KINETICS OF THE REACTION OF POLY(4-CHLOROMETHYLSTYRENE)

WITH TERTIARY AMINES AND RELATED STUDIES

A Thesis submitted to the
University of London
for the degree of
Doctor of Philosophy

by

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ABSTRACT

4-Chloromethylstyrene has been synthesised, by a known route, from p-tolunitrile. This monomer has been polymerised by initiation with azobisisobutyronitrile. Polystyrene has been chloromethylated to yield a soluble polymer containing one chloromethyl group substituted in each benzene ring. Substitution, which was slightly in excess of monochloromethylation, has been shown to be largely para to the main chain.

The polymers were characterised by determination of their intrinsic viscosities in toluene at 25°.

Chloromethylated polystyrene has been reacted with triethylphosphite and several tertiary amines to yield polymers containing benzyldiethylphosphonate and benzyltrialkyl ammonium groups respectively.

The second-order rate constants for the reaction between triethylamine and benzyl chloride, cuminyl chloride, the chloromethyl polymers and a styrene: 4-chloromethylstyrene copolymer in benzyl alcohol at 75° have been determined. The rates of the polymeric quaternizations progressively fall after about 25% reaction due to the formation of electrostatic charges on the macromolecules. The values of the rate constants are unaltered by changes in polymer molecular weight, and
(initially) by spacing out the reactive groups by inert styrene units. The deceleration is similar for both poly(4-chloromethylstyrene) and chloromethylated polystyrene.

A similar, though less marked, fall in the rate of quaternization of poly(4-chloromethylstyrene) with triethylamine at 75° in sulpholane was observed, but in dimethylformamide solvent no deceleration occurred.

The kinetic results are discussed in relation to polar and solvation effects and to the structure of the macromolecules.
ACKNOWLEDGMENTS

The work described in this thesis has been carried out in the Joseph Kenyon Laboratory of Battersea College of Technology under the supervision of Dr. C.L. Arcus. The author thanks Dr. Arcus for his kindly help and guidance throughout the course of this work.

The author also thanks the College for the tenure of a research assistantship.
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INTRODUCTION
Introduction

Although the general importance of polymer chemistry is evident from the present scale of industrial production of polymers, it is only in the past thirty or so years that an understanding has been reached of the processes of polymerisation and the properties of polymers.

It is not the purpose of this introduction to summarise the extensive literature on the various general aspects of polymer chemistry, but rather to establish briefly those facts which relate to the structure of vinyl addition polymers, especially polystyrene. Later a more detailed discussion on the chemical reactivity of macromolecules will be presented, since this is pertinent to the work to be described.

Free radical polymerisation of vinyl monomers

Many vinyl monomers readily form high molecular weight polymers in the presence of initiators, which may be anionic or cationic, or free radicals. The process of such a polymerisation has been shown to follow a typical chain reaction mechanism. The reaction can be divided into three distinct steps; initiation, propagation of the polymer chain and termination. Many workers have studied these reactions by the kinetic and other methods; in particular the polymerisation of styrene has been fully investigated. The main conclusions of the investigations may be summarised as follows.

Initiation

Compounds which dissociate thermally to give free radicals can be
used to start polymerisation, although in certain cases polymers may be
formed in the absence of an initiator simply by the action of heat, light
or other radiation.

The initiation reaction may be subdivided into two steps. Firstly
decomposition of the initiator into free radicals:

\[ I \rightarrow 2R^* \]

Benzoyl peroxide and azobis-isobutyronitrile are commonly used as
initiators and the mechanisms of their thermal decompositions have been
widely studied.

Benzoyl peroxide decomposes to yield benzoate free radicals:

\[ \text{Ph}_2\text{C} = \text{O} \cdot \text{O} \cdot \text{C} \cdot \text{Ph} \rightarrow 2\text{Ph}_2\text{C} = \cdot \text{O}^* \]

These radicals are relatively stable, but can decompose further to
phenyl radicals and carbon dioxide:

\[ \text{Ph}_2\text{C} = \cdot \text{O}^* \rightarrow \text{Ph}^* + \text{CO}_2 \]

However, in the presence of a vinyl monomer this second step may
not occur, the benzoate radicals combining instead with monomer. Analysis
of benzoyl peroxide-initiated polystyrene [1] has shown that 96% of the
end-groups are benzoate. In dilute solution polymerisation, the second
step is more likely to occur.

Benzoyl peroxide has certain disadvantages as an initiator. It
may oxidise any reactive groups (such as amino-groups) present in the
monomer and it is susceptible to induced decomposition [2].

Azobisobutyronitrile is free from these defects. It decomposes thermally by the following scheme [3], to yield isobutyronitrile free radicals and nitrogen:

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

\[
\text{CH}_3 \quad \text{C} \quad \text{N} = \text{N} \quad \text{C} \quad \text{CH}_3
\]

The azo free radical being very unstable decomposes to the isobutyronitrile radical and does not initiate polymerisation.

The second stage of initiation involves addition of the free radical (\( R^\cdot \)) to a monomer molecule (\( M \)), to yield an activated monomer free radical.

\[ R^\cdot + M \rightarrow M_1^\cdot \]

e.g. \( \text{PhCOO}^\cdot + \text{CH}_2 = \text{CH} \rightarrow \text{PhCOO} - \text{CH}_2 - \cdot \text{CH} \]

\[ X \quad X. \]

**Propagation**

Propagation involves successive addition of monomer molecules to the free radical centre of the growing polymer molecule by a chain
reaction mechanism:

e.g. \[ \text{Ph.COO.CH}_2 + \cdot \text{CH} + \cdot \text{CH} = \text{CH} \rightarrow \text{ThCOO - CH}_2 - \text{CH} - \text{CH}_2 - \cdot \text{CH} \]

\[ \text{X} \quad \text{X} \quad \text{X} \quad \text{X} \]

\[ + \text{CH}_2 = \text{CHX} \]

\[ \text{Ph.COOC.(CH}_2 - \text{CH})_n \cdot \text{CH}_2 - \cdot \text{CH} \]

\[ \text{X} \quad \text{X} \]

Termination

Deactivation of the growing polymer free radical and consequent termination of the chain can occur by either combination of two active polymer chains at their active centres, yielding polymer with two initiator fragments (R):

\[ \text{R} \cdot \cdot \cdot \text{CH}_2 - \cdot \text{CH} + \cdot \text{CH} - \text{CH}_2 \cdot \cdot \cdot \rightarrow \text{R} \cdot \cdot \cdot \text{CH}_2 - \cdot \text{CH} - \cdot \text{CH} - \text{CH}_2 \cdot \cdot \cdot \text{R.} \]

\[ \text{X} \quad \text{X} \quad \text{X} \quad \text{X} \]

or by disproportionation, involving a hydrogen atom transfer from one active chain to another. In this case the polymer molecules will contain one fragment (R):

\[ \text{R} \cdot \cdot \cdot \text{CH}_2 - \cdot \text{CH} + \cdot \text{CH} - \text{CH}_2 \cdot \cdot \cdot \rightarrow \text{R} \cdot \cdot \cdot \text{CH} = \text{CH} + \text{CH}_2 - \text{CH}_2 \cdot \cdot \cdot \text{R} \]

\[ \text{X} \quad \text{X} \quad \text{X} \quad \text{X} \]

Both types of termination have been observed. Polystyrene, azobisisobutyronitrile initiated, was found to contain almost exactly two initiator fragments per polymer molecule [4], whence it is concluded that termination occurs almost exclusively by combination.

Termination may also occur by chain transfer; that is transfer of
a free radical atom, often hydrogen, to the growing chain from some external neutral molecule. This latter may be solvent, leading to the incorporation of solvent fragments in the polymer, initiator (induced decomposition), monomer, or polymer (when chain branching occurs).
The Structure of Vinyl Addition Polymers

Free radical initiated vinyl polymers are usually linear but chain branching is possible by means of the chain transfer reaction with a 'dead' polymer chain. Chain transfer constants are very low so that little or no branching normally occurs. The best known example of non-linear polymerisation is the high pressure preparation of poly(ethylene). The infrared spectrum of the product shows the presence of as many as 5 methyl groups for each 100 methylene groups [5].

The addition of monomer to (initiator) free radical can occur in two ways, giving rise to different polymer structures:

\[ \text{M}^* + \text{CH}_2 = \text{CH} - \xrightarrow{\text{M}_x - \text{CH}_2 - \hat{\text{CH}}_2 \quad \text{I}} \xleftarrow{\text{M}_x - \text{CH} - \hat{\text{CH}} \quad \text{II}} \]

In I, but not in II, resonance between the unpaired electron and the substituent \( X \) is possible. Hence we expect I to be the more stable, and the rate of formation of I should be greater than that for II. Steric factors also favour I. For styrene polymerisation I will be especially favoured since the substituent \( X \) (phenyl) readily enters into resonance.

The formation of I exclusively during propagation would lead to the 'head to tail' structure:

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

whereas if II were to intervene appreciably the 'head to head' structure:
would make an appreciable contribution to the total structure.

That the former normally predominates has been amply shown by destructive chemical analysis of many polymers. Thus destructive distillation of polystyrene yielded no products containing phenyl groups attached to adjacent carbons [6].

From the kinetic treatment of polymerisation it has been shown [7] that the chain length of high polymer is related to the initiator concentration ([I]) and monomer concentration ([M]) by:

\[ y \propto \frac{[M]}{[I]^2} \]

\( y \) = kinetic chain length = number of monomer units consumed per active centre. Thus polymers of different average molecular weights may be prepared by varying the initiator concentration.

A further possibility of structure variation exists when considering the stereochemistry of polymer chains. A polymer:

\[ M_x \ldots \text{CH}_2 - \text{CH}_2 \ldots \text{M}_y \]

formally has a series of alternate asymmetric carbons, assuming \( M_x \) and \( M_y \) are portions of chains of different length. These asymmetric carbons can exist in both d- and l-configurations; if all d- or all l-the stereo-regular polymer is referred to as isotactic, if alternately d- and l-the polymer is syndiotactic. A random distribution of d- and l-configurations, the
atactic polymer, is the normal product of free radical polymerisations. In recent years a whole range of new catalysts have been discovered which initiate stereospecific polymerisation. Most commonly used are the Ziegler-Natta catalysts consisting usually of a transition metal halide and a Group III metal alkyl. The mechanism of the polymerisation has not yet been fully worked out, but seems to involve coordination of the monomer onto the metal, in a preferred configuration [8].

Stereoregular polymers differ in properties from their atactic isomers, being usually less soluble, highly crystalline (since they have an ordered structure) and having generally different mechanical and chemical properties.

It is now realised that conventional, free radical initiated polymers may contain stereoregular sequences in the polymer chain. Thus methyl methacrylate, polymerised using free radical initiations especially at low temperatures consists largely of the syndiotactic structure [9]. This 'local' description of a polymer chain is often referred to as the microtacticity.

Copolymerisation

The simultaneous polymerisation of two monomers, copolymerisation, has also been widely studied. The ease with which a monomer will copolymerise is expressed in its reactivity ratio $r$, the ratio of the rate constant for a radical adding to its own monomer to that of its addition to another. Some monomers which will not homopolymerise will enter
readily into copolymers e.g. maleic anhydride. Since the reactivity ratios of two monomers are usually different, the composition of the copolymer will vary during the reaction, being initially rich in the more reactive monomer, which is rapidly used up; towards the end of reaction only the less reactive monomer will remain to be incorporated into the chain.

Comparative Reactivity of Monomers

The reactivity of a substituted ethylene monomer $\text{CH}_2 = \text{CHX}$ towards a particular radical has been shown to increase in the order:

$$-\text{C}_6\text{H}_5 > -\text{CH}_2 > -\text{CO.CH}_3 > -\text{CN} > -\text{COOR} > -\text{Cl} > -\text{CH}_2\text{Y}^{-}0\cdot\text{COCH}_3 > -\text{OR}.$$  

These results may be explained on the basis of resonance stabilisation of the product radical, the phenyl group, for example, permits three extra resonance structures:

$$\text{CH}_2 - \text{CH} \quad \text{CH}_2 - \text{CH} \quad \text{CH}_2 - \text{CH}$$

The resonance stabilisation due to $X$ is much greater in the radical than in the monomer, the activation energy for addition of the substituted monomer to its radical is therefore less than for the corresponding case of the unsubstituted monomer.

The effect of more than one 1-substituent is roughly additive, but 1,2-disubstituted ethylenes are usually unreactive.
The Molecular Weights of High Polymers

Polymers prepared by free radical initiation do not consist of chains of equal length, but rather a distribution of chain lengths; consequently the polymer contains molecules of differing molecular weights. Any method of determining the molecular weight will yield an average value; the type of averaging depending on the particular method used. Methods depending on the colligative properties of particles, e.g. osmometry, yield the number average molecular weight:

\[ \bar{M}_n = \frac{\sum N_i M_i}{\sum N_i} \]

where \( N_i \) is the number of species \( i \) with molecular weight \( M_i \).

The weight average molecular weight:

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

will be obtained when a property dependent on concentration e.g. light scattering is used for molecular weight determination. Unless the polymer is monodisperse \( \bar{M}_w \neq \bar{M}_n \), the former being larger.

A unique property of high polymers is their ability, when in dilute solution, of considerably raising the viscosity of the pure solvent. This leads to the most convenient method of characterising a polymer and determining its molecular weight.

Assuming the densities of solvent and the dilute solution are the
same, the specific viscosity of a polymer, \( \eta_{sp} \) is given by:

\[
\eta_{sp} = \left( \frac{\text{flow time solution}}{\text{flow time solvent}} \right)^{-1}
\]

\( \eta_{sp} \) is concentration dependent, extrapolation of \( \eta_{sp}/c \) to zero concentration gives the limiting viscosity number (L.V.N.) \( [\eta] \):

\[
[\eta] = \eta_{sp}/c \quad c \to 0 \\
\text{..............(1)}
\]

- where \( c \) is usually expressed as g. of solute per 100 ml. solution.

On the basis that plots of \( \eta_{sp}/c \) vs. \( c \) for a given polymer solvent system are linear with slope equal to the square root of the intercept \( 0 = 0 \), Huggins [10], proposed the relation:

\[
\eta_{sp}/c = [\eta] + k_1 [\eta]^2 c, \quad K_1 \text{ is a constant.}
\]

Definition of L.V.N. by:

\[
\left[ \ln\left( \frac{\eta_{sp}}{c} \right) \right] = \left[ \eta \right] = \eta_{sp}/c \quad c \to 0
\]

has been shown by Kraemer [11] to be equivalent to (1) and leads to:

\[
\left[ \ln\left( \frac{\eta_{sp}}{c} \right) \right] = [\eta] - k_2 [\eta]^2 c. \quad \text{..............(2)}
\]

where \( k_1 + k_2 = 0.5 \).

Since usually \( k_2 < k_1 \), there is less error in using equation (2) for calculating \( [\eta] \). (However, recently Ibrahim [12], has doubted the equivalence of Kraemer's and Huggin's equations).

For a fractionated polymer, \( [\eta] \) and molecular weight are related by the equation (Mark and Houwink [13]):

\[
[\eta] = K M^\alpha
\]
- where \( k \) and \( \alpha \) are constants for the particular solvent/polymer system.

Such equations are empirical in origin; the constants \( k \) and \( \alpha \) must be predetermined for the system under study by an absolute method.

For heterogeneous polymers it can be shown [14] that if a viscosity average molecular weight is defined as:

\[
\bar{M}_v = \left[ \sum_i w_i M_i^{\alpha} \right]^{1/\alpha}
\]

\[
= \left[ \sum_i \frac{w_i M_i^{1+\alpha}}{\sum_i w_i M_i^{1+\alpha}} \right]^{1/\alpha}
\]

- where \( w_i = C_i/C \) is the weight fraction of species \( i \), then:

\[
[\eta] = k \bar{M}_v^\alpha \]

\[
...............(3)
\]

Generally \( \bar{M}_w > \bar{M}_v > \bar{M}_n \), with \( \bar{M}_v \) closer to \( \bar{M}_w \) than \( \bar{M}_n \), hence in the determination of \( k \) and \( \alpha \) by an absolute method on fractionated polymers, light scattering is preferred, since it yields \( \bar{M}_w \). When \( k \) and \( \alpha \) have thus been determined, use of equation (3) gives the viscosity average molecular weight for heterogeneous polymers.
The Reactivity of Groups attached to Macromolecules

This section discusses some aspects of the reactions of high polymers, in which a pendant side group undergoes a chemical change. Studies of degradative reactions, which involve scission of the main chain, such as depolymerisation, will be excluded.

Chemical transformations of high polymers have long been carried out, even before the structures of the polymers were known. Such reactions are of importance for a variety of reasons.

Firstly, it is possible to prepare polymers with an extended range of properties. This was early realised and led to the industrial production of modified polymers such as cellulose acetate. Such reactions are of interest where it is impossible to prepare the required polymer by polymerisation of the monomer, which either may not be known or may not readily polymerise.

