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STUDIES RELATED TO THE POLYMERISATION OF STYRENE BY PERCHLORIC ACID

by

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ABSTRACT

The interaction of styrene with $HClO_4$ has been studied in CCl_4, $CHCl_3$, CH_2Cl_2, $EtNO_2$ and $PhNO_2$.

No polymerisation occurs in CCl_4 at 0°.

The polymerisation in $CHCl_3$ at 0°, -30° and -60° is complicated by side reactions of the acid with the solvent. At 0° and low acid concentrations, however, the reaction is of first-order with respect to monomer.

The polymerisation in CH_2Cl_2 at 0° appears to follow first-order kinetics up to about the first half-life of the reaction, after which the reaction rate increases continuously. Attempts have been made to determine the nature of the propagating species. To this end, the polymerisation in CH_2Cl_2 has also been carried out in the presence of ethanol and triethylamine, and in the presence of an electric field. The effect of the "scavengers" on the polymerisation depends on the sequence of addition of the reagents involved. The electric field increases the reaction rate continuously.

The polymerisations in $EtNO_2$, and $PhNO_2$, at 0° are complicated by side reactions of the acid with the solvent.

The interaction of styrene with CF_3SO_3H in CH_2Cl_2 has been carried out at 0°, -30°, -60° and -90°. The acid, when mixed with CH_2Cl_2 alone, reacts with the solvent and something in the glass forming at least two products. The rates of the polymerisation increased with the age of the acid solutions.

An improved extraction method has been developed to prepare anhydrous $HClO_4/CH_2Cl_2$ solutions safely.

CONTENTS

To my wife Mary

CHAPTER I

General Introduction

The polymerisation of styrene by protonic and Lewis acids has been studied extensively, and these investigations have been thoroughly reviewed by Mathieson(1). Until the early nineteen sixties, the chemical interpretations of the reactions involved in these systems invariably assumed that the propagating species produced in the initiation reaction are 1-phenylethyl, and subsequently polystyryl ions. This assumption was based primarily on the orthodox formulations of the theories of ionic polymerisation(2-5). Although the ionic nature of the chain carrier was never proven, the intuitions of what would happen if styrene and an acid are mixed, were supported by the finding that for this kind of system the activation energy for the propagation is generally much lower than the corresponding activation energy for radical polymerisations. The molecular weights of the polymers produced by the ionic polymerisations are generally lower than those of polymers made by the radical polymerisation. Furthermore, the ionic nature of at least one such polymerisation seemed to be confirmed through the work of Pepper(6) who demonstrated a strong dependence of rate upon the dielectric constant of the solvent. The case of cationic polymerisations is presented most appropriately by reference to Plesch's book(1) and the reviews by Pepper(7) and Kennedy(8) which followed.

The first real challenge to the proposed ionic nature of an allegedly cationic polymerisation was that presented by Gandini and Plesch(9) for the system styrene/$HClO_4$/1,2-dichloroethane. This system had been extensively studied by Reilly and Pepper(10). Their choice of perchloric acid as the catalyst was dictated by previous knowledge that the polymerisations catalysed by a metal halide required very carefully controlled quantities of water as a co-catalyst(11). The previously investigated conventional acids, which were expected to supply their own protons, presented problems of high association in the organic solvent (e.g. chloroacetic acids)(12), irreproducibility (e.g. HCl, HBr)(13), and non-stationary kinetics (e.g. H_2SO_4)(14). It was hoped that $HClO_4$ would not exhibit these problems since it is very soluble in ethylene dichloride, it is a notoriously strong acid (hence it is expected to minimise the termination reaction), and it is a monoprotic acid. In fact, the kinetics of the polymerisation of styrene by this acid, followed in an open (though carefully guarded) dilatometer, was found to be simple and perfectly reproducible(10). The reaction rate (for $[C_8H_8] = 0.2 - 1.7M$, $[HClO_4] = (0.1\text{-}50)\ 10^{-3}M$ between 25° and -30°) was first-order in monomer and linearly proportional to the initial acid concentration. It was assumed, and later substantiated by Gandini and Plesch(15), that the initiation reaction is instantaneous. The DP of the polymers is dominated by two transfer processes, one being the transfer of a proton to a monomer giving a double-bond end-group, the other involving a cyclization reaction forming a non-propagating indanyl end-group.

