring trans 1-4 and 1-2(vinyl) addition respectively, were also used in this investigation. These bands, which have been assigned to out-of-plane hydrogen deformations are strong and relatively free from interference making them suitable as analytical bands. Absorbance at the band maximum was calculated directly from the transmittance indicated on the spectrum, using the base-line shown in figure 23.

Table 10 shows the molar absorptivities determined by Silas/

Absorption band (cm^{-1})	Assignment	Remarks
3068	$RCH{=}CH_2$	C-H stretch in vinyl groups.
3000	$RCH{=}CH_2$	" "
2980	"	" "
2912	$\rangle CH_2, \rangle CH_3$	C-H stretching.
2839	"	"
2240	$-C{\equiv}N$	nitrile stretching.
1640	$R_1CH{=}CHR_2$	cis and trans stretch.
1439	$\rangle CH_2$, $RCH{=}CH_2$	C-H in plane deformations.
1350	———	———
1305	———	———
990	$RCH{=}CH_2$	C-H out of plane deformation.
962	$R_1CH{=}CH_2$ trans.	" "
908	$RCH{=}CH_2$	" "
755	$R_1CH{=}CHR_2$ cis.	" "
720	"	" "
680	"	" "

Table 9. Infra-red peak assignments.

	Molar absorptivity (litres $moles^{-1}$ cm^{-1})		
Component	962 cm^{-1}	908 cm^{-1}	800 - 625 cm^{-1}
Trans 1-4	133	2.4	0.86
1-2 (vinyl)	6.7	184	4.7
Cis 1-4	4.4	1.9	10.1

Table 10. Molar absorptivities in calibration polybutadienes as used by Silas.

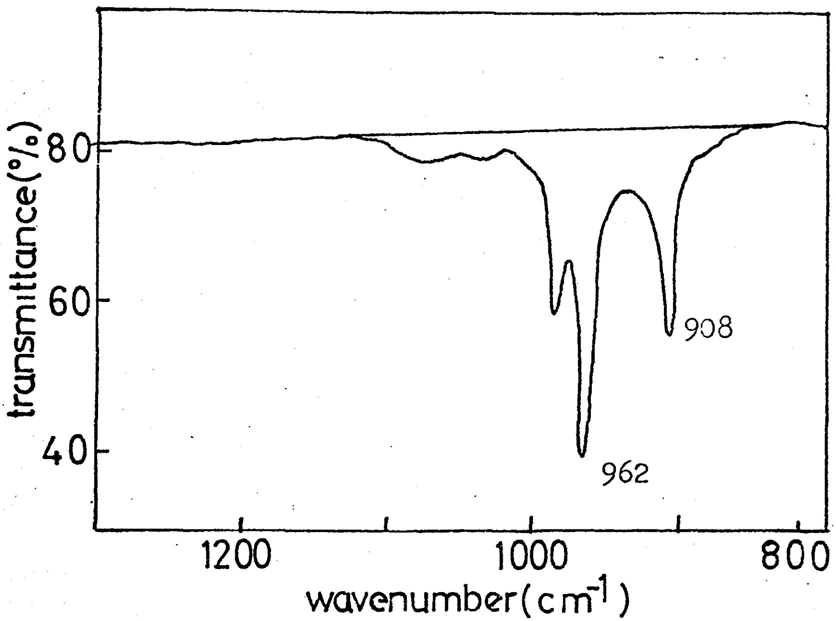


Figure 23. Analytical bands and base-line used in microstructure analysis.

Silas for the calibration polymers of high trans content, high vinyl content and high cis content respectively. Comparison of the data of table 10 with those of Hamilton [68], Binder[71], and Richardson[77] shows fairly good agreement, and it is on this basis that the data of Silas ARE used in this work. Consideration of this data reveals that the contribution of cis structures in the 962 and 908 cm^{-1} regions is small and thus the analysis of 1-4 trans and 1-2 (vinyl) composition may be carried out more easily by neglecting the contribution of cis structures in the region of the spectrum assigned to trans and vinyl structures.

The analysis then involves solving two simultaneous equations of the form;

$$a^{i} = c_1 a_1^{i} + c_2 a_2^{i}$$

which expresses the absorptivity at each analytical wavelength in terms of the fractional concentration and absorptivity of each component. Absorptivity is defined as A/bc where A is absorbance, b is path length and c is concentration. This procedure has been applied to polybutadiene and to copolymers containing 89%, 80%, 75% and 66% butadiene. The results are shown in tables 11 - 13. From these results there appears to be no pattern to the distribution of unsaturation in the polymers. It is noted however, that the concentration of butadiene entering as 1-2 (vinyl) groups remains relatively low throughout the range, and as can be seen from table 13 may in fact be decreasing with increasing acrylonitrile concentration. The 89% butadiene copolymer appears to deviate greatly from the other polymers in terms of unsaturation distribution having a substantially greater proportion of trans structures than the other polymers.

% butadiene in polymer	Molar absortivity (litres moles^{-1} cm^{-1})		c_1	c_2
	962 cm^{-1}	908 cm^{-1}		
100	66.8	27.0	0.425	0.140
89	92.1	27.9	0.685	0.143
80	56.6	13.7	0.422	0.069
75	78.5	17.4	0.586	0.087
66	84.0	17.8	0.627	0.089

c_1,c_2, are concentration coefficients.

<u>Table 11</u>. Data for infra-red microstructure analysis.

% butadiene in polymer	% trans 1-4	% 1-2(vinyl)	% cis 1-4
100	43	14	43
89	69	14	17
80	42	7	51
75	59	9	32
66	63	9	28

<u>Table 12</u>. Unsaturation distribution as % of butadiene content.

% butadiene in polymer	% trans 1-4	% 1-2(vinyl)	% cis 1-4
100	43	14	43
89	61	13	15
80	34	6	41
75	44	7	24
66	41	6	19

<u>Table 13</u>. Unsaturation distribution as % of total polymer.

Nuclear Magnetic Resonance and Microstructure

Nuclear Magnetic Resonance (NMR) is of considerable interest and importance for the study of low molecular weight organic compounds$^{78-7}$ However during the past 15 years, investigations of a variety of polymer systems have been published. These studies have dealt with solid polymers, and the spectra obtained have been of the Broad-Line type. When dissolved in suitable solvents, however, polymers give high resolution spectra in which the resonance lines are only a fraction of the width of those in the solid state $(10^{-3} - 10^{-4})^{80-86}$.

Recently much NMR work has been carried out on polymers containing butadiene, in relation to the microstructure of the polymers$^{87-94}$. It is evident that valuable information can be obtained from NMR studies of polymers, and in this work the technique is used to yield some useful distribution data.

NMR spectra from polybutadiene and a series of copolymers are shown in figures 24 - 28. Consideration of the references quoted above has permitted the peak assignments given in table 14.

In an alternating 1:1 copolymer^{92} the olefinic protons appear at 4.42 τ, the methine proton of the acrylonitrile unit (A) around 7.4 τ with the methylene protons of the butadiene unit (B) at 7.71 τ. The methylene protons of the A unit appear at 8.3 τ.

In polybutadiene (figure 24) the only system present is the BBB sequence, thus the peak at 4.59 τ is due to the presence of butadiene blocks. In the 89% copolymer the main peak is at 4.61 τ, but a shoulder appears at 4.55 τ which is possibly due to BBA sequences. The 80% copolymer has the main peak at 4.59 τ with the shoulder at 4.54 τ, while the 75% copolymer has its main peak at 4.60 τ, the shoulder at 4.55 τ, and an additional shoulder at 4.40 τ which is

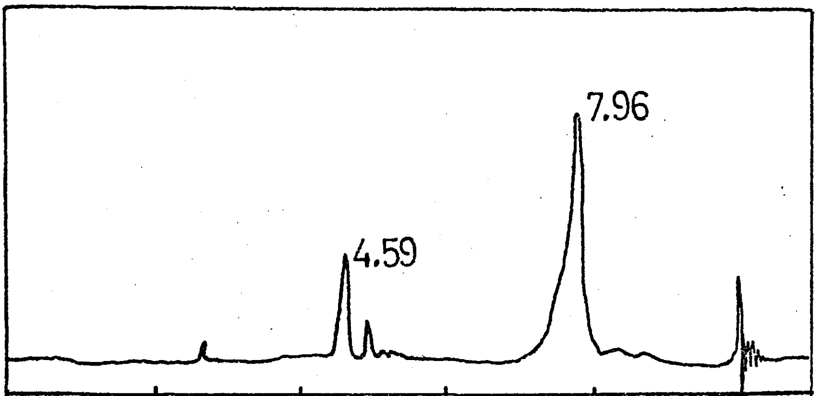


Figure 24.

polybutadiene

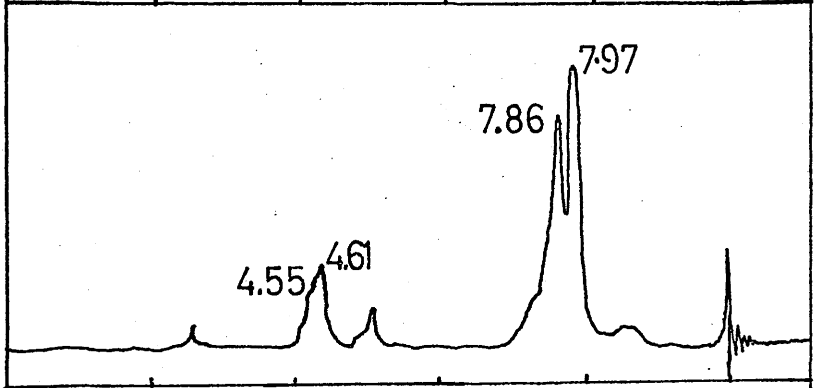


Figure 25.

89% butadiene copolymer

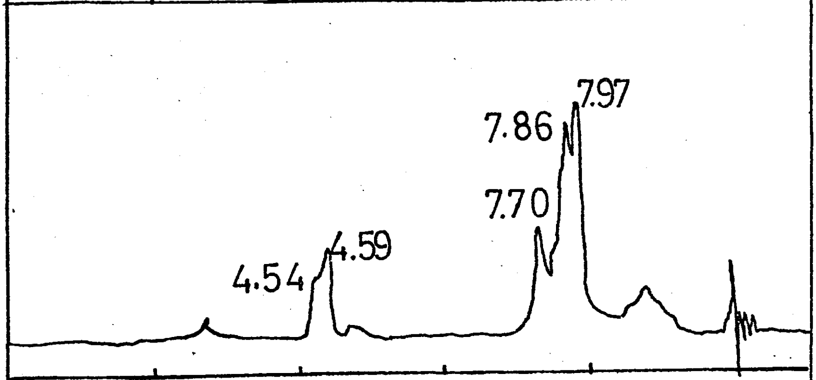


Figure 26.

80% butadiene copolymer

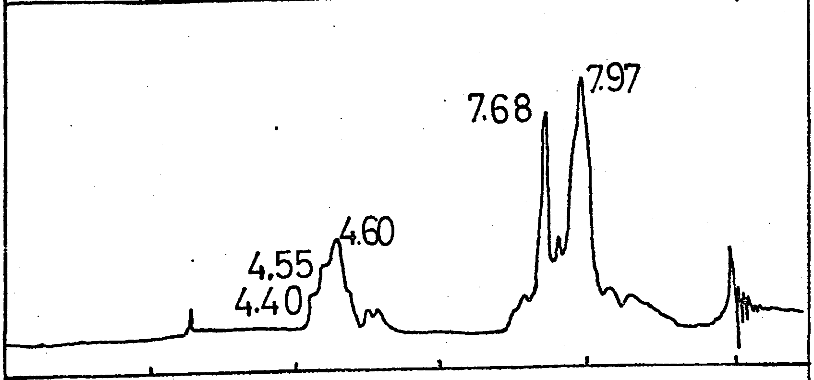


Figure 27.

75% butadiene copolymer

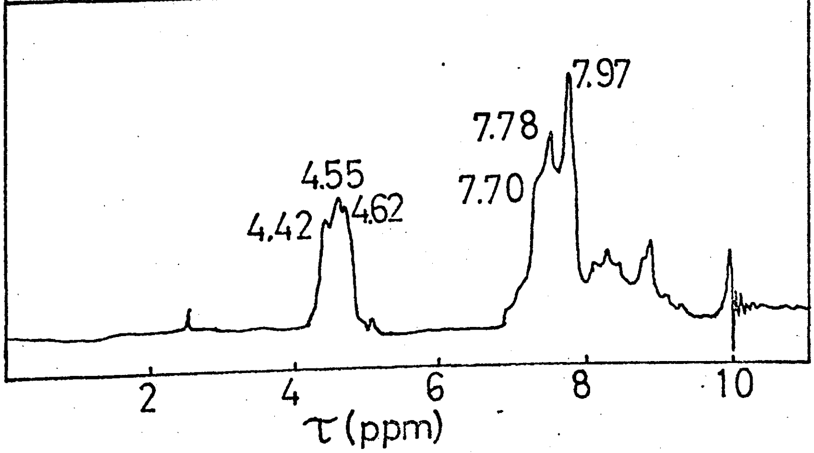


Figure 28.

66% butadiene copolymer

due to ABA sequences. In the 66% copolymer there are three close peaks at 4.42, 4.55 and 4.62 τ of approximately the same height. These are due to the sequences ABA, BBA, and BBB respectively, complemented by the possible cotactic configurations contributed by the alternating sequences.

The methine proton of A appears at 7.50 τ in polyacrylonitrile^{92}, therefore it is probable that the weak peaks around 7.5 τ in the 66% and 75% copolymers are due to BAB sequences.

The methylene protons of B units, in the homopolymer (figure 24) appear at 7.96 τ due to BBB sequences, but in the 89% copolymer this peak appears at 7.97 τ with a smaller peak at 7.86 τ due to other sequences, probably of the BBA type. The 80% copolymer has the major peak again at 7.97 τ with the BBA peak at 7.86 τ. There is a small peak at 7.70 τ with the possible emergence of a peak at 7.78 τ, all due to the other possible sequences and contributions.

In the 75% copolymer the peak at 7.68 τ has increased in intensity together with the peak at 7.77 τ. The peak at 7.86 τ can be distinguished by a shoulder. This to be expected, since as the number of the other sequences increases the peak due to BBA sequences should loose intensity.

The main peak is at 7.97 τ in the 66% copolymer and the 7.78 τ peak has increased in intensity. Although the 7.70 τ peak has also increased in intensity, it appears as a shoulder. Similarly the 7.86 τ peak can be distinguished as a shoulder.

The methylene protons of acrylonitrile units appear at 8.2 - 8.5 τ^{92}. In the 80% copolymer this peak is at 8.45 τ. As the acrylonitrile content increases the peak height increases and shifts to lower field. In the 75 and 66% copolymers the methylene proton appears as several peaks probably due to the presence of different types of sequences.

From the above considerations assignments have been collected together in table 15.

The peaks in the 5 - 5.3 τ region of the spectrum may be assigned to the olefinic protons of the 1-2 vinyl configurations of butadiene units[93], however insufficient data is available for a detailed analysis of these peaks.

Chemical shift	Assignment
4.4 - 4.6	$-C\underline{H}=C\underline{H}-$ (1-4 olefinic protons)
5.0 - 5.3	$=C\underline{H}_2$ (1-2 " ")
7.2 - 7.5	$-\underset{CN}{\underset{\vert}{C\underline{H}}}-$ (acrylonitrile methine proton)
7.7 - 8.0	$-C\underline{H}_2-$; $-\overset{\vert}{C}H-$ (present in 1-2 configuration)
8.0 - 8.5	$-C\underline{H}_2-$ (acrylonitrile methine protons)
8.5 upwards	$C\underline{H}_3-C$; $C\underline{H}_3-C-C=C$; $C\underline{H}_3-C=C$; etc.
2.75	$C\underline{H}Cl_3$ (trace in $CDCl_3$)

Table 14. NMR assignments to functional groups.

% butadiene in polymer	Sequence	Chemical shifts	
100	BBB	4.59	7.96
89	BBB	4.61	7.97
	BBA	4.55	7.86
80	BBB	4.59	7.97
	BBA	4.54	7.86
	ABA	——	7.70
75	BBB	4.60	7.97
	BBA	4.55	7.97
	ABA	4.40	7.68
	BAB	——	7.50
66	BBB	4.62	7.97
	BBA	4.55	7.78
	ABA	4.42	7.70
	BAB	——	7.50

Table 15. NMR assignments to sequences present.

CHAPTER FOUR

THERMAL ANALYSIS METHODS

Several thermal analysis techniques have been used in a preliminary investigation of the thermal breakdown patterns of the series of butadiene - acrylonitrile copolymers. The results of this study have yielded an overall view of the degradation of the system under conditions of programmed temperature increase, and from this, a temperature range was selected for a detailed examination under isothermal conditions.

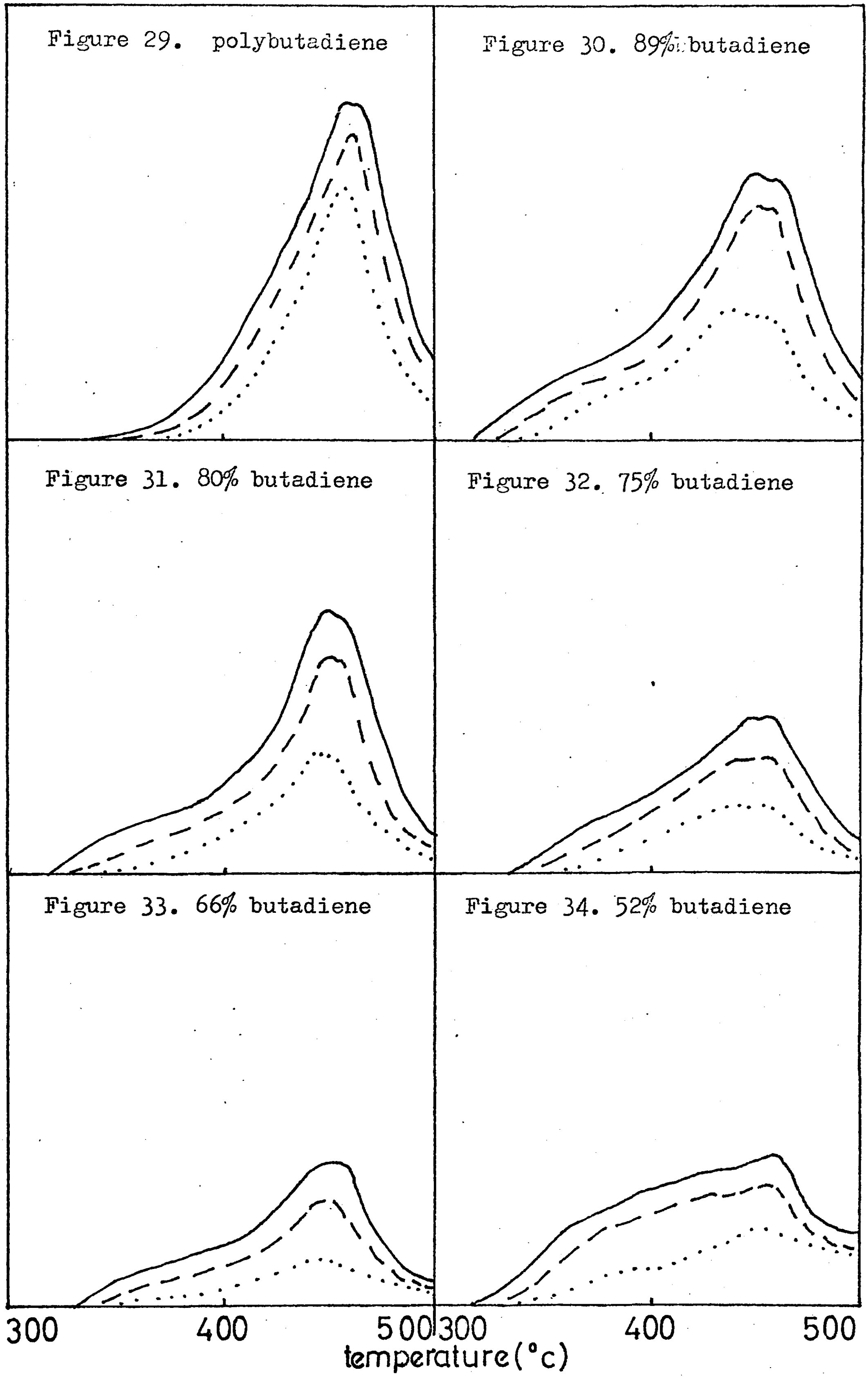
4.1 Thermal Volatilisation Analysis. (TVA).

This technique continuously measures the rate of evolution of volatile material during controlled temperature increase of the sample. Explanation of the experimental method is given in Chapter 2. The traces obtained are shown in Figures 29 - 38, and the temperatures at which rate maxima occur are listed in Table 16. The traces due to products non-condensible at -45 °C and -100 °C have been omitted for clarity, since there are no unexpected deviations of these traces in comparison with those at other temperatures.

Figure 29 shows the thermogram obtained from a sample of polybutadiene. During degradation, polybutadiene undergoes extensive intermolecular transfer reactions resulting in short chain fragments which condense on the cooled upper part of the TVA degradation tube, as the "cold-ring" fraction, and the fraction of volatile material obtained is small. The lack of coincidence in the TVA traces indicates a mixture of products with a range of volatilities. Concurrent production of all the products is indicated by the fact that the rate maximum on each trace occurs at the same temperature. This breakdown pattern is very close to that found for polyethylene and similar polymers.[9 The -196°C trace indicates that the amount of permanent gases such as hydrogen or methane produced during degradation is significant.

Figure 30 shows the thermogram of an 89% butadiene 11% acrylonitrile copolymer, from which it may be seen that the rate of production of volatiles has fallen somewhat in relation to the butadiene polymer, and a broad shoulder has appeared to the low temperature side of the main peak. Reference to figure 38 which is the thermogram of polyacrylonitrile, shows that this shoulder may be due to products formed as a result of the presence of acrylonitrile in the polymer. The rate of production of permanent gases (-196°C trace) remains significantly high, but has decreased in relation to the 0°C trace.

With decreasing butadiene content the observed trend continues (figures 30 - 33), with the main butadiene peak decreasing in significance and the acrylonitrile shoulder increasing accordingly, until with 52% butadiene (figure 34) the trace is broad with no well defined maximum. Figure 35 is that of a 41% butadiene copolymer, showing that products due to the presence of acrylonitrile are becoming much more prominent with the butadiene peak almost at a minimum. Note also that a new peak is appearing to the high temperature



<u>Figures 29 - 34</u>. TVA traces for the polymers.
—— 0°C; ----- -75°C; ······· -196°C.

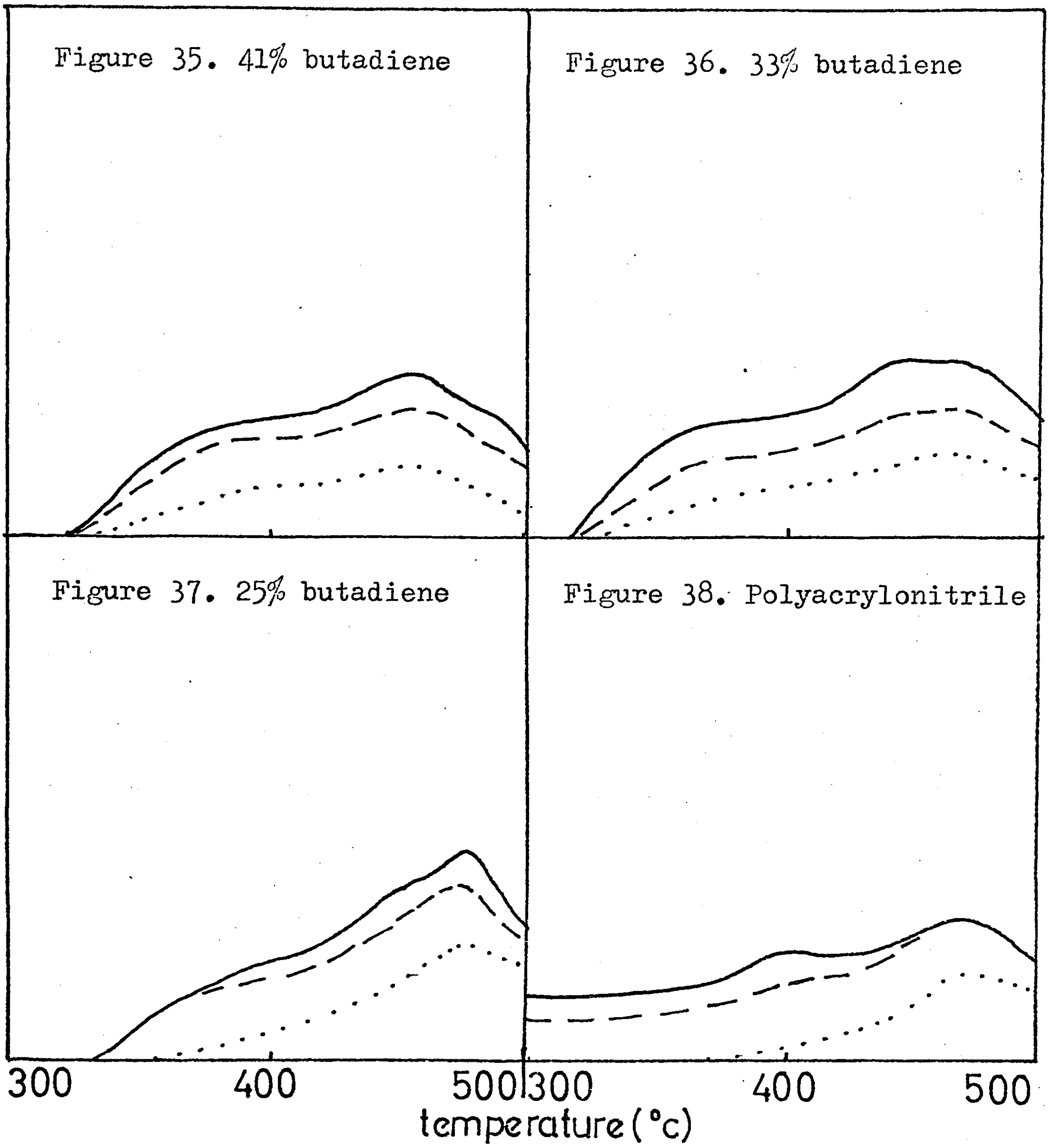


Figure 35. 41% butadiene

Figure 36. 33% butadiene

Figure 37. 25% butadiene

Figure 38. Polyacrylonitrile

Figures 35 -38. TVA traces for the polymers.

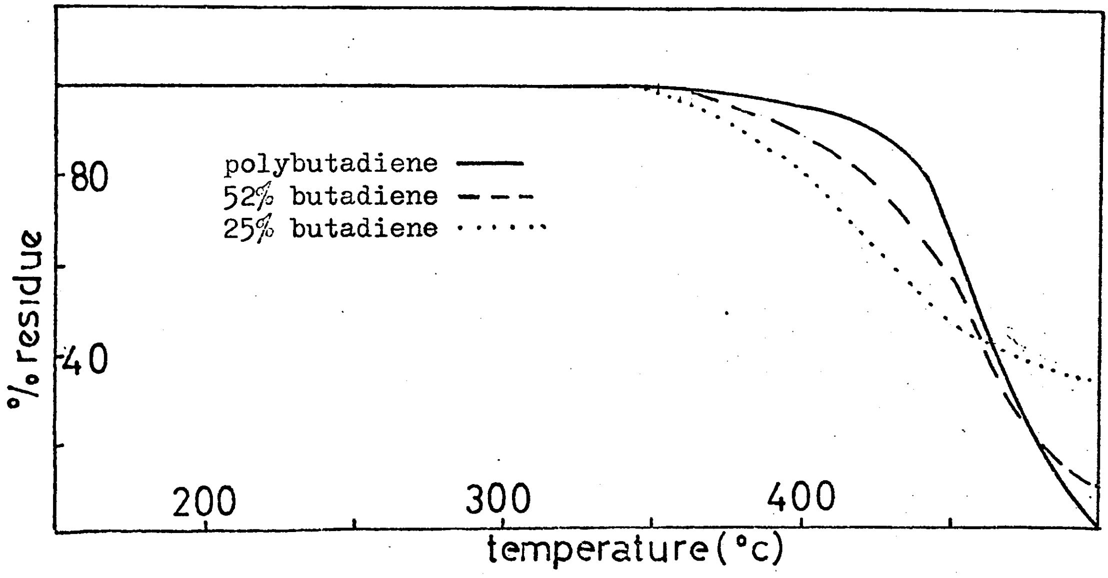


Figure 39. TGA traces for the polymers.

side of the main peak. This new peak continues to increase with increasing acrylonitrile content (figure 36) until as seen in figure 37 for a 25% butadiene - 75% acrylonitrile copolymer, the polyacrylonitrile pattern is predominating. The reason why the TVA trace for polyacrylonitrile is already off the base-line at 300°C is that the nitrile polymerisation reaction for polyacrylonitrile described in Chapter 1 occurs at about 250°C yielding a very sharp response in the TVA. Since this reaction is eliminated by the incorporation of only a few percent comonomer, the sharp response would not be expected for the copolymers in the composition range being considered in this work.

