KINETICS OF THE REACTION OF METHYL IODIDE WITH
POLY(p-N,N-DIMETHYLAMINOSTYRENE) AND RELATED STUDIES.

Being a Thesis submitted to the
University of London
for the degree of
Doctor of Philosophy
by

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August, 1963.
ABSTRACT OF THE THESIS

p-N,N-Dimethylaminostyrene has been synthesised, by a known method, from p-N,N-dimethylaminobenzaldehyde. This monomer has been homopolymerised and copolymerised with styrene by initiation with α,α'-azoisobutyronitrile. The polymeric amines have been characterised by intrinsic viscosity determinations in toluene.

A homopolymer of poly(4-vinylpyridine) was prepared, with α,α'-azoisobutyronitrile as the initiator, and characterised by intrinsic viscosity measurements in 96% ethanol.

The rate constants for the reaction between the poly(p-N,N-dimethyl aminostyrene)s and methyl iodide in dimethylformamide at 0° have been compared with those of dimethylaniline and p-isopropyldimethylaniline and methyl iodide at the same temperature and in the same solvent.

Similar kinetic measurements were made on the reaction of n-butyl bromide at 75° with poly(4-vinylpyridine) and pyridine in dimethylformamide and sulpholane and on poly(4-vinylpyridine) in dimethylformamide-sulpholane mixtures.

The initial second-order rate constant for the reaction of poly(p-N,N-dimethylaminostyrene)s with methyl iodide in dimethylformamide at 0°, is almost unaltered by change in molecular weight and by the spacing-out of amino groups by inert styrene units. Under the conditions above, the constants for dimethylaniline and p-isopropyldimethylaniline
were determined. The values imply electron release from the main chain to the side-groups in the polymers. The development of a charged envelope about the macromolecule leads to a fall in the rate of quaternisation after 20-25% reaction.

A similar fall in quaternisation rate was found for the reaction between n-butyl bromide and poly(4-vinylpyridine) in sulpholane but no deceleration was observed for the same reaction in dimethylformamide as the solvent. In solvent mixtures, progressively richer in dimethylformamide, deceleration became progressively less than that found in sulpholane.

The kinetic results are discussed in relation to the size, structure and coiling of the macromolecules.
ACKNOWLEDGMENT

The work described in this thesis has been carried out in the Organic Chemistry Research Laboratories of the Battersea College of Technology, London, S.W.11, under the supervision of Dr. C.L. Arcus, to whom the author wishes to express sincere thanks for his interest, help and guidance throughout this work.

Thanks are also expressed to Dr. T.J. Howard for the gas-liquid chromatography, to the technical staff of the College for their ready co-operation, and to the Department of Scientific and Industrial Research for a research studentship and for aid from a grant.
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HISTORICAL INTRODUCTION
ADDITION POLYMERISATION.

Historical Introduction.

It is over a hundred years since polymers ceased to be but unwanted residues which frustrated the organic chemist in his quest for higher yields of pure compounds. Polymers have very definite structures and properties of their own and in the recent decades have had a marked industrial importance.

Observations on the polymerisation of readily polymerisable vinyl monomers, such as styrene, vinyl chloride and butadiene, date back to the first isolation of the monomer in each case. Simon, in 1839, reported the conversion of styrene, to a gelatinous mass and some twenty-seven years later its depolymerisation to yield the original monomer was noted. Lemoine, therefore, put forward the view that the transformations of styrene could be likened to a reversible dissociation. The constitution of the polymers was, at that time, almost completely unknown.

In 1910, Stobbe and Poenjak, after noting that boiling-point elevations of poly(styrene) in solution were negligible, came to the conclusion that poly(styrene) was a colloidal body. They proposed a cyclic formula containing four, five or more structural units.

\[
\begin{align*}
\text{Ph} \\
\text{Ph}-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2 \\
\quad | \\
\text{Ph}-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2 \\
\quad | \\
\text{Ph}
\end{align*}
\]
Butadiene was polymerised (1911-3) by Lebedev and Skavronskaia and Harries, both of whom assigned to it a cyclo-octadiene structure after identification of succinic acid in the products obtained from the ozonide.

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

Subsequently Lebedev did propose a chain structure for poly(butadiene).

In 1920, an important paper was published by Staudinger proposing the chain formula for poly(styrene), this was a revolutionary idea because the general opinion at that time favoured rings of moderate size for vinyl polymers. Work on poly(oxymethylene) supported the chain structure.

\[
\begin{align*}
-\text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH} - \\
\text{Ph} & \quad \text{Ph}
\end{align*}
\]

Poly(styrene)

The colloidal properties of these substances were attributed entirely to the size of the molecules which he guessed might contain about a hundred units. The end-group problem was solved by postulating that the terminal valencies of long chains were inert.

Staudinger championed this viewpoint in the years which followed but his ideas were not accepted at once; investigators preferred definite ring systems to chains of uncertain length. Low molecular weight measurements, subsequently shown to be in error, seemed to support the opposition, but finally in 1926, the results of X-ray diffraction of cellulose fibres were shown by Sponsler and Dore to be consistent with a chain formula composed of a large number of units.
In 1929, Staudinger\textsuperscript{13} differentiated between linear and non-linear polymers. Infusibility and insolubility of the latter was characteristic of network structures. A year earlier Meyer and Mark\textsuperscript{14} stated that vulcanised rubber had properties which could be accounted for by the formation of covalent cross linkages.

Carothers\textsuperscript{15,16} embarked on a series of investigations which were successful in removing much of the uncertainty which was prevailing in the polymer field at the time. The object of the work was to prepare polymeric molecules of definite structures using well-established reactions and to investigate the properties of these substances in relation to their constitution. The main part of his work was in the field of condensation polymers.

Taylor and Bates\textsuperscript{17} suggested a free-radical mechanism to explain the polymerisation of ethylene; independently Staudinger\textsuperscript{18} proposed a similar scheme for liquid phase polymerisations. To the concept of vinyl polymerisation as a growth of long-chain molecules there was added by Chalmers and others the idea that the polymerisations have the characteristics of chain reactions studied by Bodenstein.

In 1930, the theoretical chemists began to invade the field. The statistical approach has since dominated the scene in the treatment of constitution, reaction and physical properties of the polymers. High polymers are far too complex for a direct mechanistic deduction of properties, even the constitution cannot always be exactly described.

It was really quite early that it was realised that there was a direct relationship between solution-viscosity and molecular weight but it was not until the mid-1940's that reliable relationships between the two were
derived. Solution-viscosities are readily measured and because of this such measurements are widely used for the characterisation of high polymers.
Structure of addition polymers.

A polymer is a large molecule built up by repetition of small simple chemical units. In some cases the repetition is linear, but in many cases the chains are branched or even interconnected to form three dimensional networks.

![Diagram](image)

Fig. 1

Branching is often the result of side reactions occurring during polymerisations, thus poly(vinyl acetate) has one branched linkage per thousand linear ones. This term is not applied to regularly repeating side-groups which are often inherent in the monomer structure, thus poly(butyl methacrylate)s are linear polymers:

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_2 - \text{C} - \text{CH}_2 - \text{C} & \\
\text{C} = 0 & \quad \text{C} = 0 \\
0 & \quad 0 \\
\text{C}_4\text{H}_9 & \quad \text{C}_4\text{H}_9
\end{align*}
\]

Cross linking occurs with a monomer which has two or more functional groups, e.g. divinylbenzene.

The length of the polymer chain is specified in terms of the number of units in the chain. The length of each chain is determined by a random process.
and consequently the lengths of individual chains vary. An experimental determination of molecular weight and chain length will give only an average value. Hence when molecular weight is referred to it is an average molecular weight.

Primary chemical bonds along normal polymer chains are entirely satisfied covalent structures. The only forces between molecules are secondary bond forces of attraction which are weak relative to the primary valencies. The high molecular weights of the polymers allow these forces to build up, by repetition, enough to impart mechanical strength to the solid substances.
The Polymerisation Process.

The polymerisation of vinyl monomers is a typical chain reaction. It can be initiated by a variety of methods typical of simple gas phase chain reactions, and it is susceptible to retardation and inhibition. In a typical addition polymerisation one act of initiation may lead to the polymerisation of thousands of monomer molecules. The characteristics of addition polymerisation suggest that the active centre responsible for the growth of the chain is associated with a single polymer molecule through addition of many monomer units. Thus there are no species intermediate between monomer and high polymer present in appreciable concentration. Of a number of postulated types of active centre, cationic, anionic and free-radical have been found experimentally. Cationic and anionic polymerisation will not however be dealt with here.

The process of free-radical polymerisation consists of three steps, firstly the generation of the free-radicals (initiation), secondly a very fast reaction whereby the monomer adds on to the free-radical, the active centre being passed on to successive monomer units (propagation) and finally a process of deactivation of the polymer chain (termination).

Initiation.

Some monomers will polymerise by the action of heat alone, here it is believed that free-radicals result from the thermal activation of a few monomer molecules. Most polymerisations, however, require the addition of a small amount of compounds known as initiators. These are generally peroxides or aliphatic azo-compounds which decompose slowly between 50-100° to yield free-radicals.
e.g. benzoyl peroxide

\[(\text{PhC}O_2)_2 \rightarrow 2\text{PhC}O_0 \cdot \rightarrow 2\text{Ph} \cdot \rightarrow 2\text{CO}_2\]

and \(\alpha,\alpha'-\text{azoisobutyronitrile}\)

\[
\begin{align*}
\text{CN} & \quad \text{CN} \\
(\text{CH}_3)_2\text{C} - \text{N} = \text{N} - \text{C} & \quad (\text{CH}_3)_2 \\
\rightarrow & \\
\text{CN} & \quad \text{CN} \\
(\text{CH}_3)_2 & \quad \text{CN} \\
\rightarrow & \\
(\text{CH}_3)_2 & \quad \text{C} \rightarrow \text{N} \rightarrow \text{N} \rightarrow & \text{C} \quad (\text{CH}_3)_2
\end{align*}
\]

\(\alpha,\alpha'-\text{azoisobutyronitrile}\) is usually chosen in preference to benzoyl peroxide, because it is free from induced decomposition.

The addition to the vinyl monomer can take place in either of two ways.

\[
\begin{align*}
R - \text{CH}_2 - \text{CH} & \cdot \\
R' & \rightarrow \text{CH}_2 = \text{CH} \\
\rightarrow & \\
R - \text{CH} - \text{CH}_2 & \cdot
\end{align*}
\]

As is true in free-radical reactions, the reaction leading to the more stable product will be favoured. Since the unpaired electron can participate in resonance with the phenyl group in Structure I but not in Structure II, it is likely that reaction I will be favoured. Steric factors also favour reaction I.
Propagation.

The free-radical growing chain can add to the monomer in one of three ways.

(1) Head-to-tail.
The occurrence of reaction I (or II) exclusively would lead to a head-to-tail structure in which the substituents occur on alternate carbon atoms. This structure requires less energy than a head-to-head, tail-to-tail arrangement.

Head-to-tail.

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

\( \text{ } \)

(2) Head-to-head, tail-to-tail.

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

\( \text{ } \)

(3) A random structure containing both arrangements.
The possibility of obtaining a regular head-to-head, tail-to-tail structure exclusively is quite remote, but it appears that an occasional monomer unit may enter in a reverse manner to provide a single head-to-head, tail-to-tail linkage.

Staudinger and Steinhofer\textsuperscript{21} found that the destructive distillation of poly(styrene) at 300\degree yielded 1,3-diphenylpropane, 1,3,5-triphenylpentane and 1,3,5-triphenylbenzene.
No product having phenyl groups on adjacent carbon atoms was found.

Such linkages can also be determined by chemical methods. In poly(vinyl alcohol) the presence of 1,2-glycol structures can be detected by the use of reagents specific for this arrangement of hydroxyl groups, such as periodic acid or lead tetra-acetate.

Marvel and Denoon and Flory and Leutner found that the consumption of the reagent is so small that the number of 1,2 glycol units cannot be detected in this way, but the result of each reaction is cleavage of the chain.

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{CH}_2-\text{CH}_2-\text{CH}_2 & \quad \text{Ph} \\
\text{CH}_2-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_2 & \quad \text{Ph} \\
\end{align*}
\]

The reduction in molecular weight accompanying the reaction is demonstrated by the decrease in viscosity of the reaction mixture. These measurements show that 1-2% monomer units react in a head-to-head, tail-to-tail manner.

It can be concluded that all the polymers so far studied contain a major proportion of head-to-tail linkages.
Termination.

Reactions in which the free-radicals are used up and the growth of the chain ceases. This can take place in several ways.

(1) By combination or coupling.

\[
\begin{align*}
-\text{CH}_2-\text{CH}^* & + \text{CH}-\text{CH}_2^* \\
\text{Ph} & \quad \text{Ph}
\end{align*}
\rightarrow
\begin{align*}
-\text{CH}_2-\text{CH}-\text{CH}-\text{CH}_2-
\end{align*}
\text{Ph} \quad \text{Ph}
\]

(2) They may undergo disproportionation with the transfer of a hydrogen atom and the formation of an unsaturated end-group.

\[
\begin{align*}
-\text{CH}_2-\text{CH}^* & + \text{CH}-\text{CH}_2^* \\
\text{Ph} & \quad \text{Ph}
\end{align*}
\rightarrow
\begin{align*}
-\text{CH}_2-\text{CH}_2 + \text{CH}^* = \text{CH}
\end{align*}
\text{Ph} \quad \text{Ph}
\]

Each of the above types are known. Recent studies by Bevington and his co-workers\textsuperscript{24} of the number of initiator fragments per molecule show that poly(styrene) terminates predominantly by coupling whereas poly(methyl methacrylate) terminates entirely by disproportionation at polymerisation temperatures above 60\textdegree and partly by each mechanism at lower temperatures.

(3) By reactions with impurities or inhibitors. This is not normally important as neither will be present in large concentrations.

(4) Chain transfer.

This is a process which increases the number of polymer molecules beyond those to be expected from the initiating radicals. It is a reaction in which a free-radical is transferred from one growing chain to another, without affecting the overall rate of reaction. The growth of the chain previously bearing the free-radical would be terminated and the molecule now bearing the radical would be capable of growing at the same rate.
k_{trans.} \quad M_x^\cdot + \text{SH} \quad \rightarrow \quad M_x^\cdot H + S^\cdot

S^\cdot \text{ proceeds to grow a new chain. Chain transfer occurs in a variety of ways.}

a) Solvent.

It usually takes place by removal of a hydrogen or chlorine atom. All solvents are susceptible to a greater or lesser extent. Carbon tetrachloride is however very prone to solvent transfer.

e.g.

\[ M_x^\cdot + \text{CCl}_4 \quad \rightarrow \quad M_x^\cdot \text{Cl} + \text{CCl}_3^\cdot \]
\[ \text{CCl}_3^\cdot + (M)_x \quad \rightarrow \quad \text{CCl}_3 M_x^\cdot \]
\[ \text{CCl}_3 M_x^\cdot + \text{CCl}_4 \quad \rightarrow \quad \text{CCl}_3 M_x^\cdot \text{Cl} + \text{CCl}_3^\cdot \]

Gregg and Mayo \(^2\) examined the formation of poly(styrene) in carbon tetrachloride and found that the polymer contained 4 chlorine atoms per molecule.

e.g.

\[ \begin{array}{c}
\text{CCl}_3 \\
\text{Ph} \\
\left( \text{CHCH}_2 \right)_x \\
\text{Cl}
\end{array} \]

Styrene is less susceptible than methyl methacrylate or vinyl acetate to such transfer.

b) Initiator transfer.

Some initiators, including benzoyl peroxide, undergo radical induced decomposition.

e.g.

\[ M_x^\cdot + (\text{PhCOO})_2 \quad \rightarrow \quad M_x - \text{OCOPh} + \text{PhCOO}^\cdot \]
-13-

α,α'-Azoisobutyronitrile is not susceptible to transfer reactions. Chain transfer has been found to occur in the polymerisation of methyl methacrylate using hydroperoxide initiators.

c) Monomer transfer.
The monomer may perform the function of the solvent of the reaction, an atom being transferred from the monomer to saturate the radical. Possibly it occurs by the transference of a proton from the $\beta$-carbon atom of the chain to the unsaturated monomer as follows:

\[
\begin{align*}
\text{X} & \quad \text{X} \\
\text{CH}_2-\text{CH} & + \quad \text{CH}_2=\text{CH} \quad \longrightarrow \\
\text{CH}==\text{CH} & \quad \text{CH}_2\text{CH}.
\end{align*}
\]

d) Polymer transfer.
Chain transfer to the polymer represents a case slightly different from the other types of transfer since it produces no new molecules but rather leads to the formation of branches on existing polymer molecules.

\[
\begin{align*}
\text{X} & \\
\text{M}_x + \text{M}_y-\text{CH}_2-\text{CH}_2-\text{M}_z & \quad \longrightarrow \\
\text{M}_x\text{H} + \text{M}_y-\text{CH}_2-\text{C}-\text{CH}_2-\text{M}_z
\end{align*}
\]

A completed polymer molecule is now capable of fresh growth. Its effect is more pronounced on molecular weight distribution than on average molecular weight.
Kinetics of radical initiated polymerisation.

In its simplest form, the process of free-radical polymerisation consists of three steps, initiation, propagation and termination. The initiator (I) was assumed to decompose into two free-radicals R* by a first order reaction.

\[ \text{k}_d \]
\[ I \rightarrow 2R^* \quad \ldots \ldots \quad 1 \]

then follows the addition of a monomer unit to form a chain radical, \( M_1^* \).

\[ \text{k}_a \]
\[ R^* + M \rightarrow M_1^* \quad \ldots \ldots \quad 2 \]

The successive steps in propagation.

\[ M_1^* + M \rightarrow M_2^* \]
\[ \text{k}_p \]
\[ M_2^* + M \rightarrow M_3^* \]

or, in general

\[ M_x^* + M \rightarrow M_{x+1}^* \quad \ldots \ldots \quad 3 \]

These are assumed all to have the same rate constant \( k_p \) since radical reactivity is presumed to be independent of chain length.

The termination step involves the mutual annihilation of the activity of two radicals. This can take place in two ways. The two chains may terminate by combination or coupling.

\[ \text{k}_{tc} \]
\[ M_x^* + M_y^* \rightarrow M_x + y \quad \ldots \ldots \quad 4 \]
for example,

\[ \text{CH}_2 - \text{CH}^\cdot + \text{CH} - \text{CH}_2 \longrightarrow \text{CH}_2 - \text{CH} - \text{CH} - \text{CH}_2 \]

Alternatively, they may undergo disproportionation, with the transfer of a hydrogen atom and the formation of an unsaturated end-group.

\[ k_{td} \quad M_x^\cdot + M_y^\cdot \longrightarrow M_x + M_y \]

for example,

\[ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \]
\[ \text{CH}_2 - \cdot + \cdot \text{C} - \text{CH}_2 \longrightarrow \text{CH}_2 - \text{CH} + \text{C} = \text{CH} \]
\[ \text{CO}_2\text{CH}_3 \quad \text{CO}_2\text{CH}_3 \quad \text{CO}_2\text{CH}_3 \quad \text{CO}_2\text{CH}_3 \]

Each type of termination is known, above.

Except where it is necessary to distinguish between the two mechanisms, the termination rate constant will be denoted by \( k_t \).

The rates of the three steps may now be written in terms of the concentrations of the species involved and the rate constants. The rate of initiation is

\[ R_i = \frac{d[M^\cdot]}{dt} = 2f \rho_d [I] \]

Where the factor \( f \) represents the fraction of the radicals formed by Eq.1 which are successful in initiating chains by Eq.2. The rate of termination is,

\[ R_t = \frac{d[M^\cdot]}{dt} = 2k_t [M^\cdot]^2 \]
In all cases, the concentration of free-radicals \([M^*]\) becomes constant very early in the reaction as the radicals are formed and destroyed at identical rates. Thus one can apply the steady state treatment whereby \(R_i = R_t\), hence Eq. 6 and 7 can be equated to solve for \([M^*]\)

\[
[M^*] = \left( \frac{f k_d [I]}{k_t} \right)^{1/2}
\]  

E..... 8

The rate of propagation is essentially the same as the rate of disappearance of the monomer, since the number of monomer molecules used up in Eq. 2 must be small compared with that used up in Eq. 3, if polymer is obtained.

Then,

\[
R_p = - \frac{d [M]}{dt} = k_p [M] [M^*]
\]  

or substituting from Eq. 8

\[
R_p = k_p \left( \frac{f k_d [I]}{k_t} \right)^{1/2} [M]
\]  

Thus the overall rate of polymerisation should, in the early stages, be proportional to 1) the square root of the initiator concentration, and 2) the first power of the monomer concentration. This will be so if the initiator efficiency is high. In the case of very low efficiency, \(f\) might be proportional to \([M]^{3/2}\), making \(R_p\) proportional to \([M]^{3/2}\)

The proportionality of the overall rate to the square root of the initiator concentration has been confirmed experimentally in a large number of cases by the work of Arnett\(^{26}\), Mayo and his co-workers\(^{27}\) and Schulz and Blaschke\(^{28}\).
Initiator efficiencies.

Strict adherence of rate of polymerisation to first order in \([M]\) indicates an efficiency of free-radicals near unity.

Arnett and Peterson\(^{29}\) determined efficiencies of \(\alpha,\alpha'\)-azoisobutyronitrile using radioactive carbon (\(^{14}C\)) by comparing the radioactive content of the polymers with the amount of initiator disappearing in the course of polymerisation. For the initiation of methyl methacrylate, vinyl acetate, styrene, vinyl chloride and acrylonitrile, \(f\) increases in that order from 0.6 - 1.0. Implicit in this method is the assumption that the initiator decomposes spontaneously, wastage of initiator by induced decomposition being negligible.

Kinetic chain length and degree of polymerisation.

The length of the polymer chain is specified in terms of the number of repeating units in the chain. This is called the degree of polymerisation (D.P.) and is represented by \(x_n\).

The kinetic chain length \(\gamma\) is defined as the number of monomer units consumed per active centre. It is therefore given by,

\[
\gamma = \frac{k_p}{2k_t} \left( \frac{[M]}{[M^*]} \right)
\]

Eliminating the radical concentration by means of Eq.9,

\[
\gamma = \frac{k_p^2}{2k_t} \left( \frac{[M]^2}{R_p} \right)
\]
For initiated polymerisation $R_p = k_p \left( \frac{f k_d}{k_t} \right)^{\frac{1}{2}} [I]^\frac{1}{2} [M]^\frac{1}{2}$

therefore

$$\gamma = \frac{k_p [M]}{2(fk_d)^{\frac{1}{2}} [I]^\frac{1}{2}}$$

The kinetic chain length is therefore inversely proportional to the square root of the initiator concentration. If no reactions take place other than those already discussed, the kinetic chain length should be related to $\bar{x}_n$, the degree of polymerisation: for termination by combination $\bar{x}_n = 2\gamma$ and for disproportionation $\bar{x}_n = \gamma$
COPOLYMERISATION

Historical introduction.

Organic compounds have been known to polymerise for well over a hundred years, but investigations into the polymerisation of two or more monomers were not begun until about 1911. It was in the quest for synthetic rubbers by the polymerisation of butadienes. The homopolymers left much to be desired and properties more like those of naturally occurring rubber were obtained by copolymerising butadiene with vinyl monomers, such as styrene. Butadiene had become readily available, from acetaldehyde via the Aldol synthesis and so was widely used industrially for copolymerisation work. Through many years of empirical experimentation, the practice of preparing many of these polymers evolved, though the principles were not understood. For a number of years the study of the reactions of copolymerisation lagged behind that of the properties of copolymers.

In the 1930's it was found that different monomers could differ markedly in their tendencies to enter into copolymers. Staudinger fractionated a vinyl chloride-vinyl acetate copolymer made from an equimolecular mixture of the two monomers. The ratios of vinyl chloride-vinyl acetate found in the fractions were 9:3, 7:3, 5:3, and 5:7. There was no 1:1 copolymer.

It was found that acrylic esters entered into copolymerisation faster than vinyl chloride, in an acrylic ester-vinyl chloride copolymer. The initial polymer formed was rich in acrylate whilst later when the ratio of acrylic ester-vinyl chloride was less than the corresponding monomer feed ratio, the polymer became rich in vinyl chloride. The change in composition was found
Maleic anhydride and other monomers which polymerise with great difficulty alone were found to polymerise readily with such monomers as vinyl chloride and styrene\textsuperscript{32}. Wagner-Jeuregg\textsuperscript{33} prepared a copolymer of stilbene-maleic anhydride; neither of these monomers would polymerise alone. High molecular weight copolymers with a 1:1 ratio of monomers were formed no matter which monomer was in excess.

In 1936 Dostal\textsuperscript{34} made the first attack on the mechanism of copolymerisation. After several unsuccessful attempts had been made to substantiate Dostal's work the kinetics were elucidated simultaneously, in 1944, by Alfrey\textsuperscript{35}, Mayo and Lewis\textsuperscript{36} and Wall\textsuperscript{37}.

The copolymer equation.

Dostal assumed that the rate of addition of a monomer to a free-radical depends only on the nature of the end-group on the radical chain. Thus monomers $M_1$ and $M_2$ lead to the formation of radicals of the type $M_1^*$ and $M_2^*$ respectively.

There are four possible ways of monomer addition in the propagation stage.

\begin{align*}
M_1^* + M_1 &\longrightarrow M_1^* & \text{Rate} = k_{11} [M_1^*] [M_1] \\
M_1^* + M_2 &\longrightarrow M_2^* & \text{Rate} = k_{12} [M_1^*] [M_2] \\
M_2^* + M_1 &\longrightarrow M_1^* & \text{Rate} = k_{21} [M_2^*] [M_1] \\
M_2^* + M_2 &\longrightarrow M_2^* & \text{Rate} = k_{22} [M_2^*] [M_2]
\end{align*}
Dostal went no further as four independent rate constants were involved. The copolymerisation equation was derived in 1944. To Dostal's reaction scheme was added the assumption of the steady state. This was applied to each radical concentration separately. The concentrations of \( M_1^* \) and \( M_2^* \) must each remain constant.

Therefore the rate of conversion \( M_1^* \) to \( M_2^* \) must be equal to the rate of conversion \( M_2^* \) to \( M_1^* \):

\[
k_{21} \left[ M_2^* \right] \left[ M_1 \right] = k_{12} \left[ M_1^* \right] \left[ M_2 \right]
\]

The rates of disappearance of the two types of monomer are given by:

\[
- \frac{d \left[ M_1 \right]}{dt} = \frac{d \left[ M_2 \right]}{dt} = k_{11} \left[ M_1^* \right] \left[ M_1 \right] + k_{21} \left[ M_2^* \right] \left[ M_1 \right] + k_{12} \left[ M_1^* \right] \left[ M_2 \right] + k_{22} \left[ M_2^* \right] \left[ M_2 \right]
\]

By defining \( r_1 = \frac{k_{11}}{k_{12}} \) and \( r_2 = \frac{k_{22}}{k_{21}} \) and combining Eq. 2 and 3 it can be shown that the composition of the copolymer being formed, at any instant, is given by,

\[
\frac{d \left[ M_1 \right]}{d \left[ M_2 \right]} = \frac{\frac{\left[ M_1 \right]}{\left[ M_2 \right]} - \frac{r_1 \left[ M_1 \right] + r_2 \left[ M_2 \right]}{\left[ M_1 \right] + r_2 \left[ M_2 \right]}}{r_1 \left[ M_1 \right] + r_2 \left[ M_2 \right]}
\]

Known as the copolymer equation.

\( \frac{d \left[ M_1 \right]}{d \left[ M_2 \right]} \) represents the ratio of the two monomers, in the increment of polymer formed when the ratio of unreacted monomer is \( \left[ M_1 \right] / \left[ M_2 \right] \). The former ratio obviously differs in general from the latter:
hence the unreacted monomer ratio will change as the polymerisation proceeds and this will give rise to a constantly changing composition of polymer being formed at each instant (unless \( r_1 \) is equal to \( 1/r_2 \)).

The equation has been verified by many experimental investigations of copolymer composition.
Monomer reactivity ratios.

The monomer reactivity ratios $r_1$ and $r_2$ are the ratios of the rate constant for a given radical adding to its own monomer to that for adding to the other monomer.