Both transfer reactions lead to an immediate regeneration of a propagating species. On the basis of spectroscopic evidence, hydrogenation and acid recovery experiments it is believed that there is no termination by recombination of ions. Hence, the rate equation of the polymerisation is given by

$$-\frac{d[C_8H_8]}{dt} = k\ [HClO_4]\ [C_8H_8] = k'\ [C_8H_8]$$

Since in this polymerisation there appeared to be no termination, and the initiation rate was believed to be so fast as not to be rate-determining, the constant $k'/[HClO_4]$ was identified with the rate-constant for the propagation reaction, i.e. $k_{(exp)} = k_p$.

The rate of polymerisation was found to be unaffected by small quantities of intentionally added water ($[H_2O]$ up to $10[HClO_4]$).

The temperature dependence of k over the range 25° to -30° fits the Arrhenius relation and permits the evaluation of the activation energy of the propagation which is $E_a = 8.3$ kcal/mole.

By varying the dielectric constant of the medium (varying the styrene/1,2-dichloroethane ratio and adding CCl_4 to the system) it was found that log k is linearly proportional to 1/D (negative slope), and E_a is linearly proportional to 1/D (positive slope). The increase of k with D is associated with a decrease in E_a.

On the basis of the above results, and taking into consideration the behaviour of related system (e.g. for styrene/H_2SO_4/1,2-dichloroethane, k = 6.7 M^{-1} sec^{-1} at 25°, whereas for styrene/$HClO_4$/1,2-dichloroethane, k = 17.0 M^{-1} sec^{-1}) Reilly and Pepper concluded that the propagating species are ion-pairs, rather than free ions. The reaction scheme proposed by these investigators was as follows:

Initiation

$$CH_2{:}CHPh + HClO_4 \xrightarrow{k_i} CH_3.\overset{+}{C}HPh\ ClO_4^-,\ R_i = k_i[P_1][HClO_4],\ \text{fast}$$

(complete in a few seconds)

Propagation

$$CH_3.\overset{+}{C}HPhClO_4^- + CH_2{:}CHPh \xrightarrow{k_p} CH_3.CHPh.CH_2.\overset{+}{C}HPhClO_4^-$$

$$R_p = k_p[P_1][P_n^+]$$

……

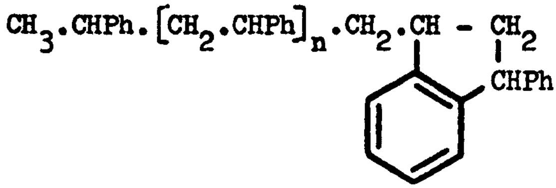
Spontaneous transfer

$$CH_3.CHPh.[CH_2.CHPh]_n.CH_2\ \overset{+}{C}HPhClO_4^- \xrightarrow{k_t} CH_3.CHPh.[CH_2.CHPh]_n.CH{:}CHPh + HClO_4$$

$$R_t = k_t[P_n^+]$$

Monomer transfer

$$CH_3.CHPh.[CH_2.CHPh]_n.CH_2.\overset{+}{C}HPhClO_4^- + CH_2{:}CHPh \xrightarrow{k_{tm}}$$

→ 

$$CH_3.CHPh.[CH_2.CHPh]_n.CH_2.CH - CH_2 + HClO_4$$

$$R_{tm} = k_{tm}[P_1][P_n^+]$$

$[P_1]$ = styrene concentration

$[P_n^+]$ = carbonium ion concentration

The conclusion drawn by Reilly and Pepper that the propagating species are ion-pairs, rather than free ions, was at variance with several of the established beliefs about cationic polymerisations. If the propagating species are ion-pairs, these must be in equilibrium with free ions. Since, on the basis of the finding in anionic polymerisation, free cations were supposed to propagate much faster than ion-pairs, most of the monomer must be consumed by free ions unless the concentration of these is very much lower than that of the ion-pairs. Whatever the concentration of the free-ions may be, since water is much more basic than styrene, the ions are expected to react preferentially with water and one would expect the reaction to be stopped by water. The very fast propagation of free ions and the sensitivity of these ions to water, has now (after Pepper's work) been well established by Williams et al.(16) who found $k_p = 3.4 \times 10^6$ M^{-1} sec^{-1} in bulk monomer at 0°.

