KINETICS OF THE ALKALINE HYDROLYSIS OF
POLY-\((m\text{-ACETAMIDOSTYRENE})\) AND SOME REACTIONS
OF POLY-\((m\text{-AMINOSTYRENE})\)

Being a Thesis submitted to the
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ABSTRACT OF THE THESIS

\textit{m}-Aminostyrene has been synthesised from acetophenone by the known route. It has been homopolymerised and copolymerised with styrene by means of 2,2'-azoisobutyronitrile as initiator.

Two homopolymers, prepared with different initiator concentrations, and the copolymer have been converted into their acetyl derivatives, and these compounds have been characterised by intrinsic viscosity determinations in benzyl alcohol and elemental analysis. A kinetic study has been made of the hydrolysis, in homogeneous solution by benzyl alcoholic potassium hydroxide at 145\degree C, of these polymeric compounds and also acetanilide and acetyl-\textit{m}-cumidide.

The rate constants for the hydrolysis of the polymeric compounds have been compared with those of acetanilide and acetyl-\textit{m}-cumidide in order to assess the contribution of the polymeric structure to the rate of hydrolysis, and to ascertain if any specifically macromolecular reactivity factors operate in the hydrolysis of those polymeric acetyl-amino compounds. It is inferred that hydrogen bonding between side-groups is an important factor.

Two homopolymers of \textit{m}-aminostyrene have been diazotised, yielding poly(\textit{m}-styrenediazonium chloride) which has been subjected to the standard diazonium reactions in which nitrogen atoms are retained in the final molecule, namely, reduction to the corresponding hydrazine, and
coupling with amines and phenols. An impure polyhydrazine was prepared. Poly(styrene-\text{-}m\text{-}diazonium chloride) undergoes azo coupling substantially to completion with \( \beta \)-naphthol, and to a considerable degree with 2,5-dimethyl- and 2,5-dimethoxy-aniline. The latter products underwent further diazotisation and coupling to yield polymeric disazo compounds.
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HISTORICAL INTRODUCTION
FREE RADICAL ADDITION POLYMERIZATION

HISTORICAL

Proteins and rubbers, examples of high molecular weight compounds have long interested chemists, because of the distinct properties shown by them, which were not found with small molecules. It was initially thought that polymeric materials were made up of small molecules held together by some "valency force", which was non operative in small molecules. This theory was initiated by Graham\(^{(1)}\) to account for the slow diffusion rates of polymeric materials and their inability to pass through semi-permeable membranes. This type of material he named colloidal.

The polymeric nature of these materials was first indicated in 1871\(^{(2)}\) but it was not until about 1930 that this view was finally accepted.

Staudinger\(^{(3)}\) in 1920 proposed chain formulae for poly(styrene) and poly(oxymethylene),

\[\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_2-\quad \text{CH}_2\text{O}-\text{CH}_2\text{O}-\text{CH}_2\text{O}\]

and decried the then accepted view of considering high molecular weight materials as aggregates of small molecules held together by some partial valency. Long-chain structures had already been
put forward for rubber by Pickles and by Lebedev for butadiene, for which Lebedev and Harries had previously indicated a cyclic structure, the cyclo-octadiene structure, as the aggregating unit.

\[
\begin{align*}
\text{CH}_2\text{CH}=\text{CH}-\text{CH}_2 \\
\text{CH}_2\text{CH}=\text{CH}-\text{CH}_2
\end{align*}
\]

Staudinger attributed the colloidal properties of polymers to their size, and suggested that the molecules might contain many hundreds of units.

He accounted for the end groups of a polymer chain with the idea that a free radical at the end of a long chain would be unreactive, a view he later modified, suggesting the free radical-ends might combine by cyclization.

Staudinger's views were supported by other authors, notably K. Meyer and H. Mark, who, together with Carothers, who published his first paper on synthetic polymers in 1929, were responsible for placing polymer chemistry on a firm chemical foundation.

The major support for Staudinger's chain concept was provided by the X-ray diffraction technique of Sponsler and Dove, who showed cellulose fibres to possess a chain structure, made from a large number of units. This method has been applied to a large number of linear polymers giving characteristic fibre patterns.

The term polymer was introduced by Berzelius who recognised
that two compounds may have the same composition, but differ, in respect to their molecular weights. The idea that polymerisation was a reaction capable of proceeding indefinitely was put forward by Carothers, who described polymers in terms of recurring units, and classified polymerisation in terms of addition or condensation polymerisation. In condensation polymerisation, a loss of a simple molecule occurs, as each polymer unit is added and hence the composition of the polymer and that of the monomer from which it was derived are different.

In addition polymerisation no loss occurs as each monomer unit is added; and the composition of the monomer and polymer are identical.

The first free radical mechanism for a polymerisation was proposed for the gas phase polymerisation of ethylene, by Taylor and Bates. Staudinger, independently of these authors, proposed a similar mechanism for liquid phase polymerisation:

\[
\text{R. CH}_2=\text{CHX} \rightarrow \text{R-CH}_2-\text{CH} \bigg[ \frac{\text{CH}_2=\text{CHX}}{X} \bigg] \rightarrow \text{R-CH}_2-\text{CH-CH}_2-\text{CH}.
\]

The mechanism was in accord with observed experimental data, notably that during the polymerisation the system contained relatively high concentrations of high polymer and unchanged monomer, and few intermediates such as dimers and trimers.

The theory of addition polymerisation was formulated by Chalmers, who, from a study of the available literature, described
addition polymerisation as a reaction taking place by a chain mechanism, in which a slow initiation step was followed by rapid propagation steps, in which a large number of monomer units were added to the growing chain.

The concept of a chain reaction has been investigated and verified by other authors namely: Marvel, Flory, Dostal and Schulz.

FREE RADICAL COPOLYMERISATION

Copolymerisation is the process in which two different vinyl monomers enter the same chain, in more or less random fashion, and in doing so, form a polymer with two different recurring units.

HISTORICAL

The study of copolymerisation phenomena has lagged behind the study of the properties of the industrially-important materials obtained in this manner.

The phenomena shown by many monomers, that of reacting more readily with one comonomer than another was first shown in the 1930's. It was found by Staudinger that on fractionation of a vinyl acetate, vinyl chloride copolymer prepared from an equimolar mixture of the two monomers, ratios of vinyl chloride to vinyl acetate of 9:3, 7:3 and 5:7 were amongst the fractions, but no fraction containing a 1:1 ratio was found. Similarly, about the same period acrylic esters were shown
to copolymerise with vinyl chloride, the acrylic ester entering into the copolymer at a faster rate than vinyl chloride giving, whilst the feed stock lasted, a copolymer rich in acrylate; the copolymer formed later was correspondingly rich in vinyl chloride. This occurred for a "stationary" monomer feed; it has been found that this type of change can be partially obviated by the gradual addition of the acrylate monomer (20).

It was also found that some monomers which showed only a slight tendency to homopolymerise, could be copolymerised quite readily, an example being furnished by maleic anhydride copolymers with styrene (21) and vinyl chloride (22).

Some cases were found where neither comonomer would homopolymerise but gave a copolymer of 1:1 ratio no matter what ratio of monomer feed was used. Examples of this behaviour are the copolymers formed between maleic anhydride and stilbene, and ethyl fumarate and isobutylene, in which the two types of unit are in strictly alternating sequence.

FREE RADICAL INITIATED POLYMERISATION

Mode of Formation of Polymers

It is now believed that this type of polymerisation has three distinct steps, designated, initiation, propagation and termination. These steps are equally applicable to polymerisation by a non free
radical mechanism, for example polymerisations effected by anionic or
cationic initiators, or by photo-activation of the monomer.

**Initiation of Polymerisation**

Pure monomers in some cases are capable of spontaneous poly-
merisation, but in most cases "active centres" must be produced in
order to promote polymerisation. This can be achieved by the intro-
duction of substances known to be decomposed by heat or light to give
free radicals. The organic peroxides, hydroperoxides and azonitriles
are amongst the most common initiators used, and are added in very low
concentration.

Benzoyl peroxide is often used; it is known to decompose
between 50-100° releasing free radicals\(^{(24,25,26)}\) in the following
manner:

\[
(\text{PhCOO})_2 \rightarrow 2\text{PhCOO} \rightarrow 2\text{Ph} + \text{CO}_2
\]

This initiator suffers from two disadvantages however:

(a) It is an oxidising agent, and this can lead to unwanted effects,
as in the polymerisation of \(m\)-aminostyrene\(^{(27)}\).

(b) It can undergo radical-induced decomposition.

\[
\text{R}-\text{CH}_2\text{-CH.} + (\text{PhCOO})_2 \rightarrow \text{R}-\text{CH}_2\text{-CH-C-COPh} + \text{PhCOO}.
\]

with the resultant termination of a growing chain.

The azonitriles, for example, 2,2'-azo-isobutyronitrile\(^{(28,29)}\),
decompose by a first order mechanism free from induced radical breakdown, in the following manner(30).

\[
\begin{align*}
\text{CH}_3 & \text{CN} & \text{CN} & \text{CH}_3 \\
\text{C} & \text{N} & \text{N} & \text{C} & \text{CH}_3
\end{align*}
\]

\[\text{CN} \quad \text{\textlongrightarrow} \quad \text{2 CH}_3\text{C.} \quad + \quad \text{N}_2\]

Other initiators are known to decompose to give free radicals, the inorganic peroxides, persulphates and permanganates, and hydrogen peroxide are often used, alone, or in conjunction with activators. Activators are often salts of metals of variable valency.

The redox systems of peroxide or hydroperoxide and reducing agents are often used in emulsion polymerisation at room temperature and below 0°C (31,32). For example, the system

\[
\text{H}_2\text{O}_2 \quad + \quad \text{Fe}^{++} \rightarrow \text{OH}^+ \quad + \quad \text{OH}^- \quad + \quad \text{Fe}^{+++} \quad (33)
\]

In the activation of a given monomer the process can occur in two ways.

(1) \( \text{R.} \quad + \quad \text{CH}_2=\text{CHX} \rightarrow \text{R-CH}_2=\text{CHX} \)

(2) \( \text{R.} \quad + \quad \text{CH}_2=\text{CHX} \rightarrow \text{R-CHX-CH}_2 \)

and the rate of formation of the two entities depends upon the relative stability of their structures. It is found that (1) predominates by virtue of the resonance stabilisation frequently afforded by the substituent in this structure as with styrene.
Polymers initiated by free radicals derived from initiators, have been shown to contain initiator fragments in the final molecule by chemical\textsuperscript{34} and physical\textsuperscript{30} methods.

**Propagation of Polymerisation**

This is the rapid growth step, and can occur by two methods.

The monomer may add to the end of a growing chain bearing a free radical in a head to head or head to tail followed by a tail to tail manner respectively, in cases of regular addition; if each monomer unit is regarded in the following manner.

1. head to head or tail to tail.

\[
\begin{align*}
R-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}- & \\
X & X & X & X & X
\end{align*}
\]

2. head to tail.

\[
\begin{align*}
R-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}- & \\
X & X & X & X & X
\end{align*}
\]

3. random addition.

\[
\begin{align*}
R-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}- & \\
X & X & X & X & X
\end{align*}
\]
It is found that energetically head to tail addition is more probable, since the new radical which is formed possesses the same resonance energy as the one it replaces, and the process is sterically more favourable. Head to head addition which would be followed by tail to tail addition involves energy changes which make it less probable.

It has been shown by various workers that head to head structures, if present, are rare. Marvel and Denoon have shown that poly(vinyl alcohol) prepared by the hydrolysis of poly(vinyl acetate), consumed very small quantities of periodic acid, which is capable of splitting 1,2 glycol units present in this case as tail to tail linkages.

-CH₂-CH(OH)-CH₂- CH(OH)-CH(OH)- CH₂-CH(OH)-

Other workers have shown that the actual consumption is so small that the number of 1,2 units cannot be determined in this manner.

The result of the reaction will, however, be cleavage of the chain, with a resultant decrease in molecular weight, which has been demonstrated by the decreasing viscosity of the reaction mixture; hence some head to head linkages are present.

In a number of other cases where the detection method is less sensitive no evidence of head to head linkages have been found, and it is concluded that for vinyl polymers head to tail linkages predominate. Staudinger has also confirmed that this is the case by pyrolysis of poly(styrene) at 300°C and analysis of the product.
The following compounds were found:

\[
\begin{align*}
\text{CH}_2\text{-CH}_2\text{-CH}_2 & \quad \text{CH}_2\text{-CH}_2\text{-CH}\text{-CH}_2\text{-CH}_2 \\
\text{C}_6\text{H}_5 & \quad \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5
\end{align*}
\]

and

\[
\begin{array}{c}
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph}
\end{array}
\]

Compounds having phenyl groups on adjacent carbon atoms were not however found, indicating the predominance of head to tail addition.

**Termination of Polymerisation**

Termination of a growing chain can occur by several methods.

(a) **Coupling**

This is the termination of a growing chain by combination of two radicals.

\[
\begin{array}{c}
\text{R-CH}_2\text{-CH}_2\text{-CH}_2 \quad + \\
\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2 \quad \text{R}
\end{array}
\]

\[
\begin{array}{c}
\text{X} \\
\text{X} \\
\text{X}
\end{array}
\]

(b) **Disproportionation**

This is an example of hydrogen transfer from one molecule to another, whereby both chains are terminated.

\[
\begin{align*}
2\text{R-(CH}_2\text{CHX)}_n\text{-CH}_2\text{-CHX}. & \quad \text{R-(CH}_2\text{CHX)}_n\text{-CH}_2\text{-CHX} \\
\text{R(CH}_2\text{CHX)}_n\text{CH}_2\text{CH}_2\text{X} + \\
\text{R(CH}_2\text{CHX)}_n\text{CH}_2\text{CH}_2\text{X}
\end{align*}
\]
It has been shown that for polystyrene (37) the mode of termination at 25° is mainly combination whilst for poly(methyl methacrylate) the mode of termination is in the ratio of disproportionation (2 parts) to combination (1 part). The data was obtained from studies using radioactive initiators, and the number of initiator fragments per molecule were estimated.

(c) Chain transfer Reactions

These reactions involve the termination of one growing chain, and the commencement of another.

For example, the solvent transfer reaction occurring when styrene is polymerised in carbon tetrachloride as solvent (40).

\[ R(CH_2-CHX)_n + CCl_4 \rightarrow R(CH_2-CHX)_n Cl + .CCl_3 \]

\[ .CCl_3 + n (CH_2=CHX) \rightarrow Cl_3C(CH_2-CHX)_n \]

Another transfer reaction involving termination is that of initiator transfer, as previously described for benzoyl peroxide.

Other transfer reactions can occur:

Monomer Transfer

\[ R-CH=CH \quad + \quad CH_2=CHX \quad \rightarrow \quad R-CH=CH \quad + \quad CH=CHX \]

\[ R-CH_2=CH \quad + \quad CH_2=CHX \quad \rightarrow \quad RCH_2=CH \quad + \quad CH=CHX \]

involving the termination of one chain and the production of a new chain radical.
Polymer Transfer

This mode of transfer causes the formation of branched chain polymers; transfer from a site on a "dead" polymer chain terminates the growing radical, and activates the other molecule.

\[
\begin{align*}
R-\text{CH}_2-\text{CH}_2 & + \text{H-C-X} \rightarrow R-\text{CH}_2-\text{CH}_2 + \text{C-X} \\
\text{X} & \quad \text{X} \\
\end{align*}
\]

giving rise to a chain radical which can add on further monomer units.

The main effect of all transfer reactions is to reduce the average molecular weight of the polymer, it does not however affect the overall rate of polymerisation since no active centres are destroyed.

Inhibition and Retardation of Polymerisation

Inhibitors and retarders are compounds which suppress normal polymerisation by reacting with chain radicals forming products which are incapable of adding more monomer.

Inhibitors react with free radicals as soon as they are generated and no polymerisation takes place where as retarders merely reduce the rate and degree of polymerisation.

Inhibitors may be free radicals which are too inert to initiate chain radicals as for example the triphenyl methyl or diphenyl picryl-hydrazyl radicals, or may be substances which react with chain radicals
giving products stabilised by resonance, as in the case of quinol or benzoquinone.

Oxygen may play the role of an inhibitor in polymeric systems by combination with chain radicals to form a peroxide which has high thermal stability and thus terminates the growing chain.

\[ 2\text{R}_n. + \text{O}_2 \rightarrow \text{R}_n\text{-C-O-R}_n. \]

The peroxide formed in some cases however is thermally unstable and decomposes to give new chain radicals, thus acting indirectly as an initiator. Copolymers in which a 1:1 ratio of oxygen to monomer was observed have been produced.\(^{(41, 42)}\) Thus, in polymerisation, oxygen can play the role of inhibitor, co-monomer or initiator, depending upon the system and the oxygen concentration.

**KINETICS OF FREE RADICAL INITIATED POLYMERISATION OF VINYL MONOMERS**

The process of polymerisation consist of three steps, initiation, propagation, and termination.

Transfer reactions have little effect upon the overall rate of polymerisation and have been neglected in this simple method of derivation of the kinetic characteristics of the system.

Initiation by an initiator \(I\), decomposing by a first order
mechanism, may be considered as occurring in two steps.

(a) Decomposition of the Initiator into two free radicals

\[ I \xrightarrow[K_D]{.} 2I^* \]  

(1)

(b) Addition of a monomer unit to form a chain radical \( M_1 \).

\[ I^* + M \xrightarrow{} M_1^* \]  

(II)

This is followed by the propagation steps, which will have the same rate constant \( K_P \), since radical reactivity is presumed to be independent of chain length. The successive steps in propagation may be represented by the general equation

\[ M_x^* + M \xrightarrow[K_P]{.} M_{x+1}^* \]  

(III)

The termination step is the removal of two radicals, which can occur by combination or disproportionation.

Combination or coupling may be represented by:

\[ M_x^* + M_y^* \xrightarrow[K_{TC}]{.} M_{x+y}^* \]  

(IV)

i.e. \[ -CH_2-CH. + .CH-CH_2- \xrightarrow{} -CH_2-CH-CH-CH_2- \]

Disproportionation involving hydrogen transfer and formation of an unsaturated end grouping may be represented by:

\[ M_x^* + M_y^* \xrightarrow[K_{TD}]{.} M_x + M_y \]  

(V)

i.e. \[ -CH_2-CH. + .CH-CH_2- \xrightarrow{} -CH_2-CH_2 + CH=CH- \]
The rates of the various steps may be written in terms of their rate constants and the concentration of the species involved. Thus the rate of initiation \( V_I \) is defined as

\[
V_I = \frac{d[M_{\cdot}]}{dt} = 2f K_D[I] \tag{A}
\]

where \([M_{\cdot}]\) is the concentration of chain free radicals, \([I]\) the initiator concentration, and \(f\) is the fraction of radicals formed by the breakdown of the initiator (eq. I) which are successful in initiating chains (eq. II).

The rate of termination \( V_T \) is defined as

\[
V_T = -\frac{d[M_{\cdot}]}{dt} = 2K_T[M_{\cdot}]^2 \tag{B}
\]

The two modes of termination are assumed to be identical for kinetic purposes.

In all cases the concentration of free radicals \([M_{\cdot}]\) becomes constant early in the reactions, as radicals are formed and destroyed at identical rates and hence the steady state condition exists

\[
V_I = V_T
\]

and hence equations A and B may be equated in order to solve for \([M_{\cdot}]\)
The propagation steps are all given the same rate constant as previously noted and the rate of propagation \( V_p \) is equal to the overall rate of disappearance of the monomer.

\[
V_p = -\frac{d[M]}{dt} = K_p[M][M^*]
\]

or substituting for \( M^* \):

\[
V_p = K_p \left( \frac{f K_p[I]}{K_T} \right)^{1/2} [M]
\]

and hence the rate of polymerisation in the early stages of reaction is proportional to the square root of the initiator concentration, and, provided \( f \) is independent of \([M]\) to the first power of the monomer concentration. These relationships hold for cases of high initiator efficiency where \( f \to 1 \), and experimental observations have confirmed them.

(a) rate dependence upon \([I]^{1/2}\), for methyl methacrylate initiated by both azobisisobutyronitrile \((30)\) and benzoyl peroxide, \((43)\) and for styrene with benzoyl peroxide, \((44)\)

(b) rate dependence upon monomer concentration for similar systems, \((30, 43, 45)\) \((f\) might be proportional to \([M]\) in cases of low initiator efficiency leading to \( V_p \propto [M]^{3/2} \).
The Initiator Efficiency $f$

This may be estimated from a comparison of the amount of initiator decomposed with the number of initiator fragments which start polymer chains. The most direct method is to analyse the polymer for initiator fragments, which may be estimated if the initiator leaves a reactive end grouping on the polymer as in the case of the hydroxyl groups left after initiation with hydrogen peroxide and ferrous iron in aqueous solution, or if the initiator is radioactively tagged.

In some cases it is more useful to determine the number average molecular weight and to calculate the number of polymer molecules formed, and to estimate $f$ from the knowledge of the mode of termination, and the number of chains:

The efficiencies of common initiators lie between 0.6-1.0 for most common monomers.

Degree of Polymerisation and Kinetic Chain Length

The kinetic chain length $V$ is defined as the number of monomer units consumed per active centre, and is given by the expression:

$$\frac{V_P}{V_1} = \frac{V_P}{V_T} \quad \text{since} \quad V_1 = V_T$$

and hence

$$V = \frac{K_P}{2K_T} \left[ \frac{M}{M^*} \right]$$
[M.] may be eliminated by substitution as in C

\[ V = \frac{K_p}{2(1 + K_D K_T)^2} \left( \frac{[M]}{[I]^2} \right) \]

and hence the kinetic chain length is proportional to \([I]^2\)

and if no other reaction takes place the kinetic chain length should be related to \(D_p\) the degree of polymerisation.

For termination by combination

\[ D_p = 2V \]

and by disproportionation

\[ D_p = V \]

This has been shown to be so in some cases but discrepancies occur which can be ascribed to transfer reactions. (46)

**Monomer Reactivity in Homopolymerisation**

The behaviour of monomers in polymerisation, can be qualitatively explained in terms of resonance, polar, and steric effects.

The tendency for a monomer to polymerise is dependent upon the substituents attached to the carbon atoms joined by the double bond. Ethylene when one hydrogen atom is replaced by chlorine polymerises readily but when symmetrically disubstituted little polymerisation occurs.

Electron-withdrawing groupings in general increase the tendency to polymerise, and have been arranged in the following order of activation:

Halogens \(<\) esters \(<\) -CN \(<\) -C_6H_5
It has also been found that except in the case of tetrafluoroethylene, an unsubstituted -CH₂ grouping is required to permit polymerisation.

The case of polymerisation of styrene is explained by the contributing forms cited earlier, but in a monomer such as CH₂=CHCl, which contains no unsaturated grouping in conjugation with the double bond, the only resonance structures are higher energy forms, whereby the radical is stabilised only to a small extent.

The effects of substitution in the vinyl part and in the aromatic nucleus of styrene have been investigated by Marvel et al. (47)

Substitution at the α and β positions in the side chain decreases reactivity and in some cases inhibits it completely, e.g. α-chlorostyrene, β-bromostyrene.

Substitution in the aromatic nucleus increases reactivity in the case of Cl, CN, or CO₂H but NO₂ decreases it. The actual orientation of a single substituent in the nucleus does not appear to have a marked effect upon reactivity; on the other hand, orientation is important in disubstitution, as in ortho chloro styrene and 2,6-dichloro styrene, both of which have markedly reduced reactivity. This is ascribed to steric hindrance between the chlorine atoms and the vinyl side chain preventing it from lying in the same plane as the aromatic nucleus.
THE KINETICS OF FREE RADICAL COPOLYMERISATION

It is found that not all vinyl compounds will undergo copolymerisation, but, in cases where copolymerisation does occur, four chain-propagation reactions are possible for a mixture of monomers $M_1$ and $M_2$, as predicted by Dostal in 1936.\(^{(48)}\) He assumed that the rate of addition of a monomer to a growing free radical is dependent only upon the nature of the end grouping bearing the free radical.

