

THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

THE THERMAL COLOURATION OF

POLYACRYLONITRILE

by

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Preface.

This thesis describes the results of research carried out, during the period October 1957 to August 1960 at the University of Glasgow in the Macromolecular Laboratory, Department of Physical Chemistry, which is under the supervision of Professor J. Monteath Robertson.

The material of chapter 3,4, and 5, has been published in a general paper read at the Symposium of the Plastics and Polymers Group of the Society of Chemical Industry at London, September 1960. A further paper on the same chapters will shortly be published in the Journal of Polymer Science, and another dealing with the subject matter of chapter 6 will appear in due course.

My thanks are due to the University of Glasgow for the award of an U.S. Rubber Company Research Studentship for the period 1957-59, and also to Courtaulds Limited for the award of a Scholarship for the period 1959-60.

My thanks are due also to the members of staff with whom I had discussion, particularly Dr. G. Eglinton for interpreting infra-red spectra. I should also like to thank Professor J. Monteath Robertson for the constant interest he has taken in this work.

Finally I wish to express my sincerest thanks to Dr. N. Grassie, under whose supervision this research was carried out, for his constant guidance, advice and encouragement throughout the course of the work.

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CHAPTER 1.

Introduction.

The degradation reactions of high polymers are of great interest industrially and commercially because of their association with the deterioration of the useful physical properties of synthetic rubbers, fibres and plastics. But these reactions have also stimulated a great deal of purely chemical interest because they often represent new types of processes or are examples of classical reactions which are modified^{1,2.} by their molecular chain environment.

The degradation reaction which occurs in polyacrylonitrile and in nitrile polymers in general, is of interest from both the industrial and purely chemical points of view. Thus, one of the disadvantages of all acrylonitrile fibres, 'Orlon', etc., is their tendency to discolour in use. The nature of the discolouration has been speculated upon and has been the subject of a considerable amount of industrial research effort. The most complete and far reaching

work has been done by Grassie and McNeill, however, on the closely related polymethacrylonitrile which undergoes a superficially similar discolouration.^{3,-8}

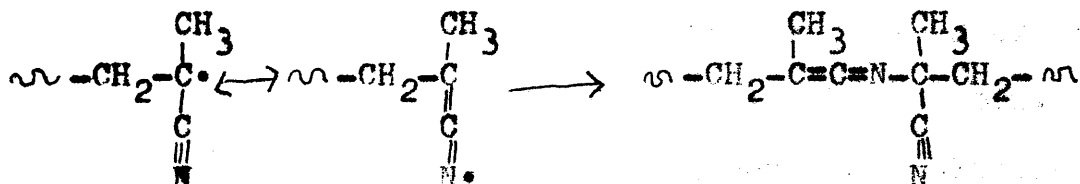
This thesis is concerned principally with the elucidation of the mechanism of the colour reaction in polyacrylonitrile making use of Grassie and McNeill's basic work on polymethacrylonitrile as an initial guide to the nature of the reaction.

Grassie and McNeill have discovered that there are three quite distinct degradation reactions which can occur in polymethacrylonitrile, namely depolymerisation, ketene - imine decomposition and colouration.

Polymethacrylonitrile is prepared from a 1:1 disubstituted monomer and so one would have predicted that it would give almost quantitative yields of monomer on degradation. It was found, however, that the yield of monomer decreased with the amount of colouration that was produced on degradation. Polyacrylonitrile is not such a disubstituted polymer and so would not be expected to give high yields of monomer on degradation. The corresponding relationship between monomer yield and extent of colouration does not then arise but it is conceivable that the degradation products will be altered

by colouration. This may, for example, explain the low yields of hydrogen cyanide obtained on degradation although, from the polymer structure and "halide" nature of the cyanide group, one would have expected some acid elimination reaction, as for example, undergone by polyvinyl chloride⁹.

Polymethacrylonitrile, polymerised at a low temperature, was found to contain appreciable amounts of ketene - imine structures^{6, 12}, produced by the reaction of the polymethacrylonitrile radical in the abnormal form, particularly in a termination step;

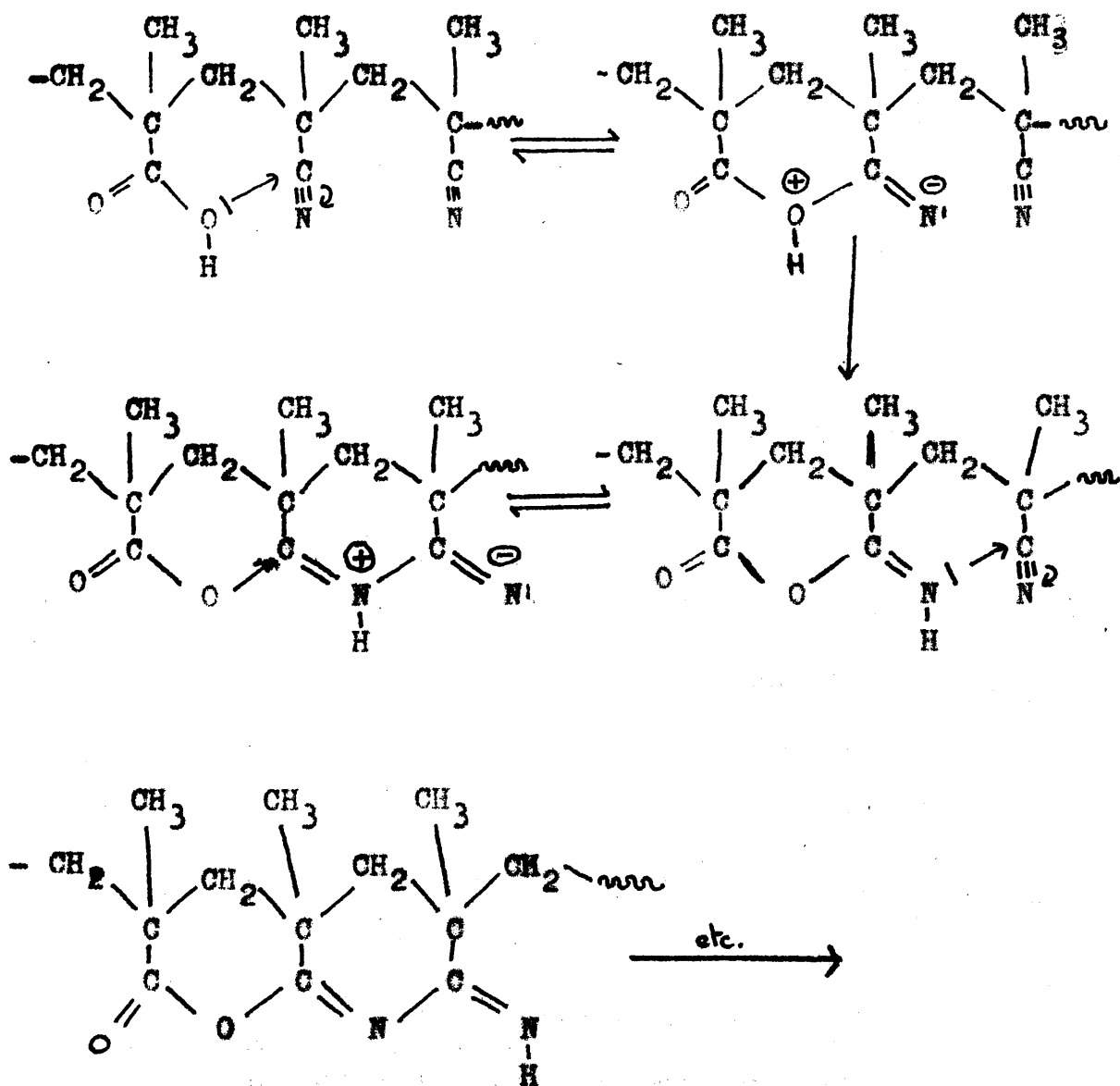


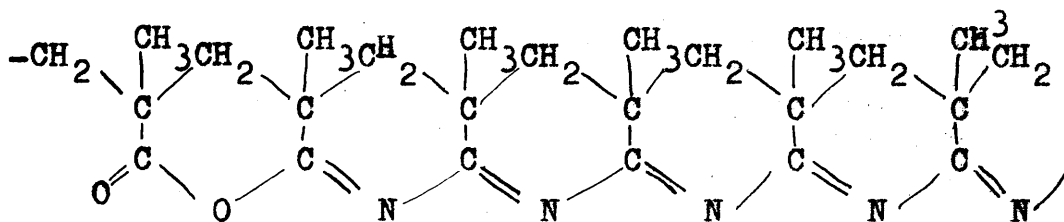
These structures are comparatively unstable and decompose readily at 90°C in solution. The stability of ketene - imine compounds is known to decrease with decreasing substitution on the parent skeleton, $\text{C}=\text{C}=\text{N}-$. It is not surprising, therefore, considering the instability of the tri-substituted form produced from methacrylonitrile that the corresponding structure, which would only be di-substituted, does not occur in polyacrylonitrile. Ketene - imine structures, however, in no way alter the

stability of polymethacrylonitrile to colouration and are not directly concerned in the general colour reaction.⁶

Before the depolymerisation temperature of polymethacrylonitrile is reached, at about 220°C, the polymer is normally found to have coloured extensively. Grassie and McNeill found that the ability to colour varied from polymer to polymer and that it was directly proportional to the amount of carbonyl impurity incorporated into the polymer.^{3,4} This carbonyl impurity in the polymer, as normally prepared, was shown to be methacrylic acid which is produced by the hydrolysis of the monomeric nitrile by traces of acetic acid and water, normally present in the monomer. Complete removal of the acidic impurity by alkaline washings prevents the colour reaction to a large extent, and if further precautions are taken, such as elimination of oxygen during polymerisation and the use of an azo compound rather than a peroxide as initiator then a polymer is obtained which does not colour significantly below the depolymerisation temperature. The rate of colouration in polymethacrylonitrile can, therefore, be controlled by using controlled amounts of methacrylic acid in carefully purified monomer. Infra-red spectrographic studies on the copolymers of methacrylonitrile

and methacrylic acid showed that the rates of colouration increased with acid concentration and that the actual initiation step of the colour reaction was a nucleophilic attack by the acid carboxylic group on the nitrile followed by proton migration, to produce an imino group which too is a nucleophilic reagent and capable of further condensation with the adjacent nitrile group ^{3,4,7}.





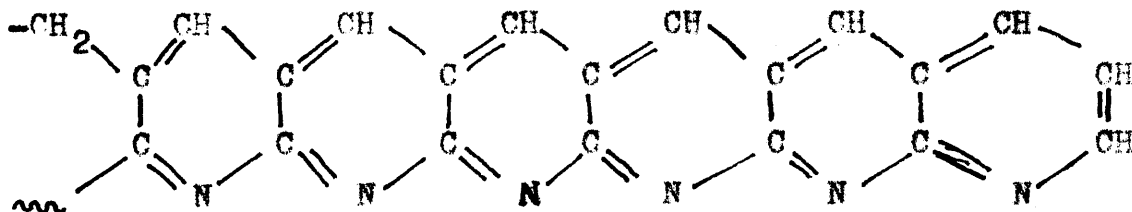
Thus the reaction is propagated along the chain resulting in a condensed ring system with conjugated carbon-nitrogen double bonds, which accounts for the gradual development of colour through the spectrum, from yellow to red.

The colour reaction, as seen from the above scheme, was considered to be ionic rather than free radical in nature. Each step in the process is complete in itself and so accounts for the slow development of colour through the spectrum. Evidence for this type of reaction is also obtained from the variety of reagents, in addition to methacrylic acid, which are capable of initiating it. External initiation studies with model compounds have shown that the following compounds were able to initiate colour.⁷

- a). Organic acids - carboxylic acids (also sulphonic)
- b). Phenols.
- c). Amides, amines, and imines.
- d). Ketones.
- e). Alkaline solutions, sodium and potassium hydroxides.

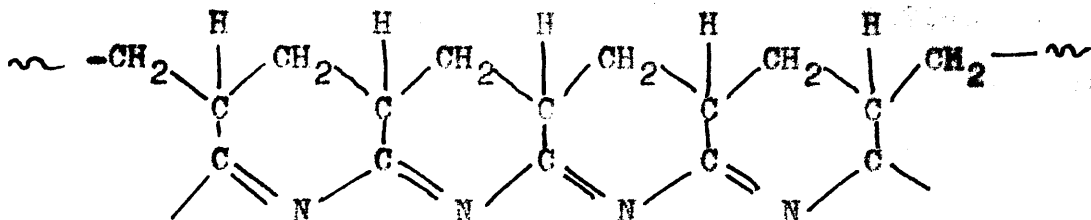
All these are nucleophilic reagents. In particular, Grassie and McNeill have shown that one can relate the ability of a substance to initiate colour with its strength as a Lewis base. This is strong evidence for the reaction given above. Hence one finds that the stronger organic acids have a weaker effect in accelerating the colouration reaction in polymethacrylonitrile.

Polyacrylonitrile undergoes the same sort of colour reaction in the same temperature range and in general, the two reactions seem to be very similar. Houtz (1950)¹⁰ studied the discolouration reaction in "Orlon" fibre. He found that the reaction occurred in an inert atmosphere, and was accelerated by the presence of air. He assigned a structure of condensed 1:8 naphthyridine rings to the colouring unit in polyacrylonitrile. His observations were based entirely on infra-red observations;



In the light of Grassie and McNeill's work on

polymethacrylonitrile this structure seems very unlikely and indeed, Burlant and Parsons¹¹, also using infra-red spectroscopy for analysis, have considered the following structure to be the colouring unit,



Although it is known that polyacrylonitrile will colour under similar conditions to impure polymethacrylonitrile and that the reactions are superficially very similar, in that an almost identical colouring unit is obtained, not much more is known about the reaction. The work described in this thesis has been aimed at a more complete characterisation of the reaction using the evidence of the polymethacrylonitrile reaction as a guide.

Presentation of the Thesis.

Apparatus and experimental techniques are described in chapter 2.

In chapter 3, the general characteristics of the effect of heat on acrylonitrile homopolymers are

described. The colour reaction was followed using the dynamic molecular still and infra-red techniques. The degradation products at a much higher temperature are partially characterised and a mode of degradation speculated upon from the point of view of the nature of these products and also of the colour reaction.

The effect of purity and mode of preparation of the homopolymers with respect to their colour stability is discussed in chapter 4. This is further elucidated by degradation experiments on copolymers of acrylonitrile and acrylic acid. The residual colouration in polyacrylonitrile is definitely shown not to be due to acidic impurities. The effect of model compounds in initiating the colour reaction in pure polymethacrylonitrile is discussed and a mode of initiation in polyacrylonitrile deduced.

Chapter 5 deals with the propagation of the colour reaction through the cyanide groups, and is discussed in detail in the light of the development of insolubility as colouration proceeds. The ability of various copolymers to develop insolubility is used to show the effect of reduced chain interaction on the reaction.

In chapter 5, copolymers of methyl vinyl ketone and acrylonitrile are shown to behave abnormally on

colouration. Chapter 6 deals with the condensation reaction in polymethyl vinyl ketone itself, and the characteristics of the thermal reaction undergone by these copolymers are explained in terms of the two reactions of the homopolymers - polyacrylonitrile and polymethyl vinyl ketone.

The colour reaction in polyacrylonitrile is summarised in chapter 8 and compared with that of polymethacrylonitrile.

Chapter 2.

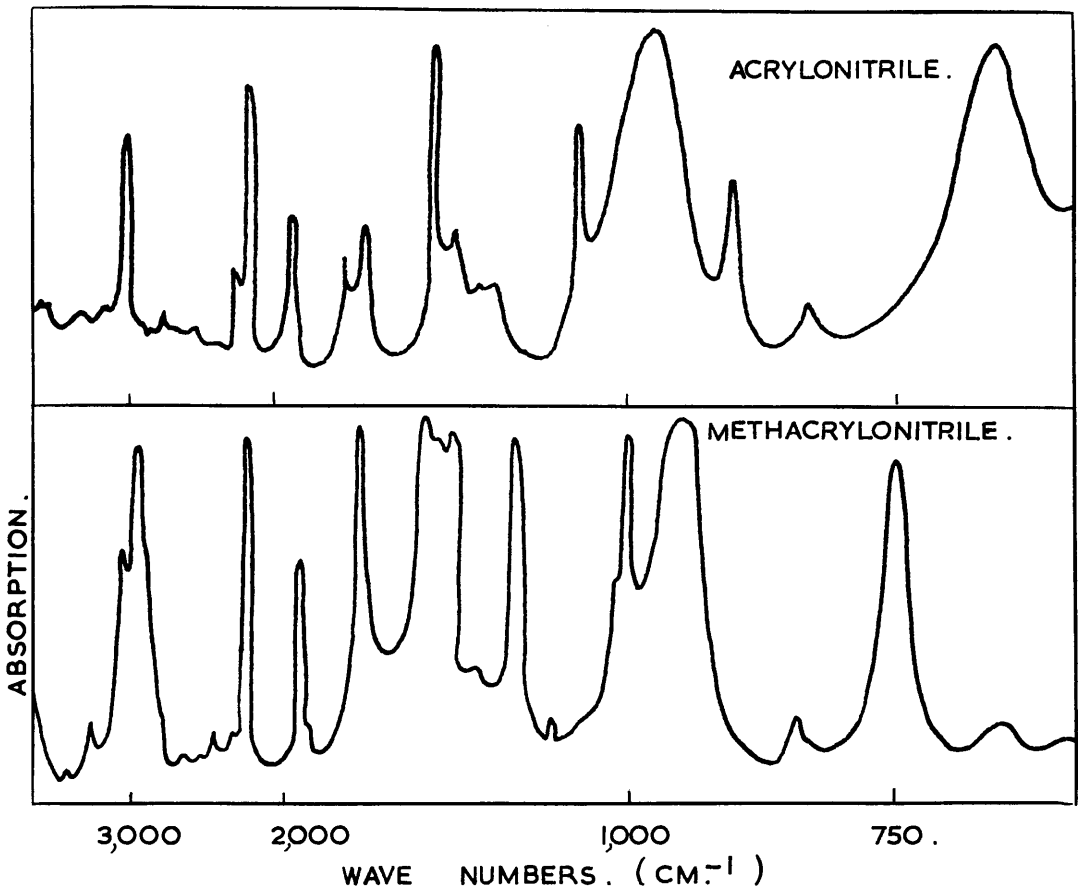
Apparatus and Experimental Techniques

1). Preparation and Purification of Reagents.

a. Monomers.

Acrylonitrile was obtained from various sources - Lights, British Drug House, Eastman Kodak, B.X. Plastics, etc. As obtained it frequently contained an inhibitor, and was purified by washing three times with dilute alkali, three times with distilled water and dried over calcium chloride. This method was found to give monomer of standard purity. The infra-red spectrum of the monomer purified in this way was identical to the spectrum assigned to acrylonitrile by Halverston, Stamm and Whalen¹³, and in particular there was no absorption in the carbonyl region.

Acrylonitrile monomer has been found to contain traces of methyl vinyl ketone, some olefins and other



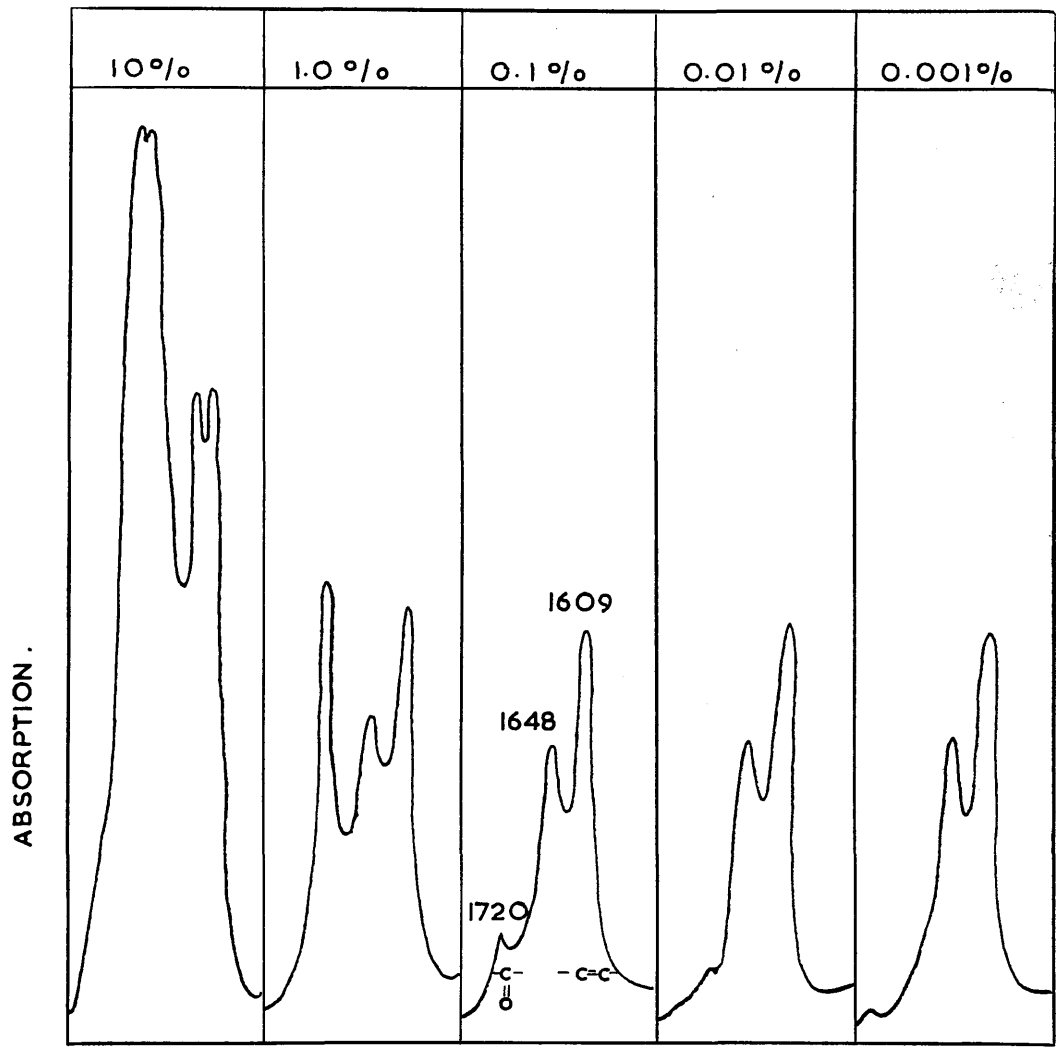
MONOMER INFRA-RED SPECTRA.

FIGURE 2-1.

cyanides. Of these only methyl vinyl ketone was considered to be a possible source of colour initiation. Also the colouration of polymethacrylonitrile as it is normally prepared has been attributed to small amounts of acid impurity³. It, therefore, seemed desirable to know the effect of small concentrations of carboxylic acid and methyl vinyl ketone on the colouration properties of polyacrylonitrile and to decide whether these two reagents could be present in acrylonitrile monomer in concentrations high enough to cause significant colouration.

Addition of known amounts of acrylic acid and methyl vinyl ketone to purified acrylonitrile showed that the infra-red spectrophotometric analysis could detect these two impurities in concentrations less than one part per thousand, see figure 2-2, and it will be shown that these concentrations do not significantly effect the colouration properties. Other organic impurities were tested for by vapour phase chromatography, a single peak was always obtained with purified acrylonitrile.

Acrylic acid (Eastman Kodak) and methyl vinyl ketone (Light or D.C.L.) were purified by drying over potassium sulphate, and distilled under pressure.



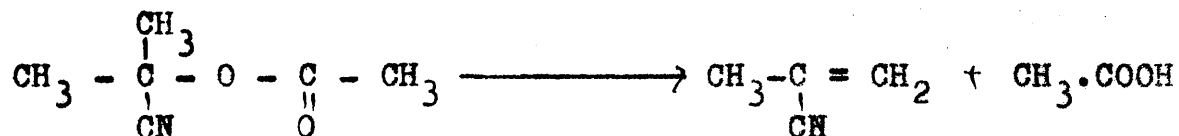
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ADDITION OF ACRYLIC ACID TO ACRYLONITRILE.

FIGURE 2-2.

Styrene (Forth Chemicals), and methyl methacrylate (I.C.I.) were purified by washing with dilute alkali, to remove the inhibitor, then with distilled water and dried over Calcium Chloride. Finally they were twice distilled under reduced pressure.

Methacrylonitrile monomer was prepared, as described by Grassie and Vance ¹⁵, by the pyrolysis of acetone cyanhydrin acetate, at 550°C.



Acetyl chloride (0.05 mol.) was added through a reflux condenser into a flask containing acetone cyanhydrin (1.0 mol.) and acetic anhydride (1.5 mol.). After a few seconds vigorous reaction set in. The reaction was kept refluxing for 30 minutes, and then allowed to stand for 30-40 hours. The mixture was fractionally distilled and the fraction boiling between 178-182°C collected. This was mainly acetone cyanhydrin acetate.

The acetate was pyrolysed in a silica tube packed with silica chips. The temperature was measured with an internal thermocouple. The acetate was added dropwise at the top of the column and the pyrolysate collected at the bottom in a water-cooled flask

vapours were condensed by passing the exit gases through a solid carbon dioxide - acetone cooled trap.

The pyrolysate was purified by neutralising the acetic acid with ammonia, 0.88, washing thoroughly with distilled water and finally, drying over calcium chloride ³. The monomer was then distilled and the product checked with infra-red spectroscopy for traces of acetic acid. Any such traces were removed by repeating the above purification procedure - washing with ammonia and water.

b. Initiator.

a:a'-azo-bis-isobutyronitrile (Eastman Kodak) was purified by twice recrystallising from ethanol, the solution filtered hot to remove insoluble polymeric material derived from the decomposition of the initiator. The crystals were filtered off and dried under vacuum.

c. Solvents.

Dimethyl formamide was stored for 1-2 hours over pellets of potassium hydroxide, dried with anhydrous calcium sulphate and then fractionally distilled. The middle portion boiling at 155°C was collected for use.

' Analar ' grade acetone was used for molecular

weight determinations. It was dried over calcium oxide and fractionally distilled.

2). Polymerisation Techniques.

Polymerisations were carried out in a pyrex glass dilatometer tubes, previously cleaned with chromic acid. A weighed amount of initiator was added and washed thoroughly into the tube with Analar acetone. The acetone was removed under vacuum.

The monomers were degassed three or four times under vacuum and distilled into a graduated tube from which a definite volume was distilled into the dilatometer tube. Finally, the tube was sealed off under vacuum.

Polymerisations were carried out in a thermostat controlled to within 0.01°C . The monomer volume contraction was followed using a cathetometer. The relationship between contraction and extent of reaction used was given by Bamford and Jenkins for acrylonitrile¹⁶, by Grassie and Vance for methacrylonitrile¹⁵, and Haward and White for methyl vinyl ketone¹⁷. These values are reproduced in table 2-1.

Approximate copolymerisation contraction factors were obtained by direct proportions from the ratios of monomers in the polymerisation mixtures. These

values were used only for following the progress of the polymerisations quantitatively. More accurate values of the percentage polymerisation, as quoted in all tables, were based on the weight of polymer produced.

Table 2-1.

Volume Percentage Contraction for 100% Polymerisation.

Temperature ° C	Acrylonitrile	Methacrylonitrile.
20.	22.5	31.1
30.	23.5	32.5
40.	24.6	33.8
50.	25.7	35.0
60.	26.7	36.7
70.	27.8	38.5
80.	28.9	40.4

Methyl vinyl ketone

25.

Most of the polymerisations were taken to about 10% conversion except in the preparation of copolymers of high acrylonitrile content, where carrying the reaction to any significant extent would have upset the monomer molar ratio in the reaction mixture, and altered the composition of the copolymer.

3). Isolation and Purification of the polymers.

Polyacrylonitrile and acrylonitrile rich copolymers, which were insoluble in the monomer mixture and in all common organic solvents, excepting dimethyl formamide, were simply isolated by filtering free of monomer and washing thoroughly with methanol. Finally, they were dried under high vacuum for several days.

No attempt was made to further purify these polymers by dissolving and reprecipitating from dimethyl formamide as this solvent was found to be an efficient colour initiating agent. Since polyacrylonitrile does not melt below colouration temperatures, traces of the solvent are difficult to remove, and so the colour stability of the polymer is greatly reduced. This is particularly so when the polymerisation is carried out in dimethyl formamide solution, in which case dimethyl formamide units presumably become directly incorporated into the chains by transfer.

Homopolymers of methacrylonitrile, and methyl vinyl ketone and copolymers of acrylonitrile which remain soluble in the monomer mixture were purified by dissolving in 'Analar' acetone and precipitating from excess methanol. The dissolution and precipitation was repeated and this product after grinding to a fine powder was

dried in vacuum.

All polymers were used in the form of finely divided powders, with the exception of polymethyl vinyl ketone which was rubber-like in properties and could not be ground. It was used in the form of a film, cast from acetone solution.

The polymerisation conditions for all polymers and copolymers are listed in the appropriate table in the appendix of this thesis. All bracketed numbers following particular polymers or copolymers, in this thesis, corresponds to the reference number in these tables.

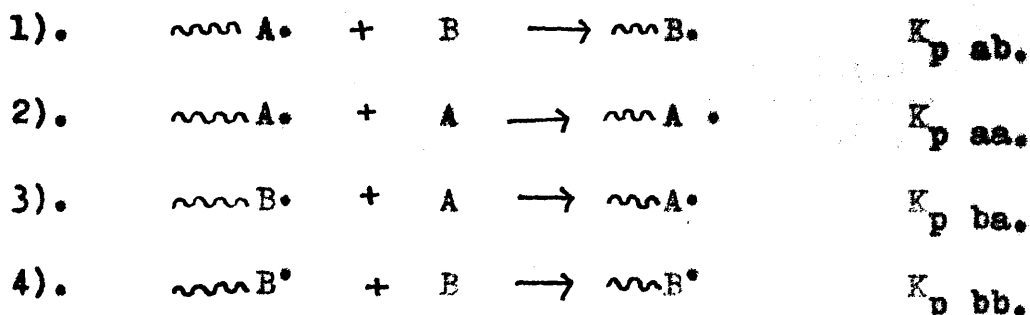
4). Copolymer Composition.

Copolymerisations involve the same reaction mechanisms as homopolymerisations, except that they are more complex. Instead of one propagation and one termination, there are now four propagation and three termination processes.¹⁸ Fortunately, the chemical composition of the copolymer is determined only by the four propagation steps, providing, of course, the molecular chains are long so that the contribution of the end groups is insignificant.

The four propagation steps for the two monomers

A and B can be represented by the equations,

Rate constants.



in which A^\cdot and B^\cdot denotes growing chain radicals terminated by units of the type A and B respectively.