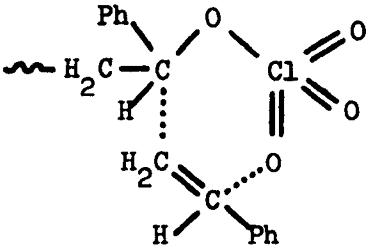
Also the activation energy for the propagation found by Reilly and Pepper was unexpectedly high. Indeed, it was even higher than for the radical polymerisation (~ 7 kcal/mole)(10). The overall activation energy for the polymerisation of styrene by $SnCl_4$ ranges between about 3 and 5 kcal/mole, depending on solvent and co-catalyst used(1).

It was primarily the unexpectedly high activation energy (leading to a correspondingly low rate-constant of propagation), and the absence of a "killing" effect of water, which led Gandini and Plesch to reinvestigate the perchloric acid catalysed polymerisation of styrene. Their technique was high vacuum adiabatic calorimetry with CH_2Cl_2 as a solvent. Their investigation yielded reproducible kinetic results(9,15), strikingly similar to those of Reilly and Pepper. In addition, conductivity measurements at 15° revealed that the polymerising reaction solution exhibited only a very low conductance, equivalent to that of a solution of the acid in the solvent alone. However, when the styrene was almost completely consumed, the conductance rose and the solution, which during the polymerisation was colourless, became yellow. The visible spectrum of this yellow solution showed a broad absorption at 424 nm. Upon scanning a polymerising solution at constant wavelength (λ = 424 nm) at 18-20° the absorbance never rose above its base-line until near the end of the reaction, at which time D_{424} increased, following at the start second-order kinetics and later changing into a first-order reaction. If a second portion of styrene was added to the yellow solution, the colour disappeared immediately, polymerisation occurred at a rate corresponding to that of the previous reaction, and the yellow colour reappeared again when the styrene was consumed. The yellow colour failed to appear when the concentration of intentionally added water exceeded that of the acid.

At the time the above experiments were carried out it was believed that the absorption at λ = 424 nm, like that observed by Jordan and Treloar(17) when styrene was added to a concentrated sulphuric-acetic acid mixture, was due to the styryl and oligostyryl secondary ions. Since the absorption at 424 nm, and the conductance, did not increase during the polymerisation, Gandini and Plesch concluded that if free ions are in the system, the concentration of these must be less than can be detected by the techniques employed. Since the colour always appeared when $[C_8H_8] = 4[HClO_4]$ it was also concluded that the propagating species is stabilized by at least 4 molecules of styrene. The propagating species was tentatively described as a perchlorate ester which, when not stabilized by styrene, dissociates into free ions. This type of polymerisation, propagated by a non-ionic, though very polar, chain carrier, was called a pseudocationic polymerisation. Hence the propagation reaction is represented as:

$$(CH_3CHPh\text{-}OClO_3)\ 4\ C_8H_8 + C_8H_8 \longrightarrow (CH_3CHPh\ CH_2CHPh\text{-}OClO_3)\ 4\ C_8H_8$$

It was suggested that the propagation was by monomer insertion via a six-membered ring, thus:



The non-ionic nature of the propagating species received support from the work of Bywater and Worsfold(18). These investigators found that whereas the $HClO_4$ could be distilled out of a $HClO_4/CH_2Cl_2$ solution, and a styrene/$HClO_4/CH_2Cl_2$ solution which had been allowed to react to completion, the $HClO_4$ could not be distilled out during a polymerisation. This indicated that during the polymerisation the acid is in a combined, non-volatile, state and is released again when the reaction is complete. However, the assignment of the absorption at 424 nm to the polystyryl ions was challenged by these and other authors(18-21).