From the series of thermograms it can also be seen that as the amount of butadiene in the polymer decreases the production of permanent gases is delayed in relation to that of other volatile products. This indicates that non-condensibles produced during the early stages of degradation of the copolymers are due to butadiene sections of the chain, since in polyacrylonitrile significant amounts of non-condensibles are produced only at temperatures in excess of about 380°C.

Table 16 demonstrates that there is a lowering of almost 30°C in the temperature at which the production of volatiles begins on going from 100% to 25% butadiene, thus the acrylonitrile units appear to be having a destabilising effect.

The main peak in the polybutadiene trace is in fact a double one, with the first peak(B_1) appearing at 461°C and the second peak(B_2) at 479°C. This peak ceases to be seen as a doublet when the butadiene content drops below 52%. From table 16, the temperatures at which B_1 and B_2 appear seem to be variable, and independent of copolymer composition. The peak at lower temperatures due to the

% butadiene in polymer	start of degradation(°C)	Peak maxima (°C)			
		A	B_1	B_2	C
100	329	—	461	479	—
89	325	414	467	479	—
80	325	402	455	473	—
75	325	396	455	467	—
66	316	396	455	473	—
52	316	396	444	461	—
41	310	390	455	455	520
33	313	396	473	473	520
25	301	396	461	461	520

Table 16. Data from TVA traces.

% butadiene in polymer	start of degradation(°C)	% residue		
		400°C	450°C	500°C
100	324	93	56	1
89	329	92	60	2
80	320	91	48	2
75	324	94	52	8
66	329	94	48	8
52	324	87	41	11
41	305	81	38	16
33	305	79	38	22
25	298	72	43	34

Table 17. Data from TGA traces.

presence of acrylonitrile(A) also appears to be independent of copolymer composition, except at the high butadiene end of the range where there may be a tendency for this peak to move to higher temperatures. Peak C, at higher temperatures, remains constant at 520°C and disappears when the butadiene content is increased above 41%. No quantitative data can be obtained about the relative amounts of volatiles, since Pirani response is not linear with pressure, and depends upon the substance giving rise to that response.

After the TVA runs were complete, polybutadiene and the 89% copolymer left no residue. However the remaining polymers left increasing amounts of residue which changed from dark brown solids for the 80% and 75% butadiene copolymers, to black chars for the polymers with butadiene contents less than 66%. The chain fragments which condensed on the cooler part of the TVA tube varied in colour from very pale yellow for polybutadiene through brown/red to dark red for the 25% butadiene polymer. The colour development is assigned to the formation of conjugated structures in the residue and chain fragments. This is discussed further in a later chapter.

The main conclusions from the TVA investigation may be summarised as follows.

1. Polybutadiene undergoes extensive intermolecular chain transfer, and the small amount of volatiles produced is a mixture of products typical of such a breakdown.
2. Incorporation of acrylonitrile lowers the temperature at which degradation starts, and reduces the amount of volatile material produced.
3. Permanent gases are produced from the start of degradation and, during the initial stages, are derived from the butadiene sections of the polymer.
4. Addition of acrylonitrile stabilizes the residue which develops colour.

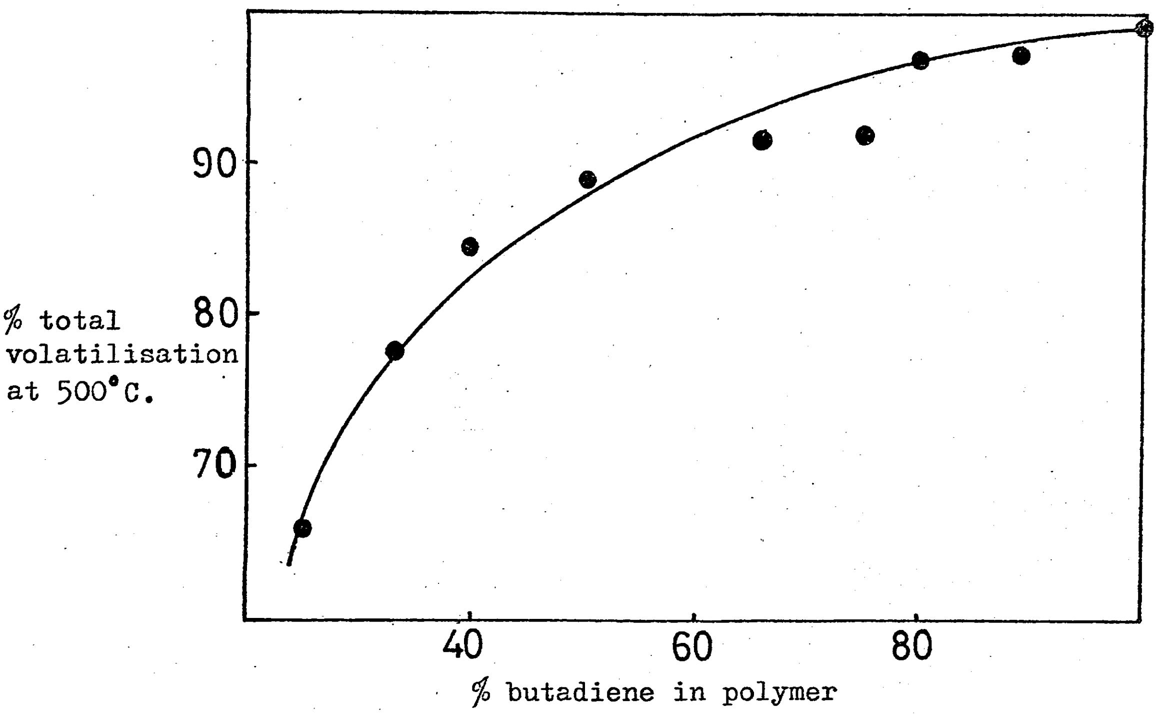


Figure 40. Volatilisation results from TGA.

5. Colour develops in the cold-ring fraction as acrylonitrile content increases.

4.2 Thermal Gravimetric Analysis (TGA).

The technique of Thermal Gravimetric Analysis (TGA), as described in chapter 2, was used to determine the general weight loss characteristics of the polymers during programmed temperature increase. The thermograms obtained from polybutadiene and two other copolymers are shown in figure 39, and table 17 lists the data from the whole range of copolymers studied.

Table 17 demonstrates that as butadiene content decreases there is a lowering of the temperature at which weight loss begins. This is consistent with the TVA analysis of these copolymers. However, although destabilisation occurs with respect to the onset of degradation, as butadiene content decreases, there is a concurrent stabilisation in the residues remaining at 500°C. Thus polybutadiene gives only 1% residue at 500°C whereas a 25% butadiene - 75% acrylonitrile copolymer leaves 34% residue. This is illustrated in figure 40.

An opposite trend exists with the residue at 400°C when a decrease in percentage residue with decreasing butadiene content is observed.

The percentage residue at 450°C, as indicated in table 17, is a combination of these two trends.

4.3 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry was used to investigate the heat changes occurring during degradation of the copolymers. The method is discussed in chapter 2, and the thermograms obtained from polybutadiene and from polymers containing 52% and 25% butadiene are shown in figure 41. Tabulated data from the complete series of thermograms is presented in table 18. The enthalpy values (ΔH) shown in this table were calculated from the equation:

$$\Delta H = \frac{E \cdot A \cdot \Delta T_s \cdot T_s}{M \cdot a}$$

where,

ΔH = enthalpy of reaction (mcal/mg)

E = Calibration Coefficient (mcal/°C-min) = 163 mcal/°C-min.

ΔT_s = Y axis sensitivity (°C/in) = 0.2°C/in.

T_s = X " " " = 50°C/in.

M = Sample mass (mg)

a = Heating rate (°C/min) = 10°C/min.

The calibration coefficient (E) for the instrument was determined by using pure samples of tin, lead and zinc whose heats of fusion are known, and which have melting transitions in the range 200 - 500°C. The procedure used may be found in the instruction manual supplied with the Du Pont DSC module. The calibration coefficient for the range within which the peak maxima occur was found to be 163 mcals/°C min.

The temperatures of start of degradation shown in table 18 were determined from the intersection of the extrapolated base-line and the side of the peak, as illustrated in figure 41 for polybutadiene. This method is fairly reliable for phase-change transitions of pure materials, but lacks reliability when the transition is of the degradation type. However this data does illustrate the destabilisation of the polymer with decreasing butadiene content, already noted from TVA and TGA.

% butadiene in polymer	Onset of degradation(°C)	Peak maximum (°C)	ΔH mcals/mg.
100	320	379	217
89	313	374	218
80	320	374	184
75	320	372	153
66	315	371	116
52	317	368	120
41	320	367	73
33	315	367	79
25	310	365	74

Table 18. Data from DSC traces.

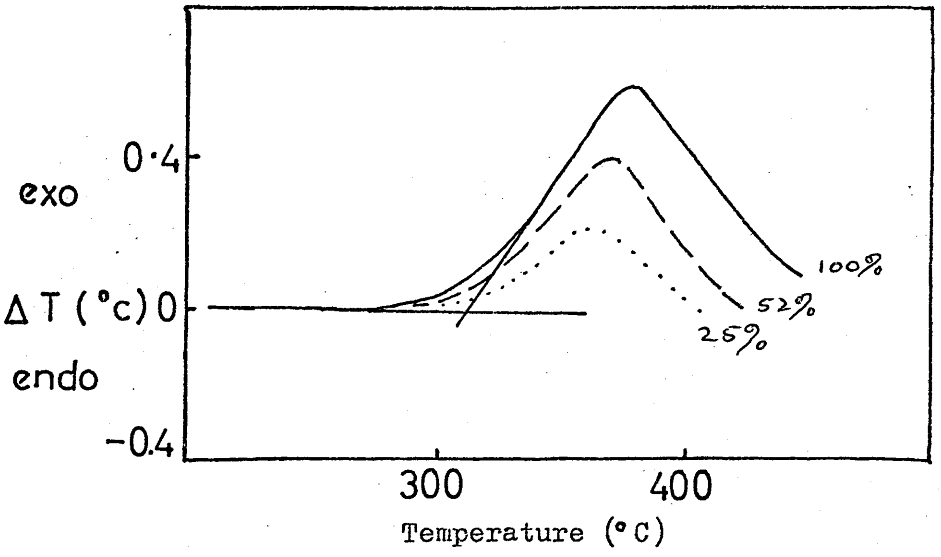


Figure 41. DSC thermograms of the polymers.

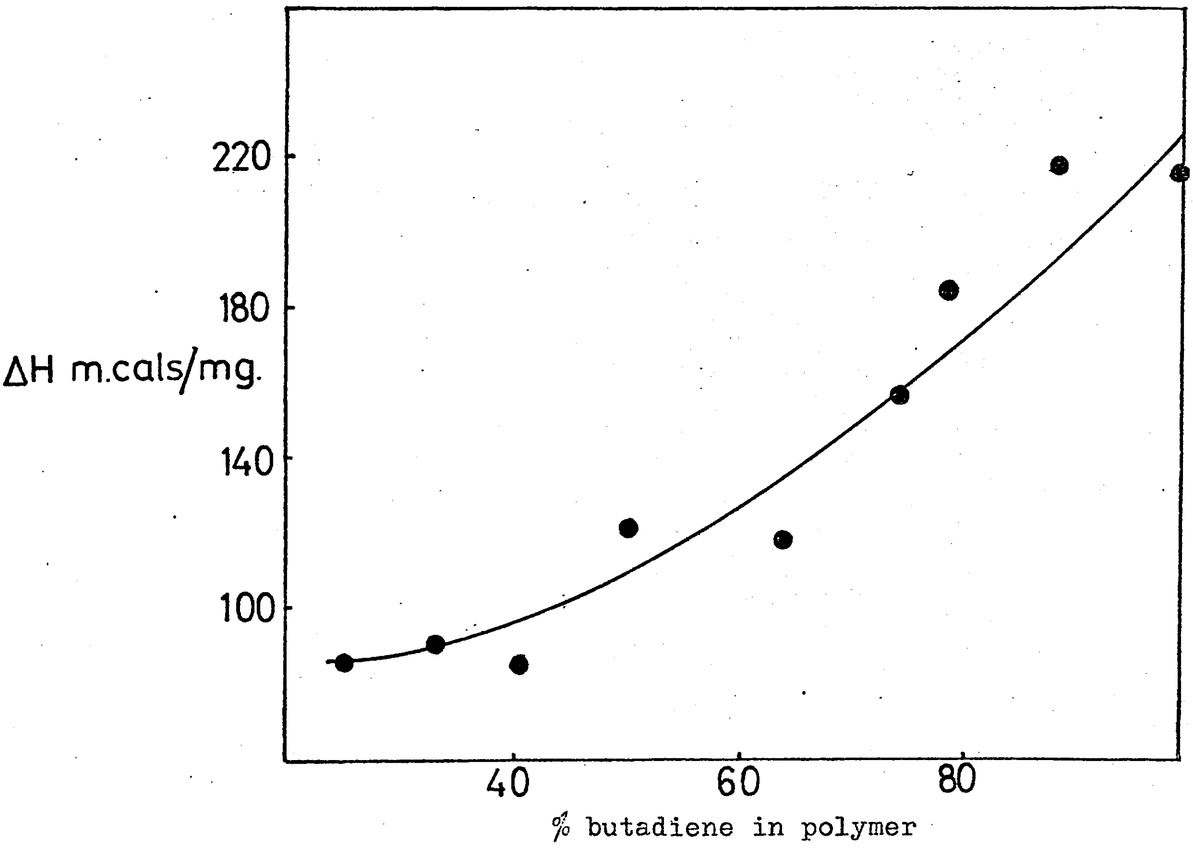


Figure 42. Enthalpy of degradation from DSC results.

Destabilisation is also seen in the temperature at which the peak maxima occur, ranging from 379°C for polybutadiene to 365°C for the polymer containing 25% butadiene. The ΔH values for the degradation are plotted against butadiene content in figure 42, and it can be see that there is a gradual decrease in the enthalpy of reaction as the butadiene content decreases. This result may be taken in conjunction with figure 40, indicating that as the amount of scission decreases and stabilisation occurs, then the ΔH of reaction decreases accordingly. The conclusion is that the scission reactions probably account for the greater part of the exothermicity.

From the application of thermal analysis methods to the copolymer system, it was decided that temperatures in the range 350 - 400°C would be suitable for initial isothermal investigations into the degradation reactions.

CHAPTER FIVE

Qualitative Analysis of the Thermal Degradation Products.

In order that methods may be devised to measure quantitatively those degradation products of interest, it is desirable that a qualitative knowledge of the products is acquired. In the present work a series of degradations were carried out for times up to twenty-four hours at temperatures in the range 350°C - 400°C using the sealed tube technique, samples of degradation products being obtained as described in chapter 2. The techniques and conditions used for the qualitative analysis are also described in chapter 2, and the results obtained are discussed here under the following headings.

1. Permanent gases.
2. Products volatile at 20°C.
3. Products liquid at 20°C.
4. Chain fragment material.
5. Polymer residues.

5.1 Permanent Gases.

The permanent gas fractions (volatile at -196°C) were analysed by infra-red spectroscopy and GLC as described in chapter 2. Figure 43 shows the infra-spectrum of the permanent gas fraction obtained from a 52% butadiene copolymer degraded for seven hours at 352°C. The only peaks are at 3018cm^{-1} and 1304cm^{-1}. These peaks, together with accompanying rotational bands, are characteristic of methane.

Figure 44 illustrates the GLC trace, obtained for these non-condensibles. The two components were identified as hydrogen and methane by comparison of the peak retention times with those of pure samples of hydrogen (7.6 minutes) and methane (11.3 minutes).

Hydrogen and methane were found to be the only components of the permanent gas fractions produced during the pyrolysis of the full range of copolymers for times between seven and twenty four hours, and at temperatures in the range 350 - 400°C.

5.2 Products Volatile at 20°C.

The fractions of degradation products volatile at 20°C were collected as described in chapter 2, and the techniques of GLC, IR and mass spectrometry were used in their analysis.

The gases produced during pyrolysis of a 52% butadiene copolymer at 352°C for periods of 8, 18, and 24 hours, were investigated and figures 45 and 46 show a representation of the infra-red spectrum of the gases obtained from the 24 hour run. The spectrum is seen to be chiefly composed of complex rotational bands, found to be due to hydrogen cyanide and ammonia by comparison with the spectra of pure samples of these materials. Ammonia is responsible for the major

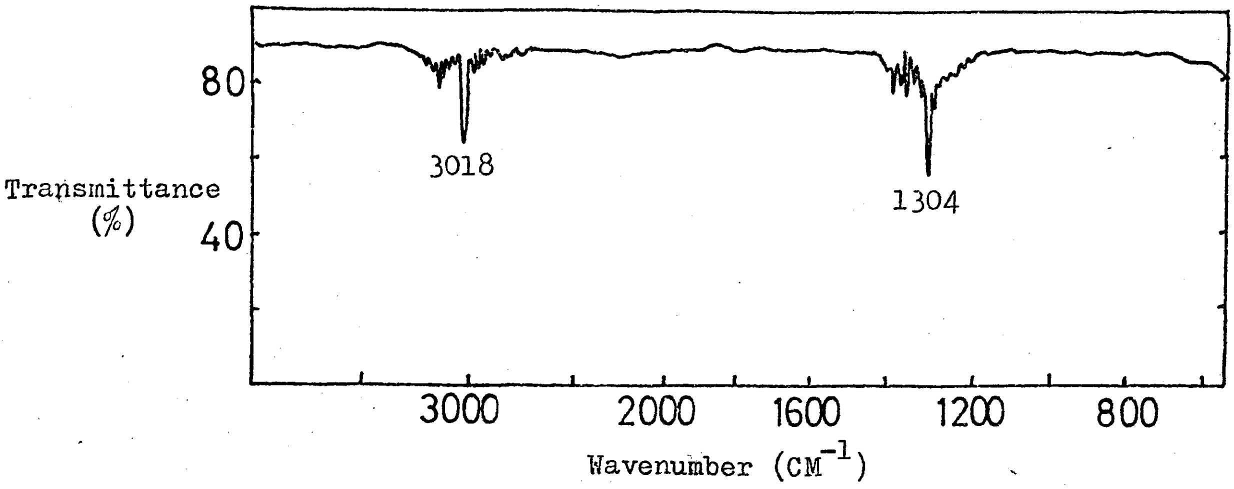


Figure 43. I.R. spectrum of permanent gas fraction from a 52% butadiene copolymer degraded for seven hours at 352°C.

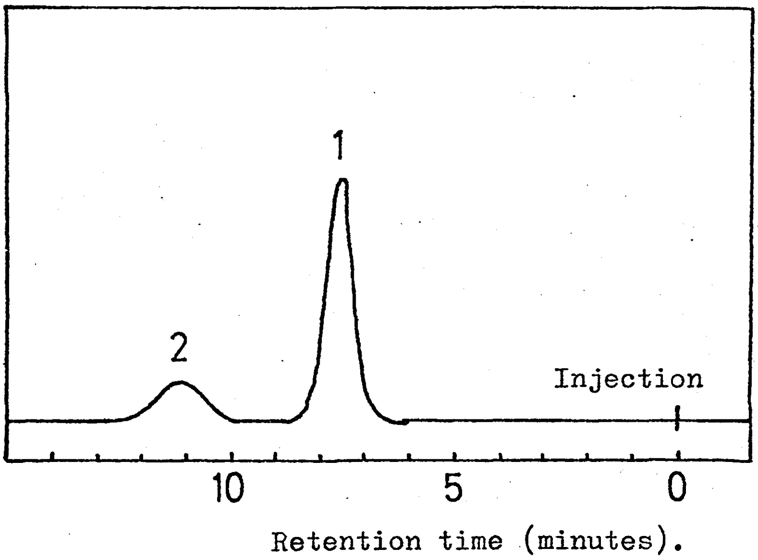


Figure 44. GLC of permanent gas fraction from a 52% butadiene copolymer at 352°C for seven hours.

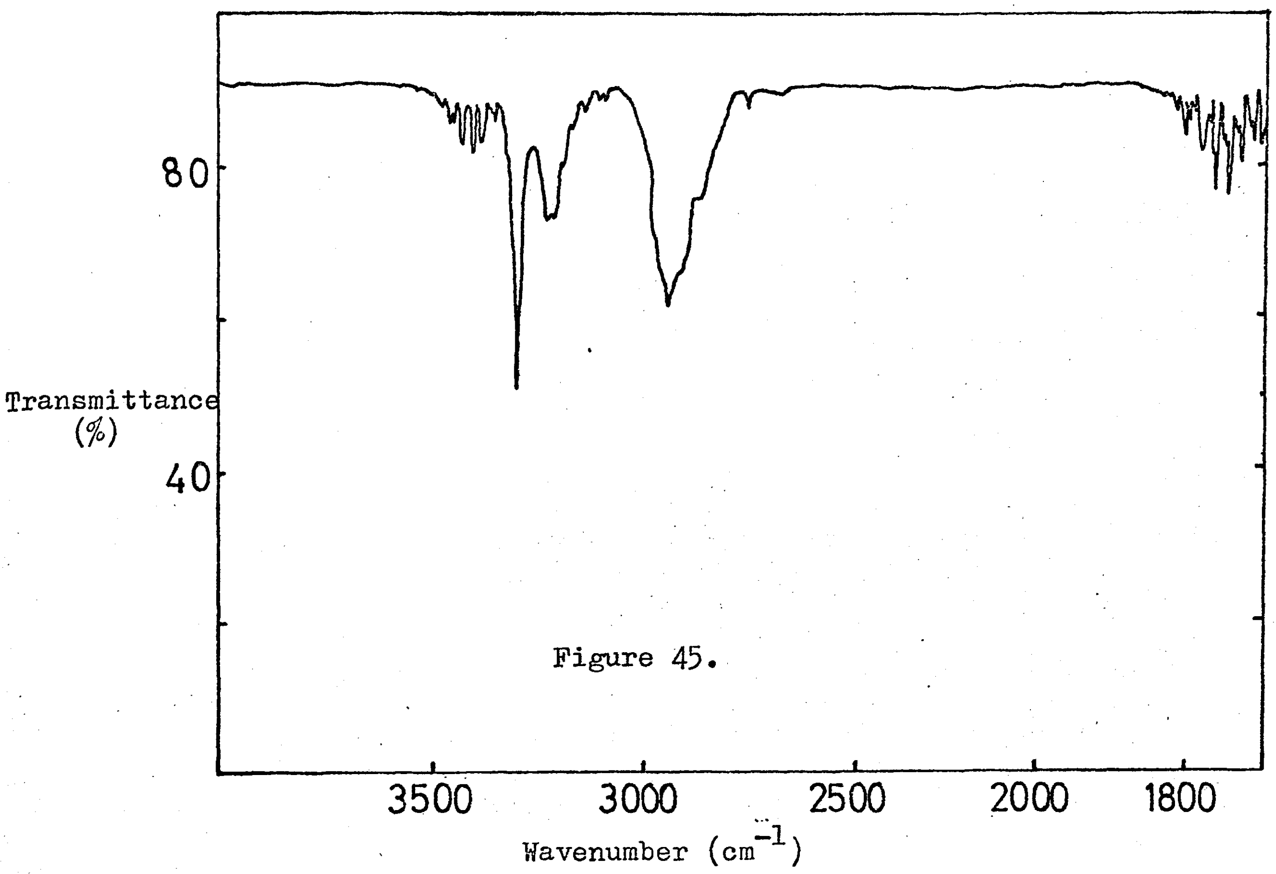


Figure 45.

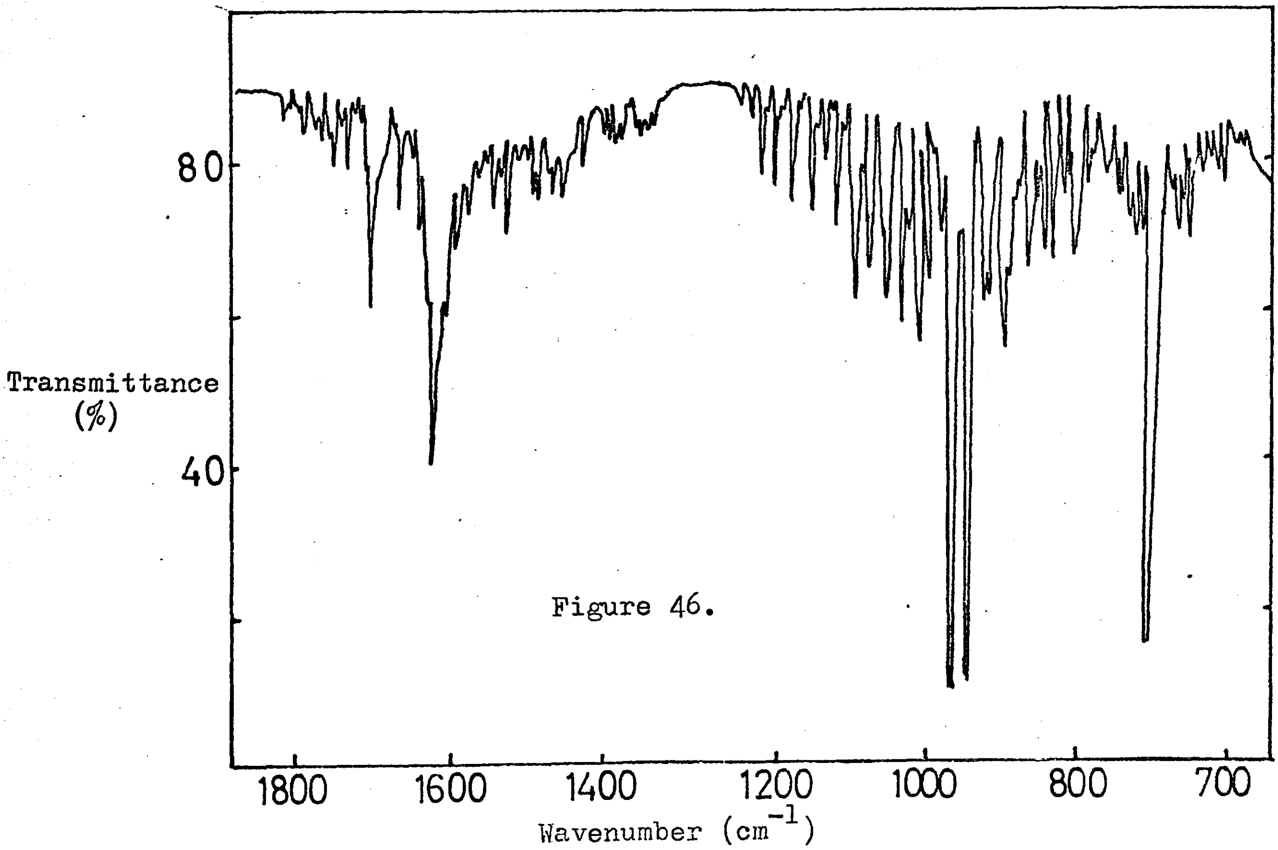


Figure 46.