Thus,

- $r_1 > 1$ means that radical $M_1 \cdot$ prefers to add $M_1$
- $r_1 < 1$ means that it prefers to add $M_2$

for example,

Styrene ($M_1$) - methyl methacrylate ($M_2$) copolymer, $r_1 = 0.52$ and $r_2 = 0.46$, each radical adds to the other monomer about twice as fast as its own.

The composition of the copolymer is independent of over-all reaction rate and initiator concentration. Reactivity ratios are unaffected, in most cases, by the presence of inhibitors, chain transfer agents and solvents.

Types of copolymerisation.

1. Ideal.

When the two radicals show the same preference for adding each monomer:

$$\frac{k_{11}}{k_{12}} = \frac{k_{21}}{k_{22}} \quad \text{or} \quad r_1 = \frac{1}{r_2} \quad \text{or} \quad r_1 r_2 = 1$$

The units will then be arranged at random along the chain, the composition of the copolymer, at all times, will be the same as the monomer feed composition.

The copolymerisation of styrene ($M_1$) and butadiene ($M_2$) was found to represent a nearly ideal arrangement. At $60^\circ$, $r_1 = 0.78$ and $r_2 = 1.39$, $r_1 r_2 = 1.08$. 

2. Alternating.

Each radical prefers to react exclusively with the other monomer,
\[ r_1 = r_2 = 0. \]

The monomers alternate regularly along the chain regardless of the composition of the monomer feed, therefore a 1:1 copolymer will be formed.

3. Actual.

Most systems lie between the ideal and alternating type of copolymerisation:
\[ 0 < r_1 r_2 > 1 \]

Another possibility in which \( r_1 \) and \( r_2 \) were both greater than unity would exist if both monomers preferred to add to their own monomer. In the extreme, two homopolymers would be formed, but there are no established cases in which the product \( r_1 r_2 > 1 \)

**Determination of monomer reactivity ratios.**

Analysis of copolymers formed from monomer mixtures at several compositions, yields the reactivity ratios. Since the monomer composition changes with conversion, it is therefore necessary to limit the copolymerisation to a very small amount. Early methods for the calculation of \( r_1 \) and \( r_2 \) were troublesome to operate but these have been superceded by a straightforward analysis of polymerisation data\(^{39}\).
MONOMER REACTIVITY IN RELATION TO STRUCTURE.

The order of reactivity of olefins towards free-radicals not only is a function of the olefin, but depends on the nature of the attacking radical.

Copolymerisation.

The relative reactivity of a monomer towards different radicals can be derived from the monomer reactivity ratio. The inverse of this ratio is a comparison of the rate of reaction of a monomer with another radical to that with its own radical.

By comparing 1/r for a series of monomers with a given radical, it is possible to arrange these monomers in order for a given radical. The same order will not necessarily be obtained for a different radical, but it will be apparent that some monomers (e.g. styrene) are consistently more reactive than others (e.g. vinyl acetate).

Mayo and Walling determined the relative reactivities of some 34 monomers and from this drew the following conclusions:

1) the effect of the 1-substituent in increasing the reactivity of monomers toward radicals are in the order,

\[ -C_6H_5 > \text{-CH} = \text{CH}_2 > -\text{COCH}_3 > -\text{CN} > -\text{COOR} > -\text{Cl} \]
\[ > -\text{CH}_2Y > -\text{OCOCH}_3 > -\text{OR} \]

2) The effect of a second 1-substituent is roughly additive,

2-chlorobutadiene and 2,3-chlorobutadiene are two of the most reactive monomers known.
3) A methyl group usually increases reactivity, e.g. methyl methacrylate $\rightarrow$ methyl acrylate.

The order of reactivity is correlated with the extent to which the product radical, $M_x\text{--CH}_2\text{--CH}^\cdot$ can be stabilised by resonance.

Three quinoid resonance structures may be written for substituted benzyl radicals obtained in poly(styrene).

\[
\begin{array}{c}
\text{As a result the radical is stabilised to the extent of about 20 K. cal.} \\
\text{Two structures of nearly equal energies can be written for allyl radicals resulting from the addition to butadiene.}
\end{array}
\]

\[
\begin{array}{c}
M_x\text{--CH}_2\text{--CH} \leftrightarrow M_x\text{--CH}_2\text{--CH} \leftrightarrow M_x\text{--CH}_2\text{--CH}
\end{array}
\]

The amount of resonance stabilisation is similar to that for a benzyl radical.

Monomers with $\text{--C=O}$ or $\text{--C=N}$ groups conjugated to a carbon-carbon double bond, have resonance structures.
These describe states of higher energy than for the normal radical structure, hence resonance energy is smaller.

When \( X = \text{Cl} \text{ or OR in } M - \text{CH}_2 - \text{CH}^* \)

the only resonance structure has a much higher energy.

\[
\begin{align*}
\text{H} & \quad \text{H} \\
M_x - \text{CH}_2 - \text{C}^+ & \quad \text{or} \\
\text{Cl}^- & \quad 0 \quad \text{or} \\
\text{or} & \quad \text{Cl}^+ \\
\end{align*}
\]

Substituents tend to stabilise the monomer as well as the radical. Resonance stabilisation is less in the monomer than in the radical.

**Homopolymerisation.**

Polymerisability of monomers depends on the substituents attached to the carbon-carbon double bond, both in type and position. Replacement of one or both hydrogen atoms on one of the carbon atoms in ethylene, by chlorine, increases the tendency for it to polymerise.

The introduction of electron withdrawing groups have been found to increase the tendency to polymerise in the following order,

\[-\text{C}_6\text{H}_5 > -\text{CN} > -\text{CO}_2\text{R} > -\text{Halogens}.\]

An unsubstituted \(-\text{CH}_2\) group in the unsaturated monomer is generally required to permit polymerisation, tetrafluoroethylene is however a notable exception to this rule.

These generalisations are only qualitative, the rates of polymerisation
having been measured under comparable conditions, but without a knowledge of
the individual processes involved. The information does give a useful guide
to the polymerisability of olefinic compounds.

Marvel and his co-workers\,\textsuperscript{41,42} investigated the effect of substitution
in the side-chain and in the aromatic nucleus of styrene and came to the
following conclusions,

1) Side-chain.

Substitution in the $\alpha$- or $\beta$-position decreases the reactivity or inhibits
polymerisation altogether.

\textit{e.g.} $\alpha$-chlorostyrene $\beta$-bromostyrene.

2) Aromatic nucleus.

Substitution by Cl, CN or CO$_2$H increases the reactivity whereas NO$_2$
decreases it.

The introduction of one chlorine atom in the ortho-position increases
polymerisation but the further introduction of a similar atom decreases
the reactivity. This has been attributed to the steric hindrance between
the chlorine atoms and the side-chain, preventing the aromatic nucleus from
lying in the same plane as the side-chain.
MOLECULAR WEIGHT DETERMINATION

Introduction.

Since nearly all high polymers are mixtures of large molecules having different numbers of monomeric units, the molecular weights are not ascertainable with the simplicity and certainty possible in lower molecular weight organic chemistry.

Methods of molecular weight determination applicable to polymers include chemical analysis of end-groups, osmotic pressure, light scattering, sedimentation and diffusion, and solution-viscosity. End-group analysis requires that the polymer contains a known number of chemically determinable groups per molecule. It has been used for the determination of carboxyl and hydroxyl or amino end-groups in poly(ester)s or poly(amide)s respectively but becomes insensitive for high molecular weights when the fraction of end-groups are too small for accurate detection. The other methods with the exception of the last are absolute methods.

The simplicity of measurement of the solution-viscosity and the usefulness of viscosity-molecular weight data are so great that viscosity measurements constitute an extremely valuable tool for the characterisation of polymers. As solution-viscosity was used in this present work it will be the only method discussed.

Solution-viscosity.

The usefulness of solution-viscosity as a measure of molecular weight has been recognised since the early work of Staudinger and his co-workers.
High polymers are unique in greatly increasing the viscosity of a solvent when present in a small concentration. The higher the molecular weight the greater the increase in viscosity, solution-viscosity is basically a measure of the size or extension in space of polymer molecules.

Measurements of solution-viscosity are usually made by comparing the efflux time \( t \) needed for a given volume of polymer solution to flow through a capillary tube with the corresponding efflux time \( t_0 \) for the solvent.

From \( t_0 \), \( t \) and the concentration of polymer solution (\( g \) per 100 ml.) the following expressions can be calculated:

- **Viscosity ratio**: \( \gamma_r = \frac{\gamma}{\gamma_0} \sim \frac{t}{t_0} \)
- **Specific viscosity**: \( \gamma_{sp} = \gamma_1 - 1 = \frac{\gamma - \gamma_0}{\gamma_0} \sim \frac{t - t_0}{t_0} \)
- **Viscosity number**: \( \gamma_{red} = \frac{\gamma_{sp}}{c} \)
- **Limiting viscosity number**: 
  \[
  \left[ \gamma \right] = \left[ \frac{\gamma_{sp}}{c} \right]_{c \to 0} = \left[ \ln \gamma \right]_{c \to 0}
  \]

The limiting viscosity number is found from the efflux times at different concentrations of polymer solution, by plotting \( \gamma_{sp}/c \) or \( \ln \gamma \) against concentration and extrapolating to zero concentration.

It has been pointed out by Mead and Fuoss\(^{50}\) and Huggins\(^{51}\) that the slopes of these plots for a given polymer solution vary as the square of the limiting viscosity number.
The specific viscosity for a dilution less than 1% is related to the limiting viscosity number by the following expression,

\[ \eta_{sp}/c = \left[ \eta \right]/(1 + B\sqrt{c}) \text{ where } B \text{ is a constant.} \]

The molecules are not close enough to overlap and some mobile ions will leave the chain, which develops net charges and expands.
Correlation between solution-viscosity and molecular weight for linear polymers.

Staudinger's prediction that the viscosity number of a polymer should be proportional to the molecular weight has needed only slight modification; the limiting viscosity number has been substituted for the viscosity number and it has been recognised that the proportionality is to a power of the molecular weight somewhat less than one.

\[ [1] = K^1 \cdot M^a \]

\( K^1 \) and \( a \) are constants determined by the double logarithmic plot of limiting viscosity number and molecular weight.

Values of \( a \) for different polymers range from 0.5 (for highly flexible polymers) to 1.0 (for stiffer polymers). For poly(styrene)s intermediate values of \( a \) are obtained depending on whether the chain molecules are extended in a good solvent such as toluene or coiled in/poorer solvent such as methyl ethyl ketone\(^{56,57}\).

Therefore \( K^1 \) and \( a \) are both functions of the solvent as well as the polymer.
It is due to their inertness and high stability that macromolecules have become of such importance, industrially. This generally requires of them no reactive groups, for example, poly(ethylene) or groups which react only under relatively vigorous conditions, for example, poly(vinyl chloride). Some do however possess reactive groups and much interest is now being shown in the preparation and reactions of these high polymers, for example, poly(acrylic ester)s. Those however with very reactive groups are difficult to prepare and consequently have received little attention, for example, poly(amine)s and poly(aldehyde)s.

When organic reactions are carried out on high polymers, the main purpose is generally of modifying the properties of the starting material, or obtaining a new polymer, inaccessible by direct synthesis. Most of these reactions are based on the transformation of the side-groups present along the polymeric chain. When these reactions are compared with similar reactions carried out on low molecular weight compounds some special characteristics become evident which are directly related to polymer structure. These characteristics may be seen from either comparative kinetic measurements or from structural organic analysis.

Methods of synthesizing polymers with reactive side-groups.

1) By synthesis of the monomer containing the desired functional group, followed by its polymerisation. This is the ideal arrangement as the position of the reactive side-group is known in the monomer and hence
the polymer has a definite constitution.

For example, poly(vinyl chloride).

The use of this method is however, restricted and suffers from the following limitations:

(a) the monomer cannot be synthesised, e.g. vinylamine and vinyl alcohol$^{58,59}$.  

(b) the monomer, containing the required functional group, can be synthesised but will not polymerise, e.g. vinylquinol.

(c) the reactive group may not be stable under the conditions of polymerisation.

2) By the preparation of an inert polymer, followed by the introduction of the required side-group by a suitable chemical reaction. For example, the nitration or sulphonation of poly(styrene).

Substitution will not be regular and thus the constitution of the product will not be well defined. Substitution usually occurs in a random manner along the polymeric chains. The product will therefore vary depending on the conditions used.

3) Another method entails the use of monomers in which the functional group is suitably protected. After polymerisation of such monomers the reactive groups may then again be liberated. Examples of this are, poly(vinyl acetate) to poly(vinyl alcohol)$^{59}$ and poly(vinylquinol diacetate) to poly(vinylquinol)$^{60}$.

It was rapidly recognised that these high polymer reactions are subject to limitations and difficulties, which are inherent in the macromolecular nature of the compounds.
(a) For the formation of a high polymer with a well defined structure it is necessary to use a reaction which proceeds with a high or quantitative yield. If not, the final product will be a copolymer of original and modified units, since in this type of reaction separation of the product from starting material and any by-products is impossible due to the nature of the macromolecule.

(b) Changes in solubility affect the reaction, the rate increases if the polymer dissolves as the reaction proceeds and decreases if precipitation of the reaction products occur. The latter case tends to give irregular substitution, the distribution of substituents being dependent on the accessibility of the reactive groups to the reagent. The choice of solvent is thus very important.

(c) High steric hindrance existing along the chain very often limits the yield of the reaction, due to coiling of the polymeric chain. This effect may be due to the volume of some substituents and of the chain itself. It may also result from a strong electrostatic repulsion of a charged macromolecule towards a reagent carrying a charge of the same sign.
Comparative kinetics.

In a comparison of the kinetics of a polymer reaction with those of related small molecules there is found to be two different types of polymer reactions, monofunctional and multifunctional.

A monofunctional reaction is one which follows a comparable course to that of the related small molecule. It refers to the reaction of the functional groups of a macromolecule in which the groups participate as individuals, for example, the hydrolysis of poly(vinyl acetate) to poly(vinyl alcohol).

A multifunctional reaction often shows a great difference to those of the simple small molecules, and implies the participation of either more than one functional group in a reaction or the tendency for intramolecular reactions to occur.

In the Arndt-Eistert diazomethane reaction on poly(methacrylyl chloride) the chain lengthening with the formation of poly(isopropenyl acetic acid) would be expected from a knowledge of the reaction of small molecules.

\[
\begin{align*}
\text{Me} & \quad \text{Me} & \quad \text{Me} & \quad \text{Me} & \quad \text{Me} \\
\text{C} & \quad \rightarrow & \quad \text{C} & \quad \rightarrow & \quad \text{C} & \quad \rightarrow & \quad \text{C} \\
\text{CCl} & \quad \text{COCHN}_2 & \quad \text{CH} = \text{C} = 0 & \quad \text{CH}_2\text{CO}_2\text{H}
\end{align*}
\]

Analysis showed the reaction on the polymer to proceed as follows,

\[
\begin{align*}
\text{Me} & \quad \text{Me} & \quad \text{Me} & \quad \text{Me} & \quad \text{Me} & \quad \text{Me} \\
\text{C} & \quad \text{CH}_2 & \quad \rightarrow & \quad \text{C} & \quad \text{CH}_2 & \quad \rightarrow & \quad \text{C} & \quad \text{CH}_2 & \quad \text{C} \\
\text{CCl} & \quad \text{CCl} & \quad \text{CCl} & \quad \text{COCHN}_2 & \quad \text{CCl} & \quad \text{CH} = \text{C} = 0
\end{align*}
\]
Yielding on hydrolysis 5 membered keto-rings without any acid properties.

Because of this tendency towards intramolecular reaction, multifunctional reactions are governed by the stereoregularity of the polymer.

Generally, monofunctional reactions have similar kinetics for both small molecules and macromolecules which are only disturbed if the electrical potential of the polymer changes. Small differences in activation energy may be due to steric and solvation effects of the polymer chains. Hiller has shown by measurement of activation energy of the acetylation of cellulose, that this reaction is similar to that carried out on ordinary alcohols.

Table (I) shows the results of Hiller and also those of another monofunctional system, the hydrolysis of poly(N-vinyl pyrrolidone)\(^{63,64}\).

<table>
<thead>
<tr>
<th>Compound</th>
<th>( E ) (K.cal. mole(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. a. Cellulose</td>
<td>10.3</td>
</tr>
<tr>
<td>b. Methanol</td>
<td>10.2</td>
</tr>
<tr>
<td>2. a. Poly(N-vinyl pyrrolidone)</td>
<td>( 25 \pm 1 )</td>
</tr>
<tr>
<td>b. N-isopropyl-2-methyl pyrrolidone</td>
<td>( 27 \pm 0.5 )</td>
</tr>
</tbody>
</table>
In the case of poly(vinyl pyrrolidone), the increasing number of electrostatic charges formed on the polymer chain when the hydrolysis proceeds is without effect on further hydrolysis; this was ascribed to the considerable distance between the carboxylate groups and the neighbouring lactam units and it was held that the ionised carboxylate side-groups are too far from each other to affect the overall shape of the molecule.

The alkaline hydrolysis of poly(methacrylamide) in which the presence of methyl side-groups assures a stretched form of the macromolecule has also been studied. The reaction slows down progressively being limited to about 70% on account of the electrostatic repulsion towards the hydroxyl groups and by hydrogen bonding which protects the amide groups.

Morawetz and Westhead illustrated the differences in rate which arise with multifunctional reactions, by finding that the introduction of methacrylic-$d$-nitranilide groups into a polymeric acid stabilised these groups to hydrolysis by $\mathbb{H}$-sodium hydroxide solution. The rate was about 1,000 times less than that of the comparable trimethylacetic- and glutaric-$d$-nitranilides. This was attributed mainly to hydrogen bonding between the acid and amide groups;
Organic structure in polymer reactions.

The nature of the reaction product must also depend on the functionality of the reaction. A chemical change of the reacting groups, which is identical with those in analogous simple substances, occurs in the case of monofunctional polymers. Kern, Schulz, and co-workers have described the transformations of poly(acrylic ester)s into poly(hydroxamic acid)s, poly(hydrazide)s, poly(hydrazone)s and of poly(acrolein) into its acetal, mercaptal, oxime and poly(acid).

The presence of several neighboring groups makes intramolecular interaction possible and consequently may change the course of the reaction completely. In the interpretation of the results of multifunctional systems the statistical calculations of Flory must be taken into account. For a bifunctional system, assuming the accessibility of all groups is equivalent and remain constant during the reaction, Flory has shown that the degree of conversion, by reaction of functional groups in pairs, must be limited to 86.5 or 81.6% respectively dependent on the polymer structure. In regular head-to-tail structure 13.5% of the functional groups become isolated and therefore cannot react intramolecularly. If on the other hand the units were orientated at random, assuming only 1,2 and 1,3 reactions in pairs, then 18.4%
of functional groups become isolated and will remain on the polymer. Experimental support has been found for these statistical calculations by Marvel and Sample\textsuperscript{75} who found that the removal of halogen atoms by zinc dust from poly(vinyl chloride) was limited to 84–86\% removal, i.e. removal from a 1,3 chain.

\[
\begin{array}{c}
\text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH} \\
\text{Cl} & \text{Cl} & \text{Cl} & \text{Cl}
\end{array}
\rightarrow
\begin{array}{c}
\text{CH}_2 \cap \text{CH}_2 \cap \text{CH}_2 \cap \text{CH}_2 \\
\text{CH} \cap \text{CH} \cap \text{CH} \cap \text{CH}
\end{array}
\]

Multifunctional interactions have been also used for synthesis of new types of polymers, mostly inaccessible by direct synthesis. For instance the Friedel-Crafts reaction makes it possible to build up into the main chain condensed aromatic rings, the condensation of poly(vinyl chloride) with aromatic hydrocarbons gives polymers containing styrene units, 1,3-methylene indene rings and unreacted vinyl chloride units\textsuperscript{76}.

\[
\begin{array}{c}
\text{CH}_2 \cap \text{CH}_2 \cap \text{CH}_2 \cap \text{CH}_2 \cap \text{AlCl}_3 \\
\text{CH} \cap \text{CH} \cap \text{CH} \cap \text{CH} \cap \text{benzene}
\end{array}
\rightarrow
\begin{array}{c}
\text{CH}_2 \cap \text{CH}_2 \cap \text{CH}_2 \cap \text{CH}_2 \\
\text{CH} \cap \text{CH} \cap \text{CH} \cap \text{CH}
\end{array}
\]

The use of aluminium chloride causes a partial depolymerisation on account of the formation of a carbonium ion along the polymer chain; in the presence of a milder and more selective catalyst (polyphosphoric acid) this degradation can be at least partially avoided.

By carrying out the Hofmann degradation on poly(acrylamide)s\textsuperscript{77} poly(amide)s can be prepared.
It is evident that all these interactions are strongly dependent on inter-group distances and consequently on the stereochemical structure of the polymer chain. All the results suggest that many reactions carried out on macromolecules may be appreciably modified and the yields improved if the reactions were carried out on a polymer with a well-defined internal and stereochemical composition.
KINETICS OF THE MENSCHUTKIN REACTION.

The reaction between an alkyl halide and a tertiary-amine, with the formation of a quaternary ammonium salt;

\[ R_2N + RX \rightarrow R_4N^+ + X^- \]

was the subject of classical investigations by Menschutkin in 1890, (whence quaternisation reactions are often known as Menschutkin reactions after that early investigator). One of the reactions studied was that between triethylamine and ethyl iodide, in a number of solvents but at only one temperature (100°). Variations in rate, of about a thousand-fold, were found; quaternisation was found to proceed more rapidly in alcohols than in hydrocarbons. The solvents were placed by Menschutkin in a series,

\[ \text{MeOH} > \text{EtOH} > \text{Me}_2\text{CO} > \text{C}_6\text{H}_6 > \text{C}_6\text{H}_{14} \]

and the same general sequence has been confirmed for the reaction between other alkyl halides and amines by a number of subsequent workers.

The quaternisation reactions were found to follow second-order kinetics, provided that both reacting species are in relatively small concentrations, the rate of reaction being proportional to the concentrations of both the reactants:

\[ \frac{dx}{dt} = k(a-x)(b-x) \]

The determination of the second-order rate constant is illustrated by some more recent work by Winkler and Hinshelwood, on the reaction between
pyridine and ethyl iodide, Table (2). The concentration of both reactants being 0.1N in the reaction mixture. The iodide ion was determined by a Volhard titration.

Reaction between pyridine and ethyl iodide in benzene at 100°.

Table (2)

<table>
<thead>
<tr>
<th>Time min.</th>
<th>$x_{mole.\cdot 1^{-1}}$</th>
<th>$k_{10^{-4}\cdot mole^{-1}\cdot sec^{-1}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>179</td>
<td>0.0120</td>
<td>1.27</td>
</tr>
<tr>
<td>420</td>
<td>0.0240</td>
<td>1.25</td>
</tr>
<tr>
<td>737</td>
<td>0.0350</td>
<td>1.22</td>
</tr>
<tr>
<td>1,054</td>
<td>0.0445</td>
<td>1.27</td>
</tr>
<tr>
<td>1,530</td>
<td>0.0530</td>
<td>1.22</td>
</tr>
<tr>
<td>2,497</td>
<td>0.0655</td>
<td>1.27</td>
</tr>
<tr>
<td>4,020</td>
<td>0.0750</td>
<td>1.24</td>
</tr>
</tbody>
</table>

It can be seen that the values of the rate constant shown in the last column are in good agreement. A second example, due to Davies, is quoted because the reactants are p-isopropylidimethylaniline and methyl iodide and thus is directly relevant to the present work.

Reaction between p-isopropylidimethylaniline and methyl iodide

in aqueous acetone at 35° - Davies.

Concentration of base and alkyl halide were 0.1 g-mole.1^{-1}.

3.63 ml. (measured at 35°) of reaction mixture were removed and titrated with 0.025N-silver nitrate solution.
Table (3)

<table>
<thead>
<tr>
<th>Time min.</th>
<th>Vol. silver nitrate-solution (ml.)</th>
<th>$k \times 10^2$ (1.g-mole$^{-1}$ min.$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>92</td>
<td>5.20</td>
<td>6.06</td>
</tr>
<tr>
<td>131</td>
<td>6.45</td>
<td>6.10</td>
</tr>
<tr>
<td>197</td>
<td>7.90</td>
<td>6.06</td>
</tr>
<tr>
<td>239</td>
<td>8.60</td>
<td>6.08</td>
</tr>
<tr>
<td>260</td>
<td>9.15</td>
<td>6.08</td>
</tr>
<tr>
<td>363</td>
<td>10.00</td>
<td>6.09</td>
</tr>
<tr>
<td>402</td>
<td>10.30</td>
<td>6.07</td>
</tr>
</tbody>
</table>

No activation energies were measured by Menschutkin as his work was carried out at a single temperature, but this was done, some years later, by Grimm, Ruf and Wolff. There was much speculation in the 1930's concerning quaternisation reactions and the relationship,

$$Rate = PZe^{-E/RT}$$

Where $E$ is the activation energy,

$P$ is the probability factor

and $Z$ is the collision number.

The effect on the reaction rate of changes in the solvent, the hydrostatic pressure, the alkyl halide and the tertiary-base were studied in relation to activation energy and the probability factor variations. A correlation was sought between $E$ and $P$ and the effect of each on the rate of reaction.
Mechanism.

It is generally agreed that in the reactions of a series of \( p \)-substituted benzene derivatives, the velocity changes are due almost entirely to changes in the energy of activation, \( E \), and not to changes in the probability factor, \( P \). Where the range of velocities with a series of \( p \)-substituted compounds is comparatively small (reaction between \( p \)-alkyl dimethylanilines and alkyl halides) it has been pointed out that the Arrhenius Equation is really inadequate and considerable care should be taken in ascribing significance to changes in \( P \). There are, however, inconsistencies in the literature concerning the influence of \( E \) and \( P \) on the rate of reaction and the following account attempts to integrate published conclusions as far as possible.

Speculations concerning the mechanisms of reactions were offered before the electronic character of the covalent bond was understood but since then much work has been done and great strides have been made in the elucidation of these mechanisms. Quaternisation reactions, having been studied and found to be of the second-order, are consistent with a reaction which is favoured by accession of electrons to a nucleophilic centre. Evans, Watson and Williams found the reaction of a series of \( p \)-substituted dimethylanilines with methyl iodide in methanol to be accurately of the second-order over the first 50% of quaternisation and the order of velocities to be:

\[
p - \text{OMe} > p - \text{Me} > H > p - \text{Cl}.
\]

The reaction is concluded to proceed by the \( S_N^2 \) mechanism.
The tertiary-amine is the nucleophilic reagent since it supplies the electron pair. Obviously a nucleophilic reagent attacks a molecule at the point of low electron density.

In the $S_N^2$ mechanism two molecules simultaneously undergo covalency change and the bonding is altered by co-ordination and heterolysis. It involves an electron transfer from the substituting agent (tertiary-amine) to the seat of substitution and from the latter to the displaced group (halide). In consequence of substitution the amine becomes one unit more positive and the halide one unit more negative.

As quaternisation is a bimolecular process the transition state involves both molecules and has two partial bonds which are longer than fully formed covalent bonds.

In the Menschutkin reaction the bonds undergoing change are partially ionic, the halide having a partial negative charge and the amine a partial positive charge. There are other changes occurring during the reaction because wherever there are changes, in the initial, transition or final state of substitution there are strong electrostatic forces of solvation in any polar solvent. These are not shown diagrammatically but energetically such
forces are in general of the same order of importance as the bonds and along with bond changes must be regarded as primary determinants of activation energy.

Since the rate of reaction can be defined in terms of the Arrhenius Equation much work has been directed towards the evaluation of the activation energy (E) and the probability factor (P). The kinetics of quaternisation reactions are of particular interest because it has been found that P is usually low and moreover markedly affected by the solvent. For example, in the reaction between aniline and bromoacetophenone the factor P varies from $4 \times 10^{-11}$ in benzene to $5 \times 10^{-5}$ in benzyl alcohol.

For other types of reaction the value of P is close to unity; very low values in the Menschutkin reaction imply that very few 'activated' collisions result in reaction. Many theories have been put forward to account for this abnormality.

Moelwyn-Hughes and Sherman have assumed that at least one of the reactants forms an unstable complex with the solvent and that the true reactant is this solvated complex. In such a case the evaluation of the product $[RJ_N][RX]$ is in error and the true value of P could be unity.