Hence the rate of incorporation of A into the chain is given by,

$$\frac{-d(A)}{dt} = K_p \text{ aa} \cdot (A) \cdot (A^\cdot) + K_p \text{ ba} \cdot (A) \cdot (B^\cdot)$$

and of B by,

$$\frac{-d(B)}{dt} = K_p \text{ bb} \cdot (B) \cdot (B^\cdot) + K_p \text{ ab} \cdot (B) \cdot (A^\cdot)$$

If it is assumed that a steady state exists then the rate of conversion of radical A to radical B is equal to the rate of conversion of radical B to radical A, that is, we assume that

$$\frac{d(A^\cdot)}{dt} = \frac{d(B^\cdot)}{dt} = 0.$$

thus,
$$K_p \text{ ba} \cdot (B^\cdot) \cdot (A) = K_p \text{ ab} \cdot (A^\cdot) \cdot (B)$$

The final copolymers will then have the composition given by the equation,

$$\frac{d(A)}{d(B)} = \frac{K_{p aa}(A^{\bullet}) \cdot (A) + K_{p ba}(B^{\bullet}) \cdot (A)}{K_{p ab}(A^{\bullet}) \cdot (B) + K_{p bb}(B^{\bullet}) \cdot (B)}$$

and putting $\frac{K_{p aa}}{K_{p ab}} = r_1$, and $\frac{K_{p bb}}{K_{p ba}} = r_2$ 19

in which r_1 and r_2 are called the reactivity ratios, the copolymer composition equation reduces to,

$$\frac{d(A)}{d(B)} = \frac{\frac{(A)}{(B)} \left\{ 1 + r_1 \cdot \frac{(A)}{(B)} \right\}}{\frac{(A)}{(B)} + r_2}, \text{ in which } \frac{(A)}{(B)}, \text{ and}$$

$\frac{d(A)}{d(B)}$, are the molar ratios of the monomers in the monomer mixture and the copolymer respectively.

This equation is limited to the instantaneous copolymer composition since the more reactive monomer will be used up more rapidly and the composition of the monomer feed, and hence the copolymer composition, will alter as the reaction proceeds. However, this effect is negligible if the conversion of monomer to polymer is kept low, that is, 5-10%.

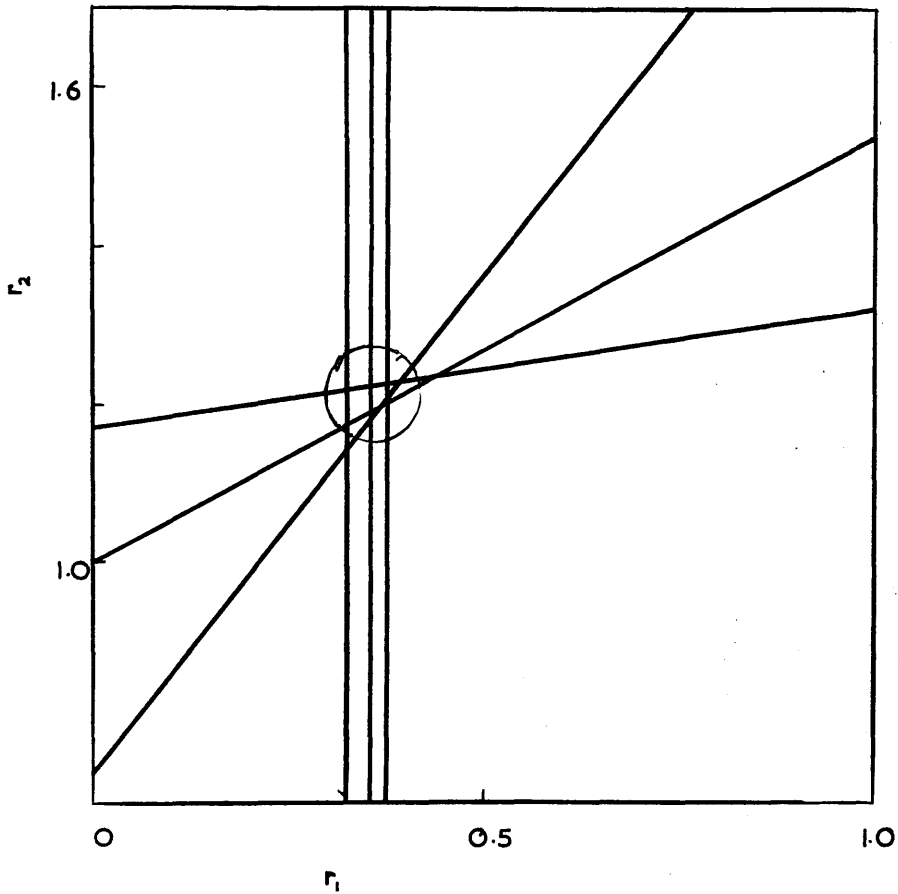
The monomer reactivity ratios are, in fact, measures of the preference of a radical to attack a

monomer of its own type rather than that of the other type. A close inspection of r_1 and r_2 allows one to predict the monomeric arrangement in the copolymer, that is, whether the monomer units are arranged randomly or whether they are as in block copolymers.

In order to make copolymers of known composition it is necessary to know the reactivity ratios for the system. These can be determined accurately only by analysis of the copolymer obtained from a known monomer mixture. r_1 and r_2 are then calculated using the copolymer composition equation above. Several experiments with different monomer feeds are usually carried out and a number of ways are available for extracting the best values of r_1 and r_2 from the results.

In the case of acrylonitrile - acrylic acid system, the copolymers were analysed by determining their nitrogen content, using Kjeldahl's method. ²⁰

0.1 - 0.5g. of copolymer was weighed in a filter paper and dropped into a 500ml. Kjeldahl flask, 3 B.D.H. mercury catalyst tablets, and concentrated sulphuric acid (15 ml.) was then added. The flask was heated over a smoky flame for about an hour, the flame temperature was raised and the heating continued for about 2 hours. On cooling, water (200 ml.) was added



REACTIVITY RATIOS: ACRYLONITRILE - ACRYLIC ACID.

$$r_1 = 0.35 \pm 0.08$$

$$r_2 = 1.19 \pm 0.08$$

Figure 2-2a

to dissolve the white solid and a 50% sodium hydroxide solution containing 10% sodium thiosulphate (60 ml.) was added via a long glass tube to give an alkaline layer in the bottom of the flask. A piece of granulated zinc was also added to prevent bumping. The flask was then connected to the distillation unit and thoroughly shaken to mix the contents. The ammonia which was then distilled off was absorbed in excess standard hydrochloric acid and back titrated against standard sodium hydroxide using screened methyl orange as an indicator. Blanks were run on the filter paper alone and the correction subtracted from the previous titrations. Analysis of pure polyacrylonitrile samples consistently gave values of 26.0% for the nitrogen content , compared with the theoretical value of 26.4%. Copolymer compositions were calculated on this former value, assuming that the percentage error in the nitrogen estimation was consistent throughout the whole range of copolymer compositions.

This gave values of $r_1 = 0.35 \pm 0.08$

and $r_2 = 1.19 \pm 0.08$, for the

reactivity ratios in the monomer system -

acrylonitrile (1), acrylic acid (2), see figure 2-2a.

All the copolymer systems used in this thesis are listed, with their relevant reactivity ratios in

table 2-2. The characteristics of the copolymers in each system are to be found in the relevant table in the appendix.

Table 2-2:- Copolymer Reactivity ratios.

Monomer System	Reactivity Ratios	References
Acrylonitrile (1). Acrylic acid (2).	$r_1 = 0.35 \pm 0.08$ $r_2 = 1.19 \pm 0.08$	above
Methyl methacrylate (1). Acrylonitrile (2).	$r_1 = 1.35 \pm 0.1$ $r_2 = 0.18 \pm 0.1$	21.
Acrylonitrile (1). Methyl vinyl ketone (2).	$r_1 = 0.61 \pm 0.04$ $r_2 = 1.78 \pm 0.22$	22.
Styrene (1). Acrylonitrile (2).	$r_1 = 0.38 \pm 0.03$ $r_2 = 0.05 \pm 0.02$	23
Acrylonitrile (1). Methacrylonitrile (2).	$r_1 = 0.266$ $r_2 = 3.42.$	Q, e scheme.

Acrylonitrile - Methacrylonitrile System.

These two monomers are too alike in structure to derive accurate reactivity ratios based on purely chemical analysis, excepting radiochemical tracer

techniques. A semi-quantitative method of calculating reactivity ratios is, however, available in Alfrey and Price's Q and e scheme. ²⁴

They considered that the rate constant for the reaction,

$$\sim\sim\sim A^\bullet + B \longrightarrow \sim\sim\sim B^\bullet$$

involving a monomer B and a growing radical A[•], could be related to the terms,

P_A - a reactivity associated with radical A[•],

Q_B - a reactivity associated with radical B[•],

e_A and e_B polar terms associated with radical A[•] and monomer B, by the equation,

$$K_{p ab} = P_A Q_B \cdot e^{-e_A \cdot e_B}$$

and assuming that the polar term is the same for the monomer as for the radical then also,

$$K_{p aa} = P_A Q_A \cdot e^{-e_A \cdot e_A}$$

from which,

$$r_1 = \frac{K_{p aa}}{K_{p ab}} = \frac{Q_A \cdot e^{-e_A(e_A - e_B)}}{Q_B}$$

and similarly,

$$r_2 = \frac{K_{p bb}}{K_{p ba}} = \frac{Q_B \cdot e^{-e_B(e_B - e_A)}}{Q_A}$$

Since pairs of monomers are involved in determining reactivity ratios, it is not possible to assign absolute values to Q and e, and arbitrary values Q = 1.0 and e = -0.8 have been assigned to styrene and all others are measured relative to this. ²⁵

In this way, each monomer is characterised

two constants from which it is possible to calculate the reactivity ratios of any copolymer system. This scheme has been applied to a wide number of systems with some limited success. It does, however, enable approximate values for the monomer reactivity ratios to be predicted.

The Q and e values of acrylonitrile and methacrylonitrile were taken as,³⁰

	Q	e
acrylonitrile	0.44	1.2
methacrylonitrile	1.15	0.9, which gave

$r_1 = 0.266$, and $r_2 = 3.42$.

5). Molecular Weight Determinations.

Osmometers.

The osmometers were of the Pinnar - Stabin design as supplied by Polymer Consultants Ltd.²⁶ The membranes were made from undried cellophane and conditioned by treatment in baths containing increasing amounts of solvent in water. Membranes used in polyacrylonitrile molecular weight determinations were conditioned to dimethyl formamide, and in polymethacrylonitrile determinations to acetone.

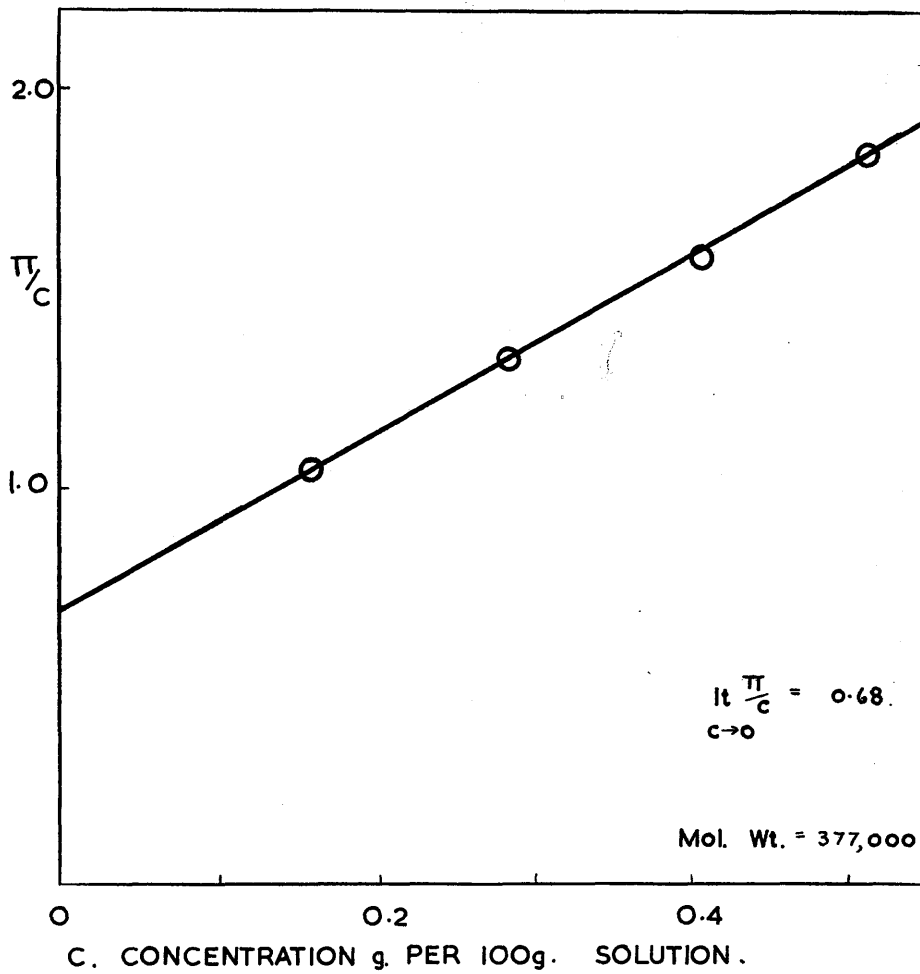
The osmometers were set up in a bath thermostated to $30.00 \pm 0.01^\circ\text{C}$. Cell constants were determined

at frequent intervals during a series of measurements.

Measurement of Molecular Weights.

A polymer solution of known concentration, approximately 1% by weight, was made up and used as a stock from which all others were prepared by weight dilution. All solutions were allowed to come to the temperature of the bath before being put into the osmometer.

Two techniques were used in the actual measurements of osmotic pressures. With polyacrylonitrile solutions in dimethyl formamide, the osmometer took 2-3 weeks to come to equilibrium. The value of the pressure at equilibrium was taken although it involved an error due to diffusion of low molecular weight material through the membranes. Fortunately, since the molecular weight of the polymer was high the error was quite small. With polymethacrylonitrile and copolymers soluble in acetone, the molecular weights were lower and diffusion quite large. Equilibrium, however, was attained much more rapidly, in fact, in several hours. The true osmotic pressure was determined graphically by following the pressure readings with time and extrapolating to the time of filling.



POLYACRYLONITRILE

MOLECULAR WT. DETERMINATION.

Figure 2-3.

Molecular Weight Determinations.

The number average molecular weight of a polymer is related to its osmotic pressure at infinite dilution by the following equation,

$$\left(\frac{\pi}{C} \right)_{C=0} = \frac{R \times T}{M_2}, \text{ in which } \pi \text{ is the}$$

osmotic pressure of the solution, C is the concentration of polymer in g.s per ml. of the solution, R is the gas constant and M_2 is the number average molecular weight of the polymer.

In order to obtain $\left(\frac{\pi}{C} \right)_{C=0}$ a series of determinations are made at different concentrations, $\frac{\pi}{C}$ is plotted against C and the curve extrapolated to zero concentration, see figure 2-3.

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

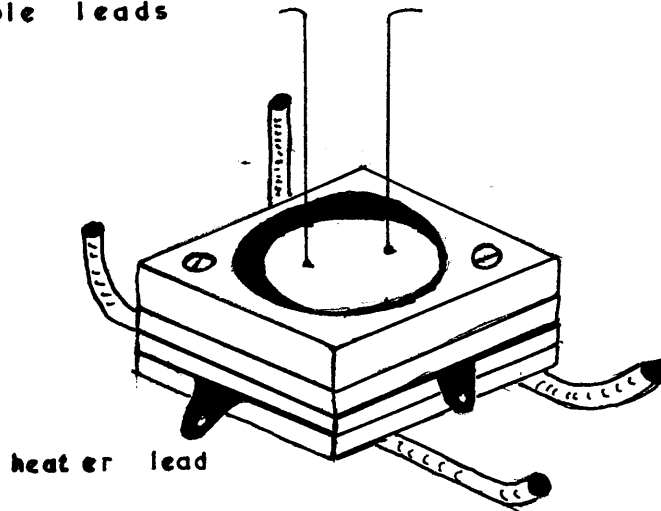
$$\text{then } \pi \text{ in atmos.} = \frac{\pi \text{ in cm.} \cdot \text{Density of the soln.}}{1033.3}$$

$$\text{but } C \text{ in g./ ml.} = \frac{C \text{ in g./100g.} \cdot \text{Density of soln.}}{100.}$$

$$\begin{aligned} \text{from which, } \text{Lt.}_{C=0} \left(\frac{\pi}{C} \right) &= \frac{L \cdot \text{Density of soln.} \cdot 100}{1033.3 \cdot \text{Density of soln.}} \\ &= \frac{L}{10.333} \end{aligned}$$

where L is the limiting value of $\frac{\pi}{C}$ in cm. and C in g.s per 100g.s of solution.

thermocouple leads



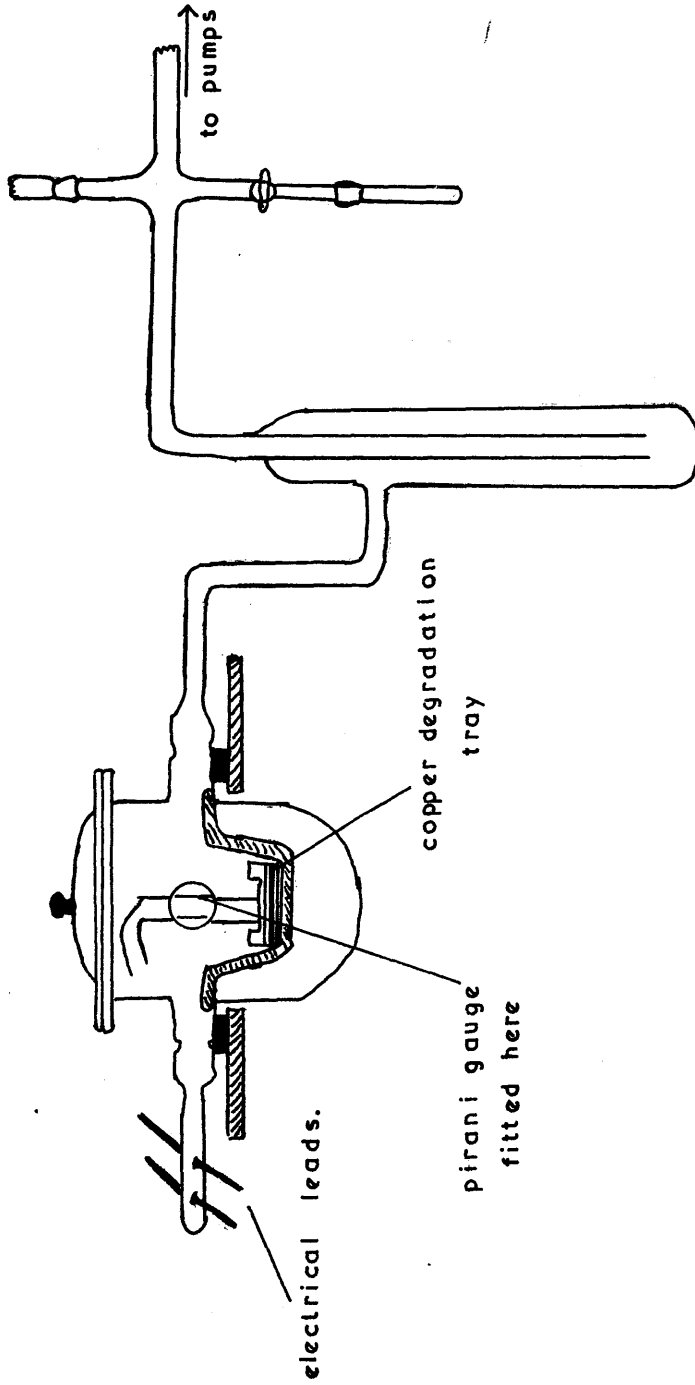
heater lead

PT. resistance thermometer lead

COPPER DEGRADATION TRAY

Figure 2-4.

Figure 2-5.



THE DYNAMIC MOLECULAR STILL

and

VACUUM SYSTEM.

so that,

$$M_2 = \frac{10.333 \cdot R. T.}{L.}$$

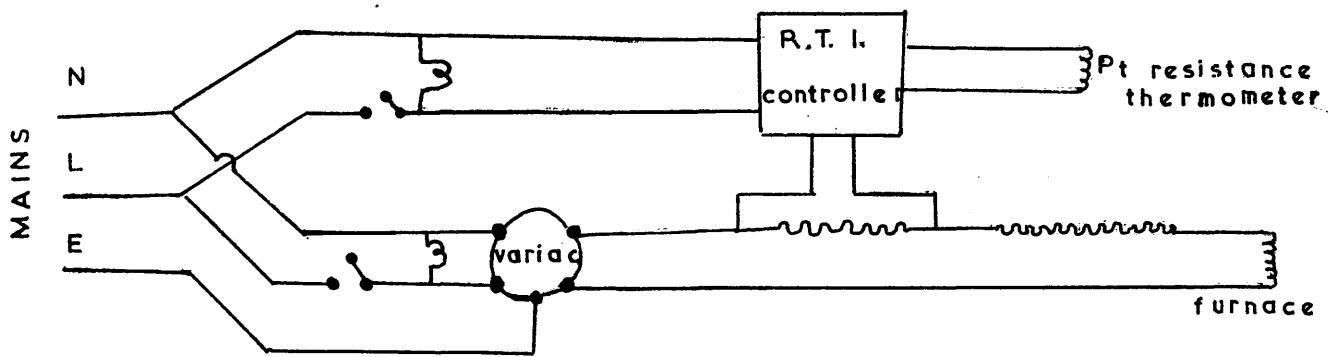
and at 30°C,

$$M_2 = \frac{257,000.}{L.}$$

6). The Dynamic Molecular Still.

The dynamic molecular still of Grassie and Melville ²⁷, with little variation was used. The glassware of the degradation apparatus is shown in figure 2-5. The still, itself, consisted of a vessel resembling in shape a desiccator with a removable ground glass flanged lid and connected to the vacuum system. The still contained a furnace block on to which a copper degradation tray could be screwed, see figure 2-4. The temperature of the block and tray was controlled by a Sunvic Resistance Controller, type R.T. 1, see figure 2-6 for the circuit diagram, and the temperature was measured by a constantan-copper thermocouple silver - soldered on to the tray.

Degradations were carried out on 0.2 g. (or less) samples of polymer covered with a fine copper powder to ensure thorough and even heating. The tray was readily removed from the furnace block and could be weighed before and after degradation.

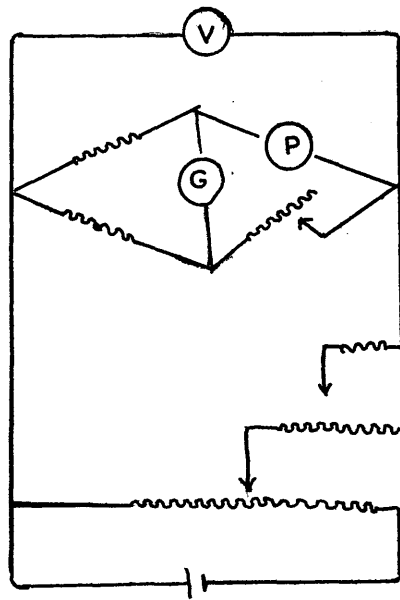
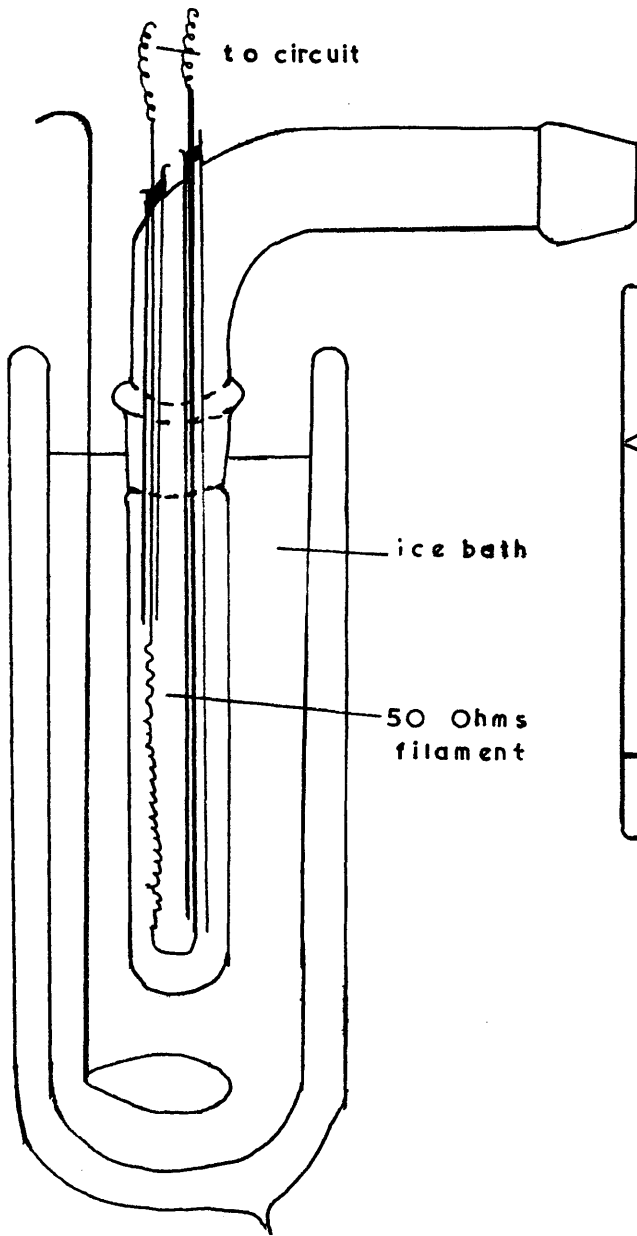


HEATING AND CONTROL CIRCUIT

Figure 2-6.

The internal pressure of the vacuum system was measured by a Pirani gauge. Some measure of the rate of evolution of volatiles from the degrading polymer is given by the small pressures built up inside the still before the vapours are condensed in the liquid air trap. The resistance of a filament in an evacuated system changes with its pressure, since it changes with the number of particles colliding with it. If V is the voltage required to give zero galvanometer deflection in a bridge circuit containing the filament, and V_0 the corresponding voltage when the apparatus is completely evacuated, then the term $(V^2 - V_0^2) / V_0^2$ is a measure of the pressure.²⁷ The gauge has to be calibrated for each substance by passing it into the still at known rates and then plotting $(V^2 - V_0^2) / V_0^2$ values against the rates. This could not be done in our own case since the volatiles evolved on degrading polyacrylonitrile are complex in composition. Nevertheless, V alone gave a useful comparison of the rates of evolution of volatiles.

McNeill²⁸ found that the Pirani gauge was extremely sensitive to changes in atmospheric conditions, in particular, to changes in temperature; accordingly he thermostated it at 0°C by immersing in melting ice, thus preventing the drift in readings he otherwise got at room temperature.



V - Voltmeter

P - Pirani gauge

G - Galvanometer

Figure 2-7.

The Pirani gauge and its electrical circuit is shown in figure 2-7. The modification adopted by McNeill was used.

Other Degradation Apparatus.

In some experiments, particularly those investigating the effect of volatile compounds on the polymer colour stability, it was more suitable to degrade the polymer samples in a flat bottomed pyrex tube, immersed in a Woods metal bath. The bath was thermostated by the Sunvic Resistance Thermometer Controller and the temperature measured by a thermocouple.

7). Infra-red Spectra Measurements.

Infra-red spectra were measured on a Perkin - Elmer, model 13, double beam spectrophotometer with a rock salt prism.

Solid State Spectra.

These were obtained using a potassium chloride disc technique. ²⁹ The potassium chloride was prepared by dissolving 'Analar' reagent in distilled water and precipitating with concentrated hydrochloric acid. It was filtered, dried and heated overnight in an oven

at 500°C. The caked potassium chloride was ground to a very fine particle size and stored in an oven, over a desiccant. Polymer was ground to pass a 120 mesh sieve and 3-4 mgs. sample was added to 200 mgs. of the dried and ground potassium chloride. The mixture was further ground together in an agate mortar under an infra-red lamp to prevent absorption of moisture. The mixture was then transferred to a disc press and compressed under a pressure of 5,000 lbs per sq. inch. In this way a transparent disc was obtained whose infra-red spectrum was measured with a pure potassium chloride disc in the reference beam of the spectrophotometer.

Solution Spectra.

These can only be measured in a small region of the spectrum, and the solvent has to be chosen which has an appropriate 'window region', that is, a region in which the solvent has no absorption bands. Any slight absorption by the solvent, however, can be counteracted by placing a cell identical to the sample, but containing only pure solvent, in the reference beam. Some idea of the extent of balancing of the two beams can be had by running the spectrum with both cells containing solvent only. This spectrum can be used as a base line in measuring the optical density of any

peak in the region.

Ethylene dichloride can be used as a solvent for polymethyl vinyl ketone and its degradation products since it has a 'window region' from 2900-1460 cm^{-1} and so could be used to measure changes in carbonyl absorption on degradation. Solutions of the polymer and its degradation products, at various stages in the reaction, were made up by weight, allowances being made for loss of volatiles during the reaction. The solutions were measured in a 0.5 mm. rock salt cell.

Gaseous State Spectra.

Volatile materials were examined spectroscopically in a gas cell with rock salt end-plates. The cell was first evacuated for several hours under high vacuum and the spectrum of the evacuated cell measured. The cell was then reconnected to the vacuum system and a small amount of it expanded into the cell. The pressure of the material in the cell was varied in order to obtain the most refined spectrum.

The spectrum of the evacuated cell provided a base line. This must be known since it is essential to show that there are no contaminants condensed in the cell which would give rise to spurious absorption. The new

peaks in the second spectrum can then be directly assigned to the volatile material.

Vapour Phase Chromatography.

Both the Griffen V.P.C. apparatus, MK 11., and the Pye-Argon Chromatograph, were used.

...polymerized... when heated in... 150°C, but at other low temperatures the... of colour is... requiring more than... change from white to light yellow. The rate... increases with temperature and at 200°C... heating is required for a similar... In general, the development of colour... spectrum, from yellow, through orange to red... occurs without autocatalysis or other... normal kinetic features.

...polymerizable powder does not melt or... heating to quite high temperatures except... pressure. A very much higher temperature... for decomposition to... take place. The... pure polymer is that...

Chapter 3.

The Degradation Reactions of Polyacrylonitrile.

1). Introduction.

Polyacrylonitrile colours when heated in vacuum above 150°C , but at this low temperature the development of colour is very slow, requiring more than 20 hours to change from white to light yellow. The rate of colouration increases with temperature and at 200°C less than 30 minutes heating is required for a similar colour change. In general, the development of colour through the spectrum, from yellow, through orange to red and brown proceeds without autocatalytic or other obviously abnormal kinetic features.