Figures 45 and 46. I.R. of volatiles at 20°C from the degradation of a 52 % butadiene copolymer at 352°C for seven hours.

peaks at 3337cm^{-1}, 1629cm^{-1}, 960cm^{-1} and 930cm^{-1} and for the accompanying rotational bands typical of XY_3 symmetric-top molecules. Hydrogen cyanide is linear in the gas phase, and the parallel and perpendicular vibrations of this molecule give rise to complex peak formations in the regions 3400-3200cm^{-1}, 1500-1300cm^{-1}, and 800-650cm^{-1}. The sharp peak at 2800cm^{-1} is also due to hydrogen cyanide, and the existence of some aliphatic material is indicated by the absorption in the region 3100-2800cm^{-1}. This analysis was also applied to the 8 and 18 hour runs, but an attempt was made to fractionate the gases evolved during degradation of the 52% butadiene polymer for 8 hours at 352°C. The fractionation was achieved by using cold traps at -100°C, -80°C, -45°C, and 0°C. At -100°C the amount of gases still volatile was small, and consisted of trace amounts of ammonia and ethylene, as shown by a strong sharp absorption at 949cm^{-1} and a weaker absorption at 1892cm^{-1}, while a band at 908cm^{-1} indicated the presence of butadiene. Weak peaks in the 750-650cm^{-1} region pointed to the possible presence of cis olefinic compounds, but definite identification was not possible. The gas fraction volatile at -80°C consisted mainly of ammonia, but the presence of trace aliphatics was indicated by absorption in the 3200-2800cm^{-1} region. Hydrogen cyanide began to appear in the fraction volatile at 45°C, and is also present together with ammonia in the sample volatile at 0°C. Analysis of the gaseous fraction obtained from the pyrolysis of a 33% butadiene copolymer for 24 hours at 352°C yielded similar results.

The degradation of a sample of polybutadiene at 352°C for twenty-four hours was carried out in the hope that the analysis of gas phase material might be easier, since no ammonia or hydrogen cyanide would be present. However, only ethylene and butadiene could be positively identified from the infra-red, together with some cis olefinic material. Definite identification of the cis material was not possible, since although band frequencies are known which identify a given olefinic configuration, these bands may be found in most low molecular weight unsaturated hydrocarbons containing that particular double bond configuration.

Samples of polybutadiene and copolymers containing 89%, 80%, 66%, 33% and 25% butadiene were pyrolysed at 400°C for seven hours, and the gaseous products volatile at 20°C were analysed. No differences were found in comparison with the analysis of products at 352°C given above.

Gas liquid chromatography was used to facilitate the identification of products volatile at 20°C during a series of degradations, and figure 47 shows the trace obtained from the gaseous degradation products of a 52% butadiene 48% acrylonitrile copolymer heated at 400°C for seven hours. The flame ionization detector of the chromatograph was not sensitive to ammonia and hydrogen cyanide was retained by the silica gel columns; thus the trace shown is that of the hydrocarbons fraction of the degradation gases. The retention time for each peak was obtained, and standard samples of the pure gases were introduced into the columns under the same conditions. Table 19 lists the gases with the same retention times as those shown in figure 47. The other copolymers in the composition range being studied, yielded the same GLC peak pattern, indicating the presence of the gases listed in table 19.

Two very broad peak structures were noted at higher retention times, indicating the presence of higher molecular weight material.

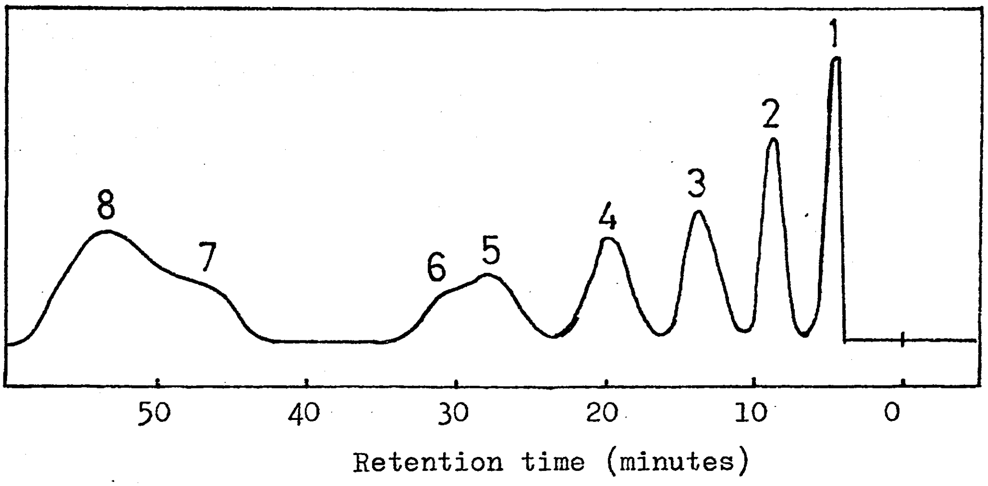


Figure47. GLC trace of volatiles at 20°C from a 52% butadiene copolymer at 400°C for seven hours.

Peak no. in Figure 47	Gas	Retention time (minutes)	Temperature (°C)
1	methane	4.0	70
2	ethane	9.3	86
3	ethylene	13.2	106
4	propane	19.7	138
5	propylene	28.2	150
6	butane	30.7	150
7	butene	47.5	150
8	butadiene	53.0	150

Table 19. GLC retention times.

Product	% butadiene in polymer					Identification method		
	100	89	52	33	25	I.R.	GLC	MS
hydrogen	*	*	*	*	*		*	
methane	*	*	*	*	*	*	*	
ethane	*	*	*	*	*		*	*
ethylene	*	*	*	*	*	*	*	
propane	*	*	*	*	*		*	*
propylene	*	*	*	*	*		*	
propadiene	*	–	*	–	–			*
butane	*	*	*	*	*		*	*
butene	*	*	*	*	*		*	
butadiene	*	*	*	*	*		*	
pentane	*	–	–	–	–			*
pentadiene	*	*	*	*	*			*
hexane	*	–	–	–	–			*
hexadienes	*	*	*	*	*			*
heptadienes	*	*	*	–	–			*
toulene	*	*	*	–	–			*
benzene	*	*	*	–	*			*
ammonia	–	*	*	*	*	*		
hydrogen cyanide	–	*	*	*	*	*		

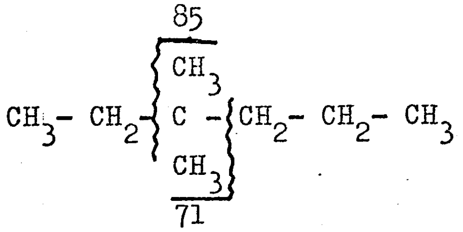
Table 20. Degradation products at 390°C. * indicates identification. The products from 80% and 66% butadiene polymers were the same as from the 89% butadiene polymer.

The technique of mass spectrometry was used to investigate the gaseous material evolved during polymer and copolymer pyrolysis, and on all occassions the results suggested a highly complex mixture of products. Figure 48 illustrates the spectrum of products volatile at 20°C produced during the degradation of polybutadiene for seven hours at 352°C. In the hope that some clarification of the spectrum might have been obtained, fractionation of the gas sample was carried out, and figures 49-52 illustrate the spectra obtained from those fractions volatile at -100°C, -80°C, -45°C and 0°C respectively. Unfortunately the spectra are still complex, most probably for the following reasons.

The molecular ion formed in a mass spectrometer, is an odd-electron species. Consider therefore the molecular ion $AB^{+\cdot}$; fragmentation may occur to give a carbonium ion and a radical,

$$AB^{+\cdot} - A^{+} + B^{\cdot} \quad \text{or} \quad A^{\cdot} + B^{+}$$

the major bond ruptures being those yielding the most stable carbonium ions and/or radicals. The above fragmentation mode illustrates the tendency of an odd-electron species to become an even-electron carbonium ion via radical elimination. Thus the molecular ions of molecules containing alkyl side-chains frequently decompose by elimination of alkyl radicals rather than by expulsion of saturated neutral hydrocarbon molecules. This is evident in the fact that, losses of methyl or ethyl radicals to give $M-CH_3$ and $M-C_2H_5$ ions, are very commonly observed in mass spectra, whereas abundant $M-CH_4$ and $M-C_2H_6$ ions are only infrequently encountered, but the relative stabilities of carbonium ions are tertiary $>$ secondary $>$ primary, therefore hydrocarbons will preferentially split at branch points. In other words the mass spectrum of a long chain linear unsaturated hydrocarbon such as N-octane (C_8H_{18}) is characterised by groups of peaks spaced 14 mass units apart (corresponding to a difference of CH_2) with the molecular ion at m/e 114. There is also a fairly regular increase in relative abundances with decreasing m/e value. However in the spectrum of the isomeric branched hydrocarbon 3-3 dimethyl hexane;

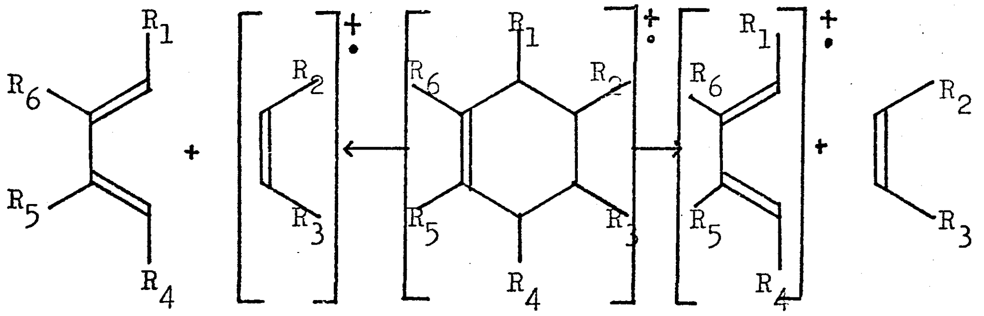


$$\mathrm{CH_3-CH_2-\underset{\underset{71}{CH_3}}{\overset{\overset{85}{CH_3}}{C}}-CH_2-CH_2-CH_3}$$

the peaks at m/e 71($C_5H_{11}^+$) and m/e 85($C_6H_{13}^+$) are enhanced by a factor of about 4 relative to the spectrum of the linear hydrocarbon since their formation corresponds to the production of tertiary carbonium ions. Fragmentation is enhanced in branched hydrocarbons and thus the linear hydrocarbon exhibits a molecular ion, while the branched hydrocarbon does not. In other words the spectrum of a mixture of linear hydrocarbons will appear simply as the spectrum of the highest member of the series with the lower members contributing to a distortion of relative abundances of ions. If that mixture also contains branched material, then the relative abundances of ions is further distorted, and the highest peak is not necessarily the molecular ion of the highest molecular weight species present. Further complications occur if unsaturated material is present. For example, a double bond induces two main types of cleavage. Firstly simple allylic cleavage giving a stable allylic carbonium ion fragment from a straight chain olefin:

$$\left[\mathrm{R-CH=CH-CH_2-R'}\right]^{+\cdot} \xrightarrow[-\mathrm{R'}\cdot]{} \mathrm{R-CH=CH-CH_2^+}$$

Secondly, cyclohexene-type systems undergo retro-Diels-Alder reactions in which charge retention may occur either with the diene portion or the ethylenic portion, depending on the nature of the substituents.



(1)

Thus in the above example if $R_1 - R_6$ were hydrogen then (1) would correspond to m/e 54 which is also the mass peak expected from butadiene. It should also be noted that in the mass spectra of compounds containing hydrocarbon chains, peaks often occur two mass units below those associated with saturated carbonium ions. These peaks are believed to be due to alkenyl cations, and thus the presence of such peaks cannot be considered as pointing to the presence of unsaturated material in the mixture.

The above considerations have made the analysis of hydrocarbon mixtures one of the most insurmountable problems at present being studied by mass spectroscopists. Nevertheless, some general comments and comparisons can be made, including identification of some products, from the presence of peaks known to be unique or virtually unique for the most likely type of products. However the analysis must be considered in the light of the foregoing discussion.

In figure 48, the gaseous products include ethane, propane, butane, as indicated by molecular ion peaks at m/e 30, 44 and 58 respectively. In the spectrum the fraction volatile at -100°C (figure 49)

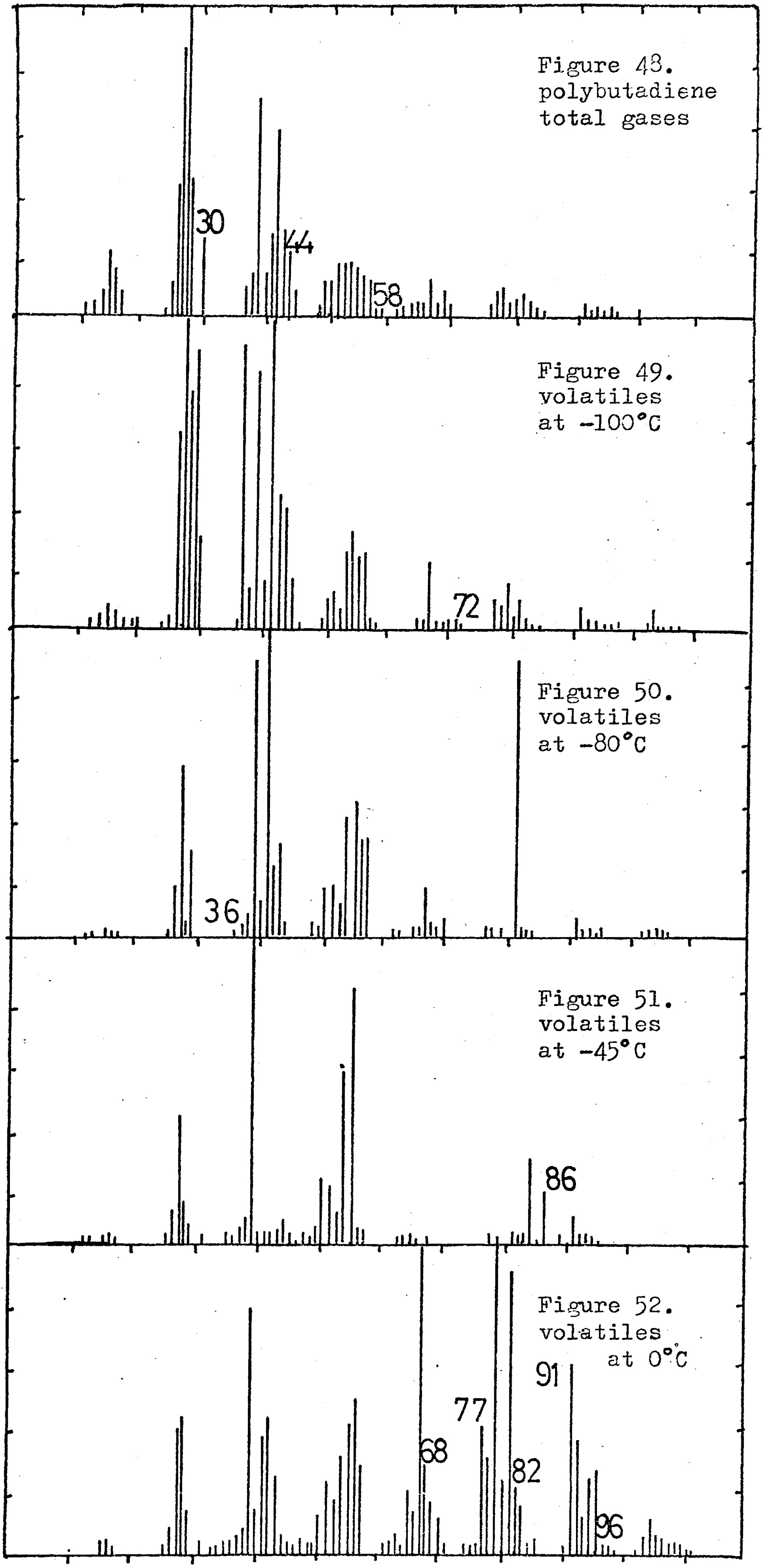


Figure 48. polybutadiene total gases

Figure 49. volatiles at -100°C

Figure 50. volatiles at -80°C

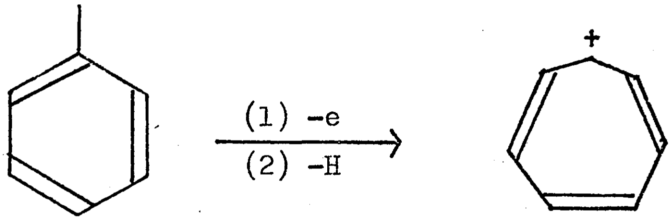
Figure 51. volatiles at -45°C

Figure 52. volatiles at 0°C

Figures 48-52.

Mass spectra of gases from polybutadiene at 352°C for seven hours.

pentane is identified by the small peak at m/e 72, and in figure 51 (Products volatile at -45°C) hexane is present as illustrated by the molecular ion peak at m/e 86. In figure 52, the peaks at m/e 92 and 91 point to the presence of toluene, m/e 91 being due to the relatively stable tropyllium ion:



Toluene Tropyllium ion.

In a similar manner peaks at m/e 78, 77, 76 and 74 are probably due to benzene. A peak at m/e 68 is most likely due to pentadienes, since no other hydrocarbon materials in the range C_5-C_8 give a peak at this point. In the same way, m/e 82 and 96 are due to hexadienes and heptadienes respectively. A peak at m/e 36 present in figures 49-52 is believed to be due to propadiene.

The spectrum of gaseous products obtained from a sample of copolymer containing 52% butadiene degraded at 352°C for seven hours was recorded together with those of the fractionated samples. The most noticeable feature was that no peak of m/e ratio higher than 96 was recorded, indicating that the maximun carbon number of the products had been reduced to some extent by the incorporation of acrylonitrile units. All the products identified from the pyrolysis of polybutadiene were also identified in this case, with the exception of pentane and hexane.

The nitrogen containing materials typical of acrylonitrile degradation have no unique peaks in the range up to m/e 110, and therefore no identification of any such products was possible.

An investigation of the mass spectra of degradation products obtained from pyrolysis of copolymers containing 87%, 80%, 66%, 33% and 25% butadiene was also carried out, indicating that even with the 25% polymer peaks as high as m/e 83 were still being recorded, illustrating the presence of material in the C_6 region.

By the application of the analytical techniques discussed above, the compounds indicated in table 20 were identified as gaseous degradation products from the degradation of the polymers. The main conclusion which must be drawn from this table is that the degradation reactions of these polymers are of a sort which yield a complex mixture of saturated and unsaturated, cyclic and acylic hydrocarbon materials.

5.3 Products Remaining liquid at 20°C.

Neither polybutadiene nor any of the copolymers yielded any products which remained in the liquid state at room temperature. The explanation probably lies in the fact that products other than residue and chain fragments amounted to only a few percent of the total sample weight, and materials which might have remained liquid such as C_5 upwards, were themselves only a small fraction of the total gas phase, hence under the conditions of reduced pressure total volatilisation was possible.

It should be noted, therefore, that even with those copolymers of high acrylonitrile content none of the products characteristic of polyacrylonitrile degradation, as discussed in chapter 1, were identified.

5.4 Chain Fragment Material.

The major fraction of degradation products consisted of the cold-ring or chain fragment material. This fraction was volatile at the temperature of degradation, but not volatile enough to pass to to the condensation limb of the degradation tube, and so condensed on the part of the tube passing through the firebrick of the oven. The cold-ring fraction was collected for examination as described in chapter 2.

The chain fragments produced during the degradation of polybutadiene in the range 350-400°C were very slightly yellow in the solid state. The number average molecular weight of the chain fragments obtained from the degradation of a polybutadiene sample at 390°C for 6 hours was 353 as determined by vapour pressure osmonetry. As the acrylonitrile content of the original polymer increased, the colour of the chain fragments produced darkened through brown/red to dark red for a 25% butadiene polymer. In solution in chloroform, these colour changes were seen to be simply a deepening of the original colour, in other words there was an increase in unsaturation giving yellow colour in the 275mμ region of the ultra-violet, but no tendency to increasing number of conjugated double bonds.
Chain fragment material remained soluble throughout the entire composition range, and their molecular weight remained in the region of 350-360.

The infra-red spectrum of the chain fragments obtained from a polybutadiene sample degraded at 390°C for 7 hours is shown in figure 53. Comparison with figure 22 for untreated polybutadiene shows that the chain fragments have lost most of the unsaturation as illustrated by disappearance of the absorption in the 750-650 cm^{-1} due to cis structures, and the marked reduction in intensity of the peaks at $962cm^{-1}$ and $908cm^{-1}$ due to trans and 1-2 (vinyl) structures respectively. Other absorption due to unsaturated structures (table 9) reduced accordingly. An increase in the relative amount of methyl groups is

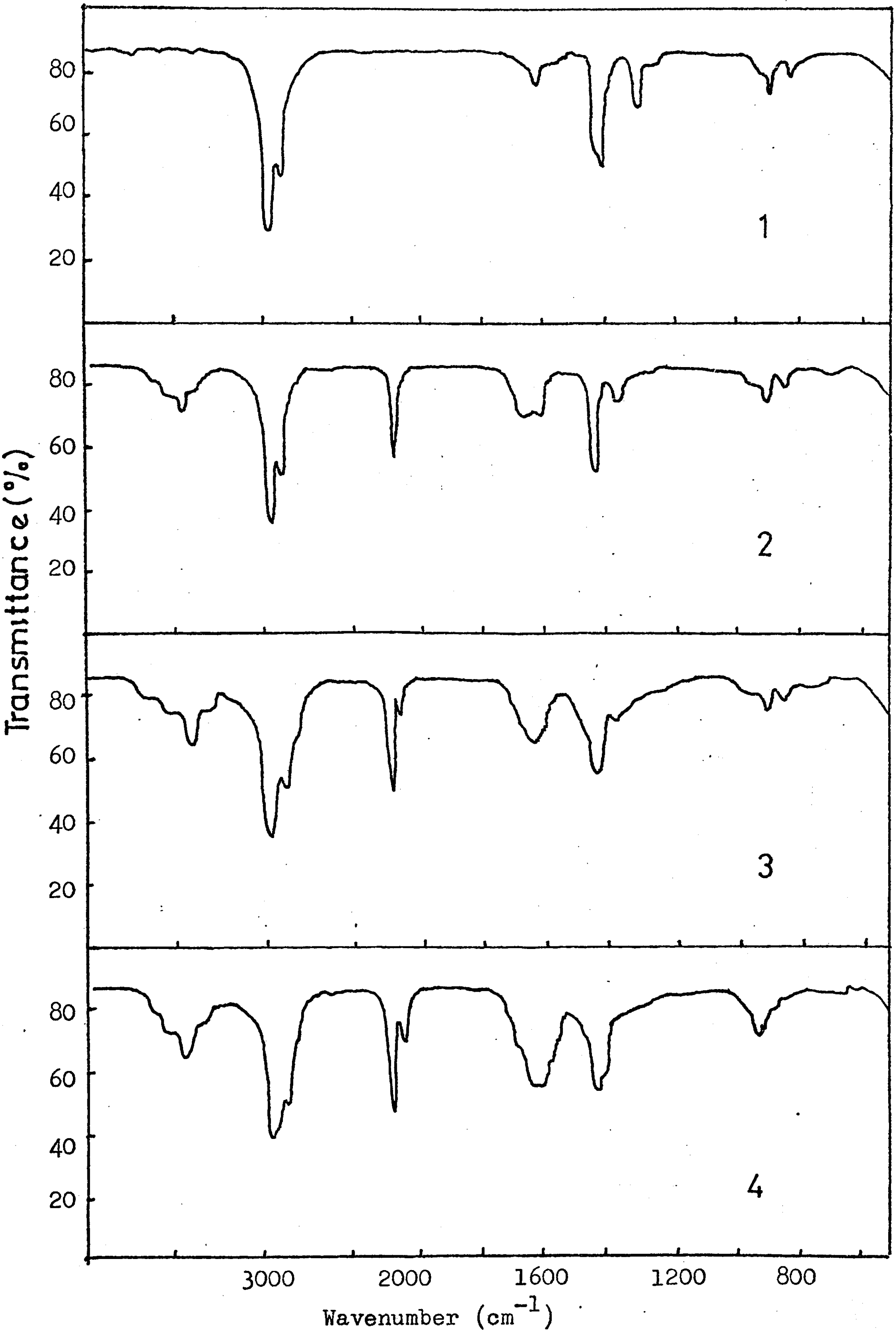
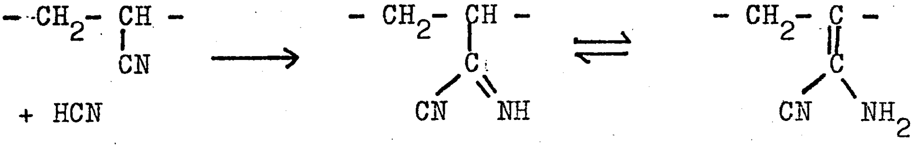


Figure 53. I.R. spectra of cold-ring fractions: 1. polybutadiene 390°C for seven hours; 2. 52% butadiene 390°C for seven hours; 3. 41% butadiene 390°C for one hour; 4. 25% butadiene 390°C for one hour.

shown by the increased absorption at 1372cm^{-1}, providing evidence for hydrogen transfer reactions occurring during degradation.

The rapid loss of unsaturation in the chain fragments was found to be almost complete after 30 minutes of treatment at 390°C.

A similar rapid loss of unsaturation occurs in the chain fragments produced by copolymer degradation, but other notable changes occur, as can be seen in figure 53 which shows the spectra of the chain fragments from a range of copolymers pyrolysed at 390°C for various times. The nitrile absorption remains at 2240cm^{-1}, but new absorptions occur at 3600, 3470, 3380, 3210, 2185, 1700-1550, and 820cm^{-1}. The most interesting band is that at 2185cm^{-1}. This band also appears in the cold-ring fraction produced during polyacrylonitrile degradation and has been assigned to unsaturated nitriles[28], although the frequency is lower than that normally associated with these structures (2240-2210cm^{-1}). The band has also been reported as characteristic of a conjugated carbon-nitrogen system[96], but other studies of nitrile group polymerisation failed to reveal additional absorption in this region[97]. Iminonitriles or amino-substituted unsaturated nitriles have been suggested by Grassie[28], since these structures exhibit reduced nitrile frequencies in the infra-red[98]. The mechanism proposed is the interaction of HCN, produced during degradation, with the nitrile groups in the chain producing α- iminonitrile structures or the corresponding tautomeric groups:



Since HCN is produced from the start of degradation of the butadiene copolymers, a reaction of this sort is possible during the degradation. The N-H bands above 3000 cm^{-1} and the absorption in the 1700-1550cm^{-1} in figure 53 can also be explained by the type of structures shown above. The broad and weak absorption at 820cm^{-1}, points to the presence of some tri-substituted olefinic structures being present, although this absorption is ill-defined and does not appear in the spectrum of the chain fragments from polybutadiene.

Attempts were made to separate the cold-ring fraction by GLC and by gel permeation chromatography (GPC), but both approaches were unsuccessful. The chain fragments were not particularly volatile at the temperatures of sample inlet and columns in the GLC (200-250°C) and no passage through the columns was detected. Using GPC, a small portion of the cold-ring fraction did pass through the column as a very broad band, but the bulk of the material remained lodged near the beginning of the GPC column. The Sephadex gel used will permit the passage and separation of material up to a molecular weight of 1200-1500, thus, since the number average molecular weight of the cold-ring fraction was about 350, no difficulty in separation had been anticipated. However the latter part of this work will discuss the extensive crosslinking which occurs rapidly in these polymers at 390°C, indicating that the cold-ring fraction formed would probably be of a complex branched nature. It is believed that this factor led to the retention of the samples in the GPC columns, and perhaps contributed to the failure of the samples to pass through the GLC columns.

The cold-ring fractions from all the polymers were found to be very susceptible to oxidative attack as illustrated by the rapid formation of bands in the infra-red due to oxygen-containing structures.

It was therefore necessary to carry out any analysis on these fractions as quickly as possible, and certainly no later than 24 hours after removal from the degradation tube.