Hinshelwood from a consideration of Eucken and Jaacks' work and Norrish account for the apparent inefficiency of the activated collisions by assuming an intermediate collision complex which can yield the final products only when conditions are favourable for stabilisation. Otherwise the complex reverts to the reactants.

Edwards has postulated, for benzene solutions, in which the product of the Menschutkin reaction is sparingly soluble, that the reaction is
primarily rapid and reversible. It was presumed that the rate of overall reaction is governed by the rate of formation of the solid product.

\[ R_N^+ + RX \rightleftharpoons R_N^+ + X^- \rightarrow \text{solid} \]

The equilibrium in solution favours the original reactants. This hypothesis takes the form of those previously put forward in that a reversibly formed intermediate is involved in the net process.

Harman, Stewart and Ruben\(^{106}\) studied the reaction between dimethylaniline and methyl iodide in which the hydrogen atoms in the alkyl halide were replaced by tritium atoms. All the radioactivity was found in the quaternary salt and none in the excess amine. The solvents used were ethanol and benzene. Ethanol as a solvent could have promoted ion separation and stabilised the initial reaction product, and therefore, the reactions were also carried out in benzene. Incomplete quaternisation of dimethylaniline in neither solvent produced radioactivity in the unreacted base. It was concluded that for these examples there is no reaction intermediate which is reversibly formed and in which iodide ion loses its identity with the methyl group to which it was originally attached. Thus Edward's mechanism is incorrect; and any other involving a reversible function of a free quaternary ammonium ion.
Structural influences.

(i) Influence of substituent groups on reactivity.

It is well known that substituents in the benzene nucleus influence aromatic reactions and many, including the Menschutkin reaction, have been investigated. The substituents change the distribution of electron densities and therefore influence the molecule by affecting bond strengths and repulsive forces. Furthermore, apart from anomalous cases, the effect of two or more substituents is approximately the algebraic sum of individual groups. \(^{107}\)

His Evans and co-workers\(^ {99}\) found that substitution in the \(p\)- or \(m\)-position in dimethylaniline altered the rate of reaction with methyl iodide in methanol by changing the energy of activation. Laidler\(^ {90}\) for the same reaction in nitrobenzene reported a similar result.

Since alkyl groups are feebly electron-repelling it would be expected that the reactivity of dimethylaniline towards methyl iodide should be enhanced by substitution of \(p\)-alkyl groups. Basic strengths should likewise be increased. The one exception is \(p\)-isobutylidimethylaniline, which has practically the same reactivity and basic strength as the unsubstituted base.

Considering the relative effects of the different alkyl groups, Davies\(^ {85}\) found for the reaction of \(p\)-alkylidimethylanilines with methyl iodide the sequence,

\[
\text{Me} \succ \text{isoPr} \succ t-\text{Bu}, \text{Et} \succ n-\text{Bu} \succ n-\text{Pr} \succ H \sim \text{iso-Bu}
\]

which is not the order expected if the sole effect of the alkyl groups is the inductive effect. Steric effects are not considered to be of importance since the substituent is so far isolated from the point of reaction. The results
point to the importance of hyperconjugation, as the sequence, Me \(\rightarrow\) isoPr \(\rightarrow\) t-Bu, is that according to the number of hydrogen atoms available for this electronic displacement.

Baker and Nathan\(^{108}\) obtained the following order for the effect of the substituents on the rate of reaction between pyridine and \(p\)-alkylbenzyl bromides,

\[
\text{Me} \rightarrow \text{Et} \rightarrow \text{isoPr} \rightarrow \text{t-Bu} \rightarrow \text{H}
\]

The sequence appears due to the superimposition of two electronic effects, an inductive effect, (which increases in the order Me \(\rightarrow\) Et \(\rightarrow\) isoPr \(\rightarrow\) t-Bu) since all are faster than the unsubstituted compound and hyperconjugation, (such electron-release towards the benzene ring would decrease in order, Me \(\rightarrow\) Et \(\rightarrow\) isoPr \(\rightarrow\) t-Bu). For \(p\)-methyldimethylaniline hyperconjugation would be represented,

![Hyperconjugation Diagram]

Superimposition of this hyperconjugative effect should thus cause either complete or at least partial inversion of the inductive order depending on the relative magnitude of the two effects. The differences in reactivity are small since the electronic effects of the alkyl groups are small and are also being relayed from a comparatively distant point.
In the Menschutkin reaction the iso-butyl group frequently causes a marked decrease in reaction rate\textsuperscript{78,109,110}, but in other cases the group has been found to behave as predicted\textsuperscript{111-113}. \textit{p}-isoButyldimethylaniline is seen to be similar in reactivity to dimethylaniline which is less than the n-or t-butyl group. The capacity for electron release of the t-butyl group is less than for the isobutyl group but this seems to be inadequate to account for a large difference in reactivity.

The order of velocity, found by Evans and co-workers\textsuperscript{99}, for nuclear substituted dimethylanilines is that normally associated with a reaction which is favoured by accession of electrons to the seat of reaction. Determination of basic strengths confirms this order\textsuperscript{114}.

\[
p-\text{OMe} \, \text{>} \, p-\text{Me} \, \text{>} \, \text{H} \, \text{>} \, p-\text{Cl}.
\]

Information as to whether changes in the rate of reaction are governed by changes in the activation energy or in the non-exponential term in the Arrhenius equation is not conclusive. Evans and co-workers\textsuperscript{99} found, Table (4), that substituents in the \textit{p}-or \textit{m}-position influence the reaction velocity by changing the activation energy and Laidler\textsuperscript{90} too found for reactions of certain nuclear substituted dimethylanilines with methyl iodide in nitrobenzene that the influence of the group is manifested in variations of \(E, PZ\) remaining practically constant; Davies\textsuperscript{55}, however, found that it was by a change in the probability term.
Reaction between methyl iodide and p-substituted dimethylanilines

\[ \text{[XC}_6\text{H}_4(\text{Me})_2] \text{ in methanol. } \text{Evans, Watson and Williams}^{99}. \]

Table (4).

<table>
<thead>
<tr>
<th>Substituent (X)</th>
<th>E (K.cal.mole.(^{-1}))</th>
<th>(\log_{10} PZ).</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-OMe</td>
<td>14.3</td>
<td>6.9</td>
</tr>
<tr>
<td>p-Me</td>
<td>14.9</td>
<td>6.8</td>
</tr>
<tr>
<td>H</td>
<td>15.2</td>
<td>6.9</td>
</tr>
<tr>
<td>p-Cl</td>
<td>16.2</td>
<td>7.0</td>
</tr>
</tbody>
</table>

Hammett and Pfluger\(^{115}\) showed that a simple relationship exists between the rate constants of one series of reactions and the equilibrium constants of another distinct though related series. Several other reaction series were later included by Hammett\(^{116-118}\), who pointed out limits to the range of structural variation permissible. Davies and Addis\(^{114}\) showed that a linear relationship held between the pK of dimethylaniline and its p-substituents (OMe, Me and Hal) in 50% alcohol and the \(\log_{10}\) of the bimolecular rate constant of the reaction between the base and methyl iodide in 90% acetone. Departures from linearity which are observed are small.
(ii) Effect of solvent on reactivity.

As stated earlier, Menschutkin proved that the combination of triethylamine with ethyl iodide proceeds more rapidly in alcohols than in hydrocarbons. He placed the solvents in the rate series,

\[ \text{MeOH} > \text{EtOH} > \text{Me}_2\text{CO} > \text{C}_6\text{H}_6 > \text{C}_6\text{H}_{14} \]

The same general sequence has been established for other quaternisation reactions, by a number of subsequent investigators. It was results such as these, and investigation of solvent effects on other reactions, that led to the theory of solvent effects on reaction kinetics put forward by Hughes and Ingold and co-workers. It is stated that a change to a more polar solvent will decrease or increase the energy of activation according as the transition state of the reaction is more or less polar than the initial state of the reactants. There may be counteracting changes in the probability factor but it is the activation energy which will dominate the reaction change.

Solvation is essentially an electrostatic phenomenon. The following assumptions were made concerning the amount of solvation to be expected in the presence of electric charges:

1) Solvation will increase with the magnitude of the charge.

2) Solvation will decrease with increasing dispersal of a given charge.

3) The decrease of solvation which will be due to a dispersal of a charge will be less than that due to its destruction on passing from the reactants to the transition state.
Concerning solvents, it has been assumed that polarity, that is, the power to solvate charges in solutes, will:

1) Increase with the molecular moment of the solvent.
2) Decrease with increased thickness of shielding of the dipole charges.

The hydroxyl group becomes a strong factor in solvent polarity, because the proton is so thinly shielded.

For the Menschutkin reaction the following should therefore be expected.

<table>
<thead>
<tr>
<th>Disposition of charges</th>
<th>Effect of activation on charges</th>
<th>Effect of increased solvent polarity on rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial state</td>
<td>Transition state</td>
<td></td>
</tr>
<tr>
<td>( Y + RX )</td>
<td>( Y^+ \ldots R \ldots X^- )</td>
<td>increased</td>
</tr>
</tbody>
</table>

Ingold therefore proposed that with a highly polar solvent the reaction rate would be faster than with a less polar solvent. Experimentally this has been found. The data has been analysed on the basis of the Arrhenius Equation and it has been confirmed that on changing the solvent there is a simultaneous change in both the activation energy \( (E) \) and the probability factor \( (P) \). Hinshelwood and co-workers found in investigations on the functional relation between the constants of the Arrhenius Equation that on passing from a non-polar to a highly polar solvent there was an increase in rate. This was concerned with a decrease in activation energy and a small increase in the probability factor. It was concluded that a correlation between \( E \) and \( P \) was unlikely to be accidental and an explanation was put forward, by these investigators, based upon general statistical principles and upon the assumption of a time interval between activation and reaction.
For the reaction between triethylamine and ethyl iodide and pyridine and methyl iodide it was found that the variation in the reaction rate is largely determined by the activation energy, the value of $P$ being comparatively constant. The results for the reaction between triethylamine and ethyl iodide are shown in the following table. The solvents are arranged in order of increasing polarity.

### Table (5).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Ethyl iodide and triethylamine</th>
<th>$E(\text{Kcal.mole.}^{-1})$</th>
<th>$\log_{10}PZ$</th>
<th>$\frac{k \times 10^5}{\text{g-mole.}^{-1} \text{sec.}^{-1}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td></td>
<td>16.0</td>
<td>4.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Toluene</td>
<td></td>
<td>13.0</td>
<td>4.0</td>
<td>25.3</td>
</tr>
<tr>
<td>Benzene</td>
<td></td>
<td>11.4</td>
<td>3.3</td>
<td>39.8</td>
</tr>
<tr>
<td>Bromobenzene</td>
<td></td>
<td>12.5</td>
<td>4.6</td>
<td>166.0</td>
</tr>
<tr>
<td>Acetone</td>
<td></td>
<td>11.9</td>
<td>4.4</td>
<td>265.0</td>
</tr>
<tr>
<td>Benzonitrile</td>
<td></td>
<td>11.9</td>
<td>5.0</td>
<td>1,125.0</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td></td>
<td>11.6</td>
<td>4.9</td>
<td>1,383.0</td>
</tr>
</tbody>
</table>

This behaviour is also found when the results of Evans and co-workers for the reaction between dimethylaniline and methyl iodide in methanol was compared with those of Laidler for the same reaction in nitrobenzene.
(iii) Variation of the alkyl halide and the base.

Menschutkin\textsuperscript{73} studied the reaction between triethylamine and a variety of alkyl halides, in acetone and in benzene.

The following order of reaction was found,

\[
\text{Me} \gg \text{Et} \gg \text{isoPr} \\
\& \quad \text{Et} \gg \text{n-Pr} \sim \text{higher normal halides}, \text{for which}
\]

the values are seen to be nearly constant.

Relative rates,

\[
\begin{array}{cccc}
\text{Me} & \text{Et} & \text{isoPr} & \text{isoPr} \\
100 & 8.8 & 0.18 \\
\text{n-Pr} & 1.7 & \text{n-Bu} & 1.2 \\
& \text{n-Hept} & 0.9 & \text{n-Oct} 0.9
\end{array}
\]

The reaction with t-Bu was frustrated by olefin formation, part of the isoPr result may have been due to this.

Methyl groups exert a positive inductive effect, so that the introduction of a methyl group in passing from methyl to ethyl iodide makes the central atom more negative; its attraction for an electron-donating reagent therefore becomes less and the observed decrease in rate is to be expected. A further decrease is found on passing from ethyl to isopropyl iodide, successive homologous additions from ethyl to the higher normal halides have but a small effect after n-butyl as the C-halogen bond strength is virtually unaltered.

The sequence of rates Me \(\gg\) Et \(\gg\) n-Pr has been confirmed by Preston and Jones for reactions of alkyl iodides with dimethylaniline and tri-isoamylamine in absolute ethanol\textsuperscript{95}. 
There are smaller rates for bromides than iodides which is due to a change in the probability factor not to a change in activation energy. Winkler and Hinselwood for the reaction between triethylamine and pyridine and alkyl halides determined the variation in activation energy with rate of reaction and the results are shown in Table (6) below.

Table (6)

<table>
<thead>
<tr>
<th>Amine</th>
<th>Iodide</th>
<th>E (K.cal.mole.⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triethylamine</td>
<td>Me</td>
<td>9.3</td>
</tr>
<tr>
<td>Triethylamine</td>
<td>Et</td>
<td>11.4</td>
</tr>
<tr>
<td>Triethylamine</td>
<td>isoPr</td>
<td>17.1</td>
</tr>
<tr>
<td>Pyridine</td>
<td>Me</td>
<td>14.3</td>
</tr>
<tr>
<td>Pyridine</td>
<td>Et</td>
<td>15.8</td>
</tr>
<tr>
<td>Pyridine</td>
<td>n-Pr</td>
<td>16.1</td>
</tr>
<tr>
<td>Pyridine</td>
<td>isoPr</td>
<td>18.0</td>
</tr>
</tbody>
</table>

The decrease in velocity and the increase in activation energy on passing from the aliphatic amine to pyridine is related to the basic strength of the amine and the availability of the unshared electrons, pyridine being a weaker base than triethylamine. Evans found the opposite effect in the reaction between dialkylalanilines and methyl iodide in methanol. The rate was found to decrease in the order

\[ \text{Me}_2 \gg \text{MeEt} \gg \text{MePr} \gg \text{Et}_2 \gg \text{EtPr} \gg \text{Pr}_2 \]
The ratio of reaction velocities taking dimethylaniline as unity was found to be comparable with the work of Thomas.

<table>
<thead>
<tr>
<th>Aniline</th>
<th>Me₂</th>
<th>MeEt</th>
<th>MePr</th>
<th>Et₂</th>
<th>Pr₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evans</td>
<td>1.0</td>
<td>0.71</td>
<td>0.41</td>
<td>0.10</td>
<td>0.046</td>
</tr>
<tr>
<td>Thomas</td>
<td>1.0</td>
<td>0.66</td>
<td>0.44</td>
<td>0.07</td>
<td>-</td>
</tr>
</tbody>
</table>

There is found to be an increase in activation energy with increase in basicity. The activation energy usually changes in the reverse manner and it therefore seems evident that some more powerful forces are operative. Several explanations have been put forward:

1) Brown and Fried suggest that the approach of an alkyl group would be hindered by the bulky alkyl substituents.

2) It has also been suggested that there is a possibility of hydrogen bond formation in the transition state complex between ethyl and higher alkyl groups and the reactive centre of the molecule.

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

This hydrogen bonding increases with EtPr and Pr₂, which is accounted for by the formation of more stable rings.
Poly(4-vinylpyridine) has been quantitatively quaternised by the addition of alkyl halides in polar solvents, but the overall kinetics do not conform to the simple bimolecular rate which accurately describes the quaternisation of monomeric pyridine derivatives. There is, of course, one fundamental difference between the two quaternisations: in the case of the monomeric compounds, reactants and products are all independent kinetic entities, while in the case of the polymer, the reactive sites are bound together on the polymer chain. Consequently, successive quaternisations must eventually occur at short distances from already quaternised sites. In solvents of high dielectric constant, many of the halide ions formed diffuse away from the pyridinium ions of the polyelectrolyte and a positive electrostatic field of high intensity builds up in the polymer coil. Experiments with a variety of dipyridyl compounds have shown that the rate of quaternisation of the second pyridine is markedly decreased by the presence of the charge on the first. Poly(4-vinylpyridine) therefore presents a case in which this electrostatic effect can be much enhanced.

The quaternisation kinetics were carried out using n-butyl bromide in sulfolane at 25, 50 and 75°C. The build-up of the bromide ion concentration was determined potentiometrically by titration with aqueous silver nitrate solution. Homopolymers of widely differing molecular weights were prepared in order to determine the dependence (if any) of the rate of quaternisation on molecular weight.
Molecular weights were determined from viscosity measurements in 95% ethanol using the equation,

\[
\left[ \eta \right]_0 = 2.5 \times 10^{-4} M^{0.68}
\]

The molecular weights of the homopolymers were evaluated and found to be as shown in Table (8).

<table>
<thead>
<tr>
<th>Code</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>m.w. x 10^-6</td>
<td>0.040</td>
<td>0.095</td>
<td>0.115</td>
<td>0.166</td>
<td>0.350</td>
<td>0.070</td>
<td>0.110</td>
<td>5.0</td>
</tr>
</tbody>
</table>

It is known that the quaternisation of 4-alkyl substituted pyridines is somewhat more rapid than that of pyridine; consequently Fuoss expected that the rate of quaternisation of the pyridyl nitrogens in poly(4-vinyl pyridine) would be about the same as 4-picoline, at least during the initial stages of quaternisation. For such reactions the rate is given by the equation,

\[
t = \frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)}
\]

The polymers in Table (8) were quaternised in propylene carbonate and in sulpholene, the concentration of the alkyl halide was about one-tenth that of the base, so that no more than 10% of the nitrogens could be quaternised. The rate of initial quaternisation proceeds normally, the second-order plots are linear and from the slopes the second-order rate constants were found.
Quaternisation by n-butyl bromide in sulpholane.

Table (9).

<table>
<thead>
<tr>
<th>Amine</th>
<th>$k \times 10^{-3}$</th>
<th>1 mole$^{-1}$ min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25°</td>
<td>50°</td>
</tr>
<tr>
<td>Pyridine</td>
<td>0.46</td>
<td>3.7</td>
</tr>
<tr>
<td>4-Picoline</td>
<td>0.85</td>
<td>6.6</td>
</tr>
<tr>
<td>4-isoPropylpyridine</td>
<td>0.90</td>
<td>7.0</td>
</tr>
<tr>
<td>Poly(4-vinylpyridine)</td>
<td>0.64</td>
<td>5.4</td>
</tr>
</tbody>
</table>

The values for the quaternisation of poly(4-vinylpyridine) are lower than the corresponding values of 4-picoline. It was concluded from these results and from those in propylene carbonate that the $\text{CH}_2\text{CHPyCH}_2$ grouping is structurally about the same as $\text{CH}_2\text{CHPyCH}_2$. Therefore there is no inherent difference in the Menschutkin reaction for substituted pyridines, whether the substituent is a simple group or part of a polymer chain.

Furthermore, the rate is substantially independent of molecular weight, but there appears to be a slight tendency for the rate to increase with increasing molecular weight.

When, however, the quaternisation is allowed to proceed essentially to completion (excess alkyl halide) a new effect appears because the rate of quaternisation rapidly drops below that corresponding to simple second-order kinetics. It has been shown$^{283}$ that if the rate of quaternisation
of a given pyridine group is independent of the charge status of its neighbours, then the kinetics should be wholly second-order, provided only that the concentration of the polymer in the rate equation be expressed as that of the repeating unit. Furthermore, it has also been shown that the rate of quaternisation of the second group in 1,3-bis(4-pyridyl)propane, $\text{PyCH}_2\text{CH}_2\text{CH}_2\text{Py}$, which is the model compound for a segment of the polymer chain, is only 0.36 times as fast as the first. Previous work has shown that the decrease is not primarily an intramolecular inductive or electromeric effect and it is thought to be due to a volume field effect produced at the site of the second nitrogen by the positive charge on the nitrogen which is first quaternised. The same field effect must also make itself felt in the quaternisation of poly(4-vinylpyridine) because the pyridyl groups, being bonded to the backbone of the polymer, cannot diffuse apart. After 50% reaction every unquaternised pyridyl group has on average both neighbours quaternised and Fuoss stated that the rate should therefore be depressed to about 1/10th of the initial rate, if the assumption is made that the field effect is additive in the exponent. An analysis of the data shows that this is indeed the case.

The poly(4-vinylpyridine) chain after 10-20% quaternisation can be symbolised as follows,

$$\cdots\text{0+0000+000+00+00000+000\ldots}$$

where '0' denotes an unquaternised site and '+' a quaternised one.

Inspection shows that there are 3 categories of unquaternised pyridine groups;
those with no quaternised neighbours, those with one quaternised neighbour and those with two quaternised neighbours. From work on model compounds the corresponding rate constants for the 3 categories were expected to be in sequence \( k_0 > k_1 > k_2 \). At the start of the reaction quaternisation begins at the rate given by \( k_0 \) which was determined, as illustrated, by experiments in which insufficient alkyl halide was present to combine with all the reactive sites. Eventually pyridines adjacent to quaternised sites become quaternised at a slower rate \( k_1 \) and finally, only pyridines with both neighbours quaternised are left and these must react by hypothesis with the slowest rate \( k_2 \).

Onsager put forward an analysis to describe the shift in population of the various categories as the reaction proceeds. The integral is in the form of an unwieldy collection of partial fractions and solution was impracticable.

The following semi-empirical solution was put forward by Fuoss to describe mathematically the proposed shift in rate control from \( k_0 \) to \( k_2 \) as time increases, \( k_1 \) being considered a mixture of \( k_0 \) and \( k_2 \).

We have,

\[
\frac{dx}{(a-x)(b-x)} = \left[ k_0 e^{-\alpha t} + k_2 (1 - e^{-\alpha t}) \right] dt
\]

Integrating

\[
f(x)/t = \frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)} / t = k_2 + (k_0 - k_2)(1 - e^{-\alpha t}) / \alpha t
\]
Where $\alpha$ is a constant depending on temperature and initial concentrations.

$\alpha$ is determined by plotting $f(x)/t$ against $(1-e^{-\alpha t})/\alpha t$ using trial values of $\alpha$ until a linear plot is obtained. Unfortunately the method is not very sensitive until 50% or more reaction and there is not much data available in this range.

Table (10) below shows some of the results obtained by Fuoss, for the quaternisation of poly(4-vinylpyridine) in sulfolane.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Temp.</th>
<th>b (mole. 1$^{-1}$)</th>
<th>r</th>
<th>$(1.$ mole.$^{-1}$ min.$^{-1}$)</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>25</td>
<td>0.263</td>
<td>2.19</td>
<td>$5.2 \times 10^{-4}$</td>
<td>$6.1 \times 10^{-5}$</td>
</tr>
<tr>
<td>H</td>
<td>50</td>
<td>0.258</td>
<td>2.19</td>
<td>$4.6 \times 10^{-3}$</td>
<td>$4.1 \times 10^{-4}$</td>
</tr>
<tr>
<td>G</td>
<td>75</td>
<td>0.241</td>
<td>2.25</td>
<td>$2.6 \times 10^{-2}$</td>
<td>$4.1 \times 10^{-3}$</td>
</tr>
<tr>
<td>G</td>
<td>75</td>
<td>0.0396</td>
<td>1.84</td>
<td>$3.0 \times 10^{-2}$</td>
<td>$4.1 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

Where $b$ is the concentration of alkyl halide and $r$ is the ratio of concentration of alkyl halide/concentration of monomoles of polymeric base.

An overall test of the equation was made by plotting $f(x)k_0t$ against $(1-e^{-\alpha t})/\alpha t$; if the ratio $k_0/k_2$ is independent of temperature and initial concentration, then all the data for the various systems studied should be on the same straight line. The results conform to this criterion, included are runs at 25, 50 and 75$^\circ$ for polymers with molecular weights ranging from 110,000 to 5,000,000. The generality, states Fuoss, of the semi-empirical equation thus appears to be established.
A recurring problem in polymer chemistry is the dependence of functional group reactivities on the reacted-or-unreacted status of neighbouring groups. As has been previously mentioned the quaternisation of poly(4-vinylpyridine) is retarded in its later stages, presumably because of the difficulty of forming a cationic group in close proximity to previously formed positive ions. The hydrolysis rates of \( \text{p-nitrophenyl methacrylate} \), \( \text{p-methoxyphenyl methacrylate} \), \( \text{methacrylate} \), \( \text{acrylamide} \) and \( \text{p-nitroacrylanilide} \) groups have been found to be enhanced by the neighbouring acrylic or methacrylic acid groups.

This problem has been treated theoretically by Keller, Alfrey and Lloyd and Arends. Following Fuoss and his co-workers where it was postulated that an unreacted functional group can be found in three distinct environments and that the rate constants for the functional group reaction are different for the three arrangements, the three rate constants were designated \( k_1 \), \( k_2 \) and \( k_3 \).

Keller determined the average fraction of reacted groups of the three different types as a function of time, by first deriving the appropriate kinetic equations and then solving them.

Alfrey and Lloyd determined quantitatively the conversion-time curves and the detailed structure of the product at any intermediate stage of reaction, for any values of \( k_1 \), \( k_2 \) and \( k_3 \). The central difficulty was inherent in the large number of simultaneous equations which were involved in the kinetic scheme. To obtain a solution of these equations certain approximations had to be made. All the kinetic expressions were developed only in terms of first-order reactions of the polymeric functional groups.
Arends\textsuperscript{137} put forward an exact solution to this problem which gave a complete description of the sequences of unreacted sites. Agreement with the solution of Alfrey and Lloyd is stated to be excellent. Further work by Keller\textsuperscript{138} confirmed that the solution of Arends satisfied the equations of Alfrey and Lloyd.
The object of the present work.

In order to add to data on the reactivity of groups attached to macromolecules the quaternisation of polymeric tertiary-amines have been studied.

Evans, Watson and Williams\textsuperscript{99} have found that the reaction for a series of $p$-substituted dimethylanilines with methyl iodide in methanol was accurately of the second order over at least 50\% quaternisation and the order of velocities

$$ p - \text{OMe} \overset{\text{Me}}{\rightarrow} p - \text{Me} \overset{\text{H}}{\rightarrow} p - \text{Cl} $$

was consistent with a reaction which is favoured by accession of electrons to a nucleophilic centre. The reaction is concluded to proceed by the $S_{n}2$ mechanism.

Harman, Stewart and Ruben\textsuperscript{106}, for the reaction of tritium-labelled methyl iodide with dimethylaniline in ethanol and in benzene, found no entry of labelled methyl into unreacted amine, whence it was concluded that the quaternisation is not reversible.

At the outset of this work, it was inferred that quaternisation is an irreversible bimolecular process and any unusual features in rate or order which were encountered in this reaction could be ascribed to the macromolecular environment.

Special characteristics due to the attachment of tertiary-amine groups to a macromolecule, it was considered, could be assessed by a comparison of the kinetics of quaternisation of the polymers with those
of the appropriate phenyl compound, and the isopropylphenyl compound, 
the latter representing the individual side-group together with the chain 
carbon atom to which it is combined and the two adjacent atoms.

Two specimens of homopolymer of different average molecular weight 
were prepared in order to study the effect of molecular weight on the 
rate and order of the reaction. The interaction of neighbouring groups 
could be determined by a comparison of the reaction of the two homopolymers 
with that of a styrene - D-N,N-dimethylaminostyrene copolymer with a 
2:1 molar ratio.

From consideration of the work by Fuoss and his co-workers\textsuperscript{123} on 
the quaternisation of poly(4-vinylpyridine), and of the results obtained 
in the above quaternisation reactions, it was decided that a further 
assessment of macromolecular reactivity could be made by an 
investigation of the effect of variation of solvent on the quaternisation 
of poly(4-vinylpyridine).
Introduction to the experimental sections.

The work has been set out in 4 main sections.

Section (1) deals with the preparation of \( \text{p-}N,N\text{-dimethylaminostyrene} \), its homopolymerisation and copolymerisation with styrene and the characterisation of the polymers, by viscosity measurements.