The former difficulty may be overcome by preparing a monomer in which the reactive group is protected. After polymerisation, the protecting group may be removed. Thus vinyl alcohol and vinylamine cannot be prepared since they spontaneously rearrange to acetaldehyde and ethylenimine respectively. However, poly(vinyl alcohol) is obtained on hydrolysis of poly(vinylacetate); and poly(vinylamine) has been synthesised \[15\] by solvolysis of poly(benzyl-N-vinyl carbamate) by hydrogen bromide in acetic acid:
Similar methods are available for the synthesis of a polymer, whose monomer does not readily polymerise. Although quinol is oxidised by free radicals to quinone, vinylquinol does polymerise to dimers and trimers, which do not readily undergo the propagation step of the polymerisation reaction; however, poly (vinylquinol) may be prepared via vinyl quinol diacetate [16]. Compounds containing thiol groups have very high chain transfer constants but thiol containing polymers have been synthesised e.g. poly (p-mercaptostyrene) by saponification of poly(p-vinylphenylthiolactate) [17].

Synthetic polymers are also useful as model systems for biologically important reactions, particularly where the analogous biological macromolecule cannot be synthesised or is unstable under the desired reaction conditions. Catalysis by polyelectrolytes is of interest here by providing a model for enzyme action [18].

Various difficulties are encountered in obtaining a well defined product from polymer reactions, arising from the macromolecular nature of the reaction. It is desirable to choose a method which, in the similar small molecule reaction, gives a high yield, side reactions being absent.
Since all groups are covalently bound to the same polymer chain a separation of different reaction products is impossible. Thus nitration of polystyrene yields a copolymer containing units of 2- and 4- nitro, 2,4- dinitro and unreacted phenyl groups.

Any side reaction occurring will also give rise to the difficulties described above. In particular intermolecular side reactions between groups on different polymer chains may result in the production of cross-linkages. Ionic chlorination of polystyrene [19], catalysed by ferric chloride, was accompanied by Friedel-Crafts alkylation, in which the carbonium ion alkylated an aromatic nucleus of another polystyrene molecule:

\[
\begin{align*}
\text{Cl} & \quad \text{FeCl}_3 & \quad \text{FeCl}_4 \\
\text{C} - \text{CH}_2 & \quad \rightarrow & \quad \text{C} - \text{CH}_2 \\
\text{CH} - \text{CH}_2 & \quad \rightarrow & \quad \text{CH} - \text{CH}_2 \\
\text{CH}_2 & \quad \rightarrow & \quad \text{CH}_2 \\
\text{CH}_2 & \quad + & \quad \text{H}
\end{align*}
\]

Often a ruling consideration in carrying out reactions on high polymers is the choice of solvent. Since both reacted and unreacted groups are attached to the same chain, the solubility properties of the
polymer alter during reaction. Precipitation is undesirable, since then some unreacted sites may not be available for reaction. In this respect cross-linking often brings about precipitation or causes 'gelling' of the polymer.

The most useful solvent will be one in which the polymer is present in an expanded conformation, thus preventing any steric blocking of unreacted groups by the main chain or already reacted groups. However, reaction may go to completion even when the polymer is not truly in solution, provided unreacted groups remain solvated and reagent is able to diffuse through the swollen polymer.

The special reactivity of groups attached to macromolecules can often be explained by intramolecular interaction of neighbouring groups, which being covalently bound to other atoms at, or near, the reaction centre, influence the reaction more than in the corresponding reaction between small molecules. Here greater distances separate the molecules which are free to diffuse through the solvent.

It is convenient to make a distinction between unfunctional reactions, when the reactive group behaves in a similar manner in both polymeric and ordinary molecules and polyfunctional reactions. In the latter functional interactions between neighbouring groups cause several groups to enter into reaction.

A bifunctional reaction may be limited in extent on account of the isolation of single unreacted groups. Flory [20] predicted statistically
that, assuming a head to tail polymer structure, for a bifunctional reaction, 13.5% of the groups would fail to react. In the dehydrochlorination [21] of poly(vinylchloride) to yield cyclopropane rings, only 84 - 86% chlorine was removable - in good agreement with the calculations.

A polyfunctional polymer reaction may not only be limited in extent but can yield unexpected products, especially when the distances between adjacent substituents favour ring formation. The Arndt-Eistert diazomethane reaction on poly(methacryloyl chloride) would be expected to yield poly(isopropenylacetic acid):

\[
\text{Me} - \text{C} - \text{COCl} \rightarrow \text{Me} - \text{C} - \text{CO} - \text{CHN}_2 \rightarrow \text{Me} - \text{C} - \text{CH} = \text{C} = \text{O} \\
\text{Me} - \text{C} - \text{CH}_2\text{CO}_2\text{H} \leftrightarrow \text{aq.}
\]

Analysis indicates that 3-keto-ketene rings are formed which, on hydrolysis and decarboxylation yield five-membered keto-rings without any acid properties [22].
The Kinetics of Polymer Reactions

The special characteristics of polymer reactions may not only be observed in the structure of the products but also in the kinetics of reaction, especially when a comparison is made with the analogous reaction between small molecules. However, special effects in a monofunctional polymer reaction may not be observed if the reacting groups are spaced well apart or if the macromolecule undergoes no great change in shape due, for example, to its becoming electrostatically charged. Thus Hiller [23] found that the activation energy for the acetylation of cellulose was similar to that for ordinary alcohols:

\[ E_a \text{ for acetylation, (K cal.mole.)} \]

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<th>Reaction</th>
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<td>Cellulose</td>
<td>10.3</td>
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<tr>
<td>Methanol</td>
<td>10.2</td>
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The alkaline hydrolyses of the lactam rings in poly-N-vinylpyrrolidone and in a model low molecular weight compound (N-isopropyl-5-methylpyrrolidone) have similar characteristics [24]:

![Reaction Diagram]
For the polymer negative charges are built up on the chain as reaction proceeds, but due to their distance apart they are without effect until 50% reaction is reached, the first order rate constant remaining constant up to this point. Later the rate falls, probably because of increasing electrostatic repulsion between carboxylate ions and attacking hydroxide ions.

This electrostatic effect is more pronounced in the alkaline hydrolysis of polymethacrylamide\[25\]. Here reaction proceeds initially at a rate similar to that of trimethylacetaamide, but after only a few percent conversion the reaction progressively slows down.

Interactions between neighbouring groups in multifunctional reactions can have large effects on the rate of a polymer reaction. Morawetz and Westhead [18] found that the rate of the base catalysed hydrolysis of p-nitroanilide ester groups is reduced about 1000 fold (compared with the trimethylacetyl ester) when these units are incorporated into an acrylic acid polymer. Intramolecular hydrogen bonding between neighbouring carboxylate groups and amino-hydrogen atoms was thought to stabilise the ester groups to attack by nucleophile.
Since the glutaryl and trimethylacetyl esters hydrolyse at similar rates it seems that two neighbouring carboxylates are required for the effect to become operative. The addition of small amounts of barium ions considerably accelerated the polymer hydrolysis, which is to be expected since barium ions will chelate with the carboxyl groups, thus reducing the hydrogen bonding and liberating the anilide groups for reaction.

Arcus [26] previously postulated a similar hydrogen bonding effect to account for the limited extent of hydrolysis (72%) of polymethacrylamide:

This interpretation was confirmed by Pinner [27] who correlated the degree of hydrolysis obtainable in methacrylamide - methacrylic acid copolymers with their initial composition.
In contrast, the hydrolysis of p-nitrophenyl ester groups, present as 1 mole %, in an acrylic acid copolymer, proceeded a million times faster compared with the trimethylacetyl ester\[23\]. Here catalysis by a single neighbouring carboxylate group was thought to result in a change in mechanism involving the formation of a favourable six-member ring transition state:

For the methacrylic acid-methacrylate ester copolymer some ester groups were found to react at a faster rate and this was interpreted by Morawetz and Gaetjens\[29\] as being due to the different stereochemical configurations of neighbouring acid groups.

Smets and de Loocker\[30\] studied the hydrolysis of partially neutralised copolymers of methacrylic acid and methylmethacrylate. They found that the reaction was catalysed by both neighbouring carboxylate and undissociated acid groups. The intramolecular nature of the reaction was demonstrated by a comparison with the hydrolysis of a methyl methacrylate (13.5 mole %) - N-vinylpyrrolidone copolymer. Even in the presence of external acid (acetic or polymethacrylic) this reaction was about 100 times
slower than the acid-ester copolymer hydrolysis. This latter reaction was however limited in extent and on the basis of structural probability calculations it was shown that neighbouring groups must be present in a particular stereochemical configuration for their catalytic effect to become operative.

These stereochemical requirements were also shown to be necessary, by Smets and Hasbain [31], in the hydrolysis of acrylic acid-acrylamide copolymers. As in the previous example, reaction proceeds in two steps, the first being 50 times more rapid than the second. The first step (up to about 40% reaction) was interpreted as being due to catalysis by neighbouring undissociated acid groups which were present in the required configuration. This stereospecificity was confirmed by the difference in behaviour of two copolymers of the same chemical composition but different internal structure. The second, slow, step had a similar rate to that of the hydrolysis of polyacrylamide by acetic acid and was therefore attributed to the action of external acid. These slower reacting amide groups together with their neighbouring acid groups were considered not to conform to the vicinalility and stereospecificity required for the fast reaction.

Smets and van Humbeck [32] have further demonstrated the stereochemical requirements for catalysis. They found that isotactic acrylic acid-methyl acrylate copolymers hydrolyse 3 - 5 times faster than atactic copolymers of the same chemical composition. The degree of conversion was
also higher in the isotactic copolymers.

These workers have also investigated the steric effects of alkyl groups present in the polymer. The rate of hydrolysis of ethyl ethacrylate-acrylic acid copolymers (alkyl substituent in polymer chain) was at a maximum when, on average, half the acid groups were neutralised, and was also directly related to the number of acid-ester-acid triads. This suggested that reaction proceeded by a concerted mechanism brought about by chain expansion due to the introduction of ethyl groups in the main chain. Both conventional and isotactic acrylic acid-tert-butyl acrylate copolymers were also studied. These hydrolyse only with mineral acid, any intramolecular interaction being absent in both cases. This stability is no doubt due to the steric hindrance of bulky tert-butyl groups present in the side chain.

In the reactions described above the kinetics are influenced by functional interactions of neighbouring groups, which must be in a preferred stereochemical configuration to have effect. On the other hand for reactions involving the production of ions along the polymer chain, the kinetics may be analysed in terms of the changes in electrical potential of the polymer molecule. Katchalsky [33] has calculated the electrical potential of polymers carrying charges along the chain and has shown [34] that the diminution in rate observed during the hydrolysis of pectin [35] is accounted for by the changes in potential during reaction.
Reactions which involve the production of positive charges along a polymer chain are of special interest in studying the effects of changing polymer electrical potential, since in these cases functional interactions between reacted and unreacted groups are unlikely. Such a case arises when a quaternization reaction is carried out on a polymer. Fuoss [36,37] and coworkers have studied the kinetics of reaction of polyvinylpyridine with $n$-butylbromide in sulpholane and propylene carbonate solvents:

\[
\begin{align*}
\text{poly-} & \quad + \quad n\text{-Bu-Br} \\
\text{ppy} & \quad \longrightarrow \quad \text{ppy} \\
& \quad | Br \\
& \quad n\text{Bu}
\end{align*}
\]

In these solvents, of relatively high dielectric constant, bromide ions will diffuse away from the polyelectrolyte, leaving the polymer chains with a high nett charge. Initially the reaction follows second order kinetics with a rate intermediate between the rates of the low molecular weight quaternizations of pyridine and 4-isopropylpyridine. This initial stage of reaction therefore has similar kinetics to normal Menschutkin reaction:
TABLE 1.

Quaternizations with n-Butyl bromide in Sulpholane [36]

<table>
<thead>
<tr>
<th>Compound</th>
<th>$10^3 x k_2$, l.mole.$^{-1}$ min.$^{-1}$venth order rate constant at 25°C</th>
<th>$E_a$</th>
<th>$\Delta S^\dagger$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyridine</td>
<td>0.46</td>
<td>16.0</td>
<td>-30.0</td>
</tr>
<tr>
<td>4-Isopropylpyridine</td>
<td>0.85</td>
<td>15.6</td>
<td>-30.3</td>
</tr>
<tr>
<td>Polyvinylpyridine</td>
<td>0.64</td>
<td>15.7</td>
<td>-30.4</td>
</tr>
</tbody>
</table>

However, the reaction soon deviates from second order kinetics, slowing down progressively as reaction proceeds. Fuoss attributed this deceleration to a volume field effect of the highly charged polymer chains produced during reaction, but could not decide on the actual process by which this effect worked.

Arcus and Hall [38] have observed a similar deceleration during the quaternization of poly-(p-M-dimethylaminostyrene) with methyl iodide in dimethylformamide solvent.

The quaternization of poly-ω-chloromethylstyrene with tertiary amines provides a further example for studying the electrostatic effect. Here a functional interaction is most unlikely to occur between an unreacted chloromethylcarbon (an electrophilic centre) and a neighbouring positively charged, reacted group.
Prior to this present work, the only kinetic study of this reaction had been carried out on the reaction of chloromethylated copolymers of styrene (crosslinked with divinylbenzene or butadiene) with pyridine or trimethylamine in dioxan [39]. Since the polymer was present in a swollen state, not in homogeneous solution, the kinetics were probably controlled by diffusion into the swollen polymer, or reaction only took place at surface sites.

Whilst the present work was in progress, Noda and Kagawa [40] published a study of the kinetics of quaternization of chloromethylated polystyrene with several tertiary amines (trimethyl-, triethyl- and tri-n-butylamines) in dimethylformamide solvent. They found that both the rate constants and activation energy for reaction were almost equal for benzyl chloride and the polymer. The reaction of the polymer with triethylamine in dimethylformamide, nitrobenzene, acetone, methylethyl
ketone and dioxan was, in all cases, found to follow second order kinetics, over the range studied, the rate constants becoming larger with increasing dielectric constant of the solvent.
The Menschutkin Reaction

The reaction between an organic halide and a tertiary amine to yield a quaternary ammonium halide:

\[ R_JN + R^- X \rightarrow R_JNR X^+ \]

was first studied kinetically by Menschutkin [41]. He found that for the reaction of ethyl iodide with triethylamine in a variety of solvents, the kinetics were of the first order in base and of the first order in iodide concentrations i.e., overall second order kinetics were followed. Subsequent workers have confirmed that this kinetic order is followed for the reaction of many amines with organic halides. The mechanism is therefore that of a bimolecular nucleophilic substitution, involving bond formation by donation of the amine-nitrogen lone electron pair, this occurring simultaneously with heterolytic fission of the carbon-halogen bond of the halide:

\[ R_JN^+ \rightarrow X \rightarrow R_JN \cdots \cdots C \cdots \cdots X \rightarrow R_JN CR_3 + X \]

The transition state for this reaction may be considered as containing stretched partial covalent bonds between the central carbon atom and the incoming and leaving groups, the nitrogen and halogen atoms carrying partial electrostatic charges. The relative degree of bond making and bond breaking at the central carbon atom in the transition state is expected to depend on the nature of the substituents R.
Some authors have claimed that the reaction proceeds to an equilibrium, since they observed a fall in the second order rate constant as reaction proceeded. Thus Edwards [2] proposed that in benzene solvent, in which the product is sparingly soluble, the Menschutkin reaction goes by a rapid reversible step which precedes the precipitation of the solid product, this latter step governing the overall rate of reaction. However, any reversibility of the reaction is ruled out by the observations of Harman, Stewart and Ruben [43]. They studied the reaction of trimethylamine with tritium labelled methyl iodide in both ethanol and benzene solvents, using an excess of base. In no case was any radioactivity found in the unreacted amine, indicating that no reverse reaction took place. Thus any mechanism which involves a reversible step is incorrect.

In a bimolecular substitution reaction prediction of the effects of substituents on the central carbon atom is not easy since bond-making and bond-breaking have the opposite electronic requirements. Thus, in the Menschutkin reaction, an electron releasing substituent will facilitate ionisation of the halide, but, on the other hand, the same substituent will make the central carbon atom more negatively charged and therefore less susceptible to attack by amine. However, Menschutkin [41] found that for the reaction of a series of alkyl iodides (R - I) with triethylamine, the rate varied in the following way:

<table>
<thead>
<tr>
<th>R</th>
<th>Me</th>
<th>Et</th>
<th>n-Pr</th>
<th>i-Pr</th>
<th>n-Bu</th>
<th>n-Heptyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative rate</td>
<td>100</td>
<td>8.8</td>
<td>1.7</td>
<td>0.18</td>
<td>1.2</td>
<td>0.9</td>
</tr>
</tbody>
</table>
Along the series Me, Et, i-Pr the inductive effect of the α-methyl groups makes the central carbon atom more negative and therefore less likely to react with nucleophile; hence the rate falls. Along the series Me, Et, n-Pr, n-Bu etc, similar effects occur, but the rate rapidly levels off, since the inductive effects of higher n-alkyl groups are very similar.

