THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

THE THERMAL DEGRADATION OF

POLYMETHACRYLONITRILE.

by

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PREFACE

The work described in this thesis was carried out in the period October 1954 to August 1957 at the University of Glasgow in the department of Physical Chemistry, which is under the supervision of Professor J. Monteath Robertson.

The material of chapter 3 has been published in the Journal of the Chemical Society, and a reprint is appended to this thesis. A second paper, at present in the press, dealing with part of the material of chapter 4, is to appear in the Journal of Polymer Science. A third paper is in course of preparation. A short general paper on the various aspects of the degradation is to be read at the International Symposium on Macromolecular Chemistry at Prague, September 1957, and will be published in the Journal of Polymer Science.

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INTRODUCTION

Twenty years ago our knowledge of high polymer degradation was limited to a few isolated systems, usually of particular industrial interest, and even in these only the general features of the reaction were understood. Nowadays the situation is much altered. Sufficient information has been accumulated to enable the various types of degradation to be classified[1], and in many cases the finer details of the degradation mechanism have been clarified to a degree that would have seemed impossible in the quite recent past. These advances in our knowledge have been made possible largely by the development of new experimental techniques such as infrared spectroscopy, and substantial improvements to older ones like measurement of high molecular weights by osmometry, or kinetic measurements under conditions of high vacuum.

TYPES OF DEGRADATION.

It is convenient at this point to survey briefly
the types of degradation which can occur.   Chemical or
physical agencies may be responsible, often both together,
the former causing such reactions as oxidation and hydro-
lysis, while degradation may be induced physically by
means of heat, light, ultrasonic radiation, mechanical
stress, or high energy radiation.

The present work was confined to thermal degradation
under high vacuum; under these conditions four main types
of reaction are commonly observed.

i) Depolymerization.   The polymer chain breaks
down by a process which is the exact reverse of the prop-
agation step in polymerization.   The reaction may be
initiated at the ends of the chains, as in the case of
polymethyl methacrylate[2], or by random scission at points
in the polymer chain, as in polybutadiene[3].   Since the
initial formation of radicals in these processes is followed
by "unzipping" of the chain, the principal product is
monomer, although side reactions may substantially reduce
the yield.

ii) Chain scission giving non-monomeric products.
Chain scission may, on the other hand, result in the

production of stable molecules rather than radicals. The
simplest examples involve rupture of "weak links" due to
structural abnormalities (other than chain ends), and a
limited rapid drop in molecular weight is observed. Poly-
styrene behaves in this way, and also depolymerizes to
monomer at the temperatures at which weak link scission
occurs[4]. A more complex example is the random scission
type in which a gradual reduction in molecular size occurs,
the main products being tetramer, pentamer, etc., monomer
appearing in appreciable amounts only after very long periods
of reaction.

iii) <u>Ester decomposition type</u>. The classical ester
decomposition reaction results in the formation of an alcohol
and an olefin. Analagous behaviour is also found in poly-
mer degradation. For example, polyvinyl chloride and
polyvinyl acetate give quantitative yields of hydrochloric[5]
and acetic[6] acids respectively, and one double bond is
formed in the carbon chain for each acid molecule expelled:

$$\sim CH_2 - \underset{\underset{OCOCH_3}{|}}{CH} - CH_2 - \underset{\underset{OCOCH_3}{|}}{CH} - CH_2 - \underset{\underset{OCOCH_3}{|}}{CH} - CH_2 - \underset{\underset{OCOCH_3}{|}}{CH} - CH_2 - \underset{\underset{OCOCH_3}{|}}{CH} \sim$$

$$\longrightarrow n\ CH_3COOH + \sim CH = CH - CH = CH - CH = CH - CH = CH \sim$$
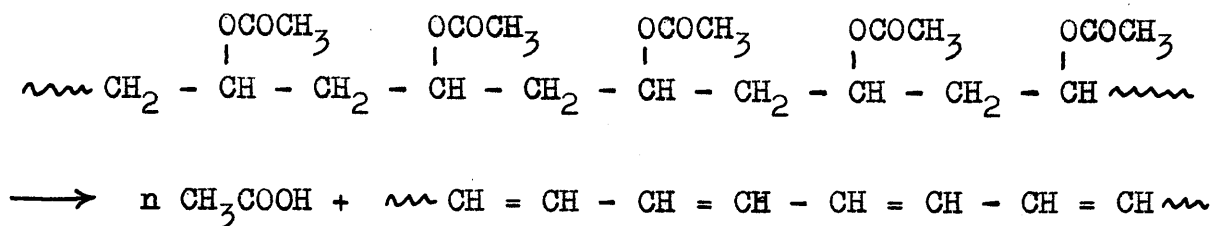
In the case of polyvinyl acetate it has been shown that the reaction is rather more complicated than the classical case: it is found that each double bond formed activates the adjacent monomer unit towards decomposition, resulting in a novel type of chain reaction.

Poly-<u>tert</u>-butyl methacrylate supplies an example in which the olefinic product is in the ejected fragment and the acid groups formed remain attached to the carbon chain:[7]

$$\sim\sim\sim CH_2 - \underset{\underset{\underset{CH_3}{\overset{|}{\underset{|}{C-CH_3}}}}{\overset{|}{\underset{O}{\overset{|}{CO}}}}{\overset{CH_3}{\overset{|}{C}}} - CH_2 - \underset{\underset{\underset{CH_3}{\overset{|}{\underset{|}{C-CH_3}}}}{\overset{|}{\underset{O}{\overset{|}{CO}}}}{\overset{CH_3}{\overset{|}{C}}} - CH_2 - \underset{\underset{\underset{CH_3}{\overset{|}{\underset{|}{C-CH_3}}}}{\overset{|}{\underset{O}{\overset{|}{CO}}}}{\overset{CH_3}{\overset{|}{C}}} - CH_2 - \underset{\underset{\underset{CH_3}{\overset{|}{\underset{|}{C-CH_3}}}}{\overset{|}{\underset{O}{\overset{|}{CO}}}}{\overset{CH_3}{\overset{|}{C}}} \sim\sim\sim$$

$$\downarrow$$

$$n\ \underset{CH_3}{\overset{CH_3}{>}}C=CH_2 + \sim\sim CH_2 - \underset{COOH}{\overset{CH_3}{\overset{|}{C}}} - CH_2 - \underset{COOH}{\overset{CH_3}{\overset{|}{C}}} - CH_2 - \underset{COOH}{\overset{CH_3}{\overset{|}{C}}} - CH_2 - \underset{COOH}{\overset{CH_3}{\overset{|}{C}}} \sim$$
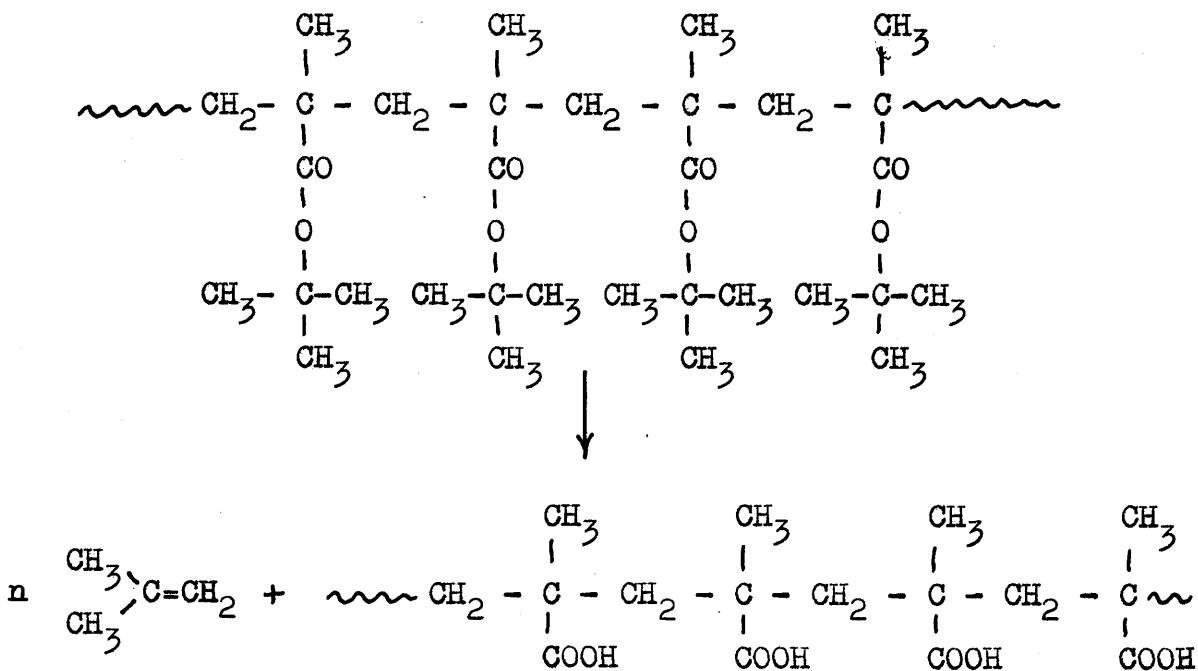
iv) <u>Substituent reactions</u>.   Reaction may also occur at reactive substituents, the carbon chain backbone remaining intact and unmodified.   For example, polymethyl vinyl

ketone loses water on heating to $270°$ due to reaction of the carbonyl group of one $-COCH_3$ unit with the methyl group of the next $-COCH_3$ side group along the chain[8]:
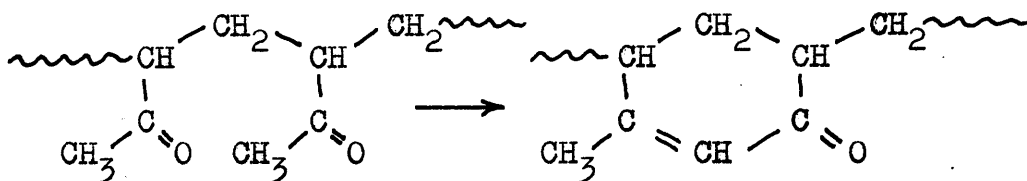
APPROACH TO SYSTEMATIC STUDY.

In any work on the breakdown of large molecules the possibility of a variety of reactions occurring is usually present. For systematic quantitative work on any one of these reactions the most rigorous precautions are necessary to exclude side reactions. Thus unless oxidation is the main feature of interest, air should be completely excluded by working under high vacuum. Conditions of high vacuum and elevated temperature are also instrumental in removing the products of degradation from the bulk of the polymer with the minimum of delay. If this is not done there is a very real danger that the products of degradation may react with the degrading material, with the formation of complicating side products.

One difficulty which always exists in studying the

thermal degradation of polymers quantitatively, and which
has not always been fully realized, is the danger of a
temperature gradient existing in the degrading material,
since polymers are poor conductors of heat.   This can be
avoided by using small quantities of polymer, and by care-
ful attention to the design of the apparatus.   A related
difficulty, less easily resolved, arises from the fact that
many of these reactions are occurring in a solid or semi-
solid state and the rate of diffusion of the products
through the polymer can become the controlling step in the
reaction.

Different degradation reactions may occur in the
same polymer at different temperatures, and it is always
desirable to select carefully temperature ranges in which
one reaction may be studied with as little complication
from others as possible.

RELATION BETWEEN POLYMER STRUCTURE AND
TYPE OF DEGRADATION.

It sometimes proves possible, nowadays, as knowledge
of these processes accumulates, to forecast how a given
polymer will behave when heated under vacuum.

Thus, generally, polymers from 1:1-disubstituted
monomers,

$$
\begin{array}{ccc}
& X & & X \\
& | & & | \\
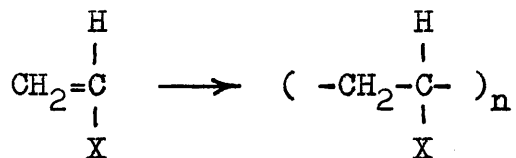CH_2{=}C & \longrightarrow & (-CH_2-C-)_n \\
& | & & | \\
& Y & & Y
\end{array}
$$
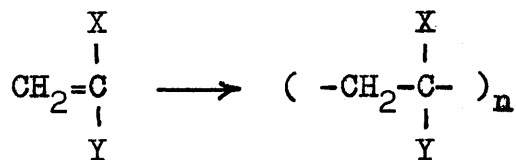
undergo depolymerization to monomer.   Examples are poly-
methyl methacrylate (and the poly-n-alkyl methacrylates
generally), poly-α-methyl styrene, and polyvinylidene
cyanide.   On the other hand, polymers from monosubstituted
monomers,

$$
\begin{array}{ccc}
& H & & H \\
& | & & | \\
CH_2{=}C & \longrightarrow & (-CH_2-C-)_n \\
& | & & | \\
& X & & X
\end{array}
$$

rarely yield large amounts of monomer.   Most depolymer-
izations proceed by a free radical mechanism, and the reason
for the different behaviour in the two types of polymer
lies in the stability of the radical present during the
depolymerization.   Free radicals would normally be expect-
ed to combine, disproportionate, or abstract a hydrogen atom
from a stable molecule.   In 1:1-disubstituted polymers,
however, there is a quaternary carbon atom at the radical
site.   This stabilises the radical and allows a greater
opportunity for the monomer-producing intramolecular dis-
proportionation reaction to occur:

$$\text{\textasciitilde\textasciitilde\textasciitilde} CH_2-\underset{Y}{\overset{X}{C}}- CH_2-\underset{Y}{\overset{X}{C}}- CH_2-\underset{Y}{\overset{X}{C}}\cdot \rightarrow \text{\textasciitilde} CH_2-\underset{Y}{\overset{X}{C}}- CH_2-\underset{Y}{\overset{X}{C}}- + CH_2=\underset{Y}{\overset{X}{C}}$$
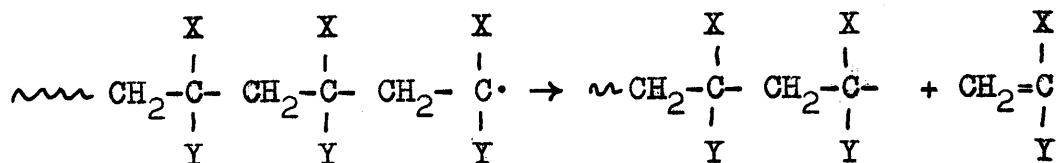
It is interesting to note that in polystyrene, which is monosubstituted, the resonance stabilization due to the phenyl group is sufficient to allow large quantities of monomer to be produced (65%).

The behaviour of polymers from monosubstituted monomers is largely determined by the greater reactivity of the radical and the availability of the reactive tertiary hydrogen atoms. Thus transfer reactions (inter- or intra-molecular) usually predominate, with the formation of trimer, tetramer, and higher fragments, and cross-linking may occur.

Ester decomposition reactions can be expected in monosubstituted polymers such as polyvinyl acetate. In the case of disubstituted polymers which contain ester groups, however, the monomer producing reaction usually sets in first. This is not unexpected if the decompos-ition temperatures of simple esters are considered. These are found to be about 500°, 450°, and 300° respectively for primary, secondary, and tertiary esters. The monomer
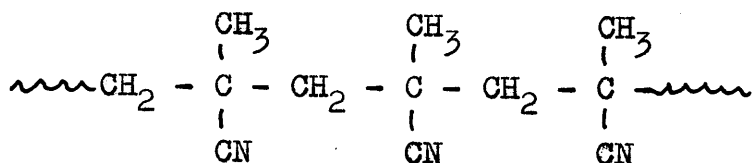
producing depolymerization usually occurs at about 200-250°. Polymers of this type, however, which contain tertiary ester groups are found to undergo an ester decomposition reaction. Thus the poly-n-alkyl methacrylates depolymerize to monomer but poly-tert-butyl methacrylate gives quantitative yields of isobutene.

When reactive substituents are present, the possibility of degradation processes involving these must always be anticipated.

A careful consideration of the polymer structure and comparison with the behaviour of other polymers of related structure will often, therefore, indicate the most likely manner of degradation. On the other hand, many of these reactions are quite unpredictable and it is becoming increasingly clear that they are due to "structural abnormalities".

POLYMETHACRYLONITRILE

The behaviour to be expected in the case of poly-methacrylonitrile

$$\sim\sim CH_2 - \underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_2 - \underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_2 - \underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}} \sim\sim$$

may now be considered.   The structure is the 1:1-disub-
stituted type, therefore monomer is to be expected as the
main product, and in view of the close similarity in
structure to polymethyl methacrylate, polymethacrylonitrile
might by comparison be expected to undergo a straight-
forward depolymerization initiated at the chain ends.

Although the nitrile substituent could be classed
as reactive there are no reactive methylene groups present
with which a condensation could occur.   One possible
reaction involving the nitrile group is an ester decompos-
ition analagous to the behaviour of polyvinyl chloride and
polyvinyl acetate (p.3) resulting in loss of hydrogen
cyanide.   This is rather unlikely, however, since depoly-
merization will be aided by the resonance stabilization of
the radical due to the presence of the nitrile substituent.

KERN and FERNOW[9] pyrolysed polymethacrylonitrile
without exclusion of air and reported monomer yields of
the order of 80% on heating the polymer to 350°. They also
found that the polymer softened at $110-120^{\circ}$, and underwent
colouration in the $120-220^{\circ}$ temperature range, passing
through yellow and orange and ultimately becoming deep red.
Monomer was not produced until 220° was reached.   Some
preliminary work by GRASSIE and VANCE[10] under conditions

of high vacuum, confirmed most of Kern and Fernow's observations, but these authors were able to obtain maximum monomer yields of only 65%.

At first sight, therefore, the behaviour of the polymer is largely as expected, but from the occurrence of colouration it is evident that the reaction is not as straightforward as with polymethyl methacrylate. It is interesting to note that a similar colouration takes place in the course of the degradation of polyvinyl chloride and polyvinyl acetate, due to the formation of the conjugated polyene residue.

AIM OF THIS WORK.

The aim of the work subsequently described in this thesis was twofold. Firstly, it was intended to make a general study of the degradation to determine if colouration and depolymerization were independent reactions which could be studied individually. Secondly, it was intended to study the production of monomer by the methods of rate and molecular weight measurement used by Grassie and Melville[2] in their detailed analysis of the mechanism of degradation of polymethyl methacrylate.
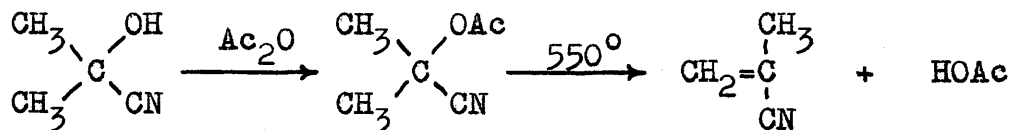
2

APPARATUS AND

EXPERIMENTAL TECHNIQUES

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1. PREPARATION AND PURIFICATION OF MONOMER.

Methacrylonitrile Preparation.

Methacrylonitrile was prepared from acetone cyan-
hydrin (I.C.I. Ltd., Billingham) by pyrolysis of the acetyl
derivative at 550°C.

$$CH_3 \diagdown \diagup OH \xrightarrow{Ac_2O} CH_3 \diagdown \diagup OAc \xrightarrow{550°} CH_2=C \diagup CH_3 \quad + \quad HOAc$$
$$CH_3 \diagup C \diagdown CN \qquad CH_3 \diagup C \diagdown CN \qquad \quad CN$$

Acetyl chloride (0.05 mol.) was added through a
reflux condenser to acetone cyanhydrin (1 mol.) and acetic
anhydride (1.5 mols.) contained in a large flask. After
a few seconds a vigorous reaction set in, causing the mix-
ture to boil. Boiling ceased after half an hour, and the
mixture was allowed to stand for 30-40 hours.

Fractional distillation of the reaction mixture
yielded acetic acid, acetic anhydride, and acetone cyan-
hydrin acetate (b.178-182°). The 140-170° fraction on
redistillation yielded a further quantity of the acetate.

Pyrolysis was carried out in a six foot long silica
tube of two inch bore, packed with silica chips, set
vertically, heated over four feet of its length and fitted
with a thermocouple to measure the temperature of the
interior (figure 1). The tube was heated to 550° and
acetone cyanhydrin acetate was run in dropwise from the top,
monomer and acetic acid being collected at the bottom.

Methacrylonitrile Purification.

First method: The first batch of monomer prepared
as above was purified by the method of GRASSIE and VANCE[11],
which consisted of pouring the pyrolysis product (monomer
and acetic acid) into a large volume of water, extracting
with ether, and distilling the dried ether extract. The
fraction boiling at 92-94° was collected, giving an overall
yield of 60-70% calculated on acetone cyanhydrin.

Second method: The pyrolysis product was placed
in a large separating funnel fitted with a reflux condenser
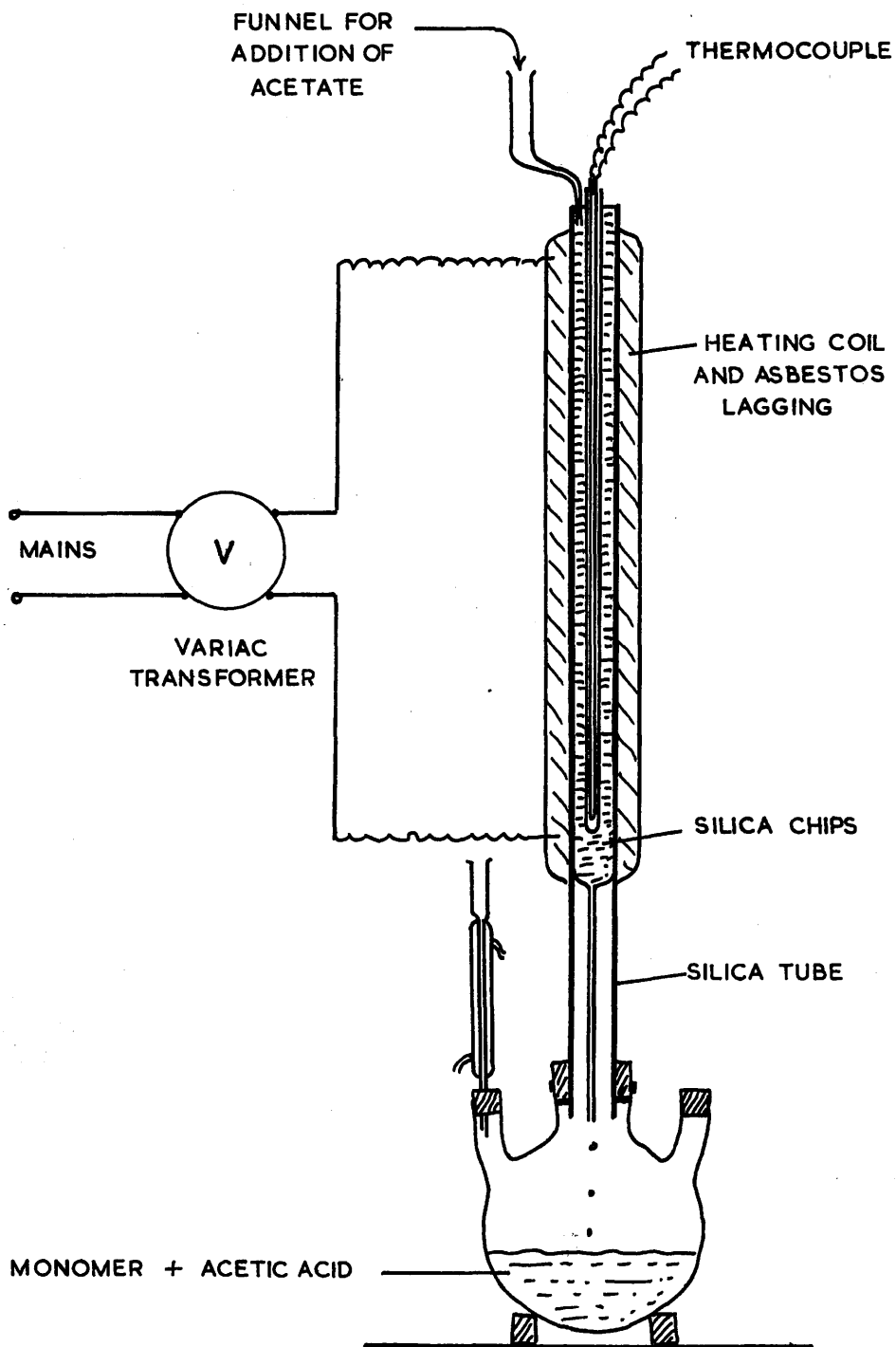and stirrer. Ammonia (d. 0.88) was added slowly through

FIGURE 1:   THE PYROLYSIS APPARATUS.

the condenser.   From time to time stirring was stopped
and the mixture was allowed to settle into two layers in
order that a portion of the lower (aqueous) layer might be
run off and tested with litmus.   When neutralization of
the acetic acid in the product was complete, the lower
layer became alkaline, and it was then run off and
discarded.   The upper layer (crude methacrylonitrile)
was washed with small portions of water, dried over calcium
chloride and twice distilled (with addition of 0.5% hydro-
quinone to prevent loss of monomer by polymerization).   A
small further quantity of monomer was obtained by ether
extraction of the washings.   Pure methacrylonitrile boils
at 89-90°.   The overall yield when this method of purif-
ication is employed is 45-50%.

2.PREPARATION OF POLYMERS AND COPOLYMERS.

Monomers.

        Methacrylonitrile was prepared and purified as
above.   Methacrylic acid (I.C.I. Ltd.) was freed from
inhibitor by distillation under reduced pressure (b. 60°/
10mm.).   Pure methacrylic acid was stored at -15°C.

Initiators.

        Azo-bis-isobutyronitrile (Eastman Kodak) was

purified by recrystallization from toluene. Benzoyl peroxide
was purified by dissolving the solid in the minimum volume
of cold chloroform, removing the small aqueous layer, and
pouring the solution into methanol.   The fine crystals
which separated were dried under vacuum.

The initiator was added to the reaction dilatometers
of known bulb volume and stem bore (previously cleaned
thoroughly with chromic acid) through a small funnel and
washed down with a little 'Analar' acetone.   The acetone
was then removed under vacuum.

Method of Filling Reaction Tubes.

a). In preparing polymethacrylonitrile. Methacrylo-
nitrile was degassed three times under vacuum, and distilled
by the usual high vacuum line cold distillation technique
into a tube calibrated in tenths of a cubic centimetre.
The dilatometer containing initiator was filled by distill-
ation of the appropriate volume from this tube, and
finally sealed off under vacuum.

b). In preparing copolymers of methacrylonitrile
with methacrylic acid.   Methacrylonitrile was degassed
and twice distilled in vacuum, first into a calibrated tube
and finally into dilatometers containing initiator.   These

were then removed from the vacuum system and a measured quantity of methacrylic acid added.   This procedure was adopted since methacrylic acid cannot easily be degassed and distilled on account of its low volatility and strong tendency to polymerize when freed from inhibitor.   The mixture was finally degassed and sealed off in vacuum.