The synthesis of \( \text{p-}N,N\text{-dimethylaminostyrene} \) was carried out as follows:

\[
\begin{align*}
\text{CHO} & \quad \xrightarrow{\text{CH(\(CH\text{)}_3\))}_2} \quad \text{CH(\(CH\text{)}_3\))}_2 \\
\text{\(N(\(CH\text{)}_2\))}_2 & \quad \xrightarrow{\text{CH} = \text{CH}_2} \quad \text{CH} = \text{CH}_2
\end{align*}
\]

The synthesis of \( \text{p-isopropyl(dimethylaniline)} \) is described by the route shown below.

\[
\begin{align*}
\text{CHO} & \quad \xrightarrow{\text{\(N(\(CH\text{)}_3\))}_2} \quad \text{\(N(\(CH\text{)}_3\))}_2 \\
\text{\(N(\(CH\text{)}_2\))}_2 & \quad \xrightarrow{\text{\(CH\text{)}_3\))}_2 \quad \text{\(CH\text{)}_3\))}_2
\end{align*}
\]

The purification of the kinetic solvent (dimethylformamide), methyl iodide and dimethylaniline is also described.

Section (2) deals with the kinetics of quaternisation of the two homopolymers, the copolymer, dimethylaniline and \( \text{p-isopropyl(dimethylaniline)} \) with methyl iodide in dimethylformamide at 0°.
Section (3) describes the preparation and evaluation of poly(4-vinylpyridine), and the preparation of n-butyl bromide salts of pyridine and poly(4-vinylpyridine).

Section (4) deals with the kinetics of quaternisation of pyridine and poly(4-vinylpyridine) in dimethylformamide and in sulpholane and of poly(4-vinylpyridine) in dimethylformamide-sulpholane mixtures by reaction with n-butyl bromide at 75°.
EXPERIMENTAL
M. p. s are corrected.

Purification of solvents.

Diethylether was dried over anhydrous calcium chloride and distilled. The fraction boiling at 34-35° was collected and stored over sodium wire.

Methanol was distilled and the fraction boiling at 64-65° was collected.

AnalaR benzene was dried over calcium hydride and distilled. The fraction boiling at 80° was collected.

AnalaR toluene was refluxed for two hours with sodium and distilled. The fraction boiling at 111°, nD 1.4940 was collected and stored over sodium wire.

96% Ethanol was distilled and the fraction boiling at 78° was collected.

Acetone was dried over anhydrous potassium carbonate and distilled. The fraction boiling at 56° was collected.
SECTION 1.

Preparation of \( p-N, N\)-dimethylamino-\( \alpha\)-methylbenzyl alcohol.

The alcohol was prepared by a Grignard reaction between methylmagnesium iodide and \( p-N, N\)-dimethylaninobenzaldehyde, according to Marvel and his co-workers\(^{139}\) but with certain modifications. The reaction was carried out in a three necked round-bottomed flask (3 L.). The centre neck contained a mercury sealed-stirrer and the two outside necks, a double surface water condenser and a dropping funnel, respectively. Calcium chloride tubes protected both the funnel and condenser from the atmosphere. Anhydrous conditions were preserved throughout.

Dry magnesium turnings (15 g.) together with sodium-dried ether (45 ml.) were introduced into the flask. Methyl iodide (90 g.), previously dried over anhydrous sodium sulphate, and sodium-dried ether (750 ml.) were shaken together in the dropping funnel. The reaction was initiated by a small crystal of iodine which was added together with a small volume of the methyl iodide solution. When the reaction was well under way the remainder of the methyl iodide solution was added at such a rate as to keep the ether gently refluxing. During the addition of the methyl iodide solution the reaction vessel was thoroughly cooled in ice.

AnalaR \( p-N, N\)-dimethylaminobenzaldehyde (75 g.), dried over phosphorous pentoxide, was dissolved in sodium-dried ether (1,200 ml.) and added slowly to the solution of the Grignard reagent. A precipitate was formed. The reaction mixture was allowed to stand overnight whereupon a grey-white solid settled out.
The product was found to be contained in this precipitate. The ethereal solution was decanted. To the precipitate was added ether (300 ml.) and ammonium chloride (60 g.) in saturated solution, ice and ammonia (d 0.88; 30 ml.). The ether layer was separated and the basic aqueous layer extracted with ether (3 x 100 ml.). The ethereal extracts were combined and washed with an aqueous ammoniacal ferrous sulphate solution (2 g. per 100 ml. of ether) for removal of peroxides. The presence of ferrous ion in excess was ascertained by testing with alcoholic dimethylglyoxime reagent.\(^{140}\)

The ethereal solution was dried over anhydrous sodium sulphate, filtered and the ether removed by a water-bath, the temperature of which was kept at approximately 45° so that no dehydration to the monomer occurred.

The alcohol was obtained as a pale-yellow solid; recrystallised from redistilled light petroleum, b. p. 40-60°, it had m. p. 58.5-59° (Marvel\(^{139}\) records 58.5-59°).

The decanted ethereal layer above yielded a further small quantity of alcohol.

There was obtained:

<table>
<thead>
<tr>
<th>Alcohol (from precipitate)</th>
<th>60 g.</th>
<th>m. p. 56.5-57.5°</th>
<th>Total Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alcohol (from decanted layer)</td>
<td>8 g.</td>
<td>m. p. 52-53°</td>
<td>62 g.</td>
</tr>
<tr>
<td>1st recrystallisation of last</td>
<td>2 g.</td>
<td>m. p. 56.5-57°</td>
<td>i.e. 75%</td>
</tr>
</tbody>
</table>

Preparation of p-N,N-dimethylaminostyrene.

Conversion of the alcohol into the corresponding styrene is somewhat troublesome, in that dehydration is not facile and the monomer readily polymerises. The best yields of the monomer were obtained when the freshly
prepared alcohol (m. p. 56°; 8 g. portions) was distilled at 5 mm. from a Claisen flask (25 ml.) with air-leak, connected to ice- and drikold-cooled receivers; heating was by micro-burner with considerable reflux from the flask neck. Various elaborations, and the use of aged alcohol, all gave smaller yields.

The product, a mixture of the monomer, alcohol and water was collected between 126-144°/5 mm. The first receiver (ice-cooled) collected mainly the monomer and alcohol whilst the second (drikold-cooled) mainly water.

In 4 runs there were obtained:

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>1st receiver</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 7.8 g.</td>
<td>4.8 g.</td>
<td>70%</td>
</tr>
<tr>
<td>2. 7.9 g.</td>
<td>4.6 g.</td>
<td>65%</td>
</tr>
<tr>
<td>3. 7.7 g.</td>
<td>4.8 g.</td>
<td>70%</td>
</tr>
<tr>
<td>4. 7.5 g.</td>
<td>4.0 g.</td>
<td>60%</td>
</tr>
</tbody>
</table>

The crude monomer was stored at 4° with 1% t-butylcatechol added. Before redistillation the monomer was dissolved in 4 volumes of light petroleum, b. p. 40-60°, and dried over anhydrous potassium carbonate. The solution was filtered, 1% t-butylcatechol added, the light petroleum evaporated, and the monomer distilled under nitrogen, at reduced pressure.

The monomer, a colourless liquid, was stored at 4° under nitrogen prior to polymerisation.
There was obtained:

<table>
<thead>
<tr>
<th>Fraction</th>
<th>b. p.</th>
<th>weight</th>
<th>n_D^{25}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-81°/0.3 mm.</td>
<td>1.60 g.</td>
<td>1.6084</td>
</tr>
<tr>
<td>2</td>
<td>81-83°/0.3 mm.</td>
<td>6.46 g.</td>
<td>1.6084</td>
</tr>
<tr>
<td>3</td>
<td>86-94°/0.5 mm.</td>
<td>1.65 g.</td>
<td>1.6078</td>
</tr>
</tbody>
</table>

The three fractions were mixed and used for the preparation of the polymers.

Total yield 30%.

**Purification of styrene.**

In order to remove the stabiliser (t-butylcatechol), styrene (250 ml.) was washed three times with 2N-caustic soda solution (250, 150 and 100 ml.) and water (250, 150 and 100 ml.), by this time the washings were neutral. The monomer was dried over anhydrous sodium sulphate, filtered and distilled under nitrogen at reduced pressure.

It had b. p. 45-46°, n_D^{25} 1.5442, and was stored at 4° under nitrogen prior to use.
Preparation of poly(p-N,N-dimethylaminostyrene).

Homopolymerisation.

\(\alpha,\alpha'\)-Azoisobutyronitrile, recrystallised from ether\(^{141}\); m. p. 103-104°,

\[
\begin{align*}
(i) & \text{ 0.0127 g.; } (ii) \text{ 0.0504 g.} \\
(ii) & \text{ 3.0186 g.; } (ii) \text{ 3.0439 g.}
\end{align*}
\]

was added to \(p-N,N\)-dimethylaminostyrene representing approximately 0.4 and 1% of initiator with respect to the monomer. The initiator was dissolved in the monomer and the polymerisations were carried out in soda glass test-tubes, sealed under nitrogen. The polymerisations were carried out for 24 hours (after which time the products were apparently solid) at 71.5 ± 1°. The tubes were broken open, revealing light-green, hard and brittle rods.

The homopolymer with 0.4% initiator will be called homopolymer (I) and the one with 1% initiator, homopolymer (II).

Copolymerisation.

\(\alpha,\alpha'\)-Azoisobutyronitrile (0.0416 g.) was dissolved in styrene (4.2033 g.) and \(p-N,N\)-dimethylaminostyrene (2.9669 g.), representing a copolymerisation mixture containing two molecular proportions of styrene to one of the aminostyrene.

Solution was attained and the polymerisation carried out in two tubes sealed under nitrogen. The conditions were identical to those for the homopolymisations and the products were brittle rods.

Purification of the homopolymers and copolymers.

1. Homopolymers.

Homopolymer (I) was crushed and dissolved in AnalaR benzene (15 ml.) giving a 20% weight by volume solution. The solution was filtered and
added dropwise to redistilled isopropanol (b. p. 81°; 60 ml.), with high speed mechanical stirring. The product precipitated in a fibrous state, was filtered and washed with isopropanol (100 ml.). The polymer was dried at 50°/2 mm. to constant weight.

There was obtained:

Homopolymer (I) - 2.4 g. i.e. 80% yield.  
Found: N, 9.50. Calc. for C_{10}H_{13}N: N, 9.52%.

Similarly,

Homopolymer (II) - 2.5 g. i.e. 80% yield.  
Found: N, 9.66. Calc. for C_{10}H_{13}N: N, 9.52%.

2. Copolymer.

The copolymer was dissolved in AnalaR benzene (38 ml.), filtered and added dropwise to mechanically stirred isopropanol (260 ml.). After filtering, the fibrous polymer was washed with isopropanol (200 ml.), dried at 50°/2 mm. to constant weight.

There was obtained:

Copolymer - 6.1 g. i.e. 84% yield.  
Found: C, 88.17; H, 8.11; N, 3.83. Calc. for C_{8}H_{8}:  
C_{10}H_{13}N as 2.00:1.00: C, 87.80; H, 8.22; N, 3.94%.

For all subsequent work the copolymer was assumed to have a 2:1 ratio of styrene to p-N,N-dimethylaminostyrene.
Determination of the limiting viscosity number of the homopolymers and copolymer.

The limiting viscosity number $[\eta]$ is defined by the following equation.

$$[\eta] = \left[ \frac{\ln \eta_r}{c} \right]_{c \to 0}$$

Now,

$$\eta_r = \frac{t_{\text{soln}}}{t_{\text{solvent}}}$$

Therefore,

$$[\eta] = \left[ 2.303 \frac{\log_{10} t_{\text{soln}} - \log_{10} t_{\text{solvent}}}{c} \right]_{c \to 0}$$

Where,

- $c$ is the concentration of the polymers in g. per 100 ml. solution.
- $t_{\text{soln}}$ is the flow-time of the solution in seconds.
- $t_{\text{solvent}}$ is the flow-time of the solvent in seconds.

The viscosity determinations on the three polymers were carried out at 25.00 ± 0.01°, using a U-tube viscometer B.S.188 No.1. The viscosity ratio of each polymer was found at four different concentrations by determining the flow-time of the solution and comparing this with the flow-time of the solvent. By extrapolation of the graph of $\ln \eta_r/c$ versus concentration, to zero concentration, the limiting viscosity number $[\eta]$ was evaluated.

Concentrations of 1.2, 0.8, 0.6, and 0.4 g. polymer per 100 ml. solution were used. The higher two concentrations were prepared by direct weighing and the lower two by dilution of the higher two. This was done by adding the solution (10 ml.) to the solvent (10 ml.) using a clean and dry pipette. Toluene was selected as the solvent.
The copolymer solution was found to have a constant flow-time over 4 hours but this was not so with the homopolymers. For the homopolymers, however, the flow-time decreased until an equilibrium value was obtained; this took up to three days. After this time the value did remain constant.

The results for a solution of homopolymer (II) are shown in Table (II) below.

**Viscosity measurements of homopolymer (II) in toluene.**

\[ c = 1.123 \, \text{g. per 100 ml. solution.} \]

Flow-time of solvent = 130.5 sec.

The solution had been made a day before any viscosity measurements were taken. The solution was adjusted to the viscometer level and the first reading taken after it had been in the thermostat for 30 min.

**Table (II).**

<table>
<thead>
<tr>
<th>Time (hr.)</th>
<th>Average flow-time (sec.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>194.5</td>
</tr>
<tr>
<td>0.67</td>
<td>193.6</td>
</tr>
<tr>
<td>1.5</td>
<td>192.8</td>
</tr>
<tr>
<td>2</td>
<td>192.1</td>
</tr>
<tr>
<td>3</td>
<td>192.1</td>
</tr>
<tr>
<td>4</td>
<td>191.5</td>
</tr>
<tr>
<td>5</td>
<td>191.3</td>
</tr>
<tr>
<td>22.75</td>
<td>189.2</td>
</tr>
<tr>
<td>24</td>
<td>189.0</td>
</tr>
<tr>
<td>25</td>
<td>189.0</td>
</tr>
<tr>
<td>26</td>
<td>189.0</td>
</tr>
</tbody>
</table>
The flow-time of the solvent was determined before and after each series of polymer solution measurements. The results for the two homopolymers and one copolymer after equilibrium had been attained are shown in Table (12).

<table>
<thead>
<tr>
<th></th>
<th>c</th>
<th>$t_{sol^n}$ (sec.)</th>
<th>$\frac{\ln \gamma_r}{c}$</th>
<th>$[\gamma]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent</td>
<td>-</td>
<td>130.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Copolymer</td>
<td>1.2060</td>
<td>240.0</td>
<td>0.5090</td>
<td>0.5650</td>
</tr>
<tr>
<td></td>
<td>0.6030</td>
<td>179.8</td>
<td>0.5325</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.8055</td>
<td>199.7</td>
<td>0.5289</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.4028</td>
<td>162.6</td>
<td>0.5467</td>
<td></td>
</tr>
<tr>
<td>Solvent</td>
<td>-</td>
<td>130.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Homopolymer (I)</td>
<td>1.194</td>
<td>220.2</td>
<td>0.4384</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5970</td>
<td>169.8</td>
<td>0.4432</td>
<td>0.4500</td>
</tr>
<tr>
<td></td>
<td>0.7930</td>
<td>185.2</td>
<td>0.4420</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.3965</td>
<td>155.8</td>
<td>0.4473</td>
<td></td>
</tr>
<tr>
<td>Solvent</td>
<td>-</td>
<td>130.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Homopolymer (II)</td>
<td>1.123</td>
<td>189.0</td>
<td>0.3303</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5615</td>
<td>157.2</td>
<td>0.3332</td>
<td>0.3375</td>
</tr>
<tr>
<td></td>
<td>0.8010</td>
<td>170.6</td>
<td>0.3322</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.4005</td>
<td>149.2</td>
<td>0.3350</td>
<td></td>
</tr>
<tr>
<td>Solvent</td>
<td>-</td>
<td>130.5</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Graph (1)

Viscosity of poly(£-N,N-dimethylamino styrene)s

Copolymer
Homopolymer (I)
Homopolymer (II)

\[ \ln \eta / \text{conc.} \]

Concentration (g per 100 ml. solution)

0.6 0.5 0.4 0.3 0.2 0.1 0.0 0.0

1.2 1.0 0.8 0.6 0.4 0.2
Preparation of \( \text{p-isopropyl(dimethylaniline).} \)

\( \text{p-isopropyl(dimethylaniline) was prepared by the action of methylmagnesium iodide on } \text{p-N,N-dimethylaminobenzaldehyde according to the method of Sachs and Sachs.} \)

Methyl iodide (100 g.) in ether (170 ml.) was added to magnesium (16 g.) in ether (50 ml.). Once the reaction had been initiated the methyl iodide solution was added dropwise, with stirring and cooling, the ether gently refluxing.

\( \text{Anal} \text{R p-N,N-dimethylaminobenzaldehyde (25 g.), previously dried over phosphorous pentoxide, was dissolved in ether (500 ml.) and added slowly. After complete addition of the aldehyde the reaction mixture was allowed to stand overnight and the ether distilled off, leaving a viscous grey oil. The flask was fitted with calcium chloride tubes and heated in an oil-bath at } 100^\circ \text{C for 8 hours. After this heating the grey oil had solidified to give a brown-red mass. The residue was decomposed by the addition of ice and concentrated hydrochloric acid (140 ml.), dropwise with considerable cooling. The aqueous layer was made ammoniacal to Congo Red, whereupon a dark red oil separated. The oil was extracted three times with ether (250, 150 and 100 ml.). The ethereal solution was dried over anhydrous magnesium sulphate, filtered and the ether evaporated leaving a dark yellow oil.}

The product was distilled twice under nitrogen at reduced pressure and the fraction boiling at \( 110^\circ/8 \text{ mm.} \) collected; it was sealed under nitrogen.
A gas-liquid chromatogram was carried out on a sample under the following conditions -

<table>
<thead>
<tr>
<th>Column</th>
<th>10% carbowax 1,000 on 109-125 celite.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp.</td>
<td>125°</td>
</tr>
<tr>
<td>Flow Rate</td>
<td>59 ml. min.⁻¹</td>
</tr>
<tr>
<td>Cylinder Pressure</td>
<td>10.2 lbs.in.⁻²</td>
</tr>
<tr>
<td>Voltage</td>
<td>1500</td>
</tr>
<tr>
<td>Attenuation</td>
<td>x 10</td>
</tr>
<tr>
<td>Chart Speed</td>
<td>6 ins.hr.⁻¹</td>
</tr>
<tr>
<td>Sample Size</td>
<td>0.025 µl.</td>
</tr>
</tbody>
</table>

The trace showed only one peak and it was concluded that the p-isopropylidimethylaniline was a pure specimen.

There was obtained:

Total yield 9.6 g. i.e. 35% yield.

<table>
<thead>
<tr>
<th>b.p.</th>
<th>weight</th>
<th>( n_D^{25} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st fraction</td>
<td>-110°/8 mm.</td>
<td>1.2 g.</td>
</tr>
<tr>
<td>2nd fraction</td>
<td>110°/8 mm.</td>
<td>8.2 g.</td>
</tr>
<tr>
<td>3rd fraction</td>
<td>110-112°/8 mm.</td>
<td>0.2 g.</td>
</tr>
</tbody>
</table>

Found, for fraction (2): C, 81.16; H, 10.12; N, 8.85;
Calc. for \( C_{11}H_{17}N \): C, 80.89; H, 10.50; N, 8.60%.

Preparation of the methiodide of p-isopropylidimethylaniline.

p-isoPropylidimethylaniline (1.0 g.) was dissolved in ether (10 ml.), to which was added a two-fold excess of methyl iodide (1.8 g.) in ether (10 ml.). A white precipitate was formed almost immediately and crystallisation was
complete after 24 hours. The product was filtered, washed thoroughly with ether and dried.

The methiodide, white crystals, was recrystallised to constant melting point by dissolving in methanol and adding ether to precipitate; it then had m. p. 204-204.5°.

**Found:** C, 47.23; H, 6.68; N, 4.55; **Calc.** for C₁₂H₂₀NI: C, 47.22; H, 6.59; N, 4.59%.

**Purification of dimethylaniline.**

Commercial dimethylaniline (150 ml.) was refluxed with acetic anhydride (65 ml.), for three hours. The mixture was then cooled and transferred to a Claisen flask fitted for distillation. The distillation was carried out under nitrogen. Some acetic acid and excess acetic anhydride passed over, followed by dimethylaniline, b.p. 192-194°.

The product, being slightly coloured was redistilled twice under nitrogen and yielded a colourless liquid b. p. 192-193°, nD²⁵ 1.5557. The dimethylaniline was sealed, under nitrogen, in ampoules. A fresh ampoule was used for each kinetic experiment.

A gas-liquid chromatogram was carried out on one of the above samples, under the following conditions.

<table>
<thead>
<tr>
<th>Column.</th>
<th>10% carbowax 1,000 on 109-125 celite.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp.</td>
<td>Flow Rate</td>
</tr>
<tr>
<td>100°</td>
<td>6.5 ml. min⁻¹</td>
</tr>
<tr>
<td>Voltage</td>
<td>Attenuation</td>
</tr>
<tr>
<td>48</td>
<td>x 0.2</td>
</tr>
</tbody>
</table>
The trace showed only one peak, and the dimethylaniline was concluded to be a pure specimen.

**Purification of methyl iodide.**

Methyl iodide (100 ml.) was dried over anhydrous sodium sulphate, filtered and redistilled. The fraction boiling at 42.0-42.4° was collected and stored in a dark bottle containing a coil of copper wire.

**Purification of dimethylformamide.**

Thomas and Rochow have investigated the purification of dimethylformamide, and the following is based on their findings.

Dimethylformamide (2 L.) was mixed with benzene (200 ml., dried over calcium hydride). The benzene was removed together with the benzene-water azeotrope by distillation at atmospheric pressure, through a 30 cm. column the temperature at the head of which was not allowed to exceed 80°.

Anhydrous magnesium sulphate (50 g., which had been heated at 300-400° in a muffle furnace for 8 hours) was added to the dimethylformamide and the whole was shaken for one day. Distillation under nitrogen through a 90 cm. vacuum-jacketed column packed with Fenske helices gave dimethylformamide b. p. 41-43°/10-12 mm., $n_D^{25}$ 1.4275.

The solvent was stored under nitrogen in a wash-bottle, the orifices of which were normally stoppered and dispensed by application of nitrogen pressure. A single stock of dimethylformamide was used in the first series of kinetic runs.
Preparation of standard silver nitrate solution.

AnalaR silver nitrate was dried in an oven at 110° for two hours and cooled in a desiccator. Silver nitrate (2.3636 g.) was weighed out accurately, dissolved in water and made up to one litre. 0.01391N-silver nitrate solution was used in all the kinetic work.
SECTION 2.

Determination of the kinetics of the quaternisation of dimethylaniline, p-isopropyldimethylaniline and poly(p-N,N-dimethylaminostyrene) by reaction with methyl iodide.

The following method of investigation has been developed; rate and order of reaction were 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, (dimethylaniline), representing the individual side-group; and (iv) the isopropylphenyl compound, (p-isopropyldimethylaniline), representing the side-group together with the chain carbon atom to which it is combined and the two adjacent atoms.

Rate-determination procedure.

The kinetic experiments were carried out at 0° in dimethylformamide as solvent. Methyl iodide (0.2720 equiv.) and the tertiary-amine (0.1360 equiv.) were weighed into separate flasks; to each dimethylformamide (5 ml.) was added; the polymeric amines dissolved in an hour at room temperature. The flasks, together with a third containing solvent, were placed in a bath of ice and water. After 30 min. the solution of the amine was added and washed into that of the methyl iodide, the whole was brought to 25 ml. with dimethylformamide, and mixed. At intervals from this point, portions (2 ml.) were transferred by syringe into methanol (45 ml.) containing 2N-sulphuric acid (6 ml.). Iodide ion was titrated potentiometrically with 0.01391 N-silver nitrate by means of a glass and a silver
At the end-point the polarity of the electrodes reversed and a change in potential of approximately 200 mv. occurred.

Ancillary determinations showed that: (a) Hydrolysis of unreacted methyl iodide was negligible under the conditions of analysis. (b) The iodide ion titres of known amounts of the quaternary salt were the same in the presence and absence of methyl iodide. (c) The dilution completely quenched the reaction; titrations, one immediately after dilution and others at hourly intervals over four hours, agreed to 0.02 ml. (1%).

It was found, from runs conducted in the absence of amine, that a slow, pseudo first-order reaction, rate constant $6 \times 10^{-6} \text{ min.}^{-1}$, occurred between methyl iodide and the solvent. The quaternisation runs were corrected for iodide ion so liberated; the corrections were small: 1.2% of the titre for the homopolymer at 8 hours.

The rate of quaternisation of dimethylaniline was determined at the beginning and end of this piece of work. The second-order constants found were in good agreement.

Reaction between the solvent and methyl iodide.

The kinetic runs were carried out: (i) with the concentration of methyl iodide equal to that used in the kinetic experiments previously described; and (ii) with the methyl iodide concentration approximately one half of that value. The two sets of data were analysed for a possible first-order character by means of the equation:

$$k = \frac{1}{t} \ln \frac{b}{b-x}$$
Where $b$ is the initial concentration of the reactant (methyl iodide) and $x$ is the decrease in concentration of the reactant after the lapse of time $t$. The value of $x$ in this reaction is the value $q_e$ used in the calculation of the correction ($q$).
Results.

Table (13).

<table>
<thead>
<tr>
<th>Time hr.</th>
<th>( x ) mole.l.(^{-1} )</th>
<th>( \ln \frac{b}{b-x} )</th>
<th>( x ) mole.l.(^{-1} )</th>
<th>( \ln \frac{b}{b-x} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-</td>
<td>-</td>
<td>0.0003</td>
<td>0.0006</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>-</td>
<td>0.0004</td>
<td>0.0008</td>
</tr>
<tr>
<td>4</td>
<td>0.0006</td>
<td>0.0009</td>
<td>0.0007</td>
<td>0.0012</td>
</tr>
<tr>
<td>8</td>
<td>0.0010</td>
<td>0.0015</td>
<td>0.0010</td>
<td>0.0018</td>
</tr>
<tr>
<td>24</td>
<td>0.0025</td>
<td>0.0040</td>
<td>0.0024</td>
<td>0.0040</td>
</tr>
<tr>
<td>48</td>
<td>0.0046</td>
<td>0.0075</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>96</td>
<td>-</td>
<td>-</td>
<td>0.0093</td>
<td>0.0153</td>
</tr>
</tbody>
</table>

Table (14).

<table>
<thead>
<tr>
<th>Time hr.</th>
<th>( x ) mole.l.(^{-1} )</th>
<th>( \ln \frac{b}{b-x} )</th>
<th>( x ) mole.l.(^{-1} )</th>
<th>( \ln \frac{b}{b-x} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0002</td>
<td>0.0009</td>
<td>0.0002</td>
<td>0.0007</td>
</tr>
<tr>
<td>2</td>
<td>0.0003</td>
<td>0.0012</td>
<td>0.0003</td>
<td>0.0010</td>
</tr>
<tr>
<td>4</td>
<td>0.0005</td>
<td>0.0019</td>
<td>0.0004</td>
<td>0.0013</td>
</tr>
<tr>
<td>6</td>
<td>0.00055</td>
<td>0.0020</td>
<td>0.0055</td>
<td>0.0018</td>
</tr>
<tr>
<td>8</td>
<td>0.0006</td>
<td>0.0022</td>
<td>0.0006</td>
<td>0.0020</td>
</tr>
<tr>
<td>24</td>
<td>0.0014</td>
<td>0.0048</td>
<td>0.0014</td>
<td>0.0046</td>
</tr>
</tbody>
</table>
The first-order rate constants \((k \times 10^6 \text{ min}^{-1})\) are shown in Table (15) below:

<table>
<thead>
<tr>
<th>Run</th>
<th>(k \times 10^6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i)</td>
<td>5.8</td>
</tr>
<tr>
<td>(ii)</td>
<td>5.8</td>
</tr>
<tr>
<td>(iii)</td>
<td>6.2</td>
</tr>
<tr>
<td>(iv)</td>
<td>6.2</td>
</tr>
<tr>
<td>Average</td>
<td>6.0</td>
</tr>
</tbody>
</table>

Because of this secondary reaction it was thought necessary to apply a solvent correction to the results previously obtained for the quaternisation kinetics.