The opposing electronic requirements of a bimolecular reaction are shown by the effects of substituents in the benzene ring on the rates of reaction of benzyl halides with tertiary amines, since here any steric effects of the substituent are minimised by removing the substituent from the site of reaction. No close correlation is found between the electron releasing or withdrawing powers of such groups and rate of reaction. Baker and Nathan [44], found the following rate order for the reaction of substituted benzyl bromides with pyridine, in dry acetone solvent:

\[
2.4\text{-di-NO}_2 \succ p\text{ alkyl} \succ H \succ p\text{-NO}_2
\]

The rate order seems to depend on the solvent since in 90% aqueous alcohol the order is:

\[
p\text{-alkyl} \succ H \succ 2.4\text{-di-NO}_2 \succ p\text{-NO}_2
\]

The p-alkyl substituted series provides an unusual rate sequence since the rate is found to increase in the order [45]:

\[
H \ll \text{Me} \succ \text{Et} \succ \text{i-Pr} \succ \text{tert-Bu}
\]
Thus, although an alkyl substituent increases the rate (compared with the unsubstituted compound), the order among the alkyl substituent series is exactly the reverse of that anticipated on the basis of the inductive effects of the alkyl groups. This unexpected rate sequence was explained by assuming the operation of the hyperconjugative effect, whereby when a methyl group is attached to a conjugated system, the C-H bond electron pair of this group can be conjugated with the rest of the system:

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

Such electron release will of course decrease in the order Me > Et > i-Pr > tert-Bu, thus explaining the observed rate order. However, the rate differences involved are small and it has been suggested [46] that they reflect changes in the solvation energies of the benzyl halides not the operation of the hyperconjugative effect.

**Solvent Effects**

The effect of solvent on the rate of the Menschutkin reaction has been shown to be important by many workers. According to the qualitative theory of solvent effects of Hughes and Ingold [47], a reaction which involves the production of ions from initially neutral reagents should be faster in a more polar solvent. In the Menschutkin reaction the polar transition state should be stabilised more, relative to the initial state, by a more polar solvent. The theory, however, ignores any specific solvent-reagent interactions, such as hydrogen bonding.
Several workers have tried to correlate the reaction rate with some property measuring the solvent polarity. Menschutkin [48] observed that the rate was faster in aromatic than in the corresponding aliphatic solvents, being particularly faster in hydroxylic solvents. For the reaction of triethylamine with ethyl iodide in various solvents his relative rates were:

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Relative rate</th>
<th>Solvent</th>
<th>Relative Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>0.13</td>
<td>Diethyl ether</td>
<td>0.57</td>
</tr>
<tr>
<td>Benzene</td>
<td>2.4</td>
<td>Phenetole</td>
<td>16.0</td>
</tr>
<tr>
<td>Propyl Chloride</td>
<td>4.0</td>
<td>Ethyl alcohol</td>
<td>27.4</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>17.4</td>
<td>Benzyl alcohol</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Kerr [49] attempted to correlate dipole moment with reaction rate but obtained only limited success. Grim, Ruf and Wolff [50] showed that rate constant varied with dielectric constant (D) over a wide range of D, but could not demonstrate a quantitative relationship. By considering only electrostatic effects Kirkwood [51] obtained such a relationship theoretically and Tommila [52] has shown that this could be used to express the effect of mixed solvents, containing acetone as one component, on reaction rate. Eagle and Warner [53] had previously correlated rate constant with D in the mixed solvent alcohol-water. However, Glasstone Laidler and Eyring [54] have suggested that in these mixed solvents the
transition state is solvated by only one of the solvent components. This suggests that any non-electrostatic forces involved would remain constant, even whilst D for the solvent varies.

Watanabe and Fuoss [55] have shown that non-electrostatic forces are not negligible, since the Kirkwood equation did not fit their results for a quaternization reaction in five solvents of relatively high D. They suggested that the transition state is probably a solvated complex and that specific short range forces were in operation. They showed that the Kirkwood equation predicts that all solvents for which D > 30 should have the same solvent effect on rate, but this is contrary to their experimental findings.

Caldin and Peacock [56] also showed that electrostatic forces alone cannot explain the solvent effect and suggested that solvents could be classified into three categories, namely: aliphatic, aromatic and hydroxylic. They attributed the high rates in aromatic solvents to the high polarizability of the benzene nucleus. Recently Reinheimer, Harley and Meyers [57] have demonstrated a linear relation between the rate constant and the polarizability of a substituent (X) in substituted aromatic solvents (Ph−X, where X = H, Cl, Br and I), and identified the Fuoss short range forces as London forces. They concluded that solvation of the transition state by interaction of the solvent with the leaving halide ion was the rate influencing factor.

It seems that the effect of solvent on rate constant involves
hydrogen-bonding, electrostatic and non-electrostatic forces, any one of which may be dominant in a given set of conditions. Consequently it does not seem likely that any single expression involving one physical property of the solvent can represent the solvent effects of an entire range of solvents.
Diethylether, dried over calcium chloride, was distilled and stored over sodium wire.

A.R. toluene was distilled (b.p. 110°) and stored over sodium wire.

Other solvents were distilled, a flat-boiling fraction being collected.

Liquid materials for kinetic study were stored under nitrogen in the dark.

Gas-liquid chromatography was performed on a Pye-Argon instrument, equipped with an ionisation detector. The conditions for analysis, unless otherwise stated, were:

- Column: 10% silicone on Celite (109-125 mesh)
- Temperature: 100°
- Flow rate: 56 ml./min.
- Cylinder Pressure: 9.5 lb./sq'
- Detector voltage: 1750 V.
- Attenuation: x 10
- Sensitivity: x 10
- Sample size: 0.1 µl.

Infrared spectra were recorded on a Grubb-Parsons instrument type GS 2A.

Microanalyses were by Dr. Alfred Berhardt, Mülheim, W. Germany.

M.p.'s are corrected, b.p.'s uncorrected.
p-Cyanobenzylchloride [58]

In a three-necked flask, carrying gas-inlet tube, thermometer pocket and reflux condenser was placed p-tolunitrile (b.p. 102°/18 mm., 171.5 g.). The flask was illuminated by a 500-watt, tungsten-filament lamp and the tolnitrile heated to 120°. Dry chlorine gas was passed into the liquid, whilst the temperature was maintained at 120-130°. Much hydrogen chloride was evolved. After 6 hours an increase in weight of 49 g. was noted. The hot liquid was filtered through a glass wool pad from a small amount of solid material into a dish, and allowed to solidify. After cooling, the crude product was twice triturated with ice-cold ethanol (100 ml.) and filtered. The solid (114 g.), recrystallised from dry ether, gave white needles of p-cyanobenzylchloride (105 g., 51%, m.p. 79.5-80.5°). In a second preparation, p-tolunitrile (163.5 g.) similarly gave p-cyanobenzylchloride (100.5 g., m.p. 80-80.5°).

4-Chloromethylbenzaldehyde [59]

(a) Anhydrous Stannous chloride [60]

A.R. hydrated stannous chloride (226 g.) was added over 15 minutes to stirred acetic anhydride (190 ml.). The mixture became hot and was stirred for a further 1.5 hours, then filtered, the solid washed with dry ether (200 ml.) and the anhydrous stannous chloride vacuum dried over calcium chloride and sodium hydroxide.
(b) **Stephen Reduction**

The reaction was carried out with mechanical stirring under anhydrous conditions.

Anhydrous stannous chloride (80 g.) was suspended in dry ether (1400 ml.) in a three-necked flask carrying gas-inlet tube, stirrer and reflux condenser. The flask was cooled in an ice/salt/drikold bath and dry hydrogen chloride passed. After 15 minutes the solid had dissolved and a heavy, yellow oil appeared. After 5 hours a colourless, homogeneous solution was obtained. Hydrogen chloride was passed for a further 30 minutes, then a solution of p-cyanobenzylchloride (50 g.) in dry ether (400 ml.) was added to the cooled mixture over 45 minutes. The pale yellow solution was resaturated with hydrogen chloride (2 hours) and allowed to attain room temperature.

After standing 6 days, with occasional stirring, a white solid had separated. The yellow ethereal layer was decanted and the solid suspended in fresh ether (750 ml.). With rapid stirring, water (750 ml.) was added over 30 minutes, when the mixture had become clear. The aqueous layer was separated and extracted with ether. To the ethereal solutions 5% aqueous sodium carbonate solution was slowly added, producing a voluminous white precipitate. When alkaline the aqueous layer was separated and extracted with ether. The combined ethereal solutions were washed with water until neutral and dried (Na₂SO₄).
The ethereal solutions from two such Stephen reductions were combined and concentrated. On cooling, white needles were deposited. After filtration these (60 g.) were recrystallised from ether to give white clusters of needles of 4-chloromethylbenzaldehyde (47 g., 46%, m.p. 70.5-71.5°).

Similarly, p-cyanobenzylchloride (100 g.) gave 4-chloromethylbenzaldehyde (55.5 g., 54%, m.p. 70.5-71.5°).

4-Chloromethyl-a-methylbenzyl alcohol[61]

Throughout this Grignard reaction anhydrous conditions were maintained.

A solution of methyl bromide (63 g.) in dry ether (210 ml.) was slowly added to a suspension of dry magnesium turnings (12.5 g.) in ether (140 ml.) containing a crystal of iodine. When reaction started the mixture was stirred and allowed to reflux gently. After 45 minutes nearly all the magnesium had dissolved.

This ethereal methyl magnesium bromide solution was cooled in an ice/salt bath and a solution of 4-chloromethylbenzaldehyde (58.5 g.) in ether (850 ml.) was added, with stirring over 2 hours. The yellow solution was allowed to warm to room temperature and then poured into iced saturated aqueous ammonium chloride solution (600 ml.), containing a little ammonia. The aqueous layer was separated, extracted with ether and the ethereal solutions washed with water until neutral and dried (Na₂SO₄).
Evaporation of the ether gave a yellow, viscous liquid. This was vacuum distilled under nitrogen in three (15 ml.) portions from a Claisen flask fitted with a vacuum-jacketed side-arm. The combined distillates yielded 4-chloromethyl-a-methylbenzyl alcohol (30.6 g., 48%, b.p. 108°/0.7 mm. nD25 1.5517) as a colourless liquid which solidified on long storage at 5°.

4-Chloromethylstyrene [61]

4-Chloromethyl-a-methylbenzyl alcohol (10.25 g.) was added to tert-butylcatechol (0.10 g.) and powdered fused potassium bisulphate (0.10 g.) contained in a small Claisen flask maintained at 200-215°/43-45 mm., under a nitrogen atmosphere. A cloudy liquid slowly distilled. After addition of the carbinol and a further fifteen minutes, the pressure was reduced to 17 mm., when a little more distillate was collected. A solid residue (0.6 g.) remained in the flask. A total distillate of cloudy liquid (b.p.t 130-142°/43-45 mm., 9.10 g.) was obtained.

In similar dehydrations there was obtained:

From carbinol (9.97 g.), distillate (8.86 g.).
From " (10.12 g.), " (8.61 g.).

The combined distillates were dried (Na₂SO₄) and redistilled under nitrogen, yielding 4-chloromethylstyrene (14.8 g., 68%, b.p. 58-59°/0.35 mm., nD25 1.5720), a clear liquid.
On gas-liquid chromatographic analysis of the monomer, a chromatogram showing a single peak at retention time 22 minutes was obtained.

**Poly(4-chloromethylstyrene)**

(1) Azobis-isobutyronitrile (0.0335 g.) was dissolved in 4-chloromethylstyrene (6.99 g.) in a soft-glass tube, which, after being alternately evacuated and flushed with nitrogen, was then sealed. The tube was heated at 60° for 94 hours, when a hard glass had formed. After cooling, the tube was broken and the contents dissolved in hot benzene (150 ml.). The solution was filtered and run into rapidly stirred methanol (1500 ml.). The precipitated polymer was filtered, washed with methanol and dried at 15 mm. over calcium chloride and paraffin wax. The white poly(4-chloromethylstyrene) (6.2 g., 89%) was further dried to constant weight at 0.1 mm., over phosphoric oxide, for analysis, viscosity measurements and kinetic work.

Found for polymerisation polymer (P.I): Cl 22.56, 22.68, calc. for C,H,Cl 23.23%.

Similarly:

(2) Monomer (6.96 g.) with azobis-isobutyronitrile (0.107 g.) heated at 70° for 23 hours gave a highly viscous syrup from which polymer (P.II) (4.4 g., 63%), Cl 22.85, 22.76 was obtained.
(3) Monomer (4.07 g.) with azobis-isobutyronitrile (0.043 g.) heated at 65° for 90 minutes gave a rubbery solid, which yielded polymer (P.III) (2.28 g., 56%), Cl 22.41, 22.44.

The final polymer was in each instance a white fibrous or powdery solid.

(4) A copolymer of styrene/4-chloromethylstyrene, supplied by Mr. N.S. Salomons, had Cl 10.44, 10.53, Calc. for C\textsubscript{8}H\textsubscript{8}C\textsubscript{6}H\textsubscript{4}Cl, copolymerised in the molar ratio 1.76:1, Cl 10.55%.

Logarithmic Viscosity Numbers and Molecular Weights of the Polymers

P.I. - P.III.

The flow times of 1% toluene solutions of the polymers were measured at 25 ± 0.02°, in an Ostwald viscometer, type B.S.188. Determinations were carried out in duplicate (except for polymer P.III). The flow times of the solutions of polymer P.I. decreased with time, falling about 0.7% after 1 day and did not reach a steady value even after 10 days. For these solutions the initial flow times were used in the calculations. The other polymer solution flow times did not fall.

The flow time of solvent toluene was measured before and after a series of determinations.

The logarithmic viscosity number was calculated from the relation:

$$\frac{[\ln(\eta/\eta_0)]}{c} = \frac{2.303}{c} \left[ \log_{10}(\text{flow time solution}) - \log_{10}(\text{flow time solvent}) \right]$$
where \( c \) is the concentration of solute in grams per 100 ml. of solution.

The intrinsic viscosity \([\eta]\) was calculated using Kraemer's equation

\[
\frac{\ln(\eta/\eta_0)}{c} = [\eta] - k_2[\eta]^2 c.
\]

\( k_2 \) being a constant for the particular solvent/polymer system, related to the Huggin's constant \( k_1 \) by

\[ k_1 + k_2 = 0.5 \]

The value \( k_1 = 0.38 \), given by Fox and Flory [62] for polystyrene in toluene was used, since the Huggin's constant for poly(4-chloromethylstyrene) is not known.

Approximate values of the viscosity average molecular weights \( \bar{M}_v \) were calculated from the relation:

\[ [\eta] = k \bar{M}_v^\alpha \]

Again the values of the constants used, \( k = 1.16 \times 10^4 \) and \( \alpha = 0.72 \) (quoted by Green [63]) were those determined for polystyrene in toluene.
TABLE 3

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solution Concentration (c)</th>
<th>Mean Flow Time (sec.)</th>
<th>Logarithmic Viscosity Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.I.</td>
<td>(1) 1.002</td>
<td>264.0 (Initially)</td>
<td>0.619 (Initially)</td>
</tr>
<tr>
<td></td>
<td>1.002</td>
<td>249.9 After 4 mos.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(2) 1.002</td>
<td>264.1 (Initially)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.002</td>
<td>251.9 After 4 mos.</td>
<td></td>
</tr>
<tr>
<td>P.II.</td>
<td>1.001</td>
<td>165.7</td>
<td>0.154</td>
</tr>
<tr>
<td></td>
<td>1.001</td>
<td>166.0</td>
<td></td>
</tr>
<tr>
<td>P.III.</td>
<td>1.000</td>
<td>169.2</td>
<td>0.174</td>
</tr>
</tbody>
</table>

The flow time of solvent toluene was 142.0 secs.

TABLE 4

<table>
<thead>
<tr>
<th>Polymer</th>
<th>[η]</th>
<th>M_N</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.I.</td>
<td>0.674</td>
<td>169,000</td>
</tr>
<tr>
<td>P.II.</td>
<td>0.159</td>
<td>22,000</td>
</tr>
<tr>
<td>P.III.</td>
<td>0.178</td>
<td>27,000</td>
</tr>
</tbody>
</table>
Polystyrene

(1) Styrene was washed three times with 2N sodium hydroxide to remove inhibitor (quinol). After being washed with water until neutral, it was dried (Na$_2$SO$_4$), and distilled under nitrogen; it had b.p. 56°/28 mm.

Purified styrene (140 g.) was dissolved in xylene (170 ml.) and dried benzoyl peroxide (0.571 g.) added. The container, a screw-top bottle, was purged with nitrogen, capped and placed in a thermostatted oven at 23°. The temperature was raised to 81° in 30 minutes. After 24 hours at 81° the bottle was removed and the viscous contents diluted with xylene (180 ml.). This solution was added slowly to rapidly stirred methanol (3.5 l.), the resulting granular precipitate filtered off, washed with methanol and vacuum dried over calcium chloride and paraffin wax. The polymer (AI) (95.5 g., 68%) was further dried (over P$_2$O$_5$ at 15 mm.) to constant weight for viscosity measurements.

Similarly:

(2) Styrene (41 g.) and benzoyl peroxide (0.200 g.) in xylene (60 ml.) gave polymer (A.II) (32.9 g., 80%).

(3) Styrene (40 g.) and benzoyl peroxide (0.800 g.) gave polymer (A.III) (37 g., 92%).