Following the polymerisation spectroscopically Bywater and Worsfold found that as the sharp styrene peak (λ = 291 nm) disappeared, a sharp peak at λ = 294 nm appeared which is associated with the unsaturated dimer of styrene. The appearance of this peak is attributed to the formation of oligostyrene molecules with an unsaturated end-group. When the styrene had disappeared, a weak spectrum, associated with the indane end-group of oligomers, emerged with the simultaneous appearance of a yellow colour and a strong absorption at 420 nm. It was shown that the colour was due to the ionization of the cyclic end-groups of the oligomers, i.e. the formation of indanyl ions. This was later confirmed by an intensive spectroscopic study of Bertoli and Plesch(22) in which they also showed that the formation of the indanyl ions requires an excess of perchloric acid, and is always preceeded by the formation of indane end-groups.

In studying the carbonium ions derived from aromatic olefins, Bertoli and Plesch(22b) have found that when excess $HClO_4$ in CH_2Cl_2 is reacted with styrene, first the unsaturated linear dimer (1,3-diphenylbut-1-ene) and then the cyclic dimer (3-methyl-1-phenylindane) are formed. If the excess of the acid does not exceed about ten times the styrene concentration, no ions are formed and the above reaction stops. If the excess of the acid is greater than tenfold an approximately equimolar mixture of the 3-methyl-1-phenylindanyl cation, and a saturated compound is formed. The mechanism of the latter reaction (supported by the second-order of the reaction) is suspected to involve a ring opening of an indane end-group giving a 1,3-diphenyl-n-butyl cation which then abstracts a hydride ion from another indane end-group giving an indanyl ion and 1,3-diphenyl-n-butane. The intermediate 1,3-diphenyl-n-butyl ions have in fact been identified and were found to absorb with a single peak at 315 nm.

If a reaction mixture is left undisturbed for several minutes it was found(23) that the absorption peak of the indanyl ion starts to decrease and simultaneously a broad peak around 450 nm appears. This new peak has been attributed to allylic carbonium ions which are formed by a hydride ion abstraction from an unsaturated polymer molecule by an indanyl ion,

i.e.

$$\sim\text{CHPh-CH}_2\text{-CHPh-CH = CHPh} + \sim\text{In}^+ + \text{ClO}_4^- \longrightarrow$$

$$\sim\text{InH} + \sim\text{CHPh-CH}_2\text{-(CPh=CH=CHPh)}^+ + \text{ClO}_4^-$$

The proposal of this reaction scheme was based on a study of allylic ions by Hofner and Pelster(24), and on similar observations made in aliphatic systems(25,26) and in analogous processes which occur in anionic polymerisations(27). Furthermore, the presence of allylic ions appears to be confirmed by the observation that if a reaction mixture is left undisturbed for several hours the 450 nm peak decreases and the solution becomes fluorescent as two new peaks appear at 390 nm and 410 nm. Upon neutralization of the reaction solution these two peaks do not disappear whereas the 450 nm peak does.

By analogy with the absorbtion spectra of diphenylpolyenes(28) the two peaks which persist after neutralization of the solution are ascribed to polyunsaturated oligomers with two to three conjugated double bonds. It was suggested that these originate from a proton abstraction from an allylic ion by some more basic species such as a highly conjugated system.

The phenomena which occur after the polymerisation of styrene is over, have frequently been observed in the course of the present work and will be referred to again in subsequent chapters of this thesis.

The polymerisation reaction which has been discussed so far (and the reactions which follow the polymerisation) were those carried out near ambient temperature. At very low temperatures (below -20°), the reactions which follow the polymerisation appear, at least qualitatively, to be the same as at room temperature. The polymerisation reaction itself, however, changes its kinetic behaviour. At successively lower temperatures the reaction exhibits a more and more pronounced fast initial stage I, followed by the usual slow stage II observed at 0°, which eventually becomes so slow that the reaction appears to have stopped right after stage I. Stage I is accompanied by the appearance of a yellow colour which disappears as soon as the slow stage II takes over (if it was present at all)(29). Since the rate of stage I is very much greater than can be accounted for in terms of the pseudocationic mechanism, it has been attributed to an ionic mechanism. Since the stage II, when observable, proceeded at the rate corresponding to the given initial acid concentration and temperature it was concluded that this reaction stage is that of a pseudocationic polymerisation.