**Solvent correction.**

We must consider the kinetic study of a reaction between the substrate \(A\), (tertiary-amine), concentration \(a\) (mole.l.\(^{-1}\)) and reagent \(B\), (alkyl halide), concentration \(b\) (mole.l.\(^{-1}\)), where a side reaction occurs between \(B\) and the solvent.

Suppose that after time \(t\) (min.), \(x\) (mole.l.\(^{-1}\)) of \(A\) have reacted and \(q\) (mole.l.\(^{-1}\)) of \(B\) have been consumed by reaction with the solvent.

**Evaluation of \(q\) and \(x\).**

Where the reaction of \(B\) and solvent is first-order with respect to \(B\), then

\[
\frac{dq}{dt} = k'(\text{conc. of } B); \ q = k' \int (\text{conc. of } B) \ dt
\]

this could be solved by plotting (conc. of \(B\)) versus \(t\), determining the
area under the curve up to \( t \), and using the value so obtained together with \( k' \) determined in blank runs.

The ratio between \( q \), as above, and \( q_e \), the experimental value in the blank runs, is given by:

\[
\frac{q}{q_e} = \frac{\text{area under } (b-x) \text{ up to } t}{\text{area under } b \text{ up to } t}
\]

\( q \) is thus smaller than \( q_e \). It was found for this set of experimental data that the numerical difference between \( q \) and \( q_e \) was negligible, and \( q \) was equated directly to \( q_e \). \( q \) having been ascertained it was applied as follows: \( x + q \) was found directly by titration and hence deduction of \( q \) yielded \( x \).

**Form of integral equation.**

We have, where \( k_q \) is the accurate instantaneous second-order constant,

\[
\frac{dx}{dt} = k_q (a-x)(b-x-q)
\]

If \( q \) is neglected, we have:

\[
\frac{dx}{dt} = k(a-x)(b-x)
\]

At values of \( x \) near 0,8a (80% reaction) the deviation of \( k/k_q = (b-x-q)/(b-x) \), from unity for a typical homopolymer was approximately 1.3%. This is within experimental error and therefore \( k \) is considered to be a sufficiently accurate value of the second-order constant, and the integrated form of

\[
\frac{dx}{dt} = k(a-x)(b-x)
\]

i.e.

\[
kt = \frac{1}{(b-a)} \ln \frac{a(b-x)}{b(a-x)}
\]

was therefore used.
Correction table.

<table>
<thead>
<tr>
<th>Time hr.</th>
<th>q/mole.l.-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0003</td>
</tr>
<tr>
<td>2</td>
<td>0.0004</td>
</tr>
<tr>
<td>4</td>
<td>0.0006</td>
</tr>
<tr>
<td>8</td>
<td>0.0010</td>
</tr>
<tr>
<td>24</td>
<td>0.0025</td>
</tr>
</tbody>
</table>

Corrected quaternisation results.

The results were plotted as $\log_{10} \frac{a(b-x)}{b(a-x)}$ versus $t$ (min.), whereby the second-order rate constant ($k$) can be evaluated, $k = \frac{2.303}{b-a} \times$ slope of the graph (mole.l.\(^{-1}\) min.\(^{-1}\)).
1. Reaction between dimethylaniline and methyl iodide, Table (16).

<table>
<thead>
<tr>
<th>Time min.</th>
<th>( x ) mole.l.(^{-1} )</th>
<th>( \log_{10} \frac{a(b-x)}{b(a-x)} )</th>
<th>( x ) mole.l.(^{-1} )</th>
<th>( \log_{10} \frac{a(b-x)}{b(a-x)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a = 0.1360 ) mole.l.(^{-1} ) ( b = 0.2667 )</td>
<td>10</td>
<td>0.0037</td>
<td>0.0059</td>
<td>0.0030</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.0052</td>
<td>0.0084</td>
<td>0.0047</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.0065</td>
<td>0.0139</td>
<td>0.0084</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>0.0131</td>
<td>0.0221</td>
<td>0.0136</td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>0.0233</td>
<td>0.0420</td>
<td>0.0242</td>
</tr>
<tr>
<td></td>
<td>280</td>
<td>0.0416</td>
<td>0.0849</td>
<td>0.0420</td>
</tr>
<tr>
<td></td>
<td>8 hr.</td>
<td>0.0585</td>
<td>0.1367</td>
<td>0.0618</td>
</tr>
<tr>
<td></td>
<td>24 hr.</td>
<td>0.1021</td>
<td>0.3937</td>
<td>0.1071</td>
</tr>
</tbody>
</table>

The figure in brackets represents time.

<table>
<thead>
<tr>
<th>Time min.</th>
<th>( x ) mole.l.(^{-1} )</th>
<th>( \log_{10} \frac{a(b-x)}{b(a-x)} )</th>
<th>( x ) mole.l.(^{-1} )</th>
<th>( \log_{10} \frac{a(b-x)}{b(a-x)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a = 0.1360 ) mole.l.(^{-1} ) ( b = 0.2667 )</td>
<td>10</td>
<td>0.0037</td>
<td>0.0059</td>
<td>0.0030</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.0052</td>
<td>0.0084</td>
<td>0.0047</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.0065</td>
<td>0.0139</td>
<td>0.0084</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>0.0131</td>
<td>0.0221</td>
<td>0.0136</td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>0.0233</td>
<td>0.0420</td>
<td>0.0242</td>
</tr>
<tr>
<td></td>
<td>280</td>
<td>0.0416</td>
<td>0.0849</td>
<td>0.0420</td>
</tr>
<tr>
<td></td>
<td>8 hr.</td>
<td>0.0585</td>
<td>0.1367</td>
<td>0.0618</td>
</tr>
<tr>
<td></td>
<td>24 hr.</td>
<td>0.1021</td>
<td>0.3937</td>
<td>0.1071</td>
</tr>
</tbody>
</table>

The final solution in each run was straw coloured.

After 24 hours the reaction was 75% complete.
Graph (2)

Reaction between dimethylaniline and methyl iodide

\[
\log_{10} \frac{a(b-x)}{b(a-x)}
\]

Time (hr.)
2. Reaction between p-isopropylidimethylaniline and methyl iodide.

Table (17).

<table>
<thead>
<tr>
<th>Time</th>
<th>(x) mole.l.(^{-1})</th>
<th>(\log_{10} \frac{a(b-x)}{b(a-x)})</th>
<th>(x) mole.l.(^{-1})</th>
<th>(\log_{10} \frac{a(b-x)}{b(a-x)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.0072</td>
<td>0.0114</td>
<td>0.0079</td>
<td>0.0133</td>
</tr>
<tr>
<td>20</td>
<td>0.0140</td>
<td>0.0234</td>
<td>0.0195</td>
<td>0.0350</td>
</tr>
<tr>
<td>40</td>
<td>0.0214</td>
<td>0.0376</td>
<td>0.0217</td>
<td>0.0394</td>
</tr>
<tr>
<td>70</td>
<td>0.0336</td>
<td>0.0642</td>
<td>0.0337</td>
<td>0.0663</td>
</tr>
<tr>
<td>140</td>
<td>0.0558</td>
<td>0.1262</td>
<td>0.0568</td>
<td>0.1334</td>
</tr>
<tr>
<td>280</td>
<td>0.0840</td>
<td>0.8504</td>
<td>0.0835</td>
<td>0.2560</td>
</tr>
<tr>
<td>8 hr.</td>
<td>0.1055</td>
<td>0.4240</td>
<td>0.1041</td>
<td>0.4268</td>
</tr>
<tr>
<td>24 hr.</td>
<td>0.1303</td>
<td>1.0400</td>
<td>0.1294</td>
<td>1.1076</td>
</tr>
</tbody>
</table>

The figure in brackets represents time.

The final solution in each run was straw coloured.

After 24 hours the reaction was 95% complete.
Graph (3)

Reaction between p-isopropylaminilinamine and methyl iodide

\[
\log_{10} \frac{a(b-x)}{b(a-x)}
\]

- Graph (i)
- Graph (ii)

Time (hr.)

0.56  0.48  0.40  0.32  0.24  0.16  0.08  0.0
### 3. Reaction between homopolymer (I) and methyl iodide.

**Table (18).**

<table>
<thead>
<tr>
<th>Time min.</th>
<th>( x ) mole.1.(^{-1} )</th>
<th>( \log_{10} \frac{a(b-x)}{b(a-x)} )</th>
<th>( x ) mole.1.(^{-1} )</th>
<th>( \log_{10} \frac{a(b-x)}{b(a-x)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.0045</td>
<td>0.0076</td>
<td>0.0060</td>
<td>0.0097</td>
</tr>
<tr>
<td>20</td>
<td>0.0088</td>
<td>0.0150</td>
<td>0.0104</td>
<td>0.0173</td>
</tr>
<tr>
<td>40</td>
<td>0.0151</td>
<td>0.0269</td>
<td>0.0167</td>
<td>0.0288</td>
</tr>
<tr>
<td>70</td>
<td>0.0244</td>
<td>0.0458</td>
<td>0.0252</td>
<td>0.0461</td>
</tr>
<tr>
<td>140</td>
<td>0.0404</td>
<td>0.0854</td>
<td>0.0404</td>
<td>0.0824</td>
</tr>
<tr>
<td>280</td>
<td>0.0599</td>
<td>0.1487</td>
<td>0.0571</td>
<td>0.1333</td>
</tr>
<tr>
<td>8 hr.</td>
<td>0.0748</td>
<td>0.2152</td>
<td>0.0734</td>
<td>0.2003</td>
</tr>
<tr>
<td>24 hr.</td>
<td>0.1070</td>
<td>0.4859</td>
<td>0.1033</td>
<td>0.4193</td>
</tr>
</tbody>
</table>

The final solution in each run was straw coloured.

After 24 hours the reaction was 80% complete.
Graph (4) shows the reaction between homopolymer (I) and methyl iodide.

The graph plots the time (in hours) against the concentration of methyl iodide.

Key points:
- Time (hr.): 0, 1, 2, 3, 4, 5, 6, 7, 8
- Concentration: 0.28, 0.24, 0.20, 0.16, 0.12, 0.08, 0.04

The graph demonstrates a linear relationship between time and concentration, indicating the reaction's progress over time.
4. Reaction between homopolymer (II) and methyl iodide.

Table (19).

<table>
<thead>
<tr>
<th>Time</th>
<th>( x ) mole.l.(^{-1} )</th>
<th>( \log_{10} \frac{a(b-x)}{b(a-x)} )</th>
<th>( x ) mole.l.(^{-1} )</th>
<th>( \log_{10} \frac{a(b-x)}{b(a-x)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.0054</td>
<td>0.0092</td>
<td>0.0054</td>
<td>0.0086</td>
</tr>
<tr>
<td>20</td>
<td>0.0087</td>
<td>0.0151</td>
<td>0.0092</td>
<td>0.0149</td>
</tr>
<tr>
<td>40</td>
<td>0.0155</td>
<td>0.0281</td>
<td>0.0159</td>
<td>0.0271</td>
</tr>
<tr>
<td>70</td>
<td>0.0234</td>
<td>0.0447</td>
<td>0.0247</td>
<td>0.0444</td>
</tr>
<tr>
<td>140</td>
<td>0.0389</td>
<td>0.0829</td>
<td>0.0418</td>
<td>0.0843</td>
</tr>
<tr>
<td>280</td>
<td>0.0575</td>
<td>0.1428</td>
<td>0.0604</td>
<td>0.1413</td>
</tr>
<tr>
<td>8 hr.</td>
<td>0.0727</td>
<td>0.2034</td>
<td>0.0774</td>
<td>0.2128</td>
</tr>
<tr>
<td>24 hr.</td>
<td>0.1049</td>
<td>0.4743</td>
<td>0.1093</td>
<td>0.4622</td>
</tr>
</tbody>
</table>

The final solution in each run was straw coloured.

After 24 hours the reaction was 80% complete.
Graph (5)

Reaction between homopolymer (II) and methyl iodide

\[ \log_{10} \frac{a(b-x)}{b(a-x)} \]

Time (hr.)
5. Reaction between copolymer and methyl iodide.

Table (20).

<table>
<thead>
<tr>
<th>Time</th>
<th>( x ) mole l. (^{-1} )</th>
<th>( \log_{10} \frac{a(b-x)}{b(a-x)} )</th>
<th>( x ) mole l. (^{-1} )</th>
<th>( \log_{10} \frac{a(b-x)}{b(a-x)} )</th>
<th>( x ) mole l. (^{-1} )</th>
<th>( \log_{10} \frac{a(b-x)}{b(a-x)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.0048</td>
<td>0.0087</td>
<td>0.0074</td>
<td>0.0107</td>
<td>0.0054</td>
<td>0.0102</td>
</tr>
<tr>
<td>20</td>
<td>0.0053</td>
<td>0.0152</td>
<td>0.0116</td>
<td>0.0174</td>
<td>0.0090</td>
<td>0.0173</td>
</tr>
<tr>
<td>40</td>
<td>0.0155</td>
<td>0.0295</td>
<td>0.0186</td>
<td>0.0290</td>
<td>0.0162</td>
<td>0.0329</td>
</tr>
<tr>
<td>70</td>
<td>0.0234 (170)</td>
<td>0.0469</td>
<td>0.0273</td>
<td>0.0450</td>
<td>0.0273</td>
<td>0.0608</td>
</tr>
<tr>
<td>140</td>
<td>0.0454</td>
<td>0.1068</td>
<td>0.0455</td>
<td>0.0848</td>
<td>0.0412</td>
<td>0.0994</td>
</tr>
<tr>
<td>280</td>
<td>0.0596</td>
<td>0.1583</td>
<td>0.0693</td>
<td>0.1559</td>
<td>0.0618</td>
<td>0.1780</td>
</tr>
<tr>
<td>8 hr.</td>
<td>0.0773</td>
<td>0.2463</td>
<td>0.0893</td>
<td>0.2444</td>
<td>0.0810</td>
<td>0.2874</td>
</tr>
<tr>
<td>24 hr.</td>
<td>0.1069</td>
<td>0.5355</td>
<td>0.1191</td>
<td>0.4995</td>
<td>0.1065</td>
<td>0.5718</td>
</tr>
</tbody>
</table>

The figures in brackets represent time.

The final solution in each run was straw coloured.

After 24 hours the reaction was 85% complete.
Graph (6)

Reaction between copolymer and methyl iodide
Summary of kinetic results.

Reaction with methyl iodide in dimethylformamide at 0°.

Table (21).

<table>
<thead>
<tr>
<th>Amine</th>
<th>(k; 10^{-3}) mole(^{-1}) min(^{-1})</th>
<th>Individual runs</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethylaniline</td>
<td></td>
<td>(i) (ii) (iii) (iv)</td>
<td></td>
</tr>
<tr>
<td>p-isoPropyl-dimethylaniline</td>
<td></td>
<td>5.0 5.1 5.1 5.1</td>
<td>5.1</td>
</tr>
<tr>
<td>Poly(p-N,N-dimethylamino-styrene) (I)</td>
<td></td>
<td>15.4 15.4</td>
<td>15.4</td>
</tr>
<tr>
<td>(II)</td>
<td></td>
<td>10.4 10.4</td>
<td>10.4</td>
</tr>
<tr>
<td>2:1 Styrene-p-N,N-dimethylamino-styrene-Copolymer</td>
<td></td>
<td>10.6 10.5 10.6</td>
<td>10.6</td>
</tr>
</tbody>
</table>
SECTION 3.

Preparation and evaluation of poly(4-vinylpyridine).

Purification of 4-vinylpyridine.

4-Vinylpyridine was dried over potassium hydroxide pellets, filtered and redistilled under nitrogen at water-pump pressure. The fraction b. p. 64-64.8°/17 mm. was collected.

A gas-liquid chromatogram was carried out on the product, under the following conditions.

<table>
<thead>
<tr>
<th>Column</th>
<th>10% carbowax 1,000 on 109-125 celite.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp.</td>
<td>Flow Rate</td>
</tr>
<tr>
<td>125°</td>
<td>57 ml.min.(^{-1})</td>
</tr>
<tr>
<td>Voltage</td>
<td>Attenuation</td>
</tr>
<tr>
<td>1500</td>
<td>x 10</td>
</tr>
</tbody>
</table>

The trace showed three very small impurities which were found to be present in an amount less than 2%.

Preparation of poly(4-vinylpyridine).

\(\alpha,\alpha'\)-Azoisobutyronitrile (0.2045 g.) was added to 4-vinylpyridine (49.39 g.) representing approximately 0.4% of the initiator. The initiator was dissolved in the monomer and the polymerisation was carried out in a number of small soda glass test-tubes, sealed under nitrogen. The polymerisation took place over 24 hours at 70°. At this time the tubes were removed from the oven and broken open, revealing a polymer, which was still slightly mobile and had a strong smell of monomer.
Purification of poly(4-vinylpyridine).

Poly(4-vinylpyridine) dissolved in redistilled t-butanol (500 ml.) after being stirred for 3 days. The polymer solution was filtered and to this AnalaR benzene (1,000 ml.) was added slowly, with high speed mechanical stirring. A gelatinous precipitate formed, the supernatant liquor was decanted and the gel was washed with benzene (3 x 100 ml.), then dissolved in redistilled t-butanol (b. p. 82°; 160 ml.) and freeze-dried.

The freeze-dryer consisted of a desiccator (8") which was insulated by means of aluminium foil and cellulose wadding. A short piece of glass tubing attached to the lid connected the desiccator to a large cold finger (2 L.), which was filled with an acetone/drikold mixture. The cold finger was connected to another acetone/drikold trap which was in turn attached to the high vacuum pump.

The solution to be freeze-dried (40 ml.) was placed in a shallow flat dish and frozen solid by packing the dish in drikold for 2 hours. The desiccator plate was also chilled. The plate and dish were brushed free of drikold and put into the insulated desiccator, which was immediately exhausted. The freeze-drying was carried out for 8 hours at 0.05 mm. The solvent was collected on the cold-finger leaving the polymer in the form of a porous, friable cake. The polymer (17 g.) was cut up and dried to constant weight at 56°/0.2 mm.

Purification of n-butyl bromide.

n-Butyl bromide was dried over anhydrous sodium sulphate, filtered and redistilled. The fraction b. p. 101.7 - 102.0°, \( n_D^{25} 1.4373 \) was collected.

A gas-liquid chromatogram was carried out on the product under the following conditions.

<table>
<thead>
<tr>
<th>Column</th>
<th>10% carbowax 1,000 on 10-125 celite.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp.</td>
<td>Flow Rate</td>
</tr>
<tr>
<td>50°</td>
<td>30 ml. min.⁻¹</td>
</tr>
<tr>
<td></td>
<td>Cylinder Pressure</td>
</tr>
<tr>
<td></td>
<td>4 lbs.in.⁻²</td>
</tr>
<tr>
<td>Voltage</td>
<td>Attenuation</td>
</tr>
<tr>
<td>1250</td>
<td>x 10</td>
</tr>
<tr>
<td></td>
<td>Chart Speed</td>
</tr>
<tr>
<td></td>
<td>12 ins.hr.⁻¹</td>
</tr>
<tr>
<td>Sample Size</td>
<td>0.025 μl.</td>
</tr>
</tbody>
</table>

The trace showed only one peak and the n-butyl bromide was concluded to be a pure specimen.

Purification of sulpholane.

Sulpholane melts at 27° and it is quite hygroscopic. It was dried by distillation at 116°/2 mm., a forerun of 20% was rejected; the main fraction had \( n_D^{40} 1.4778 \).

A gas-liquid chromatogram was carried out on the product under the following conditions.
The trace showed only one peak and the sulpholane was concluded to be a pure specimen.

**Purification of dimethylformamide.**

Dimethylformamide was purified as in Section 1 p. 86. The fraction b. p. 42°/11 mm. n_D^{25} 1.4282 was collected and stored under nitrogen in a wash bottle. Nitrogen pressure was used to release the solvent when required.

**Purification of pyridine.**

AnalaR pyridine was dried over potassium hydroxide pellets, filtered and redistilled under nitrogen. The fraction b. p. 114°, n_D^{25} 1.5058 was collected.

A gas-liquid chromatogram was carried out on the product under the following conditions.
The trace showed only one peak and the pyridine was concluded to be a pure specimen.

**Preparation of N-n-butylpyridinium bromide**

N-n-butylpyridinium bromide was prepared by refluxing Analar pyridine (8 ml.) and n-butyl bromide (17.5 ml.) in 96% ethanol (10 ml.) for 15 hours. The solution was concentrated until precipitation started, crystallisation being complete after cooling in ice. The product was filtered and washed with dry acetone. It was recrystallised from dry acetone, and had m. p. 105-105.5°. The salt is extremely hygroscopic.

The pyridinium salt was dried for 2 hours at R.T./0.1 mm.

Found: Br, 37.16. Calc. for C$_{9}$H$_{14}$N Br: Br, 36.98%.

**Preparation of poly(N-n-butyl-4-vinylpyridinium bromide)**

The quaternary salt was prepared by heating together poly(4-vinylpyridine) (2.60 g.) and n-butyl bromide (21 g.) in redistilled nitromethane (b. p. 101°, n$_{D}^{25}$ 1.3799; 60 ml.) at 60° for 4 days.

The solution was removed from the oven, whereupon the polymeric salt began to precipitate. The nitromethane was removed by distillation at water-pump pressure, and the polymeric salt was dissolved in 96%...
ethanol (70 ml.). The solution was filtered and the polymer reprecipitated by dropwise addition of the solution to redistilled dioxan (b. p. 101°; 750 ml.) with high speed mechanical stirring.

The product was filtered, washed with dioxan (200 ml.) and dried for 2 hours at 56°/0.1 mm.

Found: Br, (i) 33.04, (ii) 33.12; Calc. for C\textsubscript{11}H\textsubscript{16}N Br:

Br, 33.03\%.
Determination of the limiting viscosity number of poly(4-vinylpyridine).

The viscosity determination was carried out at 25.00 ± 0.01°C using a U-tube viscometer B.S.188 No.1. The viscosity ratio of the polymer in 96% ethanol was found at four concentrations, as in Section 1 p.79. By extrapolation of the graph of $\frac{\ln \eta_r}{c}$ versus concentration, to zero concentration the limiting viscosity number was determined.

The polymer solutions were found to have a constant flow-time over 4 hours. The flow-time of the solvent was determined before and after the series of polymer solutions.

Table (22).

<table>
<thead>
<tr>
<th></th>
<th>$c$ (g/100 ml. sol.)</th>
<th>$t_{sol}$ (sec.)</th>
<th>$\frac{\ln \eta_r}{c}$</th>
<th>[\eta]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent</td>
<td>-</td>
<td>320.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Polymer</td>
<td>1.2585</td>
<td>811.8</td>
<td>0.741</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.8085</td>
<td>603.6</td>
<td>0.787</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6293</td>
<td>531.0</td>
<td>0.807</td>
<td>0.876</td>
</tr>
<tr>
<td></td>
<td>0.4043</td>
<td>447.2</td>
<td>0.832</td>
<td></td>
</tr>
<tr>
<td>Solvent</td>
<td>-</td>
<td>319.0</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Determination of the kinetics of the quaternisation of pyridine and poly(4-vinylpyridine) in dimethylformamide and sulpholane and of poly(4-vinylpyridine) in dimethylformamide-sulpholane mixtures by reaction with n-butyl bromide.

Rate-determination procedure.

The kinetic experiments were carried out at 75±0.01° in the chosen solvent. In other respects, conditions of reaction and analysis were kept the same as for the quaternisation of poly(p-N,N-dimethylaminostyrene); tertiary-amine (0.1360 equiv.) and alkyl halide (0.2720 equiv.) were used in each kinetic run. The polymeric tertiary-amine was dissolved the day before the kinetic run. The polarity of the electrodes changed during the titration of bromide ion, the change at the end-point being smaller than for iodide and was about 80 mv.

Ancillary determinations agreed with those of Section 2 p.89.

It was found, from runs conducted in the absence of amine, that a slow approximately first-order reaction, rate constant 8 x 10⁻⁵ min⁻¹ occurred between n-butyl bromide and dimethylformamide. There was no side reaction between the alkyl halide and sulpholane, for the dimethylformamide-sulpholane mixtures the reaction was found to be slower than for dimethylformamide.

The quaternisation reaction was corrected for the bromide ion so liberated; the corrections amounted to 10% of the titre for the polymer at 9 hours.

The rate of quaternisation of poly(4-vinylpyridine) in both dimethylformamide and sulpholane was determined at the beginning and end
of the series of kinetic runs. The second-order constants found were in good agreement. The kinetics of the reaction between n-butyl bromide and both pyridine and poly(4-vinylpyridine) in sulpholane were determined both with and without the addition of the product of the reaction.

The solvent mixtures were made up by weight, the two components were weighed into separate flasks, mixed by transferring one to the other and shaking. The mixtures were kept in stoppered flasks under nitrogen, no mixture was kept for longer than 4 days.

Reaction between dimethylformamide and dimethylformamide-sulpholane mixtures and n-butyl bromide.

For the reaction between dimethylformamide and n-butyl bromide the kinetic runs were carried out as for the solvent reaction between dimethylformamide and methyl iodide. The results were analysed for a possible pseudo first-order relationship, the symbols having the same significance as before, (the value x is the value q_e used in the calculation of the correction).

<table>
<thead>
<tr>
<th>Time hr.</th>
<th>(i) b = 0.1407 mole.l(^{-1})</th>
<th>(ii) b = 0.1405 mole.l(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(x) mole.l(^{-1})</td>
<td>(\ln \frac{b}{b-x})</td>
</tr>
<tr>
<td>1</td>
<td>0.0022</td>
<td>0.0157</td>
</tr>
<tr>
<td>2</td>
<td>0.0033</td>
<td>0.0237</td>
</tr>
<tr>
<td>4</td>
<td>0.0047</td>
<td>0.0341</td>
</tr>
<tr>
<td>6</td>
<td>0.0061</td>
<td>0.0445</td>
</tr>
<tr>
<td>8</td>
<td>0.0075</td>
<td>0.0548</td>
</tr>
<tr>
<td>9</td>
<td>0.0075</td>
<td>0.0548</td>
</tr>
</tbody>
</table>
The figures in brackets represent times.

Now \( k = \frac{1}{60} x \) (slope of plot of \( \ln \frac{b}{b-x} \) min.\(^{-1}\) versus t).

The first-order rate constants \((k \times 10^5 \text{ min.}^{-1})\) are shown in the table below.

This secondary reaction necessitated the application of a solvent correction to the quaternisation results. Solvent correction determinations were carried out for each solvent and solvent mixture.
Solvent correction.

This was made essentially as for poly(p-N,N-dimethylaminostyrene), Section 2 p.92, but as the numerical differences between $q_e$ and $q$ were here appreciable, $q$ was calculated from the graphs of decrease in halide concentration versus time for both the solvent blanks and for quaternisation runs using the expression,

$$
\frac{q}{q_e} = \frac{\text{area under } b-x \text{ up to } t}{\text{area under } b \text{ up to } t}
$$

From a plot of $q$ versus time, the correction ($q$) for the reaction times were evaluated.

Form of integral equation.

Now $\frac{dx}{dt} = k \frac{q(a-x)(b-x-q)}{q}$. 

If $q$ is neglected, we have $\frac{dx}{dt} = k(a-x)(b-x)$.

At values of $x$ near 0.8a the deviation of $\frac{k}{k_q}$ from unity was approximately 6% and at 0.5a approximately 3% for the polymer reaction in dimethylformamide. For the solvent mixtures it was less and for sulpholane nil. It was decided that $k$ is a sufficiently accurate value of the second-order constant, and the integrated form of the equation was used,

$$
kt = \frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)}
$$

The results were plotted as $\frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)}$ versus $t$ (min.) whereby the second-order rate constant $k$ can be evaluated from the slope.

Evaluation of $q$ from $q_e$ (specimen determination).

The relationship between $q$ and $q_e$, the experimental value in the blank runs, is given by:

$$
\frac{q}{q_e} = \frac{\text{area under } (b-x) \text{ up to } t}{\text{area under } b \text{ up to } t} \quad \text{(Section 2 p.93)}
$$
The ratios of the areas under the plots of the concentration of alkyl halide versus time for the quaternisation experiment and the solvent blank were calculated as follows:

For the purpose of this correction the \((b-x)\) quaternisation experiment curve can be approximated to a series of straight lines, as shown by the dotted lines in the diagram. As the decrease in concentration of the alkyl halide with time in the solvent blank is a constant, or very nearly so, the ratio of the areas under \(b\) and \(b-x\) up to time \(t\) can be represented by the ratio of their ordinates at time \(t/2\).