Polyacrylonitrile powder does not melt or coalesce on heating to colouration temperatures except under high pressures. A very much higher temperature is required for decomposition to volatile materials and sintering to take place. The examination of the colour reaction in pure polymer is thus limited to the solid state, unlike that of polymethacrylonitrile which melts

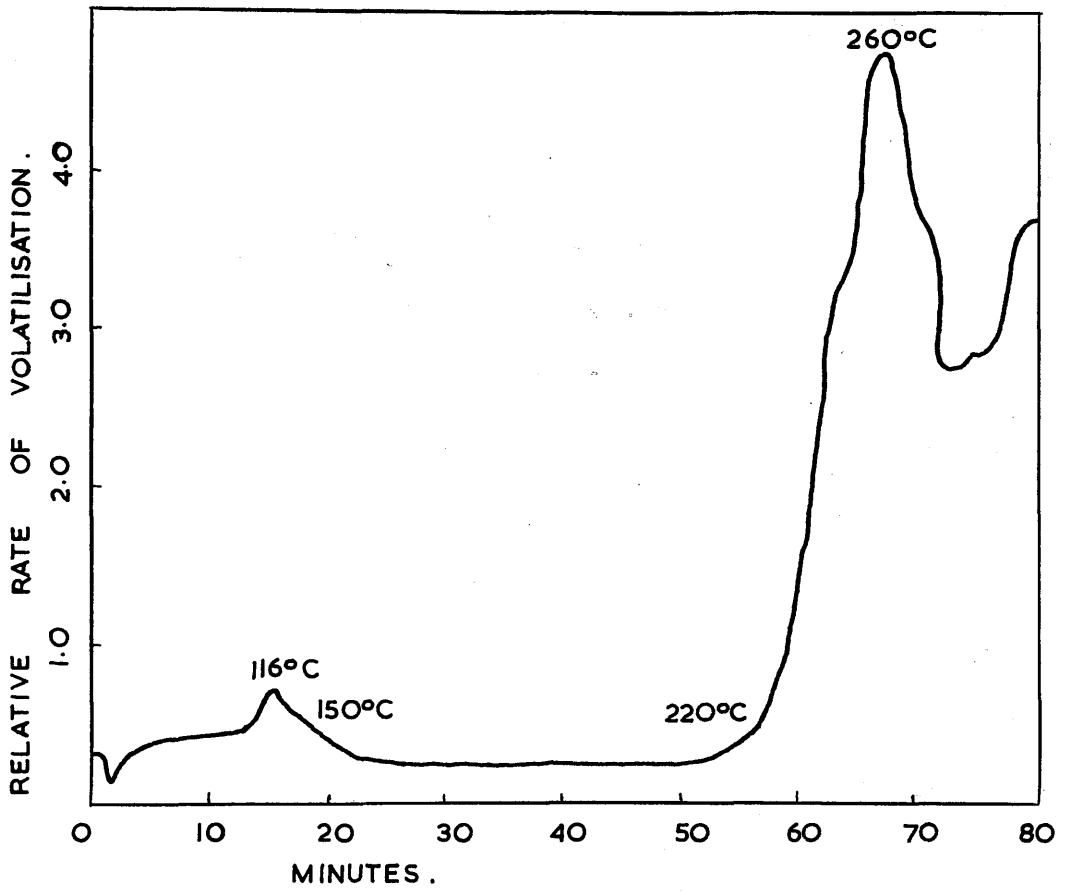


Figure 3-1.

well below any temperature at which it colours. Solution degradation measurements are also of little value since the few solvents which are available, such as dimethyl formamide and dimethyl sulphone, are themselves efficient colour initiators.

The effect of heating polyacrylonitrile (9) in the molecular still is shown in figure 3-1. Pirani gauge voltage readings give a measure of the pressure of the system and this in turn gives a measure of the rate of production of volatiles. The temperature of the system is raised at a constant rate. A small amount of volatiles is seen to be given off at about 120°C. These are mainly water and methanol which have presumably been absorbed by the polymer during its purification. No more volatiles are evolved by the polymer until about 230°C. A maximum rate of evolution appears to be reached at 260°C. From the nature of these volatile materials, which will be discussed later in this chapter, it is fairly obvious that the polymer begins to decompose to volatile materials at about 230°C. In addition, this experiment also shows that there is no detectable evolution of volatiles between 150-230°C - the temperature range in which colouration proceeds at a measurable rate. This was further verified by following the change in

weight of a polymer sample as it colours over a period of several hours at 200°C. After this treatment the polymer had become a reddish-brown in colour with less than 0.01% loss in weight. Obviously the colour reaction is not accompanied by an evolution of volatiles.

2). The Colour Reaction.

The potassium chloride disc technique was used to follow the changes in infra-red absorption which occurred during colouration. This may be done in one of two ways. Either the polymer can be incorporated into a disc and degraded in it, or the polymer can be degraded in bulk and incorporated in it, for spectral measurements. Ideally the latter, would be the more desirable but the errors involved in weighing such small quantities of polymer, mixing it with potassium chloride to a homogeneous consistency and getting an identical particle size distribution in each case, are sufficient to obscure the general trend in the spectrophotometric observations. The former technique, on the other hand, ensures that all infra-red measurements are made in identical conditions, but clearly it can be used only if the salt environment has no effect on the colour reaction. With this in mind, 0.030 g. samples of polyacrylonitrile (9),

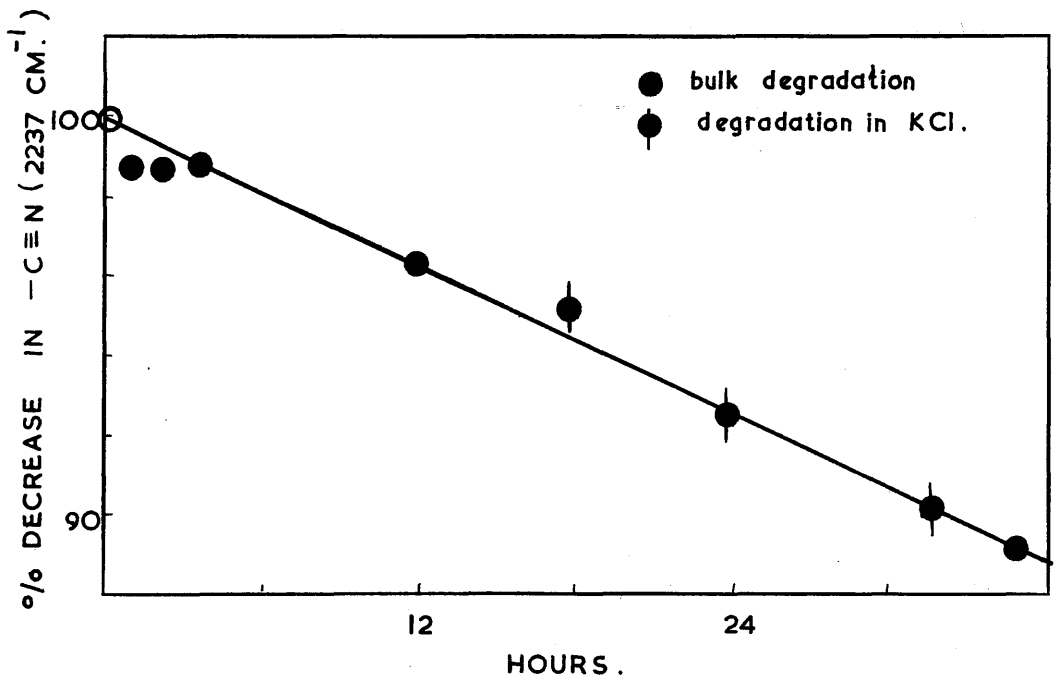


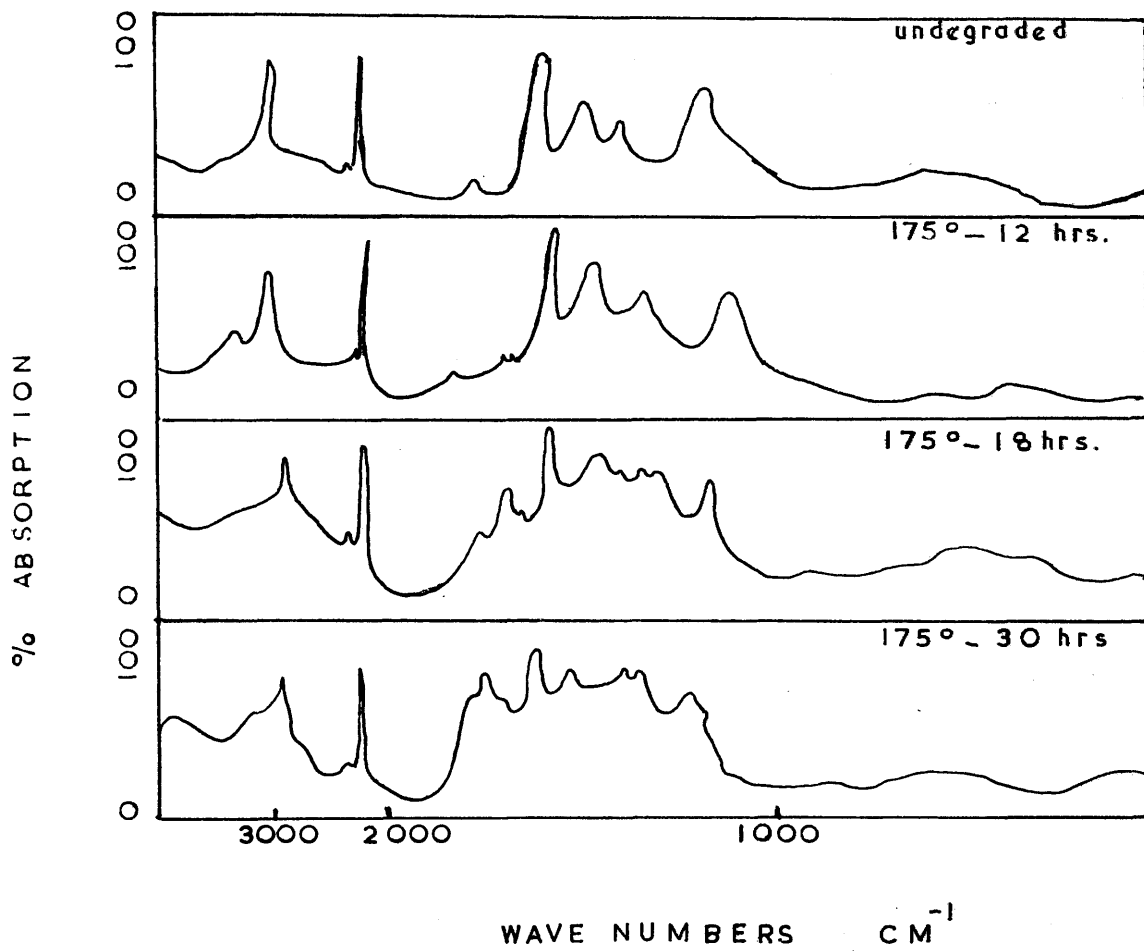
Figure 3-2.

were degraded in the molecular still at 175°C. These were removed at intervals up to 12 hours and incorporated into discs as reproducibly as possible. The disc, containing the polymer degraded at 175°C for 12 hours was then further heated and its spectrum taken at intervals up to an additional 18 hours. The kinetics of the colouration of the polymer in bulk, and when incorporated in a disc, were very much the same. This is shown in figure 3-2, where the kinetics of the cyanide condensation is followed in the two environments. There was no acceleration of the colouration reaction in the salt environment and the grinding and disc pressing also had no apparent effect. Potassium chloride clearly acts only as a diluent. Nevertheless, it was realised that because of this and the low thermal conductivity of potassium chloride, results could only be compared quantitatively when experiments were carried out under exactly identical conditions of temperature and with the same polymer - potassium chloride weight ratio in the discs.

The technique of degrading polymer while incorporated in a disc has several limitations. It can be used only if no volatiles are evolved during the degradation since these will be occluded as microscopic bubbles in the disc and cause wide scattering of the infra-

red beam. The degradation of polymethyl vinyl ketone which involves the evolution of water cannot then be followed by this method. However, even when no volatiles are evolved, the technique is limited because of the development of scatter at high wave numbers in the infra-red spectra of the coloured discs. This can be considerably alleviated by giving the reference disc of pure potassium chloride the same heat treatment. Scatter does, however, persist with the highly coloured degraded materials and seems to be an inherent property of them. Polymer degraded to an advanced stage of colouration and incorporated in a disc has much the same scatter. Nevertheless, the reaction can be studied to an advanced degree of colouration before scatter becomes appreciable or causes any significant error in the optical density measurements.

The spectrum of polyacrylonitrile along with those of degraded material is shown in figure 3-3. The absorption bands in polyacrylonitrile have been fully characterised by Liang and Krimm³¹, and a list of their assignments, for the more important peaks, is made in table 3-1. The corresponding absorption bands in polymethacrylonitrile, as found by McNeill²⁸, are noted for comparison.



IR SPECTRA OF DEGRADED POLYACRYLONITRILE

Figure 3-3.

Table 3-1.

**Infra-red Spectrum and Assignments for Polyacrylonitrile
and Polymethacrylonitrile.**

Frequency cm. ⁻¹	Assignment in PAN.	Frequency cm. ⁻¹	Assignment in PMAN.
2940	-CH ₂ stretch.	2950	-CH ₂ stretch
2870	-CH ₂ stretch.	2870	-CH ₂ stretch.
2237	-CN stretch.	2210	-CN stretch.
		2012	-C=C-N- str.
		1620	-C=C- str.
		1464	-CH ₂ bend.
1447	-CH ₂ bend.	1450	-CH ₂ bend.
		1388	-CH ₃ bend.
		1372	-CH ₃ bend.
1359	-CH ₂ wagging.		
1310	-CH bending		
1247	-CH wagging.	1210	} $\left\{ \begin{array}{c} \text{C} \\ \\ -\text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array} \right\}$ distort.
1073	overtone -CN.	980	
		843	CH ₃ rock.
778	-CH ₂ rock		
	-C-CN. stretch.		

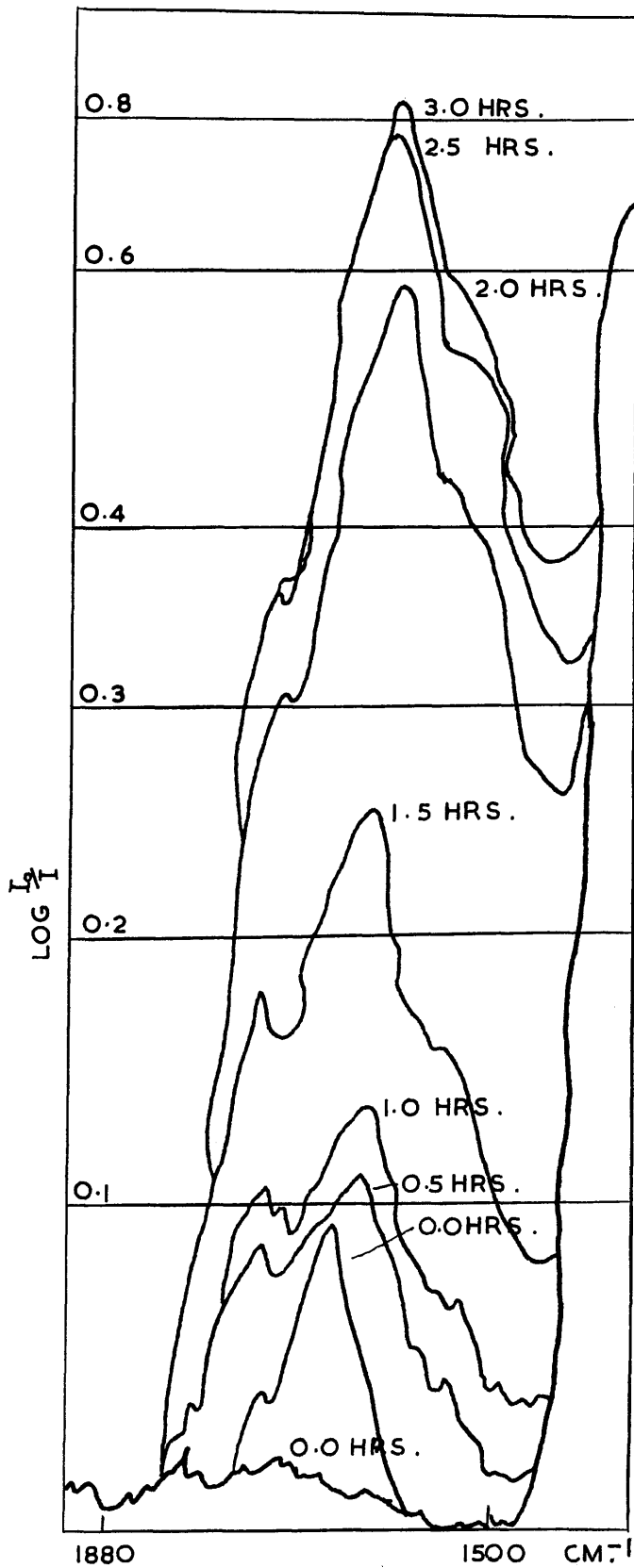
The weak absorption bands in polyacrylonitrile

at 3450 and 1626 cm.^{-1} are most probably due to traces of water absorbed by the potassium chloride of the disc. Slight heating of the disc under vacuum to a temperature well below that at which colour develops, completely removes these peaks. Similar conclusions have been reached by others.³²

The very narrow but strong absorption band at 2237 cm.^{-1} has been attributed to the cyanide stretching vibration, since according to Bellamy³³ most aliphatic nitriles are expected to absorb in the region $2250 \pm 10 \text{ cm.}^{-1}$

Obvious changes occur in the spectrum of polyacrylonitrile (9) on colouration, as seen in figure 3-3. The cyanide absorption band (2237 cm.^{-1}) decreases in intensity; while at the same time, extensive absorption develops at lower wave numbers, particularly in the region 1700-1500 cm.^{-1} . The extent of absorption in this region increases rapidly as colouration develops and at the same time it tends to move to lower wave numbers. Finally, with material degraded to an advanced stage the absorption from 1700- down to 700 cm.^{-1} is almost continuous.

The drop in cyanide absorption, the extent of absorption in the lower region and the development of colour are all inter-related. In particular, while colour develops steadily and cyanide peak intensity decreases



DEGRADATION OF
POLYACRYLONITRILE
AT 200°.

Figure 3-4.

linearly with time of heating, the intensity of absorption of the new peaks, in the region $1700-1500\text{cm.}^{-1}$ increases linearly with the percentage loss in intensity of the cyanide absorption, 2237 cm.^{-1} , see figure 4-3; the development of the new absorption bands in the region $1700-1500\text{ cm.}^{-1}$ is shown in greater detail in figure 3-4. The initial absorption at 1626 cm.^{-1} , which was attributed to traces of water in the potassium chloride disc, first disappears, although at a temperature below the colouration temperature, and is replaced by two peaks at 1670 and 1590 cm.^{-1} , initially of equal intensity. As the reaction proceeds the peak at the lower wave number increases more rapidly than the higher one until finally the higher peak is engulfed.

Absorption also develops at 3350 cm.^{-1} , as the colouration proceeds. This can only be due to the production of a nitrogen-hydrogen bond, since the alternative oxygen-hydrogen cannot be present.

It can be seen from table 3-2, in which the changes in spectra of polyacrylonitrile and polymethacrylonitrile on colouration are compared that the two reactions are very similar. In both, the cyanide absorption band is disappearing and new absorption appearing in the $1700-1500\text{ cm.}^{-1}$ region, in each case, with the same general characteristics.

Table 3-2.

Changes in the Infra-red Spectra of Polyacrylonitrile and Polymethacrylonitrile during Colouration.

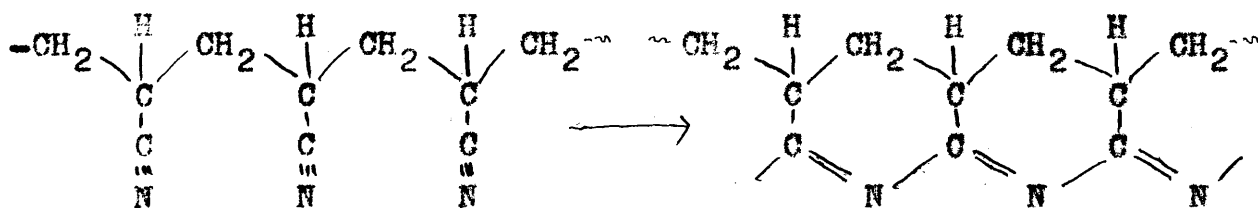
A). Disappearance or Reduction of Absorption.

In Polyacrylonitrile.		In Polymethacrylonitrile.	
Frequency cm. ⁻¹	Assignment	Frequency cm. ⁻¹	Assignment
3450	water, -OH.	3480	-OH or -N-H.
		2580	-COOH?
2237	-CN.	2210	-CN.
		2012	-C=C=N-.
1626	water, -OH.		

B). Appearance of New Absorption.

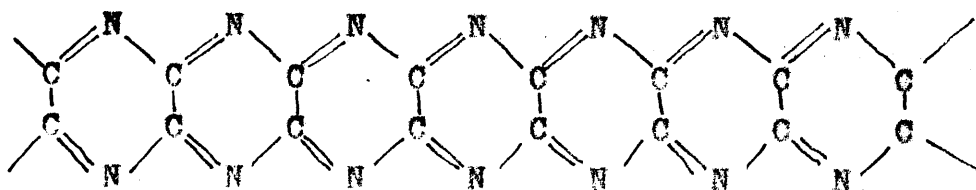
In Polyacrylonitrile.		In Polymethacrylonitrile.	
Frequency cm. ⁻¹	Assignment	Frequency cm. ⁻¹	Assignment
3350)	-N-H, =N-H.	3180	=N-H ?
3210)		3070	
2100	-C=C-CN.		
1700-1500	(-C=N-) _n	1693-1490	(-C=N-) _n .
1380, 1330		1272	
1238, 1154,		1178	
1080, 800		1133	

The colouration in polyacrylonitrile, then by analogy to the reaction in polymethacrylonitrile, appears to be caused by the condensation of cyanide units into a system of carbon-nitrogen double bonds. The development of colour through the spectrum and the shift in absorption in the $1700-1500\text{cm.}^{-1}$ region to lower wave-numbers is thus considered to be due to the development of increasing sequences of carbon-nitrogen double bonds in conjugation with one another, as more and more cyanide groups condense.



Burlant and Parsons ¹¹, La Combe ³⁴, McCartney ³⁵, and Schurz ³⁶, have all studied the colouration reaction in polyacrylonitrile and have assigned this structural type to the coloured material.

The infra-red spectrum of para-cyanogen has been examined by Bircumshaw, Talyer, and Whiffen ³⁷, and a similar interpretation has been made for its structure.



The colouration of polyacrylonitrile, in which cyanide groups are disappearing and being replaced by carbon-nitrogen conjugation, all without the evolution of volatiles, is thus envisaged as a condensation of cyanide groups into a ring system with conjugated carbon-nitrogen double bonds. Interrupting and restarting the reaction at any stage has no influence upon its course. Material of any intermediate colour can be isolated. It thus appears that the reaction proceeds from unit to unit along the chain, each intermediate structure being perfectly stable. The colour reaction, therefore, appears to be ionic rather than a radical process. This is closely similar to the behaviour of polymethacrylonitrile.

3). The high Temperature Decomposition Reaction.

Polyacrylonitrile (9) does not decompose to volatile material below 230°C. Decomposition at this temperature is, however, very slow and, in general, yields of products sufficient for analysis were obtained by degradations at a very much higher temperature.

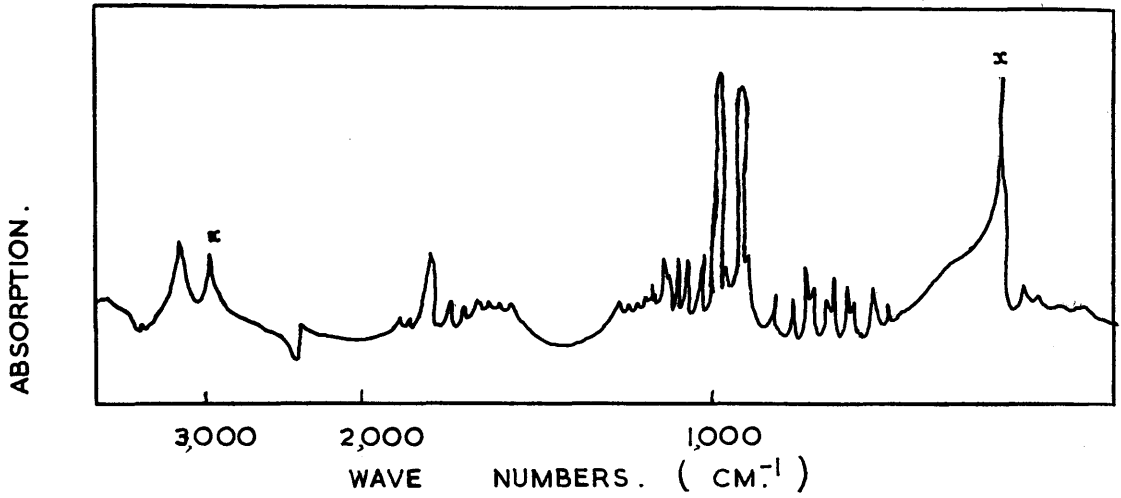
Polyacrylonitrile, on decomposition, produces gaseous, liquid and solid materials.

On degrading a typical polyacrylonitrile sample at 400°C , in an evacuated system attached to a liquid air trap, the products were conveniently divided into four portions, as follows; (1). Material gaseous at room temperature but condensed at liquid air temperature. (2). A colourless liquid fraction volatile at room temperature. (3). A reddish-brown liquid involatile at room temperature. (4). A black coke-like involatile residue. The first two fractions were condensed in the liquid air trap; the third condensed on the cool part of the reaction tube above the degrading polymer. These were analysed separately.

(1). Gas Analysis.

After cooling the residual polymer, the infra-red gas cell was attached to the system, the liquid air trap removed and the system allowed to come to room temperature. The pressure of the gaseous fraction was sufficient for infra-red spectrophotometric analysis.

The material proved to be ammonia with some hydrogen cyanide, as can be seen from figure 3-5, in which the spectrum of the gaseous product is given. It can be



GASEOUS DEGRADATION PRODUCTS — NH_3 AND HCN .

X DENOTES PEAKS DUE TO HCN GAS .

Figure 3-5.

compared with the spectra of pure ammonia and hydrogen cyanide, reproduced in figure 3-6.³⁹ hydrogen cyanide which might reasonably have been expected to have been a product and which, indeed, has been reported by others,^{11, 38, 40} was also detected in the liquid air trap, using the benzidine acetate spot test.⁴¹ This test is very much more sensitive to hydrogen cyanide than infra-red spectroscopy and will, indeed, detect concentrations of a few parts per million.

(2),(3). Liquid Analysis.

The colourless oil, fraction 2, has a molecular weight of 79 ± 1 , determined by the cryoscopic method using benzene as a solvent. The molecular weight of the coloured oil was exactly double this value, namely 160 ± 1 . Both these fractions were soluble in all common organic solvents, alcohols, benzene, carbon tetrachloride, chloroform and acetone. Their element analysis were identical, and the higher molecular weight material corresponded to the formula of the trimeric entity, $C_9H_{10}N_3$ - molecular weight 160.

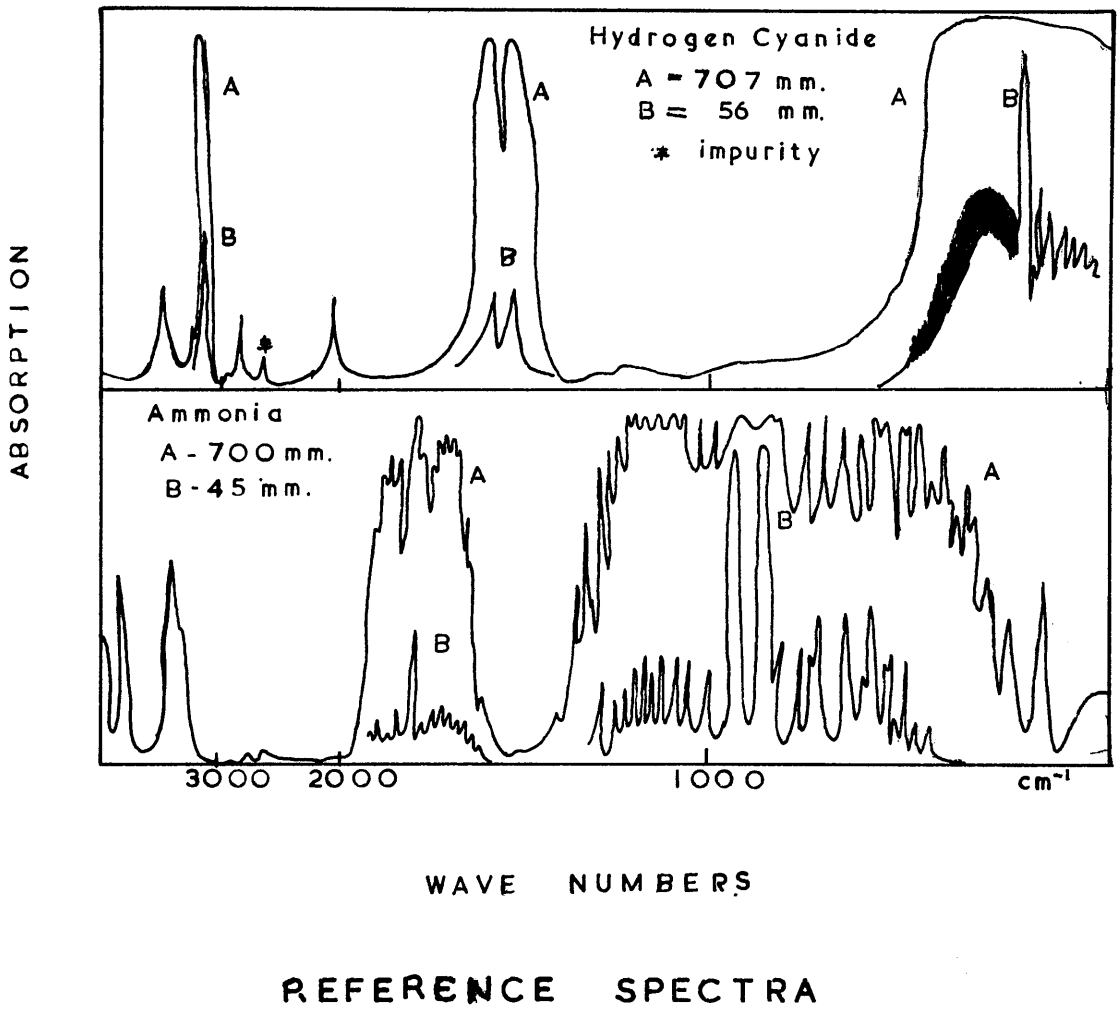


Figure 3-6.