Polymerization.

Polymerizations were carried out in a thermostat controlled to $\pm 0.1^{\circ}$, the progress of the reaction being followed by observing with a cathetometer the fall in level of the liquid in the stem of the dilatometer.

The relation between contraction and extent of polymerization for polymethacrylonitrile, obtained by Grassie and Vance[11], is given in table 1.   The same relation was assumed to hold for copolymers of methacrylonitrile containing a small proportion of methacrylic acid. The volume contraction in any given case was obtained using the data of table 1 and the equation

$$V_c = V \left[1 + 0.0014 \ (t-20) \right] \frac{\%P}{F}$$

where V = volume of monomer at 20°

t = polymerization temperature, $^{\circ}C$,

%P = extent of polymerization required

F = % polymerization/ % contraction (table 1).

Table 1

DILATOMETRIC RELATIONSHIP

Temp.(^{o}C)	% polymerization / % contraction *
20	3.22
30	3.12
40	3.04
50	2.98
60	2.88
70	2.78
80	2.68

* based on volume at 20°C.

Polymerizations initiated by photodecomposition of initiator at 30° were carried out in a thermostat with a silica window, the light source being an Osram 250v. 125w. mercury vapour lamp.

Polymerization was carried to 5% in the case of

copolymers and 10% for pure polymers, with the exception
of those prepared at 30° where polymerization was stopped
at 6% to avoid the duration becoming very lengthy.

Methacrylonitrile polymers of molecular weight
greater than 25,000 tend to separate during polymerization
and gradually form a tough gelatinous plug at the bottom
of the dilatometer.   Although there is no gel effect[11],
the formation of this plug is undesirable, firstly because
some cross-linking occurs, and secondly because attempts
to dissolve it in hot solvent result in contamination of
the polymer with a small quantity of air-polymerized
material, due to the presence of monomer and initiator in
the gelatinous mass.

The tendency of the polymer which separates to
compact itself in this way can be minimised by shaking or
stirring the mixture during polymerization.   One way of
doing this is to connect the dilatometer stem to a stirring
motor and spin the tube during reaction, stopping at inter-
vals for readings of the level to be made.

Isolation and Purification of Polymers.

Polymethacrylonitrile precipitated by pouring the
cooled reaction mixture (or mixture + acetone in the case

of less soluble polymers) into about ten times its volume
of methanol or petroleum ether (40-60°) was dissolved in
'Analar' acetone and reprecipitated.   The polymer was
dried under high vacuum.

Copolymers of methacrylonitrile and methacrylic acid
were more difficult to isolate, since the solubility
towards precipitants changed as the proportion of meth-
acrylic acid was altered.   Petroleum ether was found to
be the most satisfactory precipitant.   The copolymer,
obtained as a fine gelatinous precipitate, was reprecipit-
ated from 10:1 acetone/alcohol solution.   The gelatinous
polymer formed a brittle glass-like mass on drying in air;
this was ground to a fine powder and dried completely under
high vacuum.

Copolymer Compositions.

Copolymer compositions were calculated from the
reactivity ratios obtained for this system by GRANT[12].   At
65° these are

$$r_1 = 0.62 \neq 0.05; \quad r_2 = 1.64 \pm 0.05$$

where the subscripts 1 and 2 refer to methacrylonitrile and
methacrylic acid respectively.   Figure 2 shows the
copolymer composition curve for the system, calculated from
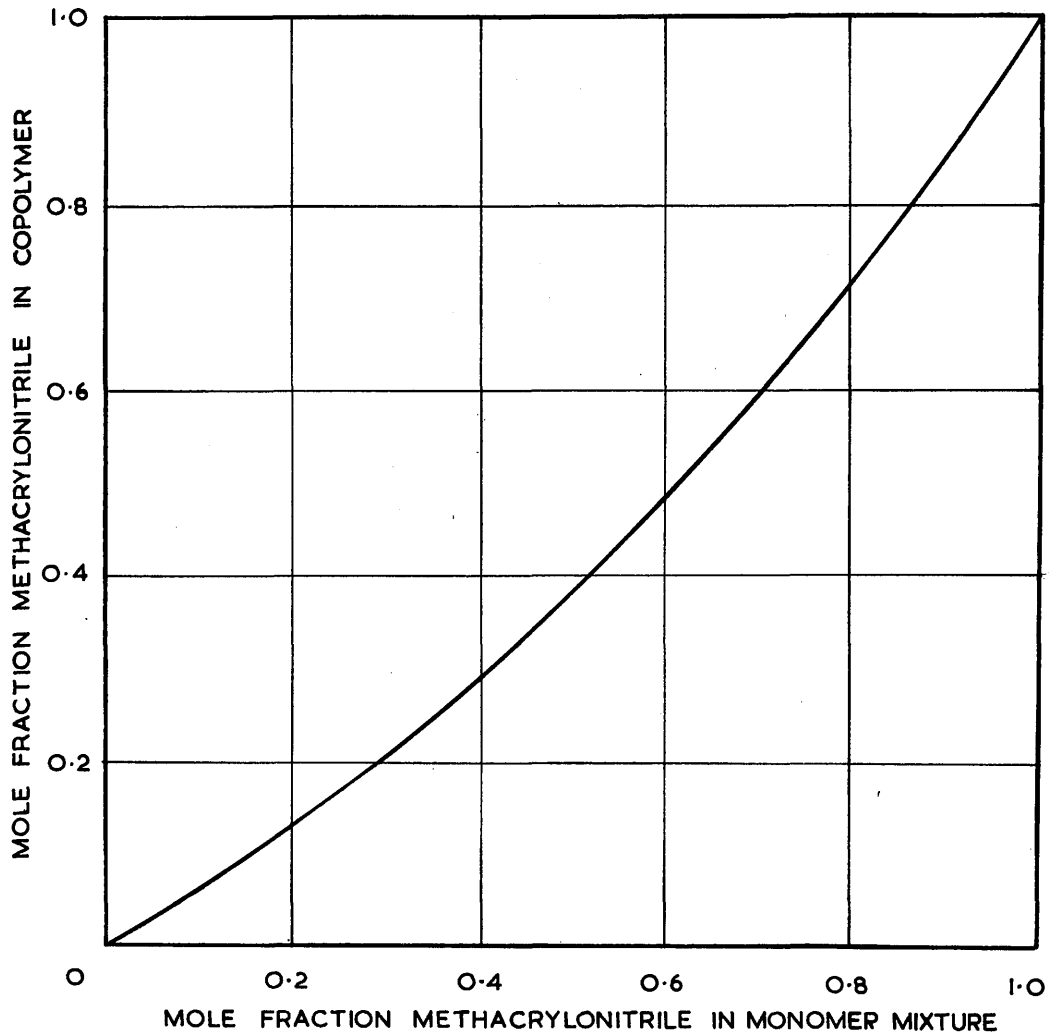
FIGURE 2 :   COPOLYMER COMPOSITION CURVE FOR THE
SYSTEM METHACRYLONITRILE-METHACRYLIC ACID.

these r values.   The compositions of the copolymers which
were prepared are given in table 2.

Table 2

COPOLYMERS OF METHACRYLONITRILE WITH METHACRYLIC ACID
0.7% w/v Azobisisobutyronitrile initiator, 65°.

| Copolymer No. | Composition Ratios* | |
	Monomer	Copolymer
1	39.5	21.2
2	8.11	5.25
3	4.05	2.57

3. MOLECULAR WEIGHT MEASUREMENTS.

i) Osmometer Design.

Osmometers of the Pinner-Stabin[13] design, supplied
by Polymer Consultants Ltd., were used.   The design is
shown in figure 3.   Two membranes are fitted, one on either
side of the glass cell, held in place by grooved metal
plates, teflon gaskets being used to seal the osmometer cell
from leaks.   Two precision bore matched capillaries of
0.56mm. diameter are fitted, one leading to the cell, the
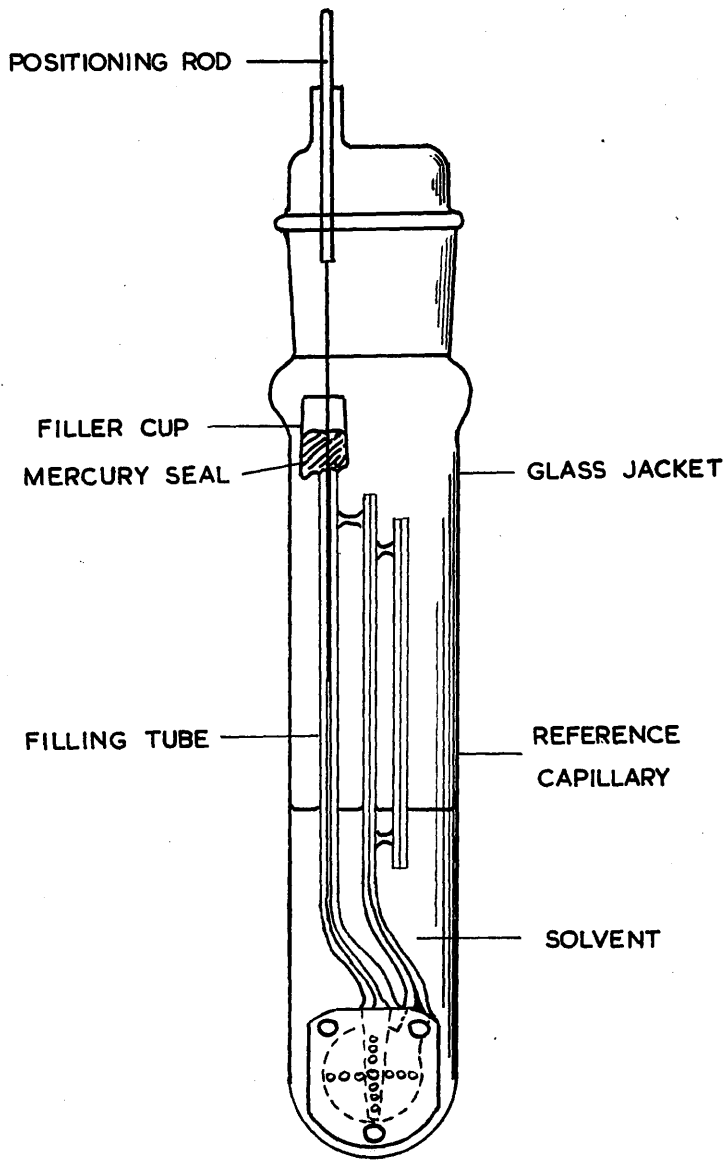
* (Methacrylonitrile)/(Methacrylic Acid)

POSITIONING ROD

FILLER CUP

MERCURY SEAL

GLASS JACKET

FILLING TUBE

REFERENCE
CAPILLARY

SOLVENT

FIGURE 3 :   THE PINNER STABIN
OSMOMETER.

other being used as a reference capillary. The cell is
filled with solution by means of the filling tube and
solvent is placed in the osmometer outer jacket. The inner
surface of the filling tube is ground and a metal position-
ing rod fits into it for adjustment of the level in the
solution capillary.

ii) <u>Solvent</u>.

'Analar' grade acetone was dried (calcium oxide)
and distilled through a spiral glass column.

iii) <u>Membrane Conditioning.</u>

Undried cellophane was conditioned by treatment in
the following baths:

1st and 2nd days	Distilled Water
3rd day	25% acetone/ 75% water
4th day	50% " 50% "
5th day	75% " 75% "
6th and 7th days	100% acetone.

iv) <u>Setting Up of Osmometers.</u>

Membranes were fitted between the teflon gaskets and
the metal plates, and the osmometer was then assembled by
bolting the plates on either side of the cell, the whole
operation being carried out under acetone to avoid drying

out of the membranes due to exposure to air[14].

The osmometer was set up in a thermostat controlled at $25° \pm 0.01°$ by a valve relay and spiral type mercury-toluene regulator. The lid was not immersed; condensation on the inside was prevented by placing a 25w. lamp about six inches above it.

To test for leaks the osmometer was filled with an approximately 1% solution of polymer of molecular weight about 50,000 to give a high osmotic pressure, free from diffusion. The difference in level of the two capillaries was observed over a period of hours. When there was no leakage this gradually became constant.

The cell constant was determined with the osmometer filled with solvent, after careful rinsing. No great variation in cell constant was found (0.00 ± 0.03 cm.) in the course of redeterminations over a period of months.

When the osmometer was being used daily it was found necessary to dismantle it about once a month and clean the capillaries thoroughly with chromic acid.

v) Determination of Molecular Weight.

Solutions of known concentration were prepared. Firstly, a quantity of polymer (about 0.3g.) was weighed

into a tared bottle, acetone was added to dissolve the polymer, and the solution was diluted with acetone to about 50 ml. This solution was then weighed and the concentration in g./100g. solution was calculated. This solution served as a stock solution from which other solutions were prepared by dilution. Different quantities of stock solution were weighed into tared 15 ml. flasks. These were then made up to 15 ml. approximately with acetone, stoppered, and stored in the thermostat at 25°. Immediately before use each flask was removed, quickly dried and weighed, thus enabling the concentration on a weight basis to be calculated.

The osmometer was rinsed with four 2 ml. portions of the solution to be used, then carefully filled. After about thirty minutes the difference in level of the capillaries was adjusted using the positioning rod to give a height about 0.5 cm. lower than the anticipated value. After a further half hour regular (15 min.) readings were commenced, these being continued until the observed osmotic pressure had become constant. With methacrylonitrile polymers of molecular weight lower than 30,000, diffusion occurred, the osmotic pressure reaching a maximum and then decreasing linearly with time. In such cases the true

osmotic pressure of the solution was determined graphically
by extrapolation to the time of filling (see appendix for
example). Molecular weights lower than 15,000 could not
be measured accurately on account of rapid diffusion of
the polymer. The dynamic method of observation and
calculation was never used since it ignores the possibility
of diffusion.

The number average molecular weight is related to
the limiting value of the /c against c plot (obtained by
observations on a series of solutions) by the following
equation:

$$\left(\frac{\pi}{c}\right)_{c\to o} = \frac{RT}{M_2}$$

where c = concentration of solution in g. solute per ml.
         of solution,

       T = the absolute temperature,

       R = the gas constant, 82.06 cc.atm. per deg.per mole,

       M_2= the number average molecular weight of the
         polymer.

Since 1 atmosphere = 1033.3 g. per sq.cm.

     π in atm.   = π in cm. x density of soln./1033.3

Since c in g./ml. = c in g.per 100g. x density of soln/ 100

$$\left(\frac{\overline{\pi}}{c}\right)_{c \to o} = L \ x \ \frac{density}{1033.3} \ x \ \frac{100}{density}$$

$$= L \ / \ 10.333$$

where L is the limiting value of $\overline{\pi}/c$ in units of cm. and

g. per 100g. solution.

Therefore M_2 = 10.333 RT/L = 10.333 x 82.06 x T/L

$$= 847.9 \ T/L$$

At 25°, $\underline{M_2}$ = 252,800 / L.

Figure 4 shows some typical osmotic pressure results for several polymers.

4. DEGRADATION APPARATUS.

a) The Dynamic Molecular Still.

The dynamic molecular still of GRASSIE and MELVILLE[2,6] was used with a slight modification.

Figure 5 shows the general arrangement of glasswork of the degradation apparatus.   The still (figure 6) consisted of an evacuated glass envelope, with removable lid, containing a furnace block onto which is screwed
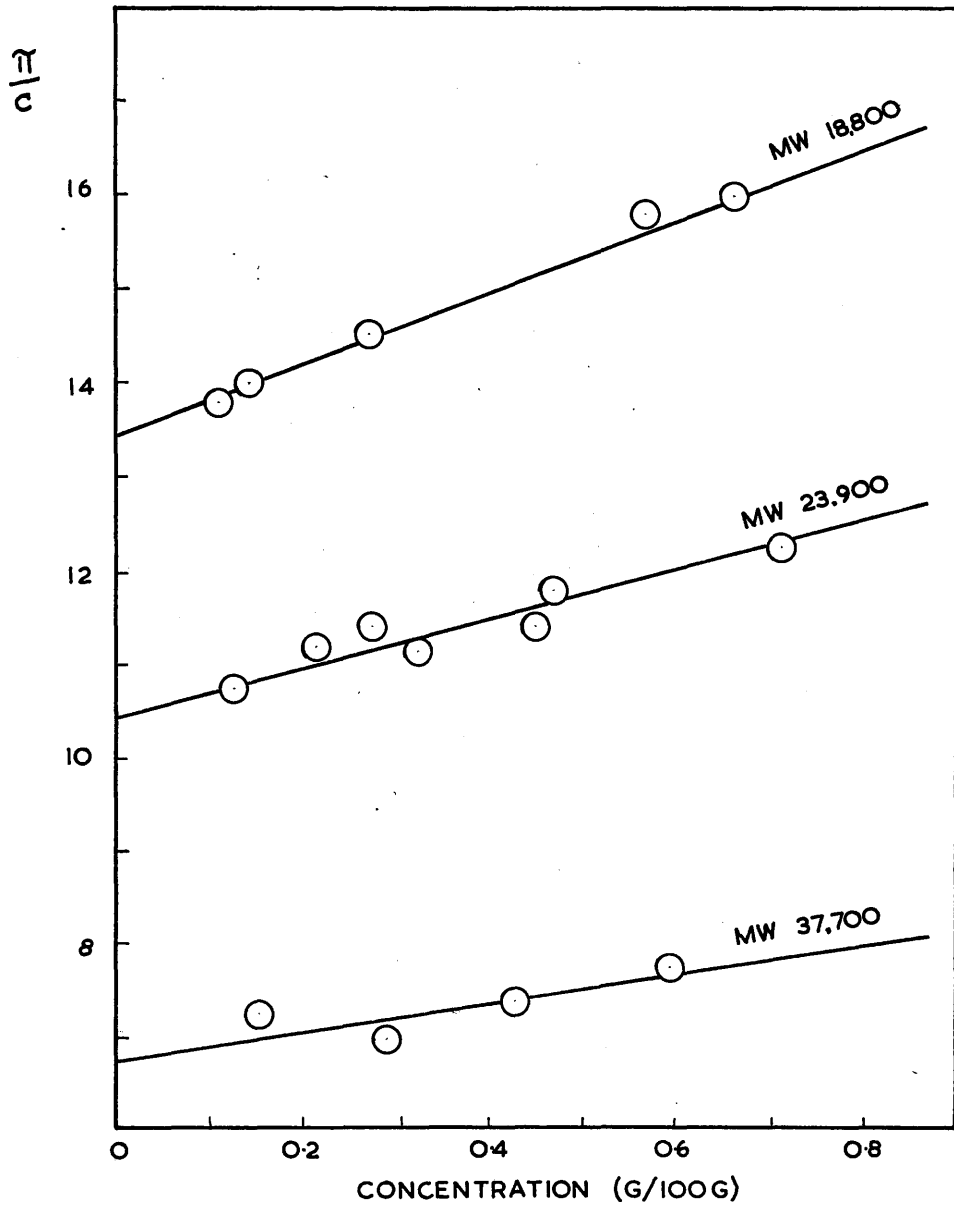
FIGURE 4 : SOME OSMOTIC PRESSURE DATA
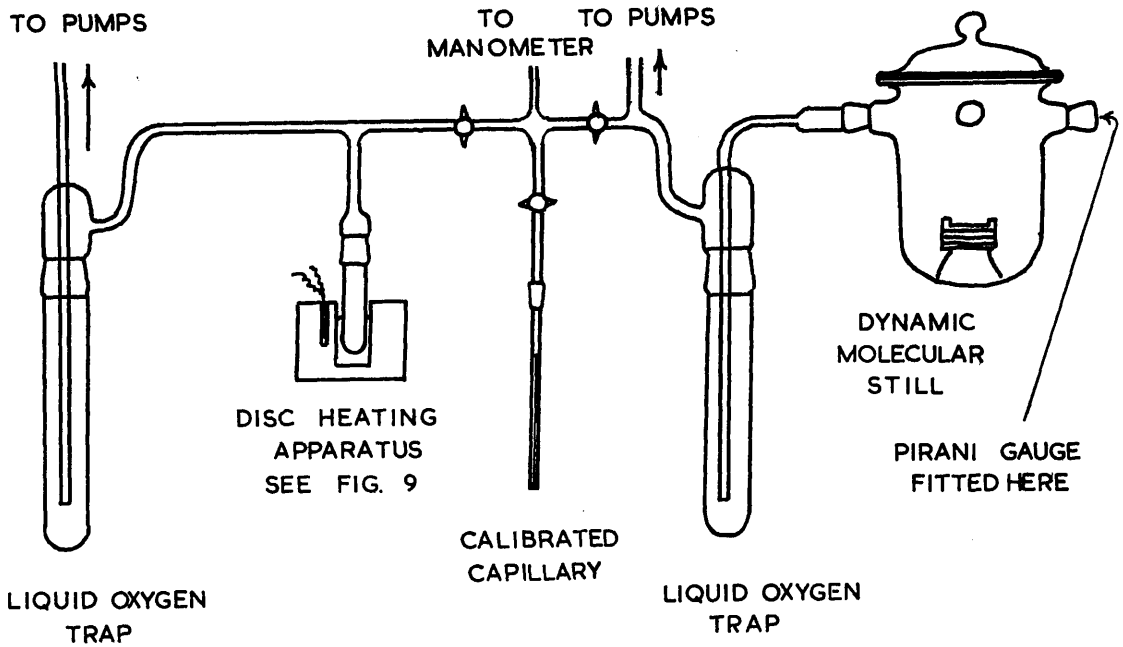FOR METHACRYLONITRILE POLYMERS.

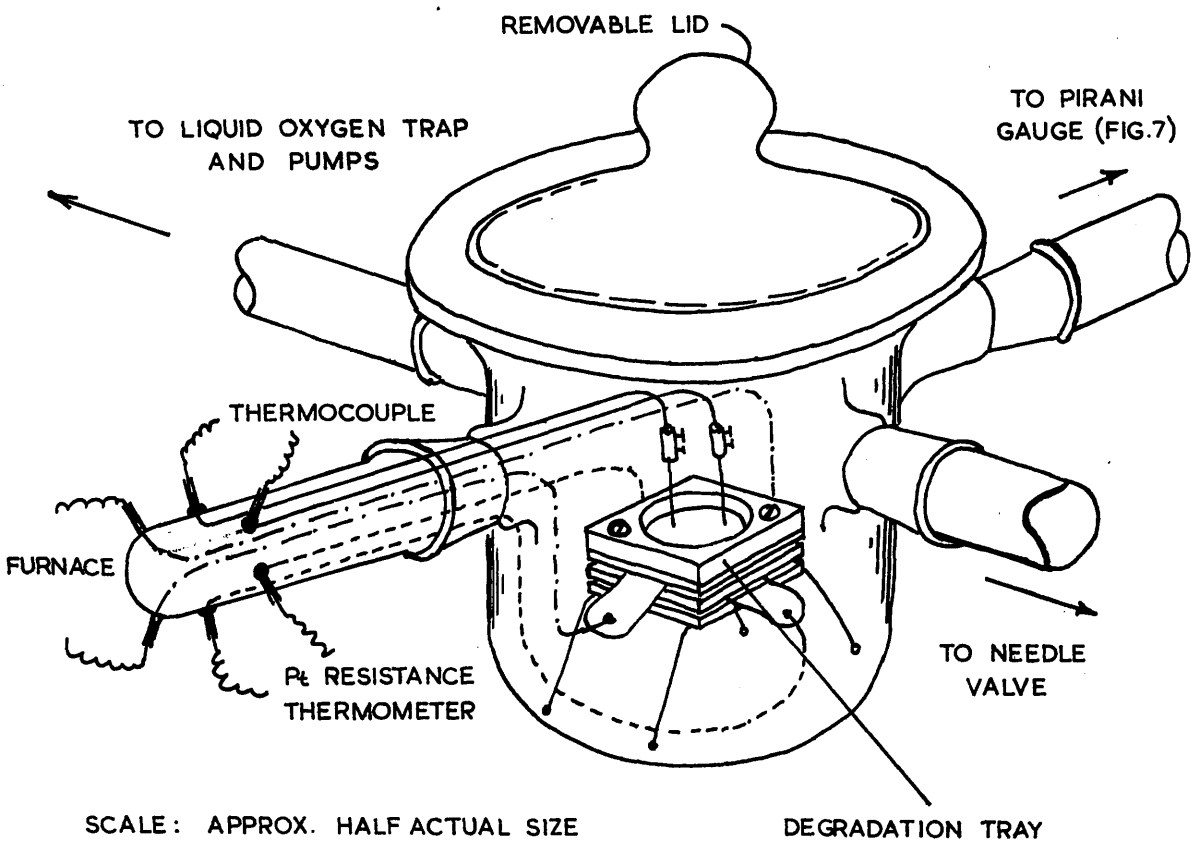FIGURE 5:   ARRANGEMENT OF GLASSWORK OF
DEGRADATION APPARATUS.

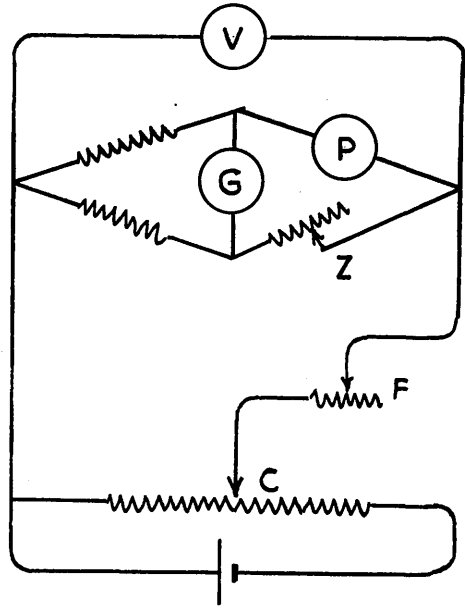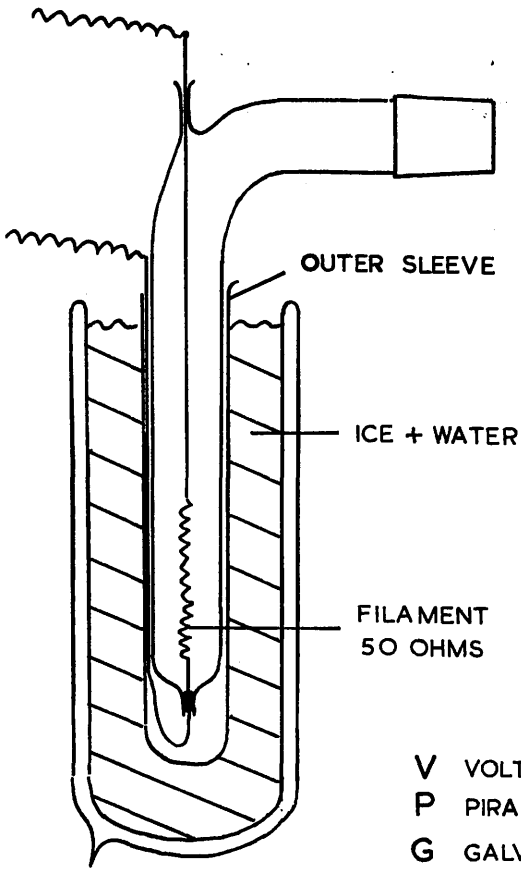FIGURE 6: THE DYNAMIC MOLECULAR STILL.