A specimen set of data for the evaluation of \(q\) from \(q_e\) is shown overleaf.
**Reaction between poly(4-vinylpyridine) and n-butyl bromide in dimethylformamide.**

Experiment (iii) Section 4 p. 124.

<table>
<thead>
<tr>
<th>Time min.</th>
<th>b-x mole. l.⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.2686</td>
</tr>
<tr>
<td>20</td>
<td>0.2646</td>
</tr>
<tr>
<td>40</td>
<td>0.2565</td>
</tr>
<tr>
<td>70</td>
<td>0.2463</td>
</tr>
<tr>
<td>140</td>
<td>0.2260</td>
</tr>
<tr>
<td>240</td>
<td>0.2047</td>
</tr>
<tr>
<td>360</td>
<td>0.1857</td>
</tr>
<tr>
<td>9 hr.</td>
<td>0.1658</td>
</tr>
</tbody>
</table>

b-x was plotted against t for the quaternisation of poly(4-vinylpyridine) and the reaction with the solvent and q evaluated as shown.
Reaction between dimethylformamide and n-butyl bromide at 75°C.

\[
\begin{array}{|c|c|c|c|c|c|}
\hline
\text{Time} & \text{I. } b = 0.2738 \text{ mole.l}^{-1} & \text{II. } b = 0.2735 \text{ mole.l}^{-1} & \text{Average } q \text{ mole.l}^{-1} \\
\text{min.} & (x) q_e \text{ mole.l}^{-1} & q \text{ molal}^{-1} & (x) q_e \text{ mole.l}^{-1} & q \text{ molal}^{-1} & \\
\hline
0 & 0.0009 & 0.0009 & 0.0010 & 0.0010 & 0.0010 \\
20 & 0.0018 & 0.0018 & 0.0018 & 0.0018 & 0.0018 \\
40 & 0.0024 & 0.0024 & 0.0025 & 0.0024 & 0.0024 \\
70 & 0.0034 & 0.0033 & 0.0034 & 0.0033 & 0.0033 \\
2 \text{hr.} & 0.0052 & 0.0047 & 0.0054 & 0.0048 & 0.0048 \\
3 \text{hr.} & 0.0065 & 0.0058 & 0.0067 & 0.0060 & 0.0059 \\
4 \text{hr.} & 0.0079 & 0.0069 & 0.0081 & 0.0070 & 0.0070 \\
6 \text{hr.} & 0.0102 & 0.0084 & 0.0103 & 0.0086 & 0.0085 \\
9 \text{hr.} & 0.0129 & 0.0101 & 0.0132 & 0.0103 & 0.0102 \\
\hline
\end{array}
\]

(x for the solvent reaction is synonymous with \(q_s\).)
From a plot of average $q$ versus time, the value of $q$ at the reaction times were determined.

<table>
<thead>
<tr>
<th>Reaction Time min.</th>
<th>$q$ mole. l. $^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.0014</td>
</tr>
<tr>
<td>20</td>
<td>0.0018</td>
</tr>
<tr>
<td>40</td>
<td>0.0024</td>
</tr>
<tr>
<td>70</td>
<td>0.0033</td>
</tr>
<tr>
<td>140</td>
<td>0.0051</td>
</tr>
<tr>
<td>240</td>
<td>0.0070</td>
</tr>
<tr>
<td>360</td>
<td>0.0085</td>
</tr>
<tr>
<td>9 hr.</td>
<td>0.0102</td>
</tr>
</tbody>
</table>

Hence the kinetic results can be corrected as shown in Section 2 p. 93 and the second-order rate constant determined.
Plot of alkyl halide concentration versus time

Graph (7)

Solvent (I) and (III)

Poly(4-vinylpyridine)

Alkyl halide conc.
(mole/l.)

Time (hr.)

0.3
0.2
0.1
1 2 3 4 5 6 7 8 9
Graph (8)

Plot of correction (q) versus time

Alkyl halide conc.
(mole/L)

Time (hr.)

0.010  0.008  0.006  0.004  0.002
1. Reaction between poly(4-vinylpyridine) and n-butyl bromide. Table (24).

**Solvent correction.**

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>(q_i) (mole.l(^{-1}))</th>
<th>(q_{ii}) (mole.l(^{-1}))</th>
</tr>
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<tbody>
<tr>
<td>10</td>
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<td>0.0015</td>
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<tr>
<td>20</td>
<td>0.0019</td>
<td>0.0019</td>
</tr>
<tr>
<td>40</td>
<td>0.0026</td>
<td>0.0024</td>
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<tr>
<td>70</td>
<td>0.0033</td>
<td>0.0031</td>
</tr>
<tr>
<td>140</td>
<td>0.0043</td>
<td>0.0041</td>
</tr>
<tr>
<td>240</td>
<td>0.0057</td>
<td>0.0055</td>
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<tr>
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<td>0.0073</td>
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<td>0.0086</td>
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**Corrected quaternisation results.**

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>(x) (mole.l(^{-1}))</th>
<th>(\frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)})</th>
<th>(x) (mole.l(^{-1}))</th>
<th>(\frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)})</th>
</tr>
</thead>
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<td>0.0033</td>
<td>0.0859</td>
<td>0.0040</td>
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<td>0.0075</td>
<td>0.1967</td>
<td>0.0073</td>
<td>0.2019</td>
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<td>0.0144</td>
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<td>0.0239</td>
<td>0.7323</td>
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<tr>
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<tr>
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<td>0.0633</td>
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Solvent correction table.

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>q(iii) and q(iv) (mole.l.(^{-1}))</th>
</tr>
</thead>
<tbody>
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<tr>
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<td>0.0018</td>
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<tr>
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<td>0.0051</td>
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<td>0.0070</td>
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<td>0.0085</td>
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</table>

Corrected quaternisation results.

<table>
<thead>
<tr>
<th>Time min.</th>
<th>x (mole.l.(^{-1}))</th>
<th>(\frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)})</th>
<th>(\frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.0043</td>
<td>0.1139</td>
<td>0.1212</td>
</tr>
<tr>
<td>20</td>
<td>0.0079</td>
<td>0.2159</td>
<td>0.2324</td>
</tr>
<tr>
<td>40</td>
<td>0.0154</td>
<td>0.4452</td>
<td>0.4461</td>
</tr>
<tr>
<td>70</td>
<td>0.0247</td>
<td>0.7600</td>
<td>0.7711</td>
</tr>
<tr>
<td>140</td>
<td>0.0432</td>
<td>1.511</td>
<td>1.503</td>
</tr>
<tr>
<td>240</td>
<td>0.0626</td>
<td>2.564</td>
<td>2.565</td>
</tr>
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<td>360</td>
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<td>3.859</td>
</tr>
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<td>0.0980</td>
<td>5.955</td>
<td>5.855</td>
</tr>
</tbody>
</table>

The final solution in each run was dark red.

After 9 hours the reaction was 72% complete.
Graph (9)

Quaternisation of poly(4-vinylpyridine) in dimethylformamide

\[ \frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)} \]
2. Reaction between pyridine and n-butyl bromide in dimethylformamide. Table (25).

Solvent correction.

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>q(i)(mole.1.⁻¹)</th>
<th>q(ii)(mole.1.⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.0015</td>
<td>0.0015</td>
</tr>
<tr>
<td>20</td>
<td>0.0019</td>
<td>0.0019</td>
</tr>
<tr>
<td>40</td>
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<td>0.0025</td>
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<td>0.0031</td>
<td>0.0031</td>
</tr>
<tr>
<td>100</td>
<td>0.0036</td>
<td>0.0038</td>
</tr>
<tr>
<td>150</td>
<td>0.0045</td>
<td>0.0046</td>
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<tr>
<td>300</td>
<td>0.0068</td>
<td>0.0070</td>
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<tr>
<td>9 hr.</td>
<td>0.0091</td>
<td>0.0094</td>
</tr>
</tbody>
</table>

Corrected quaternisation results.

(i) a = 0.1397 mole.1.⁻¹
b = 0.2752 mole.1.⁻¹

(ii) a = 0.1370 mole.1.⁻¹
b = 0.2811 mole.1.⁻¹

<table>
<thead>
<tr>
<th>Time min.</th>
<th>x mole.1.⁻¹</th>
<th>( \frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)} )</th>
<th>x mole.1.⁻¹</th>
<th>( \frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
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<td>0.0663</td>
<td>0.0023</td>
<td>0.0575</td>
</tr>
<tr>
<td>20</td>
<td>0.0050</td>
<td>0.1360</td>
<td>0.0048</td>
<td>0.1263</td>
</tr>
<tr>
<td>40</td>
<td>0.0101</td>
<td>0.2787</td>
<td>0.0100</td>
<td>0.2733</td>
</tr>
<tr>
<td>70</td>
<td>0.0170</td>
<td>0.4896</td>
<td>0.0170</td>
<td>0.4842</td>
</tr>
<tr>
<td>100</td>
<td>0.0239</td>
<td>0.7173</td>
<td>0.0238</td>
<td>0.7063</td>
</tr>
<tr>
<td>150</td>
<td>0.0334</td>
<td>1.064</td>
<td>0.0334</td>
<td>1.059</td>
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<tr>
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<td>2.092</td>
<td>0.0567</td>
<td>2.141</td>
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<tr>
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<td>0.0619</td>
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<td>0.0816</td>
<td>3.903</td>
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</table>

The final solution in each run was pale yellow.

After 9 hours the reaction was 60% complete.
Graph (10)

Quaternisation of pyridine in dimethylformamide

(i) \[ \frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)} \]

(ii)
3. Reaction between poly(4-vinylpyridine) and n-butyl bromide in sulpholane.

Table (26).

<table>
<thead>
<tr>
<th>Time min.</th>
<th>( x/\text{mole.}\text{l.}^{-1} )</th>
<th>( \frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)} )</th>
<th>( x/\text{mole.}\text{l.}^{-1} )</th>
<th>( \frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.0057</td>
<td>0.1515</td>
<td>0.0053</td>
<td>0.1458</td>
</tr>
<tr>
<td>10</td>
<td>0.0104</td>
<td>0.2847</td>
<td>0.0099</td>
<td>0.2783</td>
</tr>
<tr>
<td>20</td>
<td>0.0181</td>
<td>0.5250</td>
<td>0.0176</td>
<td>0.5145</td>
</tr>
<tr>
<td>30</td>
<td>0.0252</td>
<td>0.7654</td>
<td>0.0247</td>
<td>0.7543</td>
</tr>
<tr>
<td>40</td>
<td>0.0310</td>
<td>0.9792</td>
<td>0.0307</td>
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<tr>
<td>70</td>
<td>0.0456</td>
<td>1.598</td>
<td>0.0458</td>
<td>1.615</td>
</tr>
<tr>
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<td>0.0733</td>
<td>3.262</td>
<td>0.0712</td>
<td>3.106</td>
</tr>
<tr>
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<td>0.0960</td>
<td>5.554</td>
<td>0.0968</td>
<td>5.649</td>
</tr>
<tr>
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<td>0.1122</td>
<td>8.457</td>
<td>0.1120</td>
<td>8.354</td>
</tr>
</tbody>
</table>

The final solution in each run was green.

After 9 hours the reaction was 81\% complete.
Graph (II)

Quaternisation of poly(4-vinylpyridine) in sulpholane

\[ \frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)} \]
The polymer was dissolved in sulpholane (5 ml.) and kept at 75° for 3 days prior to the kinetic experiments.

<table>
<thead>
<tr>
<th>Time min.</th>
<th>(iii) ( x ) mole.( l )^{-1}</th>
<th>( \frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)} )</th>
<th>(iv) ( x ) mole.( l )^{-1}</th>
<th>( \frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)} )</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.1275</td>
<td>0.0050</td>
<td>0.1335</td>
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<td>0.0092</td>
<td>0.2531</td>
<td>0.0093</td>
<td>0.2585</td>
</tr>
<tr>
<td>20</td>
<td>0.0169</td>
<td>0.4898</td>
<td>0.0171</td>
<td>0.4979</td>
</tr>
<tr>
<td>30</td>
<td>0.0239</td>
<td>0.7281</td>
<td>0.0240</td>
<td>0.7350</td>
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<td>40</td>
<td>0.0299</td>
<td>0.9467</td>
<td>0.0298</td>
<td>0.9495</td>
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<td>0.0449</td>
<td>1.582</td>
<td>0.0448</td>
<td>1.590</td>
</tr>
<tr>
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<td>0.0717</td>
<td>3.180</td>
<td>0.0708</td>
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<tr>
<td>300</td>
<td>0.0958</td>
<td>5.613</td>
<td>0.0951</td>
<td>5.552</td>
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<tr>
<td>9 hr.</td>
<td>0.1114</td>
<td>8.424</td>
<td>0.1109</td>
<td>8.345</td>
</tr>
</tbody>
</table>

The final solution in each run was green.

After 9 hours the reaction was 81% complete.
Graph 12
Quaternisation of poly(4-vinylpyridine) in sulfolane

\[ \frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)} \]

Time (hr.)
4. Reaction between poly(4-vinylpyridine) and n-butyl bromide in sulpholane under Fuoss' conditions.

Poly(4-vinylpyridine) (0.0277 g.): n-butyl bromide (0.8252 g.)

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>(i) $a = 0.1066$ mole.l.$^{-1}$</th>
<th>$\frac{x}{b-a}$</th>
<th>$\ln \frac{a(b-x)}{b(a-x)}$</th>
<th>(ii) $a = 0.1055$ mole.l.$^{-1}$</th>
<th>$\frac{x}{b-a}$</th>
<th>$\ln \frac{a(b-x)}{b(a-x)}$</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.1418</td>
<td></td>
<td>0.0038</td>
<td>0.1604</td>
<td></td>
</tr>
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<td>0.2665</td>
<td></td>
<td>0.0069</td>
<td>0.2902</td>
<td></td>
</tr>
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<td>0.0123</td>
<td>0.5192</td>
<td></td>
<td>0.0126</td>
<td>0.5480</td>
<td></td>
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<td>0.7807</td>
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<td>0.0178</td>
<td>0.8058</td>
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<td>0.0220</td>
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<tr>
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<td>0.0530</td>
<td>3.260</td>
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<tr>
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<td>0.0735</td>
<td>5.982</td>
<td></td>
<td>0.0717</td>
<td>5.697</td>
<td></td>
</tr>
<tr>
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<td>0.0841</td>
<td>8.461</td>
<td></td>
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</tbody>
</table>

The final solution was green.

After 9 hours the reaction was 81% complete.
Graph (13)

Quaternisation of poly(4-vinylpyridine) in sulpholane - Fuoss' conditions

\[ \frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)} \]

Time (hr.)

(i)

(ii)
5. Reaction between pyridine and n-butyl bromide in sulpholane.

Table (28).

<table>
<thead>
<tr>
<th>Time min.</th>
<th>( x ) mole.( \text{L}^{-1} )</th>
<th>( \frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)} )</th>
<th>( x ) mole.( \text{L}^{-1} )</th>
<th>( \frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
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<td>0.2025</td>
<td>0.0072</td>
<td>0.1975</td>
</tr>
<tr>
<td>20</td>
<td>0.0142</td>
<td>0.4176</td>
<td>0.0145</td>
<td>0.4209</td>
</tr>
<tr>
<td>40</td>
<td>0.0267</td>
<td>0.8450</td>
<td>0.0271</td>
<td>0.8502</td>
</tr>
<tr>
<td>70</td>
<td>0.0427</td>
<td>1.511</td>
<td>0.0430</td>
<td>1.508</td>
</tr>
<tr>
<td>100</td>
<td>0.0553</td>
<td>2.160</td>
<td>0.0559</td>
<td>2.170</td>
</tr>
<tr>
<td>150</td>
<td>0.0719</td>
<td>3.264</td>
<td>0.0734</td>
<td>3.342</td>
</tr>
<tr>
<td>300</td>
<td>0.1034</td>
<td>6.981</td>
<td>0.1039</td>
<td>6.958</td>
</tr>
<tr>
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<td>0.1247</td>
<td>13.91</td>
<td>0.1228</td>
<td>12.47</td>
</tr>
</tbody>
</table>

The final solution in each run was pale yellow.

After 9 hours the reaction was 91% complete.
Graph (14)

Quaternisation of pyridine in sulpholane

\[ \frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)} \]

Time (hr.)
6. Reaction between poly(4-vinylpyridine) and n-butyl bromide in sulfolane in the presence of poly(N-n-butyl-4-vinylpyridinium) bromide.

The effective bromide content of the polymeric salt was determined under kinetic conditions: a solution of poly(4-vinylpyridine) (0.3572 g.) and the polymeric salt (0.8225 g.) was made up to 25 ml. in a graduated flask. Aliquots were removed and titrated potentiometrically for bromide ion.

The bromide ion concentration was found to be 0.1316 mole.\textsuperscript{-1}.

Table (29).

<table>
<thead>
<tr>
<th>Time min.</th>
<th>(\chi) mole.\textsuperscript{-1}</th>
<th>(\frac{1}{b-a}\ln\left(\frac{a(b-x)}{b(a-x)}\right))</th>
<th>(\chi) mole.\textsuperscript{-1}</th>
<th>(\frac{1}{b-a}\ln\left(\frac{a(b-x)}{b(a-x)}\right))</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.0039</td>
<td>0.1077</td>
<td>0.0037</td>
<td>0.0993</td>
</tr>
<tr>
<td>10</td>
<td>0.0085</td>
<td>0.2413</td>
<td>0.0083</td>
<td>0.2306</td>
</tr>
<tr>
<td>20</td>
<td>0.0169</td>
<td>0.5014</td>
<td>0.0168</td>
<td>0.4882</td>
</tr>
<tr>
<td>30</td>
<td>0.0241</td>
<td>0.7409</td>
<td>0.0239</td>
<td>0.7290</td>
</tr>
<tr>
<td>40</td>
<td>0.0305</td>
<td>0.9788</td>
<td>0.0305</td>
<td>0.9696</td>
</tr>
<tr>
<td>70</td>
<td>0.0465</td>
<td>1.670</td>
<td>0.0463</td>
<td>1.650</td>
</tr>
<tr>
<td>150</td>
<td>0.0738</td>
<td>3.355</td>
<td>0.0739</td>
<td>3.340</td>
</tr>
<tr>
<td>300</td>
<td>0.0978</td>
<td>5.888</td>
<td>0.0978</td>
<td>5.872</td>
</tr>
<tr>
<td>9 hr.</td>
<td>0.1120</td>
<td>8.519</td>
<td>0.1120</td>
<td>8.484</td>
</tr>
</tbody>
</table>

(i) \(a = 0.1378\) mole.\textsuperscript{-1}  
\(b = 0.2724\) mole.\textsuperscript{-1}  
Polymeric salt (0.8237 g.); corresponding to 0.1318 mole.\textsuperscript{-1} of bromide ion

(ii) \(a = 0.1375\) mole.\textsuperscript{-1}  
\(b = 0.2743\) mole.\textsuperscript{-1}  
Polymeric salt (0.8324 g.); corresponding to 0.1332 mole.\textsuperscript{-1} of bromide ion.
Graph (15)

Quaternisation of poly(4-vinylpyridine) in sulpholane in the presence of added polymeric salt

\[
\frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)}
\]
7. Reaction between pyridine and n-butyl bromide in sulpholane in the presence of N-n-butylpyridinium bromide.

The pyridinium salt (approx. 3.67 g.) was weighed out quickly, because of its very hygroscopic nature and dissolved in sulpholane (12 ml.). An aliquot (2 ml.) was taken and made up to 25 ml. with sulpholane in a graduated flask at 75°. Samples (2 ml.) were removed by syringe and titrated for bromide ion and hence the original salt solution (stock solution) was standardised. Aliquots of the stock solution (2 ml.) were used in each kinetic experiment.

The concentration of the stock solution was 0.1090 mole.l.\(^{-1}\).

### Table (30).

<table>
<thead>
<tr>
<th>Time min.</th>
<th>(x) molecule.l.(^{-1})</th>
<th>(\frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)})</th>
<th>(x) molecule.l.(^{-1})</th>
<th>(\frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.0086</td>
<td>0.2342</td>
<td>0.0072</td>
<td>0.1992</td>
</tr>
<tr>
<td>20</td>
<td>0.0154</td>
<td>0.4411</td>
<td>0.0146</td>
<td>0.4285</td>
</tr>
<tr>
<td>40</td>
<td>0.0296</td>
<td>0.9268</td>
<td>0.0274</td>
<td>0.8804</td>
</tr>
<tr>
<td>70</td>
<td>0.0462</td>
<td>1.626</td>
<td>0.0442</td>
<td>1.603</td>
</tr>
<tr>
<td>100</td>
<td>0.0588</td>
<td>2.288</td>
<td>0.0570</td>
<td>2.296</td>
</tr>
<tr>
<td>150</td>
<td>0.0755 (210)</td>
<td>3.422</td>
<td>0.0735</td>
<td>3.460</td>
</tr>
<tr>
<td>240</td>
<td>0.0900</td>
<td>4.787</td>
<td>0.0934</td>
<td>5.567</td>
</tr>
<tr>
<td>360</td>
<td>0.1120</td>
<td>8.249</td>
<td>0.1087</td>
<td>8.316</td>
</tr>
<tr>
<td>8 hr.</td>
<td>0.1217</td>
<td>11.14</td>
<td>0.1180</td>
<td>11.14</td>
</tr>
</tbody>
</table>

The figure in brackets represents time.
Graph (16)

Quaternisation of pyridine in sulpholane in the presence of N-n-butylpyridinium bromide

\[ \frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)} \]
Summary of kinetic results.

1. Reaction with n-butyl bromide in dimethylformamide at 75°.

Table (31).

<table>
<thead>
<tr>
<th>Amine</th>
<th>Individual runs</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(k; 10^{-3}1. mole^{-1} min^{-1})</td>
<td></td>
</tr>
<tr>
<td>Pyridine</td>
<td>(i) 7.2</td>
<td>7.2</td>
</tr>
<tr>
<td></td>
<td>(ii) 7.2</td>
<td></td>
</tr>
<tr>
<td>Poly(4-vinyl pyridine)</td>
<td>(iii) 10.7</td>
<td>10.7</td>
</tr>
<tr>
<td></td>
<td>(iv) 10.7</td>
<td></td>
</tr>
</tbody>
</table>

2. Reaction with n-butyl bromide in sulfolane at 75°.

Table (32).

<table>
<thead>
<tr>
<th>Amine</th>
<th>Individual runs</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(k; 10^{-3}1. mole^{-1} min^{-1})</td>
<td></td>
</tr>
<tr>
<td>Pyridine</td>
<td>(i) 21.9</td>
<td>21.9</td>
</tr>
<tr>
<td>(added pyridinium salt)</td>
<td>(ii) 23.1</td>
<td>23.0</td>
</tr>
<tr>
<td>Poly(4-vinyl pyridine)</td>
<td>(iii) 23.8</td>
<td>23.8</td>
</tr>
<tr>
<td>(added poly(pyridinium salt)</td>
<td>(iv) 25.0</td>
<td>25.0</td>
</tr>
<tr>
<td>Fuoss conditions</td>
<td></td>
<td>25.8</td>
</tr>
</tbody>
</table>
Reaction between poly(4-vinylpyridine) and n-butyl bromide in sulfolane - dimethylformamide mixtures.

(1) 80% sulfolane. Table (33).

<table>
<thead>
<tr>
<th>Solvent correction.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (min.)</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>10</td>
</tr>
<tr>
<td>20</td>
</tr>
<tr>
<td>30</td>
</tr>
<tr>
<td>40</td>
</tr>
<tr>
<td>70</td>
</tr>
<tr>
<td>150</td>
</tr>
<tr>
<td>300</td>
</tr>
<tr>
<td>9 hr.</td>
</tr>
</tbody>
</table>

Corrected quaternisation results.

<table>
<thead>
<tr>
<th>Time</th>
<th>( x ) mole.l(^{-1})</th>
<th>( \frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)} )</th>
<th>( \frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.0038</td>
<td>0.0572</td>
<td>0.0033</td>
</tr>
<tr>
<td>10</td>
<td>0.0072</td>
<td>0.2035</td>
<td>0.0065</td>
</tr>
<tr>
<td>20</td>
<td>0.0138</td>
<td>0.4037</td>
<td>0.0131</td>
</tr>
<tr>
<td>30</td>
<td>0.0202</td>
<td>0.6075</td>
<td>0.0195</td>
</tr>
<tr>
<td>40</td>
<td>0.0255</td>
<td>0.8005</td>
<td>0.0251</td>
</tr>
<tr>
<td>70</td>
<td>0.0395</td>
<td>1.361</td>
<td>0.0392</td>
</tr>
<tr>
<td>150</td>
<td>0.0661</td>
<td>2.804</td>
<td>0.0657</td>
</tr>
<tr>
<td>300</td>
<td>0.0919</td>
<td>5.190</td>
<td>0.0925</td>
</tr>
<tr>
<td>9 hr.</td>
<td>0.1102</td>
<td>8.285</td>
<td>0.1111</td>
</tr>
</tbody>
</table>

After 9 hours the reaction was 81% complete.
Graph (17)

Quaternisation of poly(4-vinylpyridine) in 80% sulphonane (i)

\[ \frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)} \] (ii)

Time (hr.)
(2) 60% sulpholane. Table (34).

Solvent correction.

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>$q_{(i)}$ and $q_{(ii)}$ (mole.l.$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.0009</td>
</tr>
<tr>
<td>10</td>
<td>0.0010</td>
</tr>
<tr>
<td>20</td>
<td>0.0014</td>
</tr>
<tr>
<td>30</td>
<td>0.0016</td>
</tr>
<tr>
<td>40</td>
<td>0.0018</td>
</tr>
<tr>
<td>70</td>
<td>0.0022</td>
</tr>
<tr>
<td>150</td>
<td>0.0031</td>
</tr>
<tr>
<td>300</td>
<td>0.0045</td>
</tr>
<tr>
<td>9 hr.</td>
<td>0.0064</td>
</tr>
</tbody>
</table>

Corrected quaternisation results.

(i) $a = 0.1367$ mole.l.$^{-1}$  
    $b = 0.2737$ mole.l.$^{-1}$

(ii) $a = 0.1368$ mole.l.$^{-1}$  
     $b = 0.2745$ mole.l.$^{-1}$

<table>
<thead>
<tr>
<th>Time</th>
<th>$x$ mole.l.$^{-1}$</th>
<th>$\frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)}$</th>
<th>$x$ mole.l.$^{-1}$</th>
<th>$\frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.0034</td>
<td>0.0891</td>
<td>0.0035</td>
<td>0.0937</td>
</tr>
<tr>
<td>10</td>
<td>0.0063</td>
<td>0.1732</td>
<td>0.0065</td>
<td>0.1789</td>
</tr>
<tr>
<td>20</td>
<td>0.0118</td>
<td>0.3346</td>
<td>0.0120</td>
<td>0.3411</td>
</tr>
<tr>
<td>30</td>
<td>0.0172</td>
<td>0.5043</td>
<td>0.0173</td>
<td>0.5066</td>
</tr>
<tr>
<td>40</td>
<td>0.0218</td>
<td>0.6591</td>
<td>0.0221</td>
<td>0.6705</td>
</tr>
<tr>
<td>70</td>
<td>0.0342</td>
<td>1.125</td>
<td>0.0346</td>
<td>1.140</td>
</tr>
<tr>
<td>150</td>
<td>0.0586</td>
<td>2.324</td>
<td>0.0591</td>
<td>2.346</td>
</tr>
<tr>
<td>300</td>
<td>0.0858</td>
<td>4.463</td>
<td>0.0861</td>
<td>4.478</td>
</tr>
<tr>
<td>9 hr.</td>
<td>0.1062</td>
<td>7.364</td>
<td>0.1063</td>
<td>7.341</td>
</tr>
</tbody>
</table>

After 9 hours the reaction was 79% complete.
Graph (18)

Quaternisation of poly(4-vinylpyridine) in 60% sulfolane

\[\frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)}\]

Time (hr.)
Table (35).

Solvent correction.