Table 3-3-

Analysis of the Coloured Oil.

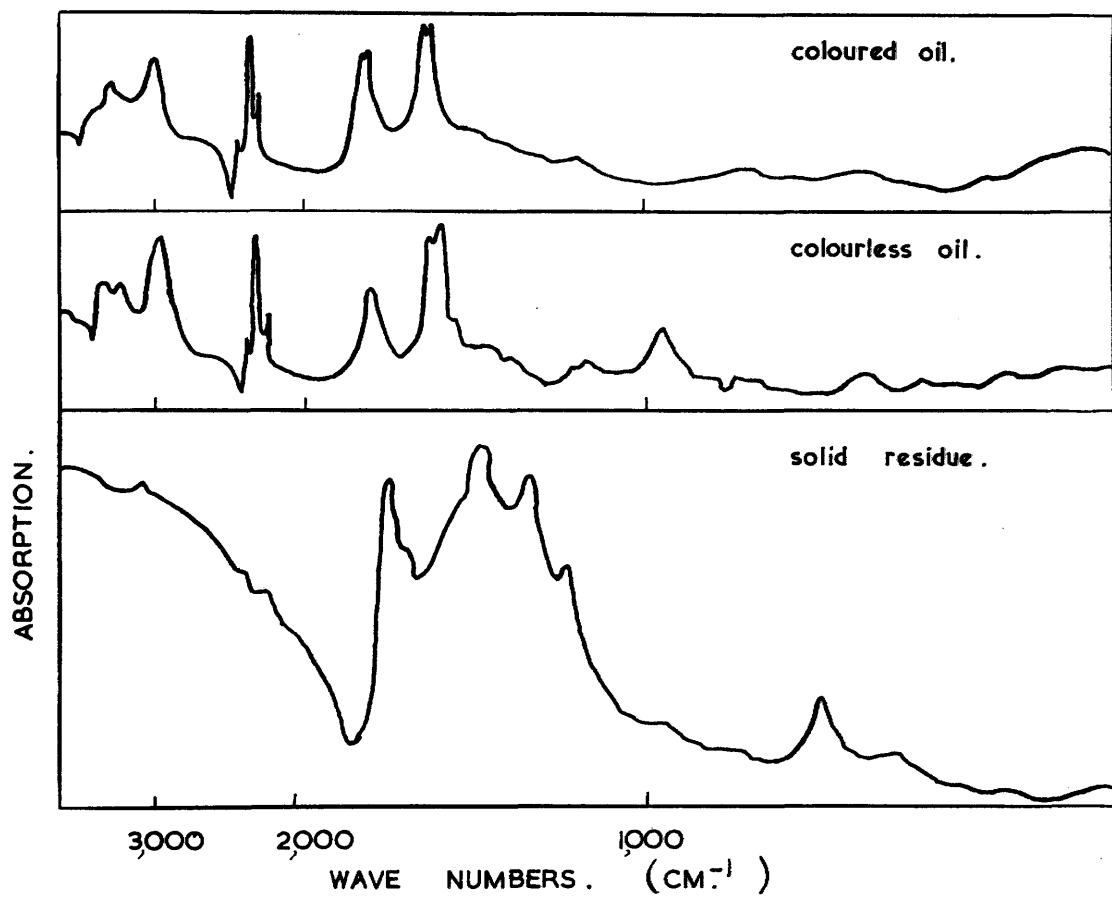
	Oil	Trimer.	
		$C_9H_{10}N_3$	
C..	67.3	67.5	%
N..	26.25	26.25	%
H..	6.32	6.25	%

The infra-red spectra of the oils, taken on liquid films, are shown in figure 3-7. They are clearly identical except for the two minor peaks at 1386 and 960cm.⁻¹ The assignments to the various peaks in the spectra are listed in table 3-4. They strongly suggest that the two materials are aliphatic nitriles with some unsaturation.

At the time of carrying out these degradation experiments Vapour Phase Chromatography was not available for further characterisation. Madorsky³⁸, has since shown, however, that these materials are complex mixtures which, as our results suggest, are derived from the basic monomeric nitrile structure.

(4). Solid Analysis.

The black charred residue is insoluble in all common organic solvents. Its infra-red spectrum shows very wide absorption with no defined peaks. It, however,



INFRA-RED SPECTRA OF DEGRADATION PRODUCTS.

Figure 3-7.

does not show any trace of cyanide absorption, although this region of the spectrum is relatively clear, (figure 3-).

Table 3-4.

Infra-red Spectra of the Degradation Products.

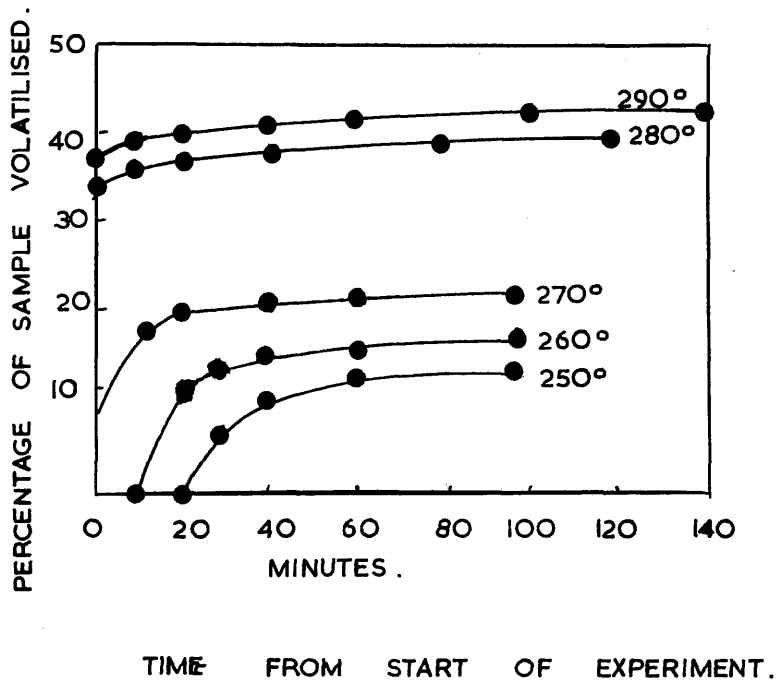
Coloured (reddish-brown) oil.

Colourless oil.

Frequency cm. ⁻¹	Assignment	Frequency cm. ⁻¹	Assignment
3570	-N-H amine		
3350	-N-H amine	3340	-N-H amine.
2945	-C-H stretch.	2945	-C-H stretch.
2825	-C-H stretch.	2825	-C-H stretch.
2230	-CN. stretch.	2230	-CN stretch.
2180	-C=C-CN stretch.	2180	-C=C-CN stretch.
1640	amine or -C=C-	1640	-C=C- or amine.
1625	amine or -C=C-	1625	-C=C- or amine.
1460	-C-H bend.	1460	-C-H bend.
1425	-C-H bend.	1425	-C-H bend.
1386	-C-C-CN overtone ?		
960	-C-H rock.		

The degradation of polyacrylonitrile to volatiles has recently been fully characterised by Madorsky and Strauss.³⁸ The volatile materials were analysed on a Mass Spectrometer. They were able to detect traces of a non-condensable gas which was hydrogen, along with considerable amounts of hydrogen cyanide but no ammonia. Burlant and Parsons¹¹, likewise, have studied the degradation of polyacrylonitrile finding as in the present work, considerable amounts of ammonia and traces of hydrogen cyanide.

Madorsky and Strauss also obtained a non-volatile coloured oil which had a molecular weight of 330 ± 9 , measured cryoscopically in dimethyl formamide solution. This molecular weight is approximately double that obtained in the present work. They, likewise, isolated a volatile liquid product which they analysed. They found it to contain mainly acrylonitrile, vinyl acetonitrile, and other aliphatic nitriles, saturated and unsaturated. The composition of the product seemed to alter on standing due to the constituents reacting together- acrylonitrile and hydrogen cyanide - to produce non-volatile materials. They offered this as an explanation of the small yield of hydrogen cyanide reported by others on degrading polyacrylonitrile.

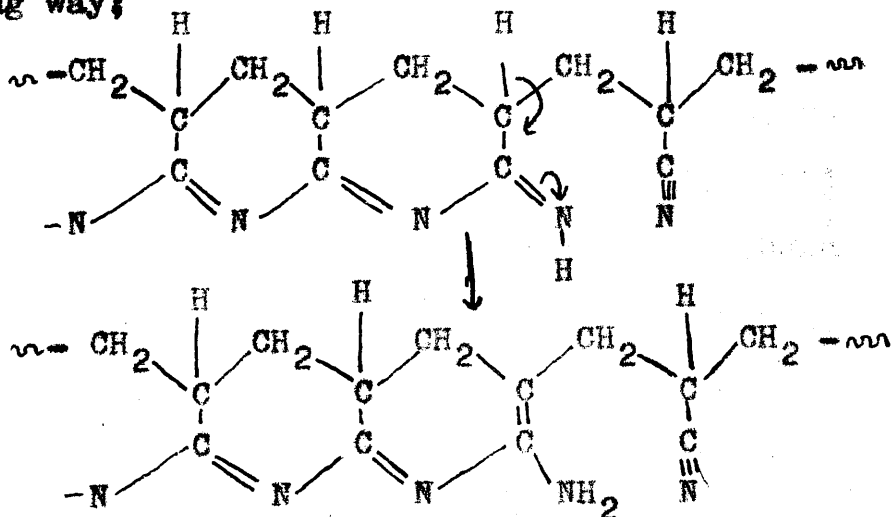


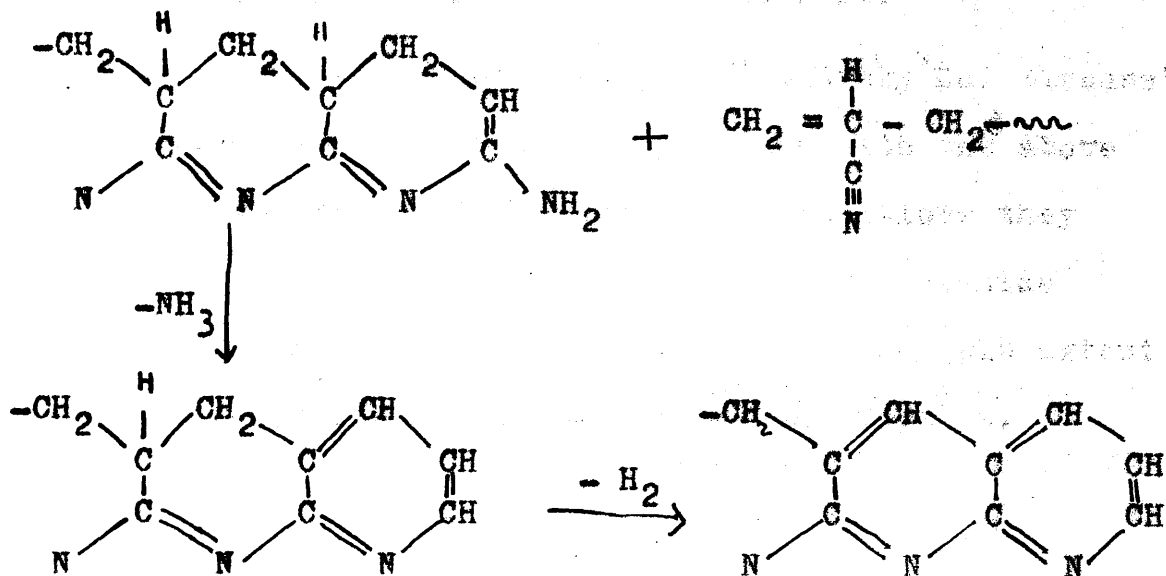
THERMAL DEGRADATION OF POLYACRYLONITRILE.

Figure 3-8.

Madorsky and Strauss' pyrolysis curves of the rates of volatilisation of polyacrylonitrile at various temperature, which are reproduced in figure 3-8, show that the polymer residue becomes stabilised as the pyrolysis proceeds. The charred residue which we obtained after the evolution of all the volatile materials, contained no cyanide groups and its infra-red spectrum had very wide absorption bands. The stabilisation of the residue and its spectrum could be explained by the production of condensed aromatic ring systems.

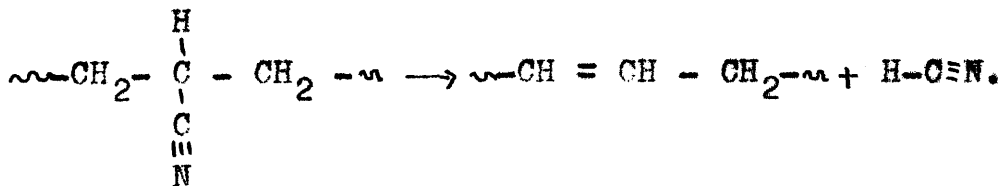
The structure causing colour in heat treated acrylonitrile polymer is considered to be a system of condensed rings terminated by an imine group. In such a system the unchanged aliphatic chain would be more vulnerable to chain scission than the ring itself. Aromatisation could, therefore, be achieved in the following way;





The above scheme is one of many which can be envisaged. It readily accounts for the production of aliphatic nitriles, both saturated and unsaturated, and of ammonia and hydrogen.

Hydrogen cyanide must be produced in an acid elimination reaction in the polymer chain,



or in the condensed ring system. If this occurs from residual cyanide groups in the chain adjacent to a condensed ring structure in the coloured polymer, the double bond so produced may promote or assist aromatisation. These speculations have not been

followed up separately in the present work.

The absence of ammonia in Madorsky and Strauss' degradation experiments does not fit in with the above picture, but perhaps the degradation conditions they adopted were so drastic as not to allow the cyanide condensation reaction to occur to any appreciable extent before the cyanide elimination reaction stops it.

Chapter 4.

Initiation Step
in the Colouration Reaction.

1). The Effect of Purity of the Monomer on the Colour Reaction.

The low temperature colouration of polymeth - acrylonitrile has been attributed to the presence of acid impurities incorporated in the polymer chain. Complete elimination of the acid impurities totally stops the colour reaction. It is not known if the colour instability of polyacrylonitrile is also due to the presence of acid type impurities.

In particular, Grassie and McNeill ³ found that methacrylonitrile monomer contained measurable amounts of acetic acid as an impurity, and if it were removed by washing with alkali the resulting polymer made from this monomer was colour stable. Acrylonitrile monomer does not, however, contain detectable amounts of acid impurities, see page 12, and figures 2-1 and 2-2, but because of the

extreme sensitivity of polymer degradation reactions to trace impurities, in general, it was considered valuable to test the effect of washing the monomer with alkali on the colouration properties of the resulting polymers. The rates of colouration of various polymers, polymerised under identical conditions - 30°C and using a:a'-azo-bis-isobutyronitrile as initiator - but using monomer obtained from different sources and purified in different ways, are shown in table 4-1. The polymers are also classified in two groups, those prepared by bulk polymerisation in which the polymer precipitated out of the monomer and those prepared by homogeneous polymerisation in which sufficient solvent was present to keep the polymer in solution.

With the exception of the polymers in group 2, the overall rates of colouration do not differ by very much. There is, however, no conclusive evidence to suggest that alkali treated monomer gives a very much more stable polymer.

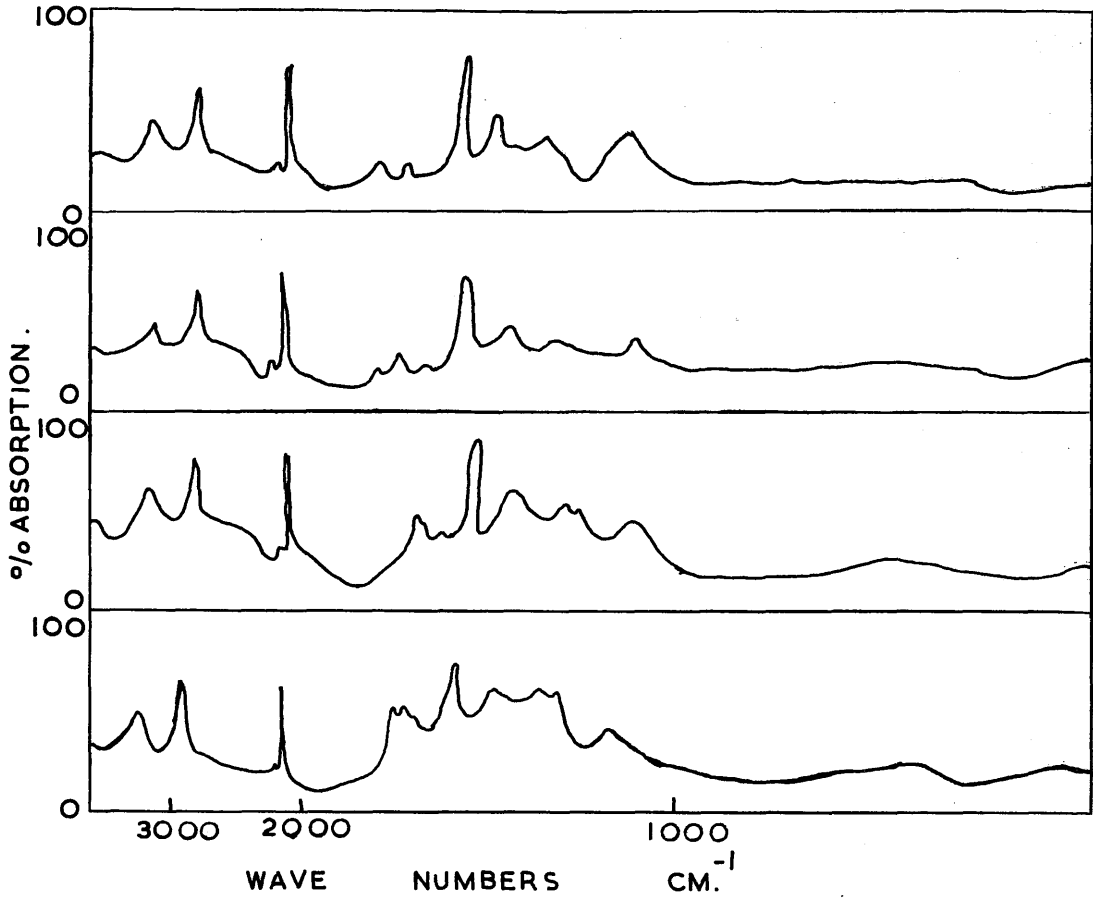
Polymer prepared in the presence of dimethyl formamide and succinonitrile, as solvents, are very much more prone to colour. The reactivity of the polymer obtained from dimethyl formamide solution is understandable - Crassie and McNeill ⁷ found that amides in general were

Group 2.

Serial No.	Monomer Source.	Polymer Preparation.	Rates % - CN / hr.
26	B.I. Plastics, OH ⁻ washed.	dmf. solvent.	20.8 ± 5.0
27	B.I. Plastics OH ⁻ washed.	succinonitrile, solvent.	too fast.

The nature of the initiation step in polyacrylonitrile is not obvious from these observations. Certainly any minute trace of acid which might be present after alkali washing would be completely ineffective in causing colouration in polymethacrylonitrile, in which concentrations of acid easily detectable by infra-red spectrophotometry are necessary. The rates of colouration of both untreated and purified monomer polymer, as in table 4-1, are so similar as to suggest that the rate is an inherent property of the polymer itself, and is quite independent of impurities.

To clarify the effect of acidic impurity on the rate of the colour reaction, copolymers of acrylonitrile and acrylic acid were studied.



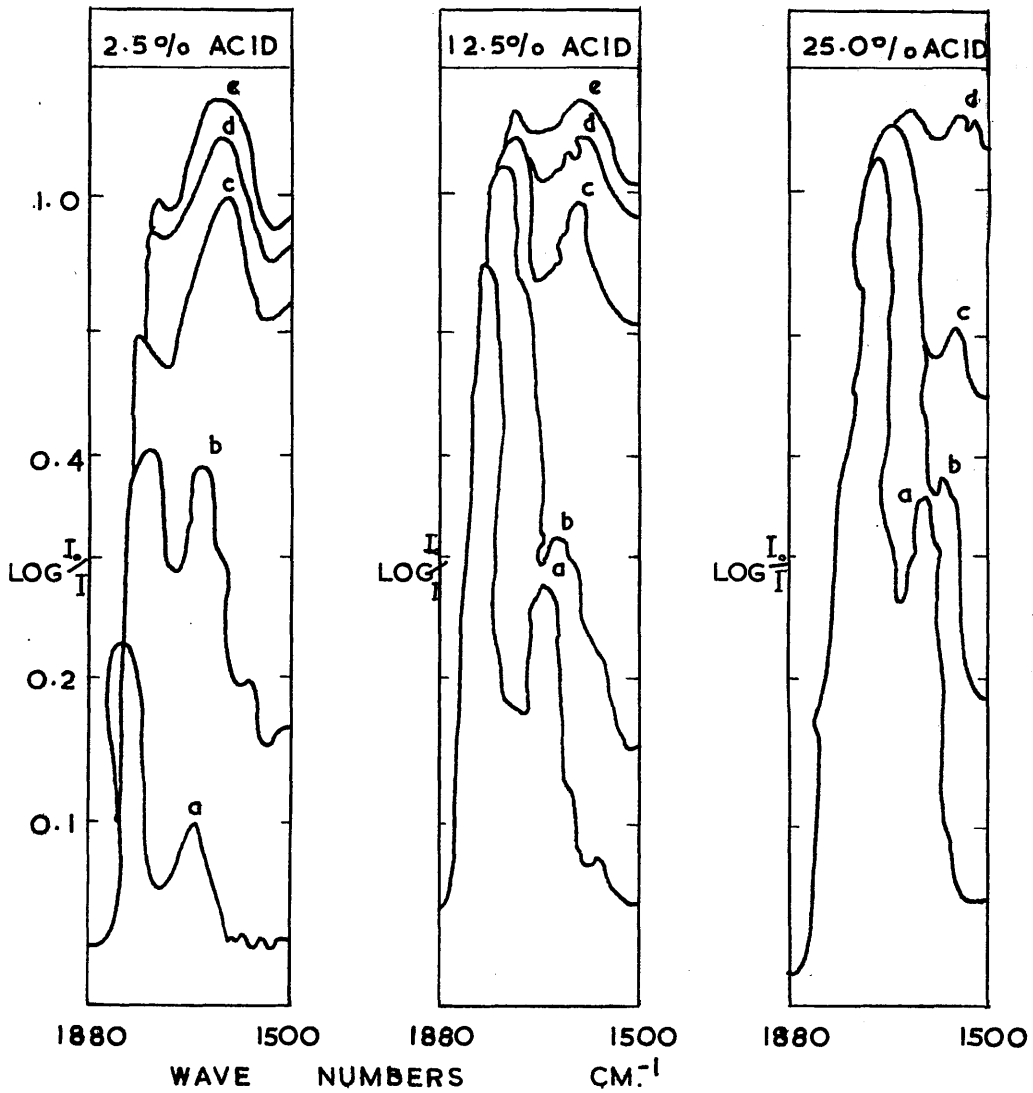
DEGRADATION OF A 1.5% ACID COPOLYMER.

Figure 4-1.

2). Spectrographic Changes during the Colouration of Acrylonitrile-Acrylic Acid Copolymers.

The changes in the infra-red spectrum of a 1.5 % acrylic acid copolymer (6) on colouration is shown in figure 4-1. Direct comparison with those in pure polyacrylonitrile, figure 3-3, shows that there is no obvious difference in the two reactions. There is the same decrease in the cyanide absorption band at 2237 cm.^{-1} , and increase in unsaturation, as shown by the absorption in the $1700\text{--}1500 \text{ cm.}^{-1}$ as colouration develops. However, it is also apparent that there is a rapid drop in the carbonyl absorption band at 1710 cm.^{-1} indicating that acid units are being used up, presumably to initiate colouration as in polymethacrylonitrile.

This is also borne out by the changes observed in the region $1700\text{--}1500 \text{ cm.}^{-1}$. This is shown in greater detail for the 2.5, 12.5 and 25.0 % acrylic acid copolymers in figure 4-2. It was noted, page 41, on studying the colouration of pure polyacrylonitrile that the two initial carbon-nitrogen double bond peaks were of equal intensity and that as colouration developed and the conjugation sequences lengthened the peak at the higher wave number (1670 cm.^{-1}) became less significant and was finally lost in favour of the lower one (1590 cm.^{-1}). With the

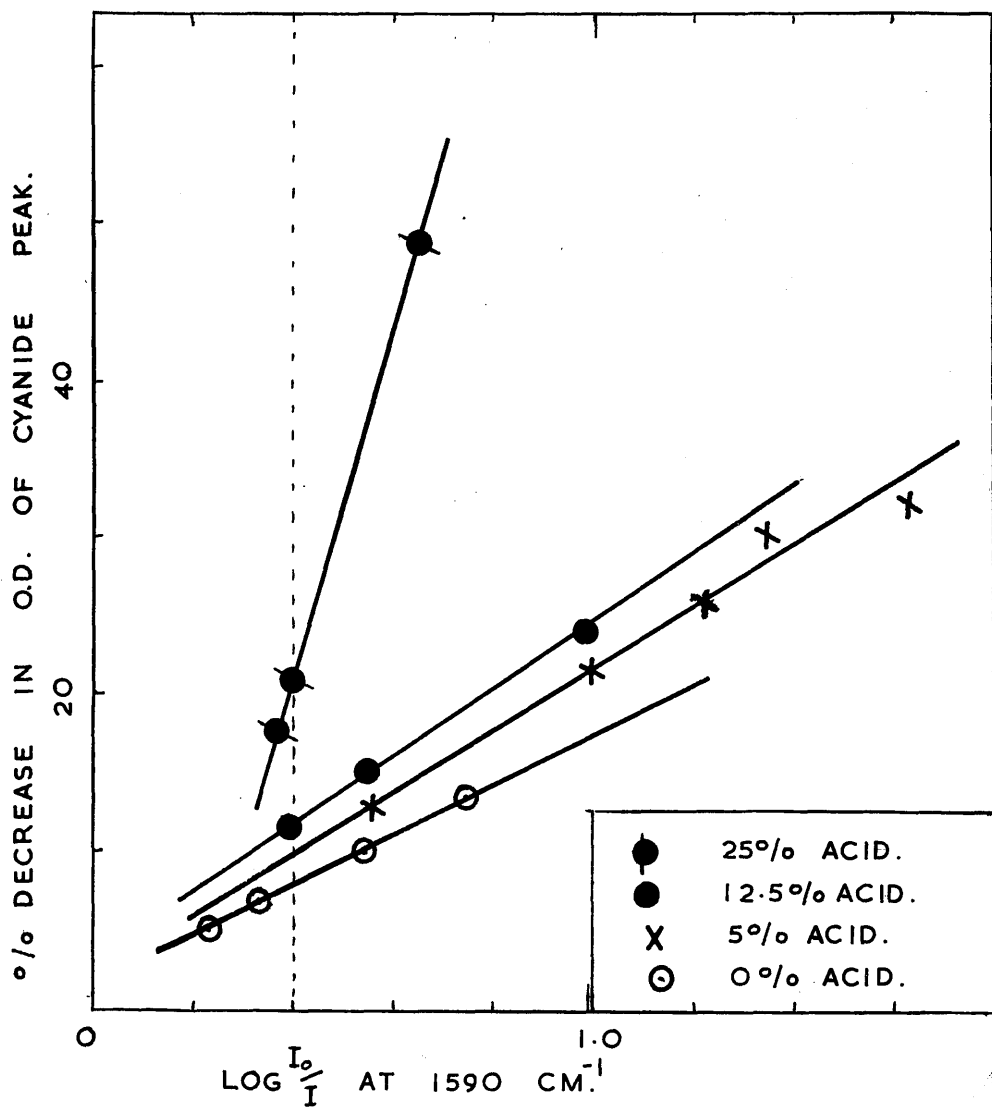


ACID COPOLYMERS DEGRADED AT 200°.

Figure 4-2.

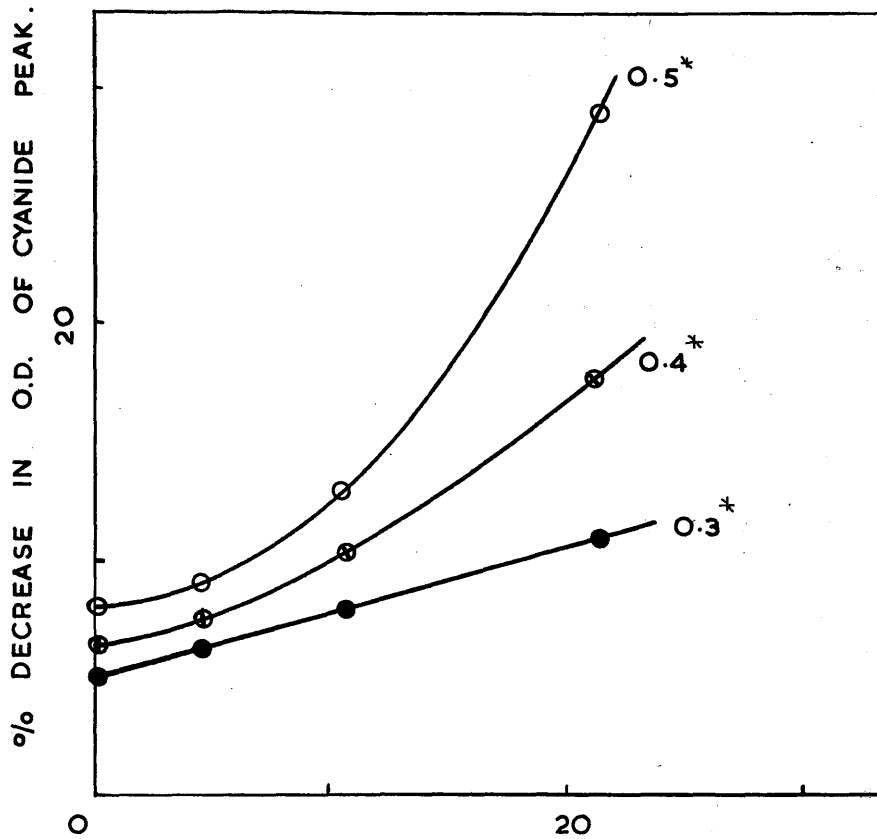
acid copolymers this is also observed but to a lesser extent because with the copolymers of high acid content the initial absorption at 1670 cm.^{-1} is very much more stronger and still makes an important contribution to the spectrum of even the most highly condensed of its degraded material. This is to be expected if acid groups are initiating the colour reaction. The more acid groups there are present the greater the number of initiating centres and so the greater the relative contribution of the less highly conjugated carbon-nitrogen double bond sequences.