FIGURE 7: DESIGN OF THERMOSTATTED
PIRANI GAUGE AND ELECTRICAL CIRCUIT.

copper degradation trays. The temperature of the furnace could be controlled to within $\pm 1^o$ using a Sunvic Resistance Thermometer Controller Type R.T.1. (for heating and control circuit see appendix). 0.1 to 0.3g. of polymer was placed in the tray and covered with freshly-reduced copper powder to ensure even heating of the polymer. The rate of evolution of volatiles was measured by the Pirani gauge in terms of the small pressure built up inside the still as the vapour travels to the liquid oxygen trap.

Pirani gauge modification. The Pirani gauge and circuit is shown in figure 7. The resistance of the filament changes with the number of particles colliding with it. If V is the voltage required to give zero galvanometer deflection at a given pressure and V_o is the corresponding voltage when the apparatus is fully evacuated, then $(V^2 - V_o^2) / V_o^2$ is a measure of the pressure. The gauge may be calibrated by passing monomer into the still at known rates by means of a needle valve, measuring V, and plotting $(V^2 - V_o^2) / V_o^2$ against the rate of flow[2]. All previous work using the dynamic molecular still was done with gauges calibrated for use at room temperature.

It was noticed that the gauge*was slightly sensitive to light and rather more sensitive to changes in room

* in the original non-thermostatted form[2]

temperature.   Changes of 3° in room temperature often occurred during a three or four hour degradation in the summer months, and this affected both V and V_o.   For example V_o changed from 0.65 at 20° to 0.62 at 25°.   It was therefore considered desirable to thermostat the gauge at 0°c.   When the thermostatted gauge was recalibrated it was found that V_o became constant.   Hence it was no longer necessary to work out $(V^2 - V_o^2) / V_o^2$ for each reading of V as above, and it was possible to read off the rate of degradation from the calibration graph of V against rate of flow of monomer (figure 8).   The use of the thermostatted gauge therefore prevents a drift in readings with changes in room temperature and also eliminates a good deal of calculation.

b) Apparatus for Heating KCl Discs.

In the experiments in which the polymer was degraded whilst incorporated in a pressed potassium chloride disc (chapter 4), heating was carried out in a specially shaped pyrex tube immersed in a Wood's metal bath, the temperature of the bath being measured by means of a thermocouple (see figure 9).   The temperature of the furnace was controlled by using the Sunvic Resistance Thermometer Controller (as for furnace of dynamic molecular still, p.32).

FIGURE 8 :   PIRANI GAUGE CALIBRATION CURVE.

TO VACUUM LINE

B 24

THERMOCOUPLE
LEADS

HEATING TUBE

FRONT   SIDE
VIEW   VIEW

HEATING COIL
AND LAGGING

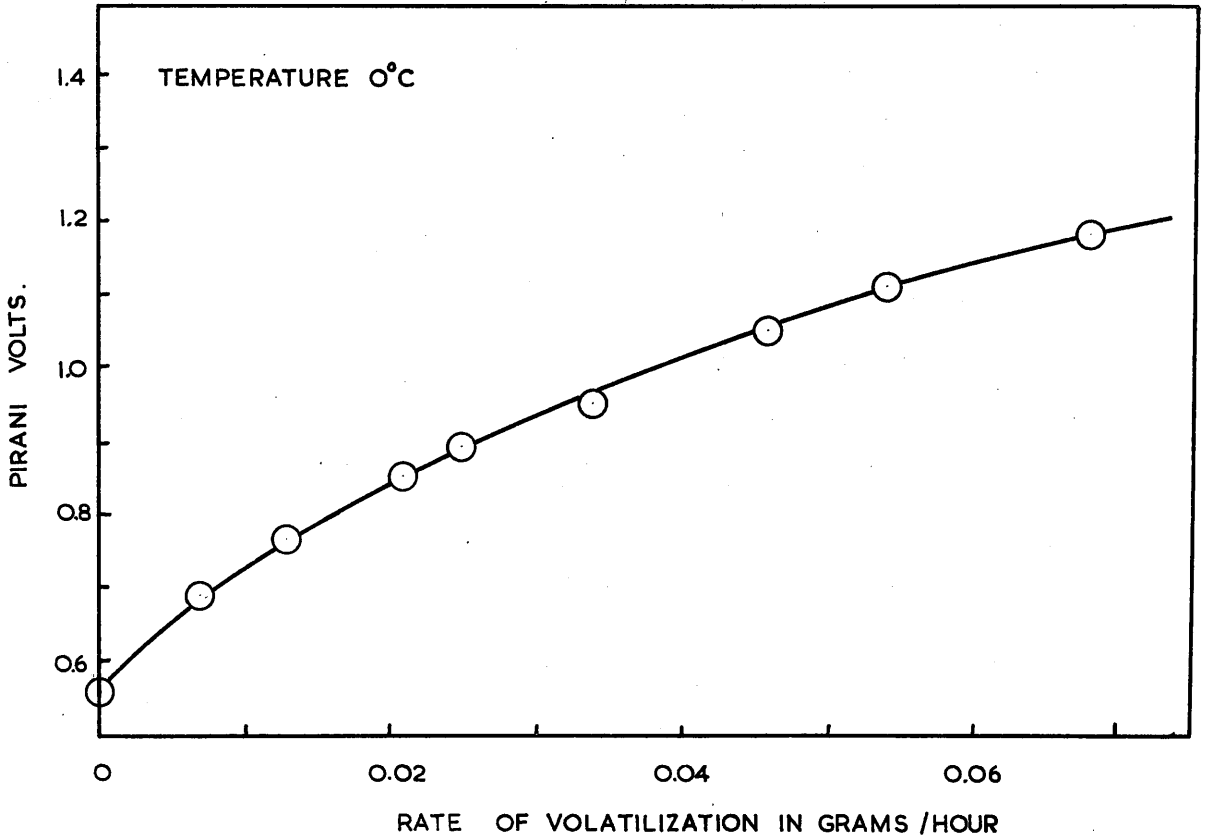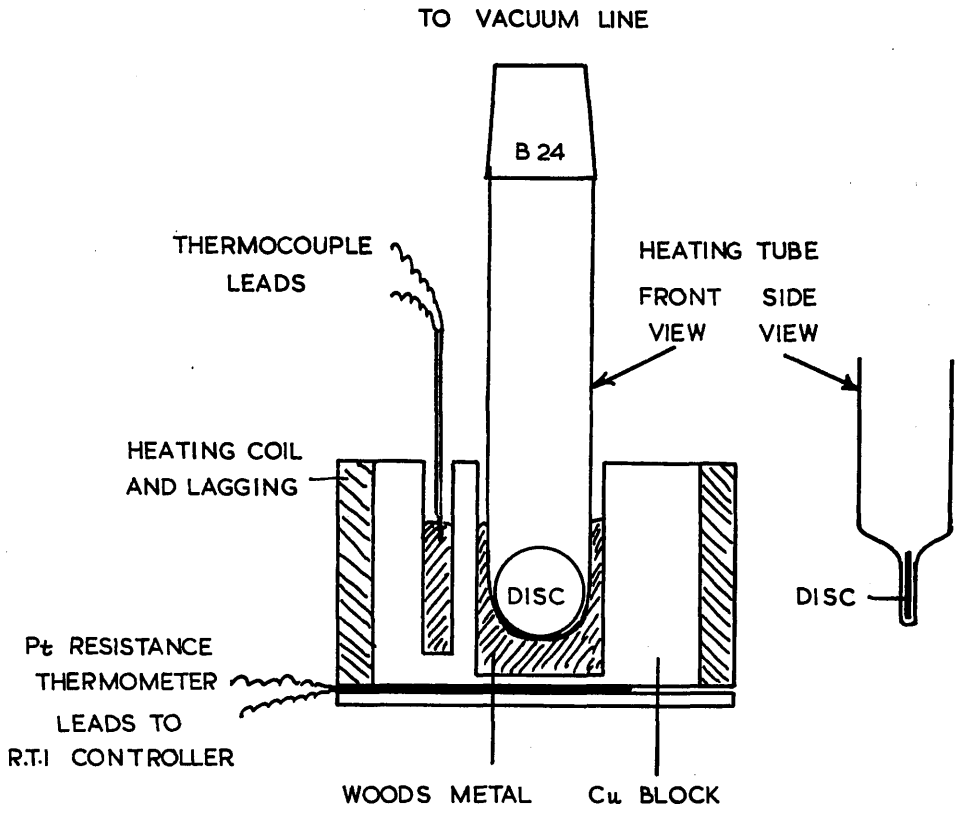DISC

DISC

Pt RESISTANCE
THERMOMETER
LEADS TO
R.T.I CONTROLLER

WOODS METAL   Cu BLOCK

FIGURE 9:   DISC HEATING APPARATUS.

c) <u>Standard Conditions for Qualitative Colouration Test</u>.

Where reference is made to the ability of a polymer sample to undergo thermal colouration it may be assumed that the following test conditions were applied: the sample was incorporated into a potassium chloride disc by the technique described below and heated for 1 hour at 150° in vacuum in the apparatus mentioned in the previous paragraph.

5. MEASUREMENT OF INFRARED SPECTRA.

Infrared spectra were measured on a Perkin-Elmar Model 13 double beam spectrophotometer with rock salt prism.

<u>Solid State Spectra</u>.

These were obtained using the potassium chloride disc technique. Potassium chloride of very fine particle size was prepared by the method of HALES and KYNASTON[15]. the polymer sample (5 to 7 mg.) was ground in an agate mortar with 300 mg. of oven-dried potassium chloride for two minutes under an infrared lamp (to prevent adsorption of water from the atmosphere). The mixture was then transferred to a disc press[16] and compressed under a

pressure of 5000 lb. per sq.in. giving transparent discs.
In the measurement of the spectrum the disc containing the
polymer was placed in the sample beam of the instrument
and a disc containing potassium chloride only was placed
in the reference beam.

Solution Spectra.

Solution spectra were measured only over small
regions of the spectrum, and solvents had to be chosen
which had appropriate "window regions" in which there was
no absorption.   The choice of suitable solvent was
further restricted by difficulties in dissolving the
polymer.   The most ideal solvents for spectroscopic work
(e.g. carbon tetrachloride, methylene chloride, and carbon
disulphide) were very poor solvents for the polymer.   The
principal solvents used were cyclohexanone and methyl
ethyl ketone.   These were purified by distillation through
a spiral column and stored over calcium chloride.

Rock salt cells of 0.5 mm. thickness were employed.
It was found necessary to use solutions whose concentrations
were from 3-8% w/v.   The sample solution was balanced
against the pure solvent in the reference beam of the
instrument.   Ideally the weak background spectrum due to
the solvent should be balanced out.   Because of the high

concentration of polymer present, however, perfect balancing, which would result in a completely flat background, could not be obtained.   In figure 10 a typical solution spectrum is compared with an "ideal" spectrum for the same region. The method used to avoid errors due to the solvent background in quantitative work was the common procedure of selecting a "ground line" from which peak heights were able to be measured accurately.   This is chosen by taking two fixed identifiable points on the spectrum (the calibration ticks made by the instrument are most suitable), one on either side of the peak, and joining these by a straight line (figure 10).   Provided measurement of the peak height under consideration is carried out from the same ground line in all cases, relative errors are largely eliminated. The same ground line technique was used in measuring CN peak heights in the quantitative work using KCl discs described in chapter 4.

It was found difficult to avoid small errors in polymer concentration when working with very small volumes of concentrated solutions.   Corrections were made for these errors in the following way.   In the reaction being studied (chapter 5), changes were observed in the absorption band at 2012 cm^{-1} The 2210 cm^{-1} band, due to nitrile
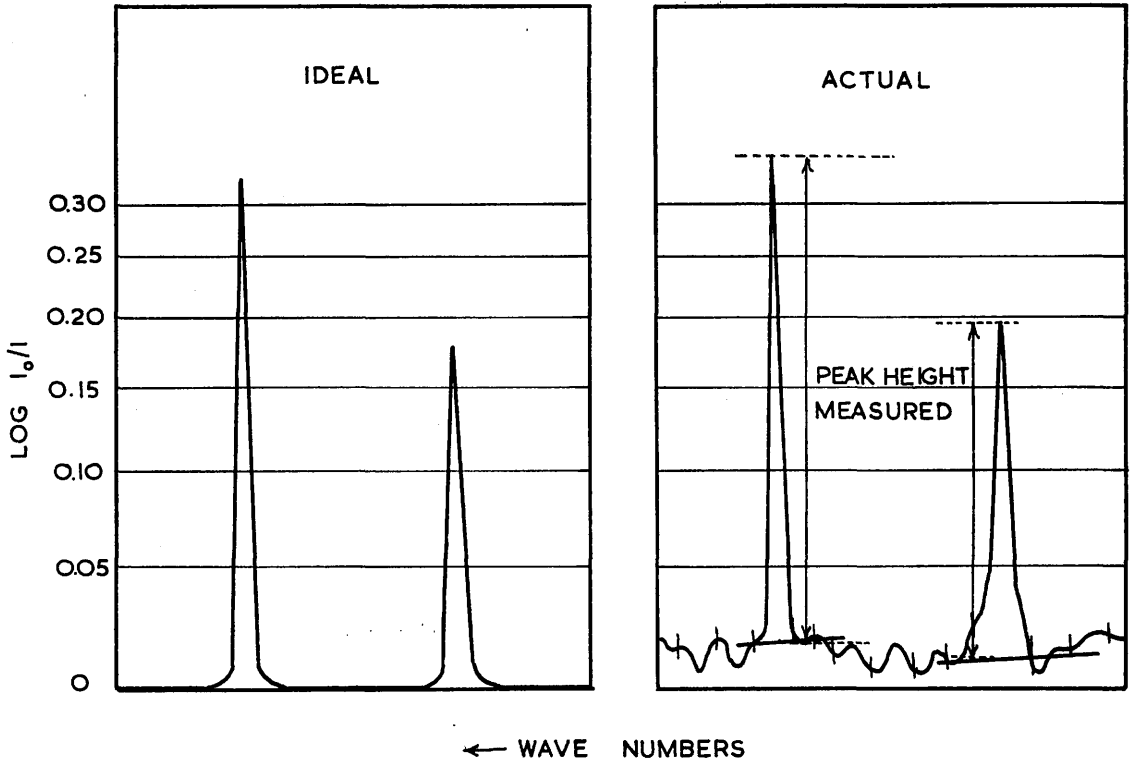
FIGURE 10: GROUND LINE TECHNIQUE.

groups, was not affected in the reaction and could be used as an internal measure of polymer concentration, enabling a small correction to be applied to the 2012 cm.$^{-1}$ peak height from observed deviations in the 2210 cm.$^{-1}$ band.

3

SEPARATION OF
COLOURATION AND DEPOLYMERIZATION

When the temperature of a methacrylonitrile polymer which
is liable to develop colour is slowly raised in vacuum, the
following general behaviour is observed. At 110° the
polymer remains clear and colourless but has softened
sufficiently for volatile material (traces of precipitant
used in the isolation of the polymer) to escape.   Above
120° the material rapidly changes colour through yellow,
orange and red to deep red.   Simultaneously the solubility
in acetone gradually decreases: yellow and orange material
from 15,000 M.W. polymer remains soluble but red material
is less readily soluble.   No further evolution of
volatile material occurs until monomer is evolved at approx-
imately 220o.   Figure 11 shows how the rate of evolution
of volatile material varies as the temperature of such a
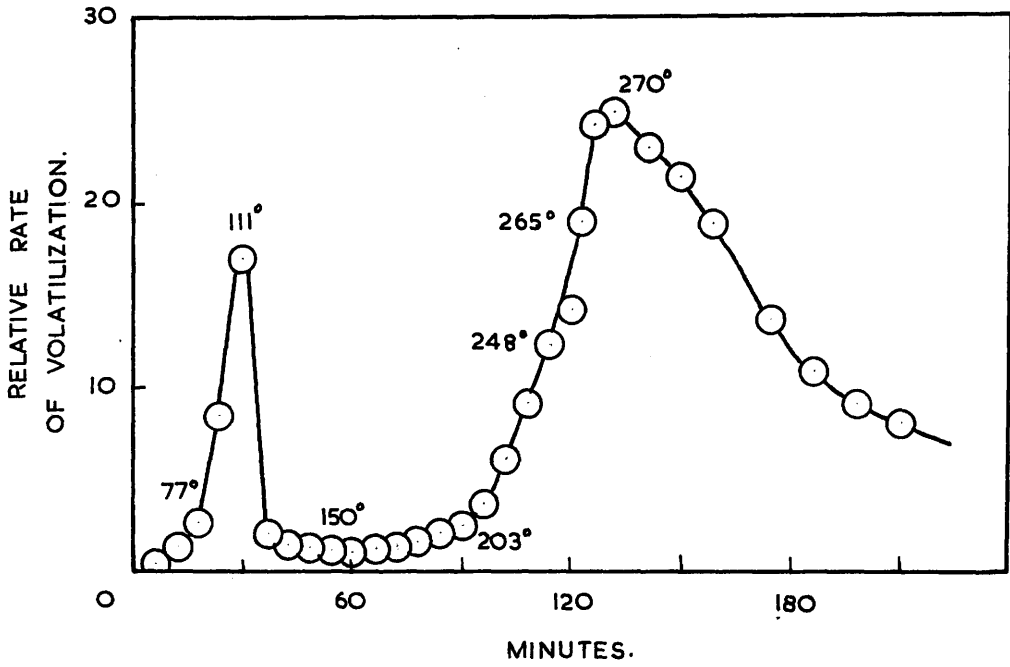polymer sample is slowly raised to 270° in the dynamic

FIGURE II.

molecular still (p.27).

While the colouration of polymethacrylonitrile has always been regarded as characteristic of the polymer, it soon became clear that the ease and extent of colouration were liable to vary widely from sample to sample. Investigation of the factors involved proves that the method of purification of the monomer, the nature of the initiator, and the presence or absence of air during polymerization may all have an effect, as shown in table 3.

Table 3

EFFECT OF POLYMERIZATION CONDITIONS ON
DEGRADATION BEHAVIOUR OF RESULTING POLYMERS.

No.	Conditions	Does polymer redden?	Max.yield monomer, 310°
A	Polymerization in air	Yes	about 55%
	Polymerization in vacuum		
B	.... from impure monomer	Yes	60-80%
C	.... from pure monomer using benzoyl peroxide initiator	Slightly	93%
D.	.... from pure monomer using azobisisobutyronitrile initiator	No	98%

It is also quite clear that the development of colour markedly affects the ultimate yield of monomer which can be obtained when the polymer is heated to high temperatures. For example the polymer referred to in figure 11, which colours readily, yields only 58% of monomer if heated rapidly to 310°, and if the extent of colouration is increased by preheating at 160° for 30 minutes the yield of monomer which can be obtained falls to 52%. On the other hand, polymer D (table 3) is converted almost quantitatively into monomer under the same conditions. Thus when colouration is absent the material appears to behave in the way which would be predicted by comparison with other polymers derived from 1:1-disubstituted monomers.

The data in table 3 suggest that colouration is associated in some way with the presence of impurities. Clearly the degradation to monomer at temperatures above 220° cannot be studied systematically until the general nature of the colour reaction has been elucidated, since it so profoundly alters the degradation properties at higher temperatures.

NATURE AND ORIGIN OF IMPURITIES.

The infrared spectra of the polymers in table 3 are shown in figure 12A-D (technique for spectroscopic work,

see p.36).   The main difference between them resides in
the band at 1720 cm.$^{-1}$, the intensity of which runs closely
parallel to the ease of colouration of the polymers.
Polymer D in which this band is absent shows no colour
reaction below 200°.   The position of the band indicates
that some type of carbonyl structure (ketone, ester, acid,
etc.) is responsible.   Carbonyl structures could occur
in polymethacrylonitrile in any one of the following ways:

i) Occlusion of ketonic solvents.

BEAMAN[17] reported a strong peak at 1710 cm.$^{-1}$ in the
infrared spectrum of polymethacrylonitrile prepared by
anionic catalysis and he attributed this to residual acetone
in the polymer films, prepared from acetone solutions,
which he used for his infrared spectroscopic measurements.
In the present work the potassium chloride disc technique
(p.36) was employed in preparing samples.   The possibility
of occlusion of solvent during purification is ruled out
since the 1720 cm.$^{-1}$ peak appears with the same intensity
when ketonic solvents have not been used in the isolation
or purification of the polymer.

ii) Decomposition of peroxidic structures.

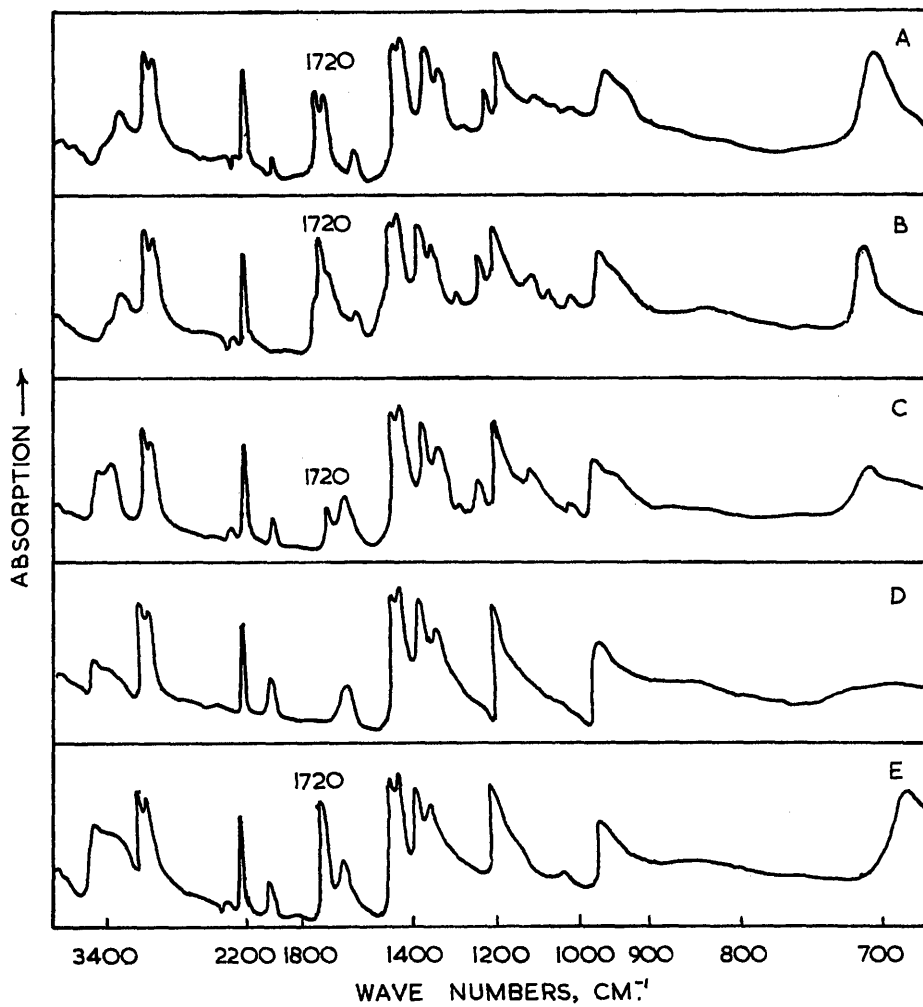This would account for carbonyl absorption in

FIGURE 12 : POLYMER SPECTRA.

air-polymerized material.   STRAUSE and DYER[18] have shown
that oxygen readily copolymerizes with methacrylonitrile.
Primarily, peroxidic structures

$$- M - M - M - O - O - M - M -$$

are undoubtedly formed, but being labile these will decom-
pose to produce other oxygenated structures containing
carbonyl groups.   The double carbonyl peak in figure 12A
is probably due to products of different modes of peroxide
decomposition.

iii) <u>Initiator fragments</u>.

PFANN, WILLIAMS and MARK[19] showed that in samples of
polystyrene initiated by benzoyl peroxide there was
absorption at 1720 cm.$^{-1}$ which varied inversely as the mol-
ecular weight.   They also noted a small peak at 1250 cm.$^{-1}$
It was concluded that benzoate end groups were responsible.
The spectrum in figure 12C (polymer C, table 3) shows weak
absorption at 1720 cm.$^{-1}$ and very weak absorption at
1250 cm.$^{-1}$, and these peaks can therefore in this case be
attributed with reasonable certainty to initiator fragments.

iv) <u>Hydrolysis of nitrile groups to carboxyl</u>.

If conditions are chosen such that (i),(ii), and
(iii) are ruled out, and carbonyl absorption is still found

to occur, the most likely explanation is that hydrolysis of nitrile groups has taken place.   This is probably the case in the polymer referred to in figure 12B above.

Since the isolation and purification procedure used for all the polymer samples was the same, and some showed colour reaction while others did not, hydrolysis cannot have occurred at that stage.   It must therefore have taken place in the monomer or in the polymer while it was still in the reaction tube.   An examination of monomer purity was therefore indicated, in particular to discover whether some acidic or basic impurity was present which might cause hydrolysis.

Nature of the Monomer Impurity.