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>( q(i) ) and ( q(ii) ) (mole.l.(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.0011</td>
</tr>
<tr>
<td>10</td>
<td>0.0013</td>
</tr>
<tr>
<td>20</td>
<td>0.0017</td>
</tr>
<tr>
<td>30</td>
<td>0.0019</td>
</tr>
<tr>
<td>40</td>
<td>0.0022</td>
</tr>
<tr>
<td>70</td>
<td>0.0030</td>
</tr>
<tr>
<td>150</td>
<td>0.0047</td>
</tr>
<tr>
<td>300</td>
<td>0.0067</td>
</tr>
<tr>
<td>9 hr.</td>
<td>0.0088</td>
</tr>
</tbody>
</table>

Corrected quaternisation results.

<table>
<thead>
<tr>
<th>Time min.</th>
<th>( x ) mole.l.(^{-1})</th>
<th>( \frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)} )</th>
<th>( x ) mole.l.(^{-1})</th>
<th>( \frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.0032</td>
<td>0.0843</td>
<td>0.0031</td>
<td>0.0854</td>
</tr>
<tr>
<td>10</td>
<td>0.0058</td>
<td>0.1585</td>
<td>0.0057</td>
<td>0.1590</td>
</tr>
<tr>
<td>20</td>
<td>0.0107</td>
<td>0.3018</td>
<td>0.0106</td>
<td>0.3013</td>
</tr>
<tr>
<td>30</td>
<td>0.0154</td>
<td>0.4468</td>
<td>0.0152</td>
<td>0.4435</td>
</tr>
<tr>
<td>40</td>
<td>0.0195</td>
<td>0.5801</td>
<td>0.0195</td>
<td>0.5825</td>
</tr>
<tr>
<td>70</td>
<td>0.0309</td>
<td>0.9915</td>
<td>0.0308</td>
<td>0.9942</td>
</tr>
<tr>
<td>150</td>
<td>0.0531</td>
<td>2.008</td>
<td>0.0536</td>
<td>2.040</td>
</tr>
<tr>
<td>300</td>
<td>0.0808</td>
<td>3.961</td>
<td>0.0810</td>
<td>3.989</td>
</tr>
<tr>
<td>9 hr.</td>
<td>0.1039</td>
<td>6.902</td>
<td>0.1042</td>
<td>6.984</td>
</tr>
</tbody>
</table>

After 9 hours the reaction was 76% complete.
Graph (19)

Quaternisation of poly(4-vinylpyridine) in 40% sulpholane

\[ \frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)} \]

(i)  

(ii)  

Time (hr.)
Solvent correction.

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>( q(i) ) and ( q(ii) ) (mole.l.(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.0013</td>
</tr>
<tr>
<td>10</td>
<td>0.0016</td>
</tr>
<tr>
<td>20</td>
<td>0.0021</td>
</tr>
<tr>
<td>30</td>
<td>0.0024</td>
</tr>
<tr>
<td>40</td>
<td>0.0028</td>
</tr>
<tr>
<td>70</td>
<td>0.0038</td>
</tr>
<tr>
<td>150</td>
<td>0.0057</td>
</tr>
<tr>
<td>300</td>
<td>0.0084</td>
</tr>
<tr>
<td>9 hr.</td>
<td>0.0115</td>
</tr>
</tbody>
</table>

Corrected quaternisation results.

<table>
<thead>
<tr>
<th>Time min.</th>
<th>( x ) mole.l.(^{-1})</th>
<th>( \frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)} )</th>
<th>( x ) mole.l.(^{-1})</th>
<th>( \frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.0026</td>
<td>0.0743</td>
<td>0.0027</td>
<td>0.0729</td>
</tr>
<tr>
<td>10</td>
<td>0.0047</td>
<td>0.1316</td>
<td>0.0049</td>
<td>0.1357</td>
</tr>
<tr>
<td>20</td>
<td>0.0089</td>
<td>0.2548</td>
<td>0.0090</td>
<td>0.2544</td>
</tr>
<tr>
<td>30</td>
<td>0.0129</td>
<td>0.3779</td>
<td>0.0130</td>
<td>0.3765</td>
</tr>
<tr>
<td>40</td>
<td>0.0168</td>
<td>0.4997</td>
<td>0.0168</td>
<td>0.4969</td>
</tr>
<tr>
<td>70</td>
<td>0.0260</td>
<td>0.8202</td>
<td>0.0260</td>
<td>0.8156</td>
</tr>
<tr>
<td>150</td>
<td>0.0481</td>
<td>1.772</td>
<td>0.0483</td>
<td>1.775</td>
</tr>
<tr>
<td>300</td>
<td>0.0752</td>
<td>3.526</td>
<td>0.0753</td>
<td>3.523</td>
</tr>
<tr>
<td>9 hr.</td>
<td>0.0990</td>
<td>6.207</td>
<td>0.0991</td>
<td>6.200</td>
</tr>
</tbody>
</table>

After 9 hours the reaction was 72% complete.
Graph (20)

Quaternisation of poly(4-vinylpyridine) in 20% sulpholane

\[
\frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)}
\]
Summary of kinetic results.

Reaction between poly(4-vinylpyridine) and n-butyl bromide in sulfolane - dimethylformamide mixtures.

Table (37).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( k \times 10^{-3} \text{ mole}^{-1} \text{ min}^{-1} ) (Individual runs)</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(i)</td>
<td>(ii)</td>
</tr>
<tr>
<td>80% sulfolane</td>
<td>20.2</td>
<td>20.0</td>
</tr>
<tr>
<td>60% sulfolane</td>
<td>16.6</td>
<td>16.5</td>
</tr>
<tr>
<td>40% sulfolane</td>
<td>14.2</td>
<td>14.2</td>
</tr>
<tr>
<td>20% sulfolane</td>
<td>12.2</td>
<td>12.1</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION
Section (1).

$p$-N,N-Dimethylaminostyrene was synthesised by a known route from $p$-N,N-dimethylaminobenzaldehyde according to Marvel and his co-workers. However, their method of decomposition was not followed and the $p$-N,N-dimethylamino-$\alpha$-methylbenzyl alcohol was isolated prior to dehydration. The yields obtained compare favourably with those of Selegny.

Conversion of the alcohol into the corresponding styrene is somewhat troublesome, in that dehydration is not facile and the monomer readily polymerises. The best yield of $p$-N,N-dimethylaminostyrene (60%) was obtained when the freshly-prepared alcohol (8 g.) was distilled at 5 mm., as previously outlined on pages 74 and 75. Various elaborations gave smaller yields; pyrolyses on the same scale and at the same pressure with: (i) the addition of iodine, powdered potassium hydroxide or syrupy phosphoric acid yielded no monomer; (ii) alcohol which had been stored in a screw-capped bottle for two months gave only a 30% yield of the required monomer.

A flash distillation procedure recommended by Wiley and Schmitt was used without success. This consisted of dropping the molten alcohol into an evacuated flask kept in an oil-bath at 150°. A mixture of alcohol and monomer came over and was collected; this was found on redistillation to be predominantly alcohol. Pyrolyses were also attempted by dropping the molten alcohol through a heated column under reduced pressure; the temperature of the column was kept between 150 and 300°, in various experiments. A small amount of monomer was collected but much dark, seemingly polymeric, material remained on the column.
Reverting to the method actually used in the preparation of the monomer, the overall yield of monomer (25%) compared favourably with those of Strassburg and his co-workers\textsuperscript{149} who used a similar method of dehydration. Wiley and Schmitt\textsuperscript{148} state that 50% yields of the monomer were consistently obtained using the flash distillation method for the dehydration stage. Marvel and his co-workers quote a 45% yield of the monomer but add a note saying that on several occasions a much lower yield of monomer was obtained.

The polymerisation of \( p-N, N\)-dimethylaminostyrene has been reported by Marvel and his co-workers who heated the monomer (1 g.) in a small tube at 120° for 24 hours. At the end of this time a hard resin, completely soluble in benzene, had formed. Wiley and Schmitt\textsuperscript{148} prepared variable capacity anion exchange resins from quaternised \( p-N, N\)-dimethylaminostyrene - styrene bead copolymers. In the present work polymerisation was successfully initiated with \( \alpha, \alpha'\)-azoisobutyronitrile at 71.5 ± 1°; two specimens of poly(\( p-N, N\)-dimethylaminostyrene) containing 0.4% and 1% of the initiator and a styrene - \( p-N, N\)-dimethylaminostyrene (2:1) copolymer containing 0.6% of the initiator were prepared. The products were light-green, hard and brittle rods, which after solution in benzene and reprecipitation into isopropanol yielded fibrous white solids.

The logarithmic viscosity-numbers \((1/c)\ln(\eta_{\text{solv}}/\eta_{\text{solv.}})\) were determined for solutions of each homopolymer and the copolymer in toluene at 25.0° at \( c=1.2, 0.8, 0.6 \) and 0.4 g. of solute per 100 ml. of solution; extrapolation yielded the limiting intrinsic viscosity \([\eta]\). The flow-times of the solutions of the copolymer did not alter with time;
those of the homopolymers fell over 3 days by up to 6% and then remained constant. It seemed that the configuration of the polymer in solution changed over this time gradually reaching some constant arrangement. The final values were used in the calculation of the logarithmic viscosity numbers. Homopolymers (I) and (II) and the copolymer have respectively $[\eta] 0.338, 0.450$ and 0.565.

The limiting intrinsic-viscosity is related to the viscosity-average molecular weight by the equation,

$$[\eta] = KM^\gamma$$

which indicates a higher molecular weight for the homopolymer having the lower initiator concentration, as would be expected (p.16) where we have that the kinetic chain length (which is directly related to the average molecular weight) is inversely proportional to the square root of the initiator concentration.

The above equation has not been evaluated for poly($\text{p-N,N-dimethylamino}$ styrene). In order to obtain numerical values permitting a comparison of molecular weights, the equation for solutions of poly(styrene) in toluene, for which Green$^{150}$ has determined the values $K = 1.16 \times 10^{-4}$ and $\gamma = 0.72$ has been applied to the limiting intrinsic-viscosities of the two homopolymers and the copolymer of $\text{p-N,N-dimethylaminostyrene}$. This leads to the values given below:

<table>
<thead>
<tr>
<th></th>
<th>m. w.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Homopolymer (I)</td>
<td>65,000</td>
</tr>
<tr>
<td>(II)</td>
<td>97,000</td>
</tr>
<tr>
<td>Copolymer</td>
<td>130,000</td>
</tr>
</tbody>
</table>
**P-Isopropylidimethylaniline** was prepared by the method of Sachs and Sachs. This consisted of reacting AnalAR \( p,N,N \)-dimethylaminobenzaldehyde with a 4 fold excess of methylmagnesium iodide. The ether was removed and the Grignard complex so formed was heated with the excess methyl magnesium iodide. The residue was decomposed, made alkaline and ether extracted. The product was distilled under nitrogen at reduced pressure after removal of the ether. It was twice redistilled and had b.p. 110°/8 mm., \( n_D^{25} 1.5304 \).

The purification of dimethylformamide by a variety of methods has been evaluated by Thomas and Rochow and it was according to their findings that this was carried out. It was stated by the above authors that dimethylformamide is difficult to purify; important impurities include water, alcohol, primary and secondary amines. It is known to decompose slightly at its normal boiling-point to give small amounts of dimethylaniline and carbon monoxide and if acidic or basic materials are present this decomposition is catalysed. There is also evidence for an addition compound DMF\( \cdot \)H\( _2 \)O which may be present in appreciable concentrations at room temperature. A chemical method was thus used to remove water from dimethylformamide and one that did not cause decomposition. Dimethylformamide was mixed with 10% benzene and the benzene was removed together with the benzene-water azetropde by distillation at atmospheric pressure. The solvent was then distilled under nitrogen at reduced pressure and stored under nitrogen in a flask the orifices of which were normally stoppered.
Section (2).

Exploratory experiments showed that the homopolymers and copolymer, both before and after quaternisation, were soluble, together with methyl iodide, in dimethylformamide at 0°C, and that reaction proceeded at convenient rates under these conditions, which were accordingly adopted.

Order and rates of quaternisation.

Representative examples of runs of dimethylaniline, p-isopropyl(dimethylaniline), and two poly(p-N,N-dimethylaminostyrene)s, and the 2:1 styrene-p-N,N-dimethylaminostyrene copolymer are shown in the Experimental Section. The logarithmic plots for dimethylaniline and p-isopropyl(dimethylaniline) are linear, and the second-order constants (k) recorded in the Table hold throughout the run. The plots for the homopolymers and copolymer are substantially linear for the first 20-25% of reaction, and then become concave towards the abcissa. The values of k given in Table (39) are derived from straight lines drawn through these first sections. The rate constants are considered to be those for the dimethylamino groups attached to the macromolecules, before the incidence of a perturbing factor, due to the accumulation of ammonium ions on the chain, has become appreciable.

The values of k for homopolymer (I), m.w. 65,000, homopolymer (II) m.w. 97,000, and the copolymer, m.w. 130,000, are nearly equal. Change in molecular weight and in the spacing of amino-groups by the insertion of inert units has thus little effect on the initial second-order constant,
for which the average value is $10.5 \times 10^{-3}$ mole$^{-1}$ min$^{-1}$. This rate, and that for $p$-isopropyldimethylaniline are respectively about twice and three times that for dimethylaniline. The results imply that quaternisation is promoted by inductive electron release towards the amino-group, and that the release from the main chain of the polymers is some fraction of that from an isopropyl group.

**Reaction with methyl iodide in dimethylformamide at $0^\circ$. Table (39).**

<table>
<thead>
<tr>
<th>Amine</th>
<th>$k \times 10^{-3}$ (mole$^{-1}$ min$^{-1}$)</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethylaniline</td>
<td>5.0 5.1 5.1 5.1</td>
<td>5.1</td>
</tr>
<tr>
<td>$p$-isoPropyl-dimethylaniline</td>
<td>15.4 15.4</td>
<td>15.4</td>
</tr>
<tr>
<td>Poly($p$-N,N-dimethyl aminostyrene (I))</td>
<td>10.4 10.4</td>
<td>10.4</td>
</tr>
<tr>
<td>(II)</td>
<td>10.6 10.4</td>
<td>10.5</td>
</tr>
<tr>
<td>2:1 Styrene-$p$-N,N-dimethylaminostyrene copolymer</td>
<td>10.6 10.5 10.6</td>
<td>10.6</td>
</tr>
</tbody>
</table>

The reaction between alkyl halides and dimethylformamide has been studied at room temperature by Kornblum and Blackwood$^{151}$. The reactions take place at a significant rate and were followed by the titration of the halide ion produced. From a solution of dimethylformamide and $t$-butyl bromide, isobutylene was isolated, since however methyl iodide and benzyl bromide liberate halide ion it is apparent that there is a
second process, nucleophilic displacement to form a salt, possibly,

\[
\begin{array}{c}
0 \quad \text{CH}_3 \\
\| \\
\text{H-C} - N - \text{CH}_3 \\
\| \\
R \\
\end{array}
\]

The reaction between methyl iodide and dimethylformamide at 25° was found by Kornblum and Blackwood to follow first-order kinetics with 10% reaction occurring in 12 days. In the present work, the reaction between methyl iodide and dimethylformamide at 0° has been found to be of the first-order in methyl iodide, and to have a pseudo first-order constant. The method by which the kinetic measurements were corrected for this side-reaction is set out in the Experimental part.

It is useful to consider the poly(styrene) main chain, the structure outside the square brackets in Fig. 2, as a substituent in the phenyl side-group and to treat it by Hammett's sigma-rho procedure.

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

Fig. 2.

It is one of the fundamental and most familiar assumptions of the science of organic chemistry that like substances react similarly and that similar changes in structure produce similar changes in reactivity. The application of this, however, requires great judgment because complications
arise from the presence of both kinetic- and potential-energy terms in the equations that determine equilibrium and rate of reaction. When attention is restricted to examples in which rate and equilibrium are determined by potential energies alone (side-group reactions of \( m \)- and \( p \)-substituted benzene derivatives) a quantitative relationship appears when two series of rate or equilibrium constants are compared, the two series differing with respect to the nature of the reacting group, and the change which it undergoes during the reaction.

The members of each series are identical in these respects but differ in the sense of a series of substituents in the \( m \)- or \( p \)-position relative to the reacting group. For example one series may be the dissociation constants of \( m \)- or \( p \)-substituted benzoic acids (e.g. \( p \)-methoxybenzoic acid), and another the rate constants for the hydrolysis of similarly substituted benzoic esters (e.g. \( p \)-methoxybenzoate). When the logarithms of the constants of one series are plotted against the logarithms of the constants of the other it was found that the points were on a straight line which obeys an equation of the form,

\[
\log k_h = \rho \log K_i + A \quad \text{...... (1)}
\]

in which \( k_h \) is the rate constant of the hydrolysis, \( K_i \) the dissociation constant, \( \rho \) the slope and \( A \) the intercept.

Similar linear relationships of greater or less precision have been found to apply to the rate and the equilibrium constants of practically all side-group reactions of benzene derivatives\(^{116-119}\). When two series of constants are both linearly related to a third, then
they are related to each other in the same way, the slope of the last relationship being the ratio of the slopes of the first two. Consequently, it is possible to relate the various series to one reference standard, for which the dissociation constants of substituted benzoic acids are especially suitable because of many accurate values now available.

Equation (1) may be simplified by conversion to the form

\[
\log k = \rho (\log K_i - \log K_i^0) + (A + \rho \log K_i^0) \quad \ldots (2)
\]

in which \( k \) is any rate or equilibrium constant and \( K^0 \) is the dissociation constant of unsubstituted benzoic acid. The quantity \( (A + \rho \log K_i^0) \) is necessarily equal to \( \log k^0 \) where \( k^0 \) is the rate or equilibrium constant for unsubstituted reactant; substitution of the definition

\[
\sigma = \log K_i - \log K_i^0 \quad \ldots (3)
\]

converts equation (2) to the form

\[
\log k - \log k^0 = \rho \sigma \quad \ldots (4)
\]

The substituent constant \( \sigma \) is by definition determined by the nature of the substituent and independent of the reaction, the constant \( k \) of which is involved in equation (4).

The reaction constant \( \rho \) is by the nature of the linear relationship a constant for all substituents and depends only on the reaction series.

For all substituents for which an accurate value of the dissociation constant of the corresponding substituted benzoic acid is available, the
value of \( \sigma \) is immediately given by the definition (3).

In the quaternisation of poly(\( p \)-N,N-dimethylanaminostyrene) all the reacting groups (A) are in the situation of the central group (Fig.2) at the beginning of the reaction. Increasingly thereafter, they may be flanked by phenyl bearing the group which is the product of the reaction.

For a substituent \( X \) in the phenyl group, the sigma constant is given by:

\[
\sigma_x = \log K_{\text{C}_6\text{H}_4X} - \log K_{\text{C}_6\text{H}_5}
\]

(5)

where \( K_{\text{C}_6\text{H}_4X} \) and \( K_{\text{C}_6\text{H}_5} \) are respectively the dissociation constant of the substituted and unsubstituted benzoic acid, in water at \( 25^\circ \). The dissociation-behaviour of poly(styrene-4-carboxylic acid) has not been recorded. However, insertion of the dissociation constants for \( p \)-isopropylbenzoic and benzoic acids\(^{153} \) in (5) yields \( \sigma_1 = -0.154 \).

(This value has been derived by the use of the best value for the dissociation constant of benzoic acid as assessed by Kortum, Vogel and Andrusow\(^{153} \) and differs slightly from Hammett's value = 0.151.)

Dissociation constant for benzoic acid in water at \( 25^\circ = 6.320 \times 10^{-5} \).

Dissociation constant for \( p \)-isopropylbenzoic acid

\[
\text{in water at } 25^\circ = 4.43 \times 10^{-5}.
\]

Further where \( \rho \) is the constant for the reaction of dimethylanilines with methyl iodide in dimethylformamide at \( 0^\circ \), \( \sigma_p \) that for the \( \sigma \)-constant for the poly(styrene) chain as a \( p \)-substituent and \( k_{\text{H}}, k_i \) and \( k_p \) are respectively the average values of the rate-constants of Table (39) for dimethylaniline, \( p \)-isopropyldimethylaniline and the
poly(p-N,N-dimethylaminostyrene)s, we have:

\[
\log k_i - \log k_H = \rho \sigma_i \quad \text{and} \quad \log k_p - \log k_H = \rho \sigma_p \quad (6)
\]

on insertion of the values above for \( \sigma_i, k_H, k_i \) and \( k_p \), there are found,

\[
\rho = -3.11 \quad \text{and} \quad \sigma_p = -0.101
\]

The last value is, rigorously, that for the main chain of \text{poly}(p-N,N-dimethylaminostyrene) considered as a \( p \)-substituent. However, the initial rates for the copolymer and homopolymers are almost identical, whence replacement of two-thirds of the dimethylamino groups by hydrogen in the polymeric substituent of Fig.2 does not appreciably alter \( \sigma_p \).

It is inferred that the value found is substantially that for the main chain bearing phenyl groups on the carbon atoms \( \beta \) and \( \delta \) to the point of attachment to the side-group under consideration. Provided that further examples confirm the above value for \( \sigma_p \), then, in a reaction of a \( p \)-substituted poly(styrene), observation of a value for \( \sigma_p \) markedly different from the normal would point to the intervention of a macromolecular factor, such as a polyelectrolyte effect or a specific secondary structure in the transition state.
Deceleration during quaternisation.

During the progress of the kinetic runs of the homopolymers and copolymer, the second-order rate constant alters little during the first part of the reaction, but thereafter falls. In graph (21) are shown the initial rates, forming the horizontal part of the plots, and the instantaneous second-order constants derived from the slopes of the second-order plots of the kinetic runs at the times when 30, 40 and 50% quaternisation had occurred. The points are the average values from the runs of each polymer. The results are shown in the Table below.

Instantaneous rate-constant versus percentage reaction.

Table (40).

<table>
<thead>
<tr>
<th>Percentage reaction</th>
<th>$k \times 10^{-3} \text{ l.mole}^{-1} \text{ min}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Homopolymer (I)</td>
</tr>
<tr>
<td>10</td>
<td>10.4</td>
</tr>
<tr>
<td>20</td>
<td>10.4</td>
</tr>
<tr>
<td>30</td>
<td>9.3</td>
</tr>
<tr>
<td>40</td>
<td>6.8</td>
</tr>
<tr>
<td>50</td>
<td>6.0</td>
</tr>
</tbody>
</table>

The rate-constants for the homopolymers are seen to fall to about 60% of the initial value when 50% quaternisation has taken place. The form of the plots indicates that the rate of deceleration with increasing quaternisation is diminishing when 50% quaternisation has been attained.
The rate-constant for the copolymer falls to about 75% of the initial value when 50% quaternisation has occurred.

The plots of $k$ versus percentage quaternisation are nearly identical for the two homopolymers, whence it is concluded that change in molecular weight, within the range above, does not appreciably affect the course of deceleration. In the copolymer, the charges are separated by distances measured along the chain, which average three times those between charges on the homopolymer at the same percentage quaternisation. This difference is associated with a less-marked, though still considerable, deceleration during the growth of a charged envelope.

A similar fall in rate has been observed by Coleman and Fuoss for the quaternisation of poly(4-vinylpyridine) by n-butyl bromide in sulfolane. It is suggested by Fuoss and his co-worker that this might be an inductive effect, wherein the positive charge on a quaternised pyridine nitrogen makes the lone pair of electrons on an adjacent pyridine group less available for reaction with alkyl halide, but inductive effects usually are considerably weakened by the interposition of even a single methylene group between charged site and reaction site. The charge on an $N^+$ might orient an approaching dipolar molecule of butyl bromide into an unfavourable position for reaction with a neighbour, or possibly the field of a nearby $N^+$ can stabilise the $N\text{ Bu}\text{ Br}$ complex in its transition state, so that decomposition into $N^+$Bu + Br$^-$ becomes less probable. Finally, the intense field of a quaternised nitrogen might increase the density of the highly polar solvent in its neighbourhood by electrostriction,
and thereby make access to the region by alkyl halide more difficult.

It is concluded, with respect to the population of dimethylaniline groups attached to the polyvinyl main chain, that quaternisation is at first essentially similar to that of dimethylaniline and p-isopropyl dimethylaniline. Electron release from the main chain is somewhat less than that from the p-isopropyl group and is expressible by the value \( \psi_p = -0.101 \). Neither change in molecular weight of the polymer, nor spacing by means of inert styrene units affect the initial rate appreciably. The accumulation of positive charge on the macromolecule as the quaternary ammonium groups are formed causes a fall in reaction rate in both homopolymers and copolymer. The effect is more marked in the homopolymers, which possess the greater charge-density at a given degree of quaternisation.
Graph (21)

Plot of instantaneous rate constants of the poly(p-N,N-dimethylaminostyrene)s versus percentage reaction

Instantaneous rate constant
\[ k \text{ (l.mole}^{-1}\text{min}^{-1}) \times 10^3 \]

Percentage reaction
Poly(4-vinylpyridine) was successfully prepared by initiation with \( \alpha,\alpha'-\)azoisobutyronitrile (0.4%) at 70°. The polymerisation took place over 24 hours in sealed tubes under nitrogen. After this time the polymer tubes were removed and broken open revealing a polymer which was still slightly mobile and had a strong smell of monomer. The polymer was purified by freeze-drying\(^{145}\) and was isolated in the form of a porous, friable cake.

The logarithmic viscosity-numbers \((1/c) \ln (\eta_{\text{sol,n}}/\eta_{\text{sol,v}})\) were determined for solutions of the homopolymer in 96% ethanol at 25.0° at \(c = 1.2, 0.8, 0.6\) and 0.4 g. of solute per 100 ml. of solution; extrapolation yielded the limiting intrinsic viscosity \([\eta]\).

The molecular weight was calculated from the limiting intrinsic viscosity by the use of the equation\(^{154}\),

\[
[\eta] = 2.5 \times 10^{-4} \ M^{0.68}
\]

and yielded a value of 164,000.

Fuoss and his co-workers\(^{129}\) found that the rate of quaternisation of poly(4-vinylpyridine) by \(n\)-butyl bromide in sulpholane was substantially independent of molecular weight and this was also found to be so for the quaternisation of poly(p-N,N-dimethylaminostyrene) by methyl iodide in dimethylformamide (Experimental Section 2.). It was therefore not thought necessary to prepare homopolymers of different molecular weight for this present work.
Poly(N-n-butyl-4-vinylpyridinium bromide) was prepared according to Fuoss and Cathers \(^{146}\) by heating together the alkyl halide and poly(4-vinylpyridine) in nitromethane, though rather more drastic conditions were used. The analyses demonstrated that the reaction had proceeded to completion (Fuoss et. al. obtained 95% reaction). Both poly(N-n-butyl-4-vinylpyridinium bromide) and N-n-butylpyridinium bromide are extremely hygroscopic.
SECTION 4.

The kinetics of the quaternisation by reaction with n-butyl bromide at 75° of pyridine and poly(4-vinylpyridine) in dimethylformamide and in sulpholane and of poly(4-vinylpyridine) in dimethylformamide-sulpholane mixtures have been studied. The quaternisation reactions between pyridine and poly(4-vinylpyridine) and n-butyl bromide in sulpholane have also been carried out with the addition of the product of the reaction. The results are shown in the Experimental Section.

The plots of the integral second-order expression against time for the quaternisation of pyridine in both solvents and for the quaternisation of poly(4-vinylpyridine) in dimethylformamide are linear, and the second-order constants \( k \) recorded in the Table hold throughout the runs. The plots for the quaternisation of the polymer in sulpholane are linear for the first 10-15% of the reaction and then become concave towards the abcissa. In the solvent mixtures the initial rate constant is lowered, and deceleration begins at approximately the same percentage reaction but is not so marked as in sulpholane. The deceleration gradually lessens until in dimethylformamide there is no deviation from the second-order kinetic equation. Addition of dimethylformamide to sulpholane therefore causes a decrease in the initial second-order constant and a lessening of the deceleration effect.

As in the quaternisation of poly(p-N,N-dimethylaminostyrene)s the values of \( k \) given in Table (41) are derived from straight lines drawn through these first sections. These rate constants are considered to
be those for the pyridinium group attached to the macromolecule before
the incidence of some perturbing factor has become appreciable.

A slow reaction between n-butyl bromide and dimethylformamide was
observed in the present work. Kornblum and Blackwood¹⁵¹ have observed
a similar slow reaction with 1-bromo-octane. Correction for the
consumption of n-butyl bromide in this side-reaction was made by the
method detailed in the Experimental Section.