The four modes of propagation may be represented by:

$$M_1^\cdot + M_1 \xrightarrow{K_{11}} (M_1)_2^\cdot \quad \text{Rate} = K_{11}[M_1^\cdot][M_1]$$

$$M_1^\cdot + M_2 \xrightarrow{K_{12}} M_1M_2^\cdot \quad \text{Rate} = K_{12}[M_1^\cdot][M_2]$$

$$M_2^\cdot + M_1 \xrightarrow{K_{21}} M_2M_1^\cdot \quad \text{Rate} = K_{21}[M_2^\cdot][M_1]$$

$$M_2^\cdot + M_2 \xrightarrow{K_{22}} (M_2)_2^\cdot \quad \text{Rate} = K_{22}[M_2^\cdot][M_2]$$

Dostal made no attempts to verify his assumption experimentally, and several attempts were made by others, but without conclusive results.\(^{(49,50,51)}\)

It was found however by Alfrey, Mayo and Wall\(^{(52,53,54)}\) in 1944, independently, that by application of Bodenstein's\(^{(55)}\) steady state hypothesis to each radical type separately so that the concentration of $M_1^\cdot$ and $M_2^\cdot$ must each remain constant, and hence the rate
of conversion of

\[ M_1 \cdot \longrightarrow M_2 \cdot \equiv M_2 \cdot \longrightarrow M_1 \cdot \]

Hence

\[ K_{21} [M_2] [M_1] \equiv K_{12} [M_1 \cdot] [M_2] \]

and the rate of disappearance of the two types of monomer is given by

\[
- \frac{d[M_1]}{dt} = K_{11}[M_1 \cdot][M_1] + K_{21}[M_2 \cdot][M_1]
\]

\[
- \frac{d[M_2]}{dt} = K_{22}[M_2 \cdot][M_2] + K_{12}[M_1 \cdot][M_2]
\]

By combination of the two equations and definition of the parameters:

\[ r_1 = \frac{K_{11}}{K_{12}} \quad r_2 = \frac{K_{22}}{K_{21}} \]

one obtains the following equation, known as the Copolymer Equation:

\[
\frac{d[M_1]}{dt} = \frac{[M_1]}{[M_2]} \cdot r_1 [M_1] + \frac{[M_2]}{[M_2]} \\
\frac{d[M_2]}{dt} = \frac{[M_2]}{[M_1]} \cdot r_2 [M_2] + \frac{[M_1]}{[M_1]}
\]

Mayo and Walling have developed the necessary experimental and mathematical techniques for the determination of the reactivity ratios of many monomers (56) by application of the copolymer equation.

Several types of copolymerisation have come to light as a result of these studies. A copolymer system exhibits "ideal" behaviour...
when the two radicals show the same preference for the addition of one monomer over the other in which case

\[
\frac{K_{11}}{K_{12}} = \frac{K_{21}}{K_{22}} \quad \text{or} \quad r_1 = \frac{1}{r_2} \quad \text{or} \quad r_1 r_2 = 1
\]

and a completely random polymer results.

In the other extreme case, each radical reacts exclusively with the other monomer i.e. \( r_1 r_2 = 0 \) and hence the monomers alternate regardless of feed-stock composition.

Most cases are found to lie between the ideal and alternating systems, i.e.

\[0 < r_1 r_2 < 1\]

Thus, in the system styrene \( M_1 \) - methyl methacrylate \( M_2 \), \( r_1 = 0.52 \) and \( r_2 = 0.46 \) and each radical end prefers to add the other monomer about twice as fast as its own.

The compositions of copolymers are independent of the initiator concentration and are unaffected by inhibitors, chain transfer agents and solvent.

**Monomer Reactivity**

Mayo and Walling\(^{(56)}\) have arranged a table of commonly occurring monomers in order of decreasing reactivity. It shows that a phenyl substituent on an olefin has the greatest effect in increasing
reactivity towards attacking radicals, and thereafter:

\[ C_6H_5 > -CH_2=CH_2 > -C-CH_3 > CN > -C-OR > Cl > -OCOCH_3 > OR; \]

in fact, vinyl ethers rarely copolymerise well. The effect of a second \(-1\)-substituent is roughly additative.

This order may be ascribed to the resonance stabilisation of the new radical formed.

In the case of the addition of the radical \(M^+\) to styrene, giving \(M-CH_2-CH_3\).

Stabilisation by resonance is equivalent to 20 K.Cals. per mole.\(^{(56)}\)

Thus when the radical stabilities differ by a large amount, as in the case of styrene and vinyl acetate, little copolymerisation is achieved.
Molecular Weights of Polymers

Polymers are mixtures of molecules of differing sizes and hence any method for the determination of molecular weight will give an average molecular weight which differs from method to method.

End group analysis and osmotic pressure, and freezing point methods dependent upon colligative properties, give a number average molecular weight defined for the ith species as $\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i}$ where $N_i$ is the number of molecules of a given molecular weight $M_i$.

Light scattering, and sedimentation techniques give weight average molecular weights defined as

$$\bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i^2}$$

The number average molecular weight is sensitive to a small percentage by weight of small molecules whilst for the weight average molecular weight the highest molecular weight species have a pronounced effect.

Viscosity and Viscosity Measurement

Polymer solutions show characteristically a high viscosity, and this solution viscosity is a measure of the size or extension in space of the polymer molecules in solution. The ease of determination, and its empirical relationship to molecular weight for linear polymers
makes it a useful tool for their characterization. The method is not
absolute, molecular weights cannot be obtained without calibration
against other methods, which will determine the empirical constants
in the viscosity molecular weight relationship.

The experimental method for the determination of solution vis­
cosity involves the comparison of the efflux times of a given volume
of solvent and of polymer solution in a standard capillary viscometer.

Several terms used in viscometry are defined as follows: the
increase in viscosity of a polymer solution over that of the solvent
is termed the specific viscosity $\eta_{sp}$ and defined as

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \frac{\text{flow time soln.} - \text{flow time solv.}}{\text{flow time solv.}}$$

The relative
viscosity or
viscosity ratio.

The reduced viscosity
or viscosity number

The inherent viscosity
or Logarithmic
viscosity number

The intrinsic viscosity
or limiting viscosity
number (L.V.N.)

where $c$ is the concentration in grams./100 ml. solution. The first
name in each case is the common name the second the name recommended
by the International Union of Pure and Applied Chemistry (1952), but which have only partially come into use.

The term intrinsic viscosity (the use of which is retained in this Thesis) was introduced by Kraemer \(^{(58)}\) for the limiting value of \(\eta_{sp}/c\) at infinite dilution. Intrinsic viscosity is independent of concentration by virtue of its extrapolation to infinite dilution.

In practice, to determine \([\eta]\) with accuracy, thermostatic control to \(\pm 0.02^\circ\), an efflux time for the solvent of greater than 100 seconds and, for accuracy in extrapolation, a range of solutions giving a relative viscosity of 1.1 - 1.5 are required.

**Dependence of Intrinsic Viscosity on Molecular Weight for Linear Polymers**

The theory and experimental basis of the relationship between viscosity and molecular weight has provoked much work and discussion, but it still remains unsettled in many respects. Staudinger\(^{(59,60)}\) first proposed for linear molecules an equation connecting reduced viscosity and molecular weight.

\[
\eta_{sp}/c = KM
\]

where \(K\) was a constant for a given substrate in a given solvent, and may be evaluated from molecular weight determination by some other method.

A double logarithmic plot of molecular weight against
intrinsic viscosity is a straight line over a large range for specimens of a given polymer of different molecular weight, but the equation

\[ \eta_{sp}/c = KM \]

(61,62,63)
does not generally apply, and the Mark-Houwink equation

\[ [\eta] = KM^\alpha \]  

(i)
is found to be of wide application.

Staudinger's original equation is thus a special case of (i) with \( \alpha \) numerically equal to 1; on detailed examination, it has only been found to apply to a limited number of condensation polymers of low molecular weight.

The constants in equation (i) have been determined for various substrates. In the case of randomly coiled polymers, \( \alpha \) will vary from 0.5 in a "theta" solvent to a maximum of about 1.0, lying in the region 0.6-0.8 for many substrates and \( K \) lies in the region 0.5 - 5 x 10^-4. It should be noted that \( K \) and \( \alpha \) are functions of the solvent as well as polymeric type.

According to Schaefgen and Flory, intrinsic viscosity leads to a viscosity average molecular weight defined as:

\[ [\bar{M}_v] = \left( \sum_{i=1}^{\infty} w_i M_i \right)^{1/\alpha} = \frac{\sum_{i=1}^{\infty} N_i M_i^{1+\alpha}}{\sum_{i=1}^{\infty} N_i M_i}^{1/\alpha} \]
dependent upon \( \alpha \) as well as the distribution of the molecular species.

It is found for many polymers that \( \bar{M}_v \) is 10-20% below \( M_w \), but in the case where \( \alpha = 1 \) \( \bar{M}_v = M_w \).
**Polyelectrolytes**

It is possible for polymers such as poly(4-vinyl-N-butyl pyridinium bromide) to dissociate in aqueous solution giving ions, and leading to large repulsive forces amongst the charged groups on the chain and extension of such a chain. In solution where the concentration is greater than 1%, the molecules are sufficiently close to overlap partially and are not appreciably extended, and the specific viscosity will therefore be as normal. When dilution proceeds, however, a net charge on the macromolecule will develop because of the mobility of the small ionic species, in this example the bromide ion, and \( \eta_s / c \) may show marked increase on dilution. The addition of a strong electrolyte tends to suppress this behaviour, and leads to normal viscosity/concentration relationship.

It can be seen then, that although viscosity is a useful method of comparison for a series of polymers of differing molecular weight, it cannot provide a method for absolute determination without calibration by means of another molecular weight determination method, such as light-scattering.
The reactions of functional groupings attached to a polymeric chain show differences from the reaction occurring when the same functional group is attached to a small molecule.

For example, the product of the reaction will be a copolymer containing reacted and unreacted functional groups in all cases except where 100% reaction occurs. This situation arises by virtue of the fact that "product" and "reactant" are joined to the same chain and separation cannot be effected.

The solubility of the reactant and product also play an important part in determining the percentage reaction; and the proximity of functional groupings on the polymeric chain often influence the course of reaction, in that frequently intramolecular rather than intermolecular reaction occurs.

Electrical charges and tactity also have marked effects on the course of reactions and these will be illustrated later.

Two types of reaction are defined for polymeric compounds, namely, mono- and multi-functional reactions, depending whether one functional group or more than one is involved in the act of reaction.

Interactions between functional groupings often enhance a tendency towards cyclization, the ring stability being a function of the nature and respective position of the substituents to one another;
For example copolymers of maleic acid and vinyl acetate\(^{(65)}\) give on alkaline hydrolysis a poly(hydroxy dicarboxylic acid), as its salt, but on acidification or acid hydrolysis in alcoholic media internal lactonisation occurs with the formation of 5 or 6 membered ring systems as is shown below.

Such interactions are often the reason for the unexpected reaction course with polymeric materials as can be shown with the following, an Arndt Eisert reaction on poly(methacryl chloride)\(^{(66)}\). It was expected to give poly(isopropenyl acetic acid) as the product by rearrangement of the intermediate diazoketone, i.e.

\[
\text{CH}_3\text{-C-COCl} \rightarrow \text{CH}_3\text{-C-CO CHN}_2 \rightarrow \text{CH}_3\text{-C-CH=CH-C}=O
\]

\[
\text{CH}_3\text{-C-CH}_2\text{-COOH} \quad \text{H}_2\text{O}
\]
Analytically the product obtained was shown to contain keto rings without acidic properties and the following reaction course was thought to be that prevailing.

\[
\begin{align*}
\text{CH}_3\text{CH}_3 & \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{CH}_3 \\
\text{CH}_3\text{CH}_3 & \xrightarrow{\text{COOH}} \text{CH}_3\text{CH}_3
\end{align*}
\]

β Keto-Ketene Rings

In many multifunctional reactions the phenomenon of limiting yield is encountered and this has been interpreted statistically by Flory, who assumes for a bifunctional system that all functional groups have equivalent and constant accessibility throughout the reaction. Reaction of functional groups in adjacent pairs may be limited in a way which depends upon polymeric structure.

Statistically it was found that for regular head to tail \((-\text{CH}_2-\text{CHX-CH}_2-\text{CHX})\) and random types of structures, the percentage of functional group which were unable to react because they became isolated were 13.5 and 18.4% respectively, and 100% reaction is only
possible where the structure is made up of units joined head to head/tail to tail, i.e. (-CH$_2$-CHX-CHX-CH$_2$-).

These calculations have been verified by the experiments of Marvel and Levesque$^{(38)}$ who found that the self condensation of poly(methyl vinyl ketone) was limited to 79-80% reaction of available carbonyl groups.

\[
\begin{align*}
\text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_2 \\
\text{CH} & \quad \text{CH} & \quad \text{CH} \\
\text{C}=\text{O} & \quad \text{C}=\text{O} & \quad \rightarrow \quad \text{H}_2\text{O} & \quad + \\
\text{CH}_3 & \quad \text{CH}_3 & \\
\end{align*}
\]

and again by Marvel and Sample$^{(68)}$ who found that the removal of chlorine from poly(vinyl chloride) by zinc dust was limited to 84-86%
Comparative Kinetics and Monofunctional Reactions

Monofunctional reactions show similar reaction kinetics to those of small molecules as has been shown by Kern and Schulz with reactions on poly(acrylic esters)\(^{(69)}\) and poly(acrolein)\(^{(70-72)}\). These results show that reactions of these types have activation energies which are almost identical to those of low molecular weight compounds, the slight differences being due to steric effects.

In this context Hiller\(^{(73)}\) has shown that in the acetylation of cellulose and the hydrolysis of its acetyl derivative the activation energy nearly corresponds to that for low molecular weight alcohols, namely 10.3 k.cal. mole\(^{-1}\) compared with 10.2.

Conix and Smets\(^{(74)}\) obtained the following results from the alkaline hydrolysis of poly(vinylpyrrolidone) and analogous small compounds.

<table>
<thead>
<tr>
<th>Substance</th>
<th>(E_a) K.Cal./mole</th>
<th>(\log P_Z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) Poly-N-vinyl pyrrolidone</td>
<td>25 ± 1</td>
<td>11.7</td>
</tr>
<tr>
<td>(ii) N-Isopropyl-2-methyl-pyrrolidone</td>
<td>27 ± 0.5</td>
<td>12.3</td>
</tr>
<tr>
<td>(iii) Co-polymer (vinyl pyrrolidone-68 maleic acid-32)</td>
<td>16 ± 1</td>
<td>6.3</td>
</tr>
<tr>
<td>(iv) N-Pyrrolidone - acetic acid</td>
<td>17 ± 0.5</td>
<td>7.3</td>
</tr>
</tbody>
</table>
The accumulation of electric charges on the polymeric chain in the case of poly(N-vinyl pyrrolidone) has no effect on the hydrolysis rate because of the distance between the carboxylate groupings and the neighbouring lactam units (8 atoms), and the carboxylate groupings are too far from one another to exert effective repulsion on one another, thereby altering the shape of the molecule, and hence the first order rate constant remains constant to greater than 50% reaction.

In the case of the copolymer and N-pyrrolidone-acetic acid in which charged maleic acid units are close to lactam units, the collision frequency for the reaction is reduced by repulsion between the negatively charged polymer chain and that of the hydroxide ion.

The electric potential of polymer molecules may increase or decrease during the course of a reaction, and influence the rate of such a reaction and Katchalsky(75) has treated this mathematically for a macromolecule carrying a given number of charges statistically distributed along a chain. The electric potential is calculated as a function of ionic strength and degree of ionisation and the overall length of the polymeric molecule. The predictions from this calculation were tested on the hydrolysis of pectinic acids(76), a reaction characterised by a strong decrease in rate constant as the reaction proceeds, and by an increase of rate constant with increase in the ionic strength of the medium. By taking into account variation of electric potential Katchalsky was able to assign an "intrinsic" rate
constant for the hydrolysis which remained valid even at 90% reaction.

Comparative Kinetics and Multifunctional Reactions

Multifunctional reactions show differences in behaviour from that expected for simple molecules, and in all cases this is dependent upon the nature of neighbouring groupings. The alkaline hydrolysis of poly(methacrylamide)\(^{(77-79)}\), for example in which the packing of the side methyl groups assures a stretched molecule. The intrinsic velocity can only be evaluated at low conversion and is similar to that for trimethylacetamide.

In this case the percentage reaction is limited to 70% and this limitation has been ascribed by Arcus\(^{(77)}\) as due to electrostatic repulsion towards the hydroxyl group; hydrogen bonding leads to the formation of the type of structure shown, and hence to stabilisation towards further attack. This idea has been confirmed by Pinner\(^{(79)}\) who correlated the degree of hydrolysis of co(methacrylic acid-methacrylamide) polymers with their initial composition, and found good agreement between the values found by experiment and those calculated from Arcus's hypothesis.
Hydrogen Bonding

a. single chain

\[
\begin{align*}
\text{Me} & \quad \text{Me} & \quad \text{Me} \\
\text{CH}_2 & \quad \text{C} & \quad \text{CH}_2 & \quad \text{C} & \quad \text{CH}_2 & \quad \text{C} & \quad \text{CH}_2 \\
\text{C} & \quad & \text{C}=\text{O} & \quad & \text{C} & \quad & \text{C}=\text{O} \\
\text{O} & \quad \text{O} & \quad \text{N} & \quad \text{(-)} & \quad \text{O} & \quad \text{O} \\
\text{H} & \quad \text{H} & \quad & & \text{H} & \quad \text{H} & \quad \text{(-)} & \quad \text{O} \\
\text{CH}_2 & \quad \text{C} & \quad \text{CH}_2 & \quad \text{C} & \quad \text{CH}_2 & \quad \text{Me} & \quad \text{Me}
\end{align*}
\]

b. between two chains

\[
\begin{align*}
\text{Me} & \quad & \text{CH}_2 & \quad \text{C} & \quad \text{CH}_2 \\
\text{C} & \quad & \text{C}=\text{O} & \quad \text{C} & \quad \text{C}=\text{O} \\
\text{N} & \quad & \text{H} & \quad \text{H} & \quad \text{(-)} & \quad \text{O} \\
\text{O} & \quad \text{O} & \quad \text{O} & \quad \text{O} \\
\text{CH}_2 & \quad \text{C} & \quad \text{CH}_2 & \quad \text{C} & \quad \text{CH}_2 & \quad \text{Me} & \quad \text{Me}
\end{align*}
\]

The hydrolysis of poly(acrylamide) however does not show this limitation in percentage reaction and it may be hydrolysed completely. Kinetic analysis shows the reaction to occur in two distinct steps the second of which is ten times slower than the first.

Smets (78) from a study of copolymers of acrylamide and vinyl pyrollidone and acrylamide and acrylic acid considers that the major
factors influencing hydrolysis in the case of poly(acrylamide) are steric and electrical charge effects.

Smets considers hydrogen bonding to be unlikely in strongly alkaline solution. The decrease in rate occurring with acrylamide at about 40% reaction he explains on the basis that at low degrees of hydrolysis the amide groupings are shielded by the neighbouring coiled neutral molecule, but the molecule at about 40% reaction takes up a stretched form due to repulsion of carboxylate ions and thus the shielding effect towards the hydroxide ion disappears, being replaced by a repulsive effect and the reaction rate falls markedly.

The behaviour of poly(methacrylamide) was compared by Smets to the behaviour of the pectinic acids. The presence of side methyl groups causes high steric hindrance along the chain, which may be considerably stretched, even at low degree of ionisation, thus the shape of the molecule varies only slightly during the course of the reaction.

The accessibility of the amide groups at low degree of hydrolysis is higher in poly(methacrylamide) than poly(acrylamide) which is coiled; which may explain the fact that log PZ is higher for poly(methacrylamide) at low conversions.

The decrease in rate constant and the upper limit is attributed both to the increasing repulsion potential and high steric hindrance. Hydrogen bonding may also contribute towards stability but it is
evident that this effect also exists in the case of poly(acrylamide) which can be hydrolysed completely, and is absent in the case of N,N'-diethyl polyacrylamide which is limited to 35% hydrolysis, and also in the case of N,N'-diethyl poly(methacrylamide) which is completely resistant to hydrolysis. Smets concludes therefore that polymeric structure has a direct influence on the alkaline hydrolysis of poly(vinylamides). The increasing negative charges along the chain exert electrostatic repulsion towards the OH⁻ ion and cause a decrease in the rate of reaction; this effect becomes appreciable in the case of poly(acrylamide) at 40% conversion; it appears with poly(methacrylamide) at low conversion. This difference has been related, above, to the more or less stretched configuration of the macromolecule during the reaction.

It has been shown by Morawetz(80) for example that if some (meth)acrylic-p-nitranilide groupings are incorporated into a polyacid molecule, the amide links are stabilised to normal alkali by a factor of one thousand when compared with trimethyl acetic and glutaric-p-nitranilides. This stabilisation has been interpreted as hydrogen bonding between amide and corresponding carboxylate groupings.
This interpretation is supported by the evidence that addition of barium ions liberates the anilide function for hydrolysis by chelation of the carboxylate grouping.

**Diazo-Reactions with particular reference to Poly(Aminostyrenes)**

Poly(aminostyrenes) have been used in the preparation of azo dyes. Oda and Urata\(^{(81)}\) have polymerised \(\text{m-aminostyrene}\) at 160° and diazotised the product in sulphuric acid, coupling with napthol AS yielding polymeric dyes. Martynoff\(^{(82)}\) diazotised poly-(\(\text{p-aminostyrene}\)), and coupled the product with phenol and dimethylaniline yielding dyes of more intense colour than those of non polymeric compounds. Similarly Grubhofer and Schleith\(^{(83)}\) have coupled a diazotised poly(aminostyrene) with protein molecules. Acid Rao and Palit\(^{(84)}\) have diazotised poly(\(\text{p-aminostyrene-methacrylic/copolymer}\) and coupled it with 2-napthol-3-6 disulphonic acid and
Kudryavtev and co-workers\(^{(85)}\) have prepared a similar dye stuff from a p-aminostyrene-acrylonitrile copolymer.

With regard to replacement reactions of poly styrene diazonium compounds work has been attempted in this context by Gregor, Dolov and Hoeschele\(^{(86)}\) on a poly-(p-aminostyrene), Parrish\(^{(87)}\) on a poly(p-aminostyrene) prepared by nitration and reduction of a lightly cross-linked poly styrene and by Manecke and Singer\(^{(88)}\), and Rao and Falit\(^{(89)}\) who used a poly-(p-aminostyrene) probably prepared by Skogseids\(^{(90)}\) method which does not guarantee that all the nitro polymer is the para isomer, it may contain ortho and di-substituted units, nor that reduction to the amino polymer is complete.

The only data available on the replacement reactions of poly diazonium compounds of known structure is that of Arcus and Halliwell\(^{(91)}\) who have subjected the polymeric diazonium compound derived from poly(\(\_\)aminostyrene) to the Sandmeyer reaction to substitute both chlorine and bromine, and iodine was substituted by warming the diazonium chloride with potassium iodide.

For the polymer replacement by Cl and Br proceeded to \(-\sim\) 85%, I to 70% and thiol to 55%.

A notable feature is that in nearly half the examples cited reaction proceeds to over 70% despite the insolubility of the final products which the authors ascribe to cross-linking by a Pschorr-type attack by some of the phenyl diazonium groups on phenyl or substituted phenyl side groups.
It can be seen therefore that "reactive" functional groups attached to polymeric chains show quite marked reactivity, provided suitable solvents are available for the reaction, but the resulting product may not be as predicted from a consideration of the conventional course of reaction on small molecules.
THE ALKALINE HYDROLYSIS OF AMIDES

Introductory

The hydrolysis of amides may be effected by acids or bases, the reaction at equivalent concentrations proceeding more rapidly in the presence of an alkali than an aqueous acid.

Kinetic studies on both the alkaline and acidic hydrolyses were first made in 1898 by Reid\(^{(92)}\) and since that time the alkaline hydrolysis of some simple aliphatic amides and some substituted benz-amides and anilides have been studied, but the subject has not attracted a great deal of attention. Normal alkaline hydrolysis has been shown to follow a bimolecular second order path, the rate being proportional to the product $[\text{amide}] [\text{base}]$.