This can be seen, figure 4-3, from the plot of the percentage decrease in optical density of the cyanide peak, 2237 cm.^{-1} against the optical density of the more highly conjugated of the carbon-nitrogen bond peaks at 1590 cm.^{-1} . The figure shows that a higher degree of condensation of the cyanide groups is required in the more acid copolymers to produce the same optical density of this peak. Indeed a plot, figure 4-4, of the percentage decrease in cyanide absorption required to produce a constant optical density of this peak, against the acid content in the copolymer can be extrapolated to zero acid content and this value is similar to that obtained from pure polyacrylonitrile. The value of the



ACRYLONITRILE - ACRYLIC ACID COPOLYMERS.

Figure 4-3



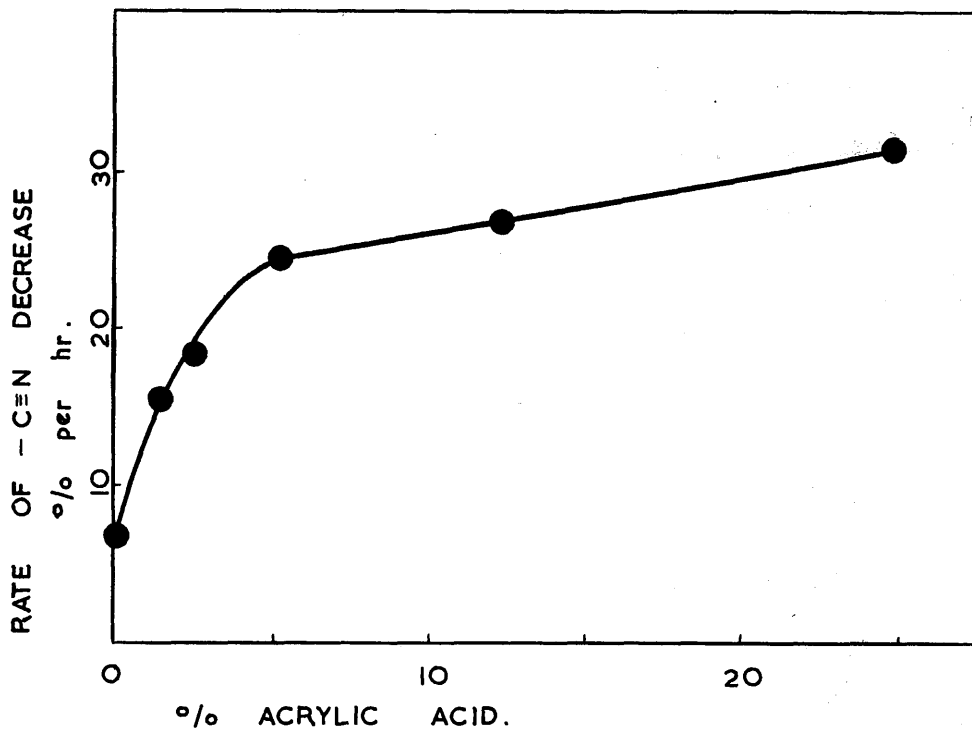
PERCENT ACID IN COPOLYMER.

* O.D. of conjugated (-C=N-) peak.

Figure 4-4.

percentage decrease in cyanide absorption required to give a constant concentration of the more highly conjugated carbon-nitrogen double bond is a measure of the number of initiating centres in the polymer, since with more initiating centres in the polymer a greater proportion of the cyanide groups have to condense to maintain the concentration of such bonds. However, it will be a complicated measure of the extent of initiation since infra-red spectroscopy gives no evidence about the distribution of the lengths of conjugation in the sequences but only measures the concentration of such bonds. It is significant that the extrapolated value should coincide with that of polyacrylonitrile itself, and also indicate residual initiation far in excess of that which might be caused by any residual acid concentration which could be present in the purified monomer.

A direct measure of the amount of initiation can be obtained, at any given temperature, from the rates of cyanide condensation, measured as percentage decrease of the optical density of the cyanide absorption band at 2237 cm.^{-1} . The rate of propagation of the colour reaction is the same in all cases and so the overall rate must be a measure of the number of propagating centres. In figure 4-5 the rate of cyanide condensation is plotted



ACID ACCELERATION OF
COLOURATION AT 200°C.

Figure 4-5.

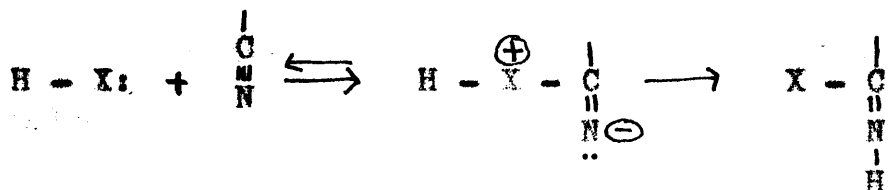
against the concentration of acid units in the copolymer. The rate appears to increase linearly, at least initially, with the acid content and to fall off rapidly with the higher concentrations. Extrapolation of this linear part to zero acid content gives a rate very similar to that of pure polyacrylonitrile. Further extrapolation to zero rate showed by direct comparison that the residual rate in polyacrylonitrile could only be produced by an acid concentration far in excess of any which could be present, in view of the complete absence of carbonyl absorption in the infra-red spectrum of acrylonitrile, either as obtained or additionally washed with alkali.

3). The Nature of the Initiation Reaction.

The above observations show that initiation of colouration in pure polyacrylonitrile cannot be accounted for in terms of acidic impurities. It seems that this residual rate at zero acid concentration must be a property of the polymer which must be capable of self initiation.

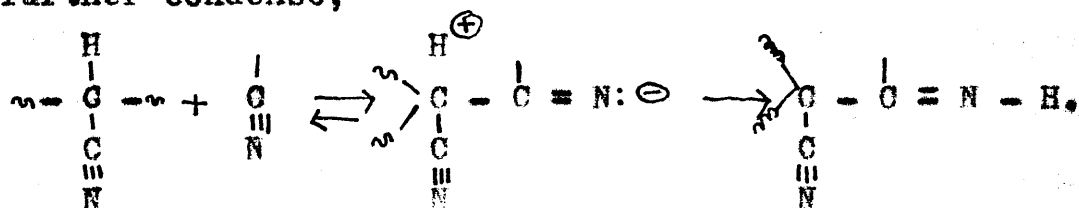
Experiments on the effects of a variety of model compounds on the initiation of colouration in polymethacrylonitrile have shown that, in general, nucleophilic reagents are necessary. In particular, it can be envisaged as a nucleophilic attack on the cyanide group followed by

proton migration producing an intermediate imino compound which itself can then act as a further nucleophilic reagent and condense with another nitrile unit;

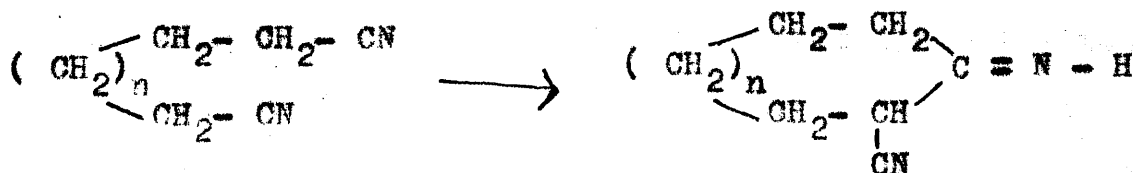


Polyacrylonitrile has such a potential nucleophilic centre in the tertiary carbon-hydrogen structure which is activated by the cyanide group and also probably by some hydrogen bonding to another cyanide group on the same or on a neighbouring chain.

This unit can act as a Lewis base and attack the cyanide group giving an intermediate imino group which can further condense;

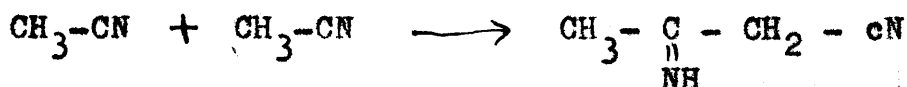


The reaction mechanism is reminiscent of a Thorpe reaction in which nitriles with an alpha hydrogen atom can be induced to condense. This has been generally used to prepare cyclic ketones from dinitriles,

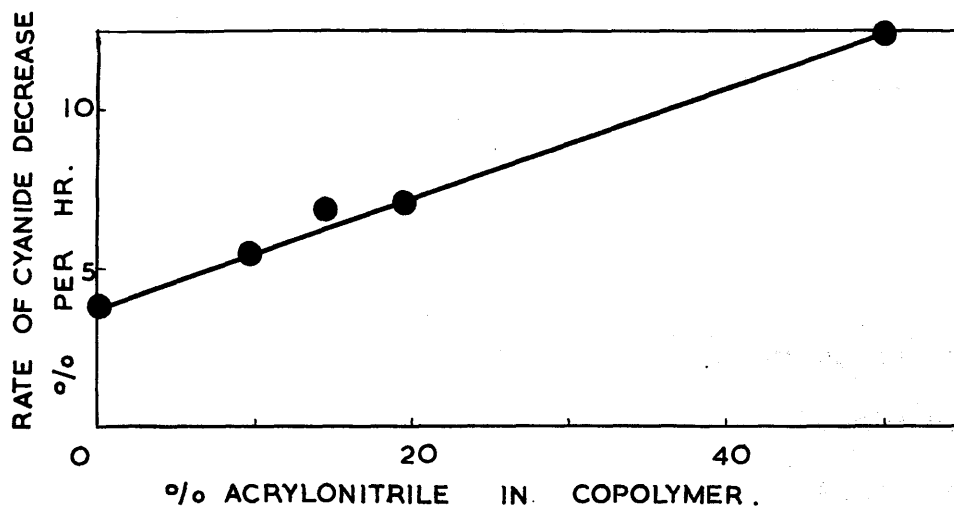


the imino-nitrile intermediate is not usually isolated as it rapidly hydrolyses to the ketone.

Mononitriles, too, undergo a similar type of condensation reaction,



If the tertiary carbon-hydrogen centre in the acrylonitrile unit is sufficiently nucleophilic to initiate the colour reaction, then clearly compounds with a similarly activated hydrogen atom must also be expected to do so. Such model compounds cannot be tested by their effects on polyacrylonitrile, however, since it already incorporates such a high concentration of tertiary carbon-hydrogen centres in its structure. The effect of model compounds was therefore tested on polymethacrylonitrile. So samples of polymethacrylonitrile were heated in the presence of a few model compounds under standard conditions. Benzoic acid, phenyl-acetonitrile, cumene were tested. Similarly acrylonitrile units should also be expected to initiate colouration in polymethacrylonitrile and so copolymers of methacrylonitrile and acrylonitrile (small concentrations) were also given the same heat treatment. In table 4-2 the nucleophilic carbon-hydrogen compounds are all seen to



INITIATION OF COLOURATION BY
ACRYLONITRILE UNITS AT 170°C.

Figure 4-6.

be efficient initiators and their efficiency relative to the typical acid initiator, benzoic acid may be compared.

Copolymers of methacrylonitrile with increasing amounts of acrylonitrile units were also degraded at 175°C, and their rates of colouration plotted against the concentration of acrylonitrile units incorporated in the chain is shown in figure 4-6. There is a steady acceleration of the reaction with increasing acrylonitrile concentration. The propagation reaction in these copolymers is likely to be the same as in pure polymethacrylonitrile, and so the acceleration can only be due to increased initiation. This, in the light of the above evidence of active hydrogen compounds initiating colouration, shows conclusively that the labile unit in polyacrylonitrile is its tertiary carbon-hydrogen bond.

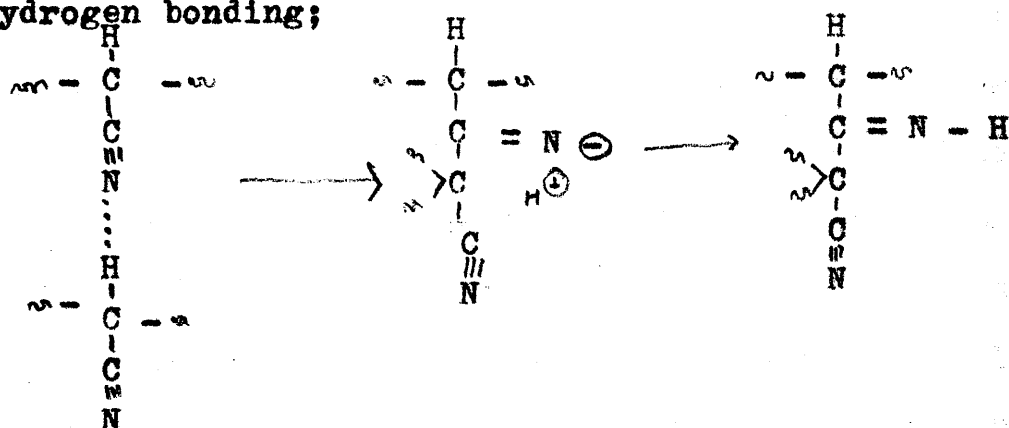
Table 4-2.

The Effect of Model Compounds on the Colouration of Polymethacrylonitrile, at 175°C.

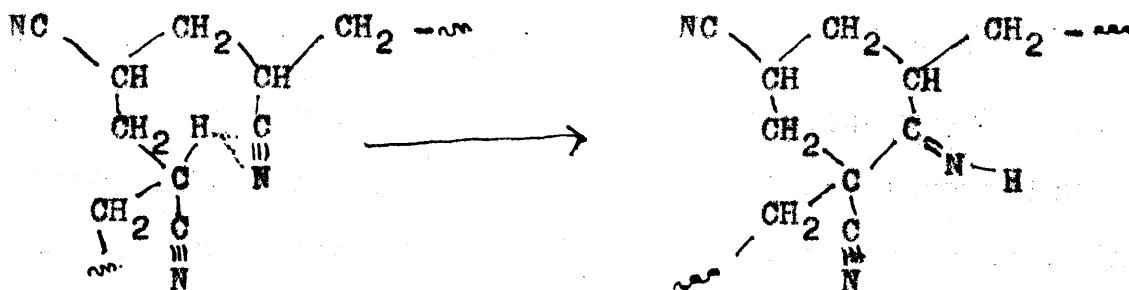
Compound Tested... Concentration...	mol. %.	Colouration.	
		30 min.	60 min.
1). Benzoic acid.	10.	dark red	dark red
2). Cumene.	10.	orange	orange-red
3). Phenyl-acetonitrile	10.	pale yellow	light red
4). Acrylonitrile copolymer.	10.	white	yellow

4). Intramolecular and Intermolecular Self Initiation.

It is possible to predict at least two ways in which initiation by these tertiary carbon-hydrogen bonds can proceed - an intermolecular and an intramolecular mechanism. From the nature of polymeric structure these seem equally possible. Fibre polymers, like polyacrylonitrile have their molecular chains packed in helixes which are intimately coiled together. Because of the small polar side groups, the intermolecular forces are strong and the chains are closely packed together. Reaction between chains should then be strongly favoured, especially in the initiation step because of the possibility of some hydrogen bonding;



Also since the chains are arranged in a spiral manner, it is quite possible that several acrylonitrile units may coil back on one another and so be available to initiate by an intramolecular mechanism. Again this process may be aided by the presence of some intramolecular hydrogen bonding:



Molecular models were made of these two possible initiation structures and also of the subsequent condensed ring systems, but all were equally strained and it was not possible to eliminate one structure in favour of the other by this means.

However, other evidence is available. Polyacrylonitrile, if heated at 140°C, for several hours slowly develops insolubility. It does not colour or appear to undergo any other physical or chemical change - its infra-red spectrum is identical with that of untreated polymer and, in particular, there is no trace of any unsaturation peaks developing. It is nevertheless completely insoluble in cold dimethyl formamide which is a very good solvent for polyacrylonitrile. If, however, the solvent and degraded polymer are heated together a gel develops and the polymer eventually dissolves completely. If, on the other hand, the polymer is degraded a stage further so that it develops a slight yellow tinge, then the polymer will not dissolve completely but will only gel in the heated

solvent. This seems to indicate that something happens to the polymer on heating but before it colours which is reversible but if it is taken to a higher conversion the polymer colours and it is no longer reversible. The change completely alters the polymer solubility in a very good solvent.

These observations were also followed by molecular weight determinations on the polymer solutions. In none of them was any substantial increase recorded in the molecular weight. Indeed, measurement on the solution obtained by heating to dissolve the insoluble polymer gave a molecular weight identical with that of the original untreated polymer.

The development of complete insolubility at 140°C would seem to indicate that considerable numbers of cross-links are being produced. The polymer remains colourless indicating that little or no cyanide condensation has taken place. Either the cross-linkages are produced on initiation or else very early on in the propagation reaction. In either case the cross-links produced are fairly labile and readily broken. This is the case when the polymer dissolves completely on heating in the presence of the solvent. If the condensation reaction is allowed to proceed further, these links become stabilised and so the polymer is no longer capable of dissolving completely but only to gel.

The stabilisation may be due to the production of very many more cross-links or the links themselves may be stabilised by further cyanide condensation, increasing the length of the conjugation sequences. Both may contribute to the further stability of these cross-links.

Molecular weight determinations on the products of degradation of copolymers of methacrylonitrile and acrylonitrile (10% mole. in the polymer) showed that no initiation cross-linkages are produced. These copolymers colour extensively and like polymethacrylonitrile remain soluble in acetone. The initiation in these copolymers must be entirely intramolecular. This is perhaps to be expected since in polymethacrylonitrile there are not the strong intermolecular forces that there are in polyacrylonitrile. The incorporation of methyl groups along the chain keeps the molecules further apart and interferes with the strong cyanide group interactions. Initiation by cross-linking would then become very much less likely. Initiation then proceeds by the only way possible, namely intramolecularly.

The above observations show that intramolecular initiation does take place when the intermolecular process is prevented, but it is not clear which occurs in polyacrylonitrile. It will be shown in the following chapter

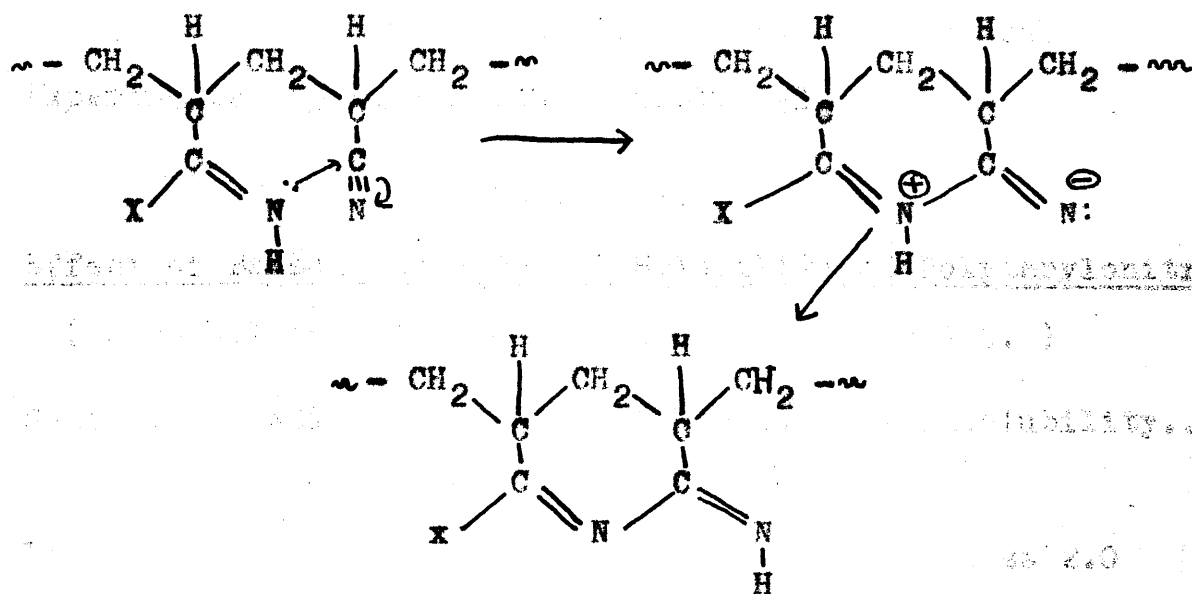
that intermolecular initiation is not necessary to account for the development of insolubility since cross-linking is also associated with the propagation step in the colour reaction.

Chapter 5.

The Propagation Reaction.

Infra-red spectrographic measurements, see chapter 3, have shown that cyanide groups are disappearing during the colouration of polyacrylonitrile without the evolution of volatiles. The reaction does, in fact, propagate by the step-wise condensation of cyanide groups into a system of condensed heterocyclic rings, associated with carbon-nitrogen conjugation.

The initiation reaction, involving the active hydrogen atom of either an acrylonitrile or a carboxylic acid unit, leads to the production of an imino intermediate which is capable of condensing further with a neighbouring cyanide group and regenerating another imino group, capable of further reaction. In this way, a system with increasing length of conjugation is produced as more and more cyanide groups condense, so accounting for the movement of colour through the spectrum, from yellow to red and brown as the reaction proceeds.



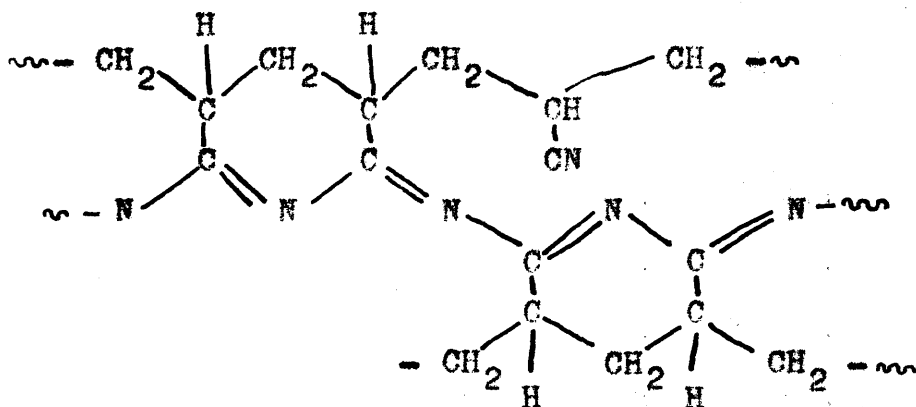
1). Insolubility in Coloured Polyacrylonitrile.

a). Acid Initiation of Colour.

Polyacrylonitrile heated in a vacuum at 120°C for several hours does not appear to undergo any chemical change. It remains just as soluble to cold dimethyl formamide as untreated polymer. There is no discoloration or any other deterioration in properties. The infra-red spectrum and limiting viscosity are unchanged. The colour reaction is clearly then not initiated at this temperature. If, however, the polymer is thoroughly mixed with benzoic acid and subsequently given the same heat treatment it is found to have coloured considerably - light yellow - and also the polymer is no longer soluble in cold dimethyl formamide. It does, however, gel in hot dimethyl formamide

great to be accounted for solely as the result of some physical change involving rearrangements of intermolecular forces.

The most obvious cross-linking process associated with propagation would consist of the reaction of a propagating imine group with a nitrile group on an adjacent chain, so that it is quite unnecessary to postulate any new type of reaction. The coloured polymer must, in fact, incorporate some structure of the type,



Molecular models of this propagating cross-link have been made and have been found not to be unduly strained.

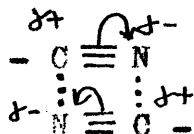
A reasonable mechanism for the production of such cross-links in the propagation step can only be deduced from a consideration of the detailed structure of the polymer. One can tentatively deduce something about the molecular architecture in cyanide polymers by

considering what is known about aliphatic nitrile in general.

Recent work ⁴³ on the nature of the intermolecular forces in aliphatic nitriles suggest that hydrogen bonding of the type,

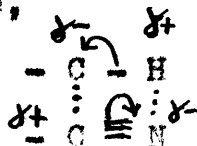


does not occur to the extent previously envisaged but instead there are much more stronger dipole interactions between nitrile groups. In particular, recent work on aliphatic mono-nitriles suggest that the molecules are associated in pairs with dipole - dipole interaction between the two nitrile groups - the groups lying with their axes antiparallel:



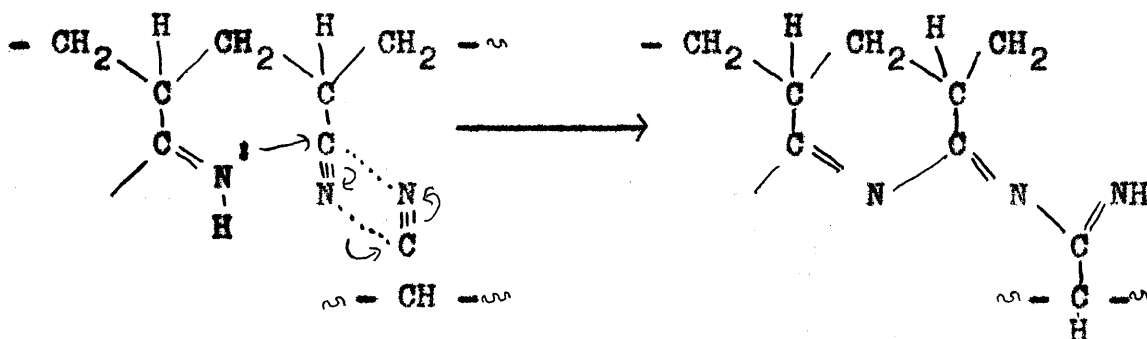
The energy of such a bond has been calculated to be about 8 k. cal. per mol., about 25% stronger than that of the strongest hydrogen bond, as found in alcohols. It readily accounts for the strong intermolecular forces in cyanide compounds in general. However, it was also found that only part of the cyanide groups in the mono-nitriles were associated in such a way. The extent of the association decreased with increasing length of the aliphatic chain. This was interpreted as indicating the

existence of an equilibrium between this type of cyanide group association and that between a cyanide group and a carbon-hydrogen dipole,



It would seem reasonable that there might be a significant contribution from the cyanide dipole pair interactions in the strong intermolecular forces in polyacrylonitrile, and that it is not entirely due to hydrogen bonding as previously considered. Other evidence in favour of dipole pair interaction is also available. Liang and Krimm ³¹ in their classification of the infra-red spectrum of polyacrylonitrile, have pointed out that the wave-number of the carbon-hydrogen stretching vibration at 2810 cm.^{-1} is inconsistent with strong hydrogen bonding, and it certainly could not account for the strong intermolecular forces in this polymer. Most of the previous work cited as evidence for hydrogen bonding in polyacrylonitrile - solubility ¹⁰, cohesive energy density, ⁴⁴ and X-ray diffraction studies ⁴⁵, only served to measure this strong interaction and could in no way infer the nature of it. One might infer from the existence of the equilibrium between the two types of dipole interaction in aliphatic nitriles that both would contribute to the molecular interaction in polyacrylonitrile.

Pairs of nitrile groups associated in this way are obviously in a most favourable configuration for taking part consecutively in the colouration propagation process. If a propagating sequence, therefore, reaches such a pair of associated nitrile groups once the first has reacted the second must be more favourably situated for reacting, even more so than the adjacent nitrile on the same chain. Thus, because of the prevalence of such group pairs, propagation cross-linking must make an appreciable contribution to the overall propagation process.



This cross-link will then propagate normally along the second chain until it cross-links again by such a mechanism.

The infra-red spectroscopic evidence suggests that a considerable proportion of the cyanide groups are associated in dipole pairs, so that the actual number of carbon-nitrogen units between each cross-link must on

the average be very small. One would then consider that polyacrylonitrile on colouration would become considerably cross-linked fairly early in the reaction. This, perhaps, explains the observed insolubility in polyacrylonitrile degraded to such a small extent as to remain colourless and makes it unnecessary to postulate initiation cross-linking as a cause of this insolubility.

The propagation reaction in polymethacrylonitrile is entirely intramolecular. This is accounted for by the polar environment. The additional methyl group, in each unit along the chain, keeps the chains further apart and inhibits dipole pair interaction between cyanide groups on neighbouring chains. Colouration in this polymer is not accompanied by the production of cross-links and so the degradation products still remain very soluble.

b). Alkaline Initiation of Colouration.

Polyacrylonitrile powder is slowly attacked by concentrated alkaline solutions with the production of a completely insoluble, highly coloured solid. In contrast, polyacrylonitrile in solution is rapidly attacked by dilute alkaline solutions with the production of the same highly coloured material which, however, remains soluble.

Colouration in solution is also accompanied by a random chain scission - the molecular weight initially rapidly dropping on colouration. 35,36.

Infra-red spectroscopic measurements on the coloured material indicate that the reaction is similar to the thermal colouration, except that the initiation is entirely by hydroxyl ion, and no self-initiation takes place.

In the solid state, however, the product is highly insoluble and so cross-links are again only produced in the propagation step. When the chains are pushed apart and the polymer-polymer interaction cut down as they are in solution, no cross-links are produced on propagation and the coloured material remains soluble. Unfortunately the chain appears to be sensitive to hydroxyl ion attack at the tertiary hydrogen: a random attack degrading the chain.

These observations are substantiated by the alkaline degradation of polymethacrylonitrile ³⁶, in both the solid and solution states. In neither case is degradation of the chain nor the production of insolubility observed. Polymethacrylonitrile has not the strong intermolecular forces to allow close approach of the chains for cross-linking to be produced, or the necessary

tertiary hydrogen atom to permit chain degradation.

c). The Thermal Self-Initiation of Colouration.

It has already been shown, page 65, that polyacrylonitrile on heating becomes completely insoluble in cold dimethyl formamide, before it begins to colour. It is, however, possible to dissolve this colourless material and also to gel coloured material by heating them in the presence of the solvent on a water bath. A technique was accordingly devised for comparing the solubilities of polymer degraded to various extents.

Polymer samples were degraded in the molecular still for periods of one hour at various temperatures. The degraded sample, 0.20 g., was placed in a graduated tube, a constant amount of dimethyl formamide (45 ml.) was added and the tube allowed to stand for 48 hours, during which time it was frequently shaken. The polymer was allowed to settle, 10 ml. of the supernatant liquid was extracted and used to determine the solubility of the polymer in the cold solvent. The remaining solution was heated for 3 hours on a water bath, at 100°C. On cooling the volume occupied by the gel was noted, the liquid filtered off and the concentration of the polymer in the

solution determined. The insolubility of the polymer was then calculated, making allowances for the volume occupied by the gel in the solution.

The development of insolubility and the decrease in volume occupied by unit weight of the gel as the colouration reaction proceeds is seen in figure 5-1 and table 5-2. Obviously, with increasing extent of reaction hot dimethyl formamide has less and less solvent power for the polymer and the gel is becoming more and more compact - it is capable of expanding to a lesser extent. This is consistent with a gradually increasing cross-link density.