Viscosity measurements on 1% toluene solutions gave the logarithmic viscosity numbers and molecular weights, by the procedure described above (pp. 48-49). The results obtained are shown in Tables 5 and 6.
### TABLE 5

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solution concentration (c)</th>
<th>Mean flow time (sec.)</th>
<th>Logarithmic Viscosity Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.I.</td>
<td>1.000</td>
<td>227.6&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.301</td>
</tr>
<tr>
<td>A.I.</td>
<td>1.003</td>
<td>227.7</td>
<td></td>
</tr>
<tr>
<td>A.II.</td>
<td>1.000</td>
<td>221.2</td>
<td>0.272</td>
</tr>
<tr>
<td>A.II</td>
<td>1.000</td>
<td>221.4</td>
<td></td>
</tr>
<tr>
<td>A.III</td>
<td>1.008</td>
<td>162.5&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.133</td>
</tr>
<tr>
<td>A.III</td>
<td>1.000</td>
<td>162.5</td>
<td></td>
</tr>
</tbody>
</table>

Flow time of solvent toluene (a) 168.6 (b) 142.0 sec.

### TABLE 6

<table>
<thead>
<tr>
<th>Polymer</th>
<th>[η]</th>
<th>$\bar{M}_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.I.</td>
<td>0.308</td>
<td>57,000</td>
</tr>
<tr>
<td>A.II.</td>
<td>0.281</td>
<td>50,100</td>
</tr>
<tr>
<td>A.III.</td>
<td>0.136</td>
<td>18,300</td>
</tr>
</tbody>
</table>
Chloromethylated Polystyrene

1. The reaction was carried out with mechanical stirring, under anhydrous conditions at a temperature of 22-25°C.

Polystyrene (AIII, 10.4 g.) was dissolved in chloromethylmethyl ether (138 g.). To the pale yellow solution powdered, freshly fused zinc chloride (43.2 g.) was added in portions of 10.8 g. at 20 minute intervals. Most of the zinc chloride dissolved and the mixture turned red-brown. After a further 2 hours a 1:1 mixture of dioxan:water (140 ml.) was slowly added, when a sticky mass separated. From the now bleached reaction mixture the polymer was extracted with benzene (70 ml.), the extract washed with water (6 x 50 ml.) and finally run slowly into rapidly stirred industrial methylated spirit (750 ml.). The precipitated polymer was filtered off, washed well with methylated spirit and reprecipitated by addition of its benzene solution (70 ml.) to methanol (700 ml.). After being washed with methanol (washings now chloride-free) the polymer, a pale yellow powder, was dried (60°/13 mm.) for 1 hour in a rotating flask. Chloromethylated polystyrene (SI) (12.0 g., 79%) was further dried (20°/10 mm.) to constant weight over calcium chloride, paraffin wax and P₂O₅.

Found: Cl 24.10, 24.22; Calc. for C₂₇H₃₅C₆Cl₂ 23.23%; Calc. for Chloromethylated polystyrene containing 5.60% di(chloromethyl) mer units, Cl 24.13%.
Similarly:

Polystyrene (AI, 36.4 g.) at reaction temperature 17-19° gave chloromethylated polystyrene (SII) (43.5 g., 82%).

Found: Cl 24.05, 24.21.

The logarithmic viscosity numbers and molecular weights were determined from viscosity measurements carried out in 1% toluene solution, as previously described.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solution concentration (c)</th>
<th>Mean Flow time (Sec.)</th>
<th>Logarithmic Viscosity Number</th>
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<tr>
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<tr>
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<td>224.1</td>
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<tr>
<td>SII</td>
<td>1.001</td>
<td>168.7</td>
<td>223.9</td>
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</table>

<table>
<thead>
<tr>
<th>Polymer</th>
<th>([\eta])</th>
<th>(M_V)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>15,200</td>
</tr>
<tr>
<td>SII</td>
<td>0.295</td>
<td>53,700</td>
</tr>
</tbody>
</table>
Pyrolysis of Chloromethylated Polystyrene

Chloromethylated polystyrene (SII, 3.20 g.) was placed in a glass bulb, connected to an air condenser. The bulb was heated strongly in a bunsen flame for 15 minutes and a dark brown distillate (1.2 g.) collected. Much hydrogen chloride was evolved and much carbon residue remained. The pyrolysate, redistilled, gave a clear, pale yellow liquid (b.p. 50-60°/0.07 mm., 0.900 g.).

Gas-liquid chromatography of the product gave a chromatogram containing one large peak of the same retention time as 4-chloromethylstyrene, as the major component. This was closely preceded by a small, second peak of 14% area of the main peak. Several other small peaks at much lower retention times were also present.

In the chromatogram of a 1:1 mixture of 4-chloromethylstyrene:pyrolysate, the area of the second peak was reduced to 4% area of the main peak.

From a second, similar pyrolysis, the redistilled pyrolysate gave a chromatogram with the second peak 8% area at the main peak. The areas of peaks of lower retention times were also reduced (relative to the main peak) to about 1/4 area of those of the first experiment.
Halogen Substitution Reactions of Chloromethylated Polystyrene

(a) Attempted reaction with sodium sulphite

Chloromethylated polystyrene (3.05 g., 0.020 moles) was suspended in a 10% NaOH solution containing crystalline sodium sulphite (5.55 g., 0.022 moles). The mixture was stirred and heated on a steam bath for 4 hours, then in an oil bath (120°) for 4 hours. After hot filtration, the undissolved polymer was washed with water and dried. The recovered polymer (2.32 g.) did not contain sulphur.

The filtrate and washings were combined and evaporated to 20 ml. After ice-cooling, a faint white precipitate separated. The pH was adjusted to pH7 (with 2N HCl) and the mixture dialysed in a cellophane tube against running water. After 4 weeks the effluent gave no precipitate with barium chloride solution. The dialysis solution was evaporated, leaving only a minute amount of (<50 m.g.) pale yellow solid.

(b) Reaction with Triethylphosphite

A solution of chloromethylated polystyrene (3.050 g., 0.020 mole) in xylene (15 ml.) was refluxed for 14 hours with triethylphosphite (3.35 g., 0.020 mole, b.p. 159-161°). Evolved gases were condensed in an acetone/drikold trap as a volatile, colourless liquid (~1 ml.).

The reaction mixture was run slowly into stirred light petroleum (b.p. 40-60°, 200 ml.). The precipitated polymer was filtered off,
dissolved in xylene (30 ml.) and reprecipitated in light petroleum. The product, filtered off and washed with light petroleum, gave pale yellow nodules (3.19 g.).

This product (1.0 g.) dissolved in benzene (7 ml.) was reprecipitated in light petroleum (100 ml.) as a fine white powder (0.70 g.).

Found P 7.54, C_{13}H_{19}O_3P requires P 12.19%. A vinylbenzylchloride: vinylbenzyldiethylphosphonate copolymer containing mer units in the ratio 1:0.973 requires P 7.54%.

The infra-red spectrum (as KBr disc) showed bands, not present in the spectrum of chloromethylated polystyrene, at:

1055, 1170, 1250 cm⁻¹

Thomas and Chittenden [64], correlating results for many organophosphorus compounds, list the following characteristic infra-red group frequencies.

\[
\begin{align*}
P-O-(C)aliphatic & \quad 950-1055 \text{ cm}^{-1} \\
P-O-(C_2H_5) & \quad \sim 1190 \text{ cm}^{-1} \\
P = O & \quad 1140-1225 \text{ cm}^{-1}
\end{align*}
\]

(c) Attempted Hydrolysis of the Phosphonated Polymer

Phosphonated polymer (0.254 g.) was refluxed with concentrated hydrochloric acid (10 ml.) for 6 hours. After filtration and washing with water, the recovered polymer did not dissolve in N NaOH. After filtration
of this mixture, the filtrate yielded no precipitate on acidification with HCl.

(d) Reaction with Trimethylamine

Trimethylamine was distilled from acetic anhydride, through soda-lime towers and condensed directly into a dioxan:methanol mixture (40:60 v/v). The amine concentration of this solution was determined by titration against standard hydrochloric acid, using methyl red indicator.

Chloromethylated polystyrene (SII, 5.083 g., 0.033 moles) was dissolved in dioxan (23 ml.) and methanol (17.7 ml.) added. Addition of trimethylamine solution (3.80N, 13.15 ml., 0.050 mole) precipitated the polymer, but reaction was allowed to proceed by immersing the flask (closed with a soda-lime tube) in a thermostat at 25°. After a few hours addition of methanol (25 ml.) gave a homogeneous solution. After 4 days the highly viscous mixture was diluted with methanol, filtered (sinter glass) and the solvent and excess amine evaporated in a rotary film evaporator (70°, 20 mm.). After 1 hour the product (7.77 g.), containing entrained solvent, was collected as pale yellow scales.

The polymer was ground to a powder and dried, in portions, over P2O5 at 80°/2 mm., to constant weight. It is very hygroscopic.

The chloride ion content was determined. Dry polymer (~0.1 g.) was accurately weighed and dissolved in water (100 ml.). The solution
was titrated against 0.100N silver nitrate, using dichlorfluorescein as indicator.

Found Cl\textsuperscript{-} 15.66, 15.31, 15.64; Calc. for poly(vinylbenzyltrimethylammonium chloride) containing 5.60\% di(quaternary ammonium) mer units: Cl 17.05\%.

Calc. for polymer in which 85.9\% mer units are quaternised, Cl 15.50\%.

The logarithmic viscosity number was calculated from viscosity measurements carried out on 1\% aqueous solution, as previously described. The flow-time did not reach a steady value; it fell by 9.0 seconds over a period of 4 days.

Initially: Mean Flow-time solution 1062.4 secs.

" water 235.2 secs.

Whence \[\ln\left(\frac{\eta}{\eta_0}\right)/c = 1.51\]

(e) Conversion of Quaternary Chloride to Hydroxide

All operations were carried out under an atmosphere of nitrogen.

Poly-(quaternary ammonium chloride) (2.228 g., 0.0105 mole) was dissolved in boiled-out water (50 ml.). A slurry of silver oxide/water (derived from silver nitrate [2.214 g., 0.013 mole.]) was added and the mixture stirred, at 20\°C, for 1 hour, and centrifuged. The brown supernatant liquid was decanted from the residue, which, after treatment with
3N HNO₃ gave a white solid, weighed as AgCl after drying to constant weight.

Wt. AgCl 1.3523 g., corresponds to:

Found Cl 15.02% in the original quaternary chloride. [Compare volumetric value: Found Cl 15.52 (mean)].

After evaporation (rotary film evaporator, 20°/20 mm.) the centrifugate gave a dark brown solid, retaining much solvent water. This, dried to constant weight (70°/23 mm.) was analysed potentiometrically for hydroxide ion.

Dried hydroxide (0.1570 g.) was heated with 0.1047N HCl (25.00 ml.) at 80° for 20 minutes. The polymer turned to a light tan colour, swelled slightly but did not dissolve. After cooling, the excess HCl was titrated potentiometrically against 0.07028N NaOH solution to pH7. The pH drifted to lower values with time.

Found: 0.00309 g.– equivalents OH, per gram.

Calc. for polymer in which 85.9% mer units are quaternary ammonium hydroxide, 0.00585 g.– equivalents per gram.

(f) Reaction with Triethylamine

Chloromethylated polystyrene (SII, 5.083 g., 0.033 mole) was dissolved in dioxan (20 ml.) and methanol (10 ml.) and triethylamine (5.00 ml., 0.037 mole) added. After 1 week at room temperature only slight precipitation had occurred. Addition of methanol (10 ml.) gave a
homogeneous solution. After a further 4 weeks triethylamine (2.50 ml., total 0.056 mole) was added and the solution heated at 60° for 17 hours. The viscous solution was then diluted with methanol (50 ml.), filtered (glass sinter) and the solvent and excess amine evaporated (rotary film evaporator, 70°/24 mm.). After further drying, pale yellow scales (9.17 g.) were obtained.

The product, containing entrained solvent, was dried to constant weight (75°/25 mm.).

Volumetric analysis for chloride ion gave erratic results. A gravimetric method was developed.

A weighed portion of dried polymer (~0.5 g.) was dissolved in water (50 ml.), concentrated nitric acid (5 ml.) and excess silver nitrate solution were added. After standing overnight the mixture was centrifuged, the silver chloride residue washed with 3N HNO₃, dried to constant weight and weighed.


Calculated for poly-(vinylbenzyltriethylammonium chloride) containing 5.60% di(quaternary ammonium) mer units: Cl 13.91%.

Calculated for polymer in which 78.14% of the chloromethyl groups are quaternised: Cl 12.33%.

Determination of the flow time of a 1% aqueous solution gave the logarithmic viscosity number as previously described. The flow time fell by 4.5% three days after making up and did not reach a steady value,
falling over a period of two weeks.

Initially: Mean Flow time solution 1105.2 secs.

" " water 235.2 secs.

Whence \( \ln(\frac{\tau}{\tau_0})/c = 1.34 \)

An aqueous solution of the quaternary hydroxide was prepared as described for the trimethylamine - quaternised polymer. From the weight of silver chloride obtained:

Found Cl 12.51%, in the original quaternary chloride [Compare gravimetric value, above].

Mr. G. Morley, of these laboratories, has found that clear, pale yellow aqueous solutions of the quaternary hydroxide, readily titrable potentiometrically, may be obtained from the quaternary chloride by use of the ion exchange resin Amberlite IRA-401.

\((g)\) Reaction with Tri-\(n\)-propylamine

The reaction was carried out as described for triethylamine, using chloromethylated polystyrene (SII 5.083 g, 0.033 mole) and tri-\(n\)-propylamine (10 ml.), the mixture being heated at 55° for 48 hours.

Analysed volumetrically, using silver nitrate and dichlorfluorescein indicator, as previously described, there was obtained:

Found Cl 11.21, 11.20
Calc. for poly-(vinylbenzyltri-n-propylammonium chloride) containing 5.60% di(quaternary ammonium) mer units, Cl 11.97%.

Calc. for polymer in which 89.91% of the chloromethyl groups are quaternised: Cl 11.21%.

Determination of the flow time of a 1% aqueous solution gave the logarithmic viscosity number as previously described.

Mean flow time solution 618.4 sec.
  " " " water  196.0 sec.

Whence \( \ln(\eta/\eta_0)/c = 1.15 \)
Purification of Kinetic Materials

Benzyl Alcohol

Benzyl alcohol (G.P.R.) was dried ($K_2CO_3$), distilled, refluxed over calcium metal for 2 hours and distilled from the calcium. The fraction collected had b.p. 203.5°, $n_D^{25}$ 1.5378.

Its gas-liquid chromatogram contained only one peak.

The peroxide content was determined as follows [45]

Benzyl alcohol (4 ml.), acetic anhydride (10 ml.) and sodium iodide (1 g.) were shaken together in a stoppered flask, and allowed to stand for 10 minutes. Water (100 ml.) was then added and the liberated iodine titrated against 0.102N $Na_2S_2O_3$.

Triethylamine

Triethylamine was dried (KOH) and distilled from sodium through a 30 cm. lagged Vigreux column. The fraction collected had b.p. 89.0° and $n_D^{25}$ 1.3979.

On gas-liquid chromatography (10% silicone on Celite column, at 38°) a chromatogram containing one peak was obtained.

Benzyl Chloride

It (G.P.R.) was dried ($Na_2SO_4$) and twice distilled under nitrogen through a 30 cm. lagged Vigreux column. The fraction collected had b.p. 65.4 - 65.8°/12.5 mm. and $n_D^{25}$ 1.5364.
Its gas-liquid chromatogram contained two peaks. The second peak was shown to be due to an impurity (<1%) having the same retention time as the three chlorotoluenes, under the conditions used.

**Cuminy1 Chloride [66]**

Redistilled cuminyl alcohol (b.p. 145-147°/31-33 mm., n_25^D 1.5188) was refluxed with concentrated hydrochloric acid for 2 hours, with stirring. After cooling ether (140 ml.) was added, then separated, washed with aqueous sodium bicarbonate, then with water until the washings were neutral. The solution was dried (Na_2SO_4), the ether evaporated and the residue twice distilled through a 30 cm. lagged Vigreux column. Cuminyl chloride had b.p. 110°/15 mm. and n_25^D 1.5213.

Its gas-liquid chromatogram showed a main peak, and the presence of a small amount of an impurity (~2%).

**Dimethylformamide [67]**

Dimethylformamide (800 ml.) was mixed with benzene [(80 ml.) dried over calcium hydride]. The benzene/benzene-water azeotrope, was distilled off, the temperature at the stillhead not exceeding 81°, through a 30 cm. lagged Vigreux column. The residue was shaken with magnesium sulphate (previously heated for 6 hours at 500°) for 2 days. After filtration,
careful fractionation through a 90 cm. vacuum-jacketed column packed with
Fenske helices, gave dimethylformamide b.p. 48°/14 mm. and nD 1.4274.
It was stored in a wash bottle under nitrogen and dispensed by application
of nitrogen pressure.

Tetramethylenesulphone (sulpholane)

The pale yellow commercial product was twice distilled under
nitrogen, a forerun of 20% (which contains any water initially present)
being rejected each time.

The product, a clear, colourless liquid, readily solidified at room
temperature. It had b.p. 106 - 108°/45 mm.
The Kinetics of Quaternisation in Benzyl Alcohol

The kinetics of reaction of the following chloro-compounds, with triethylamine at 75°, were determined:

Benzyl Chloride
Cuminyl Chloride

3 specimens of poly(4-chloromethylstyrene), polymers PI-PIII, of different molecular weights.

2 specimens of chloromethylated polystyrene, polymers SI and SII, of different molecular weights.

A copolymer of styrene: 4-chloromethylstyrene, copolymerised in the ratio 1.76:1.