The mechanism has not been fully elucidated but the following mechanistic path appears to satisfy the known facts.

\[
\begin{align*}
\text{R-C-NH}_2 + \text{OH}^- & \xrightarrow{\text{fast}} \text{R-C-NH}_2\text{OH}^- \\
\text{R-C-NH}_2\text{OH}^- & \xrightarrow{\text{slow}} \text{R-C-NH}_2 + \text{OH}^- \\
\end{align*}
\]

permits the ingress of isotopic oxygen.

\[
\begin{align*}
\text{R-CO}_2^- + \text{NH}_3 & \xrightarrow{\text{very rapidly}} \text{R-C} + \text{NH}_2^- \\
\end{align*}
\]

The reaction proceeds by a carbonyl-addition mechanism with the reversible formation of an intermediate (A) in which the carbonyl
oxygen has been made equivalent to the oxygen atom from the attacking hydroxide ion. Evidence for isotopic oxygen exchange was obtained by Bender and Ginger, and Bender and Unik (93,94) who studied the exchange occurring concurrently with the hydrolysis reaction using benzamide labelled in the oxygen PhCO$^{18}$NH$_2$. The reaction was carried out at 109° and it was found that isotopic oxygen exchange occurred five times as fast as the hydrolysis reaction.

**Aliphatic Amides RCONH$_2$ or RCONHR$^-$**

The alkaline hydrolysis of aliphatic amides has been studied to a greater extent than the hydrolysis of the aromatic amides, the principal workers in this field being Calvet (102), Meloche and Laidler (95), and Packer, Thompson and Vaughan (96).

The reaction is second order with rate $\alpha[\text{OH}^-][\text{amide}]$, as first found by Croker and Lowe (97) and by Peskoff and Meyer (98), and later workers have confirmed this rate dependence.

Packer, Thompson and Vaughan (96) in 1955 studied the alkaline hydrolysis of acetamide, propionamide, iso-butyramide, and trimethyl acetamide at 50 and 70° over a range of sodium hydroxide concentrations. The order of reactivity is as follows.

<table>
<thead>
<tr>
<th>Amides</th>
<th>$10^3 K_2$ litre$^{-1}$ mole$^{-1}$ min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp. 50°</td>
</tr>
<tr>
<td>Acetamide</td>
<td>18.4</td>
</tr>
<tr>
<td>Propionamide</td>
<td>16.6</td>
</tr>
<tr>
<td>iso-Butyramide</td>
<td>6.58</td>
</tr>
<tr>
<td>Trimethyl acetamide</td>
<td>1.53</td>
</tr>
</tbody>
</table>
indicating that it is governed by the inductive effects of the alkyl groups, the contributions by hyperconjugative electron release being extremely small. In criticism, it might be pointed out that steric hindrance would operate in the direction shown by the rates in the Table. Related data on the alkaline hydrolysis of corresponding ethyl esters by Davies and Evans (99), and Evans et al (100) are cited, and suggest the inductive effect to dictate the rate. Willems and Bruyants (101) in 1951 studied the basic hydrolysis of a series of aliphatic amides in aqueous solution at 65, 75 and 85° using initial concentrations of sodium hydroxide and amide of 0.05 mole per litre;

<table>
<thead>
<tr>
<th>Amide RCONH₂</th>
<th>Kₐx10⁴ litre·mole⁻¹·sec⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp: 65</td>
</tr>
<tr>
<td>R=CH₃</td>
<td>6.34</td>
</tr>
<tr>
<td>C₂H₅</td>
<td>5.24</td>
</tr>
<tr>
<td>n.C₃H₇</td>
<td>2.34</td>
</tr>
<tr>
<td>n.C₄H₉</td>
<td>2.00</td>
</tr>
<tr>
<td>n.C₅H₇</td>
<td>1.59</td>
</tr>
</tbody>
</table>

They find a decrease in rate constant for an increase in the number of carbon atoms in the chain.
The major study on the alkaline hydrolysis of aliphatic amides prior to these workers was made by Calvet, who studied the thermochemistry of the reactions and has evaluated numerous physical constants with respect to their solutions. He found the hydrolysis to be bimolecular; his results agreed with previous workers, notably Peskoff and Meyer, except for valeramide which unlike these authors, he found to show normal behaviour in the series.

The rate constant was found to decrease with increasing molecular weight up to butyramide and remains constant thereafter. The following rate constants were obtained at 17°.

<table>
<thead>
<tr>
<th>Amide</th>
<th>( K_2 ) litre mole(^{-1}) hour(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formamide</td>
<td>4.45</td>
</tr>
<tr>
<td>Acetamide</td>
<td>0.0692</td>
</tr>
<tr>
<td>Propionamide</td>
<td>0.0669</td>
</tr>
<tr>
<td>Butyramide</td>
<td>0.0237</td>
</tr>
<tr>
<td>Valeramide</td>
<td>0.0239</td>
</tr>
<tr>
<td>Capronamide</td>
<td>0.0237</td>
</tr>
<tr>
<td>Benzamide</td>
<td>0.0365</td>
</tr>
<tr>
<td>Monochloracetamide</td>
<td>23.2</td>
</tr>
<tr>
<td>Dichloroacetamide</td>
<td>3.35</td>
</tr>
<tr>
<td>Trichloroacetamide</td>
<td>1.10</td>
</tr>
</tbody>
</table>

It can be seen that introduction of an electronegative atom, chlorine, increases the rate. Calvet attempts to explain his results by reference to the strengths of the acids corresponding to the amide, and postulates the following general rule. The rate of hydrolysis
of an amide by alkali will be faster than another, if the acid to which it corresponds is stronger than the acid to which the other corresponds. This rule is not obeyed exactly as can be seen with benzamide, the "anomalous" result is explained by Calvet as being due to steric effects.

Laidler and Chen\(^{103}\) have made a study on the effect of pressure upon the hydrolyses of aliphatic amides and esters. They find the reactions to be kinetically second order for concentrations of both reactants equal to \(10^{-5}\) after mixing:

They obtained the following results for acetamide and propionamide at 25\(^\circ\); \(K_2\) litre. mole\(^{-1}\) sec. \(^{-1}\) \(\times 10^5\)

<table>
<thead>
<tr>
<th>Pressure lb.in(^2)</th>
<th>Acetamide</th>
<th>Propionamide</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.7</td>
<td>3.77</td>
<td>3.00</td>
</tr>
<tr>
<td>4,000</td>
<td>4.44</td>
<td>-</td>
</tr>
<tr>
<td>5,000</td>
<td>-</td>
<td>3.78</td>
</tr>
<tr>
<td>10,000</td>
<td>5.47</td>
<td>4.86</td>
</tr>
<tr>
<td>15,000</td>
<td>6.80</td>
<td>6.07</td>
</tr>
<tr>
<td>Vcm(^3) mole(^{-1})</td>
<td>-14.2</td>
<td>-16.9</td>
</tr>
</tbody>
</table>

They postulate that a mechanism of the following type, which satisfies their results, is followed.
It appears therefore that with aliphatic amides, the inductive effect of a substituent plays the major role in defining the rate of such hydrolyses, in cases where steric effects may be neglected.

THE EFFECT OF SUBSTITUENTS ON RATE OFALKALINE HYDROLYSIS OF AMIDES CONTAINING ARYL GROUPS

Amides $\text{Ar.CO.NHR}$

Reid\(^{(92)}\) first studied the alkaline hydrolysis of a series of substituted benzamides. He found that the reaction in water at 100° was retarded by electron releasing groupings and accelerated by electron attracting groupings. He also found the reaction to be sensitive to steric retardation in the ortho position, by substituents of either polarity. His results are shown as relative rates below,
the rates with NO₂ in the ortho and para position being too fast for measurement.

<table>
<thead>
<tr>
<th>Substituent</th>
<th>NH₂</th>
<th>OMe</th>
<th>H</th>
<th>I</th>
<th>Br</th>
<th>NO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>p</td>
<td>-</td>
<td>0.2</td>
<td>0.49</td>
<td>1.69</td>
<td>1.91</td>
<td>-</td>
</tr>
<tr>
<td>m</td>
<td>0.19</td>
<td>0.93</td>
<td>0.83</td>
<td>2.60</td>
<td>2.97</td>
<td>5.60</td>
</tr>
<tr>
<td>o</td>
<td>0.064</td>
<td>-</td>
<td>0.094</td>
<td>0.13</td>
<td>0.25</td>
<td>-</td>
</tr>
</tbody>
</table>

Some of the studies made by Reid have been repeated by Laidler and Meloche (95) at various temperatures between 50-100° using solutions 0.025 M in each component. It is suggested by these authors that in some cases Reid was measuring the rate of solution of the amide, and they find the following rates, a second order law being obeyed.

<table>
<thead>
<tr>
<th>Amide</th>
<th>K₂ x 10⁶ litre mole⁻¹ sec⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature</td>
</tr>
<tr>
<td></td>
<td>100.1° 90 80.3 64.5 52.8</td>
</tr>
<tr>
<td>p-Nitrobenzamide</td>
<td>2270 - 582 217 93.9</td>
</tr>
<tr>
<td>p-Chlorobenzamide</td>
<td>502 - 125 39.7 16.1</td>
</tr>
<tr>
<td>Benzamide</td>
<td>338 - 76.4 23.9 8.54</td>
</tr>
<tr>
<td>p-Methylbenzamide</td>
<td>188 - 47.5 13.1 4.66</td>
</tr>
<tr>
<td>o-Methylbenzamide</td>
<td>13.5 5.57 2.37 -</td>
</tr>
</tbody>
</table>
Rate-dependence upon substituents is similar to that stated above. Ogata and Okano\(^{(104)}\) have studied benzanides and nitriles and have come to the same general conclusions as Laidler and Meloche. Packer, Thompson and Vaughan\(^{(96)}\) have investigated the alkaline hydrolysis of a series of para alkyl benzamides, which they considered free from steric effects, and thus capable of providing information on the effect of hyperconjugative electron release upon reaction rate. The series \(p\)-toluamide, \(p\)-ethyl benzamide, \(p\)-isopropyl benzamide and \(p\)-tert.butyl benzamide was investigated with a large excess of alkali, so that the kinetics were pseudo-first order, with respect to the concentration of amide, yielding constant \(K_1\). The linear plots of \(K_1\) against \(\text{[NaOH]}\) are described by the equation, \(K_1 = K_2 \text{[NaOH]}\), where \(K_2\), the catalytic coefficient of the hydroxyl ion, is the second order rate constant for the bimolecular reaction between the amide and hydroxide ion.

All four substituted benzamides were found to be hydrolysed more slowly than the parent benzamide (see table below); with no definite reactivity order, and it was considered by the authors that it was a mixed inductive-hyperconjugative order, displaying an unusual balance of effects.
In the hydrolysis of benzamides, therefore, it can be seen that substitution in the ortho position decreases the rate, (except for the nitro-group) and substitution in the meta and para positions increases the rate when an electron-withdrawing substituent is present, and decreases the rate in the case of an electron-releasing substituent.

**Amides Ar.NH.CO.R**

The alkaline hydrolysis of anilides has been the subject of measurements in aqueous solution by Davis\(^{(105)}\) and in aqueous alcohol by Semerano\(^{(106)}\).

Davis\(^{(105)}\) studied the reaction at \(100^\circ\) only and his results are summarised below.

<table>
<thead>
<tr>
<th>Amide</th>
<th>(K_2 \times 10^2 ) litre. mole(^{-1}) min.(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzamide</td>
<td>16.3</td>
</tr>
<tr>
<td>p-Toluamide</td>
<td>10.4</td>
</tr>
<tr>
<td>p-Ethylbenzamide</td>
<td>10.8</td>
</tr>
<tr>
<td>p-Iso-propylbenzamide</td>
<td>10.6</td>
</tr>
<tr>
<td>p-Tert.butylbenzamide</td>
<td>10.8</td>
</tr>
</tbody>
</table>
### Davis Results

\[ K_2 \text{ litre mole}^{-1} \text{, hour}^{-1} \]

<table>
<thead>
<tr>
<th>Compound</th>
<th>( K_2(\text{av}) )</th>
<th>Compound</th>
<th>( K_2(\text{av}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>+ Formanilide</td>
<td>87.1</td>
<td>N.methylacetanilide</td>
<td>3.84</td>
</tr>
<tr>
<td>+ Acetanilide</td>
<td>3.20</td>
<td>N.ethylacetanilide</td>
<td>0.94</td>
</tr>
<tr>
<td>Propioanilide</td>
<td>1.93</td>
<td>+ Form-o-toluidide</td>
<td>3.39</td>
</tr>
<tr>
<td>n.Butyranilide</td>
<td>0.934</td>
<td>+ Acet-o-toluidide</td>
<td>0.709</td>
</tr>
<tr>
<td>iso Butyranilide</td>
<td>0.395</td>
<td>+Acet-m-toluidide</td>
<td>3.14</td>
</tr>
<tr>
<td>n.Valeranilide</td>
<td>0.656^*</td>
<td>+Acet-p-toluidide</td>
<td>3.11</td>
</tr>
<tr>
<td>iso Valeranilide</td>
<td>0.131^*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+ Formanilide</td>
<td>87.1</td>
<td>Acetanilide</td>
<td>3.20</td>
</tr>
<tr>
<td>+ Form-o-toluidide</td>
<td>33.9</td>
<td>Acet-o-toluidide</td>
<td>0.709</td>
</tr>
<tr>
<td>+ Form-m-toluidide</td>
<td>74.6</td>
<td>+Acet-m-toluidide</td>
<td>3.14</td>
</tr>
<tr>
<td>+ Form-p-toluidide</td>
<td>82.9</td>
<td>+Acet-p-toluidide</td>
<td>3.11</td>
</tr>
<tr>
<td>Propionanilide</td>
<td>1.93</td>
<td>n.Butyranilide</td>
<td>0.934</td>
</tr>
<tr>
<td>Propio-o-toluidide</td>
<td>0.400</td>
<td>n.Butyr-o-toluidide</td>
<td>0.207</td>
</tr>
<tr>
<td>Propio-m-toluidide</td>
<td>1.89</td>
<td>n.Butyr-m-toluidide</td>
<td>-</td>
</tr>
<tr>
<td>Propio-p-toluidide</td>
<td>1.85</td>
<td>n.Butyr-p-toluidide</td>
<td>0.656^*</td>
</tr>
<tr>
<td>iso Butyranilide</td>
<td>0.395</td>
<td></td>
<td></td>
</tr>
<tr>
<td>iso Butyr-o-toluidide</td>
<td>0.096</td>
<td></td>
<td></td>
</tr>
<tr>
<td>iso Butyr-m-toluidide</td>
<td>0.290^*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>iso Butyr-p-toluidide</td>
<td>0.276^*</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

^* Solution not complete.
+ Carried out to 98% completion.
<table>
<thead>
<tr>
<th>Compound</th>
<th>$K_2$(av)</th>
<th>Compound</th>
<th>$K_2$(av)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formanilide</td>
<td>87.1</td>
<td>Acetanilide</td>
<td>3.20</td>
</tr>
<tr>
<td>o-Chloroformanilide</td>
<td>91.9</td>
<td>o-Chloroacetanilide</td>
<td>3.10</td>
</tr>
<tr>
<td>m-Chloroformanilide</td>
<td>87.1</td>
<td>m-Chloroacetanilide</td>
<td>3.31</td>
</tr>
<tr>
<td>p-Chloroformanilide</td>
<td>88.4</td>
<td>p-Chloroacetanilide</td>
<td>3.07</td>
</tr>
<tr>
<td>Propionanilide</td>
<td>1.93</td>
<td>Acetanilide</td>
<td>3.20</td>
</tr>
<tr>
<td>o-Chloropropionanilide</td>
<td>2.07</td>
<td>o-Bromoacetanilide</td>
<td>3.31</td>
</tr>
<tr>
<td>m-Chloropropionanilide</td>
<td>2.07</td>
<td>m-Bromoacetanilide</td>
<td>3.28</td>
</tr>
<tr>
<td>p-Chloropropionanilide</td>
<td>1.52</td>
<td>p-Bromoacetanilide</td>
<td>2.97*</td>
</tr>
<tr>
<td>Formanilide</td>
<td>87.1</td>
<td>Acetanilide</td>
<td>3.20</td>
</tr>
<tr>
<td>o-Nitroformanilide</td>
<td>T.F.F.M.</td>
<td>o-Nitroacetanilide</td>
<td>T.F.F.M.</td>
</tr>
<tr>
<td>m-Nitroformanilide</td>
<td>118.9</td>
<td>m-Nitroacetanilide</td>
<td>5.45</td>
</tr>
<tr>
<td>p-Nitroformanilide</td>
<td>T.F.F.M.</td>
<td>p-Nitroacetanilide</td>
<td>T.F.F.M.</td>
</tr>
<tr>
<td>Benzanilide</td>
<td>insoluble</td>
<td></td>
<td></td>
</tr>
<tr>
<td>o-Nitrobenzanilide</td>
<td>55.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Nitrobenzanilide</td>
<td>13.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>o-Acetyl Anisidine</td>
<td>2.28</td>
<td>o-Acetylphenetide</td>
<td>2.34</td>
</tr>
<tr>
<td>m-Acetyl Anisidine</td>
<td>2.86</td>
<td>m-Acetylphenetide</td>
<td>2.90</td>
</tr>
<tr>
<td>p-Acetyl anisidine</td>
<td>3.40</td>
<td>p-Acetylphenetide</td>
<td>3.28</td>
</tr>
</tbody>
</table>

* Not completely soluble
T.F.F.M. Too fast for measurement
Semerano carried out hydrolyses of a series of anilides at various temperatures in sealed tubes under nitrogen. His results are summarised below.

\[ K_2 \times 10^4 \text{ litre mole}^{-1} \text{ min}^{-1} \]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100</td>
</tr>
<tr>
<td>Acetanilide</td>
<td>95.6</td>
</tr>
<tr>
<td>Acetyl-o-toluidide</td>
<td>39.5</td>
</tr>
<tr>
<td>Acetyl-m-toluidide</td>
<td>84.5</td>
</tr>
<tr>
<td>Acetyl-p-toluidide</td>
<td>94.3</td>
</tr>
<tr>
<td>Acetyl xylidide 2,3.</td>
<td>27.8</td>
</tr>
<tr>
<td>Acetyl xylidide 2,4.</td>
<td>32.4</td>
</tr>
<tr>
<td>Acetyl xylidide 2,5.</td>
<td>36.7</td>
</tr>
<tr>
<td>Acetyl xylidide 2,6.</td>
<td>1.99</td>
</tr>
<tr>
<td>Acetyl xylidide 3,4.</td>
<td>87.8</td>
</tr>
<tr>
<td>Acetyl xylidide 3,5.</td>
<td>80.4</td>
</tr>
</tbody>
</table>

It would appear from these results that as a general trend in the hydrolysis of anilides as with aromatic amides of the substituted benzamide series, electron attracting substituents increase
the rate, whilst, electron releasing substituents retard it. It is also apparent from the work of Semerano that dimethyl-substitution in the benzene ring decreases the rate markedly when both or one of the ortho positions are substituted, the rate being lowest when both ortho positions are filled as in 2,6-acetylxylidide.

It is apparent that inductive electronic effects although important in anilide hydrolysis, are not the sum total of effects affecting the hydrolysis rate. The rates of the isomeric chloro and bromo-acetanilides for example are not significantly in the direction predicted from inductive electron withdrawal, and it is inferred that in this case conjugative electronic effects may also play an important part in defining the rate of hydrolysis, by balancing the inductive effect of the chlorine atom, and thus decreasing its substituent effects, the chlorine functioning as a -I, + M, group.

\[ \text{Cl} \quad \text{NHCOCH}_3. \]

It should be noted that this implies increase in the nitrogen shell above an octet.

This effect would not be present in the meta position, where conjugative electron release is negligible, and indeed the rates for the meta position are very slightly in the predicted direction. However, for acetyl toluidide and propio toluidide isomers, the
rates obtained by Davis and Semerano show the ortho methyl grouping to hinder hydrolysis whilst meta and para methyl groupings cause changes in rate which seem small in relation to the possible inductive and hyperconjugative effects.

The effect of substituents upon rate of alkaline hydrolysis of aliphatic and aromatic amides may be summarised in the following general manner: Electron-releasing substituents retard the hydrolysis by diminishing the electrophilic character of the carbonyl carbon atom; bulky groupings retard the rate by steric hindrance; electron attracting groupings increase the rate.

Polymeric amides

The alkaline hydrolysis of polymeric amides is a process complicated by factors peculiar to the polymeric species. Results reported hitherto are for amides of polymeric acids, not, as in the present work, for the acyl derivatives of polymeric amines. Complications arise because of the ease of intramolecular interaction and charge effects with related molecular shape.

The literature is summarised in the previous section.
INTRODUCTION TO THE EXPERIMENTAL SECTION

The experimental section is divided into four parts. Section I deals with the synthesis of \( m \)-aminostyrene, its polymerisation and copolymerisation with styrene, and the acetylation of the poly(aminostyrenes) formed.

The route to poly-(\( m \)-acetamidostyrene) is shown below.

Also described is the acetylation of \( m \)-cumidine and the preparation of samples for kinetic studies.
Section II deals with the kinetic measurements, and related preparative studies, the thermostat bath and the experimental method used in the determination of rates of hydrolysis in benzyl alcoholic potassium hydroxide at 145°.

Section III describes reductive procedures for poly-\((m\text{-styrene-diazonium chloride})\) and the characterisation of the resultant poly-(\(m\text{-hydrazinostyrene}\)) by preparation of hydrazone derivatives.

Section IV describes coupling reactions of poly-\((m\text{-styrene-diazonium chloride})\) with phenols and amines, and disazo coupling with \(\beta\)-naphthol of the derivatives obtained from the amines.
EXPERIMENTAL
All melting points are corrected.

Purification of Solvents

Benzene was dried over anhydrous calcium chloride and distilled; the fraction b.p. 79-81° was collected.

Dimethylformamide was distilled and the fraction b.p. 152-153° collected.

Methanol was distilled and the fraction b.p. 64-65° collected.

Ethyl alcohol (96%) was distilled and fraction b.p. 78° was collected.

Drying of Analytical Samples

Samples for analysis were dried prior to despatch at temperatures between room temperature-110°, and 0.05-1.0 mm. pressure, to constant weight; the temperature was chosen with due regard to the stability of the compound. The Analyst was instructed further to dry all polymeric samples at room temperature/high vacuum before analysis.
Preparation of m-nitroacetophenone (107, 108, 109)

A wide mouthed 2 litre beaker was fitted with a paddle shaped mechanically operated stirrer. The stirrer, which was of half the diameter of the beaker, was placed in an off-centre position to ensure maximum stirring. The stirrer was driven by a multi-speed motor which was essential for thorough mixing at all stages.

The flask was surrounded by a mixture of ice, salt and solid carbon dioxide. The flask was also equipped with a dropping funnel and thermometer.

Sulphuric acid (d. 1.84; 600 ml.) was placed in the flask and cooled to -5° at which temperature it solidified. Redistilled acetophenone (b.p. 93°/21 mm; 216 g; 1.8 mole) was added from the dropping funnel at such a rate that the temperature did not exceed 5° (the sulphuric acid melted), over a period of about 30 minutes. This solution, which was dark red, was then cooled to -10° by the addition of solid carbon dioxide chippings.

A nitration mixture of nitric acid (d. 1.42; 80 ml.), and fuming nitric acid (d. 1.50; 80 ml.) in sulphuric acid (d. 1.84; 240 ml.) was added from the dropping funnel to the stirred solution of acetophenone at such a rate that the temperature did not exceed -5°.
This temperature can only be maintained by the periodic addition of solid carbon dioxide chippings to the reaction mixture. The addition of the nitration mixture was carried out over $3\frac{1}{2}$ hours.

At the end of the addition, the reaction mixture, which was now extremely viscous, was stirred with cooling (below $-5^\circ$) for a further 45 minutes.

The whole was poured on to ice (1.5 Kg.) and water (3 L.) with vigorous manual stirring.

The product was obtained after filtration as a cream solid; it was transferred to a mortar and triturated with water (3 x 300 ml.) and cold 96% ethanol (2 x 25 ml.). It was then air-dried, after pressing on a porous plate. The dried solid was recrystallised from 96% ethanol; a further crop of crystals was obtained by evaporation of the mother liquor to half its original volume.

Yield

Main crop 197 g. m.p. 78-78.5° Total 67%
Second crop 4.0 g. m.p. 77-77.5°

A total of 972 g. of acetophenone was nitrated by this method as shown below.