Pepper et al.(30) have reported that at -97° the reaction does not go to completion and that there is no further reaction after the first "flash" polymerisation. However, if the temperature of a "dead" solution of this type is raised, it will resume polymerisation at a rate characteristic of stage II at the higher temperature. The number average molecular weight of the total product from a reaction which exhibited both stage I and II, increased with conversion, but for a reaction at -97° the number of polymer chains formed per acid molecule is one. It was concluded that the stage I is a flash polymerisation by free ions with a termination which becomes reversible at temperatures above about -80°. In stage II the polymer then grows onto the polymer chains already formed.

In an attempt to identify the propagating species in stage II, Pepper et al.(31) have carried out the polymerisation of styrene by $HClO_4$ in the presence of $n\text{-}Bu_4N^+ClO_4^-$ and $Li^+ClO_4^-$. These salts reduce the rates and yields of this polymerisation. The effect on the rates of stage I and II are quantitatively different, but in both stages the rates decrease linearly with the reciprocal square-root of the salt concentration. The stage I is completely suppressible by the salt, whereas stage II is only partially suppressed. Pepper believes that the non-suppressible polymerisation of stage II is due to the propagation by ion-pairs which normally (i.e. in the absence of the salt) are in equilibrium with free ions and Plesch's covalent ester.

On the basis of the results and arguments presented in this thesis we believe that the non-suppressible propagating species are the esters and not the ion-pairs.

Although much had been learned about what happens <u>after</u> the polymerisation of styrene by $HClO_4$, there was still no clear answer as to what the propagating species is, or are, <u>during</u> stage II at low temperatures, and throughout the polymerisation at ambient temperatures. Since it has not been possible to detect the propagating species instrumentally, the approaches that have been used for their detection and possible identification required indirect methods such as studying the effect of water and perchlorate salts on the rates of the polymerisation. Another method has been tried during the original investigations of Gandini and Plesch(29). It consisted of synthesising the perchlorate ester separately and then adding it to a styrene/CH_2Cl_2 solution. Unfortunately the 1-phenylethyl perchlorate could not be prepared since it was found to be very unstable in CH_2Cl_2 alone. Hence an attempt was made to make the ester in situ by dissolving Ag ClO_4 in the styrene/CH_2Cl_2 solution and then adding 1-phenylethyl bromide. The reaction trace of the ensuing polymerisation was slightly sigmoid (presumably because the formation of the ester is not instantaneous) but otherwise was a carbon-copy of an equivalent reaction carried out with $HClO_4$. The reaction solution was colourless throughout the polymerisation and turned yellow at the end. Although the experiment showed that the reactions during and after the polymerisation are very similar to the reactions catalysed by $HClO_4$, it did not show what the reactive species are in either case.

A further method used for the identification of the nature of the propagating species in a variety of systems is that used by Ise(32) which consists of carrying out the reaction in the presence of an electric field. The system styrene/$HClO_4$/CH_2Cl_2 had not been studied by this author. If the propagating species are ion-pairs the electric field might be expected to increase their degree of dissociation (α) (the second Wien effect) and hence lead to an increased concentration of free ions. Since free ions are expected to propagate faster than ion-pairs(33), the rate of the polymerisation should increase. The rate of several of the polymerisations studied by Ise's group increased in the presence of the electric field. A lack of an electric field effect was explained in terms of α being either too high or too low for the electric field to contribute to the dissociation of the ions. A more detailed description of the results of reactions carried out in the presence of an electric field will be given in the introduction to chapter III. The results of the electric field studies have not lead to an unambiguous answer to what the nature of the propagating species are.