Table 5-2.

The Development of Insolubility in Degraded Polyacrylonitrile.
(1 hour at various temperatures.)

Temperature.	Colour.	% Insolubility.
160°C	white	81.0
170°C	off white	86.2
180°C	v. pale yellow	92.5
190°C	pale yellow	93.1
200°C	yellow	96.3

2). Insolubility in Coloured Copolymers of Acrylonitrile.

It has been shown that the ability of poly-acrylonitrile to initiate its own colour reaction and to allow cross-linking to occur during the propagation of the reaction is dependent on the polar nature of the cyanide groups. This ability is further facilitated by the strong intermolecular forces arising from these polar properties and the relatively small size of the cyanide group which allows close packing of the chains. These conditions are not found in polymethacrylonitrile or copolymers of acrylonitrile rich in methacrylonitrile due to the steric effect of the bulky methyl group. Copolymers of acrylonitrile with smaller amounts of methacrylonitrile would, therefore, give intermediate conditions in which cross-linking would be expected to occur to a limited extent. Copolymers of acrylonitrile with monomers other than cyanide monomers would also give intermediate conditions for cross-linking to occur, but they also introduce further limitations to the cyanide condensation. The presence of a non-condensable group would block the cyanide condensation reaction in a single chain, so that in the absence of a cross-link being produced, the lengths of conjugated colour-producing sequences would be limited. The effect of the foreign non-condensable group in

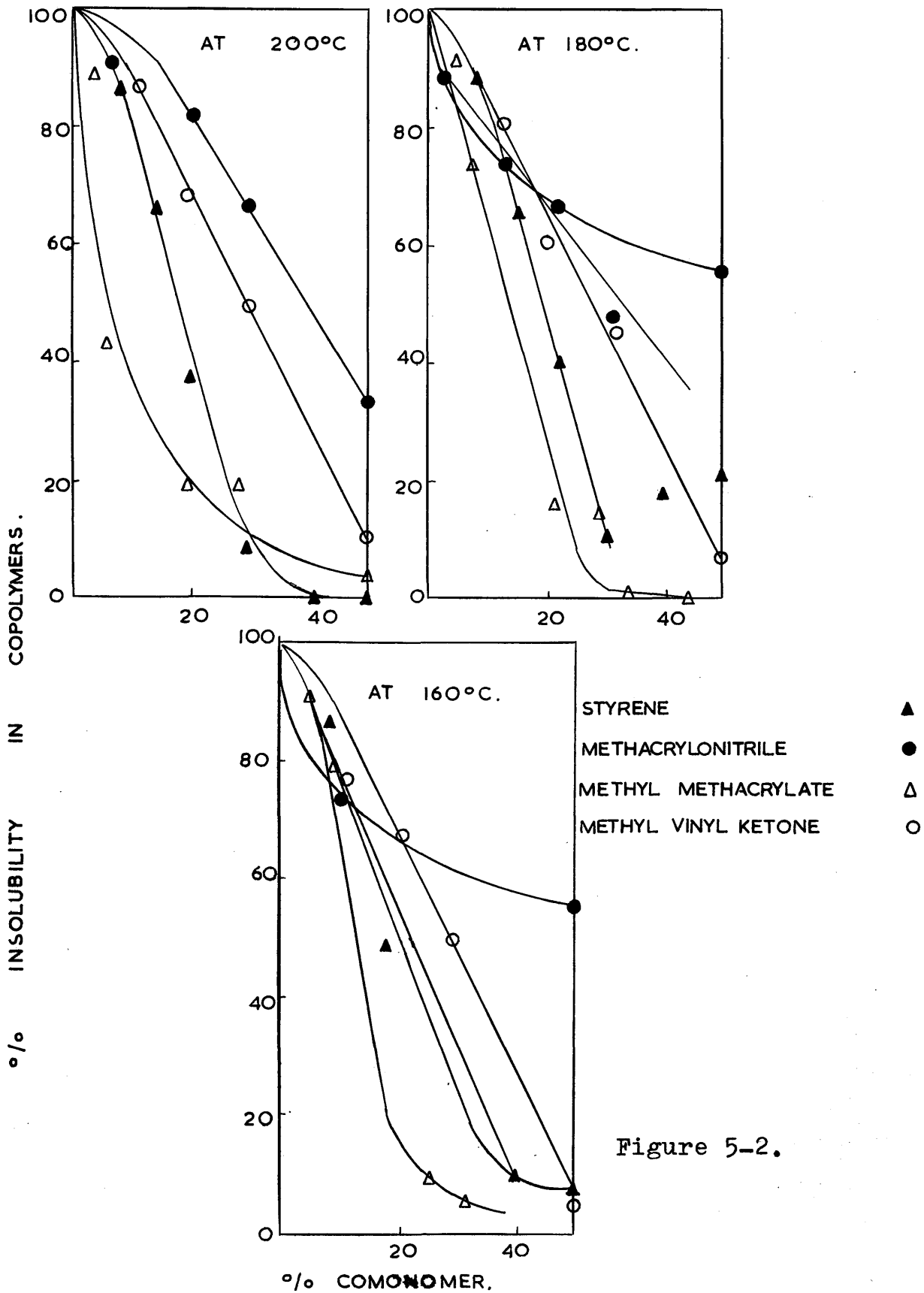
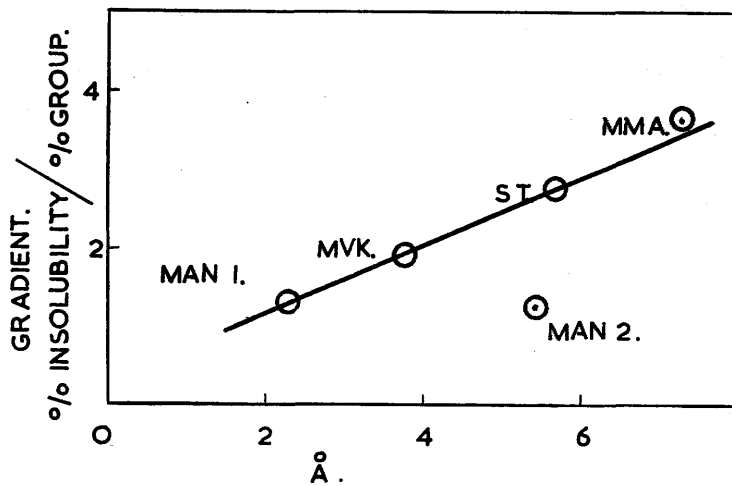


Figure 5-2.

inhibiting the colouration and cross-linking in poly - acrylonitrile is therefore of considerable interest.

Accordingly copolymers of acrylonitrile with varying amounts of 1). methacrylonitrile, 2). methyl methacrylate, 3). methyl vinyl ketone 4) styrene, were made. The details of their polymerisations and copolymer compositions are given in the tables in the appendix.

Samples of these copolymers were degraded in the molecular still in the usual fashion. The percentage insolubility at various degradation temperatures is related to the amount of foreign monomer incorporated in the chain in figure 5-2. It is obvious, from the figure, that for any one copolymer series the more impurity groups incorporated along the chain the more soluble is the resulting polymer's degradation products. The relative effectiveness of these comonomers in preventing insolubility seems to increase with its effective bulkiness. A measure of the effectiveness of a particular group in inhibiting cross-linking is given by the gradient of the linear part of the curves in figure 5-2. This value was plotted against the maximum radius of the cone of revolution that the group would sweep out when attached to the carbon atom on the chain. Figure 5-3 shows that there is a definite relationship between the



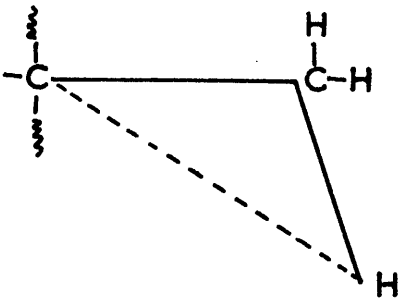
EFFECT OF GROUP SIZE ON
INHIBITING CROSS-LINKS.

Figure 5-3.

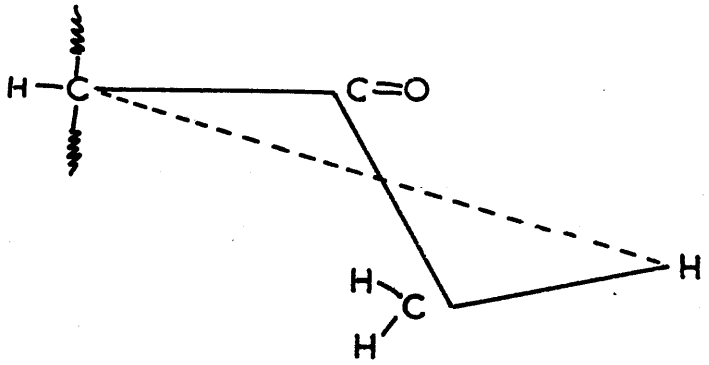
bulkiness of the group and its effectiveness in inhibiting the production of cross-links. It leads us to conclude that the effect of the impurity group is principally that of keeping the chains further apart and its effect is proportional to the group's size.

The relative sizes of the substituents were calculated using standard values for bond angles and lengths as shown below, page 83. ⁵¹ The bulkiness of the methyl methacrylate unit was determined by adding the terms for the two side groups together; however, in methacrylonitrile if one adds the two side group terms together, that is, for the methyl and for the cyanide groups, then this value predicts that methacrylonitrile is very much more effective in inhibiting cross-linking than is actually the case. If, however, one uses the methyl group term alone then its effectiveness falls into line with the others, as shown in figure 5-3. This would suggest that only the methyl group is effective in inhibiting cross-linking and that the cyanide group plays no part at all in it. This is, perhaps, to be expected in view of the part played by the cyanide group in the colouration reaction.

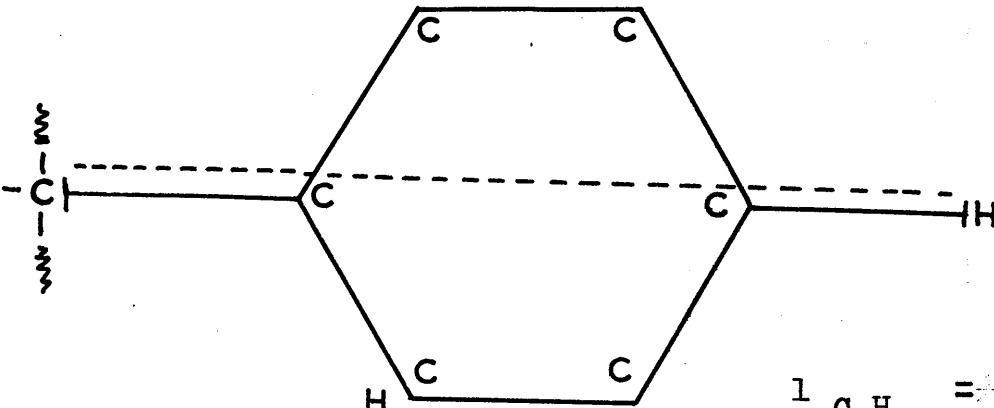
These values quoted for the bulkiness of the side groups are only relative and no implication that they are absolute is intended.



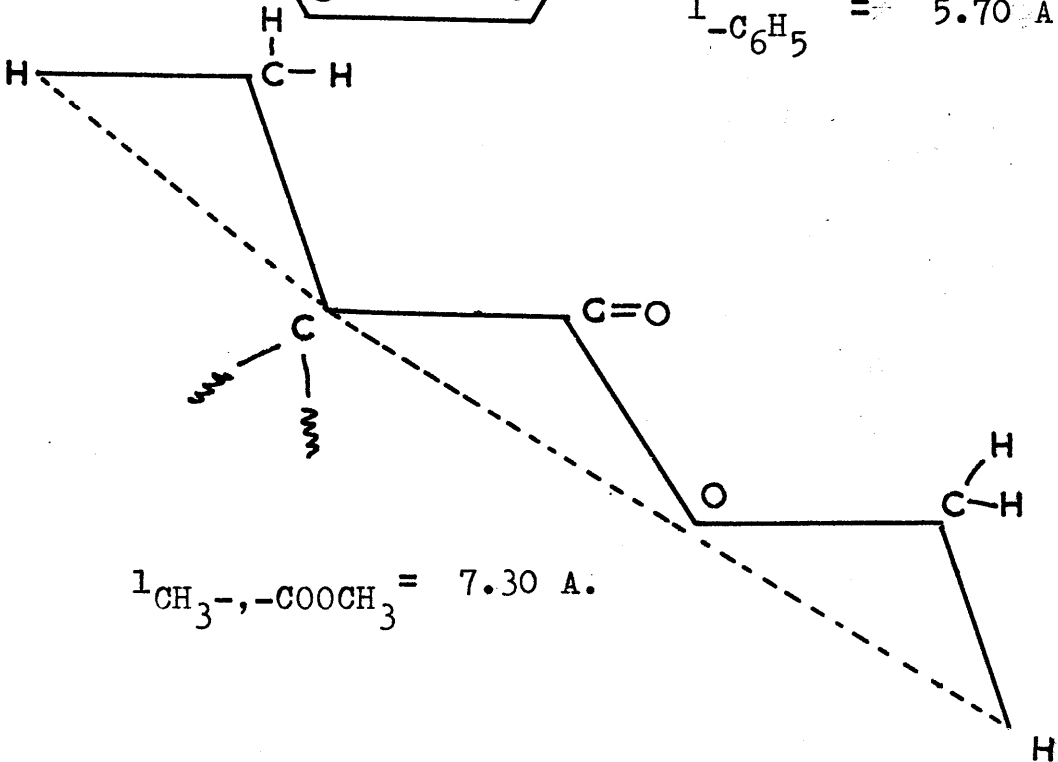
$$l_{-CH_3} = 2.4 \text{ \AA.}$$



$$l_{-COCH_3} = 3.85 \text{ \AA}$$

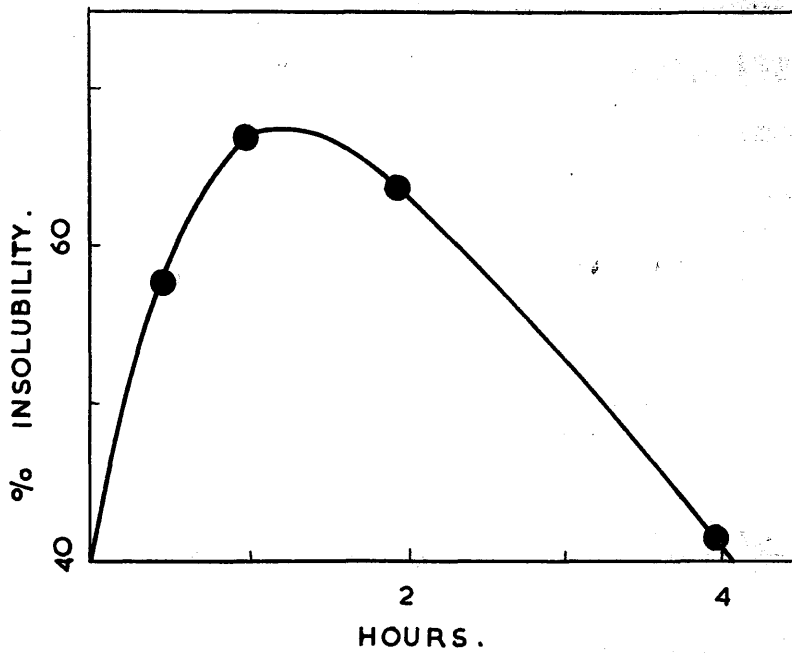


$$l_{-C_6H_5} = 5.70 \text{ \AA}$$



$$l_{CH_3-, -COOCH_3} = 7.30 \text{ \AA.}$$

Figure 5-4.



DEVELOPMENT OF INSOLUBILITY AT 160°C.
(20% METHYL VINYL KETONE.)

The development of insolubility in these copolymers was measured at 140, 160, 180 and 200°C. The curves showed surprisingly little temperature dependence, see figure 5-2. The reason for this was revealed by a series of experiments on a copolymer containing 20% methyl vinyl ketone. It was degraded at 160°C for various periods of time up to 4 hours, see figure 5-4. It obviously reaches a maximum insolubility within a hour and does not alter much on further treatment. This explains the insensitivity of the insolubility gradient to temperature, maximum insolubility is attained early in the reaction.

3). The Colour Reaction in the Copolymers.

These copolymers were also studied for their colour stability in order to determine the efficiency of the various monomeric groups in preventing colour formation. The colour stability was measured in three ways. Some approximate measure can be had from the colour obtained under standard degradation conditions, see table 5-2. A more accurate estimation can be had from infra-red spectrographic measurements, using the usual disc

technique. The rates of cyanide disappearing or of carbon-nitrogen double bond appearing were both used. The latter is, perhaps, the more accurate in detecting traces of reaction occurring in copolymers in which the colour reaction is considerably inhibited.

Table 5-3.

Colouration in Copolymers of Acrylonitrile with Monomer (B).

(degraded at 200°C for 6 hours.)

Monomer (B).	5.	10.	20.	30.	50.%mc
Styrene.	brown		yellow	white	white
Methyl Methacrylate.	orange	orange	yellow	white	white
Methyl Vinyl Ketone.	d.brown	d.brown	orange	yellow	yellow
Methacrylonitrile.	d.brown	d.brown	d.brown	d.brown	d.brown

The optical density of the conjugated carbon-nitrogen double bond absorption at 1590 cm.^{-1} produced in the copolymer after degrading for various periods of time at 200°C as plotted against the concentration of the comonomer is a measure of the amount of cyanide condensation occurring in the copolymer, see figure 5-6.

The rates of colouration, as measured by the percentage decrease in the optical density of the cyanide peak at 2237 cm.^{-1} , are plotted against the concentration

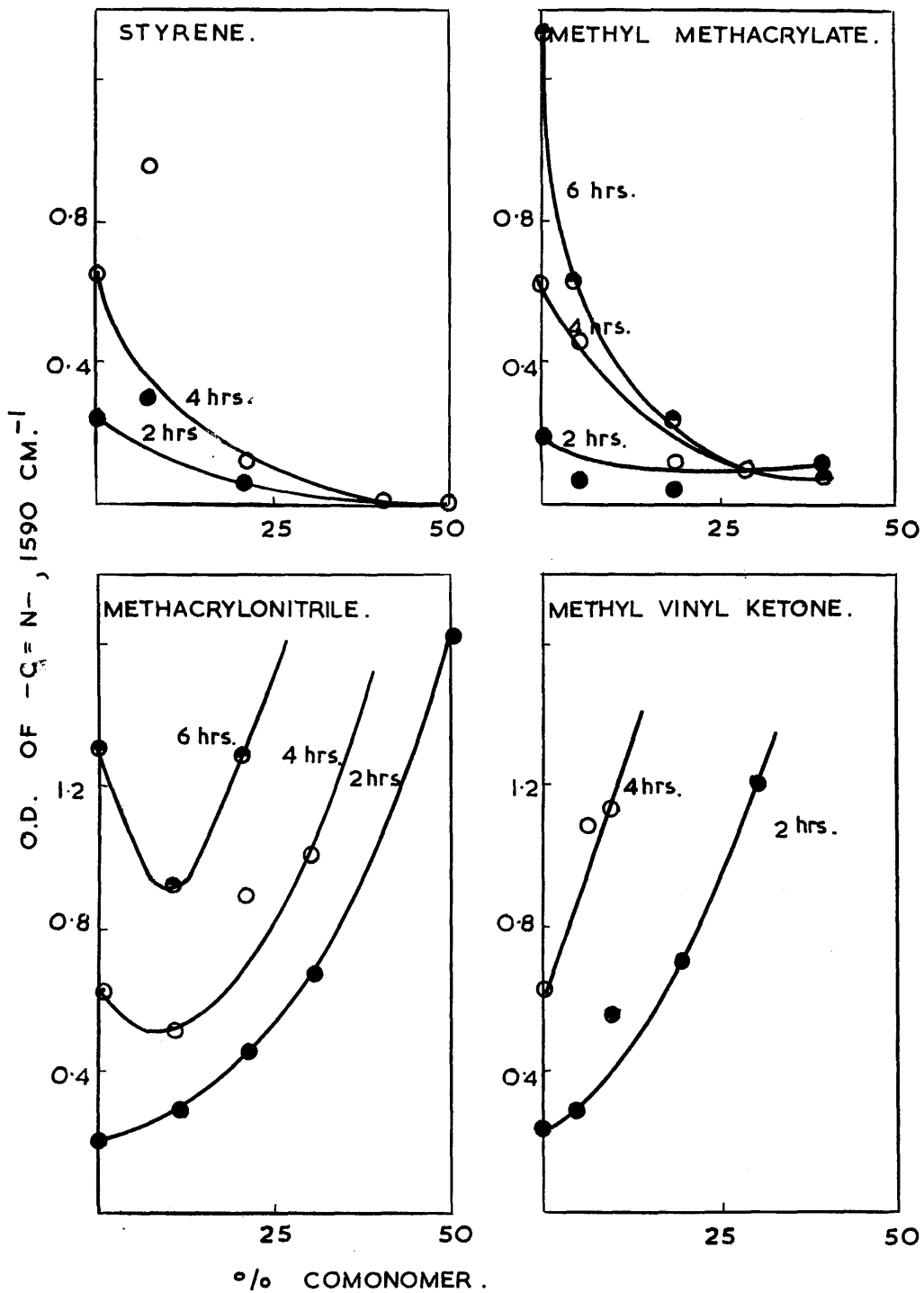


Figure 5-6.

of comonomer B, in figure 5-5.

The results can best be discussed by considering the monomers in groups.

Group 1). The Inert Monomers.

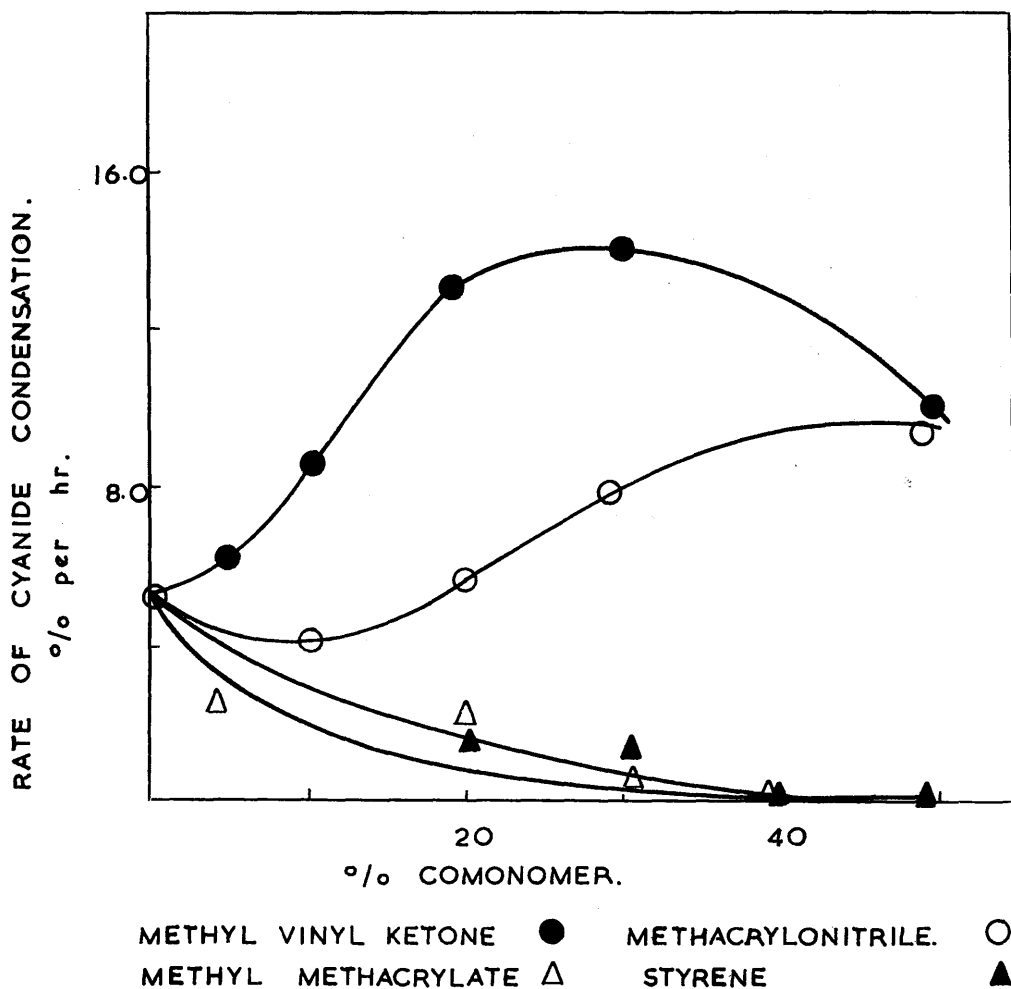
Styrene and Methyl Methacrylate.

These two monomers can be considered together since they display the same effects. The incorporation of these units along the chain cuts down the rate of colouration and the average length of the conjugated colour-producing sequences. The condensation reaction is virtually stopped by the incorporation of about 30% of these monomeric units into the chain. This can be seen from the white colour of the degraded material and also the absence of absorption in the carbon-nitrogen double bond region of the infra-red spectrum. Cyanide groups are then no longer able to condense.

Group 11). The Reactive Monomers.

a). Methyl Vinyl Ketone.

Methyl vinyl ketone copolymers behave anomalously. The incorporation of these units along the chain does not cut down the rate of cyanide condensation



EFFECT OF FOREIGN GROUPS ON RATE OF COLOURATION.

Figure 5-5.

nor the length of the conjugated sequences in the coloured material. A 50-50 copolymer still colours appreciably.

These monomer units also appear to accelerate the colour reaction, due presumably to two possible effects - increased chain mobility and increased initiation. The incorporation of methyl vinyl ketone units in the chain cuts down the strong intermolecular forces and so allows the chains to become more mobile, such that a copolymer containing approximately 20-30% methyl vinyl ketone units softens at the colouration temperature. Condensation is more favoured in the liquid than in the solid state.

Since even small amounts of methyl vinyl ketone units accelerate the reaction it seems that these units may also be capable of initiating the colour reaction. Ketones with an alpha hydrogen atom are known to initiate the colouration of polymethacrylonitrile.⁷ Initiation may involve either the enolic form of the ketone, or the tertiary hydrogen atom, it is not known which.

Since the presence of large amounts of methyl vinyl ketone units does not affect the progress of colour through the spectrum, the length of the conjugated sequences are apparently maintained, indicating that

methyl vinyl ketone units must in some way be reacting with the colouring unit in such a way as to maintain the development of conjugation. This will be discussed in the following chapter which will deal with the thermal decomposition of polymethyl vinyl ketone in more detail.

b). Methacrylonitrile.

The incorporation of methacrylonitrile units in the chain also has two effects. There is an apparent acceleration of the rate of condensation and the length of the conjugated colour-producing sequences are maintained. A 50-50 copolymer colours to the same extent as pure polyacrylonitrile, but at a faster rate.

The incorporation of methyl groups along the chain accelerates the cyanide condensation, again presumably to increased mobility of the chains. The copolymers containing higher proportions of methacrylonitrile soften at the temperature of colouration and the reaction is more favoured in the liquid state. The initial small decrease in rate as shown in figure 5-5, is no more than is to be expected from the decrease in initiation which will follow from the decrease in acrylonitrile concentration in the molecules. This monomer does not cut down the length of conjugation sequences since it

can readily take part in the propagation reaction.

The work described in this chapter shows that the propagation step in the colouration reaction involves the condensation of nitrile groups. In this way long sequences of carbon-nitrogen double bond conjugation are built up together with a condensed heterocyclic ring system. This condensation reaction is not limited, however, to the cyanide groups along any one chain but it can propagate from one chain to another producing finally a highly coloured and highly cross-linked material. The ability of polyacrylonitrile to cross-link in this fashion is due to the relatively small size of the cyanide groups. Any attempt to interfere with this intimate structure by the incorporation of bulkier or less polar groups along the chain serves to limit the amount of cross-linking which can take place. Incorporation of a monomer other than a cyanide monomer also cuts down the average length of conjugation sequences, although in the case of methyl vinyl ketone propagation can proceed through its unit in such a way as to maintain the conjugation. By including as much as 30-40 % of an inert monomer, styrene, or methyl methacrylate, in the chain it is possible to

stop the colouration reaction completely, since this amount of monomer is sufficient to prevent all intermolecular cross-linking which is essential if conjugation sequences of any significant length are to be produced.

Chapter 6.

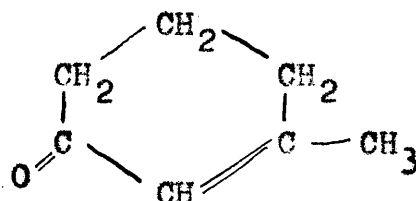
The Thermal Colouration of Polymethyl Vinyl Ketone.

1). Introduction.

Polymethyl vinyl ketone undergoes a superficially similar thermal colour-producing reaction to polyacrylonitrile, involving the interaction of the methyl ketone substituents. In the thermal colouration of polyacrylonitrile, however, the development of colour proceeds rapidly from white, through the spectrum - from yellow to red- and finally to brown and black, under extreme conditions, while polymethyl vinyl ketone becomes yellow early in the reaction deepening as it proceeds, but only in the final stages does it become red. The colour never extends as far into the red as it does in polyacrylonitrile. This is a direct result of the condensation reaction in polymethyl vinyl ketone being a random process between any pairs of methyl ketone substituents, and so the colour producing sequences must on the average be very much shorter conjugated than in polyacrylonitrile, condensed to the

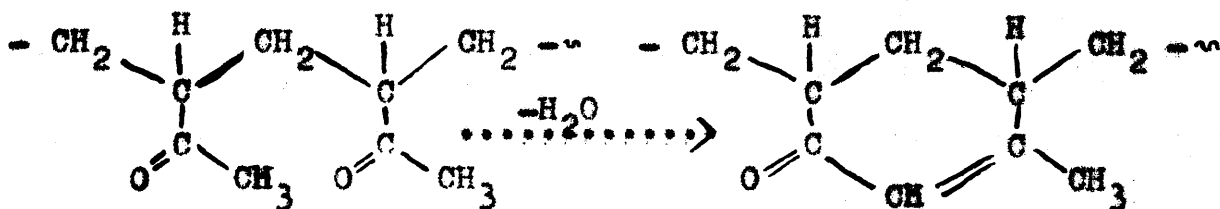
same extent, since this involves a step-wise condensation of cyanide groups along the chain. The average length of the conjugated sequences does increase in the random condensation reaction with increased condensation but because of the possibility of isolating non-reactive groups between adjacent sequences they remain relatively short, even in polymer totally degraded.