Polymer, dried to constant weight, or liquid chloromethyl compound (2.0 millimoles) was weighed into a 25 ml. standard flask and benzyl alcohol (15 ml.) added. In the case of the polymers, dissolution was allowed to occur overnight. Then triethylamine (4.0 millimole) was weighed in. Benzyl alcohol was added to the mark and, after shaking, 2 ml. samples were withdrawn by syringe and dispensed into drawn-out soft-glass tubes, which were then sealed under nitrogen. The tubes were immersed in a thermostat at 75±0.02° (zero time).

At appropriate intervals a tube was removed (time 't') and rapidly cooled in an acetone/drikold mixture to quench reaction. After being washed, the tube was crushed under 3N nitric acid (5 ml.) and 0.0200N silver nitrate (10.00 ml.) added. The mixture was shaken for 1 minute and the
excess silver ion titrated against standard thiocyanate, with ferric alum (1 ml. saturated solution) as indicator. From the titre, the chloride ion concentration \(x\) in the reaction mixture at time \(t\) was calculated.

From additional kinetic runs the following points were established:

(1) The analysis method was satisfactory: using standard sodium chloride solution, correct titres were obtained, provided the analysis mixtures were well shaken, the end-point remaining for at least one minute.

(2) Negligible reaction occurred between solvent and chlorocompound.

Samples from runs conducted in the absence of amine were titrated for chloride ion. The results showed a small but erratic production of chloride ion. This was ignored since it was <1% of the initial concentration of chlorocompound.

(3) No reaction occurred between solvent and amine. In a run conducted in the absence of chlorocompound, the amine concentration was constant over the time of the longest kinetic run.

(4) The production of chloride ion and disappearance of amine were equivalent. In a run with benzyl chloride two tubes were withdrawn at each time interval. The chloride ion concentration in one equalled the reduction of amine concentration in the other.

From the values of \(x\), values of:

\[
\frac{2.303}{b-a} \cdot \log_{10} \left( \frac{a(b-x)}{b(a-x)} \right) = f(x)
\]
were calculated, \(a\) and \(b\) being the initial concentrations of chlorocompound and amine respectively, calculated from the weights taken in each run.

Since \(k_2, t = f(x)\) is the integrated form of the second order rate-equation, plots of \(f(x)\) against time have slope \(k_2\) (the second order rate constant). Such graphs were drawn for each kinetic run and \(k_2\) determined.

The values \(a, b\) and \(x\) obtained relate to concentrations in a known volume of solvent at room temperature (taken as 20°, an average), whereas the concentrations during the run were less due to solvent expansion between 20° and 75°. The values of the rate constants \((k_2)\) obtained from the second-order plots were corrected for this solvent expansion, by determining the densities of benzyl alcohol at 20° and 75°.

The results and graphs are tabulated on pp. 71-86.

**Kinetics of Quaternisation in Dimethylformamide**

The procedure was as described for benzyl alcohol runs, with minor modifications in the method of analysis.

Before titration, to the analysis mixture was added nitrobenzene (2 ml.) and the whole shaken for one minute.

For the polymer runs, addition of A.R. potassium nitrate (5 g.) to the analysis mixture gave more stable end-points.

The extent of reaction between chlorocompound and solvent was found to be less than 2% for benzyl chloride and less than 1% for
poly(4-chloromethylstyrene), after heating at 75° for 7 hours. No
correction was applied.

The results and graphs appear on pp. 85–89.

Kinetics of Quaternisation in Sulpholane

The procedure was as described for dimethyl-formamide runs, except
that during the preparation of reaction samples, the reaction mixture was
maintained at 25–35° to prevent solidification. Consequently solvent
expansion was calculated for the range 30–75°.

The results and graphs appear on pp. 90–92.

Note on Graphs I – XII

In all the second order plots the origin for each run has been
displaced successively by 20 minutes of the abscissa from left to right.
Reaction between Benzyl Chloride and Triethylamine in Benzyl Alcohol

**TABLE 7**

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>(i) $a = 0.07778 \text{ mole.l}^{-1}$</th>
<th>(ii) $a = 0.07633 \text{ mole.l}^{-1}$</th>
<th>(iii) $a = 0.07551 \text{ mole.l}^{-1}$</th>
<th>(iv) $a = 0.07766 \text{ mole.l}^{-1}$</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>$100x$ mole.l$^{-1}$</td>
<td>$f(x)$</td>
<td>$100x$ mole.l$^{-1}$</td>
<td>$f(x)$</td>
</tr>
<tr>
<td>15</td>
<td>0.720</td>
<td>0.7103</td>
<td>0.720</td>
<td>0.719</td>
</tr>
<tr>
<td>25</td>
<td>1.190</td>
<td>1.245</td>
<td>1.180</td>
<td>1.248</td>
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<td>40</td>
<td>1.820</td>
<td>2.052</td>
<td>1.775</td>
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<td>3.685</td>
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<td>235</td>
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</table>
Graph I

Quaternization of Benzyl Chloride in Benzyl Alcohol
Reaction between Cuminal Chloride and Triethylamine in Benzyl Alcohol

### TABLE 8

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>(i) $a = 0.06233 \text{ mole.l}^{-1}$</th>
<th>$b = 0.1421 \text{ mole.l}^{-1}$</th>
<th>(iii) $a = 0.06955 \text{ mole.l}^{-1}$</th>
<th>$b = 0.1425 \text{ mole.l}^{-1}$</th>
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</thead>
<tbody>
<tr>
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<td>$100 x f(x)$</td>
<td>$100 x f(x)$</td>
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<td>0.695</td>
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<td>0.705</td>
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### Additional Table

<table>
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<tr>
<th>Time (min.)</th>
<th>(iii) $a = 0.06016 \text{ mole.l}^{-1}$</th>
<th>$b = 0.1421 \text{ mole.l}^{-1}$</th>
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<td>70</td>
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<td>140</td>
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<td>5.160</td>
<td>18.29</td>
</tr>
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</table>
Graph II

Quaternization of Cuminyl Chloride in Benzyl Alcohol

F(x)

Time (min.)
Reaction between Poly(4-chloromethylestyrene) (PI) and Triethylamine in Benzyl Alcohol

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>(i) ( a = 0.07261 \text{ mole}\cdot l^{-1} )</th>
<th>(ii) ( a = 0.07586 \text{ mole}\cdot l^{-1} )</th>
<th>(iii) ( a = 0.07482 \text{ mole}\cdot l^{-1} )</th>
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</thead>
<tbody>
<tr>
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<td>( b = 0.1480 \text{ mole}\cdot l^{-1} )</td>
<td>( b = 0.1455 \text{ mole}\cdot l^{-1} )</td>
<td>( b = 0.1469 \text{ mole}\cdot l^{-1} )</td>
</tr>
<tr>
<td>5</td>
<td>0.300 0.310</td>
<td>0.310 0.330</td>
<td>0.315 0.294</td>
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<tr>
<td>10</td>
<td>0.695 0.687</td>
<td>0.735 0.755</td>
<td>0.695 0.681</td>
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<tr>
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Reaction between Poly(4-chloromethylstyrene) (PII) and Triethylamine in Benzyl Alcohol

**TABLE 10**

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<th>Time (min.)</th>
<th>(i)  $a = 0.07494 \text{ mole} \cdot \text{l}^{-1}$</th>
<th>$b = 0.1468 \text{ mole} \cdot \text{l}^{-1}$</th>
<th>Time (min.)</th>
<th>(ii)  $a = 0.07614 \text{ mole} \cdot \text{l}^{-1}$</th>
<th>$b = 0.1462 \text{ mole} \cdot \text{l}^{-1}$</th>
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<td>$100 \times \text{ mole} \cdot \text{l}^{-1}$</td>
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<td>$100 \times \text{ mole} \cdot \text{l}^{-1}$</td>
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Reaction between Poly(4-chloromethylstyrene) (P III) and Triethylamine in Benzyl Alcohol

TABLE 1

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<th>Time (min.)</th>
<th>(i) a = 0.08139 mole.l⁻¹</th>
<th>Time (min.)</th>
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<td>b = 0.1409 mole.l⁻¹</td>
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<td>100 x mole.l⁻¹</td>
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<td>10</td>
<td>0.800</td>
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<th>(iv) a = 0.07914 mole.l⁻¹</th>
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<td>100 x mole.l⁻¹</td>
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Graph Y

Quaternization of Poly(4-chloromethylstyrene) (P4CMS) in Benzyl Alcohol

x(t)
Reaction between Chloromethylated Polystyrene (SI) and Triethylamine in Benzyl Alcohol

### Table 12

<table>
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<th>Time (min.)</th>
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<td>0.576</td>
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<td>0.942</td>
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<td>0.959</td>
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Graph VI
Quaternization of Chloromethylated Polystyrene (SI) in Benzyl Alcohol.

Time (min.)

$F(x)$
Reaction between Chloromethylated Polystyrene (SII) and Triethylamine in Benzyl Alcohol

TABLE 13

<table>
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<th>Time (min.)</th>
<th>(i) $a = 0.07962\ \text{mole.l}^{-1}$</th>
<th>(ii) $a = 0.07991\ \text{mole.l}^{-1}$</th>
<th>(iii) $a = 0.08056\ \text{mole.l}^{-1}$</th>
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<td>$b = 0.1457\ \text{mole.l}^{-1}$</td>
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<td>$100 \times f(x)$</td>
<td>$100 \times f(x)$</td>
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<tr>
<td>5</td>
<td>0.310</td>
<td>0.303</td>
<td>0.320</td>
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<tr>
<td>10</td>
<td>0.655</td>
<td>0.628</td>
<td>0.655</td>
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<td>0.950</td>
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Graph VII

Quaternization of Chloromethylated Polystyrene (SII) in Benzyl alcohol.

(iii) (i) (ii)

Time (min.)
Reaction between Polystyrene: poly(4-chloromethylstyrene) copolymer and Triethylamine in Benzyl Alcohol

### TABLE 14

<table>
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<th>Time (min.)</th>
<th>(i) $a = 0.07452 \text{ mole.l}^{-1}$</th>
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<td>$\text{mole.l}^{-1}$</td>
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<td>1.670</td>
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Reaction between Benzyl Chloride and Triethylamine in Dimethylformamide

### TABLE 15

<table>
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<th>Time (min.)</th>
<th>(i) $a = 0.07640 \text{ mole.l}^{-1}$</th>
<th>(ii) $a = 0.07676 \text{ mole.l}^{-1}$</th>
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<td>$\text{mole.l}^{-1}$</td>
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Graph VIII

Reaction between Copolymer and Triethylamine in Benzyl Alcohol

Time (min.)
Reaction between Poly(4-chloromethylstyrene) and Triethylamine

in Dimethylformamide

**TABLE 16**

<table>
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<th>Time (min.)</th>
<th>(i) ( a = 0.07654 \text{ mole.}^{-1} )</th>
<th>(ii) ( a = 0.07603 \text{ mole.}^{-1} )</th>
<th>(iii) ( a = 0.07757 \text{ mole.}^{-1} )</th>
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<td>( f(x) )</td>
<td>( 100x ) ( \text{mole.}^{-1} )</td>
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<tr>
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<td>0.350</td>
<td>0.320</td>
<td>0.335</td>
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<table>
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<th>( b = 0.1530 \text{ mole.}^{-1} )</th>
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<td>( f(x) )</td>
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<td>80</td>
<td>2.350</td>
<td>2.576</td>
<td></td>
</tr>
<tr>
<td>130</td>
<td>3.370</td>
<td>4.259</td>
<td></td>
</tr>
<tr>
<td>205</td>
<td>4.555</td>
<td>7.046</td>
<td></td>
</tr>
<tr>
<td>302</td>
<td>5.415</td>
<td>10.08</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>6.045</td>
<td>13.37</td>
<td></td>
</tr>
<tr>
<td>544</td>
<td>6.485</td>
<td>16.65</td>
<td></td>
</tr>
</tbody>
</table>
Graph X

Quaternization of Poly(4-chloromethylstyrene) (PI) in Dimethylformamide

Time (min.)
Reaction between Poly(4-chloromethylstyrene) (PI) and Triethylamine in Sulpholane

**TABLE 17**

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>(i) $a = 0.07716 \text{ mole.} l^{-1}$.</th>
<th>(ii) $a = 0.07896 \text{ mole.} l^{-1}$.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$b = 0.1461 \text{ mole.} l^{-1}$</td>
<td>$b = 0.1453 \text{ mole.} l^{-1}$</td>
</tr>
<tr>
<td>$100 x$ mole. $l^{-1}$.</td>
<td>$f(x)$</td>
<td>$100 x$ mole. $l^{-1}$.</td>
</tr>
<tr>
<td>5</td>
<td>1.940</td>
<td>2.135</td>
</tr>
<tr>
<td>10</td>
<td>2.320</td>
<td>2.698</td>
</tr>
<tr>
<td>15</td>
<td>2.890</td>
<td>3.62</td>
</tr>
<tr>
<td>25</td>
<td>3.865</td>
<td>5.66</td>
</tr>
<tr>
<td>35</td>
<td>4.460</td>
<td>7.58</td>
</tr>
<tr>
<td>50</td>
<td>5.050</td>
<td>9.27</td>
</tr>
<tr>
<td>70</td>
<td>5.645</td>
<td>11.99</td>
</tr>
<tr>
<td>100</td>
<td>6.265</td>
<td>16.12</td>
</tr>
<tr>
<td>150</td>
<td>6.860</td>
<td>22.72</td>
</tr>
</tbody>
</table>

Reaction between Benzyl Chloride and Triethylamine in Sulpholane

**TABLE 18**

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>(i) $a = 0.07836 \text{ mole.} l^{-1}$.</th>
<th>(ii) $a = 0.07898 \text{ mole.} l^{-1}$.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$b = 0.1442 \text{ mole.} l^{-1}$</td>
<td>$b = 0.1529 \text{ mole.} l^{-1}$</td>
</tr>
<tr>
<td>$100 x$ mole. $l^{-1}$.</td>
<td>$f(x)$</td>
<td>$100 x$ mole. $l^{-1}$.</td>
</tr>
<tr>
<td>5</td>
<td>0.955</td>
<td>0.933</td>
</tr>
<tr>
<td>10</td>
<td>1.615</td>
<td>1.700</td>
</tr>
<tr>
<td>15</td>
<td>1.975</td>
<td>2.172</td>
</tr>
<tr>
<td>25</td>
<td>2.815</td>
<td>3.462</td>
</tr>
<tr>
<td>40</td>
<td>3.750</td>
<td>5.323</td>
</tr>
<tr>
<td>70</td>
<td>4.985</td>
<td>8.913</td>
</tr>
<tr>
<td>110</td>
<td>6.025</td>
<td>14.03</td>
</tr>
<tr>
<td>170</td>
<td>6.875</td>
<td>22.04</td>
</tr>
</tbody>
</table>
Graph XI

Quaternization of Poly(4-chloromethylstyrene) (PI) in Sulpholane

Time (min.)
Graph XI
Quaternization of Benzyl Chloride in Sulpholane
DISCUSSION
Preparation of Polymers

Early work on the synthesis of chloromethylstyrenes did not lead to the pure 4-chloromethylstyrene.

Cerny and Wichterle [68] chloromethylated styrene but their product, on conversion to the aldehyde by the Sommelet reaction, only gave cinnamaldehyde. Hence chloromethylation had occurred only at the styrene 1-carbon atom.

Clarke, Hammerschlag and Highlands [69] described a synthesis of chloromethylstyrene in which ethylbenzene was chloromethylated, converted to chloromethylbromoethylbenzene by photobromination and finally dehydrobrominated. By a similar route Macmaster and Stowe [70] obtained a chloromethylstyrene. Chloromethylated ethylbenzene was photochlorinated to 3(chloromethyl)-α-chloroethylbenzene, which was dehydrochlorinated.

However, chloromethylation of alkylbenzenes is known to give a mixture of the o-, m- and p- substitution products. (see p. 99). The chloromethylstyrenes obtained by the last two methods consisted of mixtures of 30-40% o- and 60-70% p- isomers. The preparation of the pure p-isomer would therefore depend on the efficiency of a fractional separation in the reaction sequence. Jones [71] claimed to have prepared 4-chloromethylstyrene by fractional crystallisation of a chloromethylstyrene mixture obtained by the method of Macmaster and Stowe.

The synthesis of 4-chloromethylstyrene as the pure p-isomer has been achieved by Arcus and Salomons [61], and their method has been followed in
this work. During this reaction sequence, when treatment with aqueous solutions was required, mild conditions were maintained to minimise the possibility of hydrolysis of the chloromethyl side groups.

p-Tolunitrile was photochlorinated, as suggested by Barkenbus and Holtzclaw [58], at 120-130° until the theoretical quantity of chlorine had been absorbed. These conditions reduced the possibility of reaction beyond monochlorination.

The product, p-cyanobenzylchloride, subjected to the Stephen reaction, gave the aldimine stannichloride, which was hydrolysed to 4-chloromethylbenzaldehyde with ice-cold water.

Reaction between this aldehyde and methylmagnesium bromide gave the Grignard addition complex, which on decomposition yielded 4-chloromethyl-α-methylbenzyl alcohol.

This carbinol was dehydrated to 4-chloromethylstyrene by distillation from fused potassium bisulphate at 200-215°/43-45 mm.