The work described in this thesis is the result of the various attempts made to discover what the propagating species are _during_ the polymerisation of styrene by $HClO_4$. It appears to us now that this polymerisation, at least in CH_2Cl_2, is propagated by more than one species, i.e. the reaction is, in Plesch's terminology(34), enieidic.

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CHAPTER II

EXPERIMENTAL

PART 1 : Materials

1,a: Styrene: The commercial product (B.D.H.) was shaken with several portions of 15% aq. NaOH to remove the inhibitor. It was then washed five times with distilled water, and left standing overnight over fused $CaCl_2$. The next day it was fractionally distilled under reduced pressure, and the middle, 80% of the starting volume was collected over CaH_2. This fraction was transferred to the vacuum line (onto a fresh portion of CaH_2) and thoroughly degassed by repeated freezing and thawing. About 10% of the styrene was then distilled off and discarded. A middle fraction, about 80%, was distilled into a reservoir containing BaO (activated by heating under vacuum at 360^{o}). The "tail" fraction was also discarded. The middle fraction was kept at ice-water temperature. Keeping the styrene at liquid N_2 temperature eventually resulted in the cracking of the reservoir.

The styrene was dosed by distilling it into precision pipettes from which it was distilled into the experimental device. Styrene, for "reverse" or "second" addition experiments, was dosed by means of phials, prepared under vacuum, as published(1).