5.5 Polymer Residues.

Large amounts of residue remained after the polymers were heat-treated in the range 350-400°C. In all cases these residues were insoluble, brittle and difficult to prepare for spectral analysis by grinding. The residue produced from polybutadiene pyrolysis was pale yellow in colour and semi-transparent; some flow had occurred in the sample prior to degradation, and this molten flow was noted in all samples containing 41% or more of butadiene. Acrylonitrile content seemed to have some influence on the colour of the residue, since the 89% butadiene copolymer yielded a residue of a very much darker amber colour than that from polybutadiene. The residues darkened in colour with increasing acrylonitrile content, although there was no tendency to move towards the red end of the spectrum. At high acrylonitrile content the residues developed a blackish char-like appearance.

Figure 54 shows the infra-red spectrum of the residue obtained from pyrolysis of a polybutadiene sample at 390°C for 6 hours. The spectrum appears very similar to that of a simple unsaturated hydrocarbon. In other words unsaturation has almost disappeared, although the weak peaks at $870cm^{-1}$ and $820cm^{-1}$ point to the existence of exomethylene structures and trisubstituted olefinic structures respectively. An increase in the absorption at $1372cm^{-1}$ due to methyl groups indicates that hydrogen transfer reactions occur during degradation as discussed previously. The rapid loss of unsaturation occurs within 30 minutes when the polymer and copolymers are treated at 390°C, and treatment beyond that time shows no detectable change in the

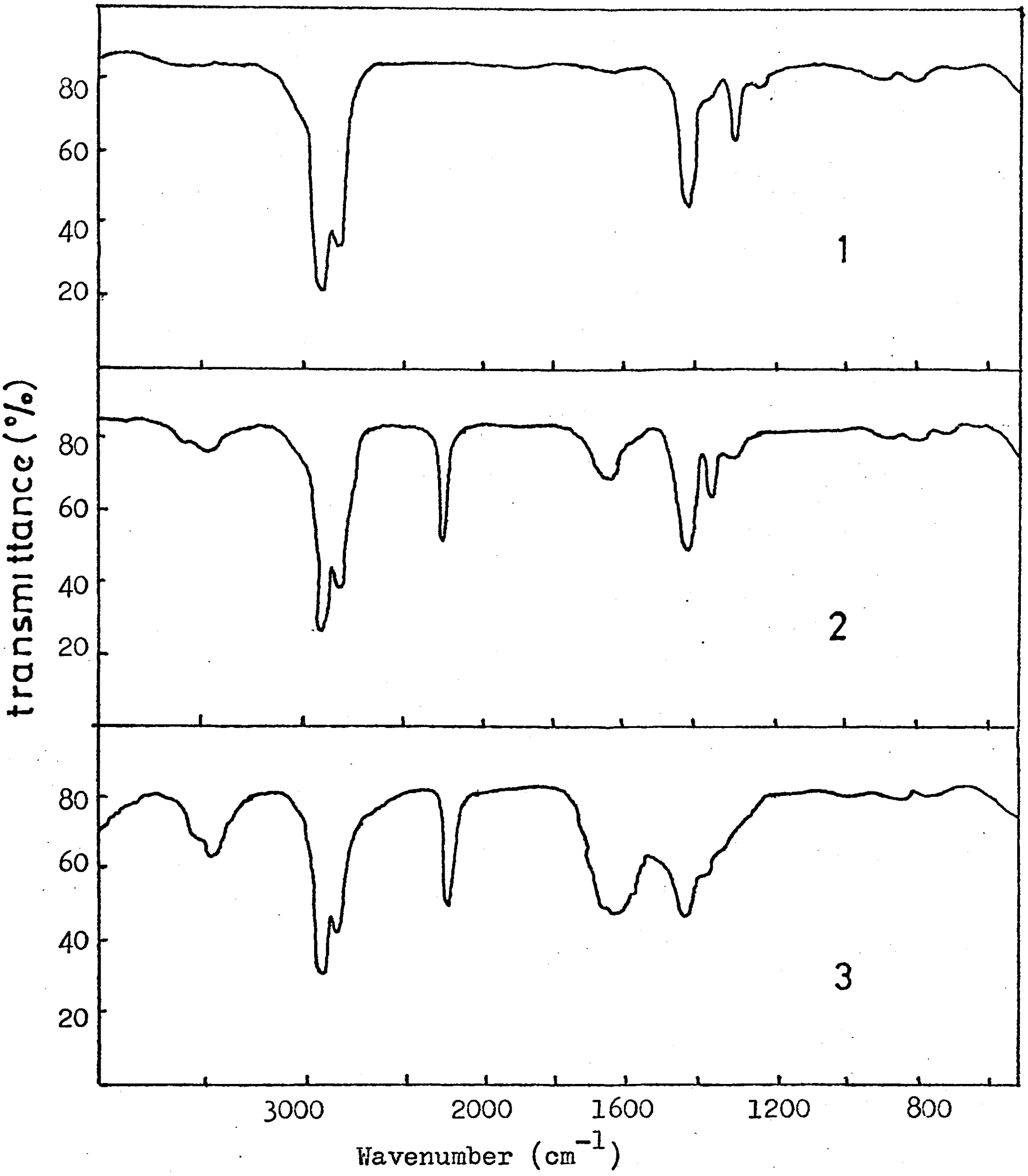


Figure 54. I.R. spectra of residues; 1. polybutadiene 6 hours 390°C; 2. 80% butadiene 4 hours; 3. 41% butadiene 6 hours.

infra-red spectrum of residue, except the complete elimination of cis trans and vinyl unsaturation.

Figure 54 also illustrates the spectra of the residues from polymers containing 80% and 41% butadiene. The spectra are similar to those of the cold-ring fractions (figure 53) and to that of the polybutadiene residue with one notable exception. The peaks at 2185cm^{-1} and 3210cm^{-1} which appeared in the spectra of chain fragments from polymers with butadiene contents less than 52%, do not appear in the residues of any of the copolymers. It is probable then that one structure is responsible for both these absorptions, and if it is an iminonitrile or amino substituted unsaturated nitrile structure as suggested in section 5.4, then some other structure containing amine or imine groups must be responsible for the remaining absorptions in the 3600-3200cm^{-1} region. Further, since the peaks in question occur only in the chain fragments and not in the residue, it is possible that the structure or structures responsible result directly from a scission reaction, or that these structures, once formed in the bulk polymer, provide weak points for scission, with retention of structural identity. A further possibility is that these structures are part of a two stage reaction which has gone to completion in the residue, but where completion has not been possible in the chain fragments due to volatilisation away from the reaction zone.

CHAPTER SIX

Quantitative Analysis of Degradation Products

In the previous chapter the identification of the products of degradation was described. It was appropriate to complement that information with quantitative measurements on the products of particular interest.

The degradations discussed in this chapter were carried out at 390°C using the sealed tube technique (chapter 2), and the complete range of copolymer composition was studied. From chapter 5, which discusses the qualitative analysis of products, it is obvious that studies must be carried out on the amounts of residue and chain fragments produced to establish the weight-loss characteristics of the degradation reaction. Also in chapter 5 it was indicated that ammonia and hydrogen cyanide might bear some important relationship to the scission reactions: thus an analysis of these two products is presented here.

The highly complex nature of the hydrocarbon gases produced has forbidden a detailed quantitative analysis of these products. However it is most likely that they arise from intermolecular transfer reactions, and since no particular product appears in any excess, it is felt that a detailed analysis of these products, would not provide much useful information in any case.

6.1. Methods of Measurement.

Weights of residue and chain fragments were obtained as described in chapter 2, which also describes the use of the constant volume manometer and infra-red calibrations to determine the pressures of gaseous material evolved.

The infra-red peak chosen for the estimation of ammonia is the rotational band at 1175cm^{-1} (figure 46). The peak at 726cm^{-1} was chosen for the measurement of hydrogen cyanide for the polymers containing 80% and 66% butadiene, however the optical density of this peak was too high to permit sufficient accuracy in the case of the 41% and 25% polymers. The peak at 713cm^{-1} was used in these cases. All optical density values were measured using the slow speed of the spectrometer together with the facility for a x10 expansion scale.

6.2 Weight Loss and Chain Fragment Formation at 390°C.

Figures 55-59 (tables 21-25) show the results from pyrolysis of polybutadiene and copolymers containing 80%, 66%, 41% and 25% butadiene. With decreasing butadiene content the rate of weight loss increases in the initial stages of reaction until with the 25% butadiene polymer 70% weight loss occurs within one hour. There is also a tendency to earlier stabilisation of the residue with decreasing butadiene content. Thus with polybutadiene after seven hours, about 30% residue remains and weight loss is continuing, whereas with the 66%, 41% and 25% butadiene, weight loss has virtually ceased after 5, 3 and 2 hours respectively.

The chain fragment curves show the expected corresponding trends and are infact almost mirror images of the residue curves. Since the residue and chain fragment curves intercept at approximately the same point on the percentage scale (~45%) then the point on the time scale at which this intercept occurs may be taken as a stability parameter for a given copolymer as shown in figure 60 (table 26). This is, of course, simply a plot of the time at which a given percentage residue remains, versus the copolymer composition. A more common way of illustrating relative stability is to present a % weight loss versus composition curve for pyrolysis over a fixed period. Figure 61 (table 27) shows such a plot for the system being studied, for one and two hours of heat treatment. The stabilisation trend of the residues can be seen by the levelling out of the 2 hour plot.

The above results further confirm that the presence of acrylonitrile units in these polymers creates a destabilising effect, as noted during thermal analysis (chapter 4). However in chapter 4 it was noted that during programmed heating to 500°C, the amount of residue remaining increased with decreasing butadiene content, whereas from the residue curves shown here the amount of residue remaining after seven hours at 390°C is higher for polybutadiene than for the other polymers. The conclusion is that the polybutadiene residue does not stabilise, and the degradation reaction continues at a measureable rate beyond seven hours.

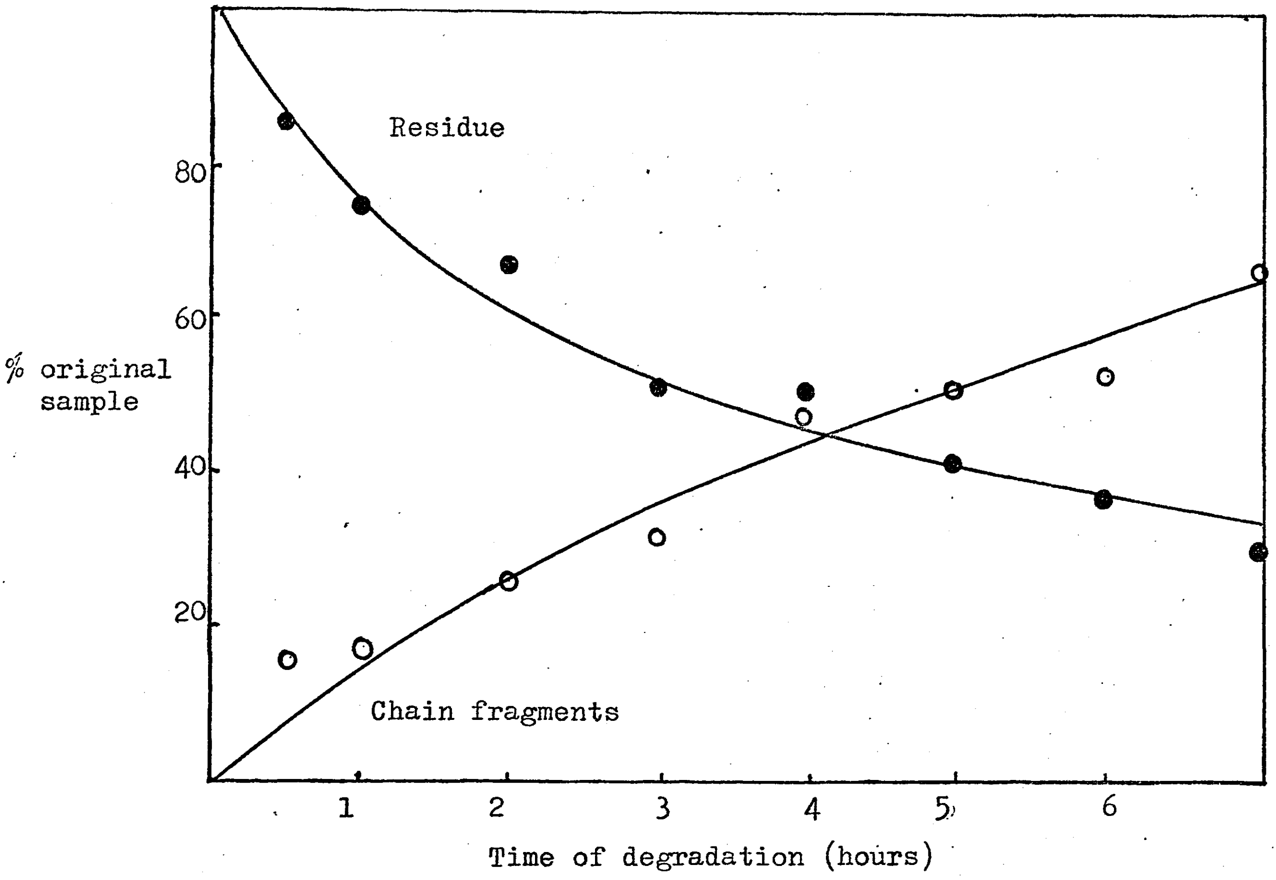


Figure 55. Residue and chain fragments plots for polybutadiene at 390°C.

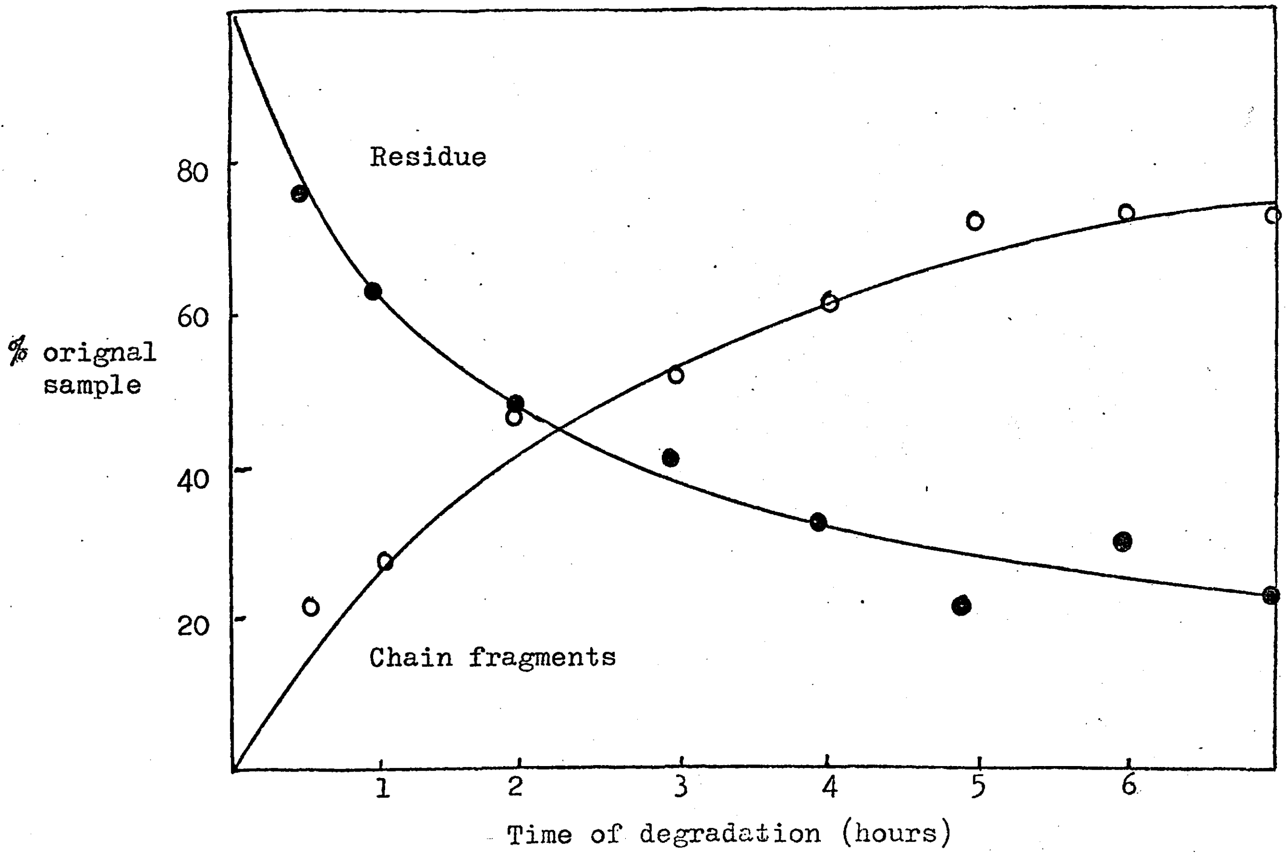


Figure 56. Residue and chain fragments plots for an 80% butadiene polymer at 390°C.

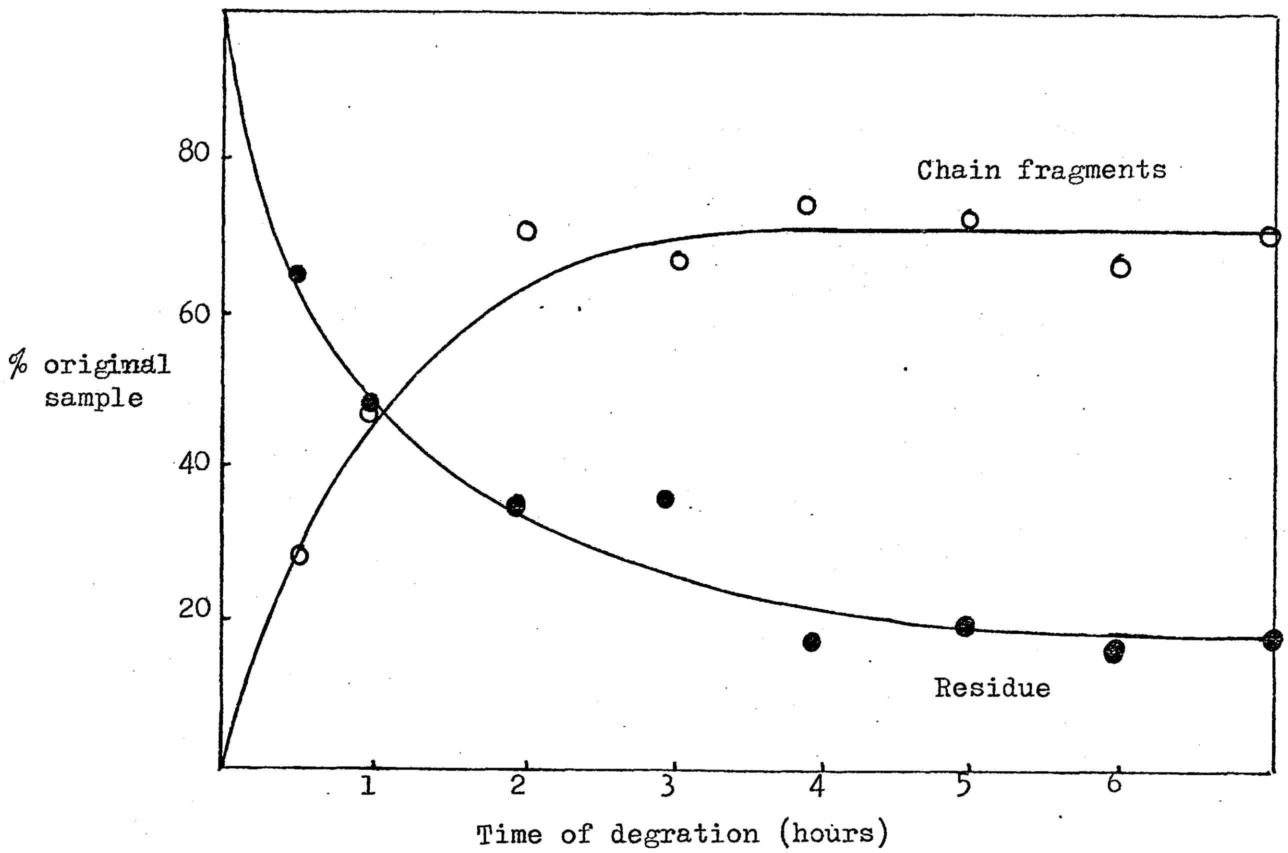


Figure 57. Residue and chain fragments plots for a 66% butadiene polymer.

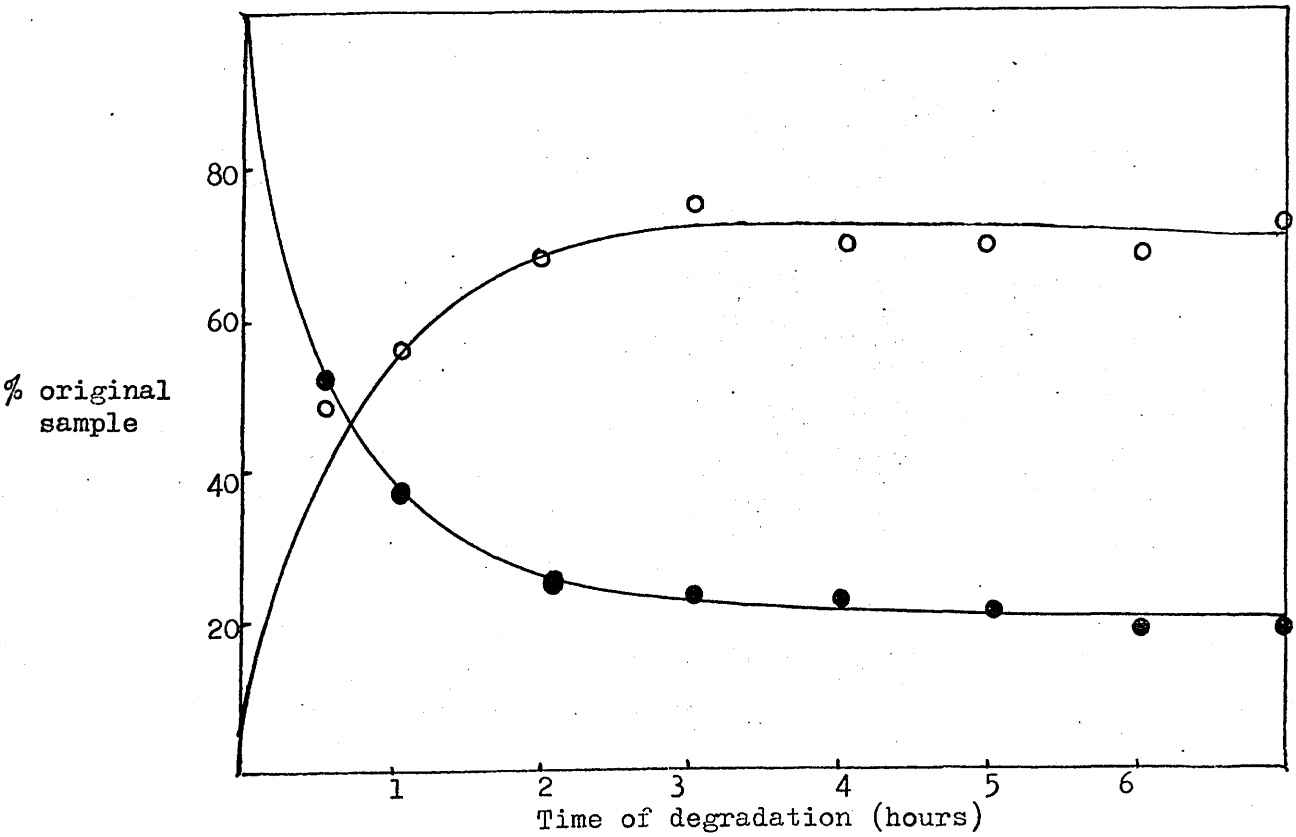


Figure 58. Residue and chain fragments plots for a 41% butadiene polymer.

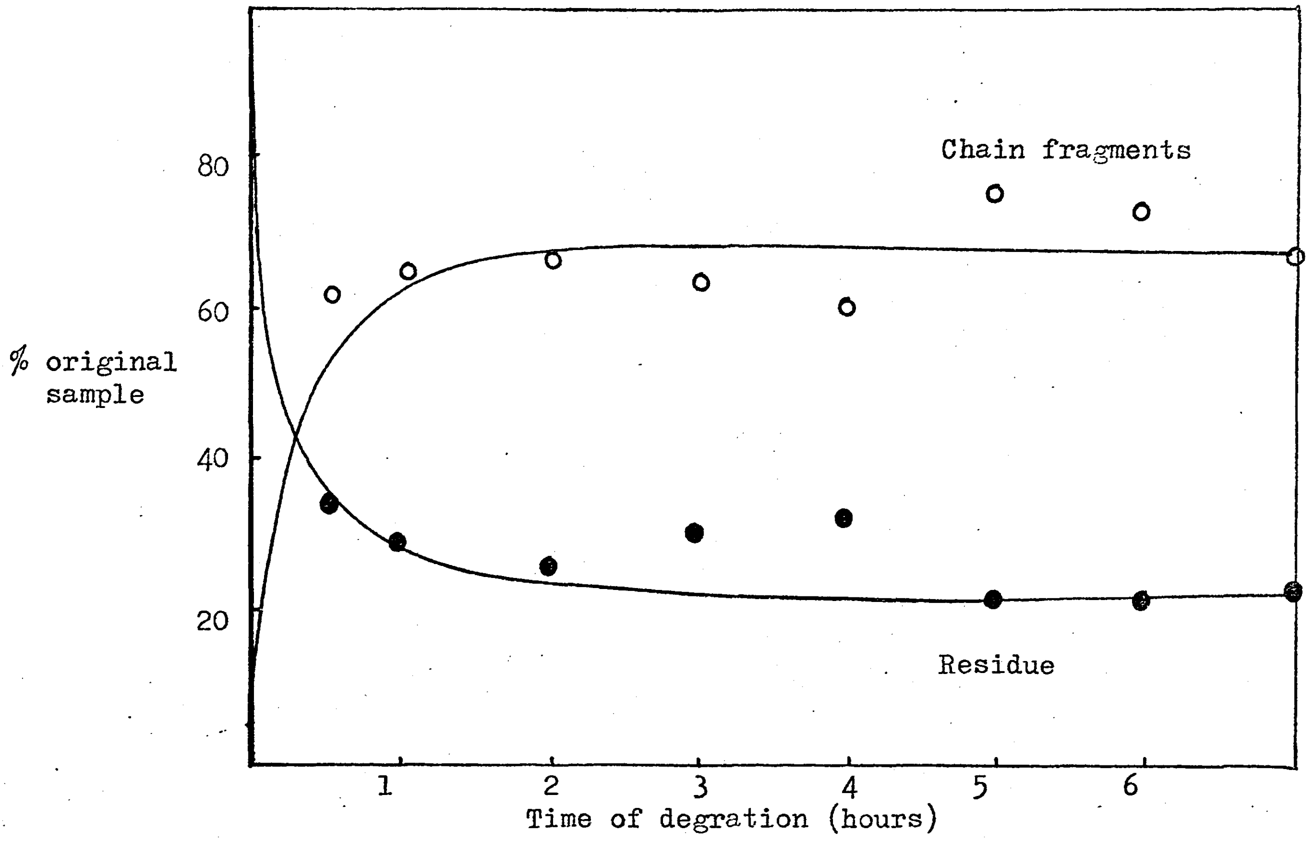


Figure 59. Residue and chain fragments plots for a 25% butadiene polymer.