<table>
<thead>
<tr>
<th>Run</th>
<th>Wt. of Acetophenone</th>
<th>Main crop of m-Nitro Acetophenone</th>
<th>2nd crop</th>
<th>Total yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>108</td>
<td>83.5g. m.p. 77.5-78</td>
<td>-</td>
<td>56</td>
</tr>
<tr>
<td>2</td>
<td>216</td>
<td>186g. m.p. 78-78.5</td>
<td>4.0</td>
<td>65</td>
</tr>
<tr>
<td>3</td>
<td>216</td>
<td>196g. m.p. 78-78.5</td>
<td>4.2</td>
<td>67</td>
</tr>
<tr>
<td>4</td>
<td>216</td>
<td>196g. m.p. 78-78.5</td>
<td>4.5</td>
<td>67</td>
</tr>
</tbody>
</table>
Preparation of α-methyl-m-nitrobenzyl alcohol

Aluminium foil (17.0 g.) dried in vacuo, mercuric chloride (0.2 g.) and isopropanol (700 ml.) dried over anhydrous potassium carbonate, were placed in a flask bearing a reflux condenser equipped with a calcium chloride tube. The mixture was boiled under gentle reflux on a hot plate until solution of the aluminium was complete (≈6 hours).

m-Nitrocetophenone (dried in vacuo, m.p. 78-78.5°; 198 g; 1.2 mole) was added when the aluminium had completely dissolved, and the mixture refluxed for a further two hours after complete solution of the ketone was attained. The excess isopropanol, and acetone formed during the reaction, were removed by distillation; the last traces were removed by distillation under slightly reduced pressure. The distillate was tested for the presence of acetone with Brady’s Reagent; a positive test was obtained. The sticky liquid product was allowed to cool and then added to vigorously mechanically stirred, ice cold, 3M sulphuric acid (2 L). The residue in the distillation flask was treated with a portion of the cold acid and the material obtained in this manner added to the main bulk.

The solution was stirred until the oil crystallised.

The buff crystalline product was collected on a filter, and ground in a mortar with water (2 x 300 ml.). It was then filtered off and air-dried. The filtrate was extracted with AnalaR benzene; the benzene was dried over anhydrous potassium carbonate, and finally
removed by distillation giving a further small yield.

The main batch of dry crude material was recrystallised from benzene, yielding the main crop (A) of crystals, a further crop (B) was obtained by evaporation of the mother liquor to half its original volume.

Yield

A, 117 g. m.p. 61-62°
B, 15 g. m.p. 59.5-60.5° 67%
From aqueous extract 2 g. -

Three other such reductions were carried out with total yields of 62, 62, and 63% respectively.

Preparation of m-nitrostyrene (113)

The apparatus used for the dehydration of α-methyl-m-nitrostyrene was that developed by Arcus and Halliwell, and is as described. It consists of a storage vessel; a separatory funnel (250 ml.) having a heating coil wound on the outside, and equipped with a mechanical stirrer and thermometer. The outlet side of the separatory funnel was joined by a polythene tube to glass tubing 100 cm. in length, held in the vertical plane. This tubing consisted of two 25 cm. lengths of 4 mm. bore separated from each other by a 50 cm. length of 2.5 mm. bore which acted as a constriction. The lower end of the 4 mm. bore tubing was attached to a glass U-tube bearing an outlet
at its lowest point which could be opened for cleaning purposes.

The other limb of this U-tube was attached, by a polythene connection, 
to the reaction chamber. This consisted of a tube of 22.5 ml. 
capacity closed at the top end by a quickfit thermometer, (0-250°) 
the bulb of which was adjacent to a T-shaped combined air inlet and 
product outlet tube which projected at right angles to the side of 
the chamber. The reaction chamber heater was wound on the outside 
of the tube, and was lagged with asbestos wool as was the storage 
vessel. The temperatures of the storage and reaction vessels were 
controlled by means of a screw clip at the U-tube reaction chamber 
connection and the setting of the outlet tap of the storage vessel.

α-Methyl-m-nitrobenzyl alcohol (25.0 g.) and orthophosphoric 
acid (AnalaR; d. 1.74; 200 ml.) and tert.-butylcatechol (0.025 g. 
were heated with manual stirring on a hot plate to 55-60° at which 
temperature the alcohol dissolves in the acid. It was then transferred 
to the storage vessel where it was heated to, and then maintained 
with stirring at 68-70°. This solution was allowed to run through 
the reaction vessel at 4.5-5 mls./minute at a reaction chamber tempe-

tature of 135 ± 2°.
At the outlet side of the apparatus the effluent from the reaction chamber was collected in a separatory funnel, the lower layer was run off and re-cycled through the apparatus.

After re-cycling, the product was added to water and steam distilled until no more m-nitrostyrene was present in the distillate (2 L), as indicated by the disappearance of milky droplets.

The distillate was extracted with AnalaR benzene, and the combined extracts, after washing with water, were dried over anhydrous potassium carbonate, with the addition of tert.-butylcatechol (0.02 g.) to inhibit polymerisation.

The benzene extracts were combined from runs carried out under similar conditions and the benzene was removed by distillation at 150 mm., under nitrogen, on a water bath. The residual oil was divided into two halves (40 g. each) for distillation.

<table>
<thead>
<tr>
<th>Distillation (l)</th>
<th>Bpt./mm.</th>
<th>( n_D^{25} )</th>
<th>Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>70-72/0.8</td>
<td>1.5807</td>
<td>2.86 g.</td>
</tr>
<tr>
<td>2</td>
<td>72-74/0.8</td>
<td>1.5808</td>
<td>24.20 g.</td>
</tr>
<tr>
<td>3</td>
<td>73-75/0.8</td>
<td>1.5808</td>
<td>7.93 g.</td>
</tr>
</tbody>
</table>

Yield 34.99 g. \( n_D^{25} \approx 1.5807 \)
Distillation (2)

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Bpt./mm.</th>
<th>( \frac{nD}{25} )</th>
<th>Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>73-75/0.8</td>
<td>1.5808</td>
<td>19.75 g.</td>
</tr>
<tr>
<td>2</td>
<td>74-75/0.8</td>
<td>1.5807</td>
<td>12.86 g.</td>
</tr>
</tbody>
</table>

Yield 32.61 g., \( nD^{25} \) \( \neq \) 1.5807

Total yield obtained from carbinol (195 g.), 67.6 g., \( nD^{25} \) \( \neq \) 1.5807, = 39%.

The alcohol (100 g.) was also dehydrated, at 135 \( \pm \) 2\( ^\circ \) = flow-rate, 5 ml./minute, without tert.-butylcatechol, and yielded the following:

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Bp./min.</th>
<th>Weight</th>
<th>( \frac{nD}{25} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>77-81/1.0</td>
<td>6.77 g.</td>
<td>1.5808</td>
</tr>
<tr>
<td>2</td>
<td>81-82.5/1.0</td>
<td>23.90 g.</td>
<td>1.5806</td>
</tr>
</tbody>
</table>

Yield 34.0%, \( nD^{25} \) \( \neq \) 1.5806.

This is the maximum yield obtained in the absence of inhibitor, and is considerably higher than the average so obtained.

\( \alpha \)-Methyl-\( m \)-nitrobenzyl alcohol (225 g.) has repeatedly been dehydrated as previously described (i.e. with tert.-butylcatechol) with consistent results.

Preparation of \( m \)-aminostyrene(111,113)

Stannous chloride dihydrate (217 g.) was dissolved in AnalaR concentrated hydrochloric acid (140 ml.) and 96% ethanol (35 ml.) in a 3-necked round bottomed 1 L flask equipped with a mercury-sealed
stirrer, a reflux condenser and a dropping funnel. The mixture was heated with stirring on a steam bath until it was gently refluxing, when \( m \)-nitrostyrene \((35.0 \text{ g.})\) in 96\% ethanol \((35 \text{ ml.})\) was added dropwise, so that only a small amount of \( m \)-nitrostyrene was present in the reaction vessel at any given time. On addition of a drop of \( m \)-nitrostyrene solution, refluxing occurred, and the steam bath was adjusted so that cessation of reflux indicated reaction to have ended, and that more \( m \)-nitrostyrene could be added. Addition of the solution was complete after an hour, and the reduction mixture was heated under gentle reflux for a further hour, when \( m \)-nitrostyrene was shown to be absent by addition of a portion of the solution to water. (The presence of \( m \)-nitrostyrene is shown by the formation of a cloudy solution.)

The solution was allowed to cool and was added to a solution of sodium hydroxide \((200 \text{ g.})\) in water \((700 \text{ ml.})\) and the whole steam distilled until no further amine was present in the distillate \((approximately 2 \text{ L})\).

The distillate was extracted with AnalaR benzene and the combined extracts were dried over anhydrous potassium carbonate with the addition of a little tert.-butylcatechol to inhibit polymerisation.

The benzene was removed by distillation under nitrogen at slightly reduced pressure, and the crude \( m \)-aminostyrene distilled at reduced pressure in an atmosphere of oxygen-free nitrogen\(^1\).
Similarly m-nitrostyrene (69.0) was reduced in this manner yielding:

<table>
<thead>
<tr>
<th>Fraction</th>
<th>R.p./mm.</th>
<th>Weight</th>
<th>nD&lt;sup&gt;25&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>68-71/0.7</td>
<td>2.31 g.</td>
<td>1.5882</td>
</tr>
<tr>
<td>2</td>
<td>71-73/0.7</td>
<td>8.66 g.</td>
<td>1.5970</td>
</tr>
<tr>
<td>3</td>
<td>73/0.7</td>
<td>2.84 g.</td>
<td>1.5824</td>
</tr>
</tbody>
</table>

Total yield 49.4%.

This distillation should be carried out immediately for maximum yield.

The yield would have been higher but the crude monomer set to a gel in the refrigerator overnight. The monomer was extracted from this with benzene, the benzene again removed by distillation at reduced pressure, and the monomer distilled with the results recorded. Polymer (3.10 g.) was obtained from the gel.

The reduction-procedure above is a revision and modification of that of Halliwell, which is subject to loss by sudden violent reaction. Two batches of m-nitrostyrene, (1) (30.6 g.), (2) (34.0 g.) were reduced by the latter method, giving:
(1) Fraction Weight $n_D^{25.5}$

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Bp./mm.</th>
<th>Weight</th>
<th>$n_D^{25.5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>74-76°/1.0</td>
<td>1.04 g.</td>
<td>1.6060</td>
</tr>
<tr>
<td>2</td>
<td>76-78°/1.0</td>
<td>9.97 g.</td>
<td>1.6048</td>
</tr>
</tbody>
</table>

Total yield 45%

(2) Fraction Weight $n_D^{25.5}$

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Bp./mm.</th>
<th>Weight</th>
<th>$n_D^{25.5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>69-70°/0.5</td>
<td>2.38 g.</td>
<td>1.6058</td>
</tr>
<tr>
<td>2</td>
<td>69-70°/0.5</td>
<td>5.89 g.</td>
<td>1.6048</td>
</tr>
<tr>
<td>3</td>
<td>80-81°/1.2</td>
<td>1.31 g.</td>
<td>1.6035</td>
</tr>
</tbody>
</table>

Total yield 35%

Purification of Styrene Monomer

Quinol-inhibited styrene (250 ml.) was washed with 2.0N sodium hydroxide (250; 150; 100 ml.) and then with water (250; 150; 100 ml.) and then dried over anhydrous sodium sulphate.

The crude styrene was distilled under reduced pressure in an atmosphere of oxygen-free nitrogen.

A fraction b.p. 43°/34 mm., $n_D^{25}$ 1.5441, was collected, and was stored at 4°.

Preparation of Homopolymers of m-Aminostyrene and a Copolymer of Styrene with Aminostyrene. (107,113)

2,2'-Azoisobutyronitrile (i) 0.0116 g; (ii) 0.0338 g. was dissolved in m-aminostyrene (i) 5.80; (ii) 6.55 g. The solutions were sealed in soft glass tubes under nitrogen and heated
at 73 ± 1° in an air oven for (i), 95; (ii) 80 minutes, until the products were apparently solid.

The tubes were cooled in solid carbon dioxide and the glass was broken away from the products; this process is facilitated by the use of solid carbon dioxide.

The products obtained, on attaining room temperature were hard clear pale yellow glasses.

Further homopolymers (iii), (iv), were prepared in exactly similar manner from:

2,2'-azoisobutyronitrile (iii) 0.0541; (iv) 0.362 g.
dissolved in m-aminostyrene (iii) 13.34; (iv) 9.07 g.
giving hard clear glasses after (iii) 828; (iv) 90 minutes respectively.

Polymerised overnight.

Copolymerisation with Styrene

2,2'-Azoisobutyronitrile (0.0504 g.) was dissolved in a well shaken mixture of styrene (7.99 g.) and m-aminostyrene (4.61 g.).

The solution was dispensed into two soft glass tubes and sealed under nitrogen. The tubes were heated in an air oven for 210 minutes. The product obtained was a hard, brittle, pale yellow glass.

In each case the tubes containing the monomer or mixture of monomers, were evacuated to 70 mm., and then filled with nitrogen using
a three-way tap system. The process was repeated three times to ensure the removal of oxygen from the tubes. The tubes were sealed with a cork and finally sealed in a coal gas/air flame.

Purification of the Homopolymers and Copolymer

Homopolymer (i) dissolved in dimethylformamide (70 ml.), giving a 10% w/v solution free from undissolved material, after gently warming on a steam bath for 90 minutes. The solution so obtained was colourless, and was added dropwise to water (500 ml.) with high speed mechanical stirring. The precipitated solid was fibrous and was filtered at the pump without filter papers, the polymer forming its own filter bed.

It was washed with water (500 ml.) and then methanol (2 x 100 ml.) and finally dried at reduced pressure over anhydrous calcium chloride and paraffin wax.

Yield: homopolymer (i): 3.07 g., 54%.# Homopolymer (ii): 3.05 g., 47%.
Homopolymer (iii): 7.04 g., 53%.
Homopolymer (iv): 4.89 g., 53%.

Found, for homopolymer (iii), N, (i) 11.54, (ii) 11.73;
Calc. for C₈H₁₉N: N, 11.76%.

Found, for homopolymer (iv), N, (i) 11.80, (ii) 11.80.

*These polymers were not analysed, they were analysed after acetylation.
The co-polymer was similarly dissolved in dimethylformamide (100 ml.) giving a clear solution free from undissolved material. It was precipitated, as above with water (1 L) and treated in the same manner as the homopolymers.

Yield: 9.58 g., 76%.

Found: C, (i) 88.61, (ii) 88.44; H, (i) 7.50, (ii) 7.44; N, (i) 3.79, (ii) 3.99;
Calc. for C₈H₆C₆H₅N = 2.35:1. C, 88.46; H, 7.69; N, 3.85%.

Acetylation of Poly-(m-aminostyrene) Homopolymers and a Copolymer with Styrene

Pyridine was redistilled from potassium hydroxide pellets.

Acetic anhydride was redistilled and a fraction b.p. 140-141° was collected.

Preliminary experiments indicated acetylation to proceed almost quantitatively in pyridine solution using acetic anhydride as the acetylating agent. It was however difficult to remove pyridine from the acetylated polymers, and as acetylating agent a mixture of acetic anhydride/glacial acetic acid was investigated. The copolymer however proved insoluble in this medium, and attention was concentrated on a search for precipitants for the pyridine solutions of poly(m-acetamidostyrene)s. Pyridine solutions of the polymers were prepared and added dropwise to the following solvents.
Solvent & Precipitant action for poly m-acetamidostyrene & Precipitant action for styrene; m-acetamidostyrene copolymer

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Precipitant action for poly m-acetamidostyrene</th>
<th>Precipitant action for styrene; m-acetamidostyrene copolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>Faint turbidity</td>
<td>milky soln.</td>
</tr>
<tr>
<td>IMS.</td>
<td>&quot;</td>
<td>milky soln.</td>
</tr>
<tr>
<td>40-60 Petroleum Ether</td>
<td>Good precipitant slight soln.</td>
<td>milky soln. and some fibrous solid.</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>Good precipitant</td>
<td>&quot;</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>Very fine precipitate</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

In both cases n-heptane proved to be the most suitable precipitant. It was however found by preliminary acetylation experiments on the homopolymer and copolymer, with attempted precipitation by n-heptane of the acetylated polymers from a pyridine solution containing water and acetic acid, that the polymeric material coagulated to a sticky mass. Light petroleum gave a similar result, and it was found that precipitation into water, giving a fibrous solid, yielded the more tractable material: it was also found that washing with methanol causes this material to form a sticky pad, and it was discontinued.

**Preparation of Poly(m-acetamidostyrene)**

Poly(m-aminostyrene) (i) (2.57 g.) was dissolved in the minimum quantity of redistilled pyridine (45 ml.) and acetic anhydride
(4.5 ml.) (100% excess) was added. This solution was heated on a steam bath for 60 minutes, in a flask bearing a reflux condenser, protected from water vapour by a calcium chloride tube. At the end of this period, water (1.0 ml.) was added and the solution further heated for 15 minutes to hydrolyse the excess acetic anhydride present.

The solution obtained after cooling was filtered by suction through a sintered glass funnel.

The filtrate obtained was then added dropwise to vigorously mechanically stirred water (400 ml.). The polymeric precipitate was fibrous and was filtered at the pump without papers. It was re-suspended in water and allowed to stand overnight. The suspension was then filtered, and the solid washed with water (1 L), then dried by desiccation over concentrated sulphuric acid for 3 days.

Yield 2.99 g., 86%.

Poly-(m-aminostyrene) (ii) (2.5 g.) was similarly acetylated with acetic anhydride (4.5 ml.) and pyridine (35 ml.); water (1.0 ml.) being subsequently added. It yielded on reprecipitation poly-(m-acetamidostyrene) (ii) 3.07 g., 89%.

ANALYSES (I)

Poly-(m-acetamidostyrene) (i)

Found:

\[\begin{align*}
C, & \text{ (i) } 73.83, \text{ (ii) } 73.97; \quad H, \text{ (i) } 6.74, \text{ (ii) } 6.95; \\
N, & \text{ (i) } 8.80, \text{ (ii) } 8.90; \quad O, \text{ (i) } 10.47, \text{ (ii) } 10.20; \\
C_{10}H_{11}NO & \text{ requires: } C, 74.50; \quad H, 6.87; \quad N, 8.69; \quad O, 9.93%. 
\end{align*}\]
(Poly-(m-acetamidostyrene) (ii))

Found:

C, (i) 74.19, (ii) 74.41; H, (i) 7.15, (ii) 7.30;
N, (i) 8.60, (ii) 8.52; O, (i) 10.11, (ii) 10.22%.

The samples were dried for analysis at 40°C/0.5 mm./2 hours, and the Analyst further dried them at room temperature/high vacuum.

It was inferred that a finite percentage of water might have been occluded in the polymers even after drying at 40°C/0.5 mm./2 hours. Thermo-gravimetric analysis on a finely ground sample dried in this manner, showed a weight-loss corresponding to 3.5%, between room temperature and 80°C, for a sample weight of 0.1204 g., subjected to a heating rate of 1°C rise per minute. It was stable then until the first "process" occurred at 240°C: complete volatilisation was achieved at 600°C.

A sample of poly(m-acetamidostyrene) was dried at 100-110°C/1 mm. for 1 - 2 hours and on thermogravimetric analysis a weight loss of 1% still occurred between room temperature and 120°C.

Samples of poly(m-acetamidostyrene) were dried at 100-110°C/0.7 mm./1 - 2 hours, and then dried by the Analyst prior to analysis; the following results were obtained: (II)

Poly-(m-acetamidostyrene) (i)

Found:

C, (i) 73.50, (ii) 73.48; H, (i) 6.92, (ii) 7.01;
N, (i) 9.01, (ii) 8.89; O, (i) 10.30, (ii) 10.30;
Poly-\((m\text{-acetamidostyrene})\) (ii)

Found:
\[
\begin{align*}
C, & \text{ (i) 73.29, (ii) 73.32; H, (i) 6.99, (ii) 6.88;} \\
N, & \text{ (i) 8.82, (ii) 9.10; O, (i) 10.51, (ii) 10.34%}.
\end{align*}
\]

**PREPARATION OF STYRENE; \textit{m\text{-acetamidostyrene copolymer}}**

Acetylation was carried out with styrene: \textit{m\text{-aminostyrene copolymer}} (8.39 g.), pyridine (125 ml.) and acetic anhydride (5.25 ml.), with subsequent addition of water (2 ml.), under exactly similar conditions to those described for the two homopolymers.

The pyridine solution containing the acetylated copolymer was added dropwise to vigorously stirred water (2 L).

The precipitated material was fibrous and was filtered easily at the pump, washed with water (2 L) and then suspended in water with occasional stirring. The suspension was allowed to stand overnight, the product was then filtered off and washed with warm water (1 L) and cold water (1 L). The product was dried by desiccation over concentrated sulphuric acid.

Yield: 8.36 g., 89\%.
PREPARATION OF ACETYL-m-CUMIDIDE FOR KINETIC STUDIES

m-Cumidine hydrochloride (8.70 g.) was dissolved in water (225 ml.) and acetic anhydride (5.7 ml.) was added dropwise to the mechanically stirred solution. The solution immediately became cloudy, and some solid was deposited on the walls of the reaction vessel. Sodium acetate trihydrate (7.49 g.) dissolved in water (45 ml.) was added to the solution which was then cooled on ice with stirring. Precipitation occurred immediately; the whole was stirred for 45 minutes, then allowed to stand on ice for a further hour.

The suspension was then filtered at the pump and the solid washed with water (1.5 L), then dried at reduced pressure over calcium chloride.

The crude material had m.p. 75.5-76.5° and weighed 7.84 g; 87% yield. Four recrystallisations from ligroin gave acetyl-m-cumidine of constant m.p. 76.5-77°. Literature values for the m.p.: 77.5-78° (114,115)
It was then dried over calcium chloride/paraffin wax yielding 5.74 g., 64%.

Found:

C, (i) 74.81, (ii) 74.94; H, (i) 8.32, (ii) 8.20;
N, (i) 8.01, (ii) 8.01; O, (i) 9.00, (ii) 9.03.

Calc. for C₁₁H₁₉NO₂:
C, 74.53; H, 8.53; N, 7.91; O, 9.03%.

PREPARATION OF ACETANILIDE FOR KINETIC STUDIES

AnalaR acetanilide was recrystallised from 2:1 v/v water and glacial acetic acid, to constant m.p. 114-114.5°C.

PREPARATION OF BENZYLALCOHOL FOR USE AS A SOLVENT IN KINETIC STUDIES

The alcohol was dried over sodium sulphate, and then distilled at reduced pressure in an atmosphere of oxygen-free nitrogen.

A fraction b.p. 94-95°C/12 mm. nD²⁵ 1.5362, was collected.
DETERMINATION OF THE INTRINSIC VISCOSITIES
OF THE ACETAMIDOSTYRENE HOMOPOLYMERS AND
ITS COPOLYMER WITH STYRENE

The intrinsic viscosity of a polymer solution is defined as:

\[ \eta_v = \frac{1}{c} \ln \left( \frac{\eta_{\text{soln.}}}{\eta_{\text{solv.}}} \right) = \frac{1}{c} \ln \eta_{\text{relative}} \]

and this may be equated to:

\[ \eta_v = \frac{2.303}{c} (\log_{10} t_{\text{soln.}} - \log_{10} t_{\text{solv.}}), \]

where \( t_{\text{solv.}} \) and \( t_{\text{soln.}} \) are the respective flow times for a given standard volume of solvent and solution through a standard capillary tube. By measuring these flow times at varying concentration a graph of \( \frac{2.303}{c} (\log_{10} t_{\text{soln.}} - \log_{10} t_{\text{solv.}}) \), the logarithmic viscosity number, against concentration (c in grams./100 ml. of solution) may be drawn. This is a straight line in normal cases with intercept \( \eta_v \), where c = 0 at infinite dilution, the limiting viscosity number or Intrinsic Viscosity.

The Dilution Method

The viscosity determinations were carried out at four concentrations using a dilution procedure.