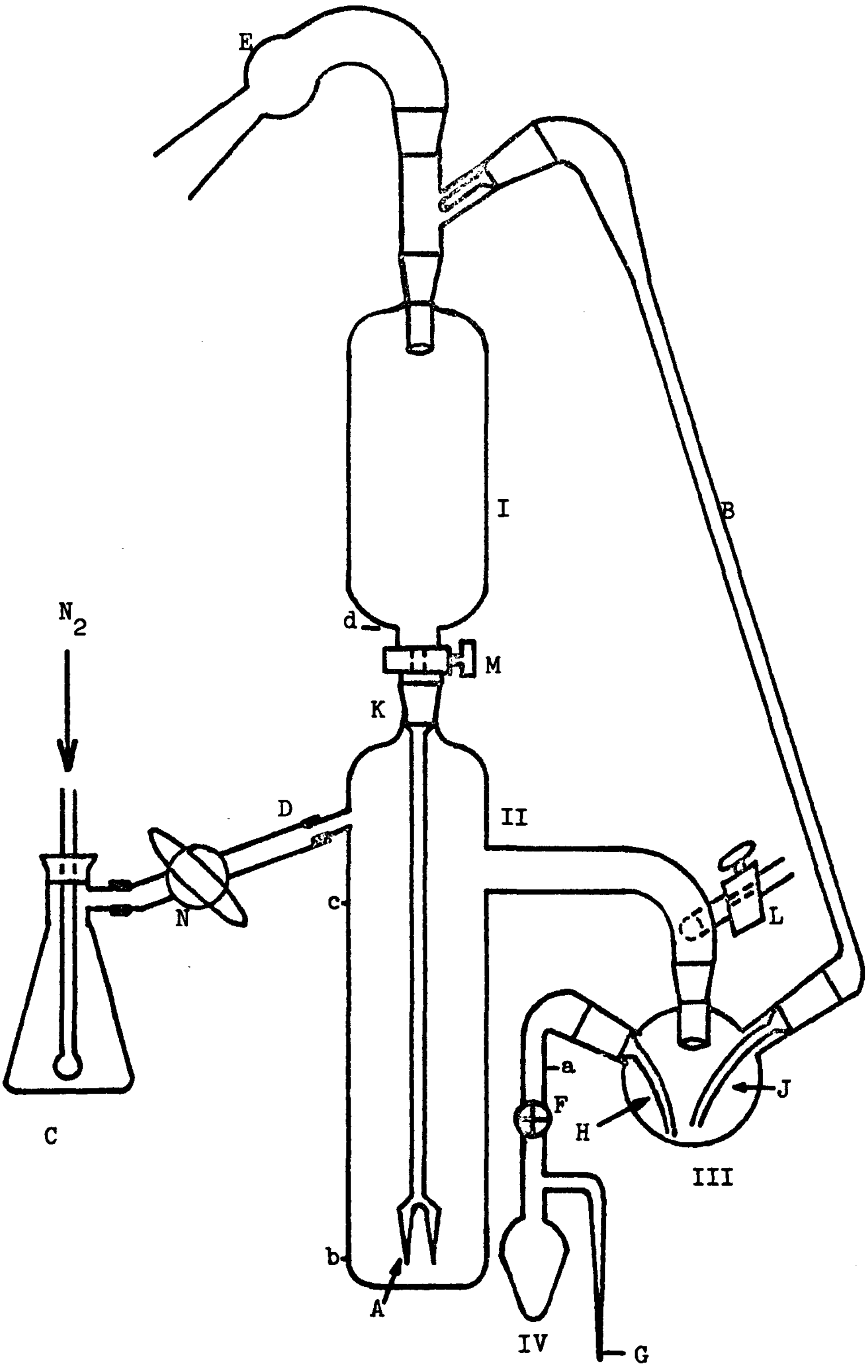
1,b: Acids

1,b,i: Perchloric acid

The previous method of preparing the dilute $HClO_4$-CH_2Cl_2 phials required the dilution of pure $HClO_4$ which was vacuum distilled out of a mixture of 20% oleum and 72% $HClO_4$(1). This procedure is somewhat hazardous since it requires working with pure $HClO_4$, which was found to explode occasionally even when working in an all-glass-no-taps system. Klages and Hegenberg(2) have obtained $HClO_4$-CH_2Cl_2 solutions by extracting the $HClO_4$ out of the oleum-H_2SO_4 mixture with CH_2Cl_2. Their procedure, based on the simple continuous extraction technique, requires heating of the increasingly concentrated $HClO_4$ -CH_2Cl_2 solution. A recent news report(3) said that this procedure has also resulted in an explosion, apparently as a consequence of overheating. Since the direct extraction method has the advantage that it does not involve the handling of pure $HClO_4$ at any stage, we have developed an extraction apparatus which does not require heating of the resulting $HClO_4$-CH_2Cl_2 solution. The apparatus is shown in Fig. II,1. It consists of a reservoir I from which the CH_2Cl_2 (and later the $HClO_4$-CH_2Cl_2) solution flows through the capillaries A into the extractor II, which contains the oleum-$HClO_4$ mixture. The CH_2Cl_2 droplets which emerge from A rise and the $HClO_4$-CH_2Cl_2 solution overflows into the receiver III. When almost no CH_2Cl_2 remains in I, the $HClO_4$-CH_2Cl_2 solution in III is pushed into I via tube B by N_2 pressure, and thus the same batch of CH_2Cl_2 can be percolated any number of times through the

Fig. II,1

The extraction apparatus for making anhydrous $HClO_4$-CH_2Cl_2 solutions



mixed acids.

A successful extraction requires the following procedure: Every glass piece of the apparatus should be cleaned with chromic acid, rinsed with distilled water only (i.e. not acetone or another organic liquid) and dried in the oven. The CH_2Cl_2 to be used in the extraction, as well as that used in saturator flask C, should be purified and must be very dry. C is a saturator for the N_2 stream in order to minimize losses of CH_2Cl_2 in the apparatus while it is purged continuously. The tube D must be of Nylon or Teflon, and not of PVC or rubber. The drying tube E should be filled with glass wool - P_2O_5. However, this should not be packed too tightly because air must readily go in and out of this tube. The collector IV is provided with a vacuum tight Teflon tap F. At the time of the assembly the capillary G, coming from IV, should be closed at the tip, and a notch must be made at a above the tap F. It is important that the tip of tube H leading into III, be lower than the tip of the tube J. None of the taps and ground-glass joints are lubricated.

At first, only II, III and IV are assembled and connected to C. The tap F must be closed. CH_2Cl_2 is added into C, and into III, just enough to close the opening of tube H. Also some CH_2Cl_2 is added into II up to the level b (about 1 cm). The system II and III should be purged with N_2.