The first batch of monomer (from which polymer B was prepared) had been purified using the method described by GRASSIE and VANCE[11].   The crude product was a mixture of monomer and acetic acid, from which monomer was isolated by pouring the mixture into water and extracting with ether. Finally the ether extract was distilled, and the monomer obtained was redistilled (p.12).   The infrared spectrum of the product obtained is shown in figure 13A.   This shows a strong carbonyl peak and broad OH absorption, indicating the presence of an acidic impurity. The material
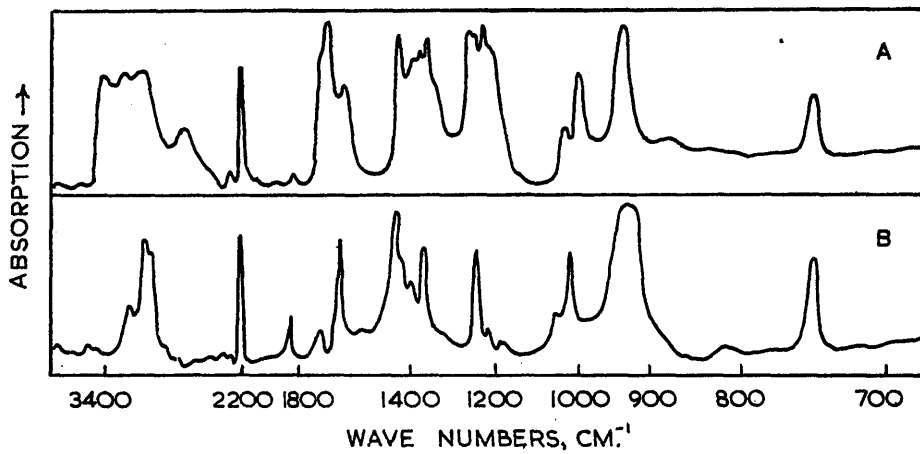
FIGURE 13 : MONOMER SPECTRA.

also shows an acid reaction to moist litmus paper.   The
acid is most probably acetic acid (b.118°) which had been
present in the ether extract. Very careful fractionation
would be required to obtain 100% pure methacrylonitrile
(b.89°) from a mixture of methacrylonitrile and acetic
acid* and the above procedure took no account of the poss-
ible presence of acetic acid in the ether extract.   Meth-
acrylic acid, the only other acidic impurity likely to be
present, boils at 163° and would be readily separable by
distillation.

A second batch of monomer was purified by neutral-
izing the crude monomer/ acetic acid mixture with ammonia,
removing the aqueous layer which separated, and drying and
twice distilling the monomer.   The spectrum of the
product, which is pure methacrylonitrile, is given in
figure 13B.   Polymer D (table 3 and figure 12), prepared
from this pure monomer, in vacuum, using an azo catalyst,
shows no colouration and no carbonyl absorption in its
infrared spectrum.

---

* Boiling point/ composition data for this system
have been obtained by YAKUBOVICH, RUDENKO, and
MERKULOVA[20].

Nature of the Impurity in Polymer from Impure Monomer.

While the impurity in the monomer is acetic acid, the impurities present in the polymer are incorporated in the chain, since reprecipitation affects neither the intensity of carbonyl absorption nor the colouration properties. The polymer must therefore contain methacrylic acid units formed by hydrolysis. A copolymer prepared from pure methacrylonitrile together with traces of methacrylic acid shows similar colouration properties and has a similar infrared spectrum (figure 12E, p.46) to polymer B from impure monomer.

The results of degradation experiments on polymers prepared from pure monomer along with traces of acetic acid and water, both separately and together, are shown in table 4, from which it may be deduced that hydrolysis

Table 4

EFFECT OF MONOMER IMPURITIES ON COLOURATION
PROPERTIES OF POLYMETHACRYLONITRILE.

Impurity	Effect on polymer
None	No colour
Water (5%)	"
Glacial acetic acid (5%)	"
Water + acetic acid (5%)	Colours

occurs under the combined influence of acetic acid and water at the elevated temperature of polymerization.   It is not clear whether hydrolysis occurs in unpolymerized monomer or in monomer units after they have been incorporated into polymer chains.

RESIDUAL COLOURATION IN PURE POLYMER.

Pure polymer initiated by $\alpha:\alpha'$-azobisisobutyronitrile does develop colour very slowly above 200°. This represents a rate of reaction many orders of magnitude less than that of the other polymers mentioned above. It does not appear to be the result of impurity in the polymer, and probably originates as a result of some structural abnormality involving monomer units themselves, such as chain ends or branches.   This slight colouration does not affect the depolymerization reaction seriously since monomer yields close to 100% can be obtained.

CONCLUSIONS.

From these results it appears that the colour reaction depends on the presence of impurities in the polymer chain, such as methacrylic acid units. The changes in the properties of the polymer seem too extensive to be

accounted for simply in terms of reaction between these few isolated impurity units, but to depend rather on changes involving many methacrylonitrile units. The methacrylic acid units probably act as centres of initiation for a process which results in the production of conjugated structures which gradually increase in length (since the colour change develops through yellow and orange to deep red.)

These experiments have defined the conditions under which colouration and depolymerization may each be studied conveniently. For depolymerization investigations at high temperatures polymers prepared from carefully purified monomer, polymerized in vacuum using an azo catalyst, are required. The colour reaction may be studied at 120-160° in copolymers of pure methacrylonitrile with traces of methacrylic acid.

4

THE COLOUR REACTION

It was concluded in the previous chapter that colouration
in polymethacrylonitrile is initiated at impurities; when
these are removed colouration at 120-160° is completely
eliminated.   The most convenient approach to a study of
the colour reaction is to prepare polymers containing known
amounts of one impurity and to take rigorous precautions to
exclude all others.   Copolymers of methacrylonitrile with
small amounts of methacrylic acid colour readily on heating.
Such copolymers are therefore ideally suited to the present
investigation since a close control can be kept over the
number of centres of initiation.

Three copolymers of methacrylonitrile and methacrylic
acid were prepared, careful attention being paid to monomer
purity, choice of initiator, and exclusion of air.   The
details of the preparation are given on pp.14-19 and the
compositions in table 5 below.   The molar ratio of the

two types of monomer unit is a measure of the proportion
of colour-initiating centres.   Copolymer 3, for example,
has 1 initiation centre for every 2.57 methacrylonitrile
units.

Table 5

COPOLYMER COMPOSITIONS.

Copolymer	Molar Ratio of Monomers*
1	21.2
2	5.25
3	2.57

* (Methacrylonitrile)/(Methacrylic Acid).

MOLECULAR WEIGHT AND SOLUBILITY CHANGES.

When copolymers of methacrylonitrile and methacrylic
acid colour thermally in vacuum, the solubility in acetone
decreases.   Data for copolymer 1, given in table 6,
show that in the early stages of the reaction the polymer
remains completely soluble.   This enables molecular
weight measurements to be made.

Table 6

MOLECULAR WEIGHT AND SOLUBILITY CHANGES

OF COLOURED COPOLYMER 1.

Time at 140°(min.)	Colour	Solubility (%)	Mol. Wt.
0	Colourless	100	14,400 ± 750
15	Yellow-orange	100	11,850 ± 750
45	Orange-red	100	12,950 ± 750
180	Deep red	80	12,750 ± 750

On prolonged heating the polymer becomes completely insoluble in acetone. Coloured material dissolves more readily in cyclohexanone than in acetone, although the opposite behaviour is true of the undegraded polymer.
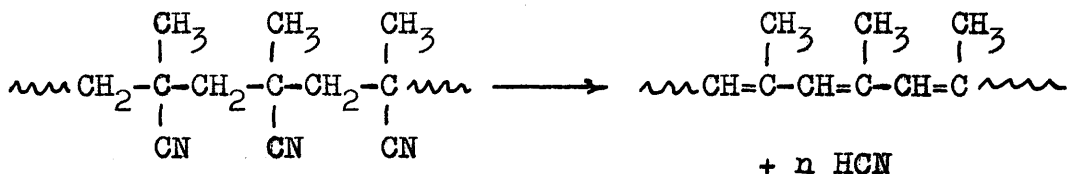
The decrease in solubility suggests that cross-linking may be taking place, either associated with the colour reaction or quite independent of it. The data of table 6, however, show that up to the point of insolubility there is no tendency for the molecular weight to increase, so the possibility of cross-linking is excluded.

The small decrease in molecular weight which occurs

in the very earliest stages of the reaction is not connected with colouration, since it occurs in most methacrylonitrile polymers, including those which do not colour at all.   The reason for this drop in molecular weight will be discussed in chapter 5.

ABSENCE OF VOLATILE PRODUCTS.

Experimental evidence has already been given to show that no volatile material is produced during colouration (p.41).   This immediately rules out the possibility, considered in the first chapter, that polymethacrylonitrile might undergo an ester decomposition type of reaction, analagous to the behaviour of polyvinyl chloride and polyvinyl acetate.   This would have involved loss of hydrogen cyanide:

$$\text{CH}_2\text{-C-CH}_2\text{-C-CH}_2\text{-C} \longrightarrow \text{CH=C-CH=C-CH=C}$$

with CH$_3$ groups above each carbon and CN groups below, converting to the conjugated system + n HCN.

but since no volatile products are produced the above reaction cannot be taking place.

The absence of cross-linking and of volatile products strongly suggests that the reaction consists of

some sort of intramolecular rearrangement.   The insolubility must result from extensive configurational changes.

CHANGES IN INFRARED SPECTRUM.

a) General.

During colouration substantial changes take place
in the spectra of the copolymers.   The changes allow the
reaction to be followed in a semiquantitative manner.

Potassium chloride discs were prepared (technique,
p.36) containing 5.6 mg. of copolymer in each case and the
infrared spectra of the undegraded materials were obtained.
The discs were then heated in vacuum at 140° in the
apparatus shown in figure 9 (p.35), heating being interrupted at intervals for measurement of the spectra.   It
is very much more satisfactory to carry out the reaction
in the disc in this way than to colour small polymer
samples individually and subsequently to prepare discs.
The latter procedure involves difficulties due to non-uniform grinding and compression of different samples of
coloured polymers and introduces the possibility of errors
in weighing and manipulating very small amounts of
material.   By adopting the former method the weight of
sample in the colouration of any one copolymer cannot vary.

The only difficulty is scattering of light at higher wave numbers in the spectrum, caused by an increase in particle size when the polymer sample is softened on heating and resolidified on cooling.   This is not serious.   It is, of course, only possible to carry out the reaction in a pressed disc because no volatile products are involved.

Table 7

CHANGES IN INFRARED SPECTRUM DURING COLOURATION.

| Disappearance or Reduction of Absorption at $(cm.^{-1})$	Structure Responsible	Appearance of New Absorption at $(cm.^{-1})$	Structure Responsible
3480	OH or NH	3180*	=NH?
2580w	COOH?	3o70	
2210m	$-C\equiv N$	1693-1490s	$(-C=N-)_n$
2012w	$>C=C=N-$	1272	
		1178	
		1133s	

* already present in undegraded copolymers 2 and 3.

Figure 14 shows the changes occurring in the spectrum of copolymer 1 at different extents of colouration. Copolymers 2 and 3 show the same general changes as copolymer 1; detail differences are discussed below. Table 7 summarizes the changes in spectra.

The general broadening of bands in the lower frequency region of the spectrum is to be expected since we are dealing in effect with a mixture of coloured and undegraded polymer.

The band at 3480 cm.$^{-1}$ may be due to the hydroxyls of the carboxyl group or more probably to traces of water. Interpretation in this region is confused by possible hydrogen bonding effects and poor resolution of the sodium chloride prism. The possibility that the spectrum may be modified by interaction between the carboxyl groups and the KCl disc on heating[21] has not been overlooked. The spectra of discs prepared from polymer which has previously been coloured do not differ appreciably from those prepared as described above.

The 2012 cm.$^{-1}$ peak, which disappears when the polymer softens, is due to ketene-imine groups, the occurrence and behaviour of which will be discussed in detail in chapter 5. They are not associated with the colour
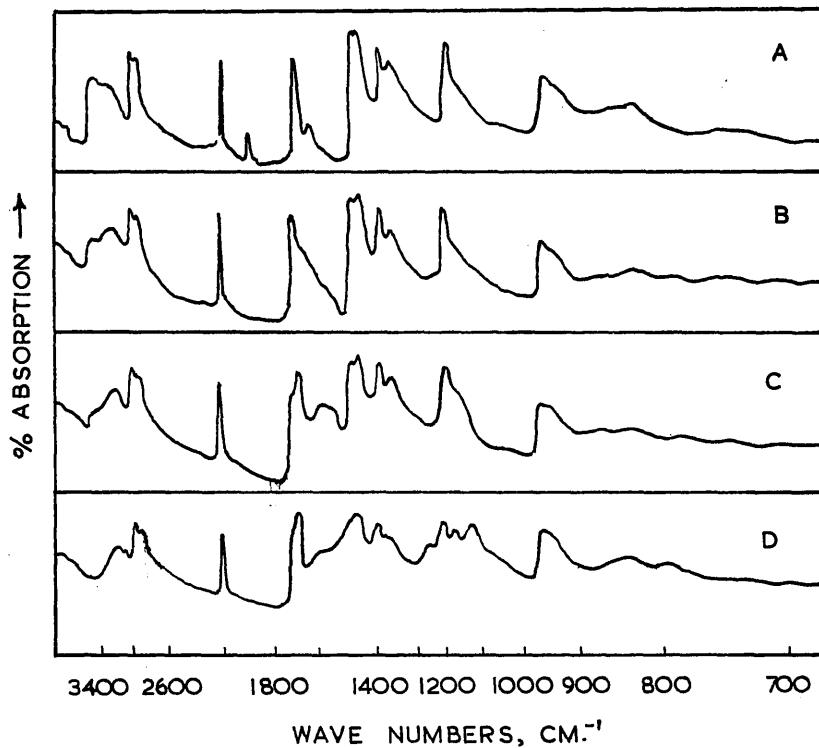
FIGURE 14: CHANGES IN INFRARED SPECTRUM DURING
COLOURATION.

COPOLYMER I.

A. UNDEGRADED, COLOURLESS
B. 3 HOURS AT 140°, YELLOW ORANGE
C. 9 " " " ORANGE RED
D. 23.5 " " " DEEP RED.

reaction, since they are also present in pure colour-stable polymethacrylonitrile.

The 2210 cm.$^{-1}$ band due to the nitrile group decreases steadily during the course of the reaction.

The interpretation of the peaks which appear during degradation is more difficult. The most significant change is the development of broad absorption in the region 1693-1490 cm.$^{-1}$

b) The Nitrile Peak.

The decrease in intensity of the 2210 cm.$^{-1}$ band during colouration of all three copolymers under discussion has been investigated quantitatively. The results are summarized in figure 15 , from which it is clear that the initial rate of disappearance of nitrile groups is roughly proportional to the number of centres of initiation (methacrylic acid units).

On the other hand, although in copolymers 2 and 3 the nitrile groups react faster, the development of visible colour is much slower. Copolymer 1 has become deep red by the time 12% of the nitrile groups have reacted, copolymer 2 is only yellow-orange after 23% reaction, while copolymer 3 is only slightly yellow at 30%
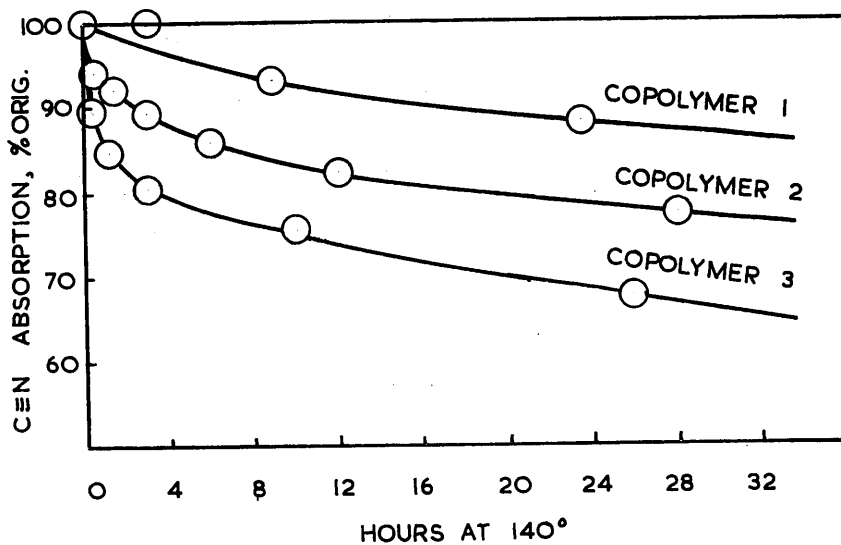
FIGURE 15: DECREASE IN NITRILE ABSORPTION (LOG I_0/I) DURING COLOURATION.

reaction.   Therefore there is some inverse relationship between the number of initiating centres and the production of visible colour.   It follows that there is a direct relation between the average length of methacrylonitrile sequences in the copolymer chain and the extent to which visible colouration passes through the spectrum towards red.

c) The Region 1693-1490 cm.$^{-1}$

During colouration new absorption appears in this region as a broad band with a peak at 1693 cm.$^{-1}$ This peak could be due to a carbonyl structure differing from that originally present (which absorbs at 1720 cm.$^{-1}$) or to C=NH.   It is not possible with the evidence presented so far to decide between these possibilities but further data which will be discussed later (p.77) indicates that C=NH is responsible.

The interpretation of the remaining part of this broad absorption band is easier.   In figure 16 the changes which occur in the 1660-1490 cm.$^{-1}$ region are shown quantitatively for each of the three copolymers. Copolymer 1 exhibits an initial increase in absorption at the higher frequency end of the region.   As the colour changes from yellow to red there is a gradual shift to
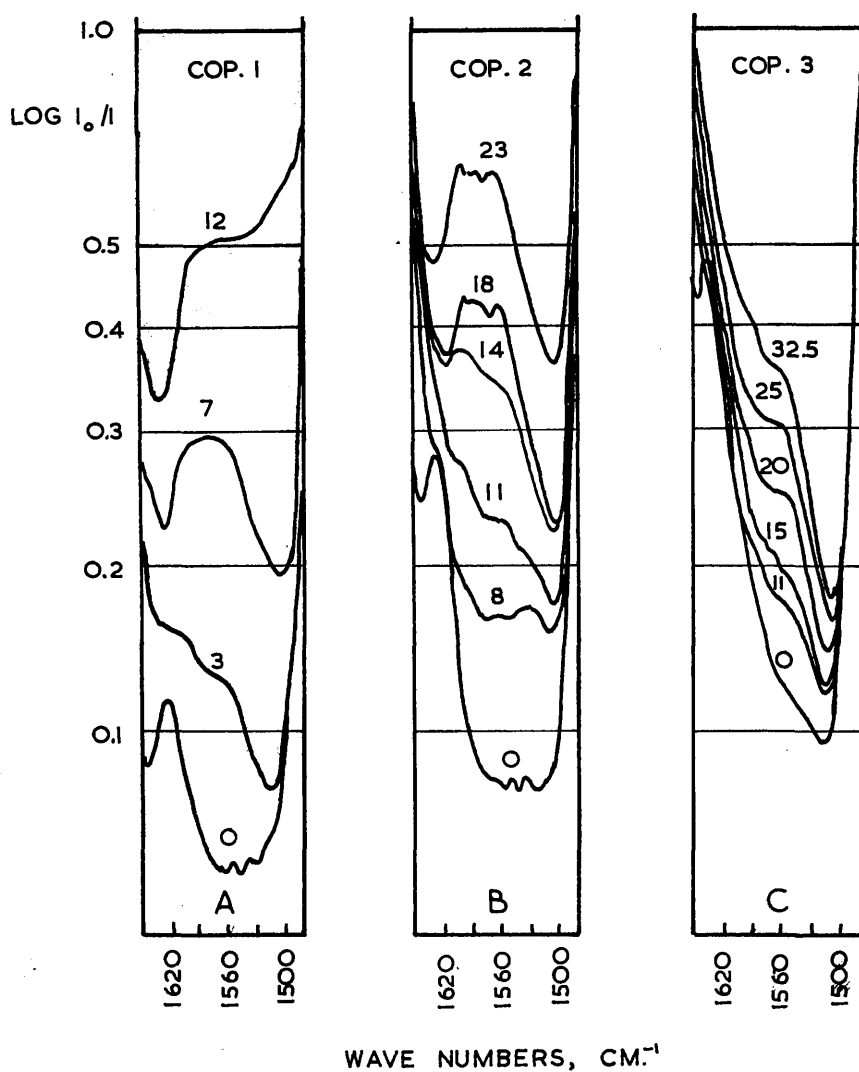
FIGURE 16: CHANGES IN INFRARED SPECTRUM, 1660-1490 CM⁻¹ REGION.

EXTENT OF REACTION (C≡N % DECREASE) INDICATED FOR EACH STAGE

lower frequencies as well as a general intensification. This can be explained on the basis of the production of conjugated sequences which gradually increase in length, a range of different lengths always being present at any given time. The movement of colour through the spectrum rather than the intensification of a single colour supports the view that the development of conjugation takes place gradually. Since nitrile groups are disappearing without chain-scission, cross-linking, or the elimination of volatile material, these must be carbon-nitrogen sequences arising by a linking up of adjacent nitrile groups along the polymer chains. BIRCUMSHAW, TAYLER, and WHIFFEN[22] have made a similar interpretation of absorption in the same region of the spectrum of paracyanogen.

If the above conclusions are correct, then in copolymers 2 and 3 in which the length of the conjugated carbon-nitrogen sequences, and hence the development of colour, must be severely restricted by the greater proportion of methacrylic acid units (1 in 5.3 and 1 in 2.6 respectively, compared with 1 in 21 in copolymer 1) which break up the long sequences of methacrylonitrile units, we should expect to find much narrower absorption bands for equivalent extents of reaction and much less

tendency to broaden to lower frequencies as reaction proceeds.   Figures 16 B and C show that these predictions are realized.   Copolymer 3 shows very little shift in absorption to lower frequencies and copolymer 2 is intermediate in behaviour between copolymers 1 and 3.

Further evidence of the close connection between the disappearance of nitrile groups and the appearance of absorption in the region under discussion is given in figure 17.   Here the optical density at 1570 $cm.^{-1}$, which can be taken as representing the concentration of $C = N$ sequences of one particular length, is shown to be directly proportional to the percentage decrease in nitrile absorption (omitting the rapid initial stage of the reaction).

REVERSIBILITY OF THE REACTION.

Thermally coloured copolymer 1 dissolves in acetone or more readily in cyclohexanone to give a correspondingly coloured solution.   Gradual reversion occurs, however, and a blood-red solution, for example, reverts to orange in two or three days at room temperature. When an attempt is made to dissolve coloured samples of copolymers 2 and 3 in cyclohexanone, the colour fades as the solid polymer
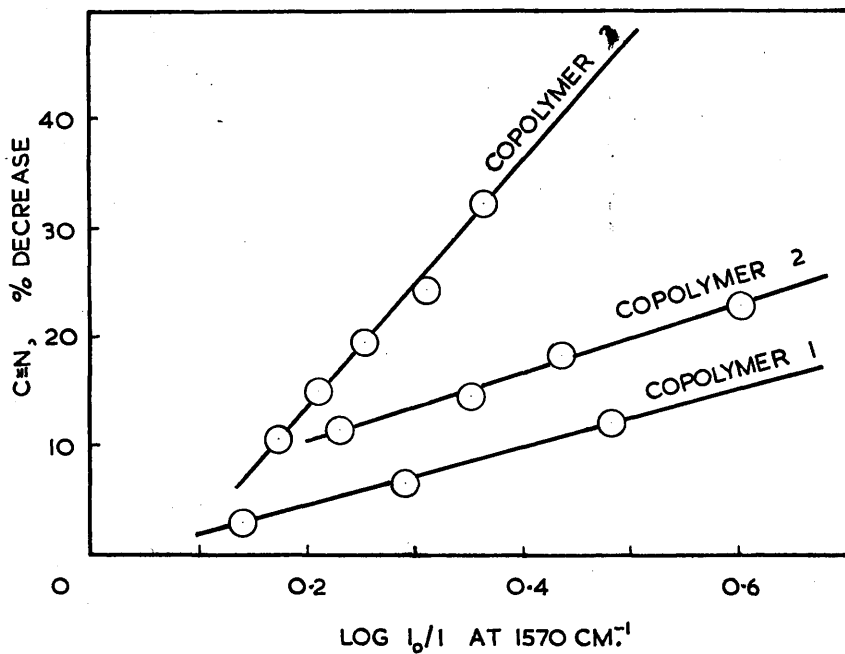
FIGURE 17.

dissolves, and a colourless or yellow solution results.
Evidently the chemical structure responsible for colour,
especially red colour, is unstable in solution.   This is
emphasized by the fact that no colouration is obtained
when cyclohexanone solutions of copolymer 1 are heated to
140-150°.

Reversion can be accelerated by treatment of
solutions in acetone with small quantities of aqueous
solutions of acids, alkalis, or salts (e.g. calcium chlor-
ide).   Thus a deep red solution of copolymer 1 fades to
pale yellow in a few seconds.   From this solution yellow
polymer can be precipitated which has an infrared spectrum
similar to that of yellow polymer obtained by thermal
colouration.

Any mechanism proposed for the reaction must there-
fore allow of a simple reverse process.

MOLECULAR STRUCTURE OF COLOURED POLYMER.

From the experimental data described above it is
proposed that intramolecular linking of adjacent nitrile
groups occurs, resulting in the structure (I).

Molecular models indicate that in polymethacrylo-
nitrile the double substituents must impose considerable

restriction to free rotation about the chain carbon-carbon bonds, and that one of the most probable configurations has nitrile groups all on one side of the chain , so that such an intramolecular reaction would be facilitated. Furthermore there is no appreciable strain in the resulting fused ring structure, since the atoms occupy almost identical spacial positions in the ring structure and in the undegraded polymer (see photographic plate).