Direct weighing of the polymers gave the concentrations c = 1.2 and 0.8% for 20 ml. of solution, and dilution by the following method
gave the two other concentrations. Solvent (10 ml.) was pipetted into a clean dry flask, the pipette cleaned and dried, and the 1.2% or 0.8% solution (10 ml.) was pipetted into this flask giving solutions of 0.6 and 0.4% respectively. The drainage time of the pipette was adjusted in the following manner in order to allow for the viscosity of the solutions.

\[
\text{New drainage time} = \text{Normal drainage time} \times \frac{t_{\text{soln.}}}{t_{\text{solv.}}}
\]

The viscosities were measured in benzyl alcohol at 25 ± 0.05°C, in a U-tube viscometer BSS.188 No. 2. The polymers were dried at 100-110°C/0.7 mm. for two hours prior to the determinations.

**Choice of Solvent**

Qualitative solubility experiments showed all three substrates to be soluble in dimethylformamide, pyridine, aniline, and benzyl alcohol. Benzyl alcohol was chosen as the solvent, since this was the hydrolysis solvent.

Benzyl alcohol was prepared as for the kinetic experiments.

The polymeric substrates dissolved with difficulty at the higher concentrations and gentle heat was applied in some cases.
Results

<table>
<thead>
<tr>
<th>Substrate</th>
<th>grams/100 ml.</th>
<th>t&lt;sub&gt;soln.&lt;/sub&gt; average seconds</th>
<th>log&lt;sub&gt;10&lt;/sub&gt; t&lt;sub&gt;soln.&lt;/sub&gt;</th>
<th>[η]&lt;sub&gt;c&lt;/sub&gt; Logarithmic Viscosity Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent (before polymer runs)</td>
<td>-</td>
<td>101.9</td>
<td>2.0081</td>
<td>-</td>
</tr>
<tr>
<td>Solvent (after polymer runs)</td>
<td>-</td>
<td>101.9</td>
<td>2.0081</td>
<td>-</td>
</tr>
<tr>
<td>2.35:1 Styrene: m-acetamidostyrene copolymer</td>
<td>1.2025</td>
<td>243.3</td>
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<td>0.4090</td>
<td>141.8</td>
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<tr>
<td>Poly(m-acetamidostyrene) (I)</td>
<td>1.2606</td>
<td>273.5</td>
<td>2.4370</td>
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<tr>
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<td>0.8485</td>
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<td>Poly(m-acetamidostyrene) (II)</td>
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<td>0.3993</td>
<td>124.7</td>
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<td>0.5065</td>
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</table>

Evaluation of [η]<sub>c</sub> or limiting viscosity number was made graphically.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Initiator Concentration</th>
<th>Intrinsic Viscosity [η]&lt;sub&gt;c&lt;/sub&gt;Lim. Visc. No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly-m-acetamidostyrene (I)</td>
<td>0.2%</td>
<td>0.93 (3)</td>
</tr>
<tr>
<td>Poly-m-acetamidostyrene (II)</td>
<td>0.4%</td>
<td>0.52 (2)</td>
</tr>
<tr>
<td>styrene: m-acetamidostyrene copolymer</td>
<td>0.4%</td>
<td>0.85 (c)</td>
</tr>
</tbody>
</table>
Determination of the Intrinsic Viscosity (Limiting Viscosity Number) of the poly-(m-aminostyrene) homopolymers (III) and (IV)

Viscosity determinations were carried out in 1.2 and 0.8% solutions and by dilution in 0.6 and 0.4% solutions, at 25 ± 0.05°, using a U-tube viscometer BSS.188 No. 1.

Each polymer sample was dried at 56°/0.05 mm. for several hours prior to the viscosity determination.

Choice of Solvent

Aniline was used as solvent; the polymers are only soluble in benzyl alcohol, aniline, pyridine and dimethylformamide. Halliwell found that dimethylformamide showed an ageing effect the viscosity decreasing with time, but aniline solutions were stable and were used for characterisation of his poly-(m-aminostyrene) polymers.

Aniline was dried over potassium hydroxide pellets, and distilled at atmospheric pressure. A fraction b.p. 183.5-184° was collected and stored under nitrogen.

Results are shown below.
Results

<table>
<thead>
<tr>
<th>Substrate</th>
<th>c grams/100 ml</th>
<th>t_{soln.} average seconds</th>
<th>log_{10} t_{soln.}</th>
<th>[\eta]_c Viscosity Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent (before polymer runs)</td>
<td>-</td>
<td>808.6</td>
<td>2.9077</td>
<td>-</td>
</tr>
<tr>
<td>Solvent (after polymer runs)</td>
<td>-</td>
<td>808.5</td>
<td>2.9077</td>
<td>-</td>
</tr>
<tr>
<td>Poly-(m-aminostyrene) (III)</td>
<td>1.1705</td>
<td>1370.0</td>
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<td>0.4503</td>
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<tr>
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<td>Poly-(m-aminostyrene) (IV)</td>
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<td>0.4035</td>
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<td>0.4624</td>
</tr>
</tbody>
</table>

Evaluation of the Limiting Viscosity number, [\eta]_o was made graphically.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Initiator Concentration</th>
<th>[\eta]_o or Lim. Visc. No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly-(m-aminostyrene) (III)</td>
<td>0.4%</td>
<td>0.47 (4)</td>
</tr>
<tr>
<td>Poly-(m-aminostyrene) (IV)</td>
<td>0.4%</td>
<td>0.47 (7)</td>
</tr>
</tbody>
</table>
SECTION II
Preparation of Solutions for Hydrolysis-Runs

1. Sodium Hydroxide

Carbonate-free sodium hydroxide was prepared in the normal manner. A concentrated solution of AnalaR sodium hydroxide (50 g.) in water (50 ml.) was prepared, from which sodium carbonate, being insoluble, was removed by filtration through a sintered glass funnel. The resulting solution was stored in a paraffin wax lined bottle, under nitrogen. A 0.1 N solution was prepared from this solution as required, from 2.25 ml. diluted to 500 ml. of solution with boiled-out distilled water. This solution was kept in a polythene bottle protected from the atmosphere by means of a soda-lime guard-tube.

2. Phenolphthalein Indicator

A 0.1% solution was prepared in a mixture of ethanol 70% and boiled out water 30%.

3. Hydrochloric Acid

A 0.06 N solution was prepared from the AnalaR 11.3 N acid by dilution with boiled-out water.

4. Methanol/Water

An equi-volume mixture of redistilled methanol and boiled-out water was prepared for use as a medium for the final back titration in the kinetic runs.
A slight acidity from the methanol was neutralised by addition of sufficient 0.1 N sodium hydroxide to give a permanent faint pink coloration with phenolphthalein indicator.

5. Benzylalcoholic potassium hydroxide

An approximately 0.28 N solution, was prepared as required for each set of hydrolysis runs by dissolving AnalaR potassium hydroxide (dried by vacuum desiccation) in dry benzyl alcohol under an atmosphere of nitrogen. (1.6 g./100 ml.).

Complete solution was effected by mechanical shaking or stirring. The resultant solution was clear and colourless.
STANDARDISATION OF SOLUTIONS

All solutions were pipetted by means of a "Pumpette".

1. Sodium hydroxide

This solution was standardised against potassium hydrogen phthalate, dried by vacuum desiccation and dissolved in boiled-out water. The solution obtained was titrated with sodium hydroxide protected from the atmosphere with a soda-lime guard-tube; phenolphthalein was used as indicator.

2. Hydrochloric acid

This solution was standardised directly against the sodium hydroxide solution.

3. Standardisation of the benzyl alcoholic potassium hydroxide

The hydrochloric acid, and sodium hydroxide solutions were used to standardise the potassium hydroxide solution, prepared from the concentrated solution in the following manner. 0.28 N benzyl alcoholic potassium hydroxide (10 ml.) was pipetted into a 20 ml. standard flask, allowing a standard drainage time of 60 seconds for the pipette in order to compensate for the viscosity of the solution. The solution was levelled with benzyl alcohol and then well shaken to ensure thorough mixing. 2 ml. samples of this solution were removed by means of a Chance all-glass 2 ml. syringe and either added directly to methanol/water (25 ml.), or sealed in capsules to be broken later
in the case of the blank determinations. 0.06 N Hydrochloric acid (5 mls.) was added to this solution and the acid remaining was titrated with 0.1 N sodium hydroxide solution contained in a 2 ml. burette, protected from atmospheric carbon dioxide by means of a soda-lime guard-tube. Phenolphthalein was used as indicator.

**DRYING OF AMIDES FOR HYDROLYSIS RUNS**

Acetanilide

Acetyl-\(m\)-cumidide

Poly-\(m\)-acetamidostyrene I

Poly-\(m\)-acetamidostyrene II

Styrene: \(m\)-acetamidostyrene copolymer

\[ 1.2 \text{ mm./room temperature/1 hour.} \]

\[ 0.8 \text{ mm./100-110}\degree/2 \text{ hours.} \]

\[ 0.8 \text{ mm./100-110}\degree/2 \text{ hours.} \]
The Thermostat Bath

Preliminary experiments indicated that a bath of working range 100-200° was required for kinetic studies. A bath capable of fulfilling these requirements was constructed, and was of the following form:

**CIRCUIT**

1. $S_1$ - Stimmer.
2. $S_2$ - Mains.
3. $S_3$ - In position $XZ$ (boost).
4. $S_3$ - In position $WY$ (control).

$S_3$ is a double-pole, double-throw 15amp arrow switch. Neon bulbs A and B indicate that the heaters are functioning when on.
A spiral mercury regulator, in conjunction with a Sunvic hot wire switch was initially used as the controlling mechanism but the temperature control so obtained was not satisfactory over periods of time exceeding a few days. This method was rejected in favour of a sealed contact thermometer (0–200° range) used in conjunction with a Sunvic electronic relay EA4, which gave trouble-free operation at 145° ± 0.05°. A non inflammable, water soluble, liquid detergent, Ucepal Pon 100 was used as bath liquid, at the elevated working temperature.

This liquid is stable to 200°, but fumes above 180° and is subject to high loss by evaporation at this temperature.

The permanent heater was made from nichrome tape and had a resistance of 70–80 ohms. It was wound on the outside of the drum containing the detergent, between two sheets of asbestos paper; the whole was then covered with a layer of Pyroma cement to secure it.

The intermittent heater was made from 30 gauge nichrome wire (200 ohms) and the heating element was coil-coiled on an asbestos former, and then placed inside a pyrex tube.

The electrical circuitry of the bath was so arranged that the bath could be heated quickly to 145° using both the permanent and intermittent heaters, controlled by the contact thermometer: accidental overheating thus being avoided. On attainment of 145°, the permanent heater was switched manually from control by the contact
thermometer, and thereafter allowed to function at a constant voltage, obtained by adjustment of a variable transformer, such as would maintain the bath slightly below 145°. The intermittent heater was now controlled by the contact thermometer, giving a simple on-off control system.

A fuse of soft solder, m.p: 180°, was incorporated into the circuit, as part of one of the leads from the mains, in order to cut off the supply in the event of a control failure.

The solder was contained in a glass U-tube immersed in the bath. Setting the Thermostat

The bath was set at approximately 145° with a non-calibrated thermometer. The bath thermometer was then allowed to equilibriate in the bath for 24 hours at a given immersion depth before calibration. Calibration was effected by reference to a standard thermometer immersed to its standard immersion depth in the bath.

Adjustments were made to the contact thermometer and variable transformer over a period of several hours until the bath was controlling at 145°, as read from the standard thermometer with its correction applied. The temperature of the bath thermometer at the given immersion depth was noted; thereafter, the bath temperature was checked daily by reference to this thermometer, and periodically by reference to the standard: no deviation was observed.

The bath has been run for periods up to 3 months without trouble; loss by evaporation was made up from time to time.
A spiral mercury regulator, in conjunction with a Sunvic hot wire switch was initially used as the controlling mechanism but the temperature control so obtained was not satisfactory over periods of time exceeding a few days. This method was rejected in favour of a sealed contact thermometer (0-200° range) used in conjunction with a Sunvic electronic relay EA^, which gave trouble-free operation at 145° ± 0.05°. A non inflammable, water soluble, liquid detergent, Ucepal Pon 100 was used as bath liquid, at the elevated working temperature.

This liquid is stable to 200°, but fumes above 180° and is subject to high loss by evaporation at this temperature.

The permanent heater was made from nichrome tape and had a resistance of 70-80 ohms. It was wound on the outside of the drum containing the detergent, between two sheets of asbestos paper; the whole was then covered with a layer of Pyruma cement to secure it.

The intermittent heater was made from 30 gauge nichrome wire (200 ohms) and the heating element was coil-coiled on an asbestos former, and then placed inside a pyrex tube.

The electrical circuitry of the bath was so arranged that the bath could be heated quickly to 145° using both the permanent and intermittent heaters, controlled by the contact thermometer: accidental overheating thus being avoided. On attainment of 145°, the permanent heater was switched manually from control by the contact
Samples were now withdrawn from this solution using a 2ml. syringe equipped with a 6" cannula of 2C S.W.G. bore. The samples were ejected into necked-down soft glass test-tubes (3' x 1/4" dia.).

The tubes were cleaned, prior to use, by the following materials, chromic acid, tap-water, distilled water, and finally redistilled methanol: the tubes were then baked dry in an oven at 110°.

Eight samples were taken for each run, and each tube was flushed out with nitrogen after filling, by means of a cannula, to ensure removal of oxygen and carbon dioxide from the tubes.

The tubes were sealed in an air/coal gas flame and then placed in a rack which allowed them to be completely submerged when it was placed in the thermostat bath.

The time at which the tubes were placed in the bath was recorded as zero in the time scale and samples were withdrawn over a period of time corresponding to 80% reaction, except for the completion runs with acetanilide which were carried to 95% reaction.

The tubes on withdrawal from the bath were immediately cooled by washing under a running tap. They were then washed with distilled water and finally dried, before being crushed under methanolic hydrochloric acid, (methanol/water, 25 ml; 0.06 N hydrochloric acid, 5 ml.).

The glass rod, used for crushing the tubes, was washed free from solution with boiled-out distilled water and removed. The solution was then titrated with 0.1 N sodium hydroxide solution, after
the addition of 3 drops of 0.1% phenolphthalein. The end-point was taken as the first permanent faint pink coloration of the solution.

**Ancillary Experiments**

It was found from preliminary experiments that a side reaction occurred between the potassium hydroxide and the solvent, leading to the diminution of the concentration of potassium hydroxide.

Blank runs were therefore made using potassium hydroxide solutions made up as for standardisation, and dispensed into tubes and sealed under nitrogen. Samples were removed at intervals of time over a period corresponding to 80% reaction for the runs being studied with the particular batch of benzyl alcoholic potassium hydroxide. These samples were subjected to treatment exactly similar to that described for the hydrolysis runs.

**Evaluation of Sample volume at 145°**

A standard 50 ml. flask was filled to the mark with distilled water, stoppered, and weighed; the temperature of the water was measured, and its density obtained from tables; the volume of the flask was then calculated.

The flask was dried and filled with 0.15 N solution of benzyl alcoholic potassium hydroxide and again weighed and the temperature noted.
Approximately, 5 ml. was removed from the flask, which was then placed in the thermostat at 145°. After 30 minutes the solution was levelled to the mark, and further checked at 30 minute intervals until no further expansion was observed. The flask was then cooled, washed free of detergent, dried and weighed.

Wt. of flask and water 77.2791 g.
Wt. of flask empty 27.4439 g.

49.8352 g. Temperature 21.0°

Density of water at 21.0° 0.99802

Hence volume of the flask = \( \frac{49.84}{0.9980} = 49.95 \text{ ml.} \)

Wt. of flask and benzyl alcoholic potassium hydroxide 79.9180 g.
Wt. of flask empty 27.4440 g.

52.4740 g. 21.0°

Density of Benzyl alcoholic potassium hydroxide at 21.0°

\( \frac{52.47}{49.95} = 1.050 \)

Wt. of flask after levelling at 145° 75.0172 g.
Wt. of flask 27.4440 g.
Wt. contained by flask at 145° 47.5732 g.
We have:

\[ V_{21} = V_t + (0.00025 V_t) \text{ (21-145)} \]

where \( V_{21}, V_t \) are volumes of the flask at 21, and 145° and 0.000025 is an average cubical coefficient of expansion for glass; leading to \( V_t = 50.10 \) ml.

Hence density of benzyl alcoholic KOH at 145°,

\[ D_{145} = \frac{47.57}{50.10} = 0.9495 \]

Thus a mass of 52.47 g. of benzyl alcoholic potassium hydroxide occupies a volume of \( \frac{52.47}{0.9495} \) ml. at 145°

\[ = 55.26 \text{ ml.} \]

Increase in volume per ml. over the 124° range

\[ = \frac{5.31}{49.95} \quad 0.1065 \text{ ml.} \]

Hence one litre would increase by 106.5 ml.

Hence one litre at room temperature occupies a volume of 1107 mls. at 145°.
TREATMENT OF KINETIC RESULTS

The hydrolysis runs were found to obey a second order law:

\[
 k_2''t = \frac{2.303}{(b-a)} \log_{10} \left( \frac{b-X}{a-X} \right) \frac{a}{b}
\]

where:  
\( t \) was time in seconds,  
\( b \) concentration of potassium hydroxide at room temperature,  
\( a \) concentration of amide at room temperature,  
\( X \) the apparent reaction variable for the hydrolysis reaction.

\( k_2'' \), \( k_2' \), and \( k_2 \) are the second order rate constants;  
\( k_2'' \), the rate constant before correction,  
\( k_2' \), the rate constant with one correction applied,  
\( k_2 \), the final corrected value for the rate constant with two corrections applied.

However, the hydrolyses are complicated by two factors for which corrections were required.

(i) There was an increase in sample volume between room temperature and \( 145^\circ \) and hence a decrease in concentration in moles/litre.

(ii) There was a secondary reaction occurring between the solvent and potassium hydroxide resulting in the decrease in concentration of the latter (2%/7 hours).

The increase in sample volume was corrected for; it involves the \( (b-a) \) term of the expression only. This correction for expansion was derived as previously described. The rate expression corrected for sample volume increase was now:
The secondary reaction was also corrected for:

The concentration of "amide [a] was known by direct weighing, that of potassium hydroxide [b] by standardisation. Back titration of the samples from the hydrolysis runs at given times gave the quantity of potassium hydroxide remaining at that time [b-X] and by subtracting from [b], X was found.

X, however, was dependent for its magnitude on two reactions, namely the hydrolysis, and reaction of potassium hydroxide with the solvent.

Hence \( X = x + q \)

where \( X \) is the apparent reaction variable measured for the hydrolysis reaction, \( x \) is the true reaction variable, and \( q \) is the reaction variable for reaction of the solvent and potassium hydroxide.

The value of \( b-q \) was evaluated from the ancillary blank experiments described earlier; a graph of \( b-q \) against time was drawn for each batch of potassium hydroxide, from which by interpolation the concentration of potassium hydroxide \( b-q \) at any given time was obtained.

Hence \( [b-q] - [b-X] = x \)

where \( X = x + q \).

The final corrected expression was of the following form:

\[
k_2t = \frac{2.303 \times 1.107}{(b-a)} \log_{10} \frac{(b-X) a}{(a-X) b} = E
\]

where \( x \) was the reaction variable for the hydrolysis run only, and 1.107 was the sample volume increase factor.
KINETIC RESULTS

The values for \(b-x-q\), \(b-q\) together with the corrected value for the hydrolysis reaction variable \(x\) are tabulated. In the final column, headed \(E\), the values of the corrected rate expression are tabulated.

\[
E = k_2t = \frac{2.303 \times 1.107}{(b-a)} \log_{10} \left( \frac{(b-x)a}{(a-x)b} \right)
\]

ACETANILIDE

Run I \(a = 0.07833\), \(b = 0.1500 \text{ moles/litre}\)

<table>
<thead>
<tr>
<th>Time</th>
<th>(b-x-q)</th>
<th>(b-q)</th>
<th>(x)</th>
<th>(E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.1386</td>
<td>0.14995</td>
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<tr>
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<td>16.84</td>
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</tbody>
</table>

Run II \(a = 0.07058\), \(b = 0.1500 \text{ moles/litre}\)

(Completion Run)

<table>
<thead>
<tr>
<th>Time</th>
<th>(b-x-q)</th>
<th>(b-q)</th>
<th>(x)</th>
<th>(E)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.14995</td>
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<tr>
<td>20</td>
<td>0.1327</td>
<td>0.1499</td>
<td>0.0172</td>
<td>2.20</td>
</tr>
<tr>
<td>35</td>
<td>0.1229</td>
<td>0.14985</td>
<td>0.02695</td>
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</tr>
<tr>
<td>60</td>
<td>0.1109</td>
<td>0.14973</td>
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</tr>
<tr>
<td>110</td>
<td>0.09686</td>
<td>0.1495</td>
<td>0.05264</td>
<td>13.06</td>
</tr>
<tr>
<td>220</td>
<td>0.08540</td>
<td>0.1490</td>
<td>0.06360</td>
<td>-</td>
</tr>
<tr>
<td>330</td>
<td>0.08058</td>
<td>0.1485</td>
<td>0.06792</td>
<td>-</td>
</tr>
<tr>
<td>420</td>
<td>0.08070</td>
<td>0.1481</td>
<td>0.06740</td>
<td>-</td>
</tr>
</tbody>
</table>
ACETANILIDE

Run III. (Completion Run). \( a = 0.07210, b = 1500 \text{ moles/litre} \)

<table>
<thead>
<tr>
<th>Time</th>
<th>b-x-q</th>
<th>b-q</th>
<th>x</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.00965</td>
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<td>0.14973</td>
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<td>0.08805</td>
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<td>0.06095</td>
<td>-</td>
</tr>
<tr>
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<td>0.08105</td>
<td>0.1485</td>
<td>0.06745</td>
<td>-</td>
</tr>
<tr>
<td>420</td>
<td>0.08007</td>
<td>0.1481</td>
<td>0.06803</td>
<td>-</td>
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Run IV \( a = 0.07360, b = 0.1413, \text{ moles/litre} \)

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<th>E</th>
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<td>0.02870</td>
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Run V \( a = 0.06780, b = 0.1409, \text{ moles/litre} \)

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ACETYLM-OCUMIDIDE

Run I  \( a = 0.06900, \ b = 0.1501, \) moles/litre

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Run II  \( a = 0.06956, \ b = 0.1501, \) moles/litre

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Run III  \( a = 0.07024, \ b = 0.1501, \) moles/litre

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ACETYL-m-CUMIDIDE

2nd ORDER I.R.E.
### POLY-(m-ACETAMIDOSTYRENE) I

**Run I**  $a = 0.07048$, $b = 0.1539$, moles/litre

<table>
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**Run II**  $a = 0.07041$, $b = 0.1539$, moles/litre

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</table>

**Run III**  $a = 0.07038$, $b = 0.1539$, moles/litre

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POLY-(m-ACETAMIDOSTYRENE)
### POLY-(m-ACETAMIDOSTYRENE) II

**Run I** \( a = 0.07083, b = 0.1526, \text{ moles/litre } \)

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**Run II** \( a = 0.07061, b = 0.1526, \text{ moles/litre } \)

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**Run III** \( a = 0.07116, b = 0.1526, \text{ moles/litre } \)

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**STYRENE: \( m \)-ACETAMIDOSTYRENE COPOLYMER**

Run I  \( a = 0.05991, b = 0.1409 \), moles/litre

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<th>( E )</th>
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<tr>
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<td>-</td>
<td>-</td>
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</tr>
<tr>
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</table>

* Tube shattered on removal

Run II  \( a = 0.6991, b = 0.1409 \), moles/litre

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<th>( b-q )</th>
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Run III  \( a = 0.06434, b = 0.1409 \), moles/litre

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STYRENE:m-ACETAMIDOSTYRENE COPOLYMER

2nd ORDER I.R.E.
SECTION III

PREPARATION OF POLY-(m-HYDRAZINOSTYRENE)

(1) Attempted Sulphite Reduction of Poly-(m-Styrene Diazonium Chloride)

In an attempt to avoid the use of a heavy metal, as in the stannous chloride reduction below, reduction by sulphite was attempted.

Diazotization of poly-(m-aminostyrene) (0.254 g.) was effected with sodium nitrite (0.155 g.) as described on p.112, the solution was stirred for 40 minutes and then added to sodium sulphite solution (3 ml.) freshly prepared in the following manner. Sodium hydroxide pellets (1.25 g.) were dissolved in water (1.5 ml.) and then made up to 9 ml., when phenolphthalein (3 drops) was added to give a permanent coloration.