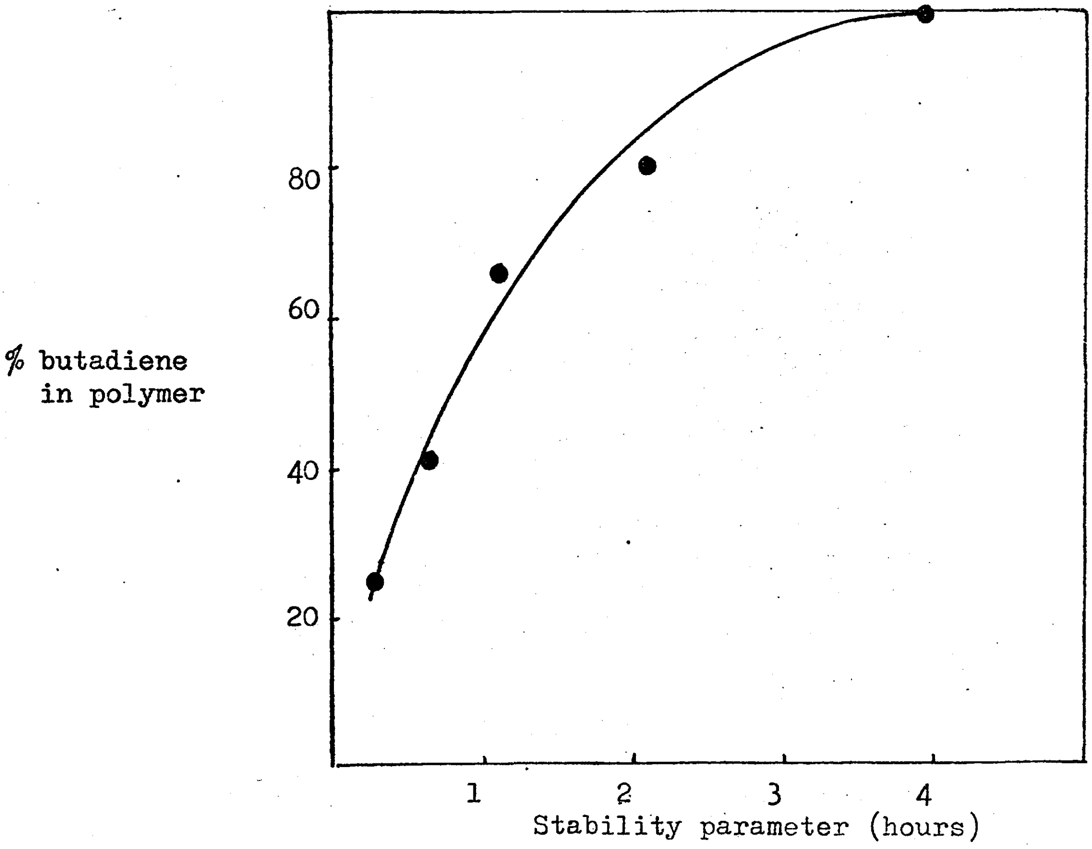


Figure 60. Stability parameters for the polymers at 390°C.

Time (hours)	% original polymer sample Residue	 Chain fragments
0	100	0
0.5	87.5	16.1
1	76.0	17.0
2	68.4	25.7
3	52.2	31.1
4	52.0	49.2
5	42.5	51.8
6	37.4	51.8
7	30.3	68.5

Table 21. Degradation data for polybutadiene at 390°C.

Time (hours)	% original polymer sample Residue	 Chain fragments
0	100	0
0.5	76.4	21.3
1	63.8	27.5
2	47.5	47.0
3	41.6	52.4
4	33.4	62.1
5	21.5	74.0
6	29.5	72.0
7	21.4	71.9

Table 22. Degradation data for an 80% butadiene polymer at 390°C

Time (hours)	% original polymer sample	
	Residue	Chain fragments
0	100	0
0.5	65.0	28.5
1	48.5	47.5
2	34.7	72.3
3	35.8	67.8
4	16.7	76.4
5	20.2	74.1
6	16.4	69.9
7	19.0	72.5

Table 23. Degradation data for a 66% butadiene polymer at 390°C.

Time (hours)	% original polymer sample	
	Residue	Chain fragments
0	100	0
0.5	52.4	49
1	37.2	56.0
2	25.3	68.6
3	23.5	76.5
4	23.3	70.4
5	21.5	70.9
6	19.1	69.4
7	19.7	74.4

Table 24. Degradation data for a 41% butadiene polymer at 390°C.

Time (hours)	% original polymer sample	
	Residue	Chain fragments
0	100	0
0.5	34.2	61.0
1	29.0	63.0
2	27.2	65.4
3	31.0	65.1
4	32.3	60.9
5	22.2	78.3
6	21.3	72.6
7	23.8	68.6

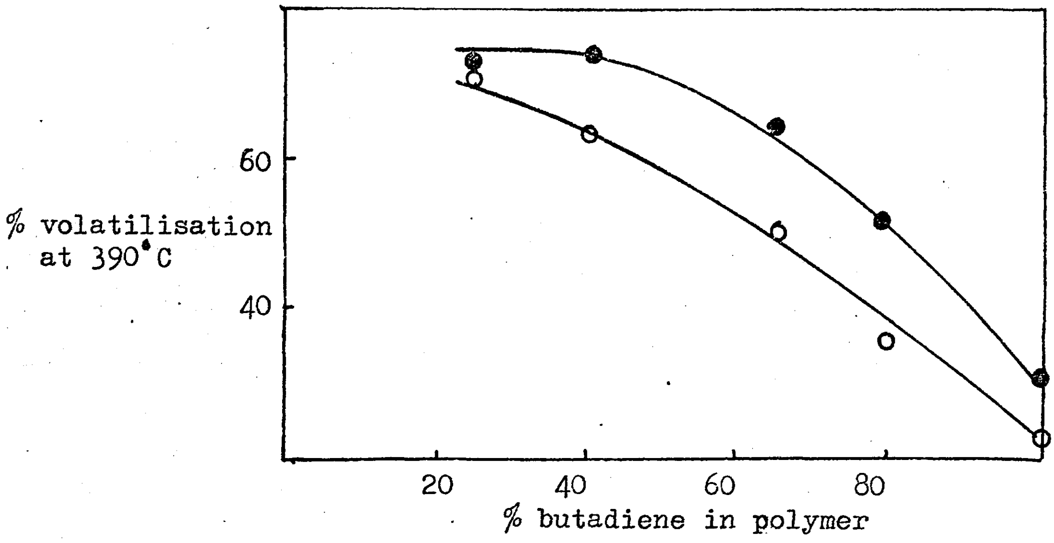
Table 25. Degradation data for a 25% butadiene polymer at 390°C.

% butadiene in polymer	Stability parameter (hours)
100	4.0
80	2.1
66	1.1
41	0.7
25	0.2

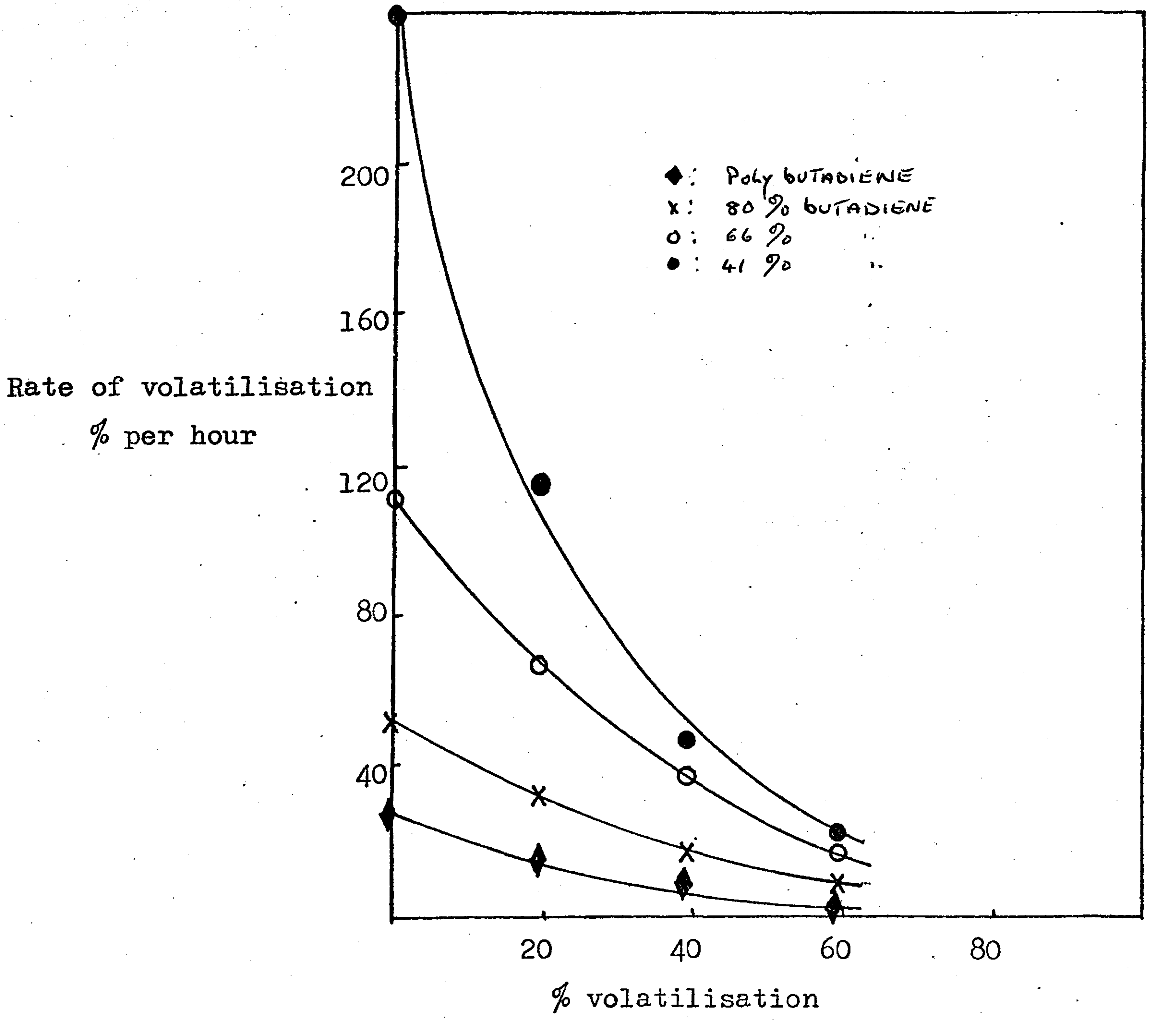
Table 26. Copolymer stability parameters.

% butadiene in polymer	% volatilisation	
	1 hour	2 hours
100	24.0	31.6
80	36.2	52.5
66	51.5	64.2
41	62.8	74.7
25	71.0	72.8

Table 27. Volatilisation data for 1 and 2 hours at 390°C.



<u>Figure 61</u>. Composition versus % volatilisation after 1 and 2 hours at 390°C



<u>Figure 62.</u> Rate of volatilisation versus % volatilisation for the polymers at 390°C.

% butadiene in polymer	% Volatilisation	Rate of volatilisation (%/hour)
100	0	27
	20	16
	40	9
	60	4
80	0	51
	20	31
	40	17
	60	8
66	0	111
	20	67
	40	37
	60	16
41	0	220
	20	116
	40	47
	60	22

Table 28. Rate of volatilisation and % volatilisation data.

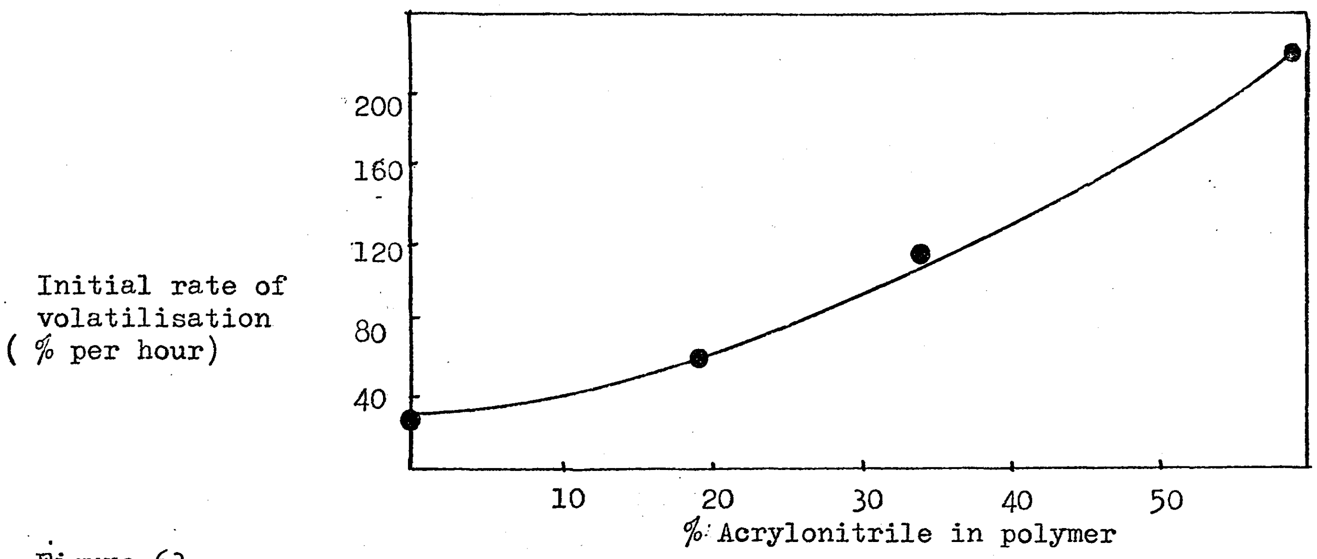


Figure 63.

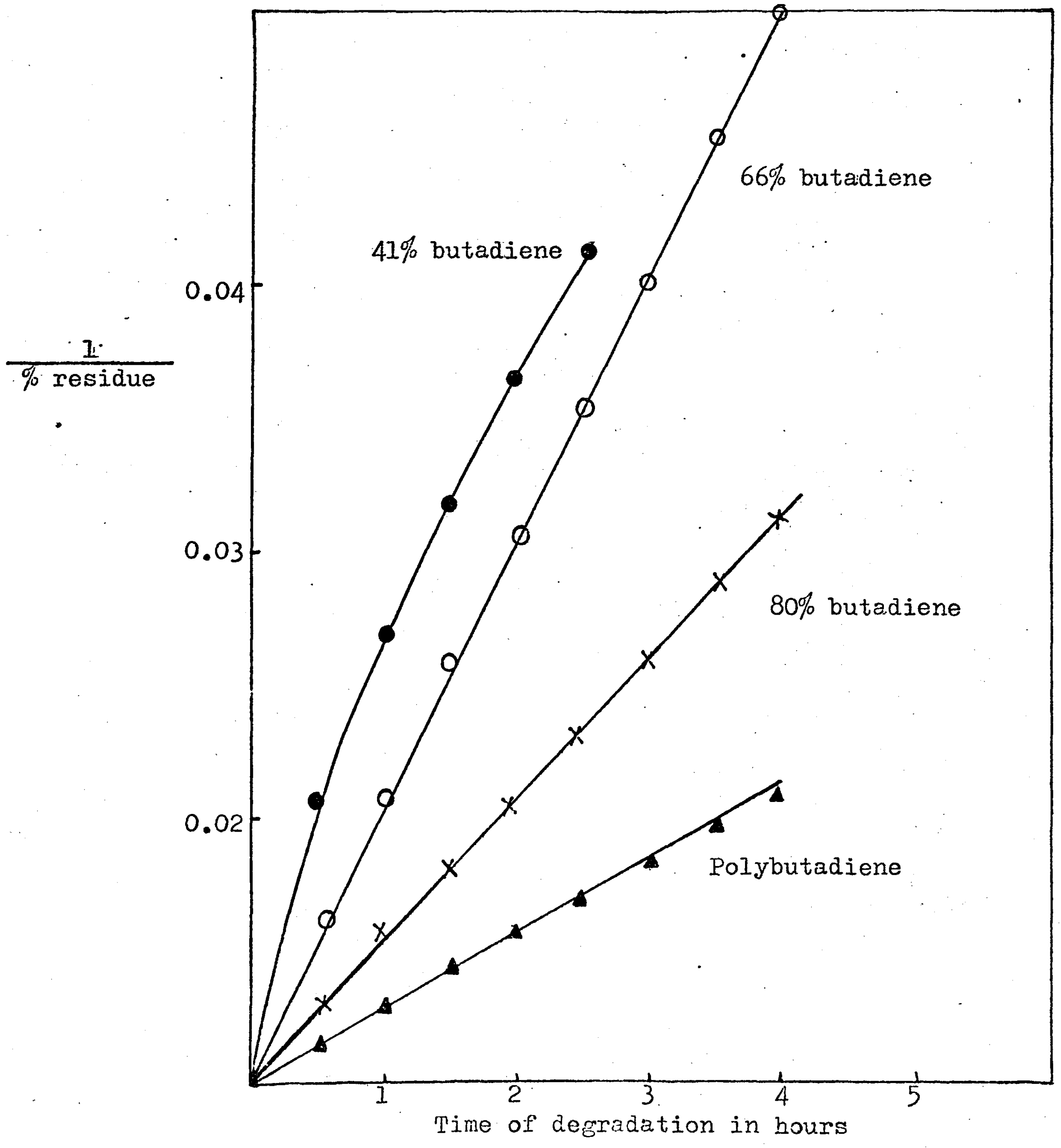


Figure 64. Second order plot for polymer degradations at 390°C.

Figure 62 (table 23) shows the relationship between the rate of volatilisation and the actual percent volatilisation for four polymers. The degradation of the 25% butadiene copolymer was too fast at 390°C to afford accurate information, however this plot does illustrate very well the effect of acrylonitrile content on the rate of volatilisation, and a plot of initial rate of volatilisation versus acrylonitrile content (figure 63) shows that this effect is non-linear with concentration. This might indicate that scission is enhanced by the presence of adjacent acrylonitrile units in the polymer.

Some kinetic information can be obtained from the available weight loss data. Figure 64 shows a second order plot for polybutadiene with respect to weight of residue remaining, and the graph is seen to approximate to second order with some slight deviation above three hours (~ 50% weight loss). The degradations of the 80% and 66% butadiene polymers are also seen to approximate to second order but the 41% polymer shows significant deviation. A first order plot for the 41% polymer also shows definite curvature. Note that the data for this polymer ARE only measured up to the 2 hour point, since beyond this point stabilisation of the residue begins. Madorsky[8] has reported that polybutadiene degradation approximates to first order, based on the same type of analysis as given above.

6.3. The formation of Gaseous Materials at 390°C.

Figures 65-69 (tables 29-33) show the total gas pressure as measured directly on the constant volume manometer (chapter 2), and the hydrogen cyanide and ammonia pressures as calculated from infra-red measurements. These gas pressures are corrected for 100mg. samples, and the plots are presented on the same scale for comparison.

The curve for polybutadiene (figure 65) represents the pressure of hydrocarbon material produced during degradation. For the remaining polymers this data could, in theory be obtained by deducting the ammonia

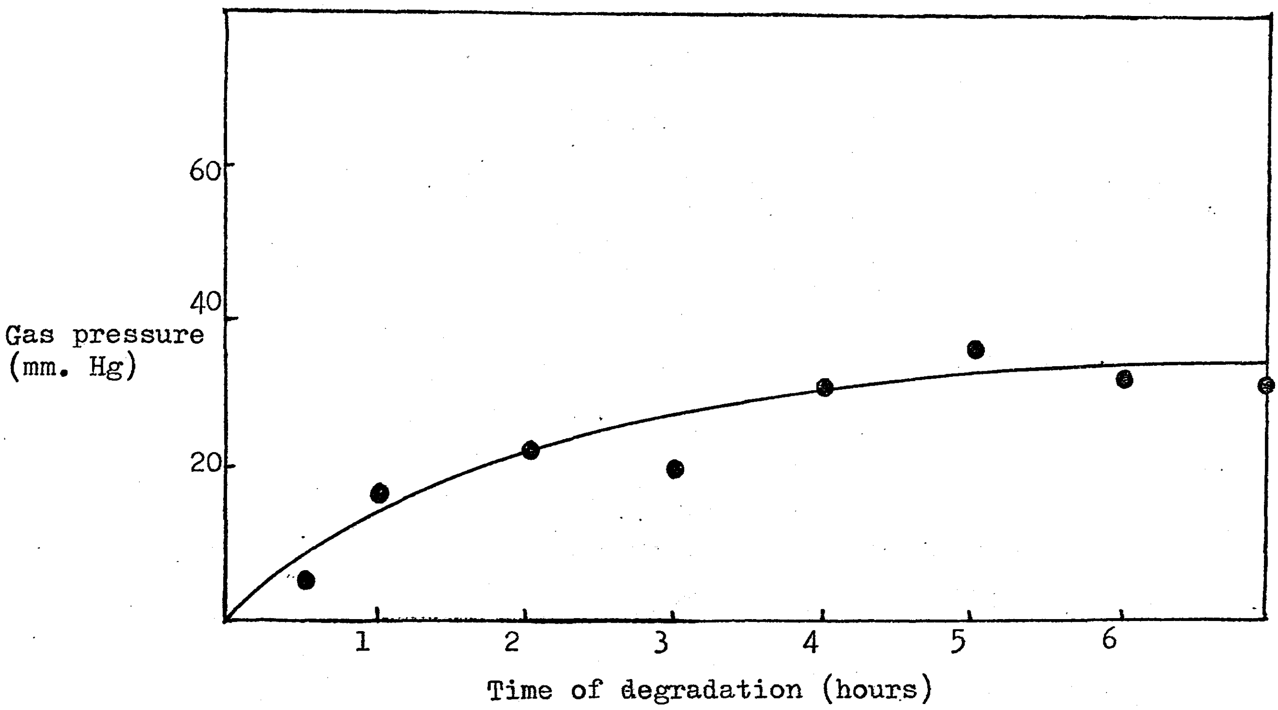


Figure 65. Gas pressures from polybutadiene degradation at 390°C.

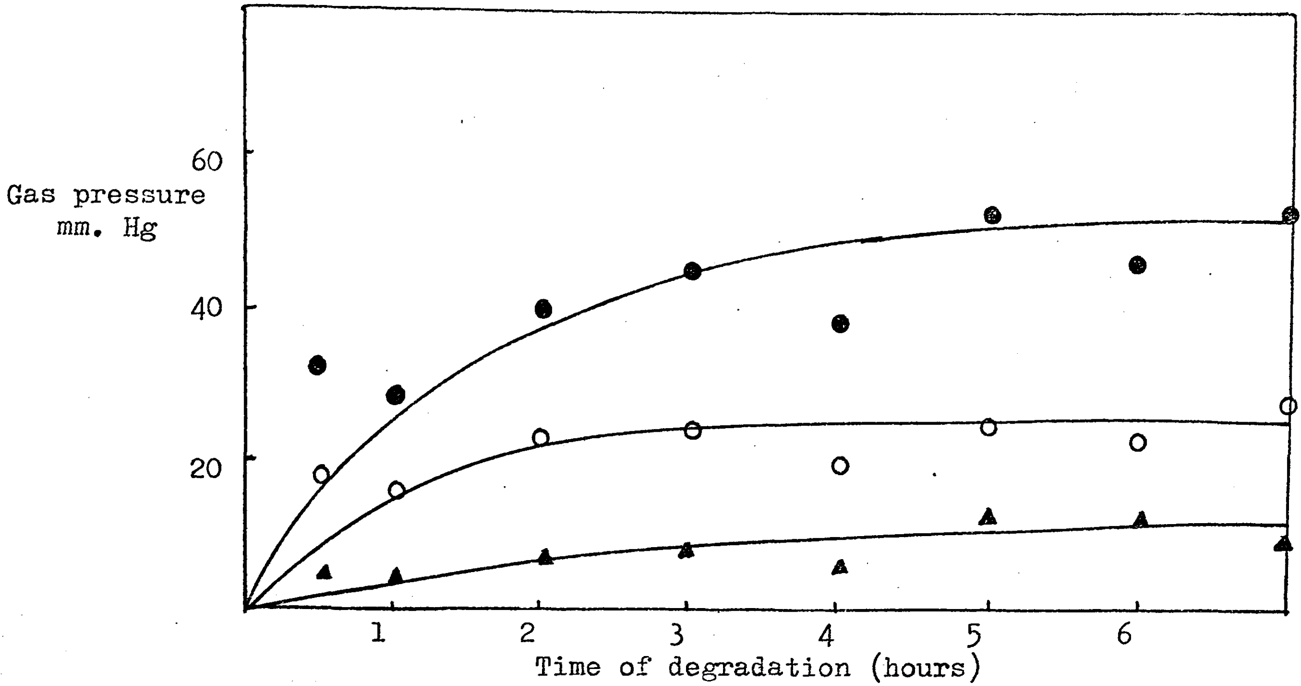


Figure 66. Gas pressures from the degradation of an 80% butadiene polymer at 390°C. (●) total gases; (o) ammonia; (▲) hydrogen cyanide.

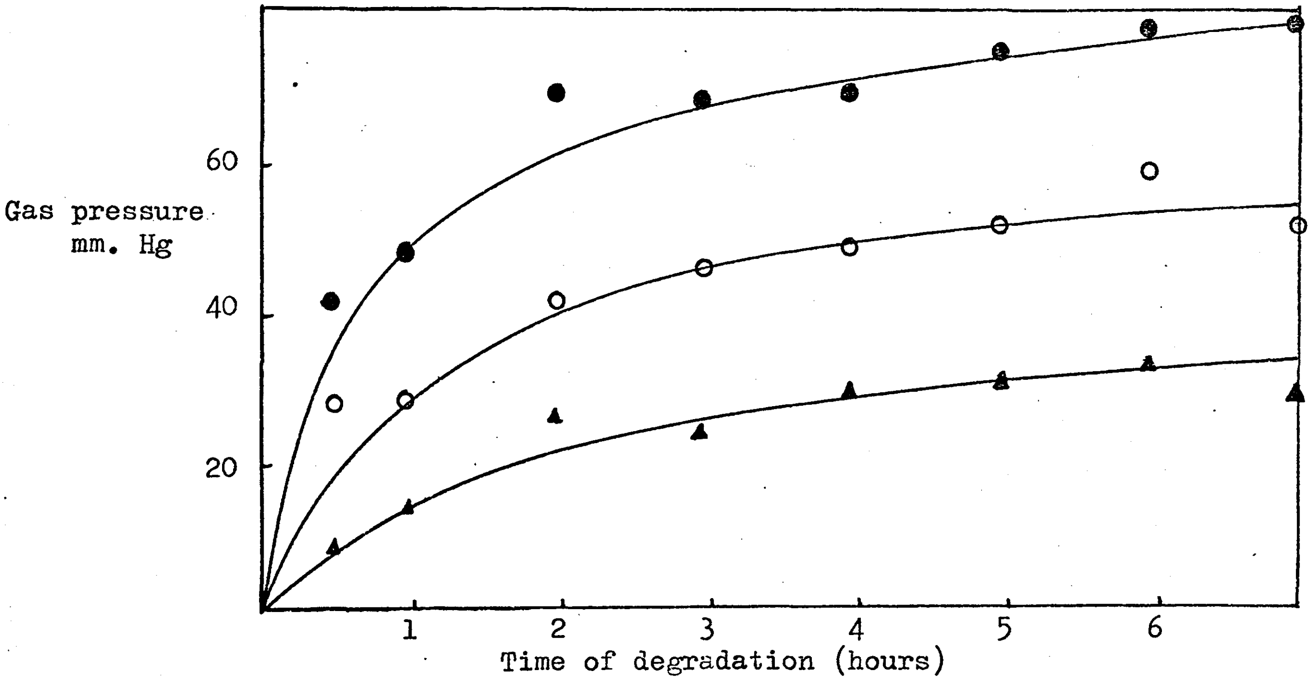


Figure 67. Gas pressures for the degradation of a 66% butadiene polymer at 390°C. For symbols see Figure 66.