(I)

(II)

(III)
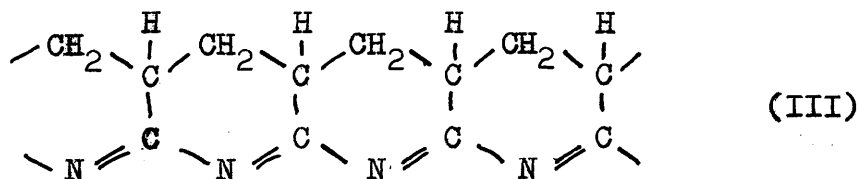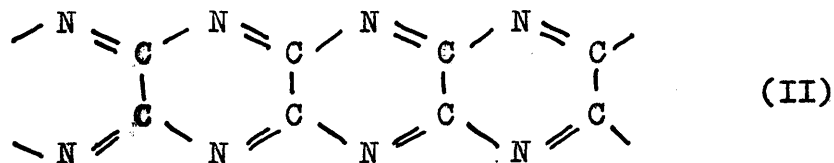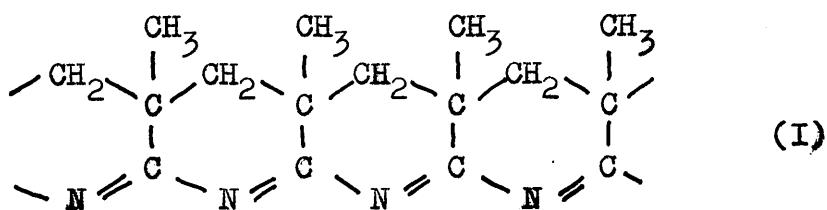
Similar structures have been proposed for para-cyanogen[22](II), alkali-degraded polyacrylonitrile[23], and recently for thermally-degraded polyacrylonitrile[24](III).

Polymerization of nitrile groups in nitriles which contain no reactive methylene group is well known in the formation of triazines, e.g. benzonitrile gives kyaphenine

PhCN ⟶

(structure showing triazine ring with Ph groups)
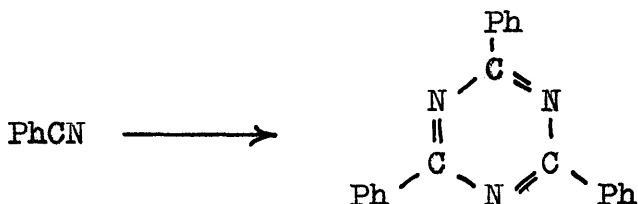
The changes in infrared spectrum which occur on thermal colouration of polymethacrylonitrile are reasonably explained by structure (I) although the assignment of the new bands at lower frequencies (below 1490 cm.$^{-1}$) to the naphthyridine-type ring systems can only be speculative.   The insolubility in acetone of extensively coloured material can be attributed to the rigidity of the fused-ring structure.

MECHANISM OF COLOURATION.

The reaction requires to be initiated, e.g. by methacrylic acid units in the polymer chains, and the rate of disappearance of nitrile groups increases with the concentration of initiating units. Visible colouration, on the other hand, is inhibited by higher concentrations

of methacrylic acid.   Other foreign units in the chain,
for example methyl methacrylate (which does not itself
initiate colouration) will restrict colouration in polymer
which would otherwise colour extensively.   It follows
that fairly long sequences of adjacent monomer units are
involved, perhaps eight to twelve units for the production
of a red colour (compare the colouration behaviour of
copolymer 2, p.62, with its composition, p.55).

Type of Mechanism - Free Radical or Ionic?

The relative slowness of the movement of colour
through the spectrum is strong evidence that the chain
reaction is not a radical one; at each stage in the
development of conjugation it is likely that relatively
stable structures exist which must be reactivated. Further
evidence for an ionic rather than radical mechanism is
found in the fact that alkali can induce a superficially
similar colouration in acetone solutions of pure poly-
methacrylonitrile.   The conditions for reversion of
colouration mentioned above also support this view.
Perhaps the best proof that the reaction is not a radical
one comes from the fact that hydroquinone does not act as
an inhibitor (and can, in fact, initiate colouration
when a trace is heated with pure polymer, p.75).

<u>Mechanism</u>.

All the experimental evidence presented above
(infrared spectra, copolymerization, solubility, etc.)
concords with the following ionic reaction scheme.

It is proposed that initiation occurs in the follow-
ing manner:
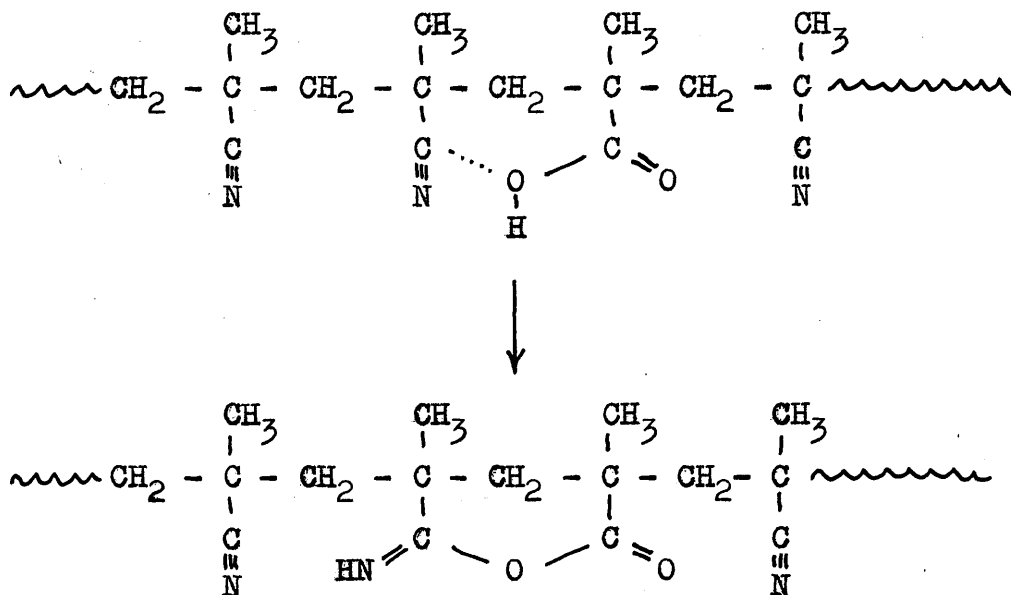
ring closure and proton migration being facilitated by
the electromeric displacements in the nitrile and carboxyl
groups.

Interaction of this sort has been observed in
<u>o</u>-cyanobenzoic acid which can be converted to phthalimide

via the isomer (IV) which can be isolated.[25]

(IV)

This is a case where the nitrile and carboxyl groups are held close together, facilitating reaction.   Molecular models of polymethacrylonitrile support the view that in the polymer chain free rotation is difficult and the two groups concerned are likely to be held in a configuration which makes it easy for them to react.

Propagation may consist of the imine group reacting in a similar way to reproduce itself one unit further along the chain.   This is reasonable since both the -COOH and -C=NH groups contain a reactive H atom capable of migration.   Thus the reaction can proceed along the chain and the structure resulting after several additions will be

This propagation reaction should be readily reversible, as is found experimentally, since the ring structure is tautomeric with the original polymer structure, and colour reversion might easily be accelerated in an ionic medium, espacially in the presence of acids and alkalis when opening of any one of the rings by hydrolysis might also occur.

COLOURATION INDUCED IN OTHER WAYS.

The above discussion was confined to colouration initiated at methacrylic acid units introduced into the polymethacrylonitrile chains by copolymerization.

If the mechanism of colouration suggested is correct, it should be possible to initiate colouration by an acid, imine, etc., not actually present in the polymer chain but simply melted together with the pure polymer. This is found to be the case. The following substances were tested and found to be capable of initiating colouration when the solids are ground together, melted, and heated to 140-180°:

benzoic acid	succinimide
stearic acid	phenol
oxalic acid	hydroquinone.

1 per cent of the initiating substance is adequate to
produce extensive colouration.

The initiation step in this case must be inter-
molecular, the mobile small molecule having easy access
to the nitriles of the chain, being followed by propagation
along the chains as before.   For example, the following
structure would result if benzoic acid were used:
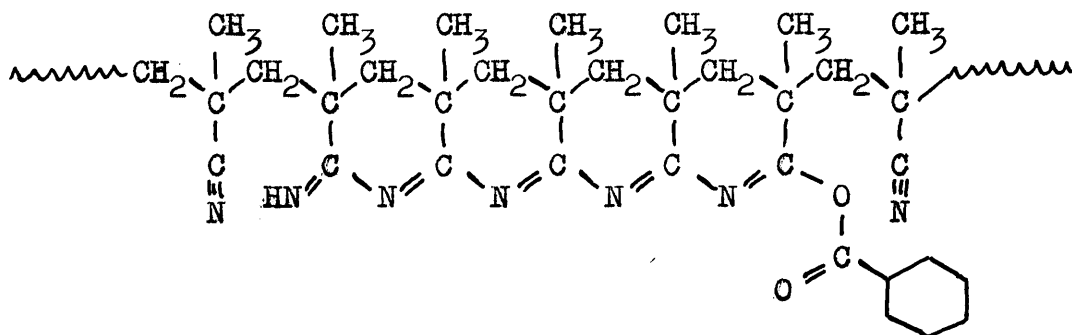
The ability of succinimide to initiate the reaction
is convincing support for the mechanism of propagation
already discussed.

The fact that such a variety of substances can
induce colouration in the polymer is of considerable
importance from the industrial point of view. Colouration
in polymethacrylonitrile has precluded its use as an
industrial material.   We now know that this reaction
can be almost completely eliminated by strict attention

to monomer purity and polymerization conditions, but the above results have shown that care must be exercised even in manipulation of the pure polymer to avoid contamination with any substance capable of causing colouration.

Phenol-initiated Colouration.

The ability of phenols to initiate colouration:
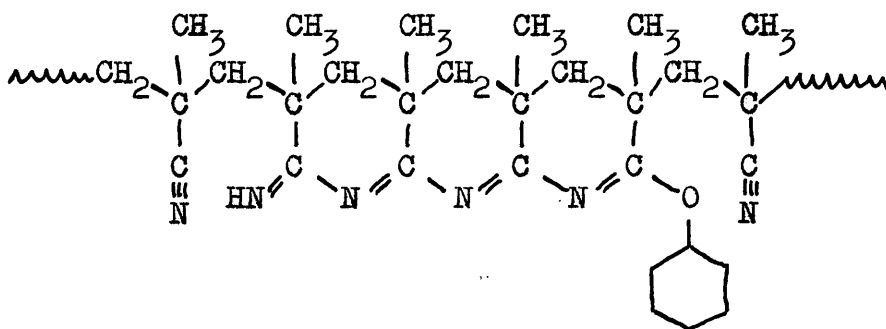
affords an opportunity to resolve a point of difficulty in the discussion of the infrared spectrum of reddened copolymer (p.64).   The 1693 cm.$^{-1}$ peak, which might be due either to a carbonyl structure or to –C=NH *, could not be assigned with certainty to either of these. Phenols do not absorb strongly in this region of the spectrum, therefore any absorption at 1693 cm.$^{-1}$ in a coloured sample initiated by a phenol must be due to –C=NH.*   On the other

---

* The only other possibility is that this peak is due to a ring vibration, but the frequency seems too high for this.

hand, complete absence of this band would indicate that
the band present in the spectrum of reddened copolymer was
due to the carbonyl group of the ring formed in the
initiation of colouration.

This was tested experimentally with pure polymeth-
acrylonitrile (polymer BN 658, see appendix) and hydro-
quinone.   It is not convenient to use phenol itself
because of difficulties in the preparation of KCl discs.
Polymer containing 2% of hydroquinone was made into a disc
with KCl and the infrared spectrum was obtained. The disc
was then heated to 150° for 1 hour (technique, p.33).
The spectrum of the resulting orange-red disc was measured.
The two spectra are shown in figure 18.   The presence of
the 1693 cm.$^{-1}$ band in the spectrum of the coloured disc
confirms that this band is due to -C=NH.

Solution Degradation by Alkalis.

When acetone solutions of pure polymethacrylonitrile
are treated with very small amounts of sodium hydroxide
solution, a yellow colour develops which ultimately
deepens to orange[23].   Larger amounts of alkali give only
pale yellow solutions because of the ability of NaOH to
cause reversion (p.69).   Assuming that the alkali-
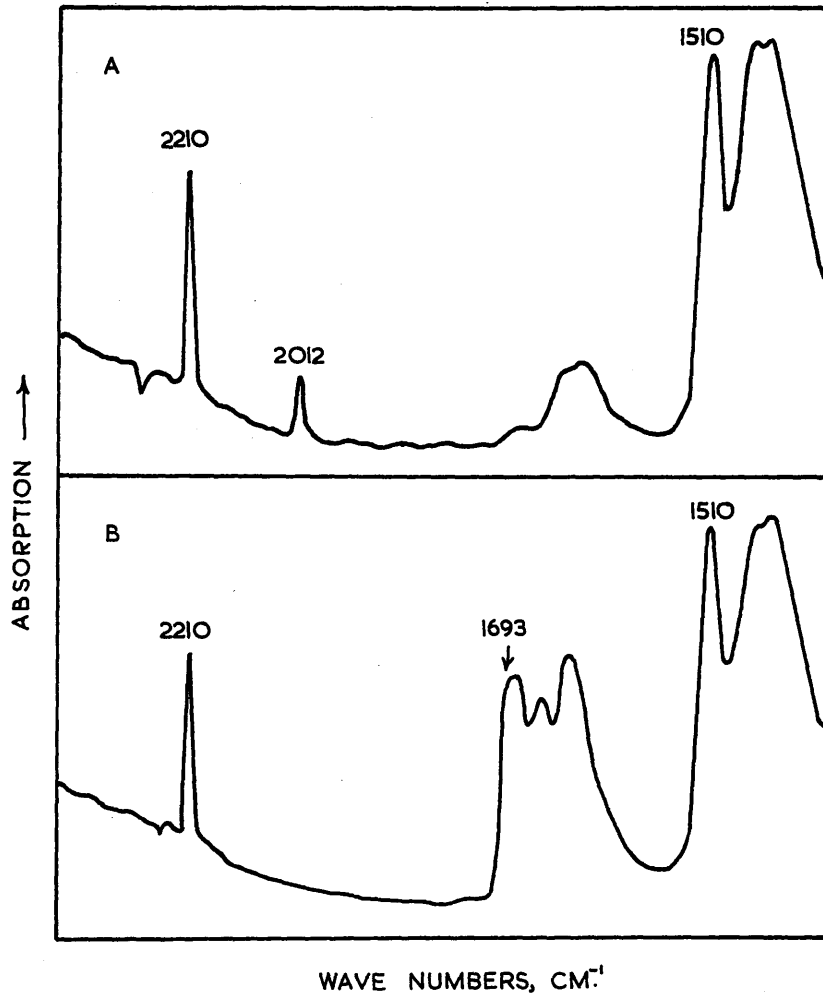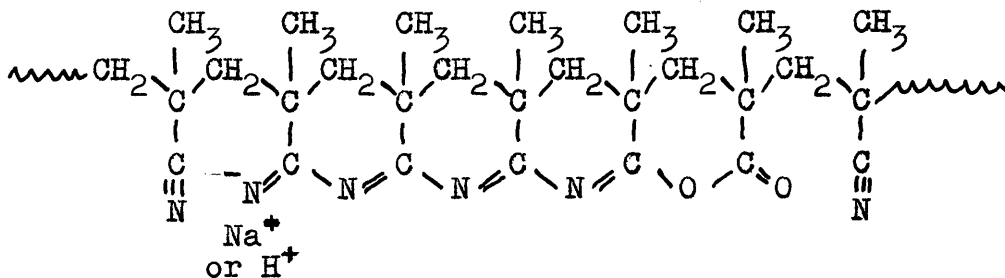initiated reaction is fundamentally similar to the thermal

FIGURE 18.

A. POLYMER + 3% HYDROQUINONE, UNDEGRADED

B. SAMPLE A, AFTER COLOURATION.

colouration of copolymers with traces of methacrylic acid, two mechanisms of initiation seem reasonable.

a). An occasional nitrile unit is hydrolysed to carboxyl and the anion initiates a colour chain:

b). A simpler initiation would consist of the addition of an OH⁻ ion to one of the nitrile groups (this occurs in the first stage of the hydrolysis reaction) followed by linking up of nitrile groups, H⁺ or Na⁺ ions at the ends of the conjugated chains being supplied from the solution:
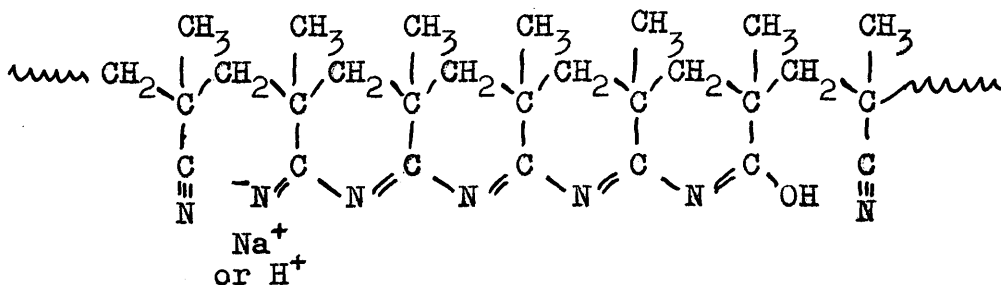
Sodium ethoxide is also capable of bringing about colouration in solution, which supports the latter mechanism.

BEAMAN[17] obtained yellow polymers by anionic
polymerization of methacrylonitrile, using sodium + liquid
ammonia, triphenylmethyl sodium, or butylmagnesium bromide
as catalysts.   It appears likely that these reagents,
in addition to bringing about anionic polymerization of
the olefinic double bond in the monomer are able to
initiate anionic polymerization of the nitrile groups
along the polymer chain in the same way as sodium hydroxide
and sodium ethoxide.

GENERAL BASE-CATALYSED NATURE OF THE COLOUR REACTION.

A review of the substances capable of initiating
colouration in polymethacrylonitrile shows that all are
bases in the Lewis sense.   The electrophilic nature of
the nitrile group therefore seems to determine the course
of the reaction, which we can describe in general terms
in the following way:
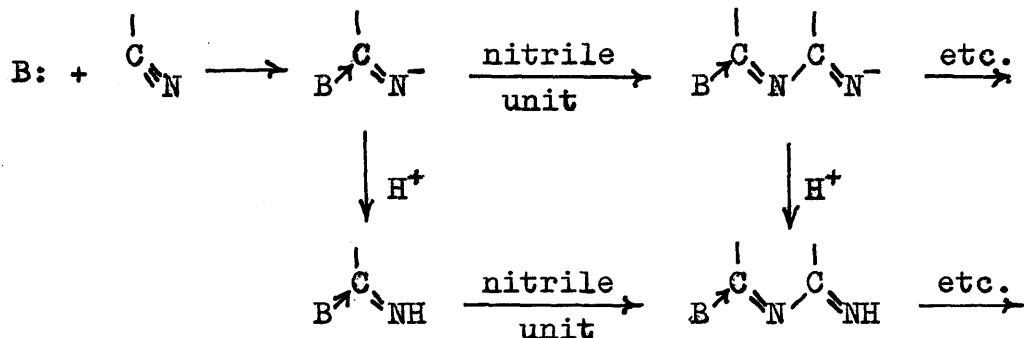
This includes the case of methacrylic acid copolymers:

$$\downarrow \text{H}^+ \text{ migration}$$

etc.
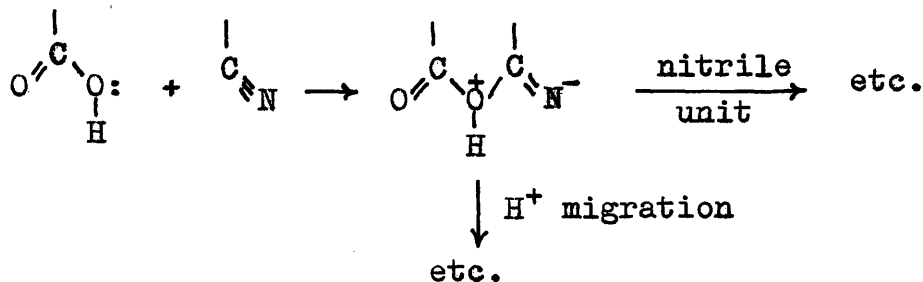
REVERSIBILITY OF COLOURATION PROCESSES.

It is possible to visualise what prevents the reaction in solution from proceeding beyond the orange stage. It is likely that an equilibrium will be set up between molecules with the original structure and those in the rigid coloured form, a range of coloured structures of different lengths always being present. In the case of the molten copolymer, the temperature is high and the mobility of the molecular chains limited by the high viscosity of the medium. The equilibrium might therefore be expected to favour the existence of quite long coloured sequences, so that the polymer will be deep red. On the other hand, in solution, at room temperature, the molecular motion will militate against the formation of the longer coloured sequences, and the equilibrium is likely to lie further towards the original colourless

structure.   Accordingly the resulting colour is nearer
orange or yellow than red.   The argument is shown in
diagramatic form below:

                    Chain rigidity increasing ——————→

ORIGINAL

STRUCTURE ————→   1 ⇌ 2 ⇌ 3 ⇌ 4 ⇌ 5 ⇌ 6 ⇌ HIGHER
No Double Bonds ———   D.B. D.B. D.B. D.B. D.B. D.B.   SEQUENCES
COLOURLESS

                    YELLOW......ORANGE.......RED...
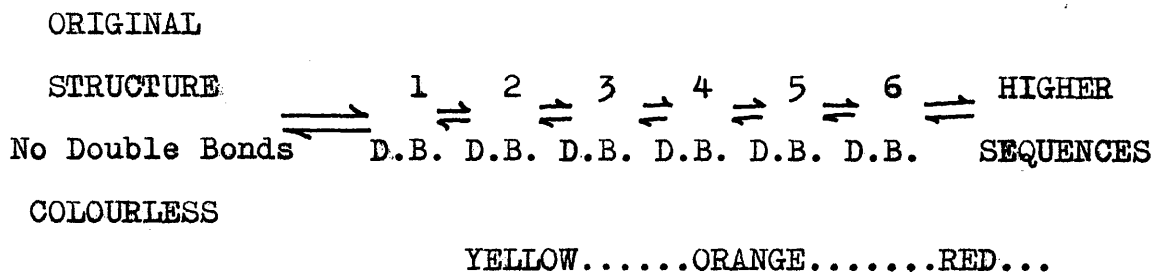
            Increasing temperature
   ——————————————————————————————————————→
            High viscosity (melt)

                    Decreasing temperature
            ←——————————————————————————————
                        and viscosity

        The fading of deeply coloured solutions of
thermally coloured copolymer is therefore explained by
an adjustment of the equilibrium to suit the new environ-
ment.

COMPARISON WITH POLYACRYLONITRILE.

$$\sim\!\!\sim\!\!\sim CH_2 - \underset{\underset{CN}{|}}{CH} - CH_2 - \underset{\underset{CN}{|}}{CH} - CH_2 - \underset{\underset{CN}{|}}{CH} - CH_2 - \underset{\underset{CN}{|}}{CH} \sim\!\!\sim\!\!\sim\!\!\sim$$
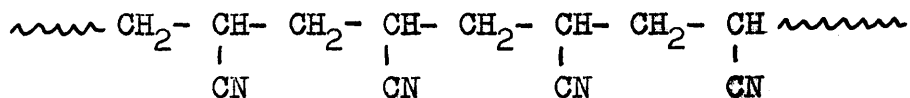
It is of interest to compare the results for the thermal colouration of polymethacrylonitrile with those recently published by BURLANT and PARSONS[24] for the pyrolysis of polyacrylonitrile, since the overall reactions have similar colouration characteristics. These superficial similarities are emphasized by the facts that their infrared spectra show a decrease in nitrile absorption as reaction proceeds, and there is evidence of new absorption in the 1650-1490 $cm.^{-1}$ region. The details of the preparation of Burlant and Parsons' polymers are not quoted but there is little carbonyl absorption in their spectrum for the undegraded material. No acidic impurity is present, therefore, and some other initiation process must operate, possibly associated with the presence of the relatively reactive tertiary hydrogen atoms which are replaced by methyl groups in polymethacrylonitrile. Molecular weight data on the colour reaction in polyacrylonitrile would be of interest in view of the part these tertiary hydrogen atoms might play in

either chain scission or cross-linking reactions.

Amine-initiated Colouration in Polyacrylonitrile.

La COMBE[26] has recently put forward a theory for
amine-initiated colouration in polyacrylonitrile, based
on the observations that the polymer heated in a closed
vessel with 3% butylamine develops a yellow colour, and
the infrared spectrum shows new bands at 1665 and 1538 cm.$^{-1}$
The theory assumes the initial formation of an amidine
structure, followed by rearrangements and ring closures:
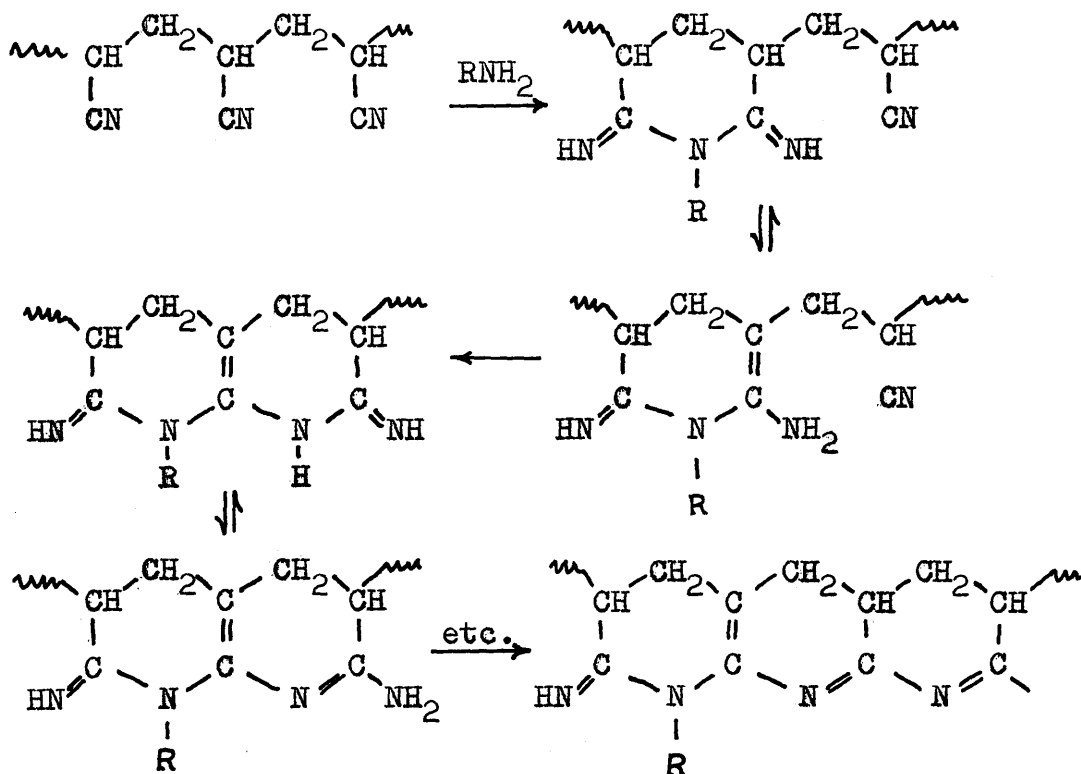
If the mechanism of colouration of polymethacrylo-
nitrile discussed in this chapter is correct, then
La Combe's theory for polyacrylonitrile seems needlessly
complicated, for the imine groups in the amidine structure
should be capable of initiating a series of ring closures.
The validity of La Combe's theory is tested by carrying
out his experiment with polymethacrylonitrile, and it is
found that this polymer also develops a yellow colour.
This would not be possible if the colouration involved
rearrangements of the type La Combe suggests.