Sulphur dioxide was passed through the solution until decolorisation occurred, and then for two minutes more.

On addition of the diazo solution, immediate precipitation occurred, to give first an orange and finally a brown suspension.

This suspension was heated slowly to 60-65°C (20 minutes) and maintained there for a further 25 minutes, giving a mobile solution of pH 1 with brown particles. This suspension was heated on a boiling water bath for seven hours giving sandy brown granules, which were filtered at the pump. The residue was washed with water, 50 ml. hot, 150 ml. cold and then dried at reduced pressure.
The Lassaigne test indicated the presence of sulphur and nitrogen, but no chloride.

Yield: 0.197 g. light pink brown solid.

The presence of sulphur indicated that conversion into the hydrazine had not occurred satisfactorily, and attention was concentrated on the use of stannous chloride.

(2) Preliminary Stannous Chloride Reduction Experiments

The stannous chloride reduction as described on p.112, was developed after use of several methods for the removal of the metal ions from the polymeric stannichloride solution.

Precipitation of the sulphides of tin by treatment with sulphur dioxide and then hydrogen sulphide was attempted, and gave only a feeble indication for tin, in conjunction with marked colour change, and this method was not pursued further.

The stannichloride was also isolated, dried, and attempts were made to redissolve the dried solid in water, followed by its reprecipitation with concentrated hydrochloric acid, leaving the tin in solution as \( \text{H}_2\text{SnCl}_6 \). This method also failed, the dried stannichloride became very difficult to dissolve in water, and the poly(hydrazine) that was "purified" in this way showed an increase in inorganic residue.

These methods were rejected in favour of precipitation of the free base from the aqueous stannichloride solution with alkali. Twice
the quantity of alkali equivalent to the hydrochloric acid and stannous chloride of the reaction was used. The precipitated poly(hydrazine) was washed with alkali and then with water until pH 7 was attained.

A cream solid which dried to an orange powder was obtained. It was subjected to combustion and gave a small residue of \( \sim 1.0\% \) white ash, yellow whilst hot. The ash was insoluble in water and acids, and gave neither a flame colour or a colour with phenolphthalein.

The dried solid gave a negative chemiluminescence test for tin, but gave a positive test for aryl hydrazines using Feigl's method, involving oxidation of the hydrazine with selenious acid, and coupling the diazonium compound formed with \( \alpha \)-napthylamine.

The dry solid was insoluble in solvents in which it dissolved when first prepared as a wet pad, with the exception of 50% aqueous acetic acid and 0.1 N hydrochloric acid in which it partly dissolved.

In order to prevent the apparent oxidation which was occurring with resultant cross-linking, the preparation was repeated with centrifugation in place of filtration, and all solutions were made from oxygen-free water, with as many operations as possible being carried out under nitrogen.

(3) Stannous Chloride Reduction of Poly-(m-Styrene Diazonium Chloride)

(In all experiments involving stannous chloride reduction, de-oxygenated water was used for aqueous washes, and the preparation of
aqueous solutions of acids and bases.)

Poly-(m-aminostyrene)III (0.597 g.) was suspended in a mixture of Analar hydrochloric acid d 1.18 (6 ml.) and water (12 ml.). The solution was warmed and the polymer coagulated to a rubbery mass. This suspension was then cooled with magnetic stirring to 0-5° and Analar sodium nitrite, (dried by desiccation over calcium chloride) (0.371 g.), dissolved in water (1/2 ml.), was then added dropwise. The suspension was cooled and stirred for 45 minutes during which time the polymer dissolved. (A slight residue of undissolved material was removed by means of a spatula at this stage).

Analar stannous chloride dihydrate (2.70 g.), was dissolved in concentrated hydrochloric acid (5 ml.) and this solution was cooled to 0° and then added dropwise to the stirred, cooled, diazonium solution. The latter changed from a highly mobile, pale yellow solution, to a viscous cream with the first drop of stannous chloride solution. The solution was stirred manually at this stage until it became mobile again, when it was magnetically stirred for a further hour with cooling.

Reduction was shown to be complete, by use of the coupling reaction between polystyrene diazonium chloride) and an alkaline solution of β-napthol. A positive reaction was given by the solution before addition of the stannous chloride solution, but 15 minutes after this addition no coupling was observed.
The suspension of the stannichloride was transferred to a centrifuge pot, the air was displaced from above the suspension by bubbling nitrogen through it. The pot was then sealed with a cork sheathed in polythene.

After centrifugation (45 minutes, 3,500 r.p.m.), the supernatent liquor was decanted and the stannichloride pad was dissolved in the minimum quantity of cold water (50 ml.); the pH at this stage was 1.

The free base was liberated from this solution by the addition of 2.5 N sodium hydroxide solution (70 ml.) which was added dropwise to the stirred stannichloride solution. A faint precipitate appeared almost immediately but dissolved, the first permanent precipitation occurring at pH 3, the pH at completion of addition was 11.

The suspension was stirred for half an hour under nitrogen, and then centrifuged. The supernatent liquor was decanted and replaced by 10N sodium hydroxide solution (100 ml.) in which the solid was re-dispersed, the pot was again sealed after flushing out the air by bubbling a stream of nitrogen through the suspension. This procedure was repeated twice with 10N sodium hydroxide, and then with water until pH 7 was attained.

After washing with water, the solid obtained was off-white in colour and was readily soluble in 0.1 N hydrochloric acid.

The solid was dried at reduced pressure over calcium chloride in a desiccator which was twice evacuated to 10 mm. and filled with
nitrogen, and then further evacuated. A brittle pale yellow-cream solid was obtained, which was only partly soluble in 0.1 N hydrochloric acid, and was insoluble in hot dimethylformamide and aniline.

Yield: 0.387 g.

Found:

C, (i) 82.79, (ii) 83.04; H, (i) 7.25, (ii) 7.05;
N, (i) 5.31, (ii) 5.45; Inorganic residue (i) 2.66, (ii) 2.46;

Recalculated with deduction for the latter:

C, (i) 85.05, (ii) 85.13; H, (i) 7.45, (ii) 7.23;
N, (i) 5.48, (ii) 5.59;

C₈H₁₀N₂ requires:

C, 71.61, H, 7.51, N, 20.88%.

**Solubility of the Poly-(m-Hydrazinostyrene)**

When freshly prepared, the wet cake was soluble in 0.1 N hydrochloric acid, but was salted out at higher concentrations, and on the addition of sodium acetate. It was soluble in aniline, and in 50% glacial acetic acid, but again salted out by sodium acetate, the precipitate redissolved on addition of more glacial acetic acid.

When freshly dried it was only partly soluble in 0.1 N hydrochloric acid, and highly swollen in aniline and dimethylformamide.
When dry and some days old it was completely insoluble.

In view of these solubility factors and the apparent oxidation which occurs on drying, it was decided to attempt the preparation of poly(hydrazone) derivatives from poly(m-hydrazinostyrene) by dissolving the wet (aqueous) poly(m-hydrazinostyrene) in 50% glacial acetic acid containing sodium acetate, insufficient to salt it out.

These preparations are described in detail overleaf.
Benzaldehyde Derivative

The poly-(m-hydrazinostyrene) was prepared by the method previously used, from poly-(m-aminostyrene)III (0.590 g.), stannous chloride (2.81 g.), sodium nitrite (0.375 g.), and 2.5 N sodium hydroxide solution (70 ml.).

The wet poly (hydrazine) was divided in half; it (4.1 g. of wet solid) was dissolved in 50% glacial acetic acid (10 ml.) containing sodium acetate (anhydrous) (0.557 g.), and this was added dropwise to redistilled benzaldehyde (0.438 g.) in glacial acetic acid (2 ml.) at room temperature. This solution was mechanically stirred for 40 minutes, and then centrifuged, the liquid decanted and the solid suspended in 50% aqueous acetic acid, twice, water, twice, and methanol, twice, followed in each instance by centrifugation.

(2 This weight of benzaldehyde corresponds to a 50% excess over that required for half the specimen, if the initial reduction was 100% complete).

On drying a buff solid was obtained; Yield: 0.133 g.

Found:

\[ \begin{align*}
C, & \quad (i) 78.22, (ii) 78.32; \\
H, & \quad (i) 6.09, (ii) 6.28; \\
N, & \quad (i) 10.66, (ii) 10.52; \\
\text{Inorganic residue}, & \quad (i) 2.35; (ii) 2.29;
\end{align*} \]

Recalculated with deduction of the latter:

\[ \begin{align*}
C, & \quad (i) 80.08, (ii) 80.15; \\
H, & \quad (i) 6.24, (ii) 6.43; \\
N, & \quad (i) 10.92, (ii) 10.76; \\
C_{15}H_{14}N_2 & \text{ requires: } C, 81.05; H, 6.35; N, 12.60%. \\
\end{align*} \]
Cyclohexanone Derivative

The remainder of the poly(hydrazine) was dissolved in 50% glacial acetic acid (10 ml.) in which sodium acetate (0.513 g.) had been dissolved. The solution was added dropwise with stirring to redistilled cyclohexanone (0.382 g.) in glacial acetic acid (2 ml.) at room temperature. Immediate precipitation occurred, and the whole was stirred and treated as in the previous experiment. On drying a yellow solid was obtained. Yield: 0.158 g.

Found:

\[ \text{C, (i) 74.13, (ii) 73.93; H, (i) 7.42, (ii) 7.42; N, (i) 9.83, (ii) 9.99; Inorganic residue (i) 2.36, (ii) 2.34; } \]

Recalculated with deduction of the latter:

\[ \text{C, (i) 75.93, (ii) 75.70; H, (i) 7.60, (ii) 7.60; N, (i) 10.07, (ii) 10.23; } \]

C\(_{14}\)H\(_{18}\)N\(_2\) requires:

\[ \text{C, 78.50; H, 8.46; N, 13.08\%. } \]
THE FISCHER INDOLIZATION REACTION (119, 120, 121, 122)

Attempted preparation of a poly("tetrahydrocarbazole")

(Method as used for 1,2,3,4 tetrahydrocarbazole) (123)

Diazotization and reduction were carried out as in the previous experiments, with poly(m-aminostyrene) (0.307 g.), hydrochloric acid (3 ml.), water (6 ml.), sodium nitrite (0.195 g.) water (1 ml.), stannous chloride (1.42 g.), hydrochloric acid (2.5 ml.).

The poly(m-hydrazinostyrene) obtained (as a wet pad), was dissolved in the minimum quantity of glacial acetic acid (2 ml.) and this solution was added to a refluxing solution of cyclohexanone (0.285 g.) dissolved in glacial acetic acid (5 ml.). A yellow precipitate immediately formed and a further 2.3 ml. of glacial acetic acid was added to fluidise the suspension. This was boiled under reflux for one hour and then filtered at the pump; the solid was washed with water and finally with redistilled methanol.

It was dried over calcium chloride/paraffin wax at reduced pressure giving a cream solid. Yield: 0.250 g.

Found:

C, (i) 78.49, (ii) 78.33; H, (i) 7.49, (ii) 7.45;
N, (i) 8.40, (ii) 8.35; Inorganic residue (i) 0.92, (ii) 0.80;

Recalculated with deduction for the latter:

C, (i) 79.23, (ii) 78.98; H, (i) 7.63, (ii) 7.51;
N, (i) 8.48, (ii) 8.42;

$C_{14}H_{15}N$ requires: C, 85.23; H, 7.67; N, 7.10%.
PREPARATION OF POLY-(m-HYDRAZINOSTYRENE HYDROCHLORIDE)

The preparation of the stannichloride was carried out with poly-(m-aminostyrene) IV (1.08 g.), hydrochloric acid (12 ml.), water (24 ml.); sodium nitrite (0.740 g.), water (3 ml.); and stannous chloride (5.70 g.), hydrochloric acid (10 ml.).

The stannichloride was dissolved in the minimum quantity of water and this solution was added dropwise to stirred 2.5 N sodium hydroxide (150 ml.) giving the free base, which was treated as before. The wet solid, obtained after washing until pH 7 was attained, was dissolved in 0.1 N hydrochloric acid giving a viscous yellow solution. The hydrochloride was precipitated by the addition of concentrated AnalaR acid (200 ml.), as a brownish pink gel. It was centrifuged, and resuspended in concentrated hydrochloric acid (150 ml.) three times with centrifugation, and finally dried over phosphoric oxide at reduced pressure with frequent renewal of the desiccant. This drying was continued until the sample was losing only 0.0006 g. per hour (78 hours).

Yield: 0.700 g. sandy yellow solid.

The dried solid was hygroscopic, and insoluble in both water and 0.1 N hydrochloric acid though highly swollen.
The chloride content was determined by the standard Volhard method. (124)

Found:

Cl, (i) 18.20, (ii) 17.78; Inorganic residue (i) 1.03, (ii) 1.11;
Recalculated on basis of average value for inorganic residue:

Cl, (i) 18.40, (ii) 17.97;

C₈H₁₁NC₁ requires:

Cl, 20.77%.

PREPARATION OF POLYHYDRAZONE DERIVATIVES (II)

Benzaldehyde Derivative

The dry poly(m-hydrazinostyrene hydrochloride) (0.201 g.) was suspended in a mixture of 50% glacial acetic acid (20 ml.) and sodium acetate (0.111 g.) and on warming on a steam bath it gave a suspension of highly swollen gel, which was added after cooling to redistilled benzaldehyde (0.187 g.) in glacial acetic acid (5 ml.). The whole was stirred for 40 minutes, and then centrifuged, and washed with water until free from chloride ion, and finally with methanol.

Yield: 0.108 g., yellow solid.

Found:

C, (i) 78.24, (ii) 78.02; H, (i) 6.31, (ii) 6.17;

N, (i) 10.47, (ii) 10.49; Inorganic residue: (i) 1.40, (ii) 1.34;
Recalculated with deduction for the latter:

C, (i) 79.33, (ii) 79.08; H, (i) 6.40, (ii) 6.25;
N, (i) 10.62, (ii) 10.63;

C₅H₁₀N₂ requires:

C, 81.05; H, 6.35; N, 12.60%

Cyclohexanone Derivative

Poly(m-hydrazinostyrene hydrochloride)(0.202 g.) was added portionwise to hot 50% glacial acetic acid (20 ml.) containing sodium acetate (0.115 g.). The swollen suspension obtained was cooled and added dropwise to redistilled cyclohexanone (0.190 g.) dissolved in glacial acetic acid (2.5 ml.). The suspension was treated as in the previous experiment.

Yield: 0.118 g.

Found:

C, (i) 75.65, (ii) 75.40; H, (i) 7.26, (ii) 7.19;
N, (i) 9.46, (ii) 9.44; Inorganic residue: (i) 1.73, (ii) 2.06;

Recalculated with deduction for the latter:

C, (i) 77.00, (ii) 77.00; H, (i) 7.39, (ii) 7.34;
N, (i) 9.63, (ii) 9.64;

C₁₄H₁₈N₂ requires:

C, 78.50; H, 8.46; N, 13.08%.
POLY-(m-STYRENE DIAZONIUM CHLORIDE) COUPLING EXPERIMENTS

Coupling with β-Napthol

Poly-(m-aminostyrene) III (0.583 g.) was dissolved in 1.0 N hydrochloric acid (25 ml.), and the solution cooled below 5°: sodium nitrite (0.332 g.) dissolved in water (10 ml.) was added dropwise with stirring. The solution was stirred for 30 minutes and tested for excess nitrous acid with starch-iodide papers. Urea, an ice-cold 5% solution (1 1/2 ml.) was then added, and the solution stirred for a further 15 minutes.

This solution was added dropwise to β-napthol (m.p., 122-123°, 0.787 g.) dissolved in 1.0 N sodium hydroxide (25 ml.) diluted with water to 200 ml. The coupling was carried out at 15° and the addition made over a period of ten minutes. Immediate coupling was observed with the first drop of diazo solution, and after completion of the addition the solution was stirred for one hour, and then filtered at the pump. At the end of one hour's stirring, excess β-napthol was shown to be present and the pH was 9.

The red solid was washed with N/50 sodium hydroxide (500 ml.) until it gave no precipitate with benzene diazonium chloride solution, and then with water until free of alkali (1 L).
It was then dried at reduced pressure/calcium chloride.

Yield: 0.769 g.

Found:

\[
\begin{align*}
\text{C, (i) } & 78.90, \ (\text{ii) } 78.95; \\
\text{H, (i) } & 5.13, \ (\text{ii) } 5.25; \\
\text{N, (i) } & 10.25, \ (\text{ii) } 10.16; \\
\text{O, (i) } & 5.84, \ (\text{ii) } 5.88;
\end{align*}
\]

\[
\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}\ 	ext{requires:}
\]

\[
\begin{align*}
\text{C, } & 78.81, \ 	ext{H, } 5.14, \ 	ext{N, } 10.22, \ 	ext{O, } 5.83%.
\end{align*}
\]

**Solubility**

Insoluble in water, benzene, carbon tetrachloride, light petroleum (b.p. 40-60°), acetone.

Swollen in cold, but insoluble in hot chloroform and ethyl acetate.

Highly swollen and part soluble in dimethyl formamide, benzyl alcohol \( \text{m-cresol} \) and formic acid, at their boiling points.

Ashing yielded no residue.

Colour of finely divided solid - bright red.

**Coupling with Amines**

Poly-(\( \text{m-aminostyrene} \)) (0.592 g. III) was diazotised under conditions similar to the previous experiment, (sodium nitrite 0.337 g; \( 1\text{ON} \) hydrochloric acid 25 ml.).

After being stirred for 30 minutes the solution (36 ml.) was divided in half, and each portion (18 ml.) was added to two separate amines, \( p\text{-xyldidine} \) and 2,5-dimethoxyaniline.
Coupling with p-Xyldine

The diazonium chloride solution was added dropwise with stirring to p-xylidine (0.348 g., redist., b.p. 210-212°), dissolved in 96% ethanol (25 ml.) at 50°. Immediate precipitation occurred with the first drop of diazo solution added, and a colour change, yellow → dark red was observed as the addition proceeded. Some of the solid appeared to dissolve to give a red solution.

The solution was stirred for 30 minutes and then cooled on ice. The solid was filtered at the pump, yielding, after washing with 0.1 N hydrochloric acid (250 ml.) a maroon solid. This solid showed a marked colour change on the addition of 2N ammonium hydroxide solution (red → orange), and it was decided that in view of the apparent ease of formation of the free base, this should be made and analysed.

The hydrochloride was suspended in 2N ammonia (150 ml.) and stirred for 30 minutes and then centrifuged. This process was repeated 3 times and each clear supernatant liquor was acidified with nitric acid and tested for the presence of chloride ion with silver nitrate.

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<th>Remarks</th>
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<td>1st supernatant</td>
<td>copious</td>
</tr>
<tr>
<td>2nd supernatant</td>
<td>diminution (considerable)</td>
</tr>
<tr>
<td>3rd supernatant</td>
<td>slight trace</td>
</tr>
</tbody>
</table>

After the 3rd "spinning down" the solid was re-suspended in ammonia and filtered at the pump, further washed with ammonia (50 ml.) and then
water.

It was then dried at reduced pressure/calcium chloride. Yield: 0.365 g.

Found:

\[
\begin{align*}
C, & \ (i) \ 77.49, \ (ii) \ 77.66; \ H, \ (i) \ 6.81, \ (ii) \ 6.90; \\
N, & \ (i) \ 9.41, \ (ii) \ 9.57; \\
C_{16}H_{17}N_3 & \text{ requires:} \\
C, & \ 76.47, \ H, \ 6.82, \ N, \ 16.72\%.
\end{align*}
\]

**Lassaigne Test**

- Nitrogen - positive test
- Chloride - very slight trace

**Solubility**

- \(m\) Cresol ) highly swollen in boiling solutions;
- Formic acid 98-100% ) slight solubility
- Dimethyl formamide )

Colour:
- finely divided free base - dull orange
- finely divided hydrochloride - purple-red

**Coupling with 2,5-Dimethoxyaniline.**

The diazonium solution (18 ml.) was added dropwise to 2,5-dimethoxyaniline recrystallised from ligroin, m.p. \(81^\circ\), (c.425 g.) under exactly similar conditions to those used for \(p\)-xylidine.
Immediate precipitation again occurred, yielding a red solution containing a gelatinous red solid. (It was much more soluble than the corresponding xylidine derivative.) Attempts to filter the solution failed, and it was centrifuged, giving a pad of red gelatinous material and a highly coloured supernatant liquid.

The solid was converted to the free base as before with 20N ammonia, washed until free of Cl⁻, and yielded on drying at reduced pressure/calcium chloride 0.453 g. of an orange red powder.

Found:

C, (i) 67.50, (ii) 67.43; H, (i) 6.32, (ii) 6.42;
N, (i) 13.51, (ii) 13.60;

C₁₆H₁₇N₃O₂ requires:
C, 67.83, H, 6.05, N, 14.83%.

Lassaigne Test

Nitrogen - positive
Chloride - slight trace

Solubility

<table>
<thead>
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<th>Compound</th>
<th>Solubility</th>
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<tbody>
<tr>
<td>m Cresol</td>
<td>( red solution</td>
</tr>
<tr>
<td>Dimethyl formamide</td>
<td>soluble on heating ( yellow</td>
</tr>
<tr>
<td>Formic acid</td>
<td>( red solution</td>
</tr>
</tbody>
</table>

Colour - the finely divided solid was bright orange-red under daylight, and brownish orange (bright) under fluorescent lighting.
Disazo Coupling

This was attempted in suspension.

Disazo coupling of poly-(m-styrene azo- p-xylidine)

The xylidine derivative (0.211 g.) (free base) was suspended in 1ON hydrochloric acid (20 ml.).

This suspension was cooled to 0-5⁰ with magnetic stirring and then diazotised with sodium nitrite (0.0609 g.) in water (12 ml.). The particles changed colour to brown as the nitrite solution was added, and after addition was complete the whole was allowed to stir for one hour. It was then added to β-naphthol (0.158 g.) dissolved in 1ON sodium hydroxide (25 ml.) diluted to 200 ml. with water, at 15⁰.

A colour change from brown to red-violet was observed as the suspension was added dropwise. After being stirred for one hour the suspension was filtered at the pump and the solid product washed with N/50 sodium hydroxide (500 ml.) and then water (1 L) and finally dried at reduced pressure over calcium chloride.

Yield: 0.229 g.

It yielded no residue on ashing.

Solubility

Highly swollen but insoluble in m cresol, formic acid, and dimethyl formamide.

Colour of finely divided solid - purple-brown (daylight) maroon under fluorescent light.
Disazo coupling of poly-(m-styrene azo-2,5-dimethoxy aniline)

The method was that used in the previous experiment. Free base (0.182 g.), sodium nitrite (0.051 g.) \( \beta \)-napthol (0.125 g.) were allowed to react at similar dilutions.

A colour change from wine red to brown was observed on addition of the nitrite solution, and when the suspension was added to \( \beta \)-napthol visible coupling was observed, giving a colour change from brown to violet.

The product was filtered at the pump, washed with N/50 sodium hydroxide (500 ml.) and then water (1 L), and finally dried at reduced pressure/calcium chloride.

Yield: 0.224 g.

Solubility

m-cresol, formic acid, DMF, partial solubility shown, highly swollen at the boiling point, violet solns.

Colour

Finely divided solid - violet-black.
RESULTS AND DISCUSSION
SECTION I

THE SYNTHESIS OF POLY-(m-AMINOSTYRENE)

The known route to the monomer m-aminostyrene from acetophenone, namely:

\[
\begin{align*}
\text{CH}_3 & \quad \text{C=O} \\
\text{CH}_3 & \quad \text{C=O} \\
\text{nitration} & \quad \text{reduction} \\
\text{CHOH} & \quad \text{CH} \\
\text{NO}_2 & \quad \text{NH}_2
\end{align*}
\]

was first reported by Matsui, and later by Arcus and Schaffer, who used m-aminostyrene as an intermediate in the preparation of m-hydrazinostyrene.

Arcus and Halliwell later modified the method of Arcus and Schaffer, so that larger quantities of α-methyl nitrobenzyl alcohol could be dehydrated by a "flow" method. Its preparation from m-nitrocinnamic acid, has been reported by Komppa and other workers, and repeated with low yields by Tutin and Mann, and Arcus and Sheffer.