The monomer gave only a single peak on gas-liquid chromatography and was inferred to be pure. It has been polymerised by the use of azobis-(isobutyronitrile) at 60-70°, as in the table below. The resulting polymers (PI, PII and PIII) were obtained as white, fibrous or powdery solids after precipitation from their benzene solutions on addition to methanol.

The polymers were characterised by determination of the logarithmic viscosity numbers of 1% solutions in toluene at 25°. Their limiting viscosity numbers were calculated using Kraemer's equation (equation 2 p. 17). Approximate values of the viscosity average molecular weights
Chloromethylation of Polystyrene

The possibility of introducing chloromethyl groups into the appropriate preformed polymer, polystyrene, has also been investigated.

The chloromethylation of aromatic hydrocarbons is well known and is a useful reaction in synthetic work since the reactive group is readily attacked by a variety of nucleophiles. The original method of Grassi and Maselli [72] used trioxymethylene and hydrochloric acid as reagent, with zinc chloride catalyst. Vavon and Bolle [73] introduced a homogeneous chloromethylation method, in which chloromethylmethyl ether was reagent. Generally, the reaction is assisted by a Lewis acid.

The application of the chloromethylation reaction to polystyrene type polymers is well known as the key step in the preparation of various anion-exchange resins, where polystyrene (usually cross-linked with divinylbenzene to ensure insolubility) is chloromethylated and the product...
treated with a primary, secondary or tertiary amine, to yield resins of various basic strengths.

Jones [74] first chloromethylated a non-cross-linked polystyrene, using chloromethylmethyl ether and zinc chloride catalyst. This method has the advantage that polystyrene, catalyst and chloromethylated polystyrene are soluble in the ether. The method used in this work is based on that of Jones.

Friedel-Crafts alkylation, also catalysed by chloromethylation catalysts, often leads to the production of diarylmethanes as a side product in the chloromethylation of aromatic hydrocarbons. In the case of polystyrene, alkylation would result in a polymer structure cross-linked by methylene bridges:

\[ +\text{CH}_2\text{ZnCl}_3 \rightarrow +\text{ZnCl}_2 + \text{HCl} \]

This is the result of chloromethylated benzene rings competing with the chloromethylmethyl ether for unreacted rings. Hence, dilution with
the ether minimises the cross-linking reaction. A sudden rise in viscosity, especially as complete monochloromethylation was approached, observed by Jones during his reactions, is evidence for the cross-linking reaction.

In the present work, in dilute ether solution, monochloromethylation was achieved with no evidence for the formation of cross-links. The polymer remained soluble throughout reaction and the product of both preparations had a logarithmic viscosity number (L.V.N.) close to that of its parent polystyrene:

<table>
<thead>
<tr>
<th>L.V.N. Polystyrene</th>
<th>L.V.N. Derived Chloromethylated Polystyrene</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.133</td>
<td>0.116</td>
</tr>
<tr>
<td>0.301</td>
<td>0.284</td>
</tr>
</tbody>
</table>

The successful preparation of poly(4-chloromethylstyrene) by chloromethylation of polystyrene requires substitution by one chloromethyl group per benzene ring in the para position. Although the product in two preparations had a chlorine content (24.13, 24.16%) close to that required for 100% monosubstitution (23.23%), not all chloromethyl groups can be assumed to be para. For the chloromethylation of alkylbenzenes by paraformaldehyde/HCl/ZnCl₂, Nazarov and Semenovsky [75] found the following isomer distributions:
Aromatic hydrocarbon | Isomer distribution in Chloromethylated Product
---|---
| x = | ortho | para |
| Ne | 51.7% | 48.3% |
| Et | 30 | 70 |
| i-Pr | 15 | 85 |
| t-Bu | 0 | 100 |

However, for chloromethylation with aqueous formaldehyde /HCl/ZnCl₂, Freeman [76] detected small amounts of meta substituted products by using a more accurate analytical technique:

<table>
<thead>
<tr>
<th>x</th>
<th>ortho</th>
<th>meta</th>
<th>para</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>45%</td>
<td>1%</td>
<td>54%</td>
</tr>
<tr>
<td>Et</td>
<td>29</td>
<td>2</td>
<td>69</td>
</tr>
<tr>
<td>i-Pr</td>
<td>12</td>
<td>3</td>
<td>85</td>
</tr>
<tr>
<td>t-Bu</td>
<td>0.1</td>
<td>6</td>
<td>94</td>
</tr>
</tbody>
</table>

The above isomer distribution data are typical of the directing influences of alkyl groups in an electrophilic substitution reaction. However, the exact mechanism and the attacking electrophile in chloromethylation reactions are not known for certain. In aqueous media (formaldehyde in aqueous acetic acid) Ogata and Okano [77] proposed that the attacking species was the hydroxymethyl cation:
Nazarov and Semenovsky [78] also came to the same conclusion, and established that under chloromethylating conditions the hydroxy group of benzyl alcohol is completely replaced by chlorine. Under the anhydrous conditions of chloromethylation by chloromethylmethyl ether it is possible that the protonated ether undergoes cleavage with the formation of a similar reactive species (the methoxymethyl cation) as under the previous conditions:

\[
\begin{align*}
\text{Cl} - \text{CH}_2\text{O-Me} & \xrightarrow{H} \text{Cl} - \text{CH}_2\text{O} + \text{Me} \\
\text{Cl} - \text{CH}_2\text{O-Me} & \xrightarrow{H} \text{Cl} - \text{CH}_2\text{O} + \text{Me} \\
\text{Cl} - \text{CH}_2\text{O-Me} & \xrightarrow{H} \text{Cl} - \text{CH}_2\text{O} + \text{Me} \\
\end{align*}
\]

It is more probable that the protonated chloromethylmethyl ether would undergo cleavage to give the chloromethyl cation as the electrophilic species, which then substitutes in the benzene molecule:

\[
\begin{align*}
\text{Cl} - \text{CH}_2\text{O-Me} & \xrightarrow{H} \text{Cl} - \text{CH}_2\text{O} + \text{Me} \\
\text{Cl} - \text{CH}_2\text{O-Me} & \xrightarrow{H} \text{Cl} - \text{CH}_2\text{O} + \text{Me} \\
\text{Cl} - \text{CH}_2\text{O-Me} & \xrightarrow{H} \text{Cl} - \text{CH}_2\text{O} + \text{Me} \\
\end{align*}
\]

However, such mechanisms are almost certainly simplifications of the processes involved in chloromethylation in the presence of zinc chloride, together with hydrochloric acid and methanol as reaction products.

From the above discussion we may expect that some ortho substitution
occurred during the chloromethylation of polystyrene. It is to be noted that the chlorine content of the chloromethylated polymers is somewhat higher than that for monosubstitution. The disubstituted groups probably contained the chloromethyl groups ortho and para to the main chain in each benzene ring. The amount of disubstitution was calculated in the following way. The product polymer contains groups of type A and B

\[ \text{In 100 polymer units, assume } (100-x) \text{ of type A and } x \text{ of type B, then:} \]

\[
\% \text{ Cl} = \frac{[(100-x) + 2x] \times 35.46 \times 100}{(100-x) \times (\text{Molecular wt. A}) + x \times (\text{Molecular wt. B})}
\]

\(x\) was found to be 5.6 for both chloromethylated polystyrenes, i.e. 5.6\% polymer side groups contained two chloromethyl groups.

However, the infrared spectra of chloromethylated polystyrene and poly(4-chloromethylstyrene) were identical. Therefore the majority of the monochloromethyl groups must have been present in the para position. Although the molecular environments of ortho and para benzene substituents are
similar it is expected that minor differences would exist between the spectrum of a polymer containing substantial amounts of both types of groups and that containing solely para groups.

In order further to assess the position of the chloromethyl groups in the substitution polymer it was pyrolysed, when some depolymerisation occurred. The redistilled pyrolysate (28% yield) was analysed by gas-liquid chromatography. In two experiments identical chromatograms were not obtained, but in both cases the major peak had the same retention time as 4-chloromethylstyrene. This was closely preceded by a smaller peak (14 and 8% area of the main peak) which may have been due to 2-chloromethylstyrene. Several smaller peaks at much lower retention times were probably due to products of fragments produced other than by depolymerisation, under the drastic pyrolysis conditions. Since on the chromatogram of a 1:1 mixture of 4-chloromethylstyrene:pyrolysate, the area of the smaller peak was reduced from 14 to 4% of the area of the main peak, it is calculated that the second peak is due to a component present as 6.6% of the pyrolysate, in one analysis and 3.7% in the second.

The evidence of infrared spectra, pyrolyses and kinetics of reaction (to be discussed later) of the chloromethylated polystyrenes indicates that ortho chloromethyl groups are present but probably to an extent of less than 10%.
Replacement Reactions of Chloromethylated Polystyrene

Before conducting the kinetic work, to be described later, some nucleophilic replacement reactions were carried out on chloromethylated polystyrene in order to obtain a qualitative idea of the reactivity of the polymer chloromethyl groups. The reactions chosen were those that proceed with facility and to completion in low molecular weight benzyl chlorides.

In these reactions the degree of conversion was calculated from the analytical results in the following way. Reaction is assumed to take place only with the monochloromethyl units to yield a product containing \(-\text{CH}_2\text{QR}\) units, where \(Q\) is the element analysed. The generalised reaction may be written:

\[
\begin{align*}
\text{CH}_2\text{Cl} & \quad \text{CH}_2\text{Cl} \\
\text{CH}_2\text{Cl} & \quad \text{CH}_2\text{Cl} \\
\text{CH}_2\text{QR} & \quad \text{CH}_2\text{Cl}
\end{align*}
\]

Group type A B C D

Assuming that per 100 units, \((100-x-y)\) are of type A, \(x\) of type B and \(y\) of type C, then:

\[
\% Q = \frac{100 \cdot y \cdot (\text{Atomic weight of } Q)}{(100-x-y) \cdot (\text{M.W. of A}) + x \cdot (\text{M.W. of B}) + y \cdot (\text{M.W. of C})}
\]
Since \( x \) is known to have the value 5.6, we may calculate the percentage conversion of monochloromethyl groups, \( y \).

The reaction of a trialkyl phosphite with an alkyl halide to yield a dialkyl phosphonate was discovered by Arbuzov [79]. The reaction can be considered as two successive nucleophilic substitutions:

\[
\begin{align*}
(RO)_3 P + R' - X & \rightarrow [(RO)_3 P + R - X] \rightarrow (RO)_2 P - R + RX \\
0 & \rightarrow
\end{align*}
\]

Firstly, addition of \( R - X \) to yield a phosphonium halide intermediate, which spontaneously breaks down (when \( R \) is alkyl) to the phosphonate. Gerrard [80] found that in the reaction of ethyl iodide with tri-(2-octyl) phosphite (from optically active \((+)-\text{octan-2-ol}\)) inversion of configuration occurred and therefore considered the second stage of the reaction to be a bimolecular nucleophilic attack of iodide ion, the electron affinity of the oxygen being increased by the positively charged phosphorus atom, whereby alkyl-oxygen fission is encouraged:

\[
\begin{align*}
R - O - + I^{-} & \rightarrow R - O - P - E t \rightarrow I - R + O = P - E t \\
\end{align*}
\]

The reaction has been extended to aromatic chloromethyl compounds by Kosolapoff [81].

Chloromethylated polystyrene underwent the Arbuzov reaction with triethyl phosphite to yield a polymer containing benzyl diethylphosphonate units. The reaction mixture, as a homogeneous solution in toluene was refluxed for 14 hours. Any side reaction between the ethyl chloride
produced and unreacted phosphite was unlikely since under the reaction conditions the volatile halide is rapidly removed from the reaction mixture.

Phosphorus analysis indicated that 49% of the chloromethyl groups had reacted. The infra-red spectrum of the product contained peaks, not present in the original polymer, at the characteristic group frequencies expected for a phosphonate.

Kosolapoff [81] has shown that phosphonates from benzyl halides are quantitatively hydrolysed by concentrated hydrochloric acid. The phosphonated polymer was heated under reflux with this acid for 6 hours, but apparently no hydrolysis occurred. It is to be noted that the polymer was insoluble in the acid, and was present merely as a suspension.

Fromm and Palma [82] reported the reaction of benzyl chloride with alkaline sodium sulphite to yield sodium benzylsulphonate. Chloromethylated polystyrene was suspended in this reagent and the mixture heated with reflux for 8 hours. The product contained no sulphur. Again, a reaction which goes well with benzyl chloride was unsuccessful with the polymer when the latter was present, not in solution, but in suspension.

Chloromethylated polystyrene has been quaternized in dioxan/methanol solution with three tertiary amines to yield polymers containing benzyltrialkylammonium chloride units. With the amines trimethylamine, triethylamine and tri-n-propylamine, 86, 78 and 90% of the chloromethyl groups respectively had reacted. In the case of the trimethylamine
quaternization, a reaction time of >10 half-lives was used, but substitution was still incomplete. However, later kinetic studies showed that the quaternization reaction slows down progressively, so that the limited extent of reaction observed in these preparative quaternizations is probably due to insufficiently long reaction times.

All three quaternized polymers were readily soluble in water. The logarithmic viscosity numbers of 1% aqueous solutions were quite large:

<table>
<thead>
<tr>
<th>Polymer SI Quaternized with R$_2$N$^-$</th>
<th>L.V.N.</th>
</tr>
</thead>
<tbody>
<tr>
<td>R= Me</td>
<td>1.51</td>
</tr>
<tr>
<td>Et</td>
<td>1.34</td>
</tr>
<tr>
<td>n - Pr</td>
<td>1.15</td>
</tr>
</tbody>
</table>

In the highly polar solvent the chloride ions are able to diffuse away from the polymer chains, causing them to carry a high effective charge. The chains therefore expand, giving rise to the high logarithmic viscosity numbers observed.

Aqueous solutions of the trimethyl- and triethylammonium hydroxide polymers have been prepared by metathetical reaction of the corresponding chloride polymers with silver oxide. Replacement of chloride by hydroxide ions was essentially quantitative.

An attempt to isolate the trimethylammonium hydroxide polymer was unsuccessful. The aqueous solution of this polymer was evaporated and
the solid dried at 70°. However, the product obtained was now insoluble in water and contained only 53% of its original hydroxide ions, as shown by potentiometric titration. Obviously some thermal decomposition of the polymer had occurred during the drying process. Hughes and Ingold [83] reported that aqueous solutions of benzyltrimethylammonium hydroxide decomposed on heating:

\[ \text{C}_{17}H_{17}\text{OH} + \text{NMe}_3^+ \rightarrow \text{C}_{17}H_{17}\text{NMe}_2 + \text{MeOH} + \frac{\text{C}_{17}H_{17}\text{NMe}_2}{2} \]

Such reactions of the polymer could lead to cross-linking by intermolecular reaction of groups of type I with chloromethyl groups also present. These reactions could account for the lower hydroxide ion content and insolubility of the solid obtained after drying.
Kinetics of Quaternization in Benzyl Alcohol

The quaternization of many benzyl halides has been found to occur by the SN2 mechanism, under a variety of conditions \([44,45,84-89]\). Even halides containing powerful electron donating substituents like methoxy \([89]\) or in polar solvents (e.g. nitrobenzene \([88]\)) do not react other than bimolecularly. Therefore it has been assumed in this work, which involves substituents with relatively weak inductive effects in only a moderately polar solvent, that the bimolecular mechanism will apply.

![Chemical Reaction]

Any deviation from second order kinetics observed in the polymer reactions can therefore be ascribed to the macromolecular nature of the reaction.

The kinetics of reaction of several chloromethyl compounds with triethylamine at 75° in benzyl alcohol solvent have been determined.

Some difficulty was encountered in the choice of solvent since, although the polymeric chloromethyl compounds were soluble in most common
organic solvents (though not in the lower aliphatic alcohols), the product of the polymer reaction, a polyelectrolyte, was only soluble in water, methanol, ethanol and, as expected, in other, highly polar solvents. A solvent was required in which both reactants and products were soluble under the conditions used; even partial precipitation of the polymer would have been undesirable, since then the reaction kinetics may have been diffusion-controlled.

The purity of liquid kinetic materials was checked by gas-liquid chromatography. The benzyl alcohol solvent was stored in a dark bottle under nitrogen since peroxides were found to be present in the solvent after long storage in air. These interfered with the measurements of rates of quaternization; therefore before each series of runs the peroxide content of the solvent was checked by titration of the iodine liberated from sodium iodide by a known amount of solvent.

In one experiment the initial peroxide content was found to equal the loss of amine after heating a 'peroxidic' benzyl alcohol/amine mixture under kinetic conditions. It is probable therefore that the peroxides interfered by reaction with the tertiary amine to yield the amine oxide. The solvent used in kinetic runs always contained < 0.002 millimoles of peroxidic oxygen per ml. i.e. < 1% of the concentration of amine used in such runs.
The chloromethyl compounds used were three homopolymers of 4-chloromethylstyrene of different molecular weight (polymers PI-PIII) two chloromethylated polystyrenes of different molecular weight (polymers SI and SII), a copolymer of styrene and 4-chloromethylstyrene, benzyl chloride, representing an individual side group of the homo-polymer, and cuminyl chloride (I) representing the side group together with the chain carbon atom to which it is combined and the two adjacent atoms, (bracketed structure in II).