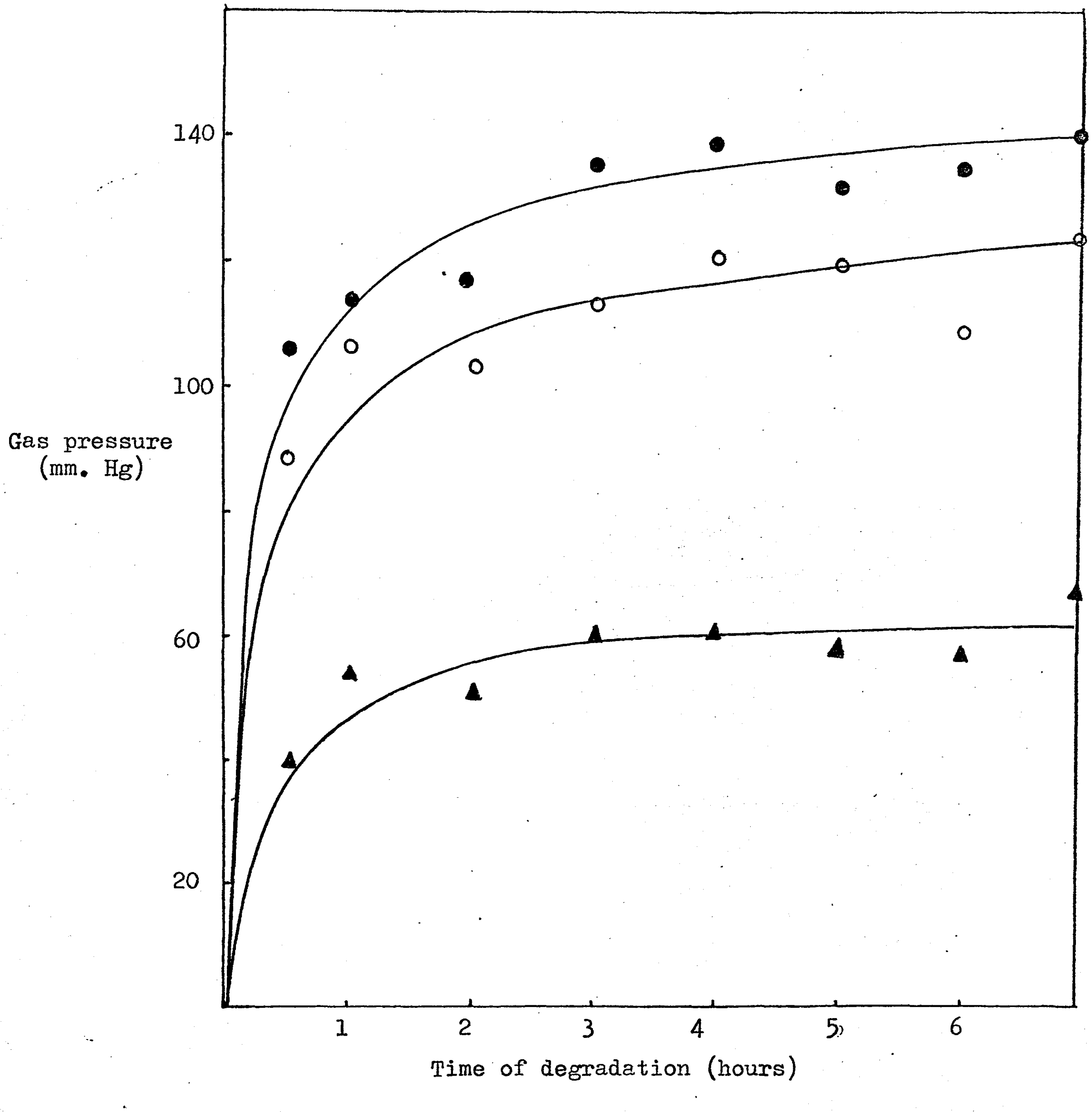


Figure 68. Gas pressures from the degradation of a 41% butadiene polymer. For symbols see Figure 66.

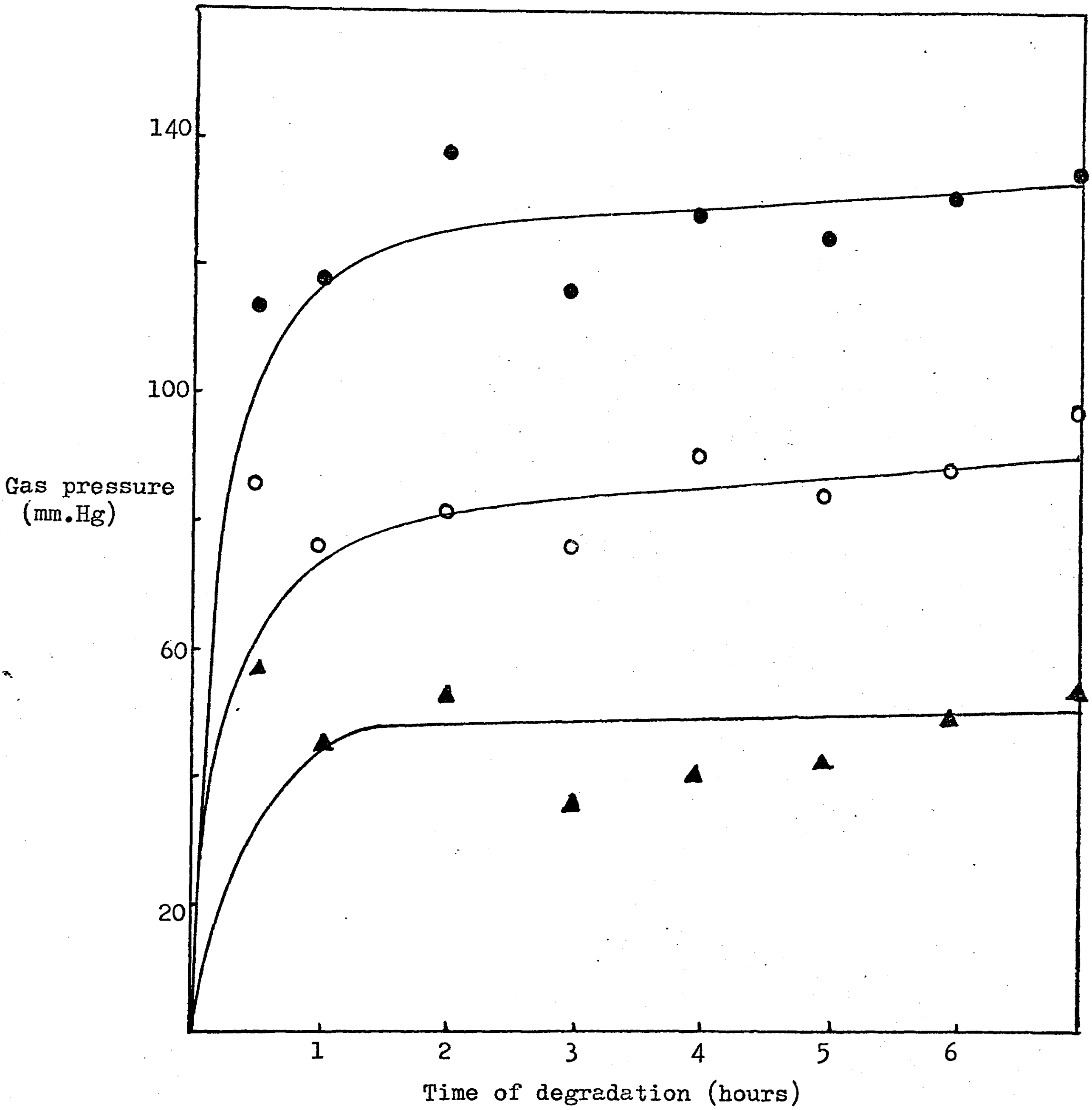


Figure 69. Gas pressures from the degradation of a 25% butadiene polymer. for symbols see Figure 66.

Time (hours)	Total gas pressure (mm. Hg)
0.5	7
1	17
2	24
3	20
4	31
5	36
6	32
7	31

Table 29. Total gas pressures for polybutadiene at 390°C.

Time (hours)	Total gas pressure (mm. Hg)	Ammonia (mm. Hg)	Hydrogen cyanide (mm. Hg)
0.5	32	17.6	4.0
1	28	15.3	3.4
2	40	23.0	6.5
3	45	24.0	8.4
4	38	19.9	5.9
5	53	24.8	12.7
6	46	22.8	11.2
7	53	27.7	7.1

Table 30. Gas pressures for an 80% butadiene polymer at 390°C.

Time (hours)	Total gas pressure (mm, Hg)	Ammonia (mm. Hg)	Hydrogen cyanide (mm. Hg)
0.5	41	27.6	8.4
1	47	27.7	13.2
2	69	41.6	25.7
3	68	45.9	23.6
4	69	48.3	28.8
5	75	51.2	31.0
6	78	59.3	32.7
7	77	51.4	28.3

Table 31. Gas pressures for a 66% butadiene polymer at 390°C.

Time (hours)	Total gas pressure (mm. Hg)	Ammonia (mm. Hg)	Hydrogen cyanide (mm. Hg)
0.5	106	87.6	39.5
1	114	105.5	53.1
2	116	102.3	50.4
3	136	113.0	59.3
4	139	120.3	60.6
5	133	119.2	57.2
6	135	108.3	56.7
7	141	123.1	65.9

Table 32. Gas pressures for a 41% butadiene polymer.

Time (hours)	Total gas pressure (mm, Hg)	Ammonia (mm. Hg)	Hydrogen cyanide (mm. Hg)
0.5	115	86.2	56.9
1	118	76.6	44.6
2	138	82.2	52.4
3	116	76.9	35.1
4	129	91.4	40.4
5	126	85.2	42.2
6	132	89.2	49.8
7	137	98.5	53.2

Table 33. Gas pressures for a 25% butadiene polymer at 390°C.

Ammonia (mm. Hg)	Hydrogen cyanide (mm. Hg)	Total measured pressure (mm. Hg)
18.9	8.9	23.0
41.4	20.9	47.0
63.6	31.7	74.9
81.6	43.5	94.5
104.1	54.5	119.0
126.1	68.0	149.2

Table 34. Individual and combined pressures of ammonia and hydrogen cyanide.

and hydrogen cyanide pressures from the total pressure. However as can be seen from the pressure curves, the sum of the ammonia and hydrogen cyanide pressures approaches close to, or exceeds, the total measured pressure, especially in the case of the 41% butadiene polymer. This effect has been reported in the production of gases during decomposition of methyl methacrylate/butyl acrylate copolymers[99].

It was decided to carry out an investigation into the possible gas phase association of ammonia and hydrogen cyanide which might lead to a decrease in overall pressure.

The constant volume manometer (fig. 6) described in chapter 2 was used, only after an additional cold finger (I) had been added between the manometer and the existing cold finger (II). Initially a certain pressure of the first gas was introduced into the constant volume (which did not include cold finger II). The gas was then condensed into cold finger II and the tap to this finger was closed. The required pressure of the second gas was then introduced into the constant volume. Both gases were then condensed into cold finger I, and allowed to evaporate together into the constant volume after closing finger II. The combined pressure could then be read accordingly.

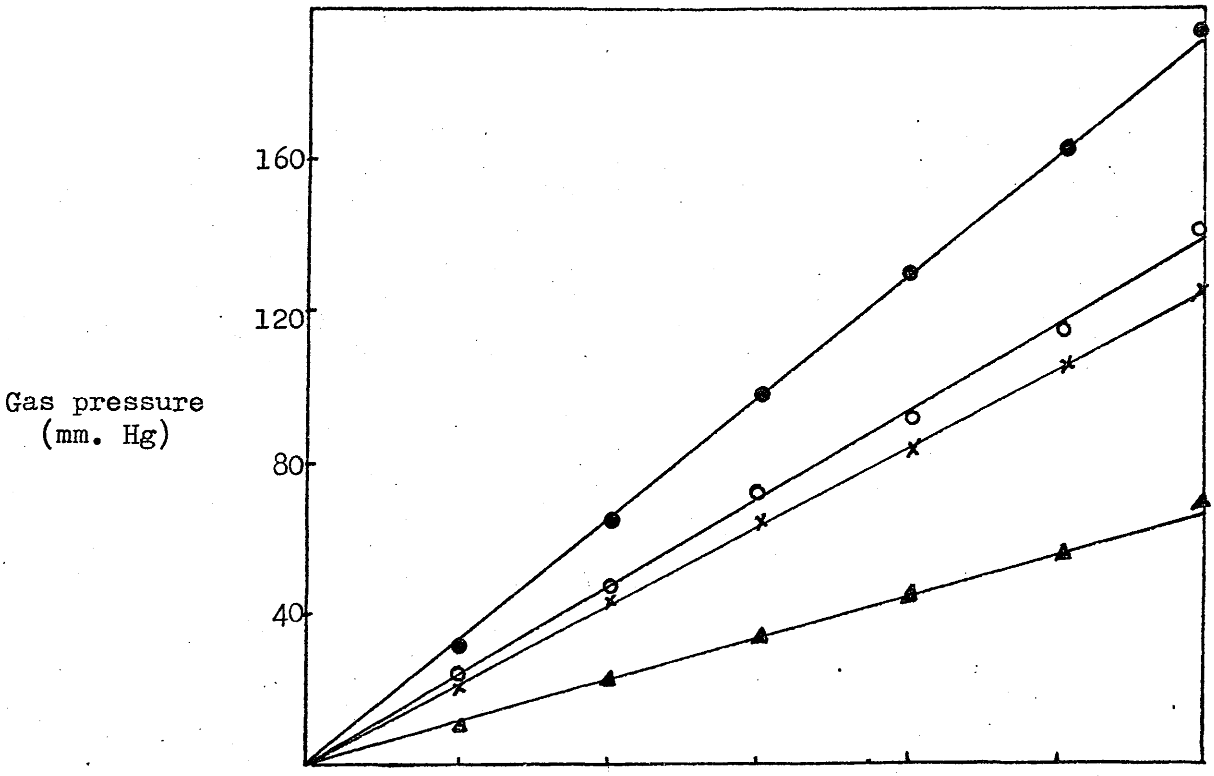
From the data of figures 66-69 it can be seen that the ratio of ammonia to hydrogen cyanide is approximately 2:1 over the copolymer range, therefore a range of pressures of ammonia and hydrogen cyanide were studied, with the ratio maintained about 2:1. Figure 70 (table 34) shows the results obtained, illustrating that there is a definite association in the gas phase between ammonia and hydrogen cyanide. The reduction in overall pressure is seen to be in the region of 26% and this deviation is not affected by increasing overall pressure, provided the ratio NH_3:HCN remains about 2:1. A series of determinations was carried out over the mole fraction range of ammonia to determine at which molar ratio, the deviation is at a maximum. The results are shown in figure 71 (table 35) and it can be seen that a maximum reduction in overall pressure of about 30% occurs when the molar ratio is 2:1 in favour of ammonia. Thus, two molecules of ammonia associate with one molecule of hydrogen cyanide in such a way as to reduce overall pressure, without removing the identity of the individual molecules, since the total pressures as measured by infra-red calibration are, in fact, as expected, therefore the total pressure readings in figures 66-69 are meaningless.

As the butadiene content of the polymers decreases, the amounts of ammonia and hydrogen cyanide are seen to increase accordingly, however with the 25% polymer the amount of gaseous material decreases. This is interpreted in terms of the acrylonitrile content in the copolymer being high enough to permit the retention of nitrogen containing structures in the polymer by their taking part in the stabilisation which occurs very rapidly with this polymer, or that the reactions producing ammonia and hydrogen cyanide are suppressed in some other way.

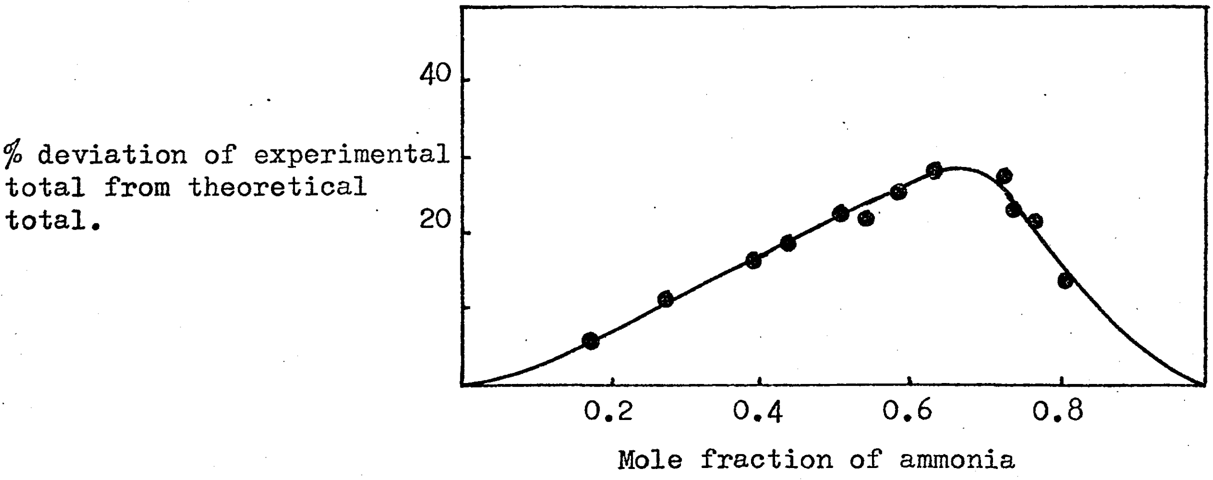
As mentioned previously, the ratio of ammonia to hydrogen cyanide remains in the region of 2:1 for the copolymers, except that with the 80% butadiene polymer the ratio is in the region of 5:1 at the beginning of degradation and falls off to about 3:1 after three hours degradation, and never reaches 2:1. This may indicate preference for ammonia production in those polymers of low acrylonitrile content, and further, that hydrogen cyanide production lags behind that of ammonia.

6.4 Pyrolysis at 355°C.

Pyrolysis experiments were carried out on a 52% butadiene polymer at 355°C for comparison and the data obtained is presented in figures 72 and 73 (tables 36, 37). This was done in order to provide some



<u>Figure 70</u>. Individual and combined pressures of ammonia and hydrogen cyanide (×) ammonia; (▲) hydrogen cyanide; (●) theoretical total; (o) experimental total.



<u>Figure 71</u>. Pressure deviations in ammonia - hydrogen cyanide mixtures.

Mole fraction of ammonia	deviation as % of theoretical total
0.181	4.92
0.286	11.44
0.398	15.69
0.452	18.50
0.520	23.05
0.550	22.40
0.597	25.80
0.637	29.00
0.733	27.80
0.755	23.00
0.780	21.90
0.815	13.80

Table 35. Pressure deviations in ammonia – hydrogen cyanide mixtures.

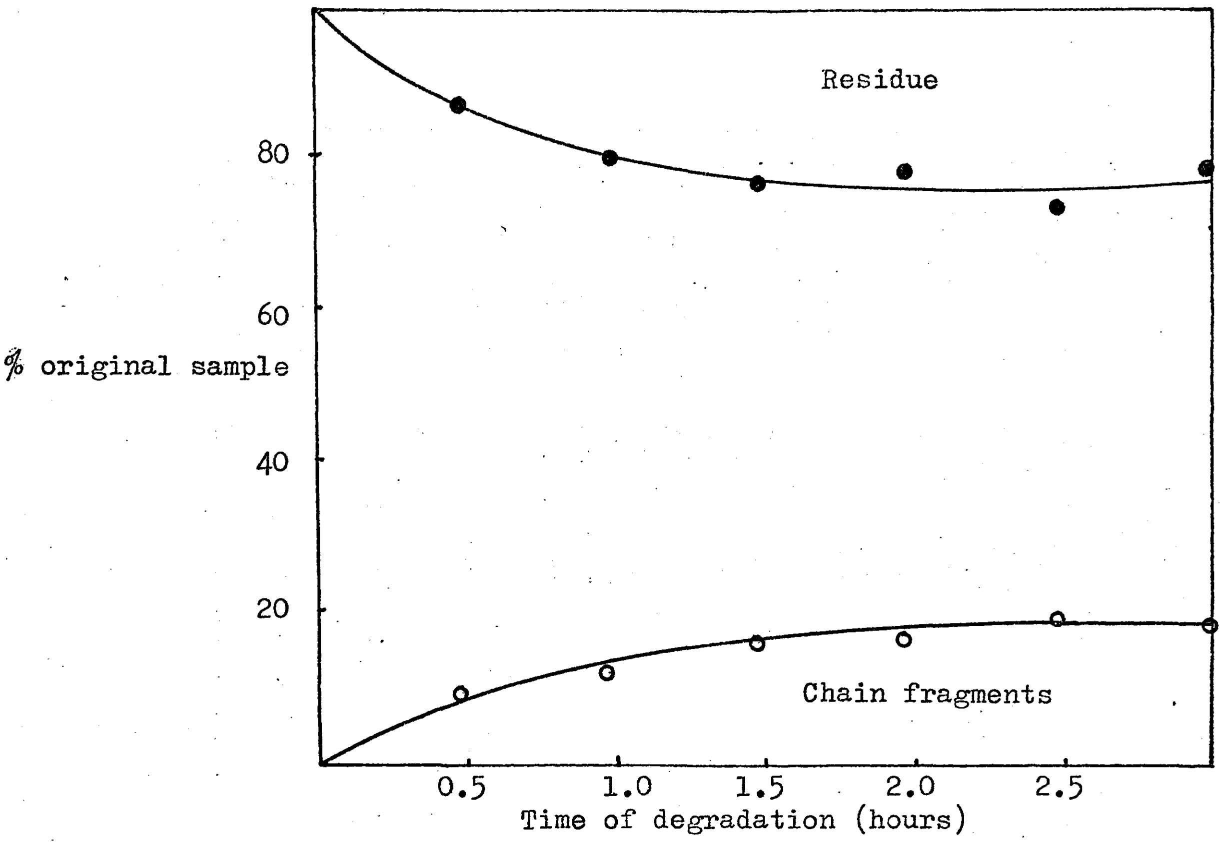


Figure 72. Residue and chain fragments plots for a 52% butadiene polymer at 355°C.

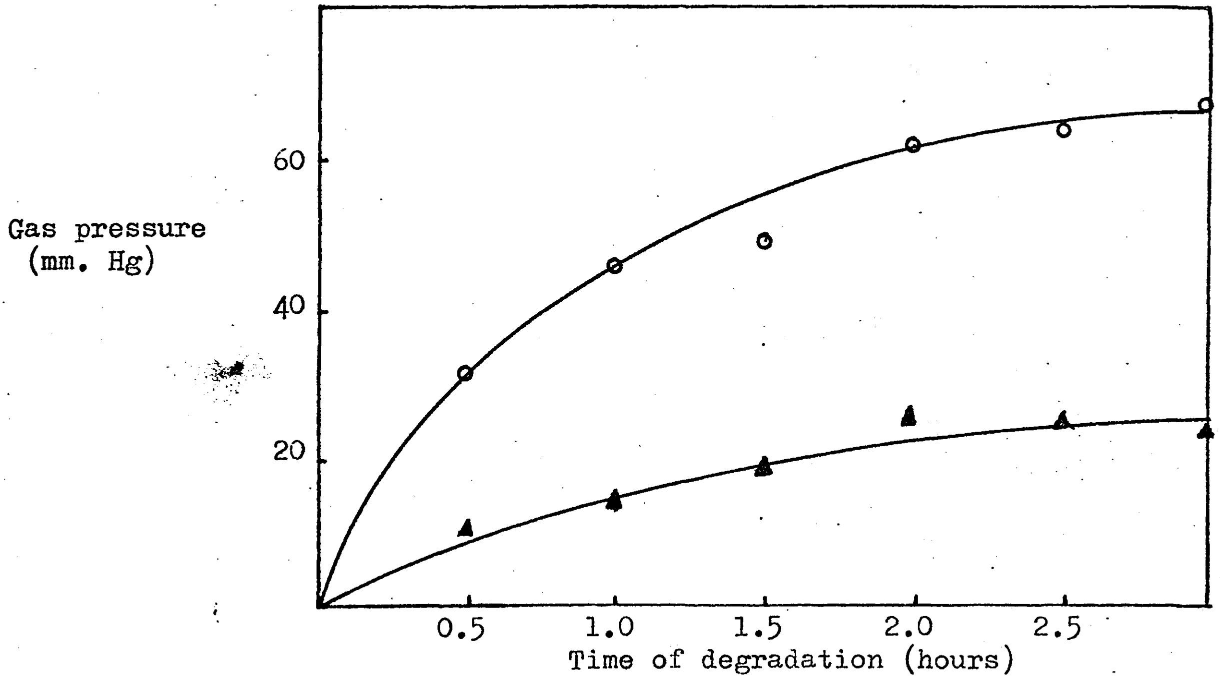


Figure 73. Gases from a 52% butadiene polymer at 355°C. (o) ammonia; (▲) hydrogen cyanide.

Time (hours)	% original polymer sample	
	Residue	Chain fragments
0.5	88.0	9.2
1.0	80.8	12.0
1.5	77.5	16.1
2.0	78.8	17.0
2.5	74.0	19.4
3.0	72.0	18.6

Table 36. Degradation data for a 52% butadiene polymer at 355°C.

Time (hours)	Ammonia (mm. Hg)	Hydrogen cyanide (mm. Hg)
0.5	30.0	9.0
1.0	44.5	12.5
1.5	48.0	17.5
2.0	60.5	24.5
2.5	63.0	24.0
3.0	66.0	22.0

Table 37. Gas pressures for a 52% butadiene polymer at 355°C.

detailed information about the production of ammonia and hydrogen cyanide over the first 25% weight loss. The hydrogen cyanide curve is clearly very shallow and almost linear over the initial stages, whereas the ammonia curve is similar in shape to those of the high temperature degradations. However hydrogen cyanide and ammonia are produced from the start of degradation as shown by the pyrolysis of a sample of 80% butadiene polymer for 21 hours at 260°C, which gave 1% volatile material including trace ammonia and hydrogen cyanide.

The weight loss curve of the 52% butadiene polymer did not conform either to first or second order kinetics.

CHAPTER SEVEN

Vinyl Group Studies

The results presented so far refer to the pyrolysis of polymers at 390°C. However, as indicated in chapter 5, rapid loss of unsaturation occurs at this temperature and thus the polymers are greatly modified before major weight loss and product evolution occur. It is therefore necessary to have some knowledge of the nature of this modification before attempts can be made to analyse high temperature data.

The loss of unsaturation at high temperatures is accompanied by insolubility and brittleness, and in the case of the nitrile containing polymers by the appearance of colour at the yellow end of the spectrum. At temperatures in the region of 260°C heat treatment for twenty hours in vacuum caused less than 1% weight loss, but insolubilit brittleness and colour also occur, and it appears that only vinyl groups disappear from the polymer. At 200°C no change is detectable in the infra-red, but the polymers are tougher and, in the case of the copolymers, slightly coloured. At 160°C no change of any kind was detected over a period of 40 hours. 230°C was chosen as a suitable temperature for studying the loss of unsaturation since at this temperature the reaction seems to proceed at a measurable rate.

TVA analysis was carried out on a sample of polybutadiene pre-heated at 230°C for 48 hours in vacuum. The trace obtained is shown in figure 74. Comparison with the trace for non pre-heated polybutadiene (figure 29) shows that the peak maxima have not changed, but a shoulder appears in the pre-heated sample at 408°C. Comparison of the TGA thermograms of the non pre-heated and pre-heated samples indicated that in the region of 400°C the rate of weight loss is slightly higher for the pre-heated sample although above this temperature the rates of weight loss are virtually identical. No change was noted in the exothermicity of degradation as measured by D.S.C. over the range up to 500°C. The only change noted in the infra-red spectrum of the pre-heated sample, was the loss of intensity in the peaks due to vinyl groups.

The following investigation was carried out to determine whether other unsaturation (including nitrile groups in the polymers) plays any part in the low temperature reaction.