The Nitration of Acetophenone

The nitration of acetophenone in various media, with varying yield has been reported by several authors.
The method used by Arcus and Schaffer (112) and Arcus and Halliwell (113) was that reported by Corson and Hazen (109) using the modifications of Morgan and Watson (108). The experimental method involves nitration with a mixture of nitric and sulphuric acids at a recommended temperature of not above 0°.

It has been found however, that to avoid a low yield of the desired product, the temperature must not rise above -5° and stirring and cooling must be efficient. An ice-salt bath was not sufficient to maintain the reaction vessel at this temperature, a mixture of Drikold, ice and salt was used. The yield obtained at this stage was 70%.

**Reduction of m-Nitroacetophenone**

Various authors (125, 112, 113) report on the reduction of m-nitroacetophenone. The method used was a modification of Lund's (110) procedure for the Meerwein Pondorf Verley reaction, the reduction of a ketonic function in a molecule by aluminium isopropoxide in isopropyl alcohol. Reduction of the carbonyl grouping can be effected in this manner without reduction of the nitro grouping, yielding the α-methy-m-nitrobenzyl alcohol.

The experimental method involves heating the ketone in an iso-propyl alcohol solution of aluminium isopropoxide. At the end of the reaction the excess alcohol, and acetone formed during the
reaction, are removed by distillation and the aluminium complex de­
composed with dilute sulphuric acid yielding \( \alpha \)-methyl-\( m \)-nitrobenzyl
alcohol. A 60% yield is obtained by this method and no further
modification has been made.

The Dehydration of \( \alpha \)-Methyl-\( m \)-Nitrobenzyl Alcohol

This dehydration stage is the most difficult in the synthesis; it has been investigated by a number of authors, with varying success, as shown in the table below.

<table>
<thead>
<tr>
<th>Method of Dehydration</th>
<th>Yield</th>
<th>Author</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphoric oxide in benzene</td>
<td>25%</td>
<td>Marvel et al</td>
<td>128</td>
</tr>
<tr>
<td>Potassium bisulphate</td>
<td>Not given</td>
<td>Matsui</td>
<td>125</td>
</tr>
<tr>
<td>Acetic anhydride/sulphuric acid</td>
<td>70%</td>
<td>Smets and Reckers</td>
<td>129</td>
</tr>
<tr>
<td>Heating alone</td>
<td>Low</td>
<td>Dahlig</td>
<td>27</td>
</tr>
</tbody>
</table>

Arcus and Schaffer\(^{(112)}\) investigated these methods of prepara-
tion and their results are summarised below, together with other experimental methods tried.
<table>
<thead>
<tr>
<th>Method of Dehydration</th>
<th>Yield and Comment</th>
<th>Compare Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic Anhydride/H₂SO₄</td>
<td>Product did not decolorize bromine in carbontetrachloride and from analysis concluded to be α-methyl-m-nitrobenzyl acetate.</td>
<td>129</td>
</tr>
<tr>
<td>20% Oleum</td>
<td>In presence of excess alcohol, alcohol obtained unchanged, and in presence of excess sulphuric acid, a gummy product obtained.</td>
<td></td>
</tr>
<tr>
<td>Refluxing with Phosphoric oxide in benzene</td>
<td>A maximum yield of 19% of the desired product obtained.</td>
<td>128</td>
</tr>
<tr>
<td>Distillation with Iodine 2% by weight at 10 mm.</td>
<td>Alcohol regained in 60% yield.</td>
<td>130</td>
</tr>
</tbody>
</table>

* A similar dehydration was effected by this method by Kenyon and Young, (130) who obtained αγ-dimethyl butadiene from αγγ-trimethylallyl alcohol by distillation with iodine.

Arcus and Schaffer found that α-methyl-m-nitrobenzyl alcohol could be dehydrated to give a 45% yield under the following optimum conditions: a mixture of ortho phosphoric acid (40 ml.), and α-methyl-m-nitrobenzyl alcohol (5 g.) was heated to 125° during the course of 12 minutes and maintained there for one minute; it was then poured
into water, and the \textit{m}-nitrostyrene finally extracted with benzene.

The dehydration of \textit{\alpha}-methyl-\textit{m}-nitrobenzyl alcohol by orthophosphoric acid has been further investigated by Arcus and Halliwell\textsuperscript{(113)} and a flow method was developed in which 25 gram samples of alcohol could be dehydrated.

A solution of the alcohol in phosphoric acid at 60° is allowed to flow through a heated reaction vessel at a given rate. An optimum flow-rate of 5 mls./min. and reaction-vessel temperature of 135° gave a maximum yield of 38%.

In this work the flow method of dehydration has been used at the optimum conditions quoted above. The method has been repeated exactly giving as a maximum yield under these conditions, \textit{m}-nitrostyrene 34%. The method was modified by the inclusion of an inhibitor, tert. butyl catechol (0.1% on the monomer weight), in an attempt to decrease losses due to polymerisation; by this means yields very slightly better than those of Halliwell have been obtained: \textit{m}-nitrostyrene 39%.

\textbf{Reduction of \textit{m}-Nitrostyrene}

This reduction has been reported by a number of authors using a variety of reducing agents. Matsui\textsuperscript{(125)} used tin and hydrochloric acid and obtained a 41% yield, Komppa\textsuperscript{(131)} used a stannous chloride
reduction, Wiley and Smith\(^{(132)}\) obtained an 84\% yield of poly-\((m\text{-}amino-\text{styrene hydrochloride})\) using zinc and hydrochloric acid.

Arcus and Schaffer\(^{(112)}\) attempted reduction by two methods, the use of hydrazine hydrate in the presence of Raney Nickel, a method developed by Balcom and Forrest\(^{(133)}\) for the selective reduction of nitro groupings to amino groupings and reduction using stannous chloride. The method of Balcom and Forrest yielded 12\% of pure \(m\text{-aminostyrene}\) and attention was turned to the stannous chloride reduction. The method used was based on the method used by Coombs\(^{(134)}\) for the reduction of 2-nitro fluorenone, and a yield of 48\% pure \(m\text{-aminostyrene}\) was obtained. Arcus and Halliwell have obtained yields of 76\% by this method.

This method has again been used but modifications have been made. The procedure described by Schaffer and Halliwell can become extremely violent, and suffers from an induction period which appears to be mechanical rather than chemical in nature.

The reaction has been modified in that the \(m\text{-nitrostyrene}\) was added dropwise in ethanol to an ethanolic solution of stannous chloride in hydrochloric acid, and in this way the violent reaction is completely eliminated. (A similar experience with stannous chloride reductions is noted by Kent and Slade.\(^{(128)}\)) The method as detailed in the Experimental part gave yields of 50\%.
Polymerisation of m-Aminostyrene

m-Aminostyrene was long ago observed to polymerise on distillation by Komppa. The first deliberate attempt at polymerisation of this monomer was reported by Matsui in 1942 who polymerised it by heating at 160°, or by allowing the monomer to stand at room temperature until it polymerised (48 hours). Oda and Urata similarly polymerised m-aminostyrene by heating at 160° under various conditions.

The first polymerisation attempted with an added initiator, decomposition of which gave free radicals, was that of Dahlig who used benzoyl peroxide. However, it proved unsatisfactory due to the oxidising ability of this initiator.

Arcus and Halliwell first polymerised m-aminostyrene in such a manner that the molecular weight of the resultant polymer could to some extent be controlled; this was achieved by initiation with 2,2'-azo isobutyronitrile, in different concentrations, at 79°. These authors also copolymerised m-aminostyrene with styrene under similar conditions. The polymers were obtained as pale yellow, slightly rubbery solids which on precipitation from dimethylformamide into water yielded white flocculent solids. The polymerisation and copolymerisation of the monomer with styrene, has been effected in like manner in this work using 2,2'-azoisobutyronitrile at a slightly lower temperature of 73° in order to increase the half life of the
decomposition of the initiator into free radicals.

The homopolymers and the copolymer with styrene, so obtained after 90, and 210 minutes respectively, were clear pale yellow, hard glasses and were readily soluble in dimethylformamide; their form contrasts to Halliwell's polymers which were polymerised over 250 minutes and 10-28 hours at 79°, yielding slightly rubbery solids.

Two homopolymers of \( m \)-aminostyrene were prepared at different initiator concentrations and were obtained in 53% yield on precipitation from dimethylformamide into water. These polymers were acetylated to give poly-(\( m \)-acetamidostyrene)s I and II used in later kinetic studies. The acetyl polymers, and hence the poly-(\( m \)-aminostyrene)s from which they were derived, were shown to have different molecular weights, by intrinsic viscosity measurements on benzyl alcohol solutions (p. 79).

Intrinsic viscosity is in general related to molecular weight by the expression,

\[
[\eta]_G \rightarrow 0 = KM^a \quad (a \text{ approximates to 0.67})
\]

and the values obtained indicate a higher molecular weight for a lower initiator concentration, as would be expected (p. 17).

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Initiator concentration</th>
<th>([\eta]\circ \text{ or LVN} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly-(( m )-acetamidostyrene) I</td>
<td>0.20%</td>
<td>0.93 (3)</td>
</tr>
<tr>
<td>Poly-(( m )-acetamidostyrene) II</td>
<td>0.40%</td>
<td>0.52 (2)</td>
</tr>
</tbody>
</table>
A copolymer of styrene and \textit{m}-aminostyrene was also prepared and after precipitation from dimethylformamide into water was obtained in 76\% yield. This was similarly converted to its acetyl derivative and characterised by intrinsic viscosity determination in benzyl alcohol.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Initiator concentration</th>
<th>([\eta]_0) or LVN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene: \textit{m}-acetamidostyrene copolymer</td>
<td>0.40%</td>
<td>0.85 (0)</td>
</tr>
</tbody>
</table>

Two other homopolymers of \textit{m}-aminostyrene were prepared; identical concentrations of initiator were used in order to prepare poly-\textit{(m}-aminostyrene\textit{)} of similar molecular weight for use in the work described in Sections III and IV. These polymers were obtained after precipitation from dimethylformamide into water in 53\% yield. Their intrinsic viscosities were measured in aniline, and indicate the polymers to have identical molecular weights.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Initiator concentration</th>
<th>([\eta]_0) or LVN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly-\textit{(m}-aminostyrene\textit{)} III</td>
<td>0.40%</td>
<td>0.47 (4)</td>
</tr>
<tr>
<td>Poly-\textit{(m}-aminostyrene\textit{)} IV</td>
<td>0.40%</td>
<td>0.47 (7)</td>
</tr>
</tbody>
</table>
SECTION II

OBJECT OF THE KINETIC INVESTIGATION

The present work is part of a more general investigation of the reactivity of polymer side-groups, in particular those attached to a polystyrene structure. Two features are looked for in reactions selected for investigation: first, that conditions can be found under which macromolecule and reagent are in homogeneous solution initially, and if practicable throughout the reaction, and second that there is general agreement on the mechanism for the reaction with comparable small molecules.

The following method of investigation has been developed; the rate and order of reaction are determined at the same solvent-composition and temperature for: (i) two specimens of homopolymer of different average molecular weight; (ii) a copolymer in which the reactive units are spaced out by inert units; (iii) the appropriate phenyl compound, representing the individual side group; and (iv) the isopropylphenyl compound, representing the side-group together with the chain carbon atom to which it is combined and the two adjacent atoms. There may be inferred from the above how far the macromolecular reaction is similar in rate and order to that for the phenyl compound; where differences are found they are ascribed to the macromolecular environment, and the effects of the following factors may be distinguishable: molecular weight, from (i) above; interaction
between adjacent reactive groups, from comparison of (ii) with (i); electron-release from the main chain, from comparison of (i) and (ii) with (iii) and (iv).

Poly-(m-aminostyrene) was employed by Arcus and Halliwell for the investigation of a representative unimolecular reaction, the decomposition of the diazonium cation, and it has now been used in the study of a bimolecular reaction, the alkaline hydrolysis of its acetyl derivative.

Preparation of acetyl-m-cumidide, and of poly-m-(acetamidostyrene) and a styrene: m-acetamidostyrene copolymer

Acetyl-m-cumidide

Acetyl-m-cumidide was obtained from m-aminocumene hydrochloride by acetylation in aqueous solution. It was obtained after recrystallisation to constant melting point in 64% yield, the melting point corresponding to those recorded in the literature.

Acetyl polymers

Two homopolymers of m-aminostyrene and a copolymer with styrene were acetylated in pyridine by acetic anhydride. Precipitation of the poly acetyl compounds from the pyridine solution was effected with water and white fibrous solids were obtained in the following yields:
The homopolymer is hygroscopic. Specimens were dried for 2 hours at 40-50°C/0.5 mm., and gave the duplicate analyses1 Exptl. p. 74

A specimen of homopolymer was heated in a thermogravimetric balance; the weight remained constant from 80°C to 240°C, whence there is no decomposition up to the latter temperature. Specimens were then dried at 100-110°C/0.7 mm. to constant weight and gave the duplicate analyses (II). Experimental p. 75. These are not superior to (I). It is believed that both drying procedures are, in fact, efficient, but that in the micro analytical laboratory, although the samples are submitted to a further drying under high vacuum at room temperature, some moisture-uptake may occur during the manipulations of the analytical procedures. When the analyses are considered as a whole, the departure from the calculated values is small. Specimens for kinetic investigation were dried for 2 hours at 100-110°C/0.8 mm. and the molecular formula of the homopolymer (C_{10}H_{11}NO)_x was used in the calculations. The copolymer was much less hygroscopic,

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly-(m)-acetamidostyrene I</td>
<td>86%</td>
</tr>
<tr>
<td>Poly-(m)-acetamidostyrene II</td>
<td>89%</td>
</tr>
<tr>
<td>Styrene: (m)-acetamidostyrene copolymer 2.35:1</td>
<td>89%</td>
</tr>
</tbody>
</table>
and its analysis did not present difficulties. In the kinetic calculations for the copolymer, the g. molecular weights of acetamido group per 1,000 g. were equated to the g. atoms of nitrogen per 1,000 g.

**Kinetic procedure**

The kinetic experiments have been performed in benzyl alcoholic potassium hydroxide solution. The kinetics are those of completely homogeneous solution. The copolymer is the least tractable material and yields a highly viscous solution. The procedure described in the experimental section yields the copolymer in solution in 0.07 N solution, the potassium hydroxide solution being 0.14 N. This solution has defined the conditions under which the rates of hydrolysis of each of the other substrates have been investigated. The temperature, 145°, was chosen with due regard for the reaction-velocity of the fastest substrate acetanilide, which is 80% hydrolysed after 140 minutes at this temperature.

The experimental procedure and method of calculation are described in detail in the Experimental part.

Two-ml. portions of the solution of the amide in benzyl alcoholic potassium hydroxide were placed in glass ampoules, which were sealed and placed in a thermostat at 145°. At intervals they were removed, crushed under methanolic hydrochloric acid, and the excess of the latter titrated with sodium hydroxide, phenolphthalein being used as indicator.
To a small extent, reaction occurred between the hot benzyl alcohol and potassium hydroxide, whereby the concentration of the latter diminished. Correction for this was made by means of runs at 145°, identical with the Kinetic runs except for the absence of an amide, whereby the concentration of alkali obtaining at intervals throughout the period of a kinetic run was determined directly.

In order to provide concentrations correct at 145°, the expansion of 0.15 N-benzyl alcoholic potassium hydroxide between 21° and 145° was determined; 1000 ml. at the former occupy 1107 ml. at the latter temperature. For the kinetic calculations, the concentration of acetamido group and potassium hydroxide are expressed in g. molecular weights per litre at 145°.
Summary of Results

Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Rate</th>
<th>% of 20.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetanilide</td>
<td>20.1</td>
<td></td>
</tr>
<tr>
<td>Acetyl-m-cumidide</td>
<td>17.8</td>
<td>89%</td>
</tr>
<tr>
<td>[Computed value for homo- and co-polymer initial rate: 18.7]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Poly-[m-acetamidostyrene] I 5.32 [28%]
Poly-[m-acetamidostyrene] II 5.53 [30%]
Styrene-m-acetamidostyrene copolymer 2.35:1.00
Initial rate 10.1 [54%]

In square brackets, as % of 18.7

Table 2

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Function</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Davis/100°/H₂O</td>
<td>[K₂ acetyl-m-toluidide/K₂ acetanilide] x 100</td>
<td>98%</td>
</tr>
<tr>
<td>Semerano/H₂O - EtOH</td>
<td>100°, 84.5/95.6 x 100</td>
<td>88%</td>
</tr>
<tr>
<td></td>
<td>110°, 180/184 x 100</td>
<td>98%</td>
</tr>
<tr>
<td></td>
<td>130°, 589/679 x 100</td>
<td>87%</td>
</tr>
</tbody>
</table>
Values for the second-order integral expression have been plotted against time (Experimental part). The results for acetanilide and acetyl-m-cumidide gave straight lines over nearly the whole reaction, showing a close adherence to the second order. Poly-(m-acetamidostyrene) I and II furnished straight lines over the greater part of the reaction, slight deceleration being indicated in the late stages. The extent to which linearity applies up to 70% reaction may be seen on inspection of the graphs; the time for this percentage reaction of acetanilide, acetyl-m-cumidide, homopolymer (I) and (II) is 95, 110, 330, 330 min., respectively. The styrene-m-acetamidostyrene copolymer gave plots in which a slight curvature is manifest throughout; the second order constant, $K_2$, derived from the initial tangential slope is recorded in Table 1; the "instantaneous" rate-constant thereafter falls progressively, though not greatly.

Comparison of the value for acetyl-m-cumidide, $17.8 \times 10^{-4}$ l. mole$^{-1}$ sec.$^{-1}$, with that for acetanilide, 20.1, shows a fall of 11% in rate on the insertion of the electron-releasing m-isopropyl substituent. This accords fairly well with Davis's and Semerano's observations (Table 2), on acetyl-m-toluidide; a greater release is to be expected from a isopropyl than a methyl group where only inductive release is to be considered, as here for a meta substituent, but the experimental condition of the present work and those of these two
authors are, all three, different.

From the rates of decomposition of benzene- and m-cumene-
diazonium chloride, and poly-(m-styrenediazonium chloride), Arcus and
Halliwell inferred that reaction was controlled by inductive release
from the m-isopropyl or m-"polymeric" substituents, and the results
permit computation of the rate to be expected for the present polymer-
hydrolyses, if only the inductive effect were important.

(139)

Hammett has found for many different reactions of a series of
substituted phenyl compounds that the following expression is applicable:

\[
\log \left( \frac{K_X}{K_H} \right) = \rho \omega
\]

where \( K_X \) is the rate for the \( X \)-substituted compound, \( K_H \) that for the
unsubstituted compound, \( \rho \omega \) a constant for the type of reaction,
and \( \omega \) a constant for the substituent which applies, in
principle, to all types of reaction.

With reference to the results of Arcus and Halliwell, and to
the present results, where:

- \( \omega_{mi} \) is the sigma constant for m-isopropyl,
- \( \omega_{mp} \) is that for the
- polystyrene main chain considered as a meta-substituent,
- \( \rho_{diaz} \) is the rho constant for the diazo-decomposition reaction,
- \( \rho_{hydrol} \) is that for the present hydrolyses,

and
$K_H$, $K_{mi}$, $K_{mp}$ are rate-constants for the reactions of

where $R = H$, isopropyl, and the polystyrene main chain, diazo-decomposition and hydrolyses being distinguished by suffixes.

We have:

$$
\log \left( \frac{K_{mi}}{K_H} \right)_{\text{diaz o}} = \rho_{\text{diaz o}} \sigma_{mi} = A; \quad \log \left( \frac{K_{mp}}{K_H} \right)_{\text{diaz o}} = \rho_{\text{diaz o}} \sigma_{mp} = B;
$$

$$
\log \left( \frac{K_{mi}}{K_H} \right)_{\text{hydrol}} = \rho_{\text{hydrol}} \sigma_{mi} = C;
$$

We wish to estimate $K_{mp}$, hydrol on the basis of inductive effects only, and this is given by:

$$
\log \left( \frac{K_{mp}}{K_H} \right)_{\text{hydrol}} = \rho_{\text{hydrol}} \sigma_{mp}
$$

$$
\rho_{\text{hydrol}} = \frac{C}{\sigma_{mi}} \quad \text{and} \quad \frac{\sigma_{mi}}{\sigma_{mp}} = \frac{A}{B} \quad \text{whence} \quad \sigma_{mp} = \frac{B \sigma_{mi}}{A}.
$$

$$
\therefore \rho_{\text{hydrol}} \sigma_{mp} = \frac{C}{\sigma_{mi}} \times \frac{B \sigma_{mi}}{A} = \frac{BC}{A}
$$

Whence,

$$
\log \left( \frac{K_{mp}}{K_H} \right)_{\text{hydrol}} = \log \left( \frac{K_{mp}}{K_H} \right)_{\text{diaz o}} \times \log \left( \frac{K_{mi}}{K_H} \right)_{\text{hydrol}} \log \left( \frac{K_{mi}}{K_H} \right)_{\text{diaz o}}
$$

Insertion of the appropriate values yields:

$$
K_{mp, \text{hydrol}} = 18.7 \times 10^{-4} \ \text{l. mole}^{-1} \ \text{sec}^{-1}
$$
The rates for the two homopolymers, which are of considerably different molecular weights, are nearly equal, but are only 28 and 30% of that estimated on a basis of inductive effects alone. The rate for the copolymer is 54% of this value. It is clear that macromolecular factors are operative in the hydrolyses of the homo- and co-polymers.

In certain circumstances a lowering of rate of reaction can occur with tightly-coiled macromolecules by shielding of the inner by the outer layers of the coil, rendering difficult the access of reagent molecules to the inner layer. Such retardation increases with increase in size of the macromolecular particles, i.e. with molecular weight. In the present instance, rate is not appreciably dependent on molecular weight, whence the circumstances above do not apply.

The presence of the polystyrene main-chain, considered as a substituent in the acetamidophenyl side-groups, might hypothetically lower the rate by steric shielding. However, this cannot offer more than a partial explanation because it is equally operative in the homopolymers and the copolymer, and the rate for the latter is nearly twice that for the former.

The results, on being compared together, imply that the proximity of \textsubscript{m}-substituted side-groups is the essential cause of a lowered rate. Further, the acetyl groups are not a necessary component, since the rate remains substantially constant as the acetamido groups are converted into amino groups. One is hence lead to consider the \textsubscript{m}-NH
groups, whether present as -NH\_2CO\_2CH\_3 or \(-\text{NH}_2\), as the essential rate-lowering substituents. The most probable mode of action of these groups is by the formation of a hydrogen bond with the carbonyl oxygen of an amido-group which is suitably placed either by adjacent attachment to the main chain or by chain-coiling.

\begin{align*}
\text{(I)} & \quad \text{HO} \quad \text{(II)} \\
\text{(III)} & \quad \text{(IV)} \\
\text{(V)} & \quad \text{(VI)} \\
\text{rapid} & \quad (\text{VII})
\end{align*}
The influence of hydrogen bonding on the successive stages of amide hydrolysis is indicated by (I-VII), in which the left- and right-hand columns contain the canonical forms contributing to the hydrogen bond.

The effect of hydrogen bonding (I and II) is to increase the electrophilic character of the carbonyl carbon atom, and hence to increase the ease with which it is attacked by the hydroxyl ion to form the transition state. In this (III and IV) hydrogen bonding opposes the breaking down into the products of hydrolysis, the conjugative electron movements of (IV) being less likely to occur than those of (III), which represents the course of normal amide hydrolysis unperturbed by hydrogen bonding. When the transition state breaks down, via V and VI, the products (VII) are those normal to alkaline amide-hydrolysis.

The suggestion is therefore put forward that hydrogen bonding reduces the probability of break-down of the transition state into the products, and in this way lowers the rate of overall reaction.

With respect to the reality of hydrogen bonding, it is desirable to place on record that poly-(m-acetamidostyrene) in the syndiotactic configuration can be placed in a conformation in which it is practicable for two series of alternate acetamidophenyl side-groups to hydrogen-bond serially as shown in photographs I and II. A rigid channel-shaped structure is formed, of which the inner and outer surfaces are shown. There is an array of hydrogen bonds along both edges.
A serially hydrogen-bonded structure is possible with the isotactic configuration, but a tight helical conformation is necessary (photographs, III and IV), and there is only a single series of hydrogen bonds.