Marvel and Levesque (1938) ⁴⁶, on investigating the structure of vinyl polymers studied the decomposition reaction in polymethyl vinyl ketone. They found that the polymer readily evolved considerable amounts of water on heating to 270°C, and treatment of this "dehydrated" material at a higher temperature gave other volatile products, from which they were able to detect small traces of 3-methyl-cyclohex-2-ene-1-one,

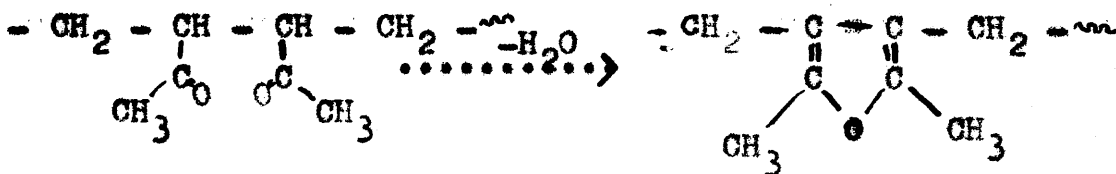


and other six membered ring ketones. They were not able to detect any furan derivatives, or other heterocyclic ring compounds. This showed conclusively that the monomer units must be arranged in the polymer in a head to tail manner and not head to head, tail to tail since the latter would have given furan derivatives, characteristic of a

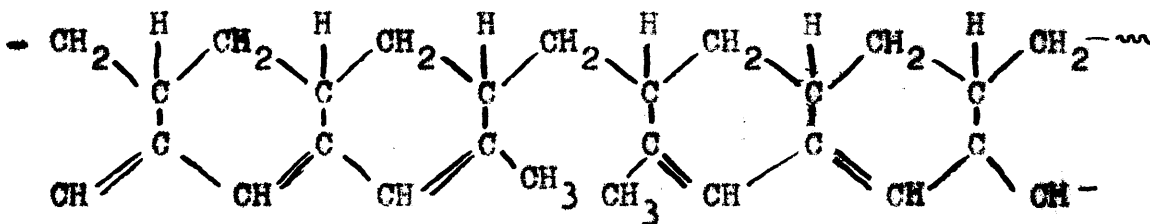
1:4 di-ketone system. The condensation and water elimination reaction was then;



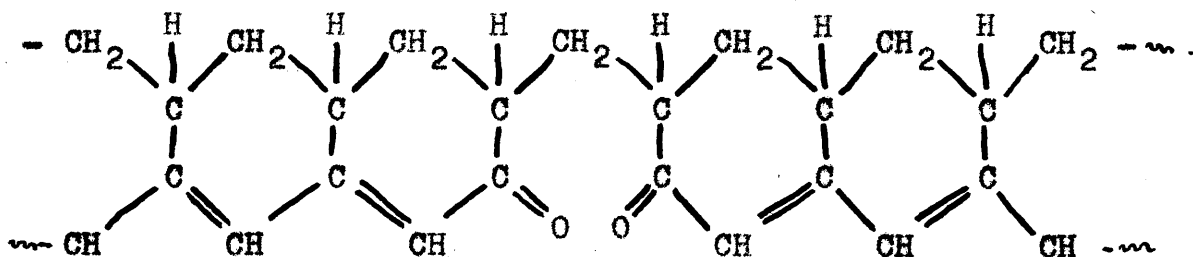
and not,



This reaction is a random condensation reaction between any two complimentary neighbouring groups. Wall ⁴⁷ and Flory ⁴⁸, independently have shown that for such a system 18.4 % of the functional groups of bifunctional substituents are isolated in the conjugation sequences and are incapable of further condensation, that is,



and also,



and, indeed, Marvel and Levesque have reported that only between 79 - 85 % of the oxygen is removed in the water elimination reaction.

2). General Characteristics.

The polymethyl vinyl ketone sample as prepared was rubber-like in properties and impossible to grind to a fine powder. The colour producing reaction as studied on this solid was found to be dependent on the polymer sample - its weight and particle size. Clearly this was due to the rate of the reaction, as measured, being controlled by the rate of diffusion of the product, water, from the polymer. This diffusion control could be eliminated, however, by using films of the polymer cast from acetone solution and covered with fine copper powder. The reaction rate, under these conditions, was found to be independent of the sample size, and hence layer thickness, at least up to the thickness necessary in these experiments.

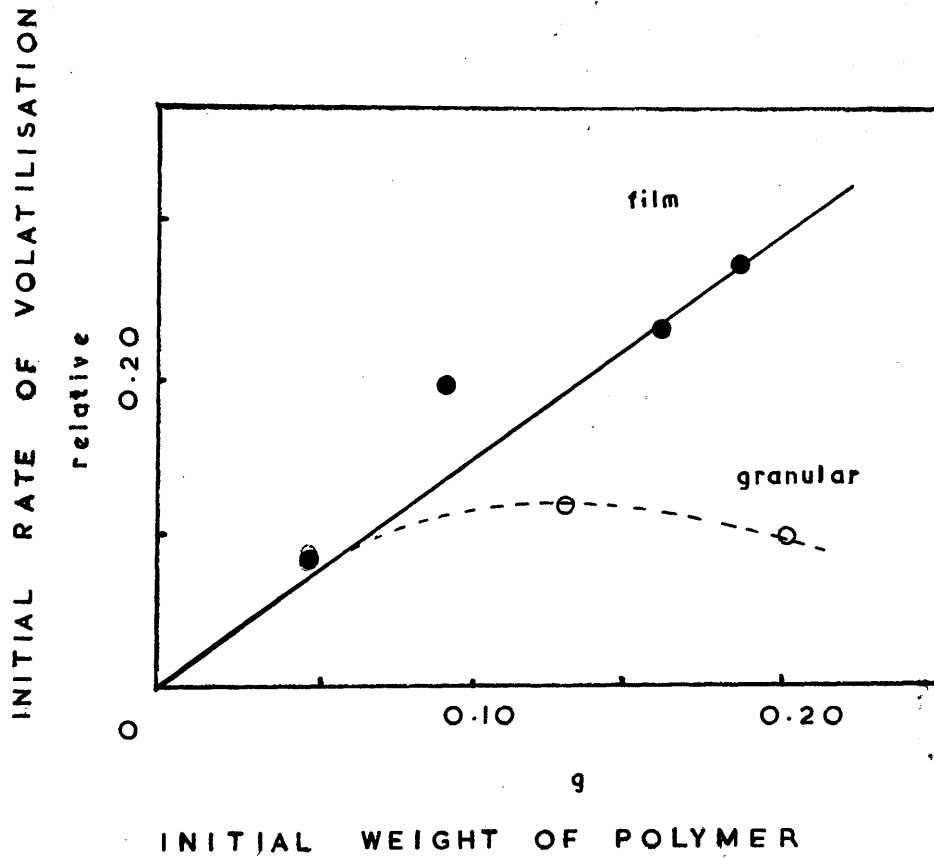
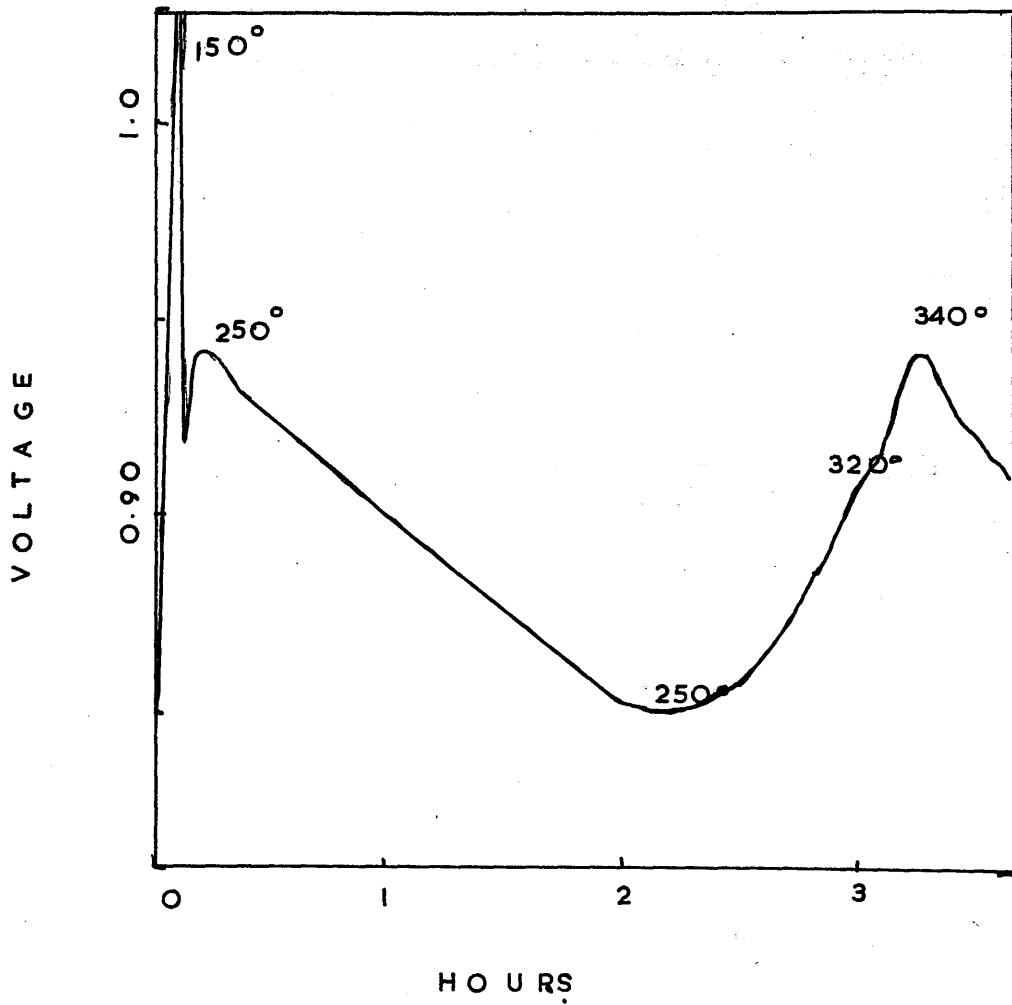


Figure 6-1.

This can be seen from figure 6-1, in which the initial rate of volatilisation, as measured by the Pirani gauge, is plotted against the sample weight, both for the polymer solid and films. The process of casting films from acetone solutions suffered from the disadvantage that the resulting polymer sample contained considerable amounts of volatile materials occluded in the polymer, which was not readily removed below colouration temperatures, even under high vacuum. This introduced a possible source of error in the weight measurements of as much as 4%.

Figure 6-2 shows a typical Pirani gauge curve for the thermal degradation of polymethyl vinyl ketone (film). The sample was rapidly heated to 250°C (heating up time - 10 minutes) and maintained at 250°C until all the volatiles had been evolved (usually 130-150 minutes). Further heating to 340°C gave a second maximum rate of evolution of volatiles. The initial peak at 180°C, during the heating up period, was due entirely to acetone (confirmed by infra-red spectroscopy and vapour phase chromatography). Casting the film from dioxan solution alters the position of this peak, and so it must be due to solvent occluded in the polymer. The rate of evolution of volatiles at 250°C decreases linearly with time. These products were shown by infra-red spectroscopy and copper



THERMAL DEGRADATION OF POLYMETHYL
VINYL KETONE

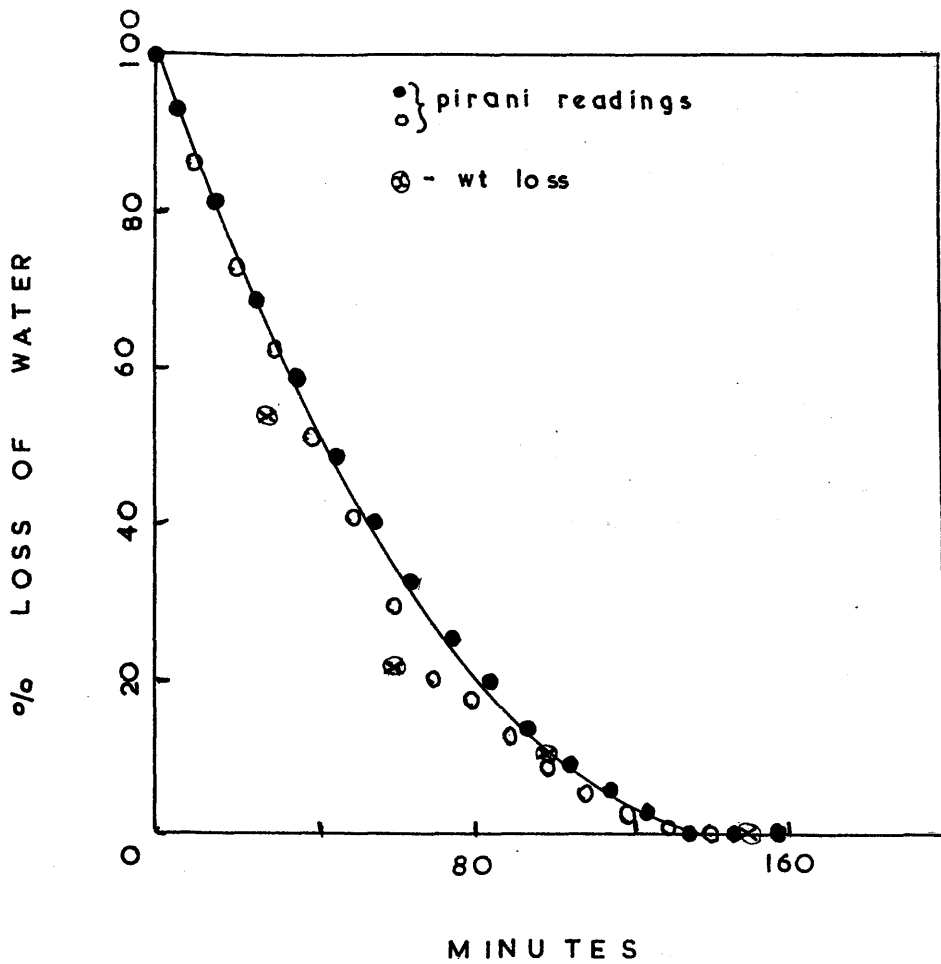
Figure 6-2.

sulphate spot test to be solely water. At 340°C yellow material condensed on the cold surface of the still. The infra-red spectrum showed that it was very similar in structure to coloured polymethyl vinyl ketone, and, in particular, to be ketonic in nature. It would seem that these were identical to the high temperature volatiles partially characterised by Marvel and Levesque.

These Pirani gauge readings indicate that polymethyl vinyl ketone undergoes two degradation reactions, one involving side group substituents, and the other involving chain degradation. Both reactions result in the evolution of volatile material, but occur in different temperature ranges. At 250°C the water elimination reaction of polymethyl vinyl ketone occurs at a measurable rate and goes to completion without the intervention of the chain degradation process which can occur only at a slightly higher temperature. Accordingly all measurements on the colour-producing reaction in polymethyl vinyl ketone were made at this temperature.

3). The Colour Reaction.

Pirani gauge readings and loss in weight of the sample was used to follow the rate of decomposition of



DEGRADATION OF POLY METHYL VINYL KET ONE

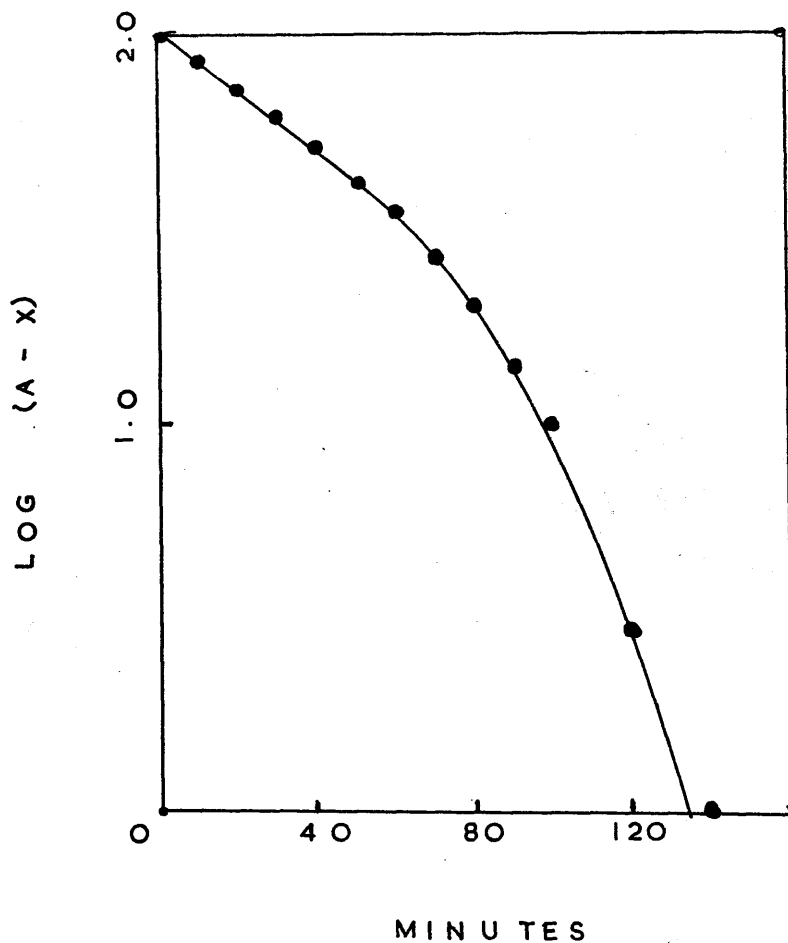
AT 250° C

Figure 6-3.

of polymethyl vinyl ketone. There was always about 20-25% loss in weight on degrading the polymer sample to completion at 250°C. The difference between this value and the theoretical one of 21.0%, as based on Flory and Wall's calculations must be due to traces of volatiles in the polymer sample. Assuming the value of 21.0% to be correct and the difference to be due to volatiles, then the extent of the reaction was calculated from the loss in weight. This is shown in figure 6-3, along with the corresponding values derived from the Pirani gauge readings. The logarithm of the concentration of the remaining condensible groups is plotted against time in figure 6-4. The reaction is seen to be first order up to about 50% reaction.

The colour reaction was also followed by infra-red spectroscopy. The infra-red spectrum of polymethyl vinyl ketone and its degradation products are shown in figure 6-5. A list of the assignments to the main absorption bands is made in table 6-1. While in table 6-2, the changes in absorption which occur on colouration are shown.

The strong absorption band at 1710 cm.^{-1} is assigned to the carbonyl bond since according to Bellamy³³ saturated aliphatic carbonyls absorb in the region $1715 \pm 10 \text{ cm.}^{-1}$. The peaks at 1356 and 1160 cm.^{-1} are assigned to the normal methyl and methyl ketone groups.



FIRST ORDER EVOLUTION OF VOLATILES

FROM POLYMETHYL VINYL KETONE

AT 25° C

Figure 6-4.

Table 6-1.

Infra-red Spectral Assignments in Polymethyl Vinyl Ketone.

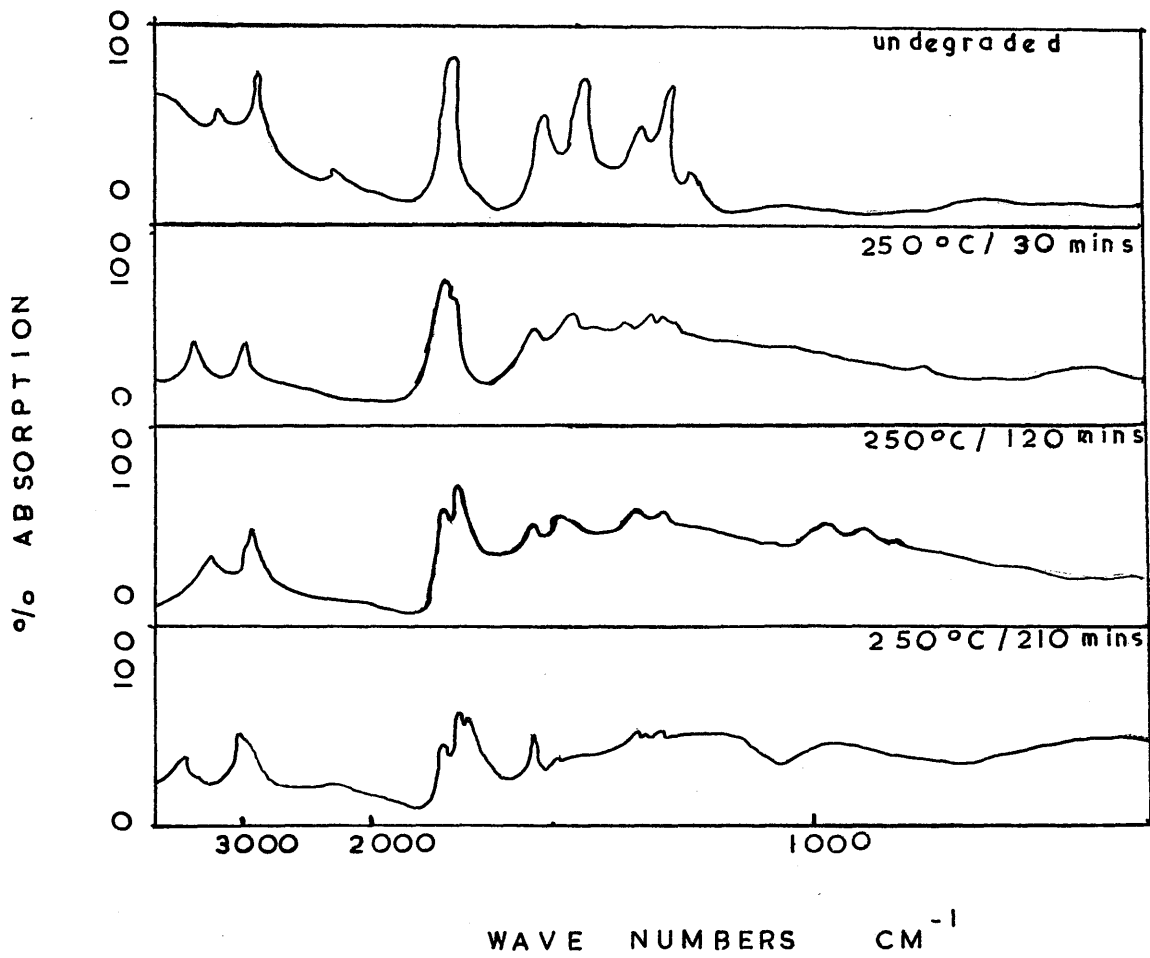
Frequency. cm. ⁻¹	Assignment.	Frequency. cm. ⁻¹	Assignment.
3550 (w)	-OH, water ?	1356 (s)	-CH ₃ bend.
3370 (w)	-OH stretch.	1238 (s)	-CH bend.
2900 (s)	-CH ₂ stretch.	1160 (s)	-CO-CH ₃
2845 (s)	-CH ₂ stretch.	1107 (w)	
1710 (s)	-C=O	960 (w),	$\begin{array}{c} \text{C} \\ \\ \text{C} - \text{C} - \text{C} \\ \end{array}$ distort.
1426 (s)	-CH ₂ bend.		

Table 6-2.

Changes in Infra-red Spectrum during the Colouration of Polymethyl Vinyl ketone.

A). Disappearance or Reduction of Absorption.

Frequency. cm. ⁻¹	Assignment.
3550	-OH , water?
1710	-C=O
1356	-CH ₃ bending.
1160	-CO-CH ₃



I. R. SPECTRA OF DEGRADED POLYME THYL
VINYL KETONE.

Figure 6-5.

Table 6-2.

B). Appearance of new absorption.

Frequency cm. ⁻¹	Assignment
1650	conjugated -C O
1615	-C=C-
1580	conjugated, -C=C-
1500- 800	wide absorption,

indefinite peaks at 1395, 1314, 1254, 1200, 1156, 1110, 1000, 840 and 808 cm.⁻¹

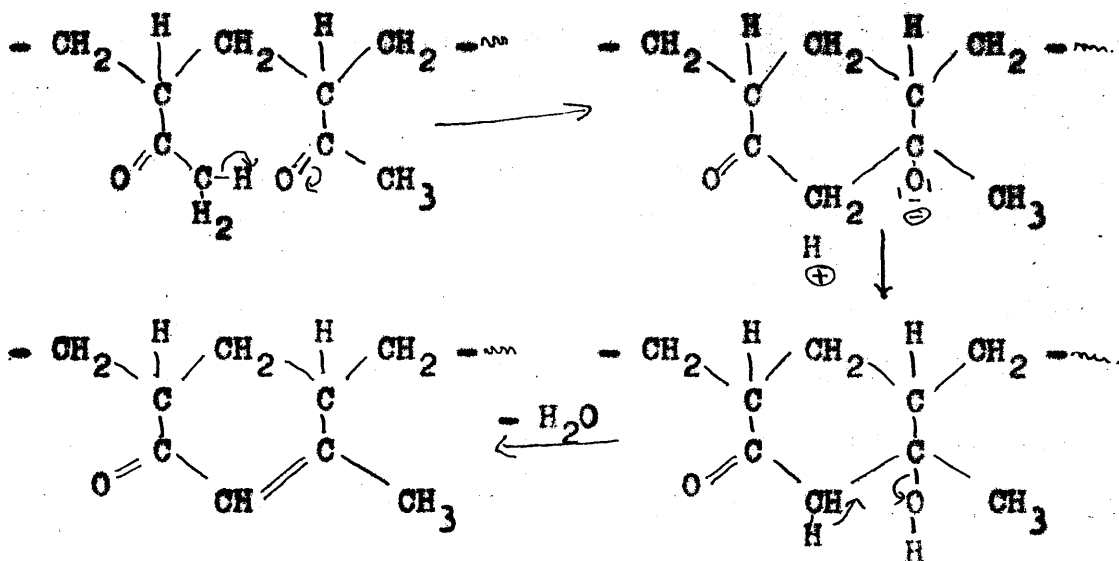
Table 6-2 shows that the carbonyl and methyl groups are disappearing with the production of new absorption in the region 1680-1500 cm.⁻¹, due to the production of unsaturated carbonyl groups and carbon-carbon double bonds, conjugated and unconjugated. This is in agreement with Marvel and Levesque's theory of an Aldol type condensation reaction followed by elimination of water, between neighbouring methyl and carbonyl groups.

The nature of the development of carbon-carbon double bond absorption, in the region 1680-1500 cm.⁻¹, is different from that of the carbon-nitrogen absorption in polyacrylonitrile, in this region. In particular, there is no observed shift in intensity from higher to lower wave-

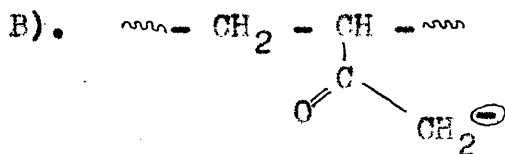
numbers as the reaction develops, as there is in polyacrylonitrile, see page 41 and figure 3-4. This is a result of the reaction in polymethyl vinyl ketone being a random process involving any two neighbouring groups, unlike that of polyacrylonitrile which is a step-wise condensation involving cyanide groups in turn along the chain. There is, thus, not the same lengthening of conjugated sequences, and so there is not the same tendency for the absorption to extend to lower wave-numbers. Similarly the colour does not show the same tendency to spread to the red end of the spectrum.

The colour reaction in polymethyl vinyl ketone would appear to be very much more simpler than that in polyacrylonitrile, since it involves only one general condensation process. It has no corresponding initiation step and each act of condensation between pairs of adjacent units is independent of all others. The reaction is also not complicated by the production of cross-links; the polymer remains soluble through the whole degradation reaction.

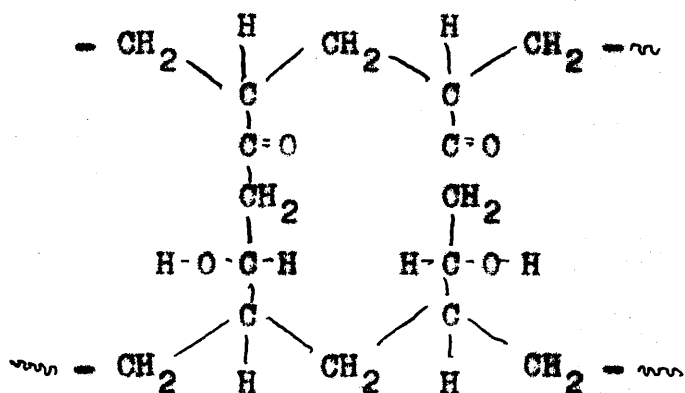
In the light of the evidence for the Aldol condensation reaction in general, ^{49,50} the reaction mechanism would appear to be,



some evidence for this postulated mechanism can be had from the fact that alkalis, particularly caustic alkalis, cause the colouration of polymethyl vinyl ketone in solution, with the evolution of heat, due in this case presumably to the enhanced activity of the ion intermediate,



in furthering the condensation reaction. However, strong alkali treatment gives a highly insoluble (cross-linked) material, whose infra-red spectrum shows the presence of considerable amounts of hydroxyl groups, that is, cross-links of this type,



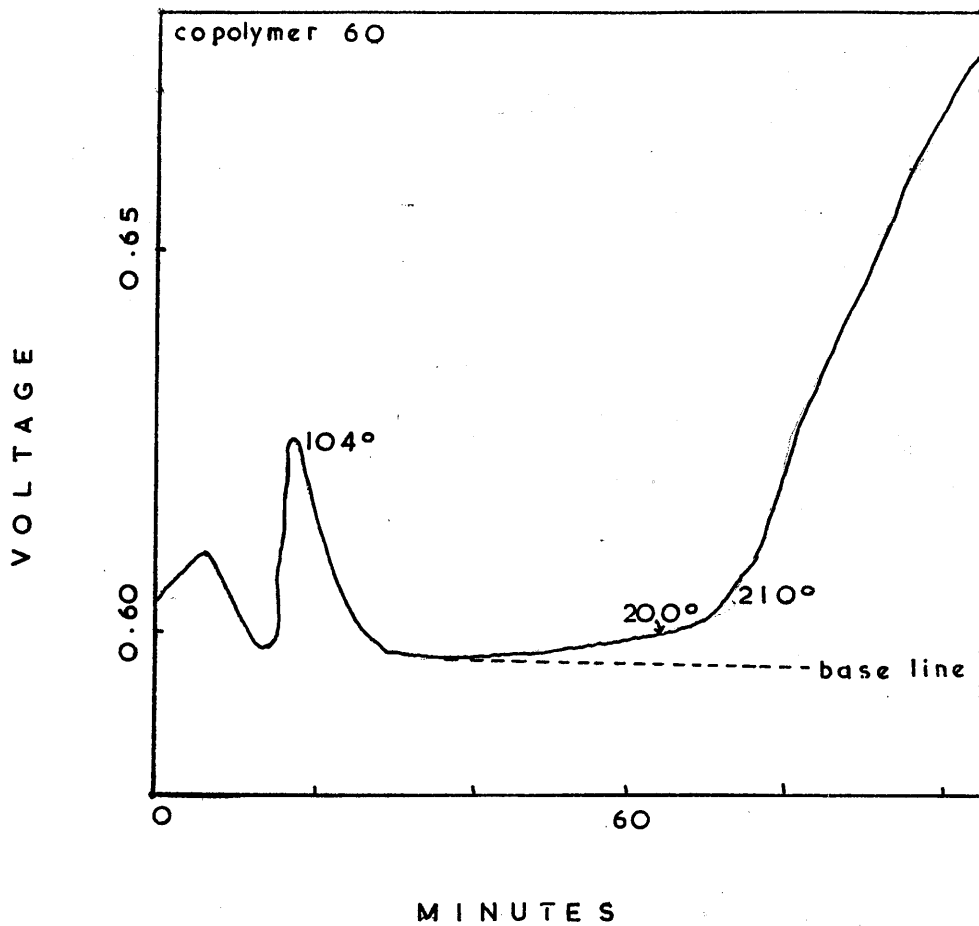
but nevertheless, further evidence for the ionic mechanism involving the methyl group of the methyl ketone.