A thin film of copolymer containing 75% butadiene and 25% acrylonitrile was cast between two salt plates fitted with a 0.007" lead spacer. The modified cell heater, which was discussed in chapter 2 (figure 8) was used. During heat treatment at 230°C, the infra-red spectrum of the polymer was recorded at 1 hour intervals up to 5 hours and thereafter at various intervals up to 96 hours. Structures indicative of oxidative attack did not appear in the infra-red until the 28 hour scan. Figure 75 shows a comparison of the infra-red spectra

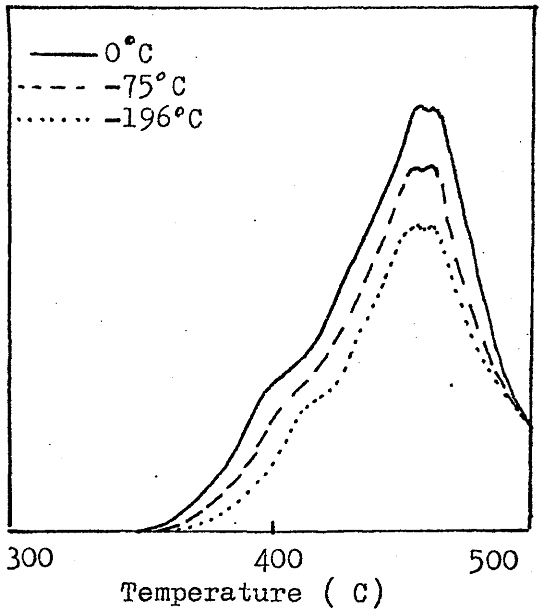


Figure 74. TVA thermogram of polybutadiene pre-heated at 230°C for 48 hours.

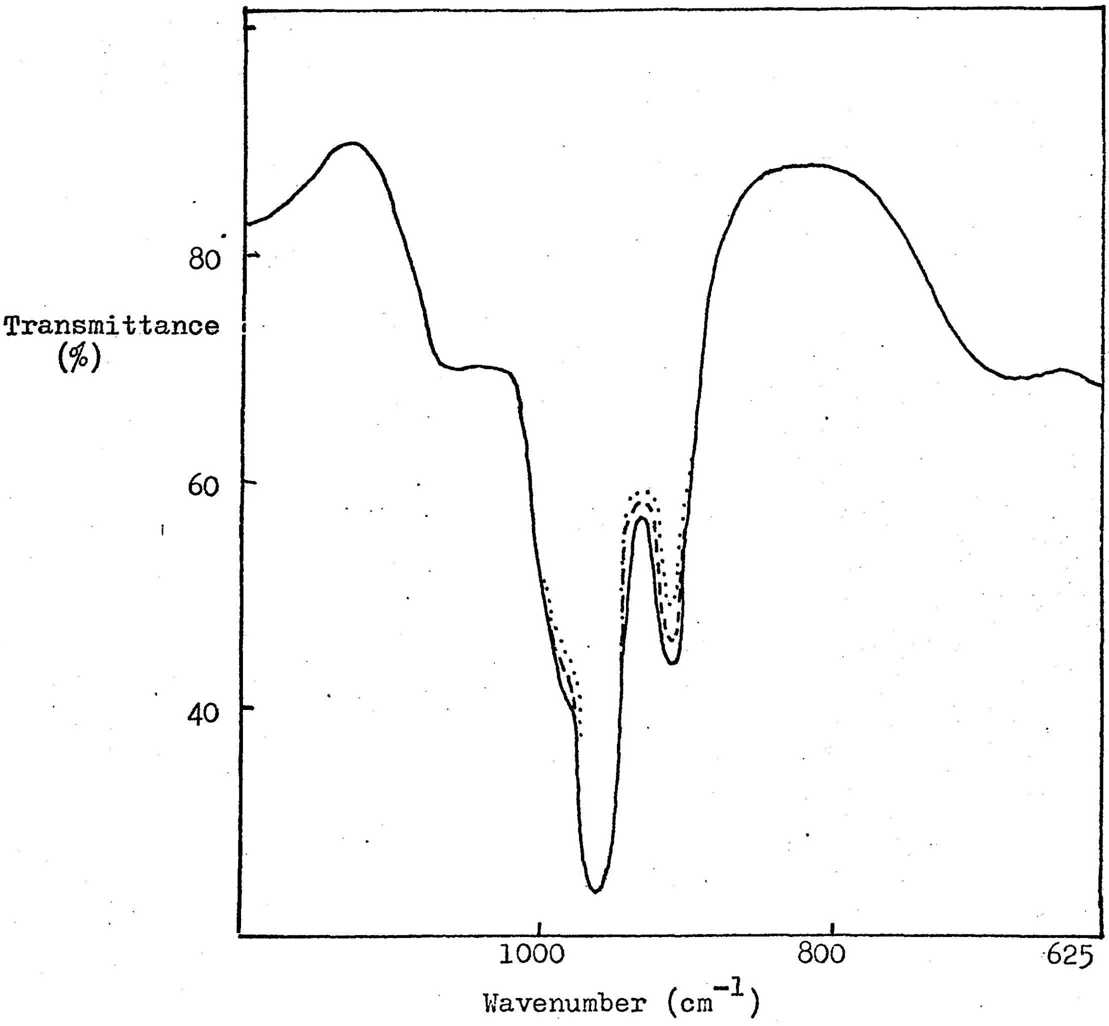


Figure 75. I.R. spectra of a 75% butadiene polymer heated at 230°C.
——— original polymer; - - - after 12 hours;
.... after 24 hours.

obtained up to 24 hours after the beginning of heat treatment. The gradual reduction in intensity of the vinyl peaks at 990 and 908cm^{-1} can be seen. No change can be detected in those absorptions due to trans and cis structures at 962 and 750-650cm^{-1} respectively. Nor was there any change in the intensity of the nitrile group resonance at 2240cm^{-1} over 24 hours.

It can be concluded then that at 230°C these polymers slowly loose vinyl group unsaturation only, the nitrile, cis and trans unsaturation remaining unaffected. The loss of vinyl groups, is not accompanied by the formation of any other structures identifiable in the infra-red.

After heating for 28 hours oxygenated structures began to appear in the infra-red, but no immediate effect was noted in the nitrile, cis, or trans absorptions, it was only after some 40 hours treatment that these absorptions began to diminish slightly. However even after 96 hours at 230°C when oxygenated structures were prominent, the drop in intensity of the cis, trans and vinyl absorptions was small in comparison to that of the vinyl group absorptions which had by then almost disappeared. Since the autoxidation of olefins does not concern unsaturation to any notable extent, the changes in the infra-red noted above are understandable.

Detailed studies were carried out on the disappearance of vinyl unsaturation in the manner described in chapter 2, using the trans group absorption at 962cm^{-1} as an internal standard. Separate films were used for each of the runs, which were carried out over periods up to 100 hours. The ratio of vinyl group absorbance to trans group absorbance ($^{V}/T$) for each of the untreated polymers was claculated by averaging the $^{V}/T$ ratios of at least ten polymer films. These average values are given in table 38. All other $^{V}/T$ determinations were converted to a percentage of the untreated $^{V}/T$ ratio for a given polymer.

% butadiene in polymer	V/T Average (untreated)
100	0.454
89	0.336
80	0.245
75	0.272
66	0.317

Table 38. Average values of V/T ratios.

Time		% vinyl groups remaining				
(hours)	% butadiene:	100	89	80	75	66
4		91	85	95	85	94
8		91	85	82	76	89
12		80	77	78	74	66
16		72	75	73	84	77
20		73	69	75	70	72
24		74	75	59	57	62
31		64	57	65	60	69
40		50	53	54	52	62
48		40	39	56	51	52
96		25	32	24	39	42

Table 39. Vinyl group loss in the polymers at 230°C.

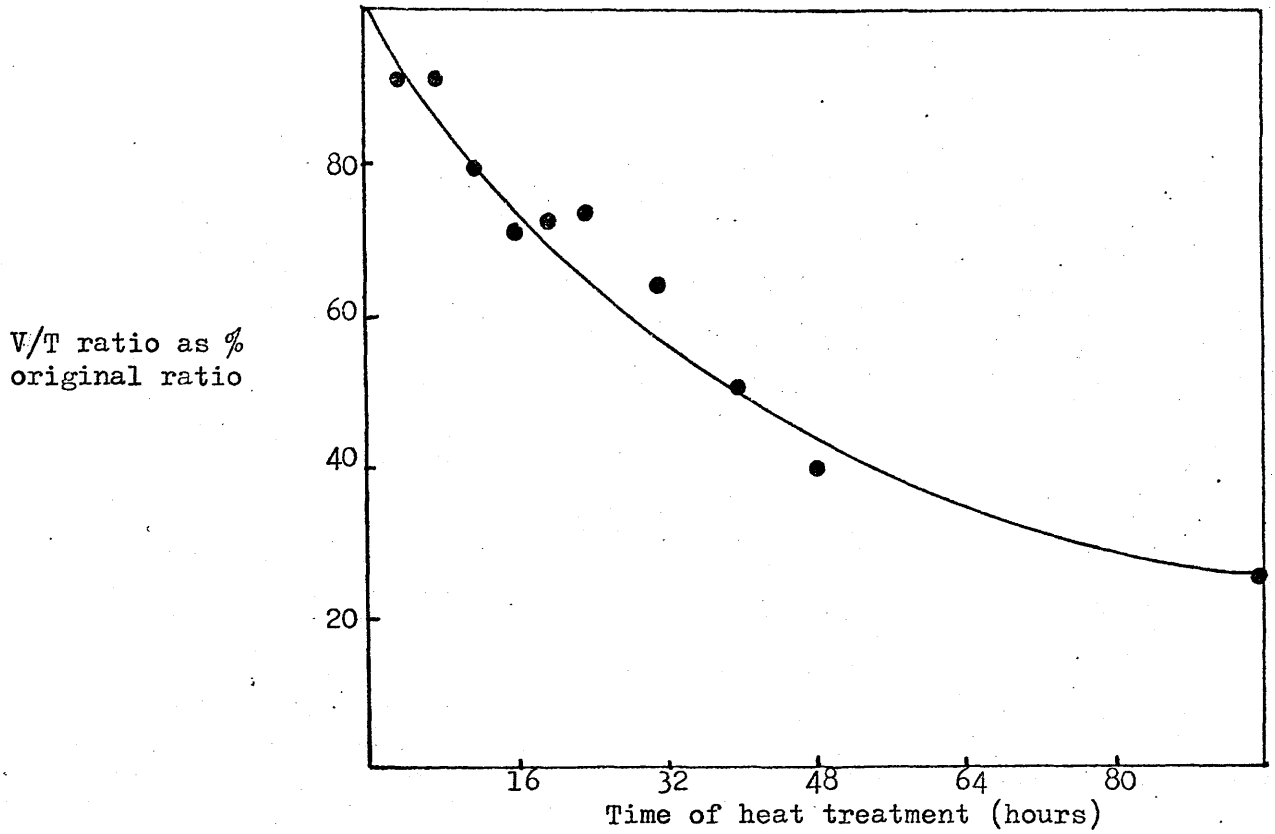


Figure 76. Loss of vinyl groups in polybutadiene at 230°C.

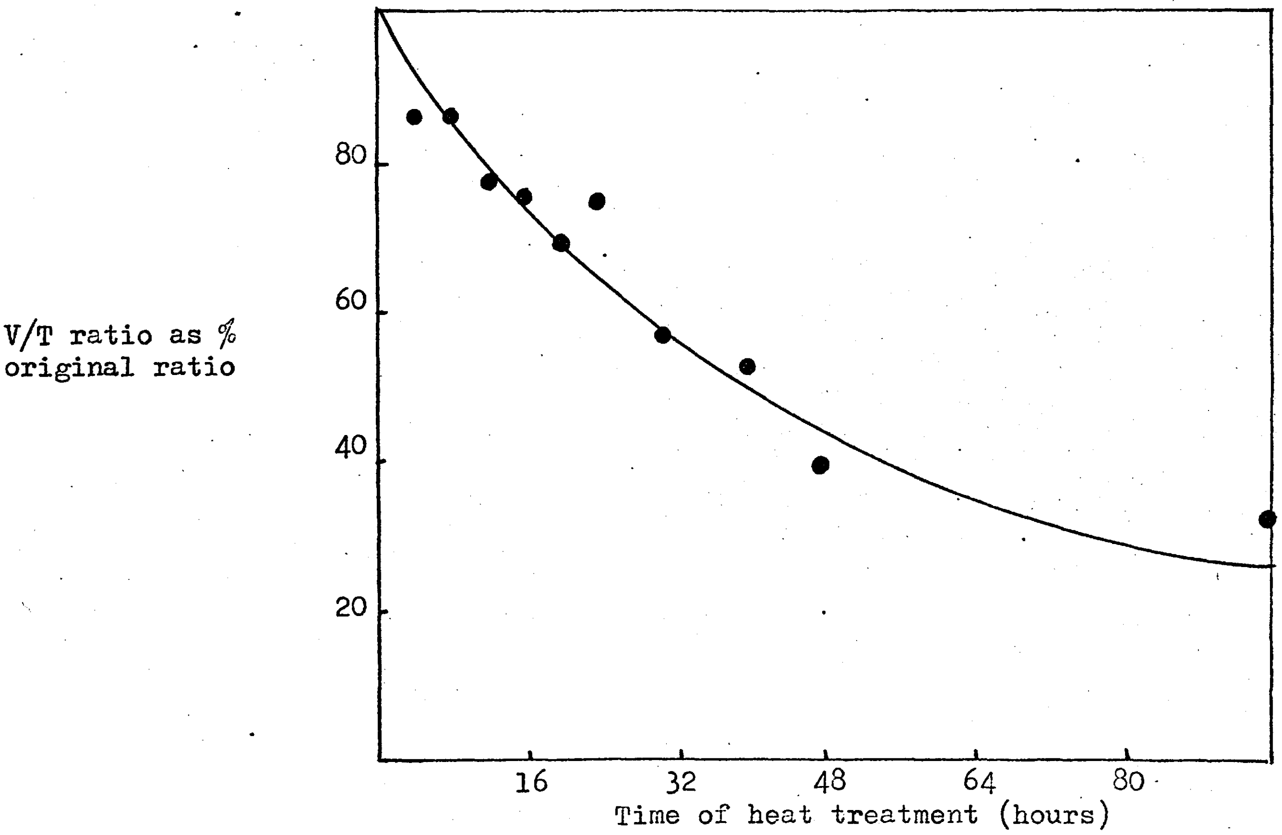


Figure 77. Loss of vinyl groups in an 89% butadiene polymer at 230°C.

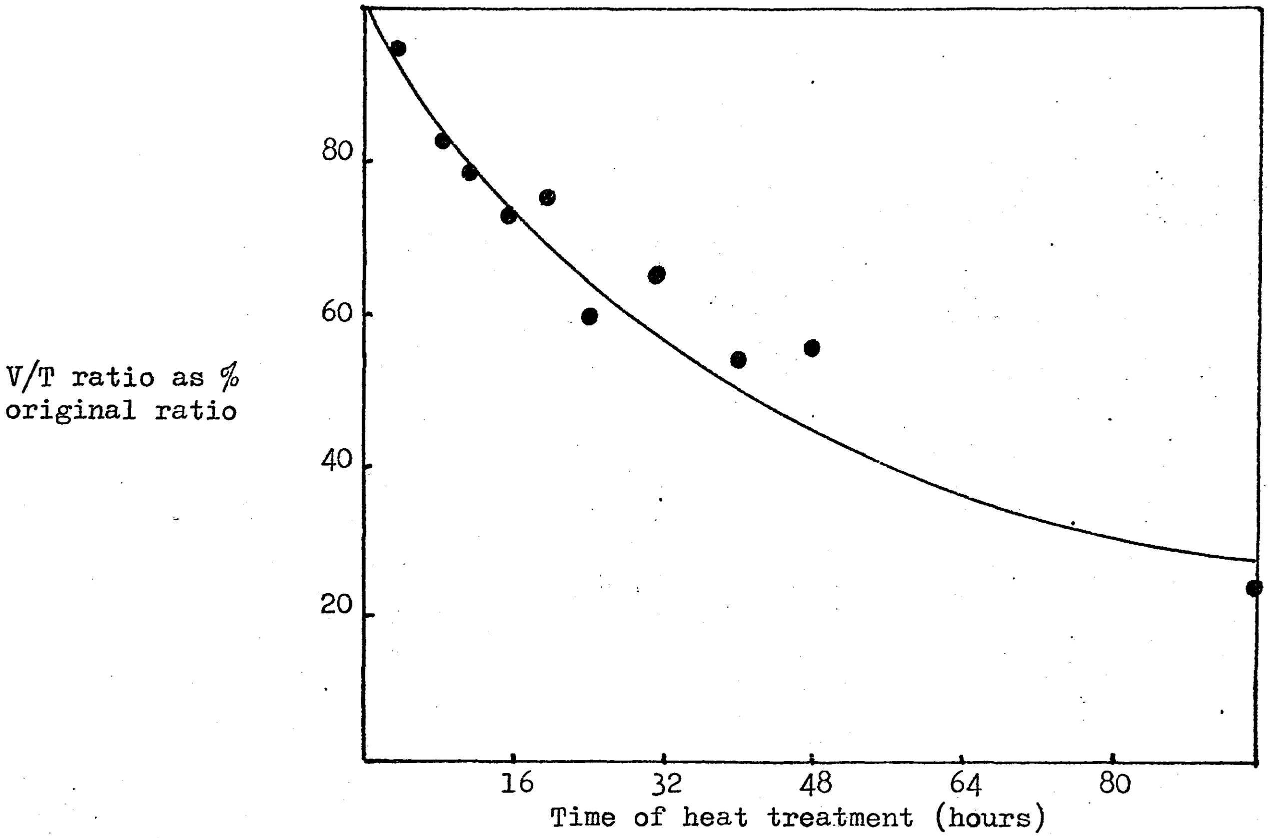


Figure 78. Loss of vinyl groups in an 80% butadiene polymer at 230°C.

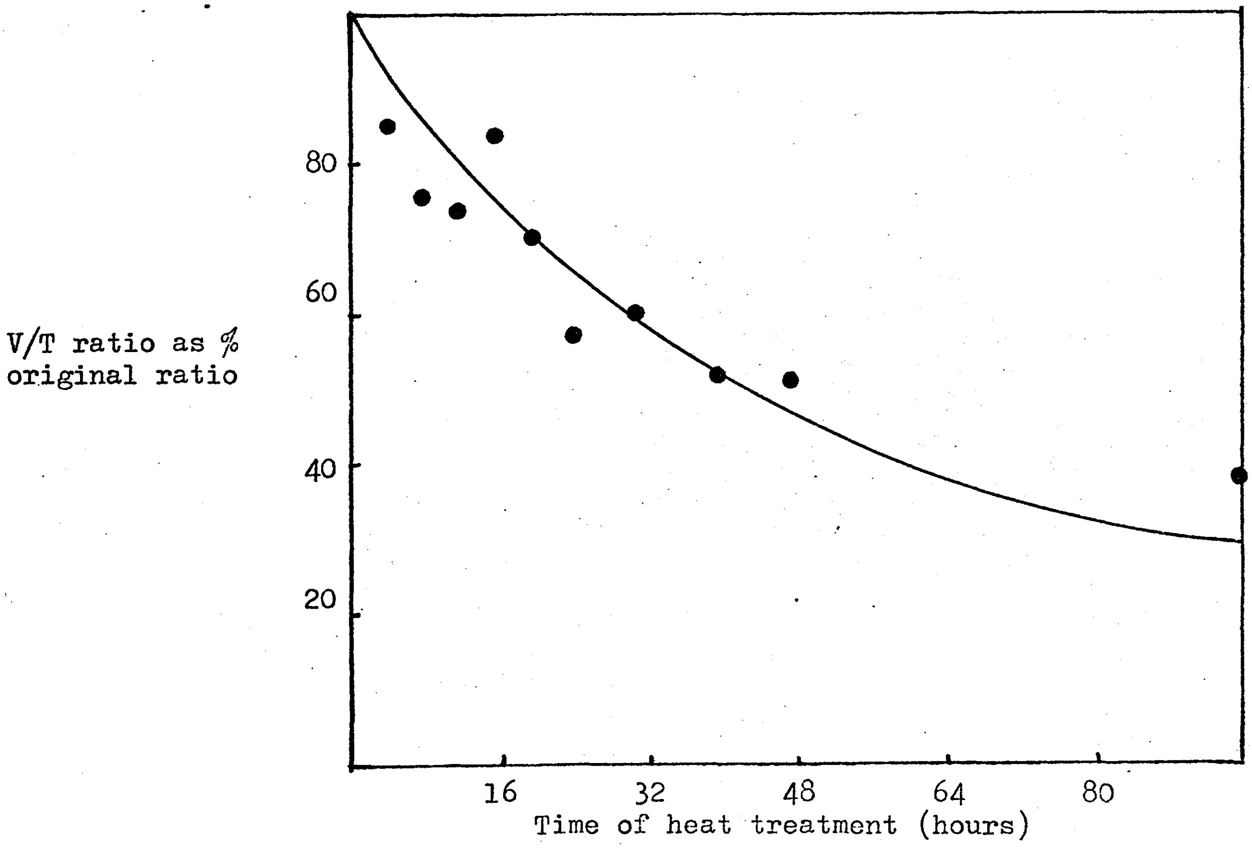


Figure 79. Loss of vinyl groups in a 75% butadiene polymer at 230°C.

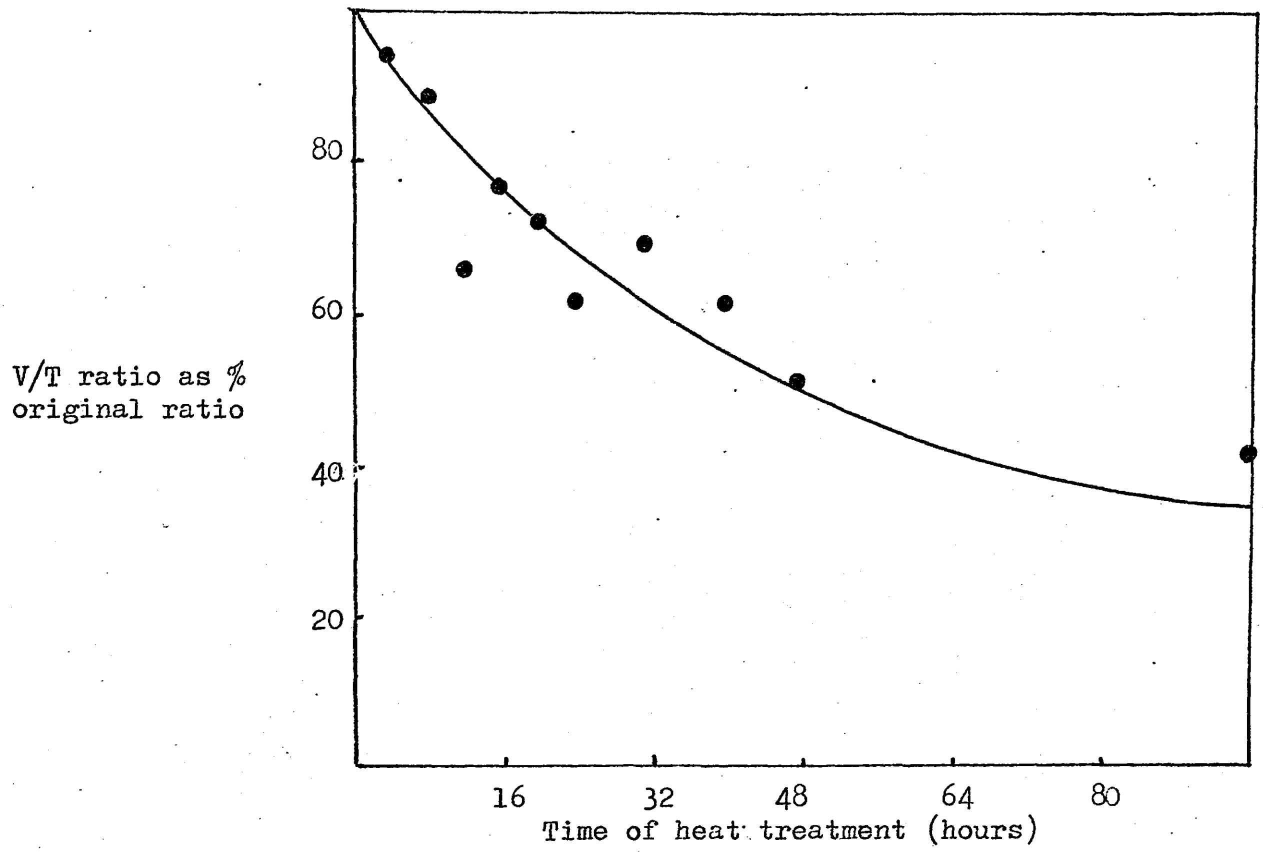


Figure 80. Loss of vinyl groups in a 66% butadiene polymer at 230°C.