![Chemical structures](image)

The kinetic results are set out in the tables and graphs on pp. 71–86. These results were calculated as described on pp. 68–69. The second order rate constants ($k_2$), obtained from the graphs and corrected for solvent expansion, are summarised in Table 19.
TABLE 19
Rate Constants for Reaction with Triethylamine in Benzyl Alcohol solvent at 75°.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$10^2k_2$ l.mole$^{-1}$.min$^{-1}$</th>
<th>Individual runs</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzyl Chloride</td>
<td>5.8, 5.6, 5.6, 5.7, 5.7</td>
<td>5.7</td>
<td></td>
</tr>
<tr>
<td>Benzyl Chloride</td>
<td>5.6, 5.8, 5.8, 5.8, 5.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cuminyl Chloride</td>
<td>9.2, 9.2, 9.3</td>
<td>9.2</td>
<td></td>
</tr>
<tr>
<td>Polymer PI</td>
<td>8.4, 8.4, 8.4</td>
<td>8.4</td>
<td></td>
</tr>
<tr>
<td>Polymer PII</td>
<td>8.3, 8.5, 8.3</td>
<td>8.4</td>
<td></td>
</tr>
<tr>
<td>Polymer PIII</td>
<td>8.3, 7.7, 7.9, 8.3</td>
<td>8.1</td>
<td></td>
</tr>
<tr>
<td>Polymer SI</td>
<td>6.8, 7.3, 7.1</td>
<td>7.1</td>
<td></td>
</tr>
<tr>
<td>Polymer SII</td>
<td>7.0, 7.1, 7.1</td>
<td>7.1</td>
<td></td>
</tr>
<tr>
<td>Copolymer</td>
<td>8.5, 8.6</td>
<td>8.6</td>
<td></td>
</tr>
</tbody>
</table>

The second order graphs are linear for benzyl and cuminyl chlorides for the whole range of reaction studied (up to about 75% reaction). For the polymers the graphs are linear for approximately the first 25% reaction then curve concave downwards. The rate constants quoted in the
table are those obtained from the first, straight portions of these graphs, replotted on a larger scale.

The average values of $k_2$ for each of the three homopolymers PI-PIII of 4-chloromethylstyrene are almost the same. Hence a variation of the molecular weight in the range 22,000 - 169,000 does not appreciably affect the initial rate of reaction. This result indicates that the rate is not controlled by diffusion of amine into the polymer coils, which are presumably sufficiently expanded to make all sites equally accessible to the reagent.

The copolymer also reacts initially at substantially the same rate as the homopolymers; spacing out of the reactive groups by, on average, 1.76 inert styrene units therefore has little effect on the initial rate of reaction.

The two chloromethylated polystyrenes also react at similar rates, although this is 15% lower than the rate for the homopolymers. This is ascribed to the ortho groups probably present in these polymers, which would be expected to be sterically less favourable for reaction, especially by the SN2 mechanism, where access by 'backside' attack of nucleophile is hindered by the close proximity of the reactive centre to the polymer main chain.

Lloyd and Durocher [90] have found that for mixed ortho and para chloromethylstyrene polymers, the ortho groups react with trimethylamine
at a slower rate than the para. However, their results cannot be exactly compared with the present work since in their system the polymers had a slightly crosslinked microgel structure (containing 0.05\% divinylbenzene) and were present as aqueous dispersions. In the present work the polymers had a linear structure and homogeneous solution was maintained throughout reaction.

The initial $k_2$ values for the homopolymers are 10\% lower than the $k_2$ value for cuminyln chloroide and 83\% greater than for the unsubstituted compound, benzyl chloride. This is consistent with the hypothesis of inductive electron release by the main polymer chain, though to a lesser extent than for the isopropyl group. Such inductive effects will be relayed through the benzene ring to the reaction centre. Inductive electron release by a p-alkyl substituent is expected to facilitate the replacement of halogen by an SN2 mechanism if one assumes that bond breaking is more important than bond making in the transition state. This may be the case in the hydroxylic solvent used, benzyl alcohol, which can hydrogen bond to the amine nitrogen (making it less nucleophilic) and also to the leaving chloride ion.

Hyperconjugative electron release from the α-hydrogen-carbon bonds in the substituted benzyl halides may also assist reaction, though this effect will occur to the same extent in both the homopolymers and cuminyln chloride.
To give a quantitative evaluation of the electron release by the main poly-4-chloromethylstyrene chain, considered as a substituent in an individual benzene nucleus, its Hammett substituent constant has been calculated. This is permissible since a para substituent is removed from the site of reaction and hence steric effects are expected to be absent.

A relationship has been found to exist between the effects of meta or para substituents in the rate constants of many side-chain reactions involving aromatic compounds [91].

Thus if for each substituent a point is plotted whose abscissa is log k for the appropriately substituted compound in one reaction and whose ordinate is log k' for the analogously substituted compound in another reaction, the resultant points lie reasonably near a straight line whose equation is:

\[ \log k = \rho \log k' + c \]  \hspace{1cm} (1)

where \( \rho \) is the slope and c the intercept.

This equation is applicable for any substituent in any two reactions which obey this relationship. If the rate constants for the unsubstituted compounds are \( k_0 \) and \( k'_0 \) then

\[ \log k_0 = \rho \log k'_0 + c \]  \hspace{1cm} (2)

Subtracting equation (2) from equation (1) for the same pair of reactions:

\[ \log \left( \frac{k}{k_0} \right) = \rho \log \left( \frac{k'}{k'_0} \right) \]  \hspace{1cm} (3)
The above argument also applies to equilibria involving meta and para substituted phenyl compounds if the rate constants are replaced by equilibrium constants in the equations.

From equation (3), applicable to any two of the reactions (or equilibria), it can be seen that any reaction (or equilibrium) may be selected as a standard with which to compare all the rest. The ionisation of benzoic acids in aqueous solution at 25° has been chosen as reference standard because of the many accurate data available for this equilibrium.

A further constant $\sigma$, characteristic of a given substituent is now defined as:

$$\sigma' = \log \left( \frac{k'}{k_0} \right)$$

Equation (3) now reduces to:

$$\log \left( \frac{k}{k_0} \right) = \rho \sigma'$$

$\sigma'$ is the substituent constant, independent of reaction type and can be interpreted as a measure the ability of the substituent to change the electron density at the reaction centre.

$\rho$, the reaction constant, is a measure of the sensitivity of the reaction in question to a change in electron density.

Before applying Hammett's method to the present data it is necessary to establish that the series of reactions under study gives a linear
Hammett plot. The data of Baker and Nathan [45, 84, 85] for reaction of substituted benzyl bromides with pyridine in acetone solvent only give a poor Hammett plot if all substituents are included [92]. (m- and p- alkyl m- and p- halogeno, m- and p- NO₂ etc.). However, if attention is restricted to alkyl substituents only, a reasonable correlation is obtained [93]. Although it is not certain that the present reaction series gives a good Hammett plot, values of the polymer substituent constant σ_p have been calculated, especially for comparison with previous work.

The value of σ_p may be obtained from equation (4) using the dissociation constant of the appropriately substituted benzoic acid, polystyrene-4-carboxylic acid, in water at 25°. This has not been recorded in the literature. However, inserting the values of the dissociation constants for p-isopropyl benzoic and benzoic acids [94]:

[Dissociation constant for benzoic acid in water at 25° = 6.320 x 10⁻⁵]

[Dissociation constant for p-isopropylbenzoic acid in water at 25° = 4.43 x 10⁻⁵].

into equation (4), we obtain σ_p = -0.154.

The ρ-constant for the reaction of benzyl chlorides with triethyl-amine in benzyl alcohol at 75° is now given by equation (5) as:

\[ \rho = \log \left( \frac{k_d}{k_H} \right) \]
where $k_i$ and $k_H$ are the average rate constants for cumylnyl and benzyl chlorides respectively. This yields $\sigma = -3.13$, which substituted into:

$$\log\left(\frac{k_p}{k_H}\right) = \sigma \sigma'$$

where $k_p$ is the average rate constant ($9.3 \times 10^{-2}$ l.mole.$^{-1}$ min.$^{-1}$) for the poly-4-chloromethylstyrene, gives: $\sigma' = -0.121$

Strictly this is the substituent constant for the main chain of poly-4-chloromethylstyrene considered as a para substituent. However, the initial rates of reaction of the homopolymers and copolymer are similar, whence replacement of the chloromethyl groups by hydrogen in the polymeric substituent does not appreciably alter $\sigma'_{p}$. Furthermore the value of $\sigma'_{p}$ obtained is close to that ($\sigma'_{p} = -0.101$) found by Arcus and Hall from kinetic data on the quaternization of poly-4-MW-dimethylaminostyrene [38].

Deceleration during the polymeric quaternizations

It was noted that for the polymer reactions the second order graphs are linear only for the first 25\% reaction. They then curve downwards towards the time axis; that is the rate of reaction fell as reaction proceeded. Values of the instantaneous rate constant ($k_i$) during the later stages of reaction were determined in the following manner.
x versus t curves were drawn for each run and the normals to the curves constructed at each 10% reaction. Conversion of the slope of the normal to that of the tangent gave \( \frac{dx}{dt} \). Substitution into the differential form of the second order rate equation:

\[
\frac{dx}{dt} = k_1 \cdot (a-x)(b-x)
\]

therefore gave values of \( k_1 \).

The mean values for each polymer are shown in tables 20, 21, and the results plotted as \( k_1 \) versus % reaction curves in graph XIII.

**TABLE 20**

Mean values of 'instantaneous' rates for chloromethylated polystyrenes in benzyl alcohol

<table>
<thead>
<tr>
<th>% Reaction</th>
<th>Polymer SI</th>
<th>Polymer SII</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>6.61</td>
<td>6.75</td>
</tr>
<tr>
<td>20</td>
<td>6.78</td>
<td>6.99</td>
</tr>
<tr>
<td>30</td>
<td>6.19</td>
<td>6.27</td>
</tr>
<tr>
<td>40</td>
<td>5.51</td>
<td>5.62</td>
</tr>
<tr>
<td>50</td>
<td>4.85</td>
<td>5.06</td>
</tr>
<tr>
<td>60</td>
<td>4.40</td>
<td>4.41</td>
</tr>
<tr>
<td>70</td>
<td>3.98</td>
<td>3.76</td>
</tr>
</tbody>
</table>
TABLE 21

Mean values of 'instantaneous' rates for homopolymers and copolymer in benzyl alcohol

<table>
<thead>
<tr>
<th>% Reaction</th>
<th>Polymer PI</th>
<th>Polymer PII</th>
<th>Polymer PI</th>
<th>Copolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>8.23</td>
<td>8.32</td>
<td>8.42</td>
<td>8.30</td>
</tr>
<tr>
<td>20</td>
<td>8.45</td>
<td>8.39</td>
<td>8.35</td>
<td>8.40</td>
</tr>
<tr>
<td>30</td>
<td>7.88</td>
<td>7.70</td>
<td>7.67</td>
<td>8.36</td>
</tr>
<tr>
<td>40</td>
<td>7.21</td>
<td>7.38</td>
<td>7.06</td>
<td>8.15</td>
</tr>
<tr>
<td>50</td>
<td>6.73</td>
<td>6.73</td>
<td>6.77</td>
<td>7.59</td>
</tr>
<tr>
<td>60</td>
<td>6.25</td>
<td>5.93</td>
<td>6.18</td>
<td>7.71</td>
</tr>
<tr>
<td>70</td>
<td>4.95</td>
<td>4.93</td>
<td>5.04</td>
<td>6.88</td>
</tr>
<tr>
<td>80</td>
<td>4.03</td>
<td>4.01</td>
<td>4.03</td>
<td>-</td>
</tr>
</tbody>
</table>

As can be seen the rate varies in the same manner for each homopolymer, the rate diminishing to 81% of its initial value at 50% reaction, and to 60% at 70% reaction. For the chloromethylated polystyrenes the initial rate is reduced to 70% of its value after 50% reaction, and to 55% at 70% reaction.
Graph XIII

Mean values of $K_i$ against % Reaction for quaternization in benzyl alcohol

Polymer
- PI
- PV
- PIII
- SI
- SII

$10^2 \times K_i$ l.mole$^{-1}$ min$^{-1}$

% Reaction
The shapes of the $k_1 - \%$ reaction curves would be expected to differ appreciably between the homopolymers and the chloromethylated polystyrenes if the latter contained a fair percentage of ortho groups. The shapes of the curves are, however, closely similar.

For the copolymer linearity of the second order graphs persists until about 50% reaction, the rate then falling to 80% of its initial value after 70% reaction.

Similar decelerations have been observed in other polymeric quaternizations: by Fuoss, Watanabe and Coleman [37] during the quaternization of polyvinylpyridine with n-butyl bromide, and by Arcus and Hall [38] in the reaction of poly(p-N,N-dimethylaminostyrene) with methyl iodide.

We may consider the reaction as proceeding in the following way. Initially groups randomly situated along the polymer chain will react and the probability of quaternization of near neighbours is small. As reaction proceeds, unreacted groups must inevitably be flanked by quaternary ammonium groups, until finally only isolated chloromethyl groups remain to react.

Clearly the presence of charged quaternary neighbours affects the rate of reaction of unreacted groups. Several explanations can be given as to how they do this, but unfortunately we cannot on present evidence, choose between them.

As reaction proceeds ions are produced and it might be argued that the changes in ionic strength of the reaction medium would affect reaction.
However, such changes would occur in the small molecule reactions also, but second order kinetics are here observed throughout reaction. Moreover a salt effect of this type would be expected to accelerate a reaction in which ions are produced from initially electrically neutral reagents.

A neighbouring positively charged quaternary ammonium group will exhibit a strong inductive electron withdrawing (-I) effect, but it is hardly likely that this will be transmitted across the three main-chain saturated carbon atoms to the neighbouring unreacted group. Indeed it has been found that the reduction in rates of quaternization of the second nitrogen compared with the first in dipyridyl compounds is similar in 1,3-dipyridylpropane (3 methylene groups), 1,2-dipyridylethane (2 methylene groups) and 1,2,3-dipyridylethylene [95]. In this last compound any electronic effect after quaternisation of one nitrogen would be transmitted through the conjugated double bond.

Thus intramolecular electronic effects are not the cause of the deceleration observed. An explanation based on the effect of the external electrostatic field caused by the charged ammonium groups is more likely to be correct. There are several ways in which this could operate; these have been discussed by Fuoss [36].

The quaternisation reaction is assumed to proceed by a bimolecular mechanism in which the incoming amino-nitrogen, benzylic carbon, and
leaving halogen atom are collinear for the transition state to have minimum energy. However, neighbouring positive charges may distort this linear arrangement by electrostatic repulsion and attraction of the partial charges in the incoming and displaced groups, thus raising the activation energy for reaction (I).

The tertiary amine will be polarised when in the electrostatic field around the partially reacted macromolecule and may be oriented in a position unfavourable for reaction, by a neighbouring positively charged nitrogen (II).

\[ \text{I} \]
\begin{align*}
 & \text{CH}_2 \text{Et}_3^+ \text{N}^- \\
 & \text{CH}_2 \text{Cl} \text{Et}_3^+ \\
 & \text{Cl} \text{Et}_3^+ \\
 & \text{N}^- \text{Et}_3^+ \\
 & \text{As}^- \text{As}^- \\
 & \text{B}^6+ \text{B}^6+
\end{align*}

\[ \text{II} \]
\begin{align*}
 & \text{CH}_2 \text{Et}_3^+ \text{N}^- \text{Et}_3^+ \\
 & \text{CH}_2 \text{Cl} \text{Et}_3^+ \\
 & \text{Cl} \text{Et}_3^+ \\
 & \text{N}^- \text{Et}_3^+ \\
 & \text{As}^- \text{As}^- \\
 & \text{B}^6+ \text{B}^6+
\end{align*}

\[ \text{III} \]
\begin{align*}
 & \text{N}^- \text{N}^- \text{CH}_2 \text{Cl} \text{N}^- \text{N}^- \\
 & \text{As}^- \text{As}^- \\
 & \text{B}^6+ \text{B}^6+
\end{align*}

\[ \text{IV} \]
\begin{align*}
 & \text{N}^- \text{N}^- \text{CH}_2 \text{Cl} \text{Cl} \text{Cl} \text{Cl} \text{N}^- \text{N}^- \\
 & \text{Cl} \text{Cl} \text{Cl} \text{Cl} \text{Cl}
\end{align*}
The electrostatic field around the poly-electrolyte may hold a layer of polarisable solvent molecules around the polymer, thus providing a barrier which the amine has difficulty in penetrating in order to reach any unreacted sites (III).

Finally it may be that the positively charged polymer carries a layer of chloride counter-ions close to it. At any reacting group breakdown from the transition state to products may be difficult since the leaving negatively charged chloride ion must move against the electrostatic field from the positively charged polymer into the negatively charged counter-ion layer (IV).
Kinetics of Quaternization in Dimethylformamide and in Sulpholane

It is evident from the previous discussion that the causes of deceleration in the polymer reactions are probably due to an extramolecular electrostatic field effect. The magnitude of this effect will obviously be dependent on the distances separating reactive groups, which are in turn dependent on the degree of solvation of the macromolecule. It was therefore considered that a variation of solvent might provide some useful information on the operation of the field effect.