4). Colouration of Methyl Vinyl Ketone and Acrylonitrile Copolymers.

On studying the effect of methyl vinyl ketone units on the colouration properties of acrylonitrile copolymers, it was found that these units accelerated the reaction and also reacted with the colouring unit in such a way as to maintain the average length of the conjugated sequences. In particular, figures 5-5 and 5-6, and table 5-3, page 85, shows that these units do not stop the colour reaction. A 50-50 copolymer can still colour appreciably.

The reactivity ratios for the system, see page 23,

$$r_1 = \frac{K_{p 11}}{K_{p 12}} = 0.61, \quad \text{and} \quad r_2 = \frac{K_{p 22}}{K_{p 21}} = 1.78, \quad (\text{1 denotes})$$



THERMAL DEGRADATION OF MVK
COPOLYMERS

Figure 6-6

acrylonitrile, and 2 methyl vinyl ketone), predict that the monomers should be arranged predominately in an alternating manner. One is then forced to accept that methyl vinyl ketone units do react to maintain the conjugation and also initiate further condensation.

The copolymers were further studied using the dynamic molecular still and Pirani gauge, with the result illustrated in figure 6-6. This shows that volatile materials are evolved at the colouration temperature, 200°C, unlike polyacrylonitrile, see page 35. The rates of volatilisation were measured by the loss in weight of the sample, and the volatile material condensed and analysed. It proved by infra-red spectroscopy to be water. In figure 6-7 the fractional percentage water evolved after one hour of degradation at 200°C is plotted against the percentage methyl vinyl ketone units incorporated in the chain. This clearly indicates that water is most readily eliminated from the copolymers of low methyl vinyl ketone content, where a considerable amount of the methyl vinyl ketone will be isolated by acrylonitrile units. As more and more methyl vinyl ketone units are added to the copolymer water is less readily evolved.

In the low methyl vinyl ketone containing copolymers there must be large segments of the chain

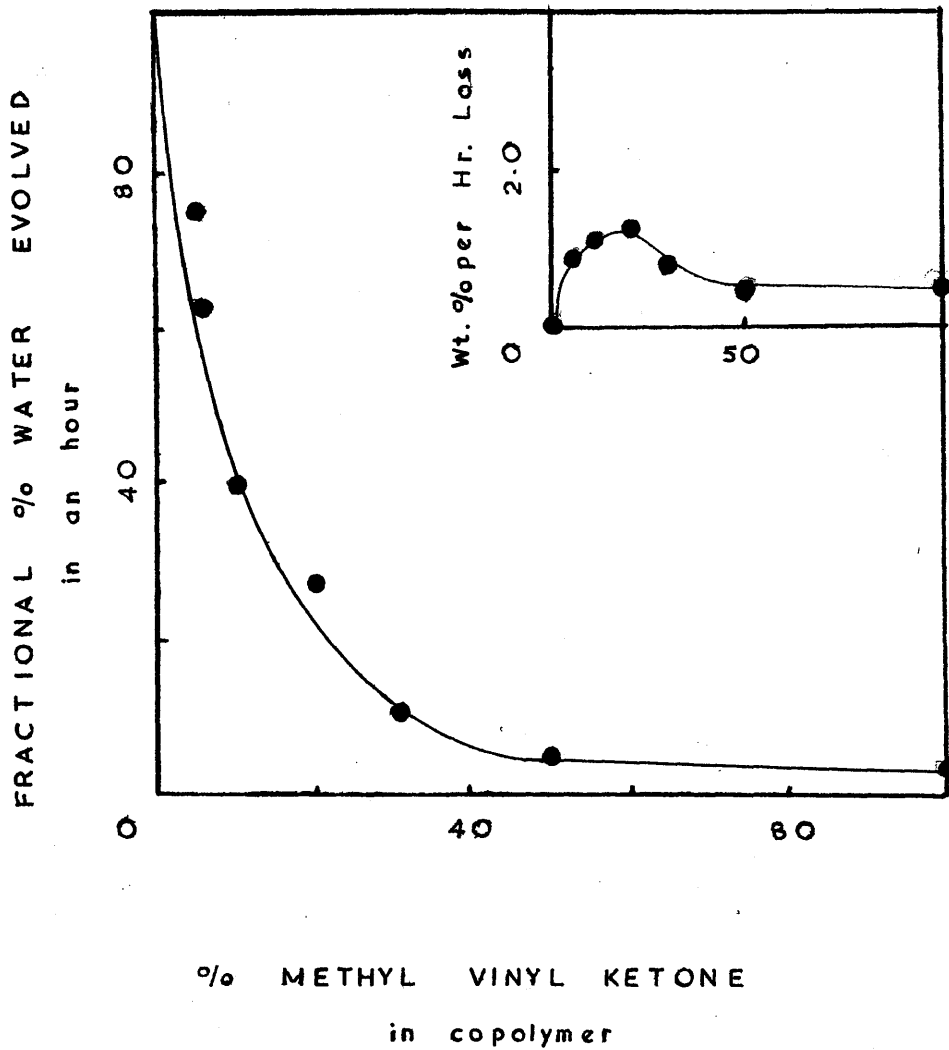
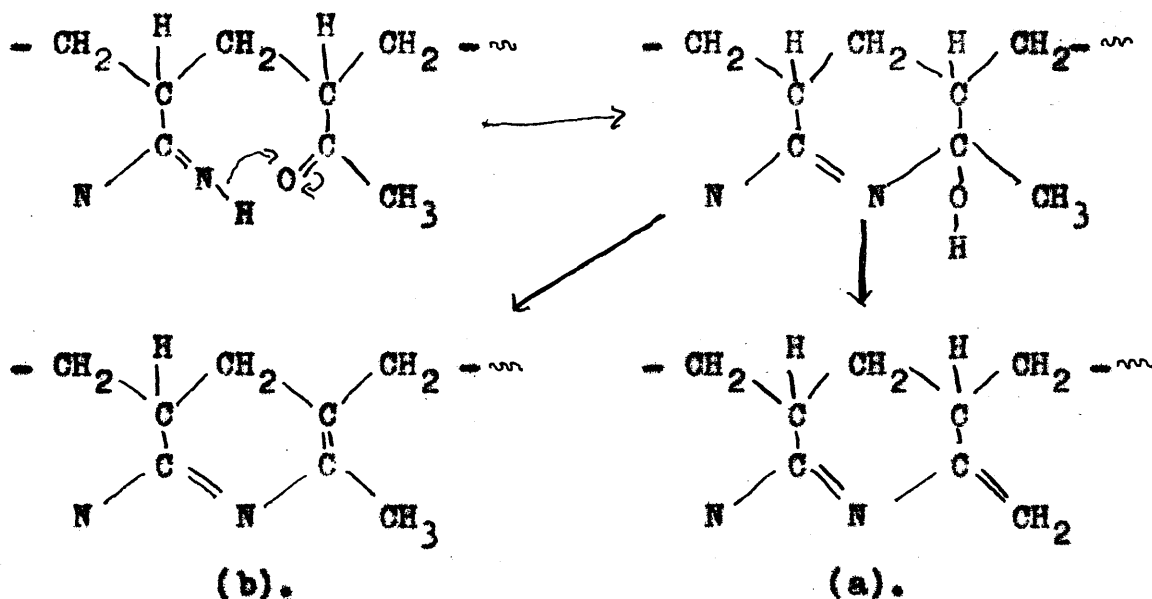
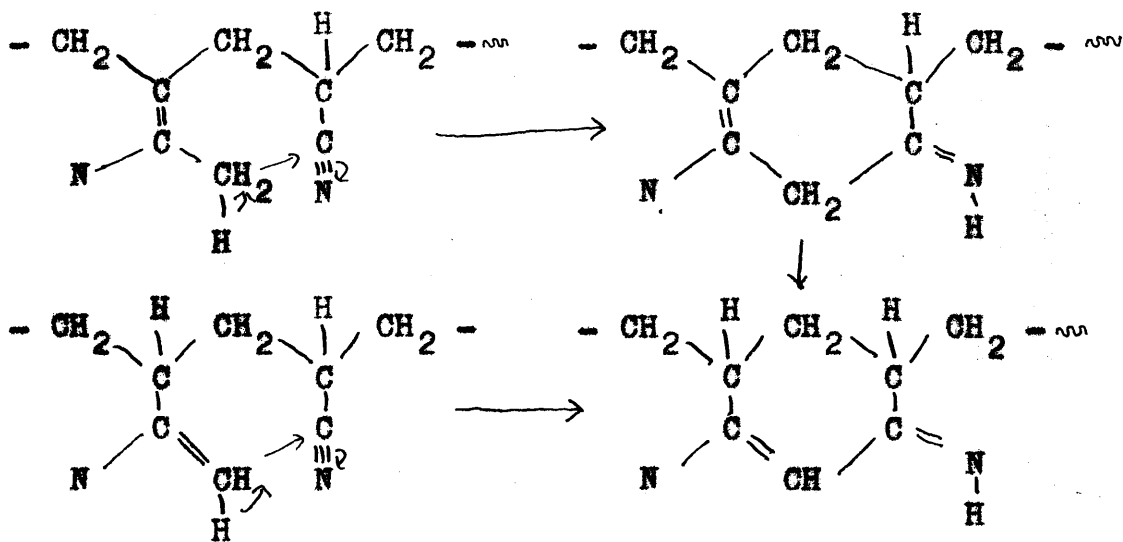


Figure 6-7.

made up entirely of acrylonitrile units, and these must be capable of condensing in the usual manner to produce the normal colour-producing carbon-nitrogen conjugation terminated by an imine group. This imine group should react readily with an isolated carbonyl group, as shown, and on eliminating water lengthen the conjugation, by the production of an exocyclic methylene group or an endocyclic double bond;



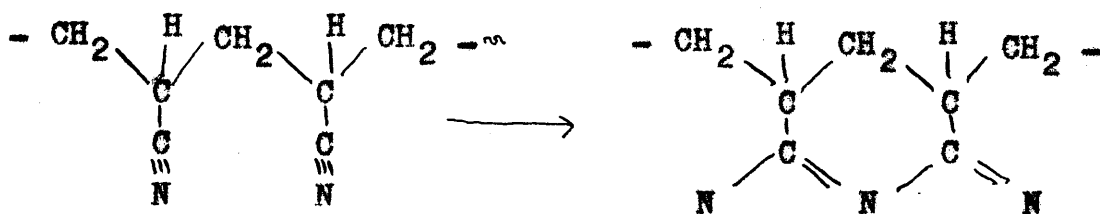
In both cases (a) and (b) the methylene and methyl groups are activated by the conjugated sequences and so ought to be capable of initiating further cyanide condensation, that is;



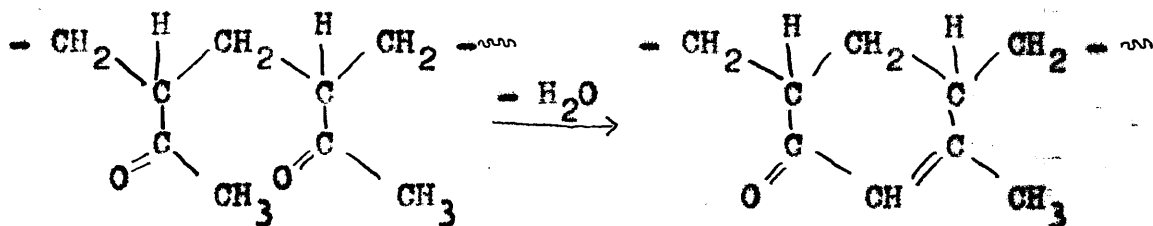
In this way an isolated methyl vinyl ketone unit would take part in the condensation reaction and maintain the conjugation. The water must be eliminated in this reaction at a faster rate than in the normal polymethyl vinyl ketone condensation.

There would appear to be four reactions occurring during the colouration of these copolymers which produce and maintain conjugation sequences.

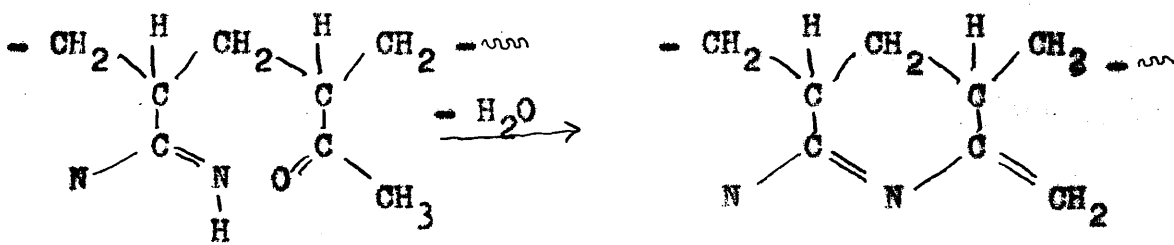
1). The cyanide condensation reaction, as in polyacrylonitrile, and so important in the colouration of the high acrylonitrile copolymers:-



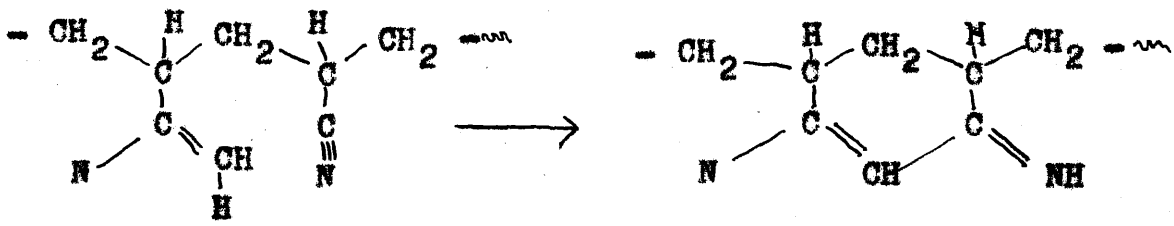
2). The methyl and carbonyl groups condensation reaction as in pure polymethyl vinyl ketone, and so important in the colouration of high methyl vinyl ketone containing copolymers. This reaction proceeds slowly at the temperature of colouration, at 200°C.



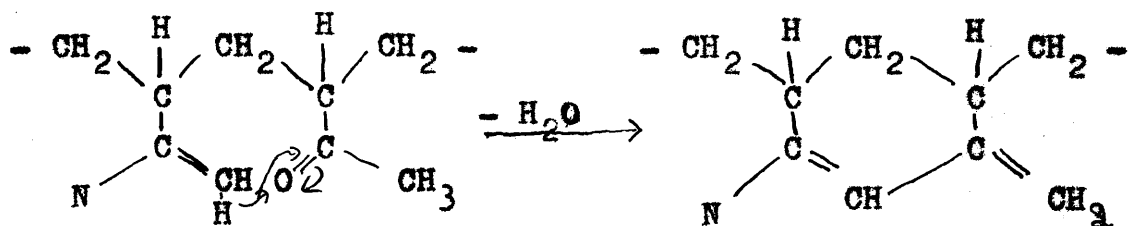
3). An elimination reaction between an imine unit and a carbonyl group. This reaction we postulate occurs at a much more rapid rate than that involving two methyl ketone units, that is reaction 2).



4). A reaction between a methyl, or methylene, group activated by conjugated double bonds in initiating cyanide condensation.



In addition to these reactions there is also a fifth, necessary to account for the colouration reaction proceeding through two or more isolated methyl vinyl ketone units.



This reaction is very similar to the normal condensation and elimination reaction of polymethyl vinyl ketone.

On the basis of reaction 3) and 5) one would expect compounds such as amines, amides, etc., to be good catalysts for the colouration reaction in pure polymethyl vinyl ketone. This is indeed the case. Model compounds (10 mol.%) were added to polymethyl vinyl ketone samples and degraded at 110°C, in a nitrogen oven, see table 6-1a. Only primary and secondary amines were found to be very efficient catalysts for the reaction; indeed, the normal reaction at this temperature was completely swamped. No other reagents, including organic acids, phenols, and tertiary amines, appreciably altered this rate. It may have been, perhaps, that the self condensation reaction was too rapid to allow these reagents to effectively catalyse the reaction. However, it did conclusively show

that amines with a free hydrogen atom were very effective in catalysing the colouration reaction.

This has been noted for the Aldol condensation reaction in general. ^{49,50} Hammett, in his book, page 344 relates, " The diacetone alcohol reaction is specifically catalysed by ammonia, and by primary and secondary amines. Tertiary amines only catalyse the reaction to an extent measurable by the hydroxyl ion concentration of their solution. " Some catalytic constants for this reaction are reproduced in table 6-2a.

Table 6-1a.

Effect of Model Compounds on Colouration of Polymethyl Vinyl Ketone, at 110°C.

1). Amides and amines.

Model Compounds. (10 % mol.)	Colour.		
	30 min.	60 min.	24 hours.
b-naphthylamine.	dark red	dark red	black
benzylamine.	orange	dark red	black
aniline.	dark red	dark red	black
diphenyl amine	dark red	dark red	black
triphenyl amine	white	yellow	orange
succinimide	white	yellow	orange
-----	white	yellow	orange

2). Other Reagents,

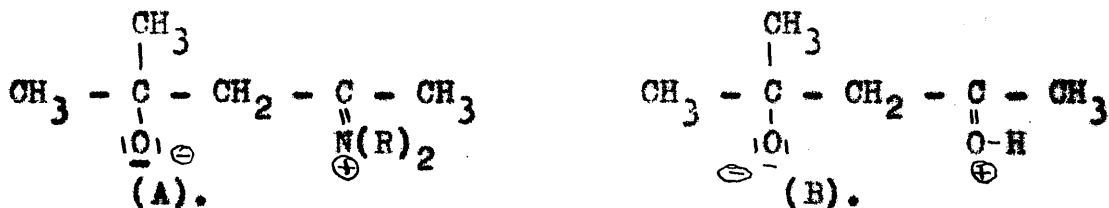
Phenol, hydroquinone, benzoic acid, benzyl cyanide, acetophenone, and cumene were all tested. There was no appreciable acceleration of the colour reaction.

Table 6-2a.

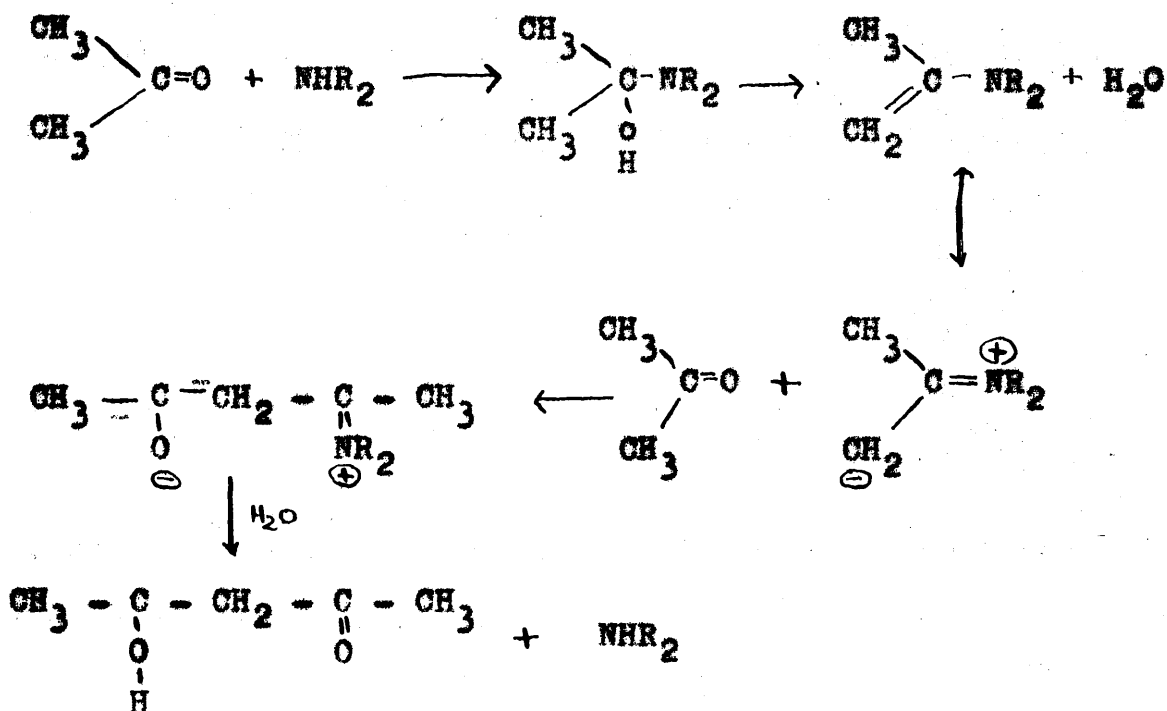
Catalytic Constants in the Diacetone Alcohol Reaction.

Catalyst.	OH ⁻	CH ₃ NH ₂	(CH ₃) ₂ NH	(CH ₃) ₃ N	(C ₂ H ₅) ₃ N
10 ⁴ k	17.8	2.22	0.147	0.	0.

It is presumed that the Aldol condensation reaction in the presence of an amine involves the production of a dipolar ion intermediate (A), which cannot be produced with tertiary amines. This immonium ion (A) accomplishes the rate determining step more quickly than would the corresponding carbonyl intermediate (B)



The path of the diacetone condensation reaction, in the presence of amines, would then appear to be:-



Other organic catalysts may catalyse the Aldol condensation and water elimination reaction in polymethyl vinyl ketone but they involve the production of the carbonyl zwitterion intermediate (B), as in the normal condensation and so their catalytic effect may not be so apparent as that of amines, which involve the more readily formed immonium ion.

Chapter 7.

Summary of the Present Work.

It is obvious from the observations made in the previous chapters that the colouration reaction in polyacrylonitrile is fundamentally the same as that in polymethacrylonitrile: the differences in the two reactions arise from the slight difference in the molecular structure of the two polymers. Polymethacrylonitrile can be colour stabilised by the elimination of initiation sites - removal of acid impurity and oxygenated structures. Polyacrylonitrile cannot be colour stabilised since it contains its own self-initiating unit, the tertiary carbon-hydrogen bond. It is, however, the same type of initiation step as in polymethacrylonitrile, since the same reagents initiate the colour reaction.

Polymethacrylonitrile remains soluble, even when degraded to an advanced stage of colouration, unlike polyacrylonitrile which becomes insoluble before it colours.

The propagation reaction is not limited to one chain but can jump from one chain to another producing a cross-link. The incidence of cross-linking is so high that the polymer becomes insoluble before the conjugation sequences become absorbing. Cross-linking cannot occur in polymethacrylonitrile since the cyanide groups on neighbouring chains are kept sufficiently remote, by the intervention of the methyl groups, as to prevent reaction between them.

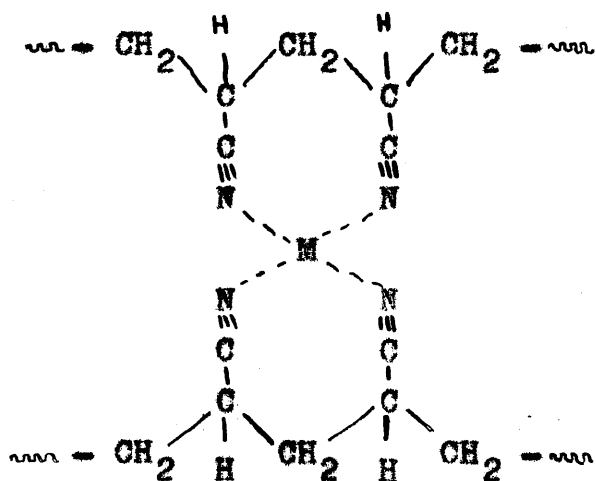
Polyacrylonitrile has been widely used as an industrial fibre but its discolouration, on thermal treatment, is a considerable problem. Particularly, since the polymer is spun from solution and most of the solvents are efficient colour initiators. This work suggests that this thermal colouration is an inherent property of the molecule, in the form of the carbon-hydrogen centres which initiate the colouration of polyacrylonitrile. The initiation of the colour reaction cannot be prevented without altering the monomer structure, and so colour stability can only be prevented by stopping the propagation process in the reaction. This could best be done by copolymerising acrylonitrile with a carefully chosen monomer.

This monomer must,

1). not, in itself, initiate the colour reaction,

2). not condense with the colouring unit, and
3). hold the chains apart to prevent initiation and propagation cross-linking. Styrene and methyl methacrylate were found to behave in the above manner, but so much of these monomers were required to stop the reaction that the copolymer lost the desired fibre properties.

To maintain fibre properties in the polymer the intermolecular forces must be maintained, to prevent colouration and propagation cross-linking the chains must be kept apart; it would seem then that fibre properties and colour stability were direct antithesis. It might be achieved, however, by chelating the cyanide groups on neighbouring chains by some metal ion complex, of the type:-



This would allow strong intermolecular attraction to be maintained and yet keep the chains quite remote

from one another. Intramolecular condensation, in such a system could be prevented by the incorporation of an inert monomer unit at frequent intervals along the chain.

Chelation of this type may possibly explain the action of large numbers of salts which have been cited as giving improved colour stability to polyacrylonitrile.

Suggestions for Future Research.

The differences between the colouration reaction in polyacrylonitrile and polymethacrylonitrile stress the effect of the second substituent on the reaction mechanism. The change from a reactive hydrogen atom, which is quite polar in nature and capable of dipole interactions with cyanide groups on neighbouring chains, to the inert bulky methyl group, considerably modifies the reaction. One goes from an almost intermolecular condensation reaction in polyacrylonitrile, to an entirely intramolecular condensation in polymethacrylonitrile. Further studies into the possible colour reaction in other alpha substituted acrylonitrile polymers would clearly be of interest.

Poly- α -chloroacrylonitrile, polyvinylidene cyanide, poly- α -phenylacrylonitrile, and poly- α -carbomethoxy-acrylonitrile, spring immediately to mind as obvious choices for such a study, since these polymers contain both polar and bulky substituent groups. These polymers may also be capable of undergoing other reactions, characteristic of the second group which may alter the colour reaction. Poly- α -chloroacrylonitrile, for example, may undergo at least three degradation reactions, namely colouration due to the condensation of cyanide groups, depolymerisation because it is a di-substituted monomer, like poly methyl methacrylate, or dehydrochlorination because it is also a substituted polyvinyl chloride. The interplay of these three reactions are of considerable interest.

APPENDIX.

List of Polymers.

A). Bulk Polymerised.

Sample NO.	Temp. °C.	Initiator Conc. % wt. per vol.	% Polymn.
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1). Polyacrylonitrile.

2	30.	0.124	6.1
9	30.	0.145	3.5
20	30	0.154	5.1
29	30	0.166	10.8
67	30	0.153	6.3

2). Polymethacrylonitrile.

32	60	0.167	14.0
40	30	0.176	5. approx

3). Polymethyl Vinyl Ketone.

70	42	0.483	10. approx.
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Initiator used in all polymerisation was

a:a'-azo-bis-isobutyronitrile.

B). Solution Polymerisation.

Sample No.	Temp. °C.	Initiator Conc. % wt. per vol.	Solvent/ Monomer vol. ratio
26 dmf	30	0.227	5.71
27 sn	65	0.241	7.31

sn - succinonitrile dmf - dimethyl formamide.

List of Copolymers.

Bulk Polymerisations.

Sample No.	Monomer Ratio A / B.	Copolymer ratio A / B.	Initiator Conc.	% B.
1). Acrylonitrile (A)-Methyl Vinyl Ketone (B).				
38	3.89	3.11	0.139	24.3
54	31.3	19.0	0.350	5.0
55	15.8	9.53	0.330	9.47
56	8.3	4.41	0.346	18.5
58	1.73	1.00	0.339	50.0
60	3.92	2.33	0.328	30.0

Sample No.	Monomer Ratio. A / B	Copolymer Ratio. A / B.	Initiator Conc.	% B.
2). Acrylonitrile (A) - Acrylic Acid (B).				
6	226.	70.4	0.149	1.4
7	115.	36.0	0.160	2.7
8	55.0	17.5	0.160	5.4
27	7.40	3.00	0.141	25.0
28	19.00	7.00	0.144	12.5
14	1.00	0.515	0.149	34.0
15	0.77	0.502	0.114	34.2
16	0.34	0.256	0.002	79.6
17	0.111	0.088	0.002	91.9

3). Acrylonitrile (A)- Methacrylonitrile (B).

47	70.2	18.8	0.350	5.5
48	14.3	3.87	0.382	20.5
49	8.57	2.42	0.354	29.3
46	33.4	8.97	0.356	10.1
35	3.5	0.975	0.502	50.6
36	0.636	0.250	0.225	80.0
37	0.306	0.111	0.348	90.0
41	0.480	0.177	0.355	85.0

Sample No.	Monomer Ratio A / B.	Copolymer Ratio A / B.	Initiator Conc.	% A
4). Acrylonitrile (B) - Methyl Methacrylate (A).				
44	0.0087	0.0467	0.316	4.44
52	0.0154	0.0807	0.314	7.46
53	0.0303	0.153	0.307	13.3
64	0.0547	0.234	0.364	19.0
65	0.111	0.393	0.316	28.2
50	0.105	0.378	0.325	27.5
66	0.378	0.925	0.289	48.1

5). Styrene (A) - Acrylonitrile (B).

43	0.00434	0.0800	0.313	7.1
59	0.00429	0.0806	0.308	7.46
61	0.00973	0.163	0.313	14.04
57	0.0168	0.252	0.327	20.14
62	0.0306	0.427	0.363	29.9
51	0.0942	0.674	0.334	40.3
63	0.348	0.955	0.368	48.9

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