Much further work is required on polyacrylonitrile,
but there is little doubt that whatever the initiation
process, e.g. a Thorpe reaction

$$>CH - \underset{\underset{N}{\|\|}}{C} \quad + \quad \overset{|}{\underset{H}{-C}} - C{\equiv}N \quad \longrightarrow \quad >CH - \underset{\underset{NH}{\|}}{C} - C{\equiv}N \quad ,$$
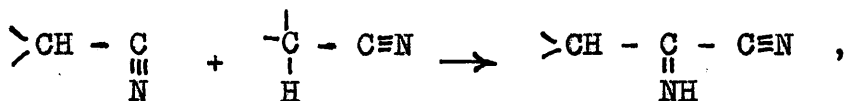
the subsequent development of conjugation proceeds in the
same way as in polymethacrylonitrile.

ADDENDA.

A very recent paper by MARSH and MARTIN[34] on the alkaline hydrolysis and polymerization of hydrogen cyanide is of interest in connection with the general picture of the colour reaction discussed in this chapter.   These authors found that in ammoniacal solutions of HCN with (HCN) > 0.02N and pH values less than 10, heating to 110° resulted in the formation of up to 71% of coloured products believed to be polymeric, in addition to the products of hydrolysis.   No colouration was obtained at pH values above 10.   This behaviour is closely comparable with the colouration and reversion behaviour in polymethacrylo-nitrile.

The hydrolysis reaction takes place as follows:

$$H \doteq C \equiv N \quad \xrightarrow{H_2O} \quad H - C = NH \longrightarrow H - C = O \quad + NH_3$$
$$\underset{OH^-}{\uparrow} \qquad\qquad\qquad \underset{OH}{|} \qquad\qquad \underset{OH}{|}$$

The intermediate clearly might be capable of initiating a colour reaction in a similar manner to the imine group in the polymer (cf. p.73,80,81) :

$$H - C = NH \quad \xrightarrow{HCN}$$
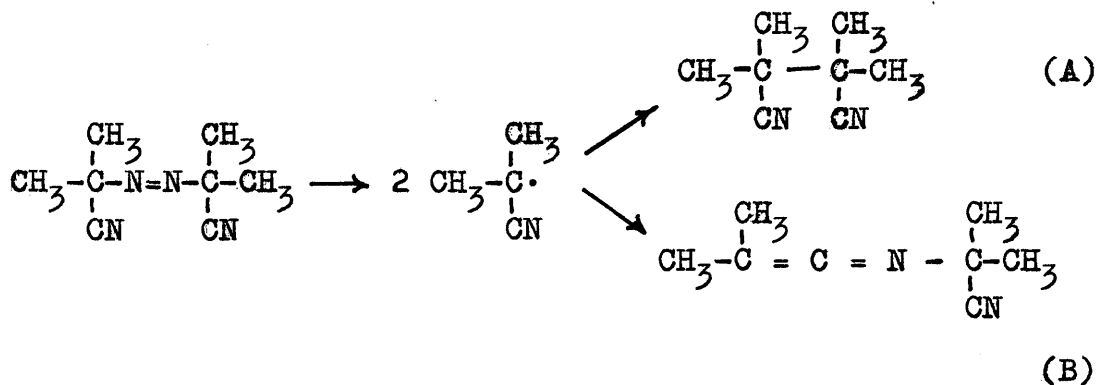$$\underset{OH}{|}$$

5

KETENE-IMINE STRUCTURES

In the course of work on the separation of colouration and depolymerization (chapter 3) a peak was detected at 2012 $cm.^{-1}$ in the infrared spectrum of polymethacrylonitrile. This appeared in all the polymers examined, regardless of the conditions of polymerization, but the intensity of absorption varied from one polymer to another. Reprecipitation did not affect the intensity of the peak. It is therefore not due to foreign molecules and must be assigned to some structure present in the polymer chain. The peak disappears rapidly on raising the temperature of the polymer to its softening point (120°C).

Absorption at 2012 $cm.^{-1}$ cannot be accounted for on the basis of the normal structure of the polymer, since none of the groups present absorb at all in this region,
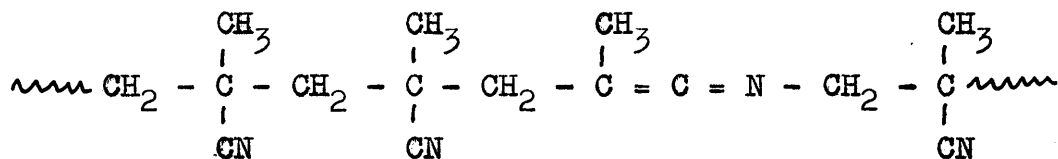
nor as an overtone or combination tone of bands at lower
frequencies.   No impurities which might appear in the
chain by copolymerization could be expected to absorb in
this region.   Very few groupings absorb around 2000 cm.$^{-1}$
Those which do are of the general type $\geq$C=C=X, where X
may be C,O,N, or S.   The disappearance of the structure
when the polymer softens leaves no doubt that one of
these labile structures is present.   Of the few possib-
ilities, the existence of ketene-imines $\geq$C=C=N- in the
polymer chain is most easily explained, and the evidence
from chemical reactions of the labile structure, discussed
in this chapter, supports this conclusion.

The occurrence of ketene-imines in polymethacrylo-
nitrile has also been discovered independently by TALAT-
ERBEN and BYWATER[27].   In the course of a study of the
decomposition of azo-bis- isobutyronitrile these workers
found that in addition to the expected radical combination
product, tetramethyl succinodinitrile (A), there was a
substantial quantity of a labile second product,
N-(2-cyano-2-propyl)-dimethylketene-imine (B), formed by
reaction of the initially formed cyanoisopropyl radical
in the form $(CH_3)_2$C=C=N$^{\bullet}$.

Talat-Erben and Bywater observed that the growing

$$CH_3-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-N=N-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \longrightarrow 2\ CH_3-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}\cdot$$

$$CH_3-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \qquad (A)$$

$$CH_3-\overset{\overset{CH_3}{|}}{C}=C=N-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

$$(B)$$

end of a polymethacrylonitrile chain has a similar
structure to the cyanoisopropyl radical, and deduced that
ketene-imine structures would be likely to occur in the
polymer:

$$\text{wwww } CH_2-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\overset{\overset{CH_3}{|}}{C}=C=N-CH_2-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{ wwww}$$

An examination of the infrared spectrum of the
polymer revealed the 2012 $cm.^{-1}$ peak, and the lability of
the structure responsible confirmed the accuracy of their
deduction.

CHEMICAL REACTIONS.

The stability of ketene-imine groups to oxygen was
tested by bubbling dry oxygen through a solution of the

polymer in methyl ethyl ketone for 24 hours, the 2012 cm.$^{-1}$ peak height being measured before and after the experiment (technique for solution infrared measurements, p.37). No change was detected.
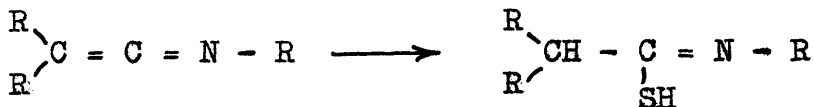
The stability to ultraviolet light was also tested. Ketene-imine structures were unaffected by irradiating the polymer in monomer solution for 12 hours at 30° (using an Osram 250v.125w. mercury vapour lamp).

STEVENS and FRENCH[28] have prepared a number of simple ketene-imines and studied some of their reactions. They found that water, chlorine, and methanol added to the C=C bond:
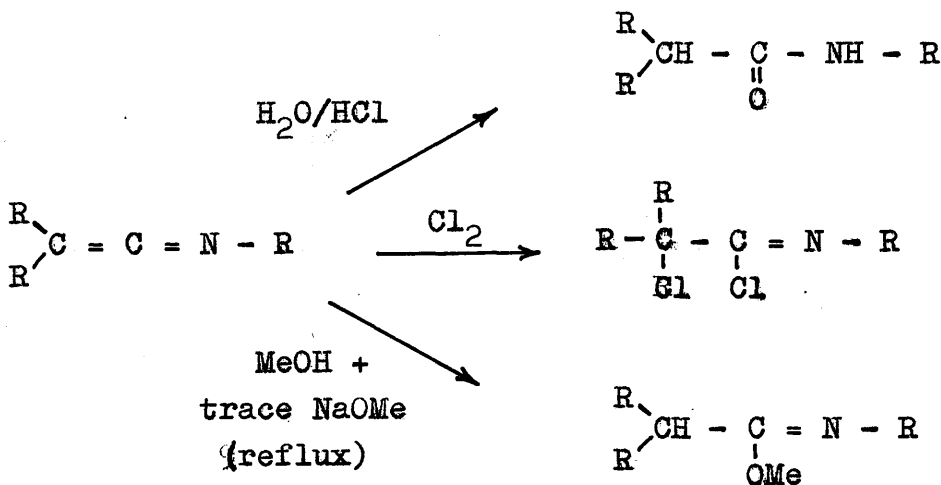
DIJKSTRA and BACKER[29] report reaction of ketene-

imines with hydrogen sulphide (sodium sulphide crystals were used):

$$\begin{array}{c} R \\ R \end{array} C = C = N - R \longrightarrow \begin{array}{c} R \\ R \end{array} CH - \underset{\underset{SH}{|}}{C} = N - R$$

These authors also report addition of many organic compounds.

The reactions with water, chlorine, methanol, and hydrogen sulphide were tested with the polymer (BN 251, see appendix).

1). Water.   To 10 ml of a 2.5% solution of polymer in acetone was added 3 drops of water and 2 drops of concentrated hydrochloric acid.   The solution was stirred for 15 minutes and the polymer was then precipitated (pet. ether) and dried in vacuum.

2). Chlorine.   Chlorine was bubbled through a 2.5% solution of polymer in methylene chloride for 5 minutes.   The solution became yellow-green due to dissolved chlorine after 1 minute.   The polymer was isolated as before.

3). Methanol.   (a) To 10 ml of a 2.5% solution of polymer

in acetone was added 1 ml of methanol. The
solution was allowed to stand overnight before
isolation of the polymer.

(b) The experiment was repeated with the
addition of approx 0.25g. of sodium to give some
sodium methoxide in the solution. An intense
yellow colour, due to colour initiation by the
NaOMe (p.80) developed.

4). <u>Hydrogen Sulphide</u>. To 10 ml of a 2.5% solution of
polymer in acetone was added a small crystal of
sodium sulphide and 5 drops of water. The
solution was stirred for 15 minutes and the
polymer was isolated.

In these experiments the only way of detecting
reaction is by infrared spectroscopy. It is easy to
tell if the ketene-imine structures have reacted (dis-
appearance of 2012 cm^{-1} peak) but it is not possible to
identify the structures formed with any certainty. The
number of ketene-imine structures present is very small
(of the order of 1 per molecule) and this makes ident-
ification of the products of reaction by any other means
quite impossible. In fact it is only if the products
show strong absorption that they can be identified at all.

The spectra of the polymers isolated in the above experiments were compared with that of the original polymer; the results are summarized in table 8.

Table 8

KETENE-IMINE REACTIONS.

Sample	2012 cm.$^{-1}$ peak	New Absorption at
1	Reduced	1680, 1620 cm.$^{-1}$
2	Absent	1680 cm.$^{-1}$
3a	Unaffected	None
3b	Absent	1700-1570 cm.$^{-1}$ (due to colour reaction)
4	Absent	1620 cm.$^{-1}$

It will be seen that no peaks due to C-Cl, C-S, or S-H were detected. This is not surprising in view of the small concentration present.   The new peaks which can be detected all agree well with what would be expected if the ketene-imines in the polymer reacted in the same way as simple ketene-imines (essentially these are C=N peaks).

THERMAL DISAPPEARANCE REACTION.

Ketene-imine structures are stable in the solid
polymer but disappear when the polymer softens ($120^{\circ}C$).
In solution they are very much more labile.   At 90°,
80% of the ketene-imines disappear in 1 hour, at 65° a
similar extent of reaction takes about 16 hours, and even
at room temperature slow reaction occurs.   Figure 19
illustrates the disappearance of ketene-imines at 90° in
cyclohexanone.

Infrared Spectral Measurements.

The only convenient measure of the concentration
of ketene-imines present in the polymer at any given time
is the intensity of absorption at 2012 $cm.^{-1}$ in the infra-
red spectrum.   It is only possible to study changes in
concentration since to measure the actual concentration
it would also be necessary to know the absolute number of
ketene-imines present in a given weight of polymer.

The technique used in the measurement of infrared
spectra of polymer solutions is described on pp.37-39.
Prior to the experiments described below, Beer's Law was
tested and found to be strictly obeyed at 2012 $cm.^{-1}$ over
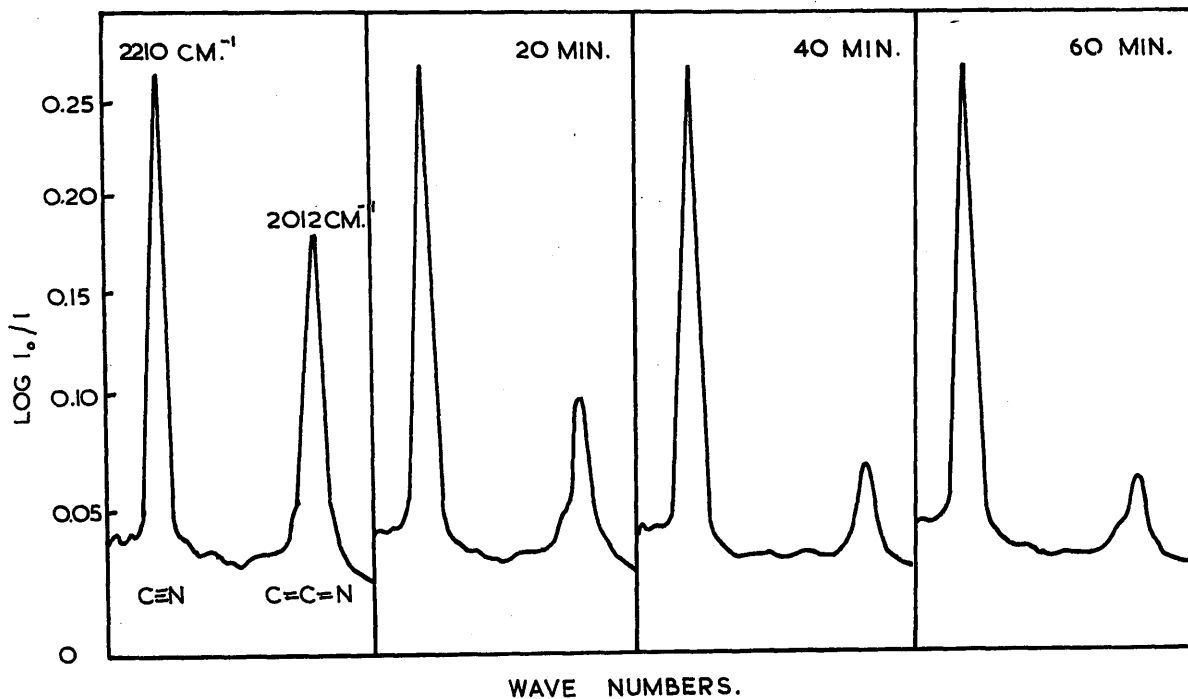the range of polymer concentrations used (figure 20).

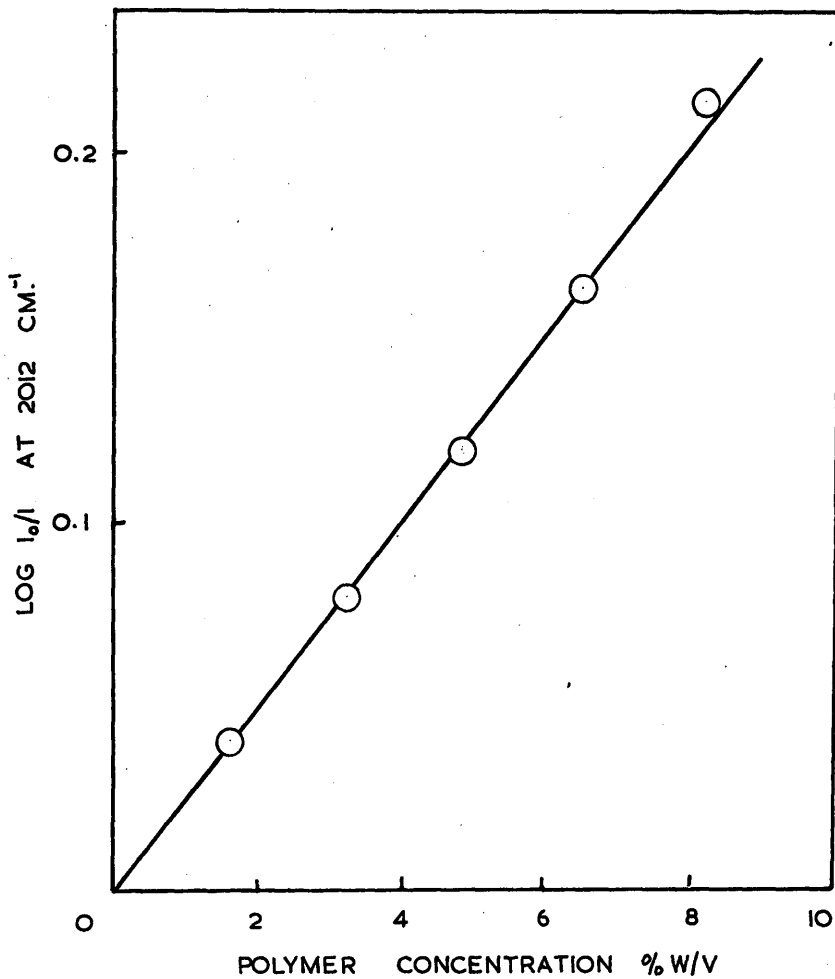FIGURE 19: DISAPPEARANCE OF KETENE-IMINE ABSORPTION AT 90°.
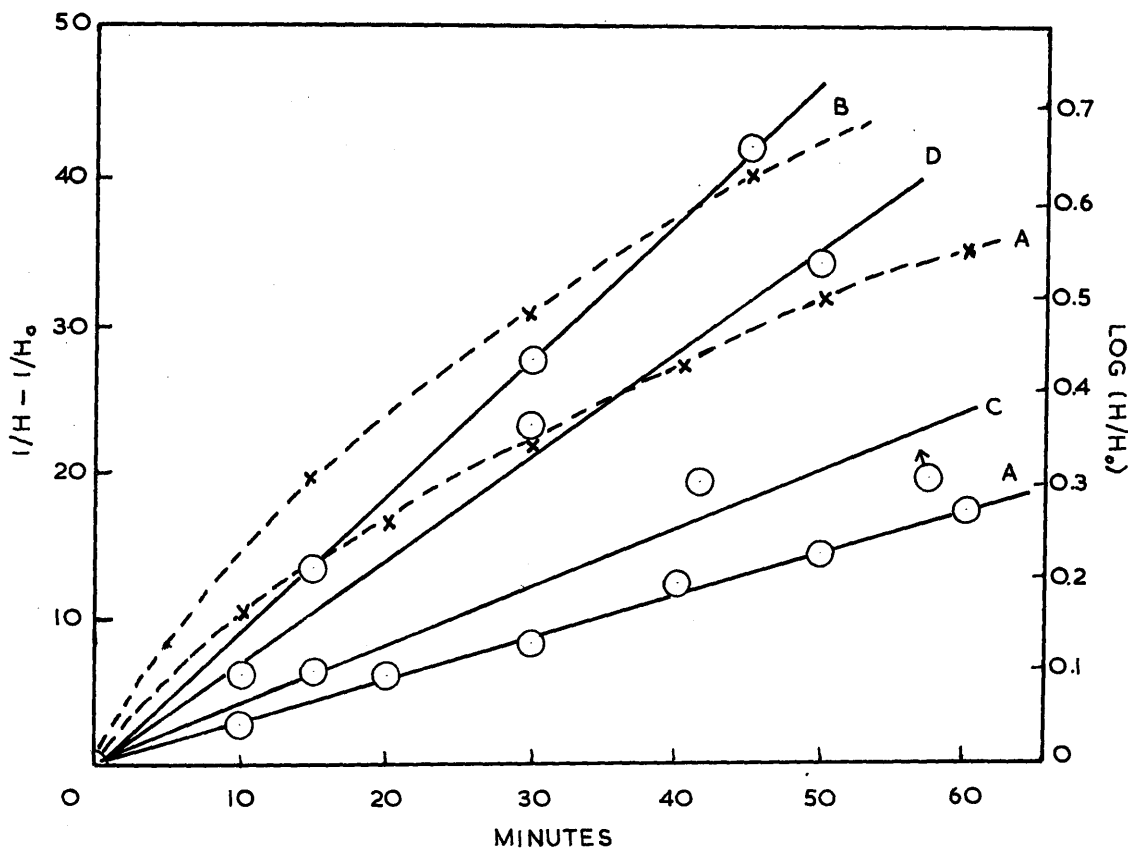
FIGURE 20 : VERIFICATION OF BEER'S LAW.

FIGURE 21: KINETIC PLOTS.

IN CYCLOHEXANONE, 90°. ----x----FIRST ORDER, —O— SECOND ORDER

H = LOG I_o/I AT 2012 CM.$^{-1}$ USED AS A MEASURE OF CONCENTRATION.
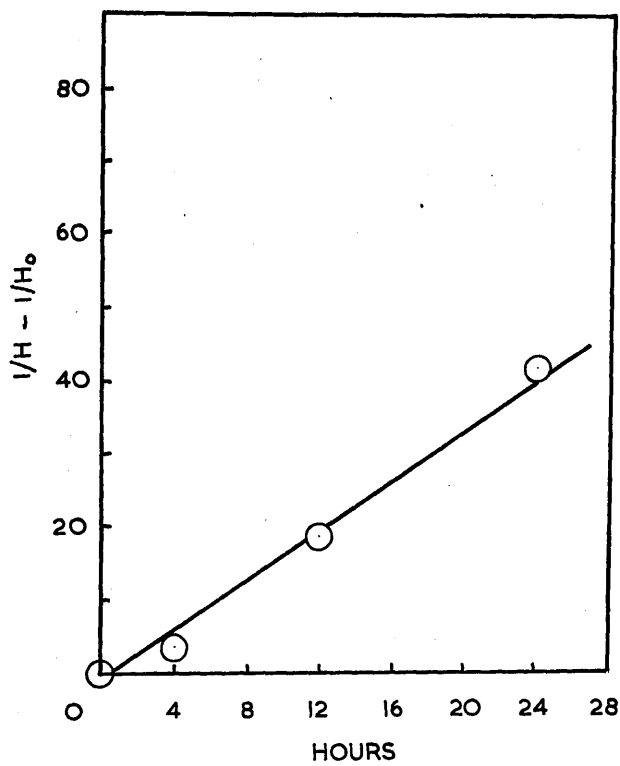
FIGURE 22: SECOND ORDER KINETIC PLOT, 65°.

7.5 % SOLN. IN CYCLOHEXANONE

Kinetics of Thermal Disappearance.

The kinetics of the thermal disappearance of ketene-imine structures were studied in cyclohexanone solution at 90° and at 65° using polymer BN 659 (see appendix).

For each series of experiments, four or more 1 ml portions of the polymer solution were degassed and sealed under vacuum. These were then immersed in a thermostat at the required temperature for varying lengths of time. On removal from the tank the tubes were cooled rapidly and opened. The infrared absorption in the region 2300-1900 $cm.^{-1}$ was measured quantitatively for each sample.

Using the 2012 $cm.^{-1}$ peak height (log I_0/I) as a measure of ketene-imine concentration, the results were tested for first and second order kinetics. Figure 21 shows the results in the case of 7.5% and 3.75% solutions (A and B) of polymer at 90°. Clearly the disappearance of ketene-imines is a second order reaction. The results for experiments at 65° again give a linear second order plot (figure 22).

Effect of Viscosity.

The slopes of the lines in figure 21 represent

relative values of the rate constant for the reaction
since we are dealing only with relative concentrations.
Comparison of lines A and B shows that the rate constant
increases when the polymer concentration is reduced by
half.   Since the ketene-imine structures are incorpor-
ated into the polymer chains, it is reasonable to picture
the process as being viscosity-controlled in the same way
as the bimolecular termination step in polymerization
which results in the well-known "gel effect". In support
of this, when the reaction is carried out with a 7.5%
solution containing 3.75% of "reactive" polymer in which
ketene-imines are present and 3.75% of "inert" polymer in
which all the ketene-imine groups have been destroyed by
melting, line C is obtained, whose slope is comparable
with that of line A for a 7.5% solution of reactive
polymer.

A further test of the viscosity dependence of the
reaction consists of adding a foreign polymer to the
solution to increase the viscosity.   Figure 21D shows
the effect of adding 2% of polymethyl methacrylate (MW
179,000) to a 3.75% solution of polymer.   A drop in
rate constant is again revealed.

The viscosities of 7.5% and 3.75% solutions in

cyclohexanone of the polymer used in these tests were measured for comparison with the relative rate constants obtained from the slopes of the lines in figure 21. The results, shown in table 9, indicate an approximate relationship between η_{sp} and the reciprocal of the rate constant.
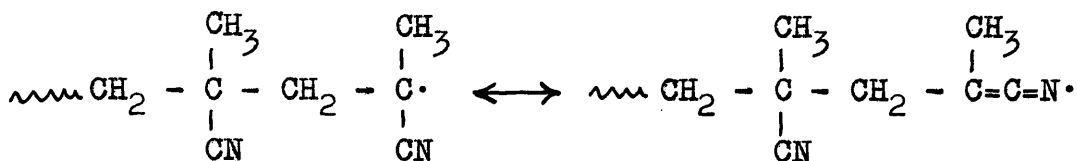
<div align="center">

Table 9

EFFECT OF SOLUTION VISCOSITY ON
RELATIVE RATE CONSTANT.