**Table (41).**

1. Reaction with n-butyl bromide in dimethylformamide at 75°.

<table>
<thead>
<tr>
<th>Amine</th>
<th>Individual runs</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(k; 10⁻³ l.mole.⁻¹ min.⁻¹)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(i) (ii) (iii) (iv)</td>
<td></td>
</tr>
<tr>
<td>Pyridine</td>
<td>7.2 7.2</td>
<td>7.2</td>
</tr>
<tr>
<td>Poly(4-vinyl pyridine)</td>
<td>10.7 10.8 10.7 10.7</td>
<td>10.7</td>
</tr>
</tbody>
</table>

2. Reaction between poly(4-vinylpyridine) and n-butyl bromide in
sulpholane-dimethylformamide mixtures.

<table>
<thead>
<tr>
<th>Solvent (percentage by weight)</th>
<th>Individual runs</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(k; 10⁻³ l.mole.⁻¹ min.⁻¹)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(i) (ii)</td>
<td></td>
</tr>
<tr>
<td>80% sulpholane</td>
<td>20.2 20.0</td>
<td>20.1</td>
</tr>
<tr>
<td>60% sulpholane</td>
<td>16.6 16.5</td>
<td>16.6</td>
</tr>
<tr>
<td>40% sulpholane</td>
<td>14.2 14.2</td>
<td>14.2</td>
</tr>
<tr>
<td>20% sulpholane</td>
<td>12.2 12.1</td>
<td>12.2</td>
</tr>
</tbody>
</table>
3. Reaction with n-butyl bromide in sulpholane at 75°.

<table>
<thead>
<tr>
<th>Amine</th>
<th>(10^{-3}) mole(^{-1}) min(^{-1})</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyridine</td>
<td>21.9, 21.9</td>
<td>21.9</td>
</tr>
<tr>
<td>Pyridine + pyridinium salt</td>
<td>22.9, 23.1</td>
<td>23.0</td>
</tr>
<tr>
<td>Poly(4-vinylpyridine)</td>
<td>24.0, 23.8, 23.8, 23.8</td>
<td>23.8</td>
</tr>
<tr>
<td>Poly(4-vinylpyridine) + poly(pyridinium salt)</td>
<td>25.0, 25.0</td>
<td>25.0</td>
</tr>
<tr>
<td>Poly(4-vinylpyridine) - Fuoss' conditions</td>
<td>25.7, 25.8</td>
<td>25.8</td>
</tr>
</tbody>
</table>

The initial rate constants found for the quaternisation of poly(4-vinylpyridine) and pyridine by n-butyl bromide in sulpholane are close to those of Coleman and Fuoss\(^{123}\), as shown in the table below.

Table (42).

<table>
<thead>
<tr>
<th>Amine</th>
<th>(10^{-3}) mole(^{-1}) min(^{-1})</th>
<th>Present work</th>
<th>Coleman and Fuoss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyridine</td>
<td>21.9</td>
<td>22.4</td>
<td></td>
</tr>
<tr>
<td>Poly(4-vinylpyridine)</td>
<td>25.8, 26.0</td>
<td>25.8</td>
<td>26.0</td>
</tr>
<tr>
<td>Poly(4-vinylpyridine) [(c = 0.3752) g./25 ml. sol.]</td>
<td>23.8</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

1 The nearest of the concentrations employed by Fuoss to that of the present work.

2 Concentration of the present work.
The results obtained for the two polymer concentrations indicate that the rate of quaternisation of poly(4-vinylpyridine) by n-butyl bromide in sulpholane at 75° is somewhat dependent on polymer concentration.

The addition of the quaternary salt to the reaction mixture in both the quaternisation of pyridine and poly(4-vinylpyridine) in sulpholane increased the initial rate by 5%.

Rate of quaternisation in solvents of different dielectric constant.

The initial second-order rate constants for the quaternisation of pyridine, 21.9 x 10⁻³ l.mole⁻¹ min⁻¹ and poly(4-vinylpyridine), 23.8 x 10⁻³ l.mole⁻¹ min⁻¹, by n-butyl bromide in sulpholane at 75° are higher than those for the corresponding reactions of pyridine, 7.2 x 10⁻³ l.mole⁻¹ min⁻¹, and poly(4-vinylpyridine), 10.7 x 10⁻³ l.mole⁻¹ min⁻¹, in dimethylformamide. Menschutkin⁷³ (p.53) and subsequent workers¹⁵⁵ have found that the quaternisation reaction goes faster the higher the dielectric constant of the solvent. The above results obtained in sulpholane and in dimethylformamide are in accord with the published dielectric constants for the two solvents - sulpholane (42.0 at 50°)¹²³ and dimethylformamide (36.7 at 25°)¹⁵⁶.

Menschutkin placed the solvents in the rate series,

\[
\text{MeOH} \succ \text{EtOH} \succ \text{Me}_2\text{CO} \succ \text{C}_6\text{H}_6 \succ \text{C}_6\text{H}_{14}
\]

for the reaction between triethylamine and ethyl iodide at 100°.
Table (45).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dielectric constant at 25°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>32.6</td>
</tr>
<tr>
<td>Ethanol</td>
<td>24.3</td>
</tr>
<tr>
<td>Acetone</td>
<td>20.7</td>
</tr>
<tr>
<td>Benzene</td>
<td>2.3</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>1.9</td>
</tr>
</tbody>
</table>

It is not always possible to say whether solvent influence is governed by van der Waal's or electrostatic forces, the former being governed by the internal pressure of the system and the latter by the dielectric constant. Kirkwood, neglecting non-electrostatic forces, derived an expression relating rate constant to the dielectric constant of the solvent and dipole moment of the species involved in the reaction. Where the transition state complex is more polar than the reactants an increase in dielectric constant is usually found to give a corresponding increase in rate. Solvent influence has also been correlated with the internal pressure of the system, increase in this factor increasing the rate, and so it is clear that these non-electrostatic forces play an important part in rate determination and cannot be neglected.

For many solvents these factors vary in approximately the same manner; polar solvents have high internal pressures and high dielectric constants; hence such media favour reactions in which the transition state is more polar than the reactants, of which the Menschutkin reaction is one.
Deceleration during quaternisation.

During the progress of the quaternisation of poly(4-vinylpyridine) in sulphonolane and in dimethylformamide-sulphonolane mixtures, the second-order rate constant alters little during the first part of the reaction (10-15%) but thereafter falls. There is no deceleration for the quaternisation reaction in dimethylformamide and the deviation decreases as the percentage of dimethylformamide in solvent mixtures is increased. In graph (22) there are shown the initial rates, forming the horizontal part (dotted lines) and the instantaneous second-order constants derived using the equation, \( \frac{dx}{dt} = k(a-x)(b-x) \) and substituting the values of \( \frac{dx}{dt}, (a-x) \) and \( (b-x) \) when 10-70% quaternisation has occurred. \( \frac{dx}{dt} \) is determined by taking the slopes of a plot of \( x \) versus \( t \) at times for 10-70% reaction. The results are shown in the table below.

**Table (44).**

<table>
<thead>
<tr>
<th>Percentage Reaction</th>
<th>100</th>
<th>80</th>
<th>60</th>
<th>40</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>23.5</td>
<td>19.2</td>
<td>15.9</td>
<td>13.8</td>
<td>12.1</td>
</tr>
<tr>
<td>20</td>
<td>21.2</td>
<td>18.5</td>
<td>15.8</td>
<td>13.7</td>
<td>12.0</td>
</tr>
<tr>
<td>30</td>
<td>20.8</td>
<td>18.1</td>
<td>15.7</td>
<td>13.5</td>
<td>12.0</td>
</tr>
<tr>
<td>40</td>
<td>20.3</td>
<td>18.1</td>
<td>15.7</td>
<td>13.4</td>
<td>12.0</td>
</tr>
<tr>
<td>50</td>
<td>19.5</td>
<td>17.4</td>
<td>15.4</td>
<td>13.4</td>
<td>12.0</td>
</tr>
<tr>
<td>60</td>
<td>18.0</td>
<td>16.1</td>
<td>15.1</td>
<td>13.3</td>
<td>11.8</td>
</tr>
<tr>
<td>70</td>
<td>15.0</td>
<td>15.4</td>
<td>14.5</td>
<td>13.3</td>
<td>11.9</td>
</tr>
</tbody>
</table>
The rate constant for the quaternisation of poly(4-vinylpyridine) in sulpholane is seen to fall to about 50% of its initial value when 70% reaction has taken place. The form of the plot indicates that the rate of deceleration with increasing quaternisation is still increasing when 70% quaternisation has been attained. The deceleration for the reaction in the solvent mixtures is not so marked and the trend is towards a constant second-order quaternisation rate as found for the reaction in dimethylformamide.

Fuoss and his co-workers\textsuperscript{129} put forward a semi-empirical solution for the deceleration found in the quaternisation of poly(4-vinylpyridine) by n-butyl bromide. The solution makes use of the idea of three rate constants ($k_0$, $k_1$, and $k_2$) describing the three categories of unquaternised nitrogen (p.62). $k_1$ was then postulated to be a mixture of $k_0$ and $k_2$ and the following expression was proposed to describe mathematically the required shift in rate control from $k_0$ to $k_2$ as $t$ increases,

$$\frac{dx}{(a-x)(b-x)} = \left[ k_0 e^{-\alpha t} + k_2 \left(1 - e^{-\alpha t}\right) \right] dt \quad \ldots \quad (1)$$

which integrates to,

$$f(x)/t = \frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)/t} = k_2 + \frac{(k_0 - k_2)(1 - e^{-\alpha t})}{\alpha t}$$

The constant ($\alpha$) was determined by plotting $f(x)/t$ against $(1 - e^{-\alpha t})/\alpha t$, trial values of $\alpha$ being used. If as Fuoss suggests the final rate constant ($k_2$) takes control at approximately 50% quaternisation,
then $\alpha$ must be of the order of $1/t^{1/2}$ the reciprocal of the time for half quaternisation. The value of $\alpha$ which yields a straight line is used in the determination of $k_0$ and $k_2$.

The determination of $\alpha$ was carried out using the results which were obtained for the quaternisation of poly(4-vinylpyridine) in this present work [run (i) p.128].

<table>
<thead>
<tr>
<th>Percentage reaction</th>
<th>$f(x)/t \times 10^2$</th>
<th>$(1-e^{-\alpha t})/\alpha t$ when $\alpha = 3.10^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>2.80</td>
<td>0.976</td>
</tr>
<tr>
<td>20</td>
<td>2.54</td>
<td>0.950</td>
</tr>
<tr>
<td>30</td>
<td>2.35</td>
<td>0.915</td>
</tr>
<tr>
<td>40</td>
<td>2.25</td>
<td>0.873</td>
</tr>
<tr>
<td>50</td>
<td>2.18</td>
<td>0.825</td>
</tr>
<tr>
<td>60</td>
<td>2.07</td>
<td>0.778</td>
</tr>
<tr>
<td>70</td>
<td>1.85</td>
<td>0.660</td>
</tr>
</tbody>
</table>

When $\alpha = 3.10^{-3}$ a linear plot was obtained for the values at 30, 40, 50, 60 and 70\% reaction. The values at 10 and 20\% reaction did not however lie on this straight line. The intercept at $t = 0$ yielded a value of $k_2 = 2 \times 10^{-3}$ l.mole.\(^{-1}\)min.\(^{-1}\). This value cannot however be justified experimentally.

The equation was further tested in the manner outlined below,

$$\frac{dx/dt}{(a-x)(b-x)} = k_0 e^{-\alpha t} + k_2 (1-e^{-\alpha t}). \quad ....... (1)$$
There are two unknowns in equation (1) and hence by taking the experimental values at two different reaction times the expression can be solved for and $k_2$.

At time $t$, \( \frac{dx}{dt} \) will be given the value $B$ and at time $t'$ \( \frac{dx}{dt} \left( \frac{a-x}{(a-x)(b-x)} \right) \) will be given the value $C$. $dx/dt$ was determined by taking the slope of the $x$ versus $t$ plot at times $t$ and $t'$.

Therefore we have,

\[ B = k_0 e^{-\alpha t} + k_2 (1 - e^{-\alpha t}) \] \hspace{1cm} \text{(2)}

\[ C = k_0 e^{-\alpha t'} + k_2 (1 - e^{-\alpha t'}) \] \hspace{1cm} \text{(3)}

Eliminating $k_2$ from (2) and (3)

\[ k_2 = \frac{B - k_0 e^{-\alpha t}}{(1 - e^{-\alpha t})} = \frac{C - k_0 e^{-\alpha t'}}{(1 - e^{-\alpha t'})} \] \hspace{1cm} \text{(4)}

Therefore

\[ B - C = e^{-\alpha t} (k_0 - C) - e^{-\alpha t'} (k_0 - B) \] \hspace{1cm} \text{(5)}

Which can be simplified by putting

\[ B - C = L \]
\[ k_0 - C = M \]
\[ k_0 - B = N \]

We have therefore,

\[ L = Me^{-\alpha t} + Ne^{-\alpha t'} \] \hspace{1cm} \text{(6)}

By inserting trial values of $\alpha$, and plotting $L$ against $Me^{-\alpha t} + Ne^{-\alpha t'}$, the value of $\alpha$ can be found for which $L = Me^{-\alpha t} + Ne^{-\alpha t'}$, $k_2$ can then be determined.
The plot of \( \frac{dx}{dt} \) versus \( k_0 e^{-\alpha t} + k_2 (1-e^{-\alpha t}) \) should equate at the two reaction times (percentage reaction) selected and also at any other reaction time if this semi-empirical solution is satisfied.

Equation (6) was solved for values at 30% and 60% quaternisation for the reaction between poly(4-vinylpyridine) and n-butyl bromide in sulpholane at 75° in runs (i) and (ii) p.128.

Table 46.

<table>
<thead>
<tr>
<th>dx/dt</th>
<th>(a-x)(b-x)</th>
<th>1.mole.(^{-1})min.(^{-1})</th>
<th>t(min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run (i)</td>
<td>Run (ii)</td>
<td>Run (i)</td>
<td>Run (ii)</td>
</tr>
<tr>
<td>20.7 x 10(^{-3})</td>
<td>20.6 x 10(^{-3})</td>
<td>18.0 x 10(^{-3})</td>
<td>18.2 x 10(^{-3})</td>
</tr>
<tr>
<td>60</td>
<td>61</td>
<td>192</td>
<td>204</td>
</tr>
</tbody>
</table>

\( \alpha \) was calculated from the above data using the initial rate constant for the reaction which had values of 24.0 x 10\(^{-3}\)1.mole.\(^{-1}\)min.\(^{-1}\) and 23.8 x 10\(^{-3}\)1.mole.\(^{-1}\)min.\(^{-1}\) respectively.

<table>
<thead>
<tr>
<th>Run (i)</th>
<th>Run (ii)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha ) = 0.0110</td>
<td>( \alpha ) = 0.0122</td>
</tr>
</tbody>
</table>

On substitution of \( \alpha \) into equation (2), there are found for runs (i) and (ii) \( k_2 = 17.2 x 10^{-3} \)1.mole.\(^{-1}\)min.\(^{-1}\) and 17.7 x 10\(^{-3}\)1.mole.\(^{-1}\)min.\(^{-1}\). These values found for \( k_2 \) are higher than the instantaneous rate constants found experimentally for 70% quaternisation in both runs.

The expression \( k_0 e^{-\alpha t} + k_2 (1-e^{-\alpha t}) \) can now be calculated at 10-70% quaternisation. The values found for the Fuoss expression and
for \( \frac{dx}{dt} \) are shown in Table (47). \( \frac{dx}{dt} \) was plotted against \( k_0 e^{-\alpha t} + k_2(1-e^{-\alpha t}) \) to test the validity of this semi-empirical solution and the result is shown in graph (23).

Table (47).

<table>
<thead>
<tr>
<th>( \frac{dx}{dt} ) (i) ( 10^{-3}; \text{ mole.}^{-1}\text{ min.}^{-1} )</th>
<th>( k_0 e^{-\alpha t} + k_2(1-e^{-\alpha t}) )</th>
<th>( \frac{dx}{dt} ) (ii) ( 10^{-3}; \text{ mole.}^{-1}\text{ min.}^{-1} )</th>
<th>( k_0 e^{-\alpha t} + k_2(1-e^{-\alpha t}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>23.6</td>
<td>22.9</td>
<td>23.6</td>
<td>22.8</td>
</tr>
<tr>
<td>21.1</td>
<td>21.8</td>
<td>21.1</td>
<td>21.7</td>
</tr>
<tr>
<td>20.7</td>
<td>20.7</td>
<td>20.6</td>
<td>20.6</td>
</tr>
<tr>
<td>20.4</td>
<td>19.6</td>
<td>20.3</td>
<td>19.6</td>
</tr>
<tr>
<td>19.5</td>
<td>18.8</td>
<td>19.6</td>
<td>18.8</td>
</tr>
<tr>
<td>18.0</td>
<td>18.0</td>
<td>18.2</td>
<td>18.2</td>
</tr>
<tr>
<td>14.5</td>
<td>17.4</td>
<td>15.9</td>
<td>17.9</td>
</tr>
</tbody>
</table>

If the Fuoss expression holds \( \frac{dx}{dt} = k_0 e^{-\alpha t} + k_2(1-e^{-\alpha t}) \) and the graph should be a straight line. The only values which fall on the expected straight line (dotted line) are those values at 30\% and 60\% quaternisation which have been used to determine \( \alpha \). The sigmoid character of the curve indicates that the semi-empirical expression of Fuoss does not fit the experimentally determined results.

It is considered that a better approach to this problem might be given by Arend's\textsuperscript{137} recent three rate-constant equation. A theoretical approach has been made to chemical reactions which are carried out on a polymer chain \( \text{e.g.} \) the hydrolysis of poly(vinyl acetate) to give
Graph (23)

Quaternisation of poly(l-vinylpyridine) in sulpholane
- run (i) solid circles
- run (ii) open circles

\[ \frac{k_0 e^{-\alpha t} + k_2 (1-e^{-\alpha t})}{10^{-3}; \text{mol}^{-1} \text{min}^{-1}} \]
poly(vinyl alcohol) or the quaternisation of poly(4-vinylpyridine) with the realisation that the rate of reaction at a given site may depend on whether or not the adjacent site has reacted.

The assumptions were made that three rate constants are sufficient to characterise the kinetics of the polymer chain. In the same way as Fuoss and his co-workers\textsuperscript{129} the constants $k_1$, $k_2$ and $k_3$ were designated as the reaction rate constants associated with a reactive site flanked (1) by two unreacted sites, (2) by one reacted and one unreacted site and (3) by two reacted sites. Further assumptions are that no reverse reaction takes place and that the reaction is carried out in the presence of a large excess of reactant (pseudo first-order kinetics), any change in concentration of the small molecule being neglected.

A sequence of reacted and unreacted sites can be visualised and if one of these sites is picked at random then the probability of picking a reacted site is just the fraction of sites which have reacted ($f$). Conversely the probability of picking an unreacted site is just (1$-f$). Within the framework there are the sequences,

\begin{align*}
-0-0-0-  ,  & -0-0-X- \\
-X-0-0- ,  & -X-0-X-
\end{align*}

Where 0 represents an unreacted site and X a reacted one. Since no 'handedness' can be ascribed to the reactive sites,

\begin{align*}
-X-0-0-  \text{ is equal to }  & -0-0-X-
\end{align*}

Each sequence is assigned a probability on the basis that the centre site was picked in the random choice.
In the derivation a set of probabilities were defined around these representative sequences and from these were derived the kinetic statements of reaction, the degree of conversion as a function of the rate constants and time.

When a functional group reaction involves a small molecule as a co-reactant the concentration of this second species will usually also influence the reaction velocity. If it is present in a swamping excess it can be incorporated into the rate constants \( k_1, k_2 \) and \( k_3 \) as a common constant factor, if not the expression would involve second-order kinetics and contain another variable. The use of a computer is essential for solution of Arend's equation, and this is not practicable within the scope of this Thesis. It is not, therefore, possible to give a mathematical 'fitting' equation at the present time, and the question whether or not it would be possible to give exact physical expression to the values of the second and third constants must be left unanswered.
Processes leading to deceleration.

The following has been established before. Reaction of poly(4-vinylpyridine) with n-butyl bromide at 75° proceeds at an instantaneous second-order rate, which is related to the percentage reaction as shown in Graph 22: in sulpholane, after an initial period, there is considerable deceleration; this is progressively less so in dimethylformamide-sulpholane mixtures increasingly rich in the former, and there is no deceleration in dimethylformamide. However, in dimethylformamide at 0°, the reaction of methyl iodide with poly(p-N,N-dimethyl-aminostyrene) is subject to deceleration. Some suggestions towards an explanation are now discussed.

In the initial stages of the reaction the quaternisation is undoubtedly a random process along a given polymer chain, and the probability of the quaternisation of near neighbours is small. But as the reaction proceeds, unquaternised nitrogens inevitably must have quaternised neighbours: the results of the present work and also the results of Coleman and Fuoss have shown that, under the specified conditions, the quaternary ammonium centres are able to slow down the reaction of the remaining tertiary-amino groups.

General experience has shown dimethylformamide to be an exceptionally good polymer solvent, and it is now postulated that, although its dielectric constant is less than that of
sulpholane, it is superior to that solvent in its capacity to solvate poly(4-vinylpyridine) and to expand the conformation of the molecules into loose coiling. This means that any effect promoted by tight coiling and proximity of side-groups will be less in dimethylformamide than in sulpholane.

Possible explanations of the deceleration of the poly(4-vinylpyridine) - n-butyl bromide reaction in sulpholane were discussed inconclusively by Coleman and Fuoss¹², and these suggestions, together with others, are now discussed in the light of the last paragraph.

(1) This deceleration might be due to an inductive effect¹², wherein the positive charge on a quaternised pyridine nitrogen makes the lone pair of electrons on an adjacent pyridine group less available for reaction with alkyl halide.

\[
\text{(-I)}
\]

Inductive effects, usually, are considerably weakened by the interposition of even a single methylene group between the charged site and the reaction site. The inductive route in this case is very long and this therefore renders it unlikely
as the cause of the deceleration. Loosening of coiling does not obviously alter the magnitude of this effect.

(2) The charge on an $\text{N}^+$ might orient an approaching dipolar molecule of alkyl halide into an unfavourable position for reaction with a neighbour$^{123}$.

\[
\begin{align*}
\text{CH}_3 - \text{CH} - \\
\text{N}^+ \quad \text{N}^+
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2 \quad \text{CH} \\
\text{Br} - \text{O} - \text{H} \\
\text{H} \quad \text{CH}_2
\end{align*}
\]

The Br might be pulled aside by a neighbouring $\text{N}^+$ and it would be more difficult to get a linear transition state ($\text{N}^+ \ldots \text{O} \ldots \text{Br}$). This would increase the activation energy of the quaternisation reaction and hence the rate would be slowed down. Heavy solvation and a more diffuse coiling would be expected to diminish this effect.

(3) Coleman and Fuoss$^{123}$ put forward a suggestion which is somewhat obscure, but may mean that, in the transition state, the bromide ion escapes with difficulty from the general positive field of the pyridinium cations. Clearly heavier solvation and a more diffuse coiling will render escape easier.
The intense field of the quaternised nitrogens might orient the highly polar solvent molecules around them in such a way as to make access to the polymer chain by the alkyl halide more difficult. The quaternary salt formed by this reaction will undoubtedly be highly solvated and the solvent molecules may be oriented as shown below:

\[
\begin{align*}
\text{Solvent molecules} & \quad \delta^- \quad \delta^+ \\
\text{Alk} - X & \quad \delta^+ \quad \delta^- \\
\text{A} - \text{B} & \\
\end{align*}
\]

The dipolar alkyl halide molecules may well not be able to get to the unreacted sites because of the barrier of positive charges of the solvent molecules. It is not clear how loose coiling, dependent itself on heavier solvation, would affect this situation.
(5) The existence of a dense counterion layer (of bromide ions) would be expected to render more difficult the breakdown of the transition state into the products:

\[
\text{Br}^{-}\text{Counterion layer}\]

it is necessary to generate a new bromide anion in the volume occupied by the existing counterions. Increased solvation and a diffuse coiling would make this deterrent factor less effective.

(6) n-Butyl groups are quite large and hence some general steric hindrance might be postulated, which becomes effective in a contracted coil. If this is important, it clearly is not effective in the poly(4-vinylpyridine) reaction in dimethylformamide, due presumably to open coiling.

In the case of the poly(p-\(N,N\)-dimethylaminostyrene) - methyl iodide reaction the increase in steric hindrance in passing from,

\[
\text{N(CH}_3\text{)}_2 \quad \text{to} \quad \text{N}^+(\text{CH}_3)_3 \quad \text{I}^{-}
\]

is not large, leading one to doubt steric hindrance as a major cause of deceleration.
In conclusion, the supposition that dimethylformamide is superior to sulpholane as a solvent, leading to more open coiling of poly(4-vinylpyridine) in the former, provides an explanation of deceleration if processes (2), (3) and (5) previously mentioned, are important. For poly(p-N,N-dimethyl-aminostyrene) in dimethylformamide at 0°, it can only be concluded that coiling does not reach that degree of diffuseness at which these processes cease to be operative.

Further work would be necessary to assess the relative importance of the six processes listed, and would probably require determination of the dimensions of the coiled molecules under different conditions by light-scattering or ultracentrifuge studies.
SUMMARY
p-N,N-Dimethylaminostyrene and p-isopropyldimethylaniline have been synthesised by known routes with certain modifications.

Poly(p-N,N-dimethylaminostyrene) and a styrene - p-N,N-dimethylaminostyrene 2:1 copolymer have been prepared by bulk polymerisation using \( \alpha,\alpha' \)-azoisobutyronitrile as the initiator at concentrations 0.4 and 1% by weight for the homopolymers and 0.6% by weight for the copolymer. Intrinsic viscosity determinations in toluene at 25.0° and substitution in Green's equation for polystyrene gave molecular weights of 65,000 and 97,000 for the homopolymers and 130,000 for the copolymer.

The initial second-order constant for the reaction of poly(p-N,N-dimethylaminostyrene) with methyl iodide in dimethylformamide at 0°, \( 10.5 \times 10^{-3} \text{l.mole.}^{-1} \text{min.}^{-1} \), is almost unaltered by change in molecular weight and by the spacing out of amino groups by inert styrene units. Under the conditions above, the constants for dimethylaniline and p-isopropyldimethylaniline are 5.1 and \( 5.4 \times 10^{-3} \). These values imply electron release from the main chain to the side-groups in the polymers, for which the Hammett sigma function is evaluated at \( \sigma_p = -0.101 \). After 20-25% reaction, the development of a charged envelope about the macromolecule leads to a fall in the rate of quaternisation.

Poly(4-vinylpyridine) was prepared by bulk polymerisation using \( \alpha,\alpha' \)-azoisobutyronitrile as the initiator (0.4% by weight). Evaluation by viscosity measurements in 96% ethanol at 25.0° led to a molecular weight of 164,000. The preparation of the n-butyl bromide salt was carried out by heating poly(4-vinylpyridine) with the alkyl halide in nitromethane.
at 60° for 4 days. The analyses demonstrated that the reaction had proceeded to completion.

The initial second-order constants were determined for the quaternisation of poly(4-vinylpyridine) by n-butyl bromide at 75° in sulfolane, 23.8 l.mole.\(^{-1}\) min.\(^{-1}\), and dimethylformamide, 10.7 l.mole.\(^{-1}\) min.\(^{-1}\), and also in dimethylformamide-sulfolane mixtures. Under the conditions above, these constants were determined for the reaction of pyridine in sulfolane, 21.9 \(x 10^{-3}\) and in dimethylformamide, 7.2 \(x 10^{-3}\). The plots of the integral second-order expression against time for the quaternisation of the polymer in sulfolane are linear for the first 10–15\% of the reaction and then become concave towards the abcissa. In the solvent mixtures progressively richer in dimethylformamide the initial rate constant is progressively lowered, and deceleration begins at approximately the same percentage reaction but is not so marked as in sulfolane. The deceleration gradually lessens until in dimethylformamide there is no deviation from the second-order kinetic equation. Addition of dimethylformamide to sulfolane therefore causes a decrease in the initial second-order constant and a lessening of the deceleration effect.

The kinetic results are discussed in relation to the size, structure, and coiling of the macromolecules.
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