The present polymers are formed by a simple free-radical process and are hence essentially atactic; short runs of syndiotactic configuration frequently broken by unordered sections most probably represent the stereochemical constitution. This, together with thermal agitation, renders it unlikely that extensive highly-ordered hydrogen-bonded structures, as in the photographs, were present in the hydrolysis-solutions. Nevertheless, a considerable average degree of hydrogen bonding within the coiled macromolecules may have prevailed, the distribution of hydrogen bonds at any instant being conditioned by the proximity of interacting groups, itself dependent both on closeness of points of attachment to the main chain, and the bringing together of groups, more widely attached, by coiling.

In the copolymer, the nitrogenous side-groups are separated by, on average, 2.35 inert styrene units. The chance of proximity, suitable for hydrogen bonding, between an amido- and another nitrogenous group is thereby lessened, but, from the rate for the copolymer, interaction is still considerable. There must be, in the copolymer, a statistical distribution of the actual numbers of styrene units.
separating the acetamidostyrene units. Some of the amido groups will therefore be subject to more, some to less, than the average degree of hydrogen-bonding interaction. The former will react less readily than the latter, and to this is ascribed the slight fall in the "instantaneous" second order constant as hydrolysis of the copolymer proceeds: the more easily hydrolysed groups tend to react during the earlier stages of reaction, leaving the less easily hydrolysed to contribute largely to the later stages.
Section III

The polymeric styrenediazonium chloride has been prepared by diazotisation of poly-\((m\text{-aminostyrene})\) in homogeneous solution in hydrochloric acid, and attempts have been made to prepare poly-\((m\text{-hydrazinostyrene})\) from this by standard reductive processes, namely, sulphite and stannous chloride reductions.

(111) Schaffer prepared the monomer \(m\text{-hydrazinostyrene}\) by diazotising \(m\text{-aminostyrene}\), followed by reduction with stannous chloride. He found that the sulphite reduction failed, giving products which contained sulphur and nitrogen but no halogen, and concluded that the bisulphite had attacked the vinyl groups to give sulphonic acid groups in material of uncertain composition. The stannous chloride reduction however proceeded giving a 39% yield of \(m\text{-hydrazinostyrene}\).

**Poly-(m-hydrazinostyrene)**

**Attempted Sulphite Reduction**

This reduction proceeds in three stages:
- first a diazo-, then a hydrazino-sulphonate is formed, and the latter is converted to the hydrazine hydrochloride

\[
\begin{align*}
\text{ArN}_2\text{Cl} & \xrightarrow{\text{Na}_2\text{SO}_3} \text{Ar.N:NSO}_3\text{Na} & \xrightarrow{2\text{H}} & \text{ArNH.NHSO}_3\text{Na} \\
& + \text{NaCl} & & + \text{NaHSO}_4
\end{align*}
\]
This method was applied to poly-(m-styrenediazonium chloride) and gave a product which contained sulphur and nitrogen but no halogen, which indicated failure of conversion to the poly-(m-hydrazinostyrene hydrochloride). This may be related to the insoluble nature of the precipitate produced on addition of the diazo solution to the sulphite solution thereby tending to terminate reaction.

Stannous Chloride Reduction

ArN₂Cl + 2SnCl₂ + 4HCl → ArNH₂NH₂.HCl + 2SnCl₄.

This reduction was effected by the addition of stannous chloride dihydrate in concentrated hydrochloric acid at 0°C, to ice-cold poly-(m-styrenediazonium chloride) solution. A precipitate, considered to be the salt of poly-(m-hydrazinostyrene) and stannichloric acid (ArNH₂NH₂.HCl + 2SnCl₄, was formed and was isolated as a white gelatinous solid on centrifugation. It gave a positive chemiluminescence test for tin and dissolved in cold water, which indicated it to be the stannichloride derivative. Attempts were made to liberate the free base from the stannichloride, and to free it from "occluded" tin, a process which proved to be far more difficult with the polymeric hydrazine, which cannot be extracted into simple organic solvents, than the analogous procedure with low molecular weight aryl hydrazines.

Three methods were attempted:

(i) Dissolution of the polymeric stannichloride in dilute hydrochloric acid followed by treatment with sulphur dioxide, and after removal of excess sulphur dioxide, with hydrogen sulphide.
No precipitate was obtained, and the solution became highly coloured.

(ii) Attempted solution of dried stannichloride in water, followed by the addition of concentrated hydrochloric acid in an attempt to precipitate the hydrochloride, and to leave the tin in solution as \( \text{H}_2\text{SnCl}_6 \).

This method also failed, giving products with increased inorganic residue; further, on drying, the stannichloride became difficult to dissolve again in water.

(iii) Precipitation of the free base with alkali.

This method gave products having inorganic residues of \( \pm 1\% \), and the material obtained in this manner gave a positive test for aryl hydrazines by Feigl's(118) method. It was also subjected to the chemiluminescence test for tin which was found to be negative. The inorganic residue obtained on ashing was insoluble in acids and alkalis and was yellow when hot, and white when cold indicating it to be stannic oxide. In view of the failure of the former, sensitive test, the tin must presumably be combined in some way with the polymer.

After drying, the polymeric hydrazine became insoluble in solvents in which it dissolved when first prepared as a wet pad, indicating cross linking to have occurred during drying probably by atmospheric oxidation. Aryl hydrazines are known to be subject to atmospheric oxidation, and Chattaway has shown that two reactions can take place, namely:
(1) Main reaction

\[ 2RNH_2NH_2 + O_2 \rightarrow 2RH + 2N_2 + O_2 \]

(2) Subsidiary reaction

\[ 2RNH_2NH_2 + O_2 \rightarrow RR + H_2 + 2N_2 + 2H_2O \]

with the resultant production of an aromatic hydrocarbon derived from the benzene or diphenyl series respectively. This oxidation occurs readily when a large surface area is open to attack as in the case of a liquid film or a finely divided solid; the latter is the case with poly-(m-hydrazinostyrene).

That oxidation occurs on drying and standing is shown as follows:

(1) Reduction was found to be complete after 15 minutes, as the capacity to couple with \( \beta \)-naphthol had then ceased.

(2) On comparison of the theoretical and determined nitrogen contents for poly-(m-hydrazinostyrene) with those for its derivatives prepared without isolation of the poly-(m-hydrazinostyrene) from the reaction media, the following is seen:

**Poly-(m-hydrazinostyrene)**

**Found:**

- \( N, (i) 5.48, (ii) 5.59; \)
- \( C_8H_{10}N_2 \) requires \( N, 20.88\% \).
Benzaldehyde derivative

Found:

N, (i) 10.92, (ii) 10.76;

C<sub>15</sub>H<sub>14</sub>N<sub>2</sub> requires: N, 12.60%.

Cyclohexanone derivative

Found:

N, (i) 10.07, (ii) 10.23;

C<sub>14</sub>H<sub>18</sub>N<sub>2</sub> requires: N, 13.08%.

These values show the dried poly-(m-hydrazinostyrene) has lost 73.5% of its theoretical nitrogen content; the benzaldehyde derivative 14.0% and the cyclohexanone derivative 22.4%. Thus, although the conversion to the derivatives is not 100%, oxidation is much less in solution than with the free solid base.

The Fischer Indolization reaction

This reaction was attempted by boiling cyclohexanone and poly-(m-hydrazinostyrene) in acetic acid, and its interpretation is complicated by oxidation, the unknown percentage of reaction between cyclohexanone and available hydrazino groupings, and the unknown percentage of cyclisation to the poly-(tetrahydrocarbazole), which involves the loss of a nitrogen atom.

The analyses of the product are:
Found:

\[ C, (i) 79.23, (ii) 78.98; \ H, (i) 7.63, (ii) 7.51; \]
\[ N, (i) 8.48, (ii) 8.42; \]

\[ \text{C}_{14}\text{H}_{15}\text{N} \text{requires:} \]
\[ C, 85.23; \ H, 7.67; \ N, 7.10\%. \]

Bearing in mind that conversion into the poly-(\text{m-hydrizinostyrene}) from the poly(aminostyrene) and thence into the cyclohexanone derivative is unlikely, from the previous experimental results, to have been complete, the analytical data indicate cyclisation to have been incomplete.

**Poly-(\text{m-hydrizinostyrene hydrochloride})**

In an attempt to reduce the oxidation occurring on drying poly-(\text{m-hydrizinostyrene}), its hydrochloride was prepared, since it was likely that this derivative would show greater stability to oxidation than the parent compound.

Comparison of the observed and theoretical chlorine contents

**Found:**

\[ \text{Cl}, (i) 18.40, (ii) 17.97; \]

\[ \text{C}_8\text{H}_{11}\text{NCl} \text{requires: Cl, 20.77\%;} \]

indicate that conversion to the hydrochloride was 87.6\%, and hence loss by oxidation was 12.4\%, which is considerably smaller than during isolation of the free base. Derivatives were accordingly
made from the dried solid, which did not however dissolve in the reaction media, but was used as a suspension of highly swollen gel.

**Benzaldehyde Derivative II**

Found:

\[
\begin{align*}
\text{N, (i) } & 10.62, \ (ii) \ 10.62; \\
\text{C}_{15}\text{H}_{14}\text{N}_2 \text{ requires: } & \text{N, 12.60%}.
\end{align*}
\]

**Cyclohexanone Derivative**

Found:

\[
\begin{align*}
\text{N, (i) } & 9.63, \ (ii) \ 9.64; \\
\text{C}_{14}\text{H}_{18}\text{N}_2 \text{ requires: } & \text{N, 13.08%}.
\end{align*}
\]

The results are similar to those obtained for the derivatives of the free base. Together they suggest that cyclohexanone reacts less readily with poly-(m-hydrazinostyrene) than benzaldehyde under comparable conditions. This leads, in the cyclohexanone derivative, to further slight oxidation of the unreacted hydrazino side-groups on drying.

The possibility exists that the conversion of poly-(m-styrene-diazonium chloride) to poly-(m-hydrazinostyrene) is restricted to 87% by virtue of stannous chloride reacting only with pairs of diazonium groupings to form \((\text{Ar.NH.NH}_2^+)_2\text{SnCl}_6^2-\) the intermediate stannichloride.
SECTION IV

The course of some azo-coupling reactions of poly-(m-styrene-diazonium chloride) have been studied. Azo-coupling experiments with diazonium compounds derived from poly-(aminostyrene) homopolymers have been reported.

For example, Martynoff \(^{(82)}\) prepared a poly-(p-aminostyrene) by thermal decarboxylation of p-aminocinammic acid, diazotized the polymer, and found it to couple substantially completely with phenol and dimethylaniline. Oda and Urata \(^{(81)}\) polymerised m-aminostyrene by heating to 160°, dissolved the polymer in concentrated sulphuric acid and diazotized the resultant solution, and, after dilution, effected coupling with 2-hydroxy naphthalene-3-carboxyanilide (Napthol A.S.). The high temperature of polymerisation, together with the drastic method required for solution of the polymer so obtained, indicate it to be a non-linear poly-(m-aminostyrene).

The polymers prepared for this work were initiated at 73° using 2,2'-azoisobutyronitrile (p. 69), and were readily soluble in 1.0 N hydrochloric acid. The polymers were diazotized using the normal, direct method for soluble primary aromatic amines.

Coupling was attempted with \(\beta\)-naphthol, 2,5-dimethoxyaniline, and 2,5-dimethylaniline (p-xyldidine). The amines were chosen because they are substituted directly to yield the p-aminoazo compounds, and
because they and B-napthol couple once only; thus the complication of two azo groupings attached to the same molecule of a phenol or amine with the formation of a cyclic or cross-linked structure was avoided.

A solution of poly-(m-styrenediazonium chloride) was reacted with alkaline B-napthol and yielded poly-(m-styreneazo-B-napthol). The analyses of this compound shown below indicates conversion to be complete.

Found:

C, (i) 78.90, (ii) 78.95; H, (i) 5.13, (ii) 5.25;
N, (i) 10.25, (ii) 10.16; O, (i) 5.84, (ii) 5.88;

\[ \text{C}_{18}\text{H}_{14}\text{N}_2\text{O} \] requires:

C, 78.81, H, 5.14, N, 10.22, O, 5.83%.

Similarly a poly-(m-styrenediazonium chloride) solution was reacted with ethanolic solutions of 2,5-dimethyl-, and 2,5-dimethoxy-aniline at 50°, using Troger and Westerkamp's method for low molecular weight compounds; poly-(m-styreneazo-2,5-dimethylaniline) and poly-(m-styreneazo-2,5-dimethoxyaniline) were precipitated from solution. The extent of coupling with the above amines was not complete, and was complicated by side-reactions of uncertain course, and it was not possible to compute from the analysis figures (shown below) the exact extent of coupling.
Poly-(m-styreneazo-2,5-dimethylaniline)

Found:

C, (i) 77.49, (ii) 77.66; H, (i) 6.81, (ii) 6.90;
N, (i) 9.41, (ii) 9.57;

C$_{16}$H$_{17}$N$_3$ requires:

C, 76.47, H, 6.82, N, 16.72%.

Poly-(m-styreneazo-2,5-dimethoxyaniline)

Found:

C, (i) 67.50, (ii) 67.43; H, (i) 6.32, (ii) 6.42;
N, (i) 13.51, (ii) 13.60;

C$_{16}$H$_{17}$N$_3$O$_2$ requires:

C, 67.83, H, 6.05, N, 14.83%.

The extent of coupling may be approximately obtained by comparison of the determined nitrogen content and the theoretical value for the fully coupled unit, expressed as a percentage.

The values so obtained, are 57 and 91% for 2,5-dimethyl- and 2,5-dimethoxyaniline respectively. These figures indicate a greater susceptibility to electrophilic attack in the case of 2,5-dimethoxyaniline as would be expected, the rate of electrophilic attack being greater with methoxy than methyl substituents.

The final product of reaction in each case was virtually
insoluble in the reaction medium, yet conversions were high based upon the calculation made with the nitrogen analyses. Another example of similar behaviour can be cited in the replacement reactions carried out by Arcus and Halliwell\(^{(91)}\) on poly-(m-styrenediazonium chloride) and it may similarly be inferred that the following factors tend towards high conversion, namely: that rate of reaction is fast relative to precipitation, and that the polymer in solution as a polyelectrolyte which has polar character, promotes association of reagent with reactive groups on the macromolecule before precipitation, and the continued solvation of these groups in the precipitate allows reagent to diffuse into the locally swollen macromolecule.

It was previously indicated that the uncertain course of side-reactions was responsible for inability to compute the exact extent of coupling. In the media chosen for reaction of the amines, two side-reactions other than coupling are possible:

(i) \[ \text{Ar.N}_2\text{Cl} + \text{EtOH} \rightarrow \text{Ar.OEt} + \text{HCl} + \text{N}_2 \]

(ii) \[ \text{Ar.N}_2\text{Cl} + \text{EtOH} \rightarrow \text{ArH} + \text{N}_2 + \text{HCl} + \text{CH}_3\text{CHO} \]

The second of these reactions however, the reduction of an aromatic diazonium compound to the hydrocarbon, is unlikely, since this reaction is facilitated by electron-attracting substituents, and the reaction is carried out at a much higher temperature or in
the presence of a metallic catalyst.

The first reaction, the production of an ether, in this case a phenetole derivative cannot be neglected.

In order to investigate the hypothesis that the coupling reaction was accompanied by a competing side-reaction producing an ether, whence the product of coupling was a copolymer of coupled and phenetole-type units, the following method was used. Two vertical axes were drawn on graph paper at right angles to, and at either end of a horizontal axis. Each of the vertical axes was given a 0-100% scale, and zero in each case was the intersection with the horizontal axis. The horizontal axis was also given a scale of 0-100% in either direction. The theoretical values of C, H, N, and O were plotted independently on separate vertical axes for (a) the completely coupled unit and (b) the unit completely in the phenetole form. This plot was made for both substrates. The two values for each C, H, N, and O were then joined by tie lines. The figures obtained on analysis were then plotted on a similar vertical scale and were moved horizontally until the best possible fit with the intersected tie lines was obtained. The percentage of each component in the copolymer was read off from the horizontal scale.

These results were converted to a molar ratio of each component and the theoretical analysis figures of such a copolymer were then calculated; the results are shown below.
Product derived from poly-(m-styrenediazonium chloride)
and 2,5-dimethylaniline

Found:
C, (i) 77.49, (ii) 77.66; H, (i) 6.81, (ii) 6.90;
N, (i) 9.41, (ii) 9.57.

\[ \text{C}_{16}\text{H}_{17}\text{N}_3 : \text{C}_{10}\text{H}_{12} \text{O} \text{ in a molar ratio of } 1:1.23 \text{ requires:} \]
C, 78.40, H, 7.37, N, 9.69, O, 4.54%.

Product derived from poly-(m-styrenediazonium chloride)
and 2,5-dimethoxyaniline

Found:
C, (i) 67.50, (ii) 67.43; H, (i) 6.32, (ii) 6.42;
N, (i) 13.51, (ii) 13.60;

\[ \text{C}_{16}\text{H}_{17}\text{N}_3 \text{O}_2 : \text{C}_{10}\text{H}_{12} \text{O} \text{ in a molar ratio of } 1:0.21 \text{ requires:} \]
C, (i) 69.15, H, 6.25, N, 13.36%.

whence it can be seen that a much better fit to the analysis figures
is obtained with this hypothesis in the case of the less reactive
substrate, whilst the fit for the more reactive substrate is only
slightly improved. This hypothesis will be further discussed in
the section dealing with disazo coupling.

Disazo coupling reactions

Since, in small molecules of the \( p \)-aminoazo-series, the free
amino-grouping may be diazotized and coupled again, it seemed feasible that the analogous polymeric compounds should also be capable of this behaviour.

In order to investigate this possibility, poly-\((m\text{-styreneazo-2,5-dimethylaniline})\) and poly-\((m\text{-styreneazo-2,5-dimethoxyaniline})\) were suspended in dilute hydrochloric acid and then diazotized and coupled with alkaline \(\text{β-naphthol}\). That coupling had occurred was evident from the colour change which occurred, from orange to purple brown and violet black respectively. This is indicative of increased conjugation in the molecule as would be expected on disazo coupling.

It was not practicable to determine the extent of such coupling from the analyses since disazo coupling involves a reduction in nitrogen content, and nitrogen can easily be lost in other side-replacement reactions, but, from the colour evidence, disazo coupling was shown to have occurred.

The analyses of these compounds are complicated in that the hypothesis, previously invoked to account for the analyses of the products of the first diazotization and coupling, must clearly be operative here. Hence, the theoretical analysis figures shown are those calculated on the assumption that the product of disazo coupling is a copolymer of disazo-coupled units (for a 100% conversion) and the same molecular ratio as before of phenetole units.
Disazo coupling of poly-(m-styreneazo-2,5-dimethylaniline)

Found:

C, (i) 76.43, (ii) 76.20; H, (i) 5.84, (ii) 5.72;
N, (i) 9.59, (ii) 9.59;

$C_{26}H_{22}N_4O$: $C_{10}H_{12}O$ in a molar ratio of 1:1.23 requires:
C, 78.11; H, 6.29; N, 9.59; O, 6.09%.

$C_{26}H_{22}N_4O$ requires:
C, 76.83; H, 5.46; N, 13.78; O, 3.93%.

Disazo coupling of poly-(m-styreneazo-2,5-dimethoxyaniline)

Found:

C, (i) 69.92, (ii) 70.05; H, (i) 5.42, (ii) 5.23;
N, (i) 12.59, (ii) 12.47;

$C_{26}H_{22}N_4O_3$: $C_{10}H_{12}O$ in a molar ratio of 1:0.21 requires:
C, 71.85; H, 5.26; N, 11.93%.

$C_{26}H_{22}N_4O_3$ requires:
C, 71.22, H, 5.06, N, 12.78%.

* These are the completely coupled units based on 100% conversion to the monoazo compounds.

It is concluded that, in general, the hypothesis of ethyl ether formation cannot be proved or disproved from these results.
Its main recommendation is that it accounts well for the analysis figures of the monoazo derivative of 2,5-dimethylaniline. It does not however appear to be of particular use for the disazo compounds, but this may be because the "theoretical" figures are based upon 100% conversion of the copolymers into the disazo compounds, which is unlikely in view of the insolubility of the initial polymers.
SUMMARY

m-Aminostyrene has been synthesised by the known route, with modifications which have slightly improved the yield of m-nitrostyrene on dehydration of α-methyl-m-nitrobenzyl alcohol, and have eliminated the violent reaction occurring on reduction of m-nitrostyrene by the original method.

Poly-(m-aminostyrene) and a styrene-m-aminostyrene 2.35:1.00 copolymer have been prepared by bulk polymerisation at 73°C, 2,2'-azo-isobutyronitrile being used as initiator at two concentrations 0.2 and 0.4% for the homopolymers, and 0.4% for the copolymer.

The polymers have been converted by acetic anhydride and pyridine into their acetyl derivatives, and these compounds have been characterised by analysis and intrinsic viscosity determinations in benzyl alcohol.

The rates of hydrolysis of the two poly-(m-acetamidostyrene) homopolymers and the copolymer with styrene, and those of acetonilide and acetyl-m-cumidide in benzyl alcoholic potassium hydroxide have been determined at 145°C, all are of the second order, except that, for the copolymer, the plot of the second order integral against time shows throughout a slight curvature indicative of deceleration.

The rate constants are:
From a comparison of these rates it is inferred that, in the hydrolyses of the m-acetamidostyrene homopolymers and copolymer:

The rates of hydrolysis of homopolymers (I) and (II), and the copolymer, are respectively 28, 30, and of a value which can be computed if only inductive release from the main chain were operative. These values indicate a special effect, dependent on the macromolecular structure, to be operative. The effect is almost independent of molecular weight, but is much more pronounced for the homo- than the co-polymer. The lowering of rate is inferred to be due, mainly, to hydrogen bonding between the oxygen atom of the acetyl group and \(-\text{NH}\)- groups, both those of the original acetamido and of the derived amino groups being effective. The effect of hydrogen bonding is to lessen the probability of breakdown of the transition state in the alkaline hydrolysis. Such hydrogen bonding would clearly be more effective in the homo- than the co-polymer, owing to the spacing-out
of nitrogenous groups in the latter.

There must be, in the copolymer, a statistical distribution, about the mean of 2.35, of the actual number of styrene units separating the acetamido-styrene units. Some of the acetamido groups will be subject to less-than-average hydrogen bonding, and hence will react more rapidly than others. The former will tend to react during the first stages of hydrolysis, and to this is attributed the small diminution in the rate-constant during the progress of hydrolysis of the copolymer.

Two further homopolymers of m-aminostyrene prepared under identical conditions (0.4% of initiator) have been shown to have essentially similar molecular weights. These polymers have been diazotised and subjected to the standard diazonium reactions in which nitrogen is not lost from the molecule, namely, reduction to the corresponding hydrazine and coupling with amines and phenols.

The percentage reduction to the hydrazinostyrene has been calculated from the chlorine content of its hydrochloride, whence the reduction was found to be 88% complete.

A similar percentage reaction has been obtained from elemental analyses of its hydrazone derivatives.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>% reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzaldehyde</td>
<td>86%</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>78%</td>
</tr>
</tbody>
</table>
The extent of conversion into poly-(m-hydrazinostyrene), or to its derivatives, has been discussed with reference to (a) the oxidation of aryl hydrazines,

(b) the possible limitation of reaction, statistically, to 87%, which could result by stannous chloride reacting with pairs of diazonium groupings during the reduction stage.

Poly-(m-styrenediazonium chloride) has also been coupled with β-naphthol, 2,5-dimethoxyaniline, and 2,5-dimethylaniline (p-xylidine) and the extents of coupling have been approximately computed from the elemental nitrogen analyses:

<table>
<thead>
<tr>
<th>Coupling agent</th>
<th>% coupling</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-naphthol</td>
<td>100%</td>
</tr>
<tr>
<td>2,5-dimethoxyaniline</td>
<td>91%</td>
</tr>
<tr>
<td>2,5-dimethylaniline</td>
<td>57%</td>
</tr>
</tbody>
</table>

The difference in percentage coupling occurring with 2,5-dimethoxy- and 2,5-dimethylaniline has been related to the electron releasing ability of the methoxy grouping. The results obtained for analyses have been discussed with reference to possible side reactions which might occur during coupling.

The amino-azo polymers derived from these amines have been further diazotised and coupled with β-naphthol. Marked colour changes indicate the formation of disazo polymers.
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