</div>

Polymer Concn. (%w/v)	Relative Rate Constant	Reciprocal of Rate Constant	$\eta_{sp}(90^{\circ})$
7.5	0.28	3.6	1.385
3.75	0.96	1.05	0.485

MODE OF FORMATION.

Ketene-imine structures in the polymer must arise through the radical chain end reacting as if the odd electron were present on the nitrogen atom:

$$\sim\sim CH_2 - \underset{CN}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}} - CH_2 - \underset{CN}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}\cdot \quad\longleftrightarrow\quad \sim\sim CH_2 - \underset{CN}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}} - CH_2 - \overset{CH_3}{\overset{|}{C}}=C=N\cdot$$

It is not clear, however, whether the radical reacts in this way in propagation, termination or both. This will depend on the relative values of the energies of activation for addition of a monomer unit at the nitrogen or carbon atom in the radical end. If ketene-imines are formed in propagation we can say that the reactivity of the radical towards addition at the nitrogen atom is less than, but comparable with the reactivity towards addition at the carbon atom. On the other hand, if termination is involved, the reactivity towards addition at the nitrogen atom must be so much less that only another radical will react at this position.

The following theoretical treatment allows the nature of ketene-imine formation to be tested experimentally, by relating the proportion of ketene-imines in the polymer to the initiator concentration.

It is assumed that we can regard the system as containing two different radical ends, a normal type, and an isomeric ketene-imine type. It is further assumed
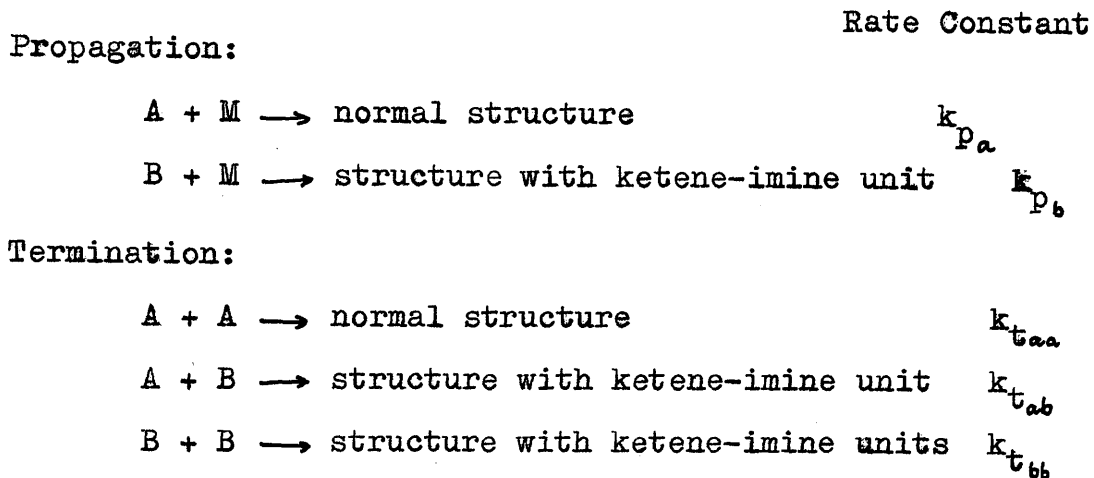
that the concentration of the latter is very small
compared to the normal type.

Let A be the normal type of radical end,

   B " " abnormal " "   "   "

   M represent monomer.

The total radical concentration is (A) + (B),

and (B)/(A) = K, where K is a constant.

$\therefore$ (B) = K(A).

The possible propagation and termination steps are:

                                                Rate Constant

Propagation:

   A + M $\longrightarrow$ normal structure k_{p_a}

   B + M $\longrightarrow$ structure with ketene-imine unit k_{p_b}

Termination:

   A + A $\longrightarrow$ normal structure $k_{t_{aa}}$

   A + B $\longrightarrow$ structure with ketene-imine unit $k_{t_{ab}}$

   B + B $\longrightarrow$ structure with ketene-imine units $k_{t_{bb}}$

Hence, $\dfrac{\text{Ketene-imine structures}}{\text{Normal monomer units}}$ =

$$\frac{\text{Rate of formn. of ketene-imine structures in prop.\& term.}}{\text{Rate of polymerization}}$$

$$= \frac{k_{p_b}(B)(M)}{k_{p_a}(A)(M)} + \frac{k_{t_{ab}}(A)(B) + k_{t_{bb}}(B)(B)}{k_{p_a}(A)(M)}$$

$$= \frac{k_{p_b}}{k_{p_a}} K + \frac{k_{t_{ab}} K(A)^2 + k_{t_{bb}} K^2(A)^2}{k_{p_a}(A)(M)}$$

$$= \frac{k_{p_b}}{k_{p_a}} K + \frac{k_{t_{ab}} K(A) + k_{t_{bb}} K^2(A)}{k_{p_a}(M)}$$

$$\frac{d(A+B)}{dt} = 0 = Zc - \left\{ k_{t_{aa}}(A)^2 + k_{t_{ab}}(A)(B) + k_{t_{bb}}(B)^2 \right\}$$

$$= Zc - \left\{ k_{t_{aa}}(A)^2 + k_{t_{ab}} K(A)^2 + k_{t_{bb}} K^2(A)^2 \right\}$$

$$= Zc - (A)^2 \left(k_{t_{aa}} + K k_{t_{ab}} + K^2 k_{t_{bb}} \right)$$

where Z is a constant and c is the initiator concn.

Let $y = \left(k_{t_{aa}} + K k_{t_{ab}} + K^2 k_{t_{bb}} \right)$

$$\therefore (A) = \sqrt{\frac{Zc}{y}}$$

$$\therefore \frac{\text{Ketene-imine structures}}{\text{Normal monomer units}} = \frac{k_{p_b}}{k_{p_a}} K + \left\{ \frac{k_{t_{ab}} K Z^{1/2}}{y^{1/2}} \right\} c^{1/2} + \left\{ \frac{k_{t_{bb}} K^2 Z^{1/2}}{y^{1/2}} \right\} c^{1/2}$$

$$= \underline{R + (P + Q) c^{1/2}}$$

where R, P, and Q are constants.

Thus if a series of polymers is prepared at a fixed temperature, and the relative concentration of ketene-imine structures measured in each case, the nature of the plot of the latter against the square root of the initiator concentration will indicate whether these structures are formed in propagation, termination or both. If all ketene-imines are formed in propagation, the plot of their concentration against $c^{1/2}$ should be a line parallel to the $c^{1/2}$ axis, that is, the concentration would be independent of the amount of initiator. On the other hand formation exclusively in the termination step would give a straight line through the origin. If both are involved the result would be a line of positive slope making a positive intercept on the ketene-imine concentration axis.

Before this method can be applied experimentally, however, account must be taken of the complication introduced by the lability of the ketene-imine structures in solution. While methacrylonitrile polymers may most conveniently be prepared catalytically at 60-80°, ketene-imines are very unstable at these temperatures, and substantial reaction occurs in the course of the polymerization. Thus a considerable proportion of the

ketene-imine structures formed will have decomposed, and the above theoretical treatment is therefore inapplicable.

Fortunately, this difficulty can be overcome by preparing polymers by photodecomposition of initiator at $20-30^\circ$. At these temperatures thermal decomposition of ketene-imine structures is negligible, provided the duration of polymerization does not exceed about 48 hours. The monomer does not polymerize photochemically at 30°, and ketene-imines are stable to ultra-violet light (p.91).

Data for a series of polymers prepared by photo-decomposition of benzoyl peroxide at 30° are given in table 10 and in figure 23. It is clear from figure 23 that ketene-imines arise almost entirely in termination, since a good straight line can be drawn through the origin or making a small intercept on the ketene-imine concentration axis. Slight deviation from linearity at high initiator concentrations might be explained by reaction of some of the ketene-imine structures with the initiator.

The reactivity towards addition at the nitrogen atom in the growing chain must therefore be very small compared to that for addition at the carbon atom, and reaction at the former, when it does occur, almost always occurs with another radical rather than a monomer molecule.
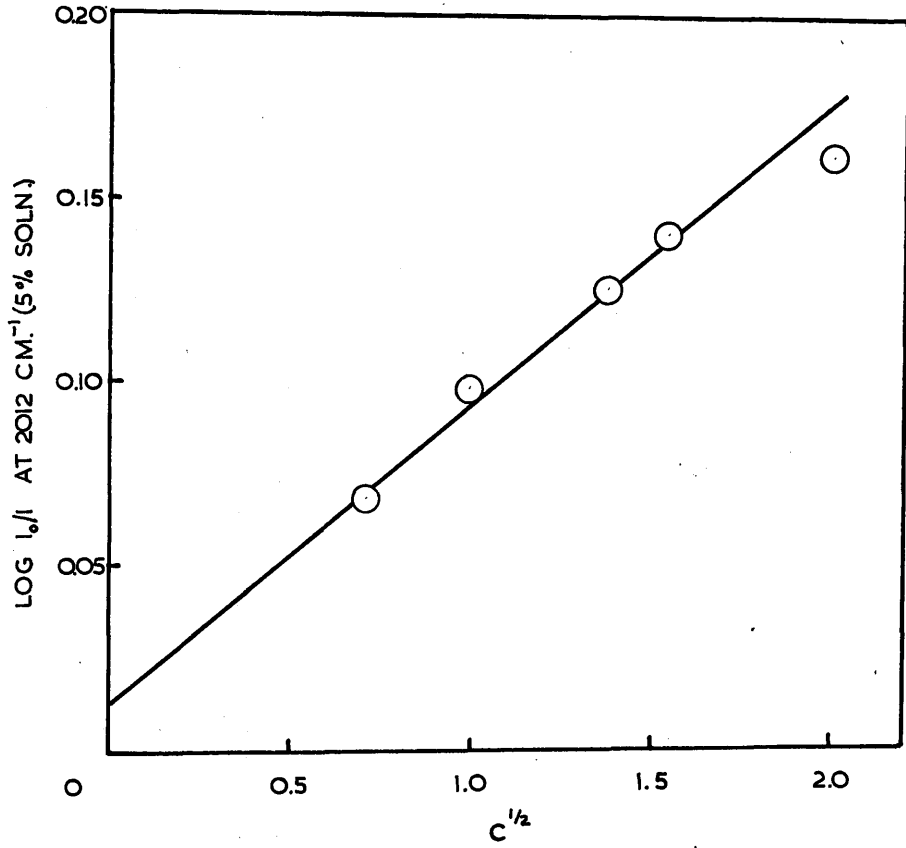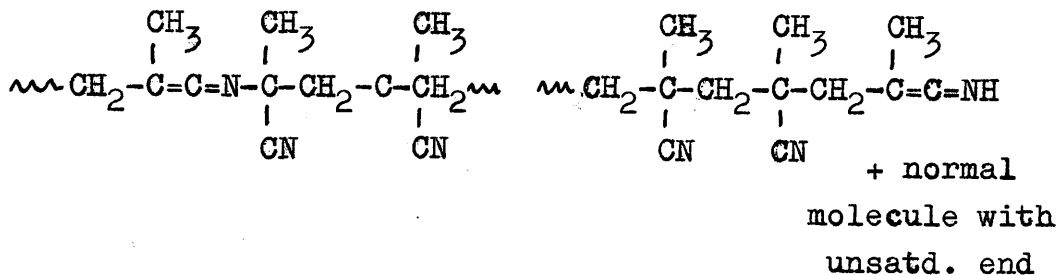
FIGURE 23.

Table 10

POLYMERS PREPARED AT 30°

BY PHOTODECOMPOSITION OF BENZOYL PEROXIDE.

No.	Initiator Concn % w/v	$c^{\frac{1}{2}}$	Rate %/hour	$\log(I_0/I)$ at 2012 cm.$^{-1}$ (5% soln. in cyclohexanone)
BZ 301	0.50	0.707	0.126	0.069
BZ 302	1.90	1.380	0.213	0.125
BZ 303	4.00	2.000	0.293	0.161
BZ 304	1.00	1.000	0.158	0.099
BZ 305	2.40	1.551	0.222	0.140

While it has been shown that ketene-imines are formed in termination, it is less easy to decide whether combination or disproportionation is involved. The structures which would result in each case are shown below. The ketene-imine formed in combination has a substituent on the nitrogen atom whereas the other has not. In the simple ketene-imines, those of the type $R_2C=C=NH$ have been found to be extremely unstable.

CH₃ structures with formulas:

CH₃   CH₃   CH₃   CH₃ CH₃ CH₃

$\sim\sim CH_2-C=C=N-C-CH_2-C-CH_2\sim\sim$ $\sim\sim CH_2-C-CH_2-C-CH_2-C=C=NH$

CN   CN   CN   CN

+ normal
molecule with
unsatd. end

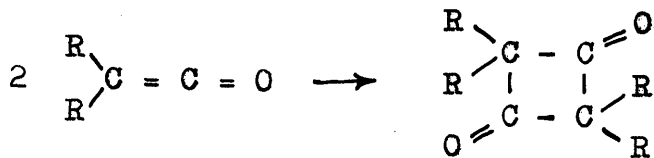COMBINATION   DISPROPORTIONATION

It seems more likely that the more stable N-substituted structure formed in combination will be present in the polymer. Furthermore, it will be shown that there is a drop in molecular weight associated with the thermal disappearance of ketene-imines in the polymer (see below). This is difficult to explain if the reactive structures are situated at the chain ends.

The possibility of a mixture of both types of ketene-imine structure being present is remote, since a double peak would be expected in the infrared spectrum. Only one very sharply defined peak is present.

MODE OF DISAPPEARANCE.

It has been shown that ketene-imine structures disappear thermally in solution by a reaction which strictly obeys second order kinetics. This at once suggests

that a dimerization process analagous to the behaviour of
ketenes

$$2 \quad \begin{matrix} R \\ R \end{matrix}\!\!>\!\!C = C = O \quad \longrightarrow \quad \begin{matrix} R \\ R \end{matrix}\!\!>\!\!\begin{matrix} C - C \!=\! O \\ | \quad | \quad R \\ O \!=\! C - C \!<\! \begin{matrix} R \\ R \end{matrix} \end{matrix}$$

is taking place, and this seems even more likely in view
of the formation by simple ketene-imines of products
believed to be dimers[28]. However, when the molecular
weight change on ketene-imine disappearance is measured,
instead of the expected rise in molecular weight, a fall
is observed. Table 11 presents some preliminary data
for a few polymers.

Table 11

MOLECULAR WEIGHT CHANGES ON KETENE-IMINE DISAPPEARANCE.

Polymer	$\log I_0/I$ 2012 cm.$^{-1}$ (7.5% soln)	Undegraded Mol.Wt. ($\pm$ 750)	Degraded Mol.Wt. ($\pm$ 750)	Degraded Mol.Wt. % orig.
BN 251	0.150	18,800	14,750	78
BZ 303	0.242	17,750	11,000	62
BZ 301	0.104	17,050	14,200	83

The possibility that a dimer is initially formed, but decomposes readily, was considered. In the polymers in table 11, ketene-imine structures had been destroyed at elevated temperatures (60-110°). In an attempt to detect initial formation of dimer a solution of polymer was allowed to stand at room temperature for two months, in the course of which considerable reduction in the ketene-imine concentration would occur. The molecular weight was measured before and after the experiment. Values of 17,750 and 15,500 respectively were obtained. Therefore formation of dimer cannot be detected even when the disappearance of ketene-imine structures takes place at room temperature.

The simplest mode of disappearance of ketene-imine structures involving chain scission is as follows:

$$\sim\sim CH_2-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\overset{\overset{CH_3}{|}}{C}=C=N-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2\sim\sim$$

$$\downarrow$$

$$\sim\sim CH_2-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH=\overset{\overset{CH_3}{|}}{\underset{\underset{CN}{|}}{C}} \quad + \quad HC-CH_2-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2\sim\sim$$
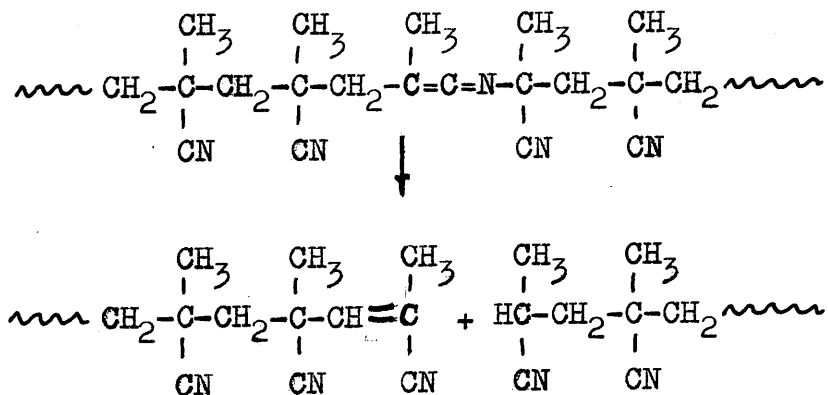
This results in the formation of similar end
structures to disproportionation in a normal termination
step.   It is not clear, however, why such a chain
scission reaction should be strictly second order with
respect to the very small number of ketene-imines present
unless the reaction involves the transient formation of
dimer, immediately followed by scission in both molecules
involved.

The infrared spectrum of polymethacrylonitrile
shows weak absorption at 1620 cm.$^{-1}$, which might be attrib-
uted to C=C end structures.   The assignment cannot be
made unambiguously, however, since polymers often show
absorption in this region due to traces of water.   It is
significant, nevertheless, that this band shows a slight
increase in intensity on ketene-imine disappearance, which
is in accordance with behaviour of the type suggested.
No other changes in spectrum may be observed.

ABSOLUTE NUMBER OF KETENE-IMINE STRUCTURES.

It would be interesting to know precisely how many
ketene-imine structures are present in a given weight of
polymer, but so far no method has been found of obtaining
this information.   Talat-Erben and Bywater estimated

that about 30 mole% of the cyanoisopropyl radicals reacted
in the ketene-imine form (p.89).   In the polymer,
however, it is clear that there can be no more than one
ketene-imine structure per molecule if these are formed
in the termination process, and not every termination step
may result in the formation of a ketene-imine structure.

It is tempting to speculate that for every ketene-
imine structure which disappears thermally a molecule
splits into two fragments.   We could therefore argue as
follows.

Let J = no. of ketene-imines per monomer unit

j = no. of ketene-imines per molecule

M_o = undegraded molecular weight

M_d = degraded molecular weight.

We have $j = J M_o$

$1/M_o \propto c^{1/2}$,   and $J \propto c^{1/2}$

(since $J = R + (P+Q)c^{1/2}$
and $R = 0$ by expt.)
cf. p.105

$\therefore J = $ const. x $1/M_o$

$\therefore j = $ const.

Also, $M_d/M_o = 1/(j+1)$ $\therefore$ $M_d/M_o = $ const.

By measuring M_d/M_o, we could find j .

The data of table 11 are inadequate to justify or condemn this approach. Assuming a value of 0.75 for M_d/M_o we obtain $j = 0.33$, i.e. 1 ketene-imine unit per 3 molecules, which seems not unreasonable.

6

THE DEPOLYMERIZATION REACTION

The relationship between polymer structure and type of degradation was discussed in chapter 1, and it was predicted that polymethacrylonitrile should degrade to monomer in high yield.   Polymethacrylonitrile does indeed degrade to monomer at temperatures over 220°, but the yield is affected by the colouration reaction, as discussed in chapter 3.   When colouration is extensive the yield of monomer may be as low as 50-60%.   These results clearly indicate that in studying degradation to monomer methacrylonitrile polymers of the highest purity are required.   Pure polymers, prepared in vacuo from rigorously purified monomer using azobisisobutyronitrile as initiator, give almost quantitative yields of monomer at 310°.   The reaction proceeds at a convenient rate for study at 250°.

The very close similarity in structure between polymethacrylonitrile and polymethyl methacrylate, both of which are derived from 1:1-disubstituted monomers, each containing a methyl substituent and a strongly electron-attracting substituent, makes it seem quite likely that the mechanism of degradation to monomer is the same in both cases.

GRASSIE and MELVILLE[1,2] made an extensive study of the degradation of polymethyl methacrylate.   Their conclusions were based principally on evidence provided by two types of measurement,

 i) Rates of production of monomer, measured continuously during the course of degradation using the dynamic molecular still (p.27),

 ii) Changes in number average molecular weight, measured osmotically, as the reaction proceeded.

From data obtained in these ways, Grassie and Melville were able to show (a) that degradation was initiated at the ends of the chains, (b) that each chain, once initiated, degraded completely to monomer, (c) that one of the two types of end resulting from disproportionation in the termination step in polymerization was more susceptible to degradation than the other.   Further work, by GRASSIE

and VANCE[30], in which the proportion of saturated and
unsaturated ends was varied by transfer to benzene, showed
that it was the unsaturated end which was the more
susceptible to degradation.

The intention in this part of the present work was
to apply the same methods to polymethacrylonitrile. The
time available, however, has allowed only some preliminary
experiments to be carried out, and the results of these,
discussed below, represent only a beginning in the study
of the degradation to monomer in polymethacrylonitrile.

Degradation of a sample of the polymer in the
dynamic molecular still at once reveals a number of
difficulties.   These will be considered under the head-
ings of Residual Colouration, Insolubility, and Gaseous
Product of Degradation.

RESIDUAL COLOURATION.

Mention has already been made (p.52) of the fact
that even pure polymethacrylonitrile shows some colour-
ation at temperatures over 200°.   Since almost quantit-
ative yields of monomer may be obtained on raising the
temperature to 300°, it follows that the extent of this

colouration must be very small, probably no more than 1% of the weight of polymer.

The structure responsible for initiating this colouration is probably some architectural feature of the polymer chain, since it is unlikely that any impurity could now be present in the polymer, in view of the very rigorous precautions taken in the preparation, and the absence of any unusual features in the spectrum of the polymer.   The most obvious points at which some abnormal structure capable of initiating colouration might be present are at the chain ends.   The expected end struct- ures in the polymer are methyl groups from the initiating cyanoisopropyl radical (A), and unsaturated (B) and saturated (C) ends if termination is by disproportionation. If ketene-imine breakdown occurs in the way suggested (p.112) this also will give rise to stuctures (B) and (C).

$$CH_3-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}\sim\sim\sim$$

(A)

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

(B)

$$H-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}\sim\sim\sim$$
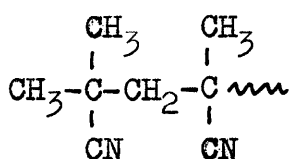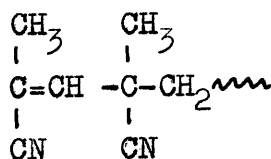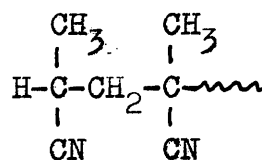
(C)

It will be noticed that structure (C) possesses a terminal hydrogen atom activated by a nitrile group.

It is possible that this may react with a nitrile group in another molecule to form -C=NH (Thorpe Reaction) which can then propagate the colouration process.
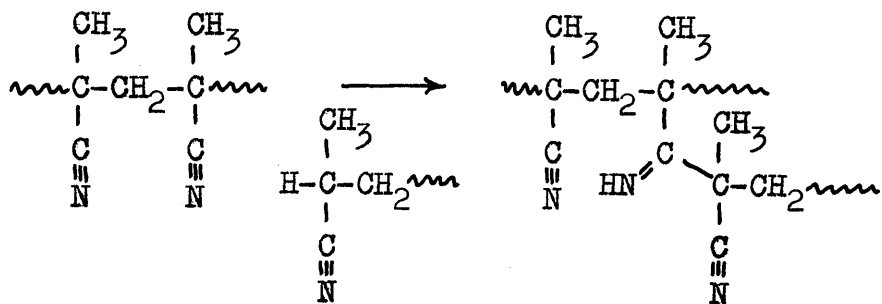
If residual colouration does arise by an inter-molecular reaction an increase in molecular weight should occur.   A sample of polymer BN 658 was heated to 204° for 5 hours and the molecular weight of the red polymer (which was completely soluble) was measured. The values of the molecular weight before and after colouration were 23,900 $\pm$ 500 and 24,700 $\pm$ 500, respectively. Allowing for an initial drop in molecular weight due to reaction of ketene-imine structures an increase in molecular weight of 20-30% is indicated.   The above mechanism may therefore be considered as a reasonable possibility.

If residual colouration is due to reaction at the ends of chains, then its effect on degradation to monomer may be out of all proportion to the small number of

monomer units actually involved in the coloured structures,
since it is possible that the monomer-producing reaction
is itself initiated at chain ends.

INSOLUBILITY.

In the course of the depolymerization reaction the
polymer gradually becomes completely insoluble.   For
example, when polymer BN 658 (see appendix) is degraded
at 249° the residual polymer is completely insoluble in
acetone by the time 40% of monomer has been collected
(table 12).   This means that it is not possible to
follow the change in molecular weight of the residue
throughout the reaction as was done by Grassie and Melville
for polymethyl methacrylate.

Table 12

SOLUBILITY AND MOLECULAR WEIGHT DATA FOR
POLYMER BN 658 DEGRADED AT 249°C.

% Degradation	Fraction Insol. % original wt.	M.W.of Soluble Portion
0	0	23,900 $\pm$ 500
16	19	18,100 $\pm$ 1,500
25	35	20,900 $\pm$ 1,500
39 (6 hours)	55	——

It is not clear what causes insolubility to develop. The amount of colouration which occurs seems quite inadequate to account for it. Possibly some independent cross-linking reaction is involved.

The extent of insolubilization during depolymerization is less when the reaction is carried out more rapidly. For example,.when the polymer referred to in table 12 is degraded at 280° to 71% conversion (30 mins) the residue amounts to only 16% of the original weight of polymer. The rate of reaction at 280° is too fast, however, to allow the depolymerization to be studied systematically.

The development of insolubility does not appear to prevent degradation to monomer. Thus although the residue may be completely insoluble at 40% conversion, it is still possible to obtain further substantial quantities of monomer. This contrasts with the insolubility resulting from impurity-initiated colouration, considered in chapter 3, when the monomer yield was very much reduced.

GASEOUS PRODUCT OF DEGRADATION.