The kinetics of reaction between poly(4-chloromethylstyrene) (polymer PI) and triethylamine have been determined in dimethylformamide and in tetrahydrothiophen-1,1-dioxide (sulpholane) solvents. For a close comparison with the results obtained in benzyl alcohol solvent, similar concentrations of reagents and reaction temperature (75°) were used. The kinetics of reaction of benzyl chloride have also been determined under the same conditions.

The results were calculated as previously described (pp. 68-69) and are set out in the tables and graphs on pp. 85-92.

The second order rate constants obtained are summarised in table 22.
TABLE 22

Reaction between chloromethyl compounds and triethylamine
at 75°.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Chloromethyl Compound</th>
<th>$10^2 x k_2$ l.mole$^{-1}$min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethylformamide</td>
<td>Benzyl chloride</td>
<td>2.03, 1.99</td>
</tr>
<tr>
<td></td>
<td>Polymer PI</td>
<td>3.60, 3.70</td>
</tr>
<tr>
<td>Sulpholane</td>
<td>Benzyl chloride</td>
<td>13.1, 12.9</td>
</tr>
<tr>
<td></td>
<td>Polymer PI</td>
<td>20.0, 21.6</td>
</tr>
</tbody>
</table>

For the dimethylformamide runs the second order plots are linear throughout reaction for both benzyl chloride and the homopolymer. For the runs in sulpholane, the graphs for benzyl chloride are linear, but those for the homopolymer start to curve concave towards the time axis after about 10% reaction. For these last runs the polymer rate constants quoted in the table are the initial values.

In both solvents the values of $k_2$ for the homopolymer are greater than those for benzyl chloride, as was found in benzyl alcohol solvent. Again inductive electron release by the polymer main chain is probably the reason for these higher rates.
The values of the 'instantaneous' rates of polymer quaternization in sulpholane have been calculated as described on p.118 and are tabulated below (Table 23).

**TABLE 23**

Mean values of 'instantaneous' rates for polymer PI in sulpholane

<table>
<thead>
<tr>
<th>% Reaction</th>
<th>$10^2 x k_i$ l.mole$^{-1}$.min$^{-1}$</th>
<th>% Reaction</th>
<th>$10^2 x k_i$ l.mole$^{-1}$.min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>23.9</td>
<td>50</td>
<td>20.1</td>
</tr>
<tr>
<td>20</td>
<td>21.4</td>
<td>60</td>
<td>15.8</td>
</tr>
<tr>
<td>30</td>
<td>22.1</td>
<td>70</td>
<td>15.4</td>
</tr>
<tr>
<td>40</td>
<td>19.7</td>
<td>80</td>
<td>14.3</td>
</tr>
</tbody>
</table>

Although decoloration starts early in reaction the rate only falls to 74% of its initial value after 70% reaction.

It is evident that both the initial rates and kinetic form of the polymer reactions are highly dependent on the solvent used. This 'solvent effect' must operate in a complicated way because of the probable continual changes in solvation of the macromolecule during reaction.
For dimethylformamide we may postulate that throughout reaction the polymer is so well solvated that the individual molecules are expanded sufficiently to ensure that considerable distances separate neighbouring side-groups. Consequently the electrostatic field effect, dependent on these distances, is inoperative, thus accounting for completely second order kinetics. The fact that such a reaction course is followed in dimethylformamide and not in benzyl alcohol also argues against the intramolecular inductive effect which, if operative, would occur in both solvents.

The polarity of the solvent will also be of importance in these ion-producing quaternization reactions. Many studies have shown that the Menschutkin reaction proceeds at a faster rate in more polar solvents [41, 42, 53, 88, 96, 97].

Dielectric constant (D) has often been used as a measure of solvent polarity and correlations between rate and D have been observed for quaternization reactions. For example the data of Norris and Prentiss[96] on the reaction of ethyl iodide with pyridine shows that rate increases with increasing D. (Table 24).
TABLE 24

Reaction of Ethyl Iodide with Pyridine

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Relative Rate</th>
<th>Solvent</th>
<th>D</th>
<th>Relative Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₆</td>
<td>2.3</td>
<td>Methanol</td>
<td>33</td>
<td>2.5</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>35</td>
<td>Ethanol</td>
<td>24</td>
<td>1.4</td>
</tr>
<tr>
<td>Acetone</td>
<td>21</td>
<td>n-Propanol</td>
<td>20</td>
<td>1.1</td>
</tr>
</tbody>
</table>

The effect of the solvent polarity in the present reactions is shown in Table 25 which summarises the mean initial rate constants obtained in the three solvents used; the published values of the dielectric constants are also shown.

TABLE 25

<table>
<thead>
<tr>
<th>Solvent</th>
<th>D²⁰</th>
<th>10² x k₂ l.mole⁻¹.min⁻¹ mean initial values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Benzyl chloride</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>13.1</td>
<td>5.7</td>
</tr>
<tr>
<td>Dimethylformamide</td>
<td>37.6</td>
<td>2.0</td>
</tr>
<tr>
<td>Sulpholane</td>
<td>42.0</td>
<td>13.0</td>
</tr>
</tbody>
</table>

[Note (a): the superscript figure refers to the temperature at which D was determined. D²⁰ for sulpholane has not been determined, but D usually increases with decreasing temperature. Therefore sulpholane is still]
expected to have the highest D at 20°, the temperature quoted for D of the other two solvents].

These results show that the variation of rate for a particular compound does not parallel the change in dielectric constant. This may be due to the specific solvent-reactant interactions previously mentioned in connection with benzyl alcohol.

Fuoss and Coleman [36] observed a similar anomaly in the quaternization of pyridine with n-butyl bromide. The rate of reaction in sulpholane (D = 42) was almost twice that in propylene carbonate (D = 65). They attributed the unexpectedly high rate in sulpholane to specific short range forces which were superimposed on the longer range electrostatic forces.

The polarity of dimethylformamide, as measured by D, is intermediate between that of benzyl alcohol and of sulpholane, yet it is in dimethylformamide that the kinetics of polymer reaction show an extreme of behaviour in the sense that it is only in this solvent that the kinetics are completely second order.

In a polar solvent, as the polymeric reaction proceeds, it is expected that the chloride ions will diffuse away from the polyelectrolyte, which will be well solvated, thus leaving the macromolecule with a higher effective charge. Hence electrostatic field effects will be more pronounced and the deceleration greater. On the other hand the larger the
macromolecular change, the more the chains will expand due to intramolecular electrostatic repulsions, thus facilitating reaction. It is not clear therefore, how a change to a more polar solvent will affect the course of reaction. This uncertainty is reflected in the apparently anomalous position of dimethylformamide, when compared with benzyl alcohol and sulpholane as solvents for quaternization.

It was hoped to clarify the role of solvent polarity by using solvents of low dielectric constant. Both benzene ($D = 2.3$) and anisole ($D = 4.3$) were tried but at the concentrations employed the partially reacted polymer was precipitated after about 20% reaction.
Analysis of Polymer Kinetics

The derivation of kinetic expressions which describe polymer reactions in which the rate of reaction of a reactive side group is dependent on the status of neighbouring groups is not straightforward. This is so because the population of each type of group in a given reaction is continually changing throughout reaction.

The first analysis of this problem was given by Fuoss, Watanabe and Coleman [313] to explain their results on the quaternization of polyvinylpyridine. They postulated that the reaction is controlled by three rate constants, $k_1$, $k_2$ and $k_3$ which are the constants for reaction of unreacted groups flanked by zero, one and two already quaternized neighbours respectively. The analysis unfortunately proved to be impractical owing to the complicated nature of the integrated rate equation involved. They therefore suggested a semi-empirical solution based on only the two rate constants $k_1$ and $k_3$. This solution was however not very sensitive until after 50% reaction, when on average unreacted groups were flanked by two quaternized groups and hence reaction proceeded at rate $k_3$.

Their final equation was found to fit the experimental data for a wide range of polymer molecular weights and concentrations and enabled estimates of $k_1$ and $k_3$ to be made. However, their equation does not
appear to be generally applicable since further data on the same reaction obtained by Hall [100] could not be reproduced by the equation.

The problem has been given a more exact mathematical treatment in recent publications. In all treatments it was assumed that three rate constants are sufficient to define the kinetics; these constants were defined as above.

The method is, however, subject to certain limitations as it only accommodates reactions which are of first order with respect to macromolecular side groups (all of which must also be initially unreacted) and of zero order in small molecule reagents; it therefore does not accommodate changes in concentration of the latter. Also differences in rate associated with stereochemical configuration are not taken into account. Further, the analysis only considers the effect of the two nearest neighbours on a reactive group, but it is possible that groups situated further along the chain are more important in intramolecular interactions, especially if reaction is carried out in a poor polymer solvent, where the polymer is in a coiled not an open configuration.

Keller [101] designated the fractions of unreacted groups at time 't' with 0, 1 and 2 reacted neighbours as $N_0$, $2N_1$, and $N_2$, and considered the rates at which they change, $dN_i/dt$. The equations were based on the unproven assumption that for an unreacted neighbour of an unreacted group the fraction $N_0/(N_0 + N_1)$ of such neighbours have two unreacted neighbours.
and the remaining fraction \( \frac{N_1}{N_0 + N_1} \) have one unreacted neighbour. This enabled equations of \( \frac{dN}{dt} \) to be set up in terms of the \( Ni \)'s and the three \( k \)'s. Explicit results could only be obtained, as \( R \) (average fraction of reacted groups), \( N_0, N_1 \) or \( N_2 \) versus \( t \) curves, when \( \frac{k_2}{k_1} \) and \( \frac{k_3}{k_1} \) were integral.

Alfrey and Lloyd [102] based their method on the rate of change of \( n \)-member unreacted sequences \( (N_n) \) and obtained in infinite series of differential equations, which could only be solved by making further assumptions. In the first, applicable when \( k_2 < k_1 \), the polymer chain was replaced by a closed loop model of finite size (e.g. 10 units), and a closed set of differential equations obtained. In the second two new variables were introduced: \( N \), the total number of sequences and \( M \), the number of unreacted sites. \( \frac{dM}{dt} \) and \( \frac{dN}{dt} \) were written down and the \( \frac{dN}{dt} \) equations rewritten using the variable \( N \). This yielded \( n + 2 \) equations in \( n + 3 \) unknowns, and this set of equations was only solved by making one further assumption: that for moderately large sequences, the numbers of sequences of adjacent size \(-N_{n-1}, N_n \) and \( N_{n+1} \) are related by an arithmetic progression where:

\[
N_{n+1} = 2N_n - N_{n-1}
\]

A closed set of equations was then obtained which could be solved e.g. for a 12 x 12 set of equations by computer. The results were given
as graphs of the $N_n$'s versus the conversion $(1 - \theta)$ for different values of the three rate constants. When $k_1 = k_2 = k$ an exact solution was obtained.

The above derivations both involve certain approximations but Arends[103] has published an exact solution, which can be more readily compared with experimental results. He derived a set of probabilities ($P$) of sequences for four different types:

$$-0-0-0- \quad -0-0-X- \quad -X-0-0- \quad -X-0-X-$$

$$P_3 \quad P_2 = P_2 \quad P_1$$

where 0 represents an unreacted group

$$X \quad \text{" \ a reacted group.}$$

and of $P_n$, a sequence containing $n$ unreacted sites, on the basis that the probability of picking a site at random is just the fraction of sites that have reacted ($f$). He then established relationships between the probabilities, and the kinetic statements were written down by counting all the possible ways of forming and destroying a sequence (for $P_1$, $P_2$ and $P_3$). Thus $dP_1/dt$, $dP_2/dt$ and $dP_3/dt$ were obtained. For $df/dt$, it was said that for every sequence of greater length than one, there are $n-2$ sites which react at rate $k_1$, and two sites which react at rate $k_2$. For unit sequences the rate is $k_3$ by definition.
By equating the kinetic statements to the probabilities and substituting $G = 1-f$, a first order differential equation in $G$ was obtained. After integration, the integral was expressed as an infinite series and evaluated by computer. This enabled $G$ vs. $t$ curves to be drawn; substitution of the numerical values of $G$ and $\frac{dG}{dt}$ into previous equations gave the detailed distribution of unreacted sequences at different conversions. Solution of the equation for the special case of $k_1 = k_2$ gave exactly the same answer as that derived by Alffrey and Lloyd. For other values of $k_1$, $k_2$ and $k_3$ agreement between the $G - t$ curves of both authors was also very good.

As previously mentioned the above derivations of a kinetic equation all assume constant concentration of small molecule reagent. Before comparing experimental data which conform to second-order kinetics with the above theory it is necessary to compensate for changes in the small molecule concentration by transforming from linear to concentration-dependent time units according to:

$$t'' = \int_0^t [B]dt$$

where $[B]$ is the concentration of the small molecule as a function of time. This can be performed graphically.

Arend[104] has analysed the data of Coleman and Fuoss on the quaternization of polyvinylpyridine and, presumably on the basis of the
two constant equation of these authors being applicable, assumed $k_1 = k_2$; this assumption simplified the calculations. By adjusting the values of $k_3$ he fitted the experimental $G$ versus $t$ curve, for one temperature, to his theoretical curve and obtained the value of $k_3$ giving the best fit. By assuming a constant ratio of $k_1$ to $k_3$ for other temperatures, he obtained good agreement between experimental and calculated values of $k_3$ at these other temperatures also. However a discrepancy appears to arise between the analyses of Coleman, Watanabe and Fuoss and of Arends, in that the ratio $k_3/k_1$ obtained by the former authors was $\sim 1/10$, the same ratio found by the latter being $\sim 1/3$.

In the present reaction the assumption $k_1 = k_2$ cannot be made; therefore the analysis in terms of Arend's three constant equation is more complex. It was hoped to simplify the problem by simulating the differential form of the theoretical rate equation on an analogue computer. By adjusting the parameters $k_2$ and $k_3$ ($k_1$ being simply the initial rate) it was hoped to obtain $G - t$ curves and to fit one of these to the experimental data, thus obtaining estimates of $k_2$ and $k_3$. It became clear, however, that to obtain reasonably accurate values of $k_2$ and $k_3$ by this procedure it was necessary to have experimental data of high precision for the later stages of the reaction. This, unfortunately, is impracticable, as the data for this region necessarily depend on small differences between titrations, and it is concluded that reliable values of $k_2$ and $k_3$ cannot be obtained by the above mathematical procedure.
SUMMARY

4-Chloromethylstyrene has been synthesised, by a known route, from p-tolunitrile. Bulk polymerisation of this monomer with azobisisobutyronitrile as initiator at concentrations of 0.5, 1.5 and 1.0% by weight yielded poly(4-chloromethylstyrenes), polymers PI, PII and PIII. The intrinsic viscosities of these polymers in toluene at 25° were determined and from these values approximate values of the viscosity average molecular weights were calculated (p.49) as: PI 169,000, PII 22,000, PIII 27,000.

Two polystyrenes, of different molecular weight, have been chloromethylated using chloromethylmethyl ether and zinc chloride to yield polymers SI and SII, whose molecular weights, calculated as before, were: SI 15,200, SII 58,000. The chloromethylated polystyrenes were soluble and hence free of cross-linkages. Analysis indicated that they contained, on average, just more than one chloromethyl group per benzene ring and infrared spectroscopy, pyrolysis and kinetic studies of these polymers showed that the bulk of these groups are present para to the polystyrene main chain.

Reaction of chloromethylated polystyrene with trimethyl-, triethyl- and tri-n-propylamines in dioxan-methanol solution yielded polymers containing benzyltrialkyl ammonium groups in which 86, 78 and 90% of the
chloromethyl groups had reacted respectively. These polyelectrolytes had high logarithmic viscosity numbers in aqueous solution.

Reaction with triethylphosphite, in toluene solution, yielded a polymer containing benzyldiethylphosphonate groups in which 49% of the chloromethyl groups had reacted.

The initial values of the second-order rate constants for the reaction between triethylamine and poly(4-chloromethylstyrene) (8.3 x 10^{-2} \text{l.mole}^{-1}\text{min}^{-1}) in benzyl alcohol at 75° have been determined and compared with the values of the second-order rate constants for the low molecular weight model compounds, benzyl chloride (5.7 x 10^{-2}) and cuminyl chloride (9.2 x 10^{-2}). These values imply electron release by the polystyrene main chain, for which the Hammett sigma constant is evaluated as \( \sigma_p = -0.121 \). The lower initial rate constant for chloromethylated polystyrene (7.1 x 10^{-2}) is attributed to some ortho chloromethyl groups probably present in this polymer.

After about 25% reaction the rates of the polymeric quaternizations fall, due to the production of electrostatic charges on the macromolecule. These charges probably retard further reaction by an external 'field effect', though how this effect operates is not clear. The deceleration is similar for both poly(4-chloromethylstyrene) and chloromethylated polystyrene. (Graph XIII).
The values of the rate constants are unaltered by changes in polymer molecular weight, which suggests that the polymeric reactions are not diffusion controlled. Further, spacing out of the reactive chloromethyl groups by inert styrene units, as in a 4-chloromethylstyrene: styrene copolymer, also does not alter their initial rate of reaction.

The rate of reaction of poly(4-chloromethylstyrene) with triethylamine at 75° in sulpholane falls after only about 10% reaction, though the deceleration is less marked than in benzyl alcohol. In dimethylformamide the same reaction shows no deceleration. The values of the second order rate constants in the three solvents used (p.129) do not correlate with the dielectric constants of the solvents.
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