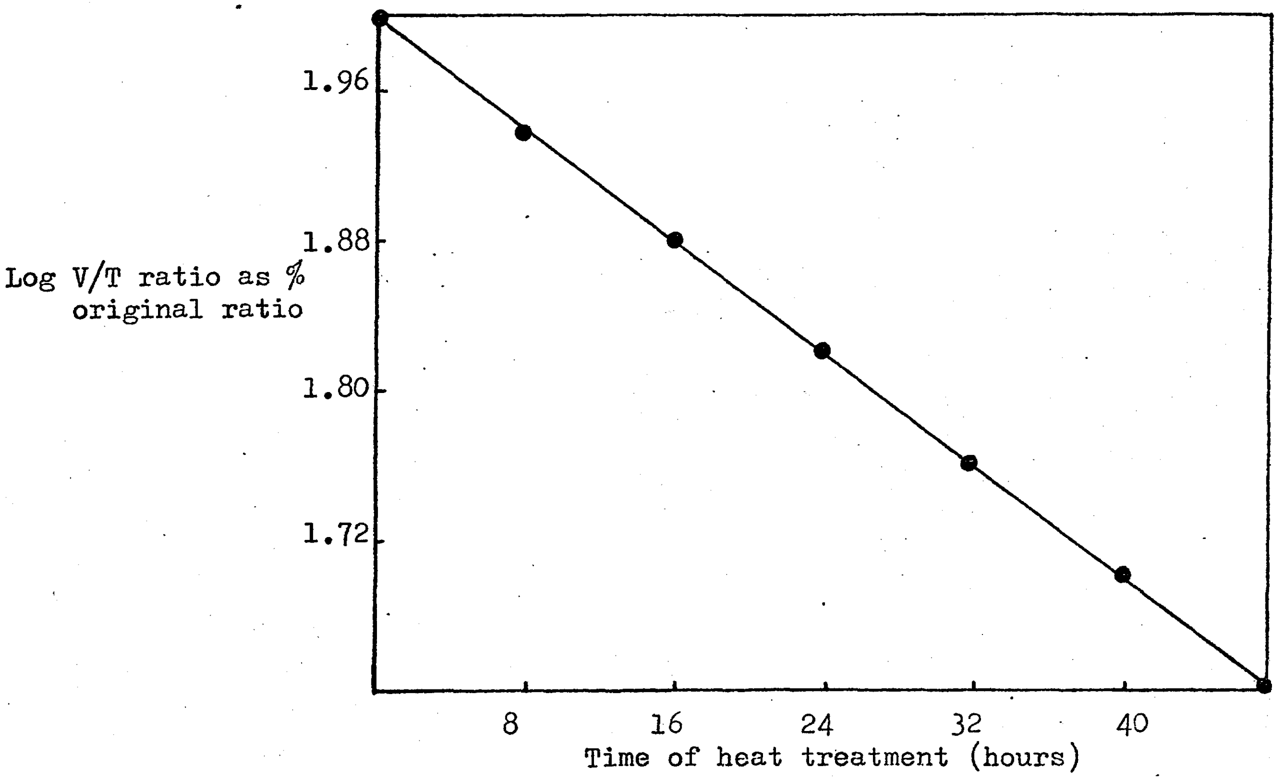
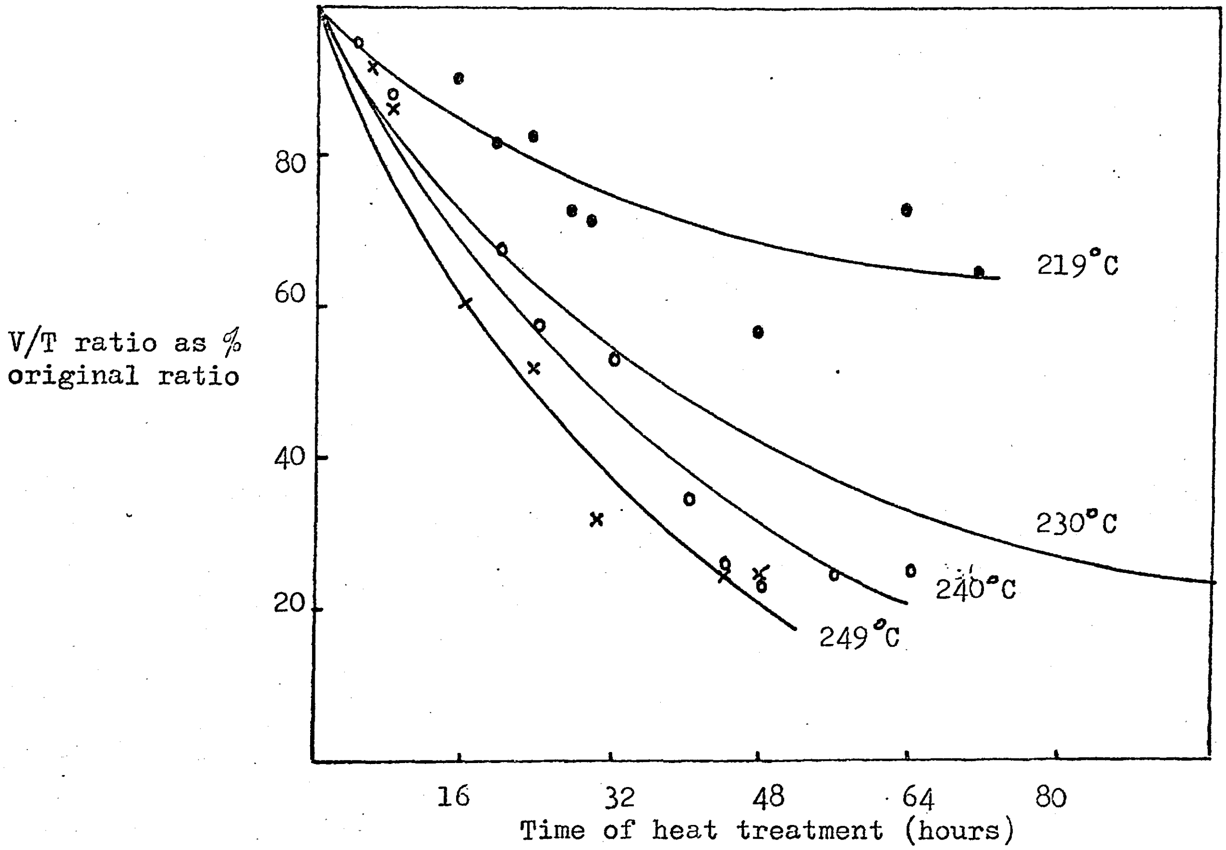
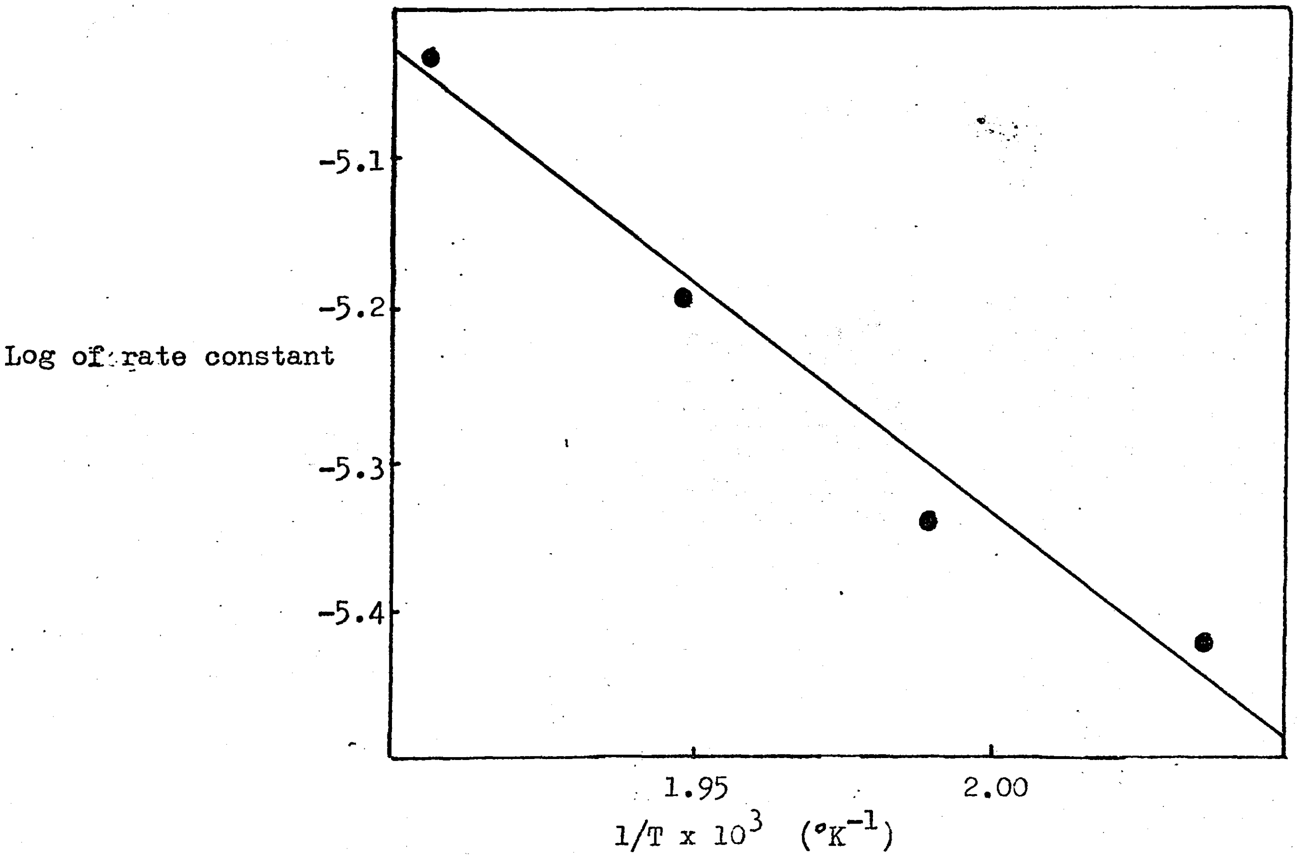


Figure 81. First order plot for vinyl group loss at 230°C.



<u>Figure 82.</u> Loss of vinyl groups in polybutadiene at several temperatures.



<u>Figure 83.</u> Activation energy plot for loss of vinyl groups.

Time		% vinyl groups left		
(hours)	Temperature(°C)	219	240	249
4		—	95	—
6		—	—	—
8		—	88	86
16		90	—	60
20		82	68	—
24		83	—	50
28		73	58	—
30		72	—	32
32		—	54	—
40		—	35	—
44		—	27	25
48		57	24	25
56		—	25	—
64		73	26	—
72		65	—	—

Table 40. Vinyl group loss for polybutadiene at several temperatures.

Temperature(°C)	Rate constant (k) x 10^6 (secs^{-1})
219	3.86
230	4.70
240	6.43
249	9.32

Table 41. Rate constants for vinyl group loss in polybutadiene.

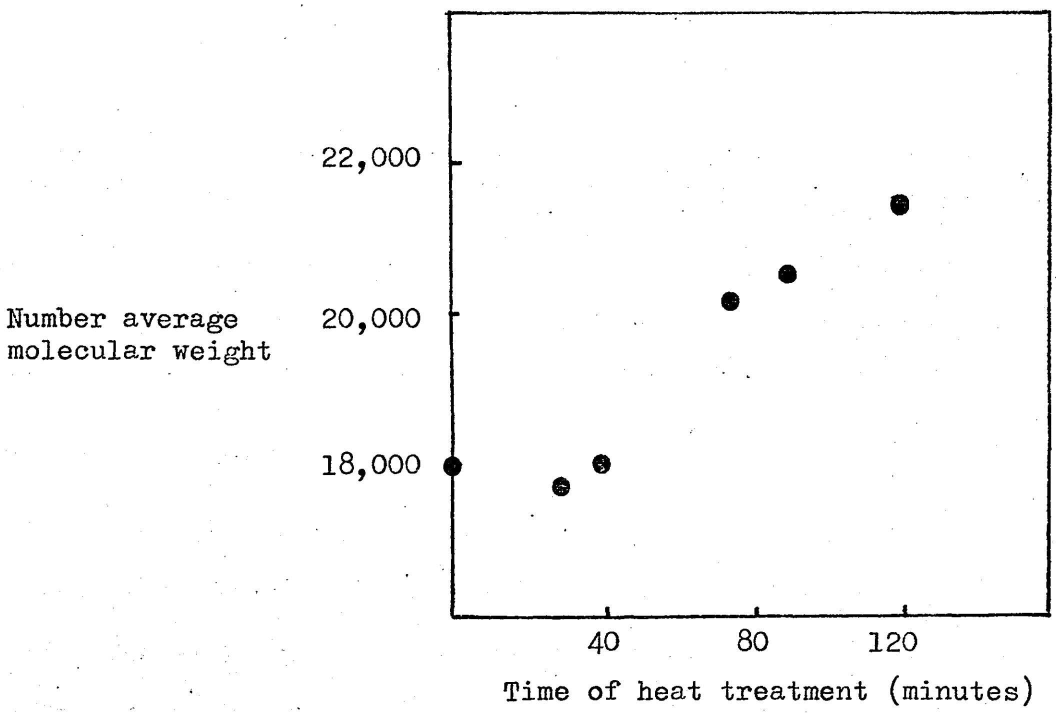


Figure 84. Molecular weight increase in polybutadiene at 230°C.

Figures 76-80 (table 39) show the vinyl loss curves for the range of polymers studied. They are clearly virtually identical over the first 50% loss in vinyl concentration. and, since these polymers differ in the initial concentration of vinyl groups (chapter 3), this result points to the vinyl loss pattern conforming to first order kinetics. The vinyl loss curves of all the copolymers were tested for first and second order kinetics and found to be strictly first order as shown in Figure 81.

Activation energy studies were carried out on polybutadiene, in the hope that some further insight into the reaction might be obtained. The vinyl group concentration was followed at 219°C, 240°C, and 249°C and the results obtained are shown in figure 82 and table 40, together with those obtained previously at 230°C. The increase in rate of reaction with increasing temperature is clearly seen. Each of the curves was found to conform to first order kinetics over the first 48 hours, although some slight deviations in the first few hours and above 40 hours could be seen. From each of the first order plots, a rate constant was calculated as in table 41.

An Arrhenius plot for this data is shown in figure 83. From this an activation energy of 15.0 K.cals./mole was calculated.

Some molecular weight studies were carried out on a sample of polybutadiene heated at 230°C in vacuum for periods up to 2½ hours. At this time gelling had occured and no further molecular weights could be measured. Results are recorded in figure 84 over the first 2 hours. The conclusion is that the loss of vinyl unsaturation in these polymers at 230°C is a reaction which involves an increase in molecular weight of the polymer, that is, some kind of cross-linking reaction.

Studies were carried out using free-radical inhibitors to determine whether or not the reaction is molecular or radical in nature. The following inhibitors were used:

Diphenyl picryl hydrazyl (DPPH).

1-4 Diamino anthraquinone (DAAQ).

2, 2' - Methylene - bis (4, ethyl - 6 tertiary butyl phenol) (MBP)

Vinyl loss curves were obtained as before in presence of each of these inhibitors. Runs were carried out over periods up to 76 hours at 230°C on polybutadiene samples containing inhibitor concentrations of 0.005%, 0.01%, 0.05%, 0.1%, 0.15% W/W. As a result of these investigations no effect whatsoever was observed on the rate at which vinyl groups disappear from the polymer. However, it was considered possible that this might be due either to instability of the inhibitors at 230°C or to the fact that they might volatilise fromthe polymer films at this temperature. Tests showed that DPPH does decompose slowly at this temperature, but that DAAQ and MBP are stable. Both these inhibitors were volatile to some extent at 230°C in vacuum, but further tests indicated that when trapped in a polymer film between two salt plates, there was no tendency to volatilise. However determinations were carried out in which large quantities of inhibitor were placed in the degradation tube with a polybutadiene film also containing inhibitor. This was done to create a pressure of gas phase inhibitor, in the event that there might be some undetectable volatilization out of the film of polymer. The results of these tests failed to show any inhibition of the vinyl reaction, and it was therefore concluded that the reaction is non-radical in nature.

CHAPTER EIGHT

REVIEW

8.1 The Degrading Species.

Investigations into the mode of polymerisation, the distribution of monomer sequences and types of unsaturation have provided a fairly reliable picture of the structures of the present polymers and copolymers.

A new set of reactivity ratios has been calculated and shown to be in agreement with those obtained by Vaille and co-workers[66], who have studied the copolymerisation of butadiene and acrylonitrile in dimethyl formamide solution. However Vaille has presented evidence for penultimate and anti-penultimate unit effects in this system, which have not been observed in the bulk polymerisation of these monomers in the present work. It is thus most likely that the effects noted by Vaille are in some way due to the influence of solvent.

Sequence distribution analysis has been applied successfully to this system, and has shown that these polymers tend to deviate from randomness towards alternation between the limits 25% - 90% butadiene content. Some evidence is found for a tendency to blocking when the butadiene content is 25% or less.

The distribution of trans 1-4, cis 1-4 and 1-2 (vinyl) unsaturation in the polymers does not show any pattern, except that the concentration of butadiene entering as 1-2 (vinyl) structures remains low, and may be decreasing with increasing acrylonitrile content. There also appears to be lowering of the cis 1-4 content at the same time. The explanation of this might be a preference for a growing chain terminated by an acrylonitrile radical to react with butadiene monomer to give the trans 1-4 structure, a combination which would produce the lowest steric hinderance between the nitrile group and the butadiene. Such a case might mean that the reactivity ratios for the system are not as simple as at first thought. In other words there would be three reactivity ratios relating to an acrylonitrile terminated growing radical coresponding to 1-2, cis, and trans 1-4 addition of the butadiene molecule. This suggests the possibility that the butadiene radical at the end of a growing chain might also be expected to vary in reactivity depending on its configuration. This would correspond to a four comonomer system with sixteen propagation reactions and twelve reactivity ratios.

The 89% butadiene polymer has a substantially greater proportion of trans unsaturation than the other polymers studied. Whether or not there is any theoretical significance in this could perhaps be settled by a study of the microstructure of a greater number of butadiene-acrylonitrile copolymers in the range 80-100% butadiene.

A study of the nuclear magnetic resonance spectra of these polymers in which measured chemical shifts have been compared with those of an alternating 1:1 polymer[92], and polyacrylonitrile[92]; has confirmed the presence of the monomer triad sequences predicted by the distribution analysis of chapter 3.

8.2 Low Temperature Reaction.

At temperatures between 200-260°C, the butadiene homopolymer and copolymers crosslink by a non-radical reaction involving the 1-2 (vinyl) groups in the polymer. No other functional groups in the polymer are involved. The resulting polymer appears to have some weak or strained structures causing an increase in the rate of degradation over the initial stages of TVA and TGA programmed to 500°C.

The reaction causing the disappearance of vinyl groups is first order with respect to vinyl group concentration, and has an activation energy of 15 K.cals per mole.

The disappearance of unsaturation in isoprene polymers has been studied by Tkáč and his co-workers[100] at temperatures above 300°C, where evidence was found for cis-trans isomerisation and cyclisation during pyrolysis of 1-4 polyisoprene. This is supported by the recent work of Golub[101], which also yields some evidence for the same reactions occurring in 1-4 polybutadienes. The samples used in this case were of high cis and high trans content, and at temperatures as low as 200°C cis-trans isomerisation was found to occur, leading to an equilibrium cis:trans ratio of 31:69 at 260°C.

In the present work no evidence has been found for isomerisation, but bearing in mind that the polymers used were not stereospecific, some isomerisation may occur without much overall change in the concentration of cis and trans structures. It is noticeable that at temperatures in the region of 390°C, the unsaturation disappears very quickly leaving none of the evidence considered indicative of cyclisation[101]

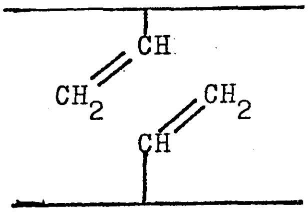
/cyclisation[101], i.e. bands in the infra-red at $975cm^{-1}$ and $819cm^{-1}$.

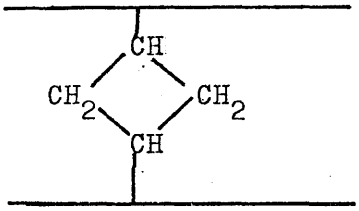
Golub[101] claims that in degraded polybutadiene the appearance of the above bands points to cyclic structures, but both these bands are present in the spectrum of the untreated polymer, and in fact the band at $975cm^{-1}$ (10.3μ) has been arrowed in the spectrum presented in his paper. The supporting evidence given in his paper for cyclisation is the development of a broad characteristic resonance in the NMR with peaks at 8.45τ and 8.75τ which Golub assigns to various non-equivalent methylene groups in saturated rings. It is true that such resonances would occur in this region, but other possibilities include:

$$C\underline{H}_3-C=C\ ,\quad C\underline{H}_3-C-C=C\ ,\quad C\underline{H}_3-C\ ;$$

$$-C-C\underline{H}_2-C-C=C\ ,\quad -C-C\underline{H}_2-C\ ,\quad C-C\underline{H}-C$$

These structures need not necessarily be part of cyclised units, and therefore the evidence presented cannot be considered as conclusive. The use of radical scavengers has no effect on the rate of disappearance of vinyl groups; thus the only apparent explanation is the interaction of two or more vinyl groups in a molecular type reaction. One possible reaction, is that between two vinyl groups to yield a C_4 ring structure:





A crosslink of this type would be strained and might explain the slight destabilisation of the polymer as noted in thermal analysis. An extension of this would be interaction between three vinyl groups to give a C_6 ring as a crosslink, but the overall concentration of vinyl groups (~14%) seems too low to permit such chance interaction in the molten state.

Based on the observations it is difficult to postulate any other mechanism for the low temperature disappearance of vinyl structures other than a non-radical post-polymerisation reaction, involving the linking up of a string of vinyl groups in some way.

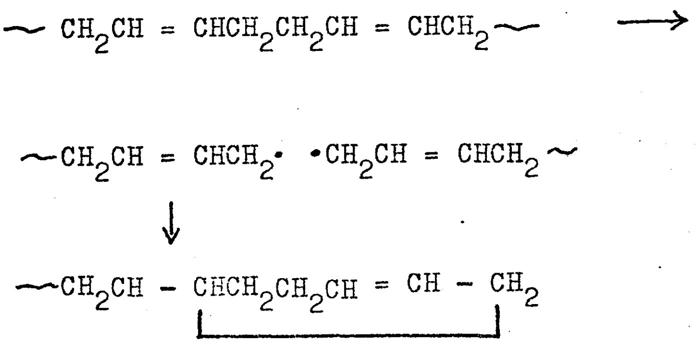
8.3 Degradation During Programmed Thermal Analysis.

Some conclusions can be drawn from the application of thermal analysis methods discussed in chapter 4.

The polymers undergo extensive intermolecular chain-transfer to yield large quantities of chain fragment material, and small amounts of volatile products typical of the breakdown of polyethylene. The temperature at which degradation starts is lowered by incorporation of acrylonitrile which also causes the formation of yellow colour in the residue and chain fragments together with stabilisation of the residue at 500°C. The permanent gases i.e. hydrogen and methane, are produced from the start of degradation and are derived from the butadiene portions of the polymer during the initial stages.

8.4 High Temperature Reaction.

During the warm up period and the initial stages at 390°C, the polymers become greatly modified due to the rapid loss of unsaturation. Cis and trans structures probably disappear via cyclisation reactions, although no evidence can be presented to support this:



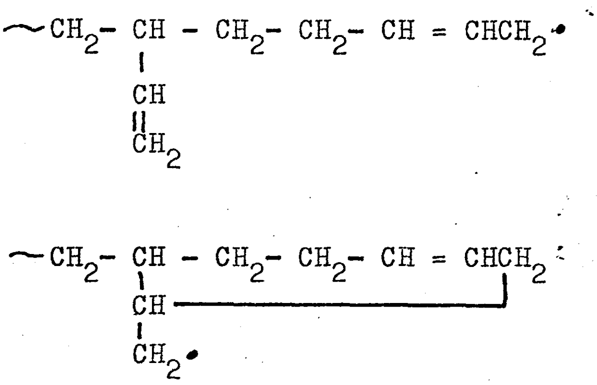
$$\sim CH_2CH = CHCH_2CH_2CH = CHCH_2\sim \longrightarrow$$

$$\sim CH_2CH = CHCH_2\cdot \quad \cdot CH_2CH = CHCH_2\sim$$

$$\downarrow$$

$$\sim CH_2CH - \underbrace{CHCH_2CH_2CH = CH - CH_2}$$

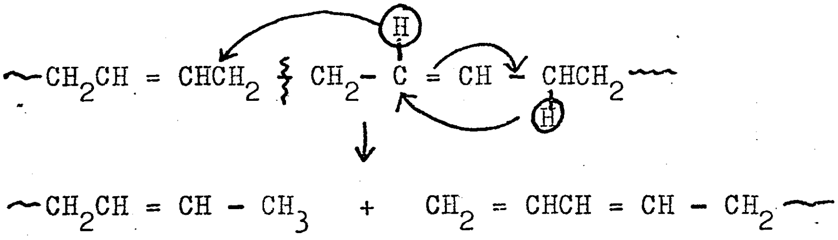
The vinyl groups in the polymer probably react in the same way as they do at low temperatures or by cyclisation leading to a seven membered ring:



$$\sim CH_2-\underset{\underset{CH_2}{\overset{\|}{CH}}}{\overset{|}{CH}}-CH_2-CH_2-CH=CHCH_2\cdot$$

$$\sim CH_2-\underset{\underset{CH_2\cdot}{|}}{CH}-CH_2-CH_2-CH=CHCH_2$$

Hydrogen transfer reactions also occur producing additional methyl groups and conjugation, as indicated by the slight yellowing of the polymer:



$$\sim CH_2CH=CHCH_2 \wr CH_2-\overset{H}{C}=CH-\underset{H}{C}HCH_2\sim$$

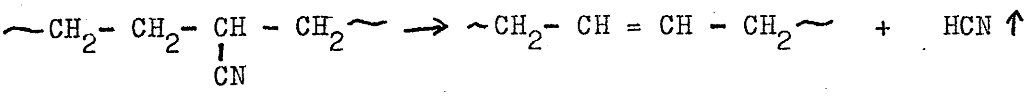
$$\downarrow$$

$$\sim CH_2CH=CH-CH_3 \quad + \quad CH_2=CHCH=CH-CH_2\sim$$

This colouration is enhanced by the incorporation of acrylonitrile units which must therefore act as weak points for chain scission.

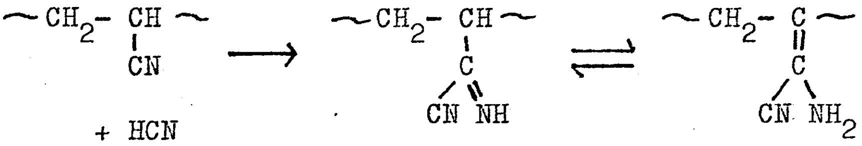
The scission and transfer reactions outlined above account for the complex mixture of hydrocarbons produced during degradation, with benzene and toluene being formed via aromatisation of cyclic structures.

Hydrogen cyanide is probably produced in a reaction analogous to dehydrochlorination in poly (vinylchloride):



$$\sim CH_2-CH_2-\underset{\underset{CN}{|}}{CH}-CH_2\sim \longrightarrow \sim CH_2-CH=CH-CH_2\sim \quad + \quad HCN\uparrow$$

It has been pointed out (chapter 5) that the action of hydrogen cyanide on the acrylonitrile units in the chain may lead to the formation of α- iminonitrile structures or the corresponding tautomeric group:



$$\sim CH_2-\underset{\substack{|\\ CN}}{CH}\sim \;+\; HCN \longrightarrow \sim CH_2-\underset{\substack{|\\ C\\ \diagup\ \ \diagdown\!\!\diagdown\\ CN\quad NH}}{CH}\sim \;\rightleftharpoons\; \sim CH_2-\underset{\substack{\|\\ C\\ \diagup\ \ \diagdown\\ CN\quad NH_2}}{C}\sim$$

(1)

A structure such as (1) may then lead to the formation of ammonia. Infra-red studies of the chain fragment material support this suggestion.

To conclude, the thermal degradation of polybutadiene and butadiene-acrylonitrile copolymers may be summarised as follows.

At low temperatures (230°C) the polymers crosslink in a non-radical reaction by means of the vinyl groups in the polymer. At higher temperatures this reaction occurs much more quickly and the cis and trans unsaturation is lost probably via cyclisation reactions. Random scission and hydrogen transfer lead to the production of large quantities of chain fragments together with small amounts of a complex mixture of saturated and unsaturated hydrocarbon gases. Hydrogen cyanide is produced by an elimination reaction leading to conjugation while ammonia may be formed from amine groups in the polymer which have resulted from the interaction of hydrogen cyanide with acrylonitrile units. The presence of acrylonitrile units destabilises the polymer with respect to the start of degradation and enhances colour formation at the yellow end of the spectrum. However polymers of high acrylonitrile content tend to leave greater amounts of residue.

At low temperatures (230°C) the polymers crosslink in a non-

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SUMMARY

This thesis describes some thermal studies of the butadiene - - acrylonitrile copolymer system. A series of copolymers was prepared by free-radical bulk polymerisation processes, the butadiene contents ranging from 25% to 100%. The polymerisation data were used to produce a new set of reactivity ratios, which in turn led to an analysis of the sequence distribution of monomer units in the polymers. Infra-red and nuclear magnetic resonance spectroscopy were used to establish the microstructure of the polymers.

Several thermal analysis methods were employed in an investigation of the degradation characteristics of these polymers during programmed heating to 500°C.

Detailed isothermal studies have been carried out in the region of 350 - 400°C to establish what changes occur in the polymer residue and what products are produced.

Quantitative investigations in this temperature range have yielded data on the weight loss characteristics, chain fragment production and the formation of gaseous products. A gas phase association between two of these products, ammonia and hydrogen cyanide, was noted and some information relating to this phenomenon has been obtained.

Part of this work also concerns the loss of vinyl groups from those polymers which occurs during heating in the region 200 - 260°C, producing a crosslinked polymer structure.

The results of the work described in this thesis may be briefly reviewed as follows.

The reactivity ratios for the copolymerisation of butadiene and acrylonitrile in bulk at 60°C are:

$$r_{\text{butadiene}} = 0.5 \qquad r_{\text{acrylonitrile}} = 0.07$$

These ratios are in agreement with recently published data for the solution polymerisation of these monomers.

Sequence distribution analysis has shown that these polymers tend to deviate from randomness towards alternation between the limits 25% - 90% butadiene content. Some evidence has also been found for a tendency to blocking when the butadiene content is 25% or less.

From microstructure studies it appears that the distribution of 1-4 trans, 1-4 cis and 1-2(vinyl) groups in the polymers does not conform to any pattern except that the 1-2(vinyl) content does not rise above 14%.

Low temperature studies have established that vinyl groups in the polymers disappear in a crosslinking reaction which is non-radical in nature. The rate of disappearance of these structures follows first order kinetics and the reaction has an activation energy of 15 Kcals/mole.

At higher temperatures this reaction occurs much more quickly and the cis/trans unsaturation is lost, probably by cyclisation reactions. Random scission and hydrogen transfer reactions lead to the production of large quantities of chain fragment material, together with small amounts of complex mixtures of hydrocarbon gases, both saturated and unsaturated. Hydrogen cyanide is produced by an elimination reaction leading to conjugation, while ammonia may be formed from amine groups in the polymer which have resulted from the interaction of hydrogen cyanide with acrylonitrile units. The Presence of acrylonitrile units destabilises the polymer with respect to the start of degradation, and enhances colour formation at the yellow end of the spectrum. However polymers of high acrylonitrile content tend to leave greater amounts of residue.