When a sample of polymethyl methacrylate is

degraded in the dynamic molecular still (p.27) and the rate of volatilization is plotted against time of degradation, the curve obtained has the form shown in figure 24. The first peak occurs when the polymer softens sufficiently for the escape of the volatile material trapped in the polymer during its isolation.   As the polymer approaches the degradation temperature the walls of the still become warmed sufficiently by radiation for the release of adsorbed gases, and a second peak occurs, due partly to this material and partly to monomer.   Figure 24 shows how the curve then becomes approximately linear, and by extrapolation of the linear portion to the time when the degradation temperature was first reached the initial rate of degradation may be found.   This procedure was used by Grassie and Melville.

When polymethacrylonitrile is degraded in the same way, the rate/time curves seldom have the ideal form of figure 24.   Figure 25 illustrates the type of curve obtained in the degradation of 0.3g. samples of polymers BN 651 and BN 658.   When the area under this curve, which represents the weight of polymer degraded, is compared with the loss in weight of the degradation tray containing the polymer, and with the weight of monomer
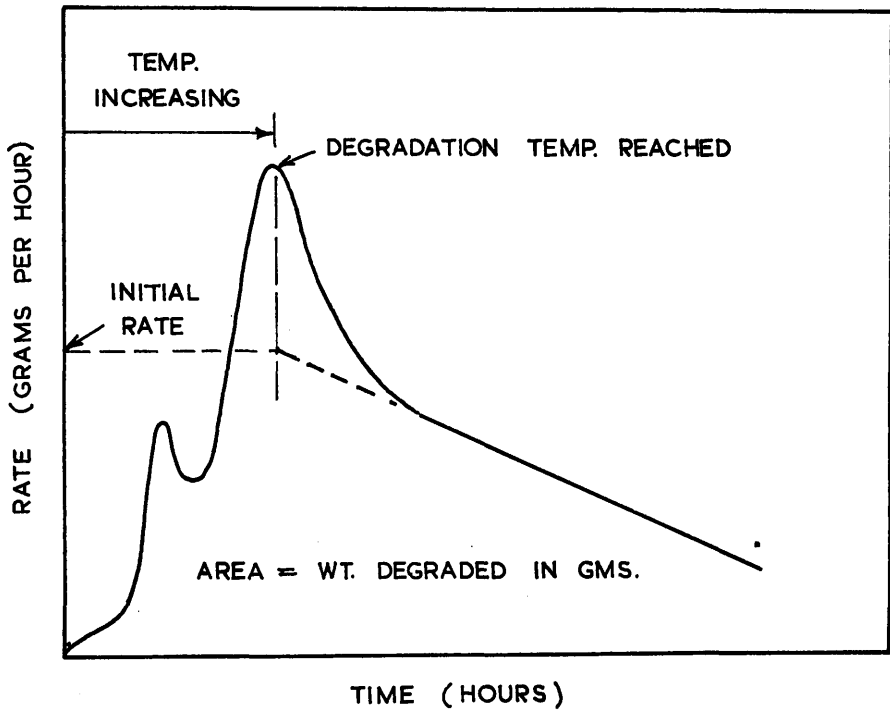
FIGURE 24.
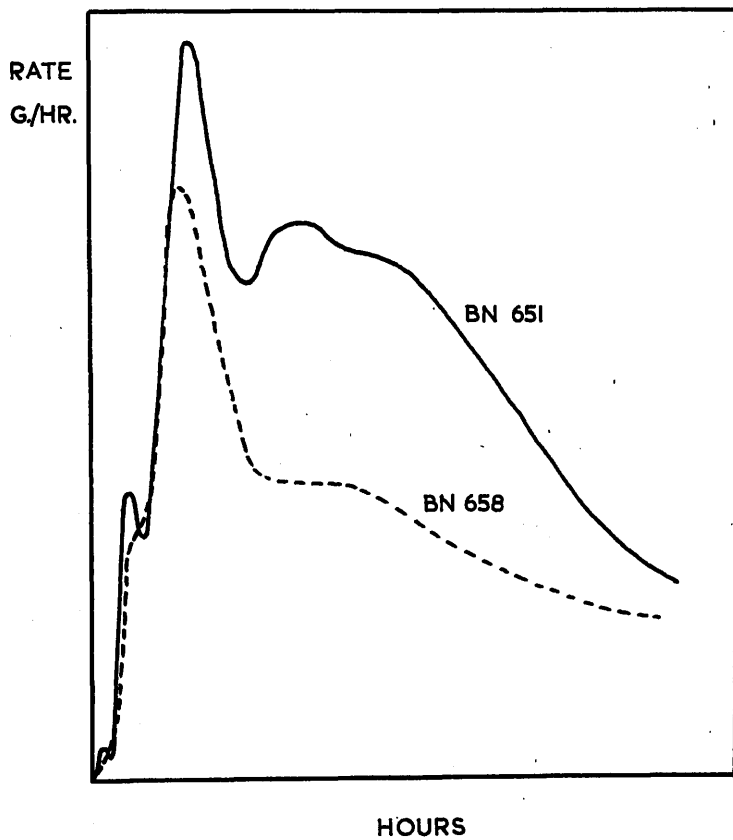
FIGURE 25.

collected a discrepancy is revealed.   Table 13 gives
some results obtained in degradations at 249°.

Table 13

COMPARISON OF EXTENTS OF DEGRADATION

MEASURED IN DIFFERENT WAYS (249°).

	Extent of Degradation		
Polymer	by loss in wt. of tray	by wt. of monomer collected	by area under Pirani plot
BN 651	45 %	43 %	48 %
BN 658	28 %	27 %	30 %
BN 658	16 %	15 %	20 %

These results show a definite trend. The monomer
yield is always slightly less than the loss in weight of
the degrading polymer.   This at once suggests that a
gaseous material is being produced which does not condense
effectively at liquid oxygen temperature (arrangement of
the degradation apparatus is given in figure 5, p.29).

The yield calculated from the area under the rate/time plot is always higher than the measured value by the other methods.   These experiments were carried out with a 10 mm. bore tap between the pumps and the apparatus. Earlier experiments using a 6 mm. bore tap had revealed even more serious discrepancies between the yields calculated by area and those measured in other ways, and the greater the weight of polymer degraded the worse the discrepancy became.   Clearly a gaseous product , non-condensable in liquid oxygen, is being produced, and the speed of its removal from the still by the pumps * has a considerable influence on the extent of its effect on the Pirani gauge.

The presence of the gaseous product is further demonstrated by closing the tap between the apparatus and the pumps, so that degradation occurs in a closed system. The Pirani gauge then indicates a continuous increase in pressure.

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* See figure 5 (p.29).   Once the apparatus has been evacuated the liquid oxygen trap serves as a pump for removal of condensable degradation products.   Non-condensable products, however, must be pumped out of the whole system by the vacuum pumps.

Nature of the Gaseous Product.

An attempt was made to identify the gaseous product by collecting some of it in an infrared gas cell, although it is difficult to obtain sufficient of the material to measure the spectrum. One gram of polymer (BN 657) was degraded at 310° for 6 hours in the apparatus shown in figure 26. The apparatus was thoroughly evacuated before degradation commenced, then tap E was closed, so that degradation was carried out in a closed system. The trap F was surrounded by liquid oxygen. A small pressure registered on the manometer at the end of the experiment. This represents the pressure due to the products at -182° (table 14).

Table 14

PRESSURE DUE TO PRODUCTS OF DEGRADATION.

Temperature ($^{\circ}$C)	Pressure (mm.)
-182	7.8
-78	14.0
0	28.5
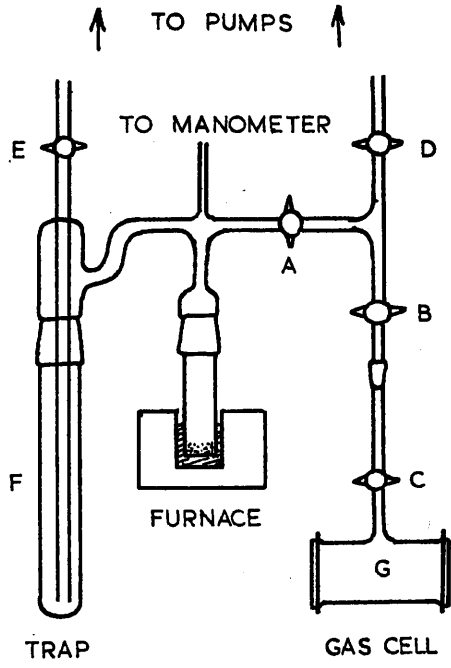
FIGURE 26.

The infrared cell G was then closed and removed from the system for measurement of the spectrum. Tap A was closed and the liquid oxygen was replaced by solid carbon dioxide/ methanol. The infrared cell was replaced and the air in section B-C of the apparatus was pumped out through D. Tap D was closed and taps A and C opened. The manometer registered an additional pressure. The spectrum of the gas in the cell was again measured. Finally the CO_2 was replaced by ice-water and a third spectrum obtained.

Table 15

SPECTRUM OF GAS COLLECTED ($cm.^{-1}$).

3070 w	1462 m
3000 s	1446 m
2950	1342 m (broad)
1845 w	1306 s
*1715 w	966 m
*1635 m	**927 vs
*1620 m	712 m

* 1715, 1635, 1620 probably due to traces of acetone and water, appear in third spectrum only.
** 927, 966 and 712 peaks appear to greater intensity, relative to other peaks, in third spectrum.

All three spectra were very weak due to the small amount of gas present, but it was clear that the same materials were present in each case. Table 15 lists the frequencies of the peaks detected.

The peaks obtained indicate clearly that the product is a hydrocarbon, and the only hydrocarbons which might be expected not to condense effectively in liquid oxygen are methane, ethane, and ethylene. The spectra of ethane and ethylene do not correspond at all well with the data of table 15. Methane, however, shows very few peaks in its spectrum (table 16) and all of these agree well, both in position and intensity, with peaks obtained.

Table 16

PEAKS IN THE SPECTRUM OF

METHANE $(cm.^{-1})$.

3000 s	1345 m (broad)
2950	1305 s
1600 w	

It therefore seems likely that methane is present, but the remaining peaks in table 14 still have to be

explained.   These may be accounted for very well if a
small amount of monomer were present, since they
correspond with the strongest bands in monomer. (Monomer
peak frequencies are quoted in the appendix - allowance
must be made for the fact that these are for the liquid
state).   The fact that these peaks show to a greater
intensity in the third spectrum ($0^{o}C$), relative to the
other peaks, supports this view, since some monomer is to
be expected in this case (vap.pres. 17.5mm. at $0^{o}C$.).

Further work is required before the products can
be isolated and identified conclusively.   Gas chrom-
atography appears to offer the best method of dealing
with the problem.   The results of the present experiment,
however, suggest methane as the only product other than
monomer.

RESULTS OF SOME DEGRADATION EXPERIMENTS.

Some molecular weight and rate measurements in the
degradation of samples of polymethacrylonitrile have been
made, from which, bearing in mind the complicating factors
already discussed, a few tentative conclusions may be
drawn.

Table 12 (p.121) gives the results of molecular

weight measurements made on the soluble portion of the
polymer residue at different extents of degradation.
There is clearly no evidence for a steep drop in molecular
weight in the early stages of the reaction, suggesting
that the reaction does not involve weak link scission
(apart from ketene-imine decomposition at lower temper-
atures), but that as with polymethyl methacrylate volatile
material is liberated from the chain ends.

This tends to be confirmed by the data in table 17
which illustrates the effect of initial molecular weight
on the rate of the reaction.

Table 17

EFFECT OF MOLECULAR WEIGHT ON
INITIAL RATE OF VOLATILIZATION AT 256°.

Polymer	Molecular WT.	Init.Rate (%/hr.)
BN 601	33,700	22
BN 651	15,900	35
BN 701	ca.14,000	40

Clearly the rate bears some inverse relationship to the initial molecular weight, that is, some direct relationship to the number of chain ends.

PHOTOCHEMICAL DEGRADATION.

Degradation in polymethacrylonitrile can be induced photochemically at 170-200°, the product being monomer. The reaction has not been studied in detail, but it has been shown that when colouration occurs the rate of the reaction rapidly falls to zero.

CONCLUSIONS.

The depolymerization reaction in polymethacrylonitrile has been shown to bear a close resemblance to that of polymethyl methacrylate in that the product is almost exclusively monomer and the reaction appears to be initiated at the chain ends. The reaction, however, is considerably complicated by side reactions resulting in colouration, insolubility, and the production of a gas, probably methane, which does not condense effectively at liquid oxygen temperature. These side reactions may or may not be related.

There is scope for much further work on the depolymerization of polymethacrylonitrile, and some suggestions are given below of lines of study which might prove fruitful.

The production of methane might conveniently be studied by gas chromatography. Rate measurements could be made for monomer production if the apparatus were re-designed for fast pumping, to remove methane. Determination of energies of activation for these two processes might reveal a relationship. On the other hand, production of methane may be related to colouration - for example, by aromatization of the ring structures by loss of angular methyl groups and adjacent hydrogen atoms:
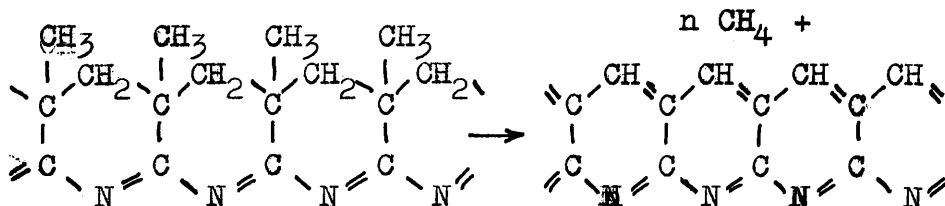
and this might be tested by degrading extensively coloured material. The insoluble residue formed in degradation might also be examined spectroscopically.

7

GENERAL DISCUSSION

While it is often possible to predict how a polymer will degrade from a consideration of its structure, there are numerous cases where the polymer is much less stable than would be anticipated or where quite unexpected degradation reactions take place.   It is becoming increasingly evident that these instances of unexpected behaviour are nearly always due to the presence in the polymer chain of a very small proportion of abnormal structures (1% or less). Thus it is often found that the molecular weight of a polymer will undergo an initial sharp drop after which the polymer remains comparatively stable until the temperature is further raised.   On the other hand, the abnormal structures may be associated with the initiation step in a chain process which may result in extensive breakdown or modification of the polymer structure.

Structural abnormalities in polymers can originate in four ways, and degradation reactions may be associated with the structures formed in any of these ways.

(i)   Impurities can become incorporated into the polymer chain through copolymerization.   Polyethylene contains small amounts of carbonyl structures which are believed to be present due to copolymerization with traces of carbon monoxide present as an impurity in the monomer. The sharp but limited drop in molecular weight which occurs in polyethylene at temperatures far below that at which, from an inspection of the polymer structure, degradation might be expected, has been shown to be associated with these carbonyl structures.[31]

(ii)   Abnormal structures must inevitably be present at the ends of chains, and these are often the sites for degradation, possibly because the structure present is susceptible to reaction, or perhaps simply because of the greater opportunities for thermal motion.   In polymethyl methacrylate, for example, degradation is initiated preferentially at the unsaturated end formed in disproportionation in the termination process in polymerization[1,30].   In

polyvinyl acetate, however, the different types of
end present seem to be equally susceptible to
degradation[33], and the preference for degradation
at the end structures in this case must be attrib-
uted simply to the greater thermal motion.

(iii)   Abnormal structures may also arise in the
polymerization process.   Polystyrene probably
provides an example of this type.   This polymer
shows the sharp drop in molecular weight in the
early stages of degradation often associated with
the presence of weak links.   The nature of the
reaction has not yet been clarified but it is
possible that weak structures arise by abnormal
steps in the polymerization.   Possibilities are
head to head linkages[32]

$$\sim\sim\sim CH_2 - CH - CH - CH_2 - CH_2 - CH \sim\sim\sim$$
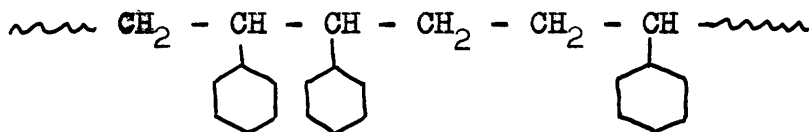
or structures resulting from polymerization through
the benzene ring:

$$\sim\sim\sim CH_2 - CH - CH_2 - CH = \!\!\!\bigcirc\!\!\!- CH_2 - CH \sim\sim\sim$$
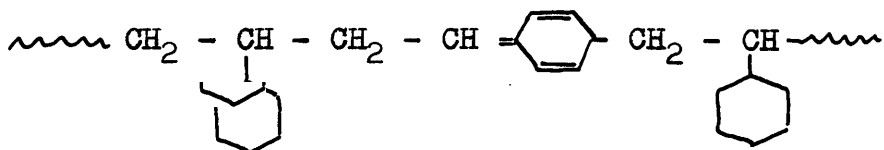
(iv)   Chemical modification of the polymer may take

place after it has been prepared.   Oxidation

reactions are the commomest examples of this type.

Natural rubber, for example, undergoes a substantial

drop in molecular weight upon reaction with a very

small percentage of its weight of oxygen.

The thermal degradation reactions of polymethacrylo-

nitrile, discussed in this thesis, provide a particularly

good example of the very great importance of small

concentrations of abnormal structures.   Three quite

distinct reactions may be observed in the temperature

ranges $20-120^{\circ}C$, $120-220^{\circ}C$, and above $220^{\circ}C$, respectively,

and each of these is associated with a different structural

irregularity.

$20-120^{\circ}C$.

In the low temperature range, in solution, or at

the softening point of the polymer ($110-120^{\circ}$), ketene-

imine structures disappear with an accompanying limited

decrease in molecular weight.   This is an example of

the breakdown of a weak link present because of an abnormal

termination step in the polymerization process,, in which

the growing radical reacts in the form

$$\mathbf{\sim\sim\sim} CH_2-C(CH_3)\ C=C=N\cdot$$
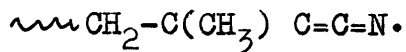
with another radical with the formation of a ketene-imine structure in the polymer chain.   The disappearance of ketene-imine structures has been shown to be a second order reaction whose rate is strongly dependent on the viscosity of the medium.

120-220°C.

Above the softening point of the polymer, rapid discolouration may occur, through yellow and orange to deep red.   This is due to the linking up of adjacent nitrile groups to form conjugated sequences.   This chain reaction provides an example of the occurrence of degradation because of the presence in the polymer of an impurity which acts as an initiating centre.   The reaction may be initiated at methacrylic acid units which are often present in polymethacrylonitrile as it is usually prepared.   The reaction can also be initiated by a variety of substances, not necessarily incorporated in the polymer chain, which are all bases in the Lewis sense.   A general mechanism has been proposed for the reaction which is essentially an anionic polymerization of a nitrile under specially favourable steric conditions.

Above 220°C.

Above 220°, rapid depolymerization to monomer occurs and yields approaching 100% can be obtained, provided care is taken to suppress the colouration reaction by rigorous purification of the monomer and polymerization under high vacuum with an azo catalyst. This depolymerization process is superficially similar to that which occurs in polymethyl methacrylate, being initiated most probably by radical formation at the chain terminal structures. This is therefore an example of a third type of abnormal structure in polymethacrylonitrile - the chain ends - being responsible for a degradation reaction.

A full investigation of the depolymerization has yet to be made, but there is already evidence of some interesting complications. A small amount of colouration, not due to impurities of the type already discussed, occurs above 200°C; this may be associated with reaction at one particular type of end structure. Insolubilization and the production of traces of a gas which is probably methane also occur. Possible methods of approach to the study of these reactions have been indicated, and it seems likely that further dependence on structural irregularities will be revealed.

APPENDIX

LIST OF POLYMERS

Polymer	Temp. °C	Initiator and concn. % w/v		% Polym.	Av.Rate %/hr.	log I_0/I at 2012cm.$^{-1}$ (7.5% soln)	Mol. Wt.
BN 251*	25	A	0.2	2	0.05	0.150	18,800
BZ 301*	30	B	0.5	6	0.126	0.104	18,200
BZ 302*	30	B	1.9	6	0.213	0.188	17,100
BZ 303*	30	B	4.0	6	0.293	0.242	17,750
BZ 304*	30	B	1.0	6	0.158	0.145	–
BZ 305*	30	B	2.4	6	0.222	0.211	–
P 601	60	B	0.25	12.5	0.32	–	–
P 701	70	B	0.75	12	1.50	–	–
BN 601	60	A	0.1	10	0.39	0.014	33,400
BN 651	65	A	0.7	10	1.75	0.076	15,900
BN 657	65	A	0.1	10	0.37	–	–
BN 658	65	A	0.2	11	0.95	0.037	23,900
BN 659	65	A	1.25	10	2.1	0.150	12,800
BN 6510	65	A	2.0	10	3.07	0.208	–
BN 6511	65	A	1.1	10	(2.4)	0.150	–
BN 6512	65	A	0.41	10	1.40	0.081	–
BN 6513	65	A	0.06	10	0.44	0.038	–
BN 701	70	A	1.0	11	3.7	0.095	–

* Photodecomposition of initiator

A = Azobisisobutyronitrile   B = Benzoyl Peroxide.

INFRARED SPECTRA

Principal peaks in the spectra of
methacrylonitrile and polymethacrylonitrile.

MONOMER		POLYMER	
3090 m		3700 w	
2945 / 2915 } s	C-H str.	2950 / 2870 } s	C-H str.
2190 s	C≡N str.	2210 s	C≡N str.
1870 m	940 overtone	2012 w-m	C=C=N
1620 s	C=C str.	1620 w	C=C str
1448 vs	CH_3 def.	1464 / 1450 } s	CH_2 def.
1380 s	CH_2 bend		
1270 s	CH rock ?	1388 / 1372 } s	CH_3 def
1023 s	-C-C≡N bend ?		
940 vs	=CH_2 wag	1210 s / 980 m }	-C-C-C- distortion
748 s		843 w	CH_3 rock ?
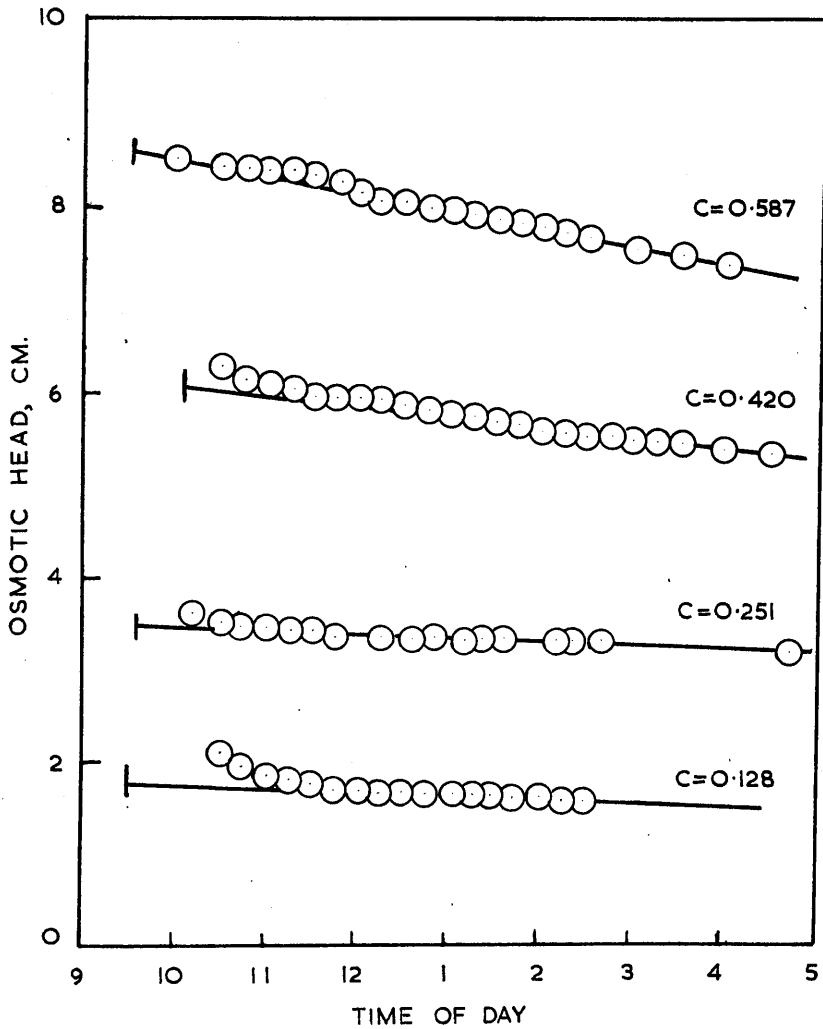
OSMOTIC PRESSURE DATA FOR BZ 302, SHOWING
DIFFUSION AND METHOD OF EXTRAPOLATION TO
TIME OF FILLING.

R.T.1
CONTROLLER

Pt RESISTANCE
THERMOMETER

N
MAINS

L,

E

VARIAC
TRANSFORMER

FURNACE
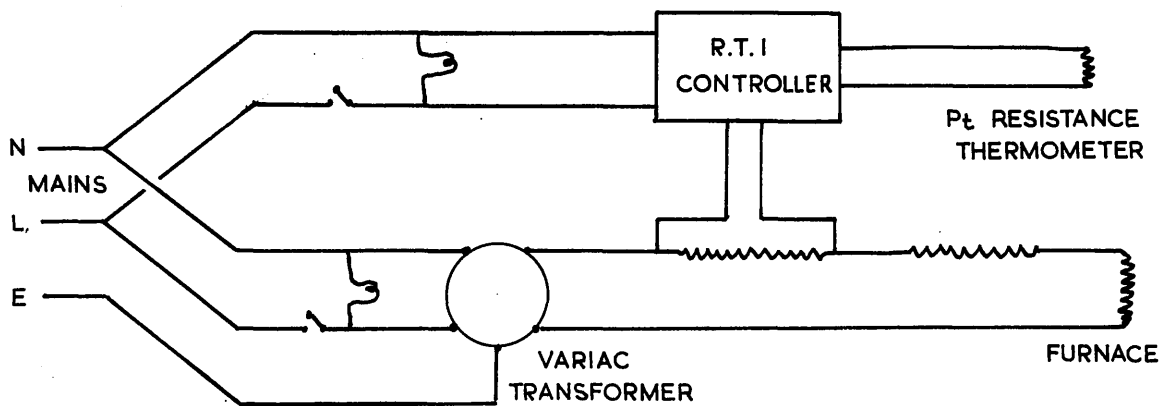
HEATING AND CONTROL CIRCUIT.

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PHOTOGRAPHIC PLATE

Molecular models of undegraded (left) and coloured (right)
polymethacrylonitrile, showing the almost identical spacial
arrangement of the atoms.

White = hydrogen, black = carbon, grey = nitrogen.