In a large tube the 72% $HClO_4$ is added dropwise into the fuming H_2SO_4. The total volume of this mixture should not exceed the volume which can be taken up by II between the levels b and c.

The H_2SO_4-$HClO_4$ mixture is then poured into II via a long narrow necked funnel, whose tip extends below the level of the CH_2Cl_2. The most important part of the procedure is the taking-out of the funnel. The funnel must be lifted out making sure that no drops are left at the joint K.

Now the rest of the apparatus is assembled, reservoir I containing approximately 50 ml of CH_2Cl_2. In doing so one must make sure that tap L is open so that the N_2, which must continue purging II and III, has an outlet.

Tap M can now be opened to let the CH_2Cl_2 go through the capillaries A. The size and number of these capillaries determines to some extent the efficiency of the extraction. However, the more capillaries one has, the more difficult it is to get the CH_2Cl_2 to come through all of them simultaneously. Our apparatus has two capillaries. It takes approximately 20 minutes for 50 ml of CH_2Cl_2 to go through these capillaries.

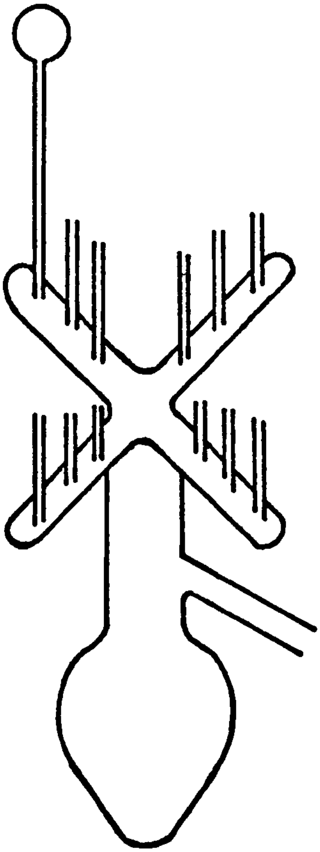
The tap M should be closed before the level of the CH_2Cl_2 reaches d. This is to ensure that tap M can never dry out which otherwise could result in an area where the $HClO_4$ could become concentrated. Having closed M, tap N is closed slightly to reduce the rate of flow of N_2. Now tap L is closed very gradually. As it is closed, the N_2 pressure will push the $HClO_4$-CH_2Cl_2 solution in III through B back into I. Taps L, N and M are fully opened again, and this completes one cycle.

In our apparatus, five cycles result in a $HClO_4$-CH_2Cl_2 solution of about 1M. Since this concentration was high enough for our purposes, the extraction was usually discontinued after the fifth cycle. Further concentrating of the solution can be achieved when the solution is being degassed on the vacuum line.

Once the fifth cycle is completed, tap M is closed, and then tap F is opened. While tap L is closed very slowly, the solution will go into tube H. At this moment the tip of the capillary G is broken off. When all the solution in III has been transferred to IV, L is opened slightly and G is sealed off again quickly with a hot flame. Then L is opened completely and tap F is closed firmly. The assembly IV is broken off at a and the tubing which leads to tap F is washed with distilled water by means of a syringe. Now IV can be fused to the vacuum line either via a tipping device (Fig. II,2) from which the solution can be transferred directly into phials, or via a manifold with a series of ampoules (each provided with a break-seal) in which the solution can be stored. In the process of degassing the solution it is recommendable that the narrow tubing, which leads to the capillary G, be sealed off again under vacuum since the previous fusing of the capillary does not provide a reliable, vacuum-tight closure. Furthermore, it

Fig. II,2

The tipping device



Phials of 1 to 3 ml capacity
are fused to all the vertical
tubes shown.

is advisable that the apparatus be dismantled as soon as possible, especially at tap M.

The $SO_4^=$ content of solutions made by this extraction technique was tested by the standard turbidimetric technique. The sulphate content of the solutions never exceeded $[SO_4^=]/[HClO_4] = 0.001$. The best solution ever obtained had $[SO_4^=]/[HClO_4] = 0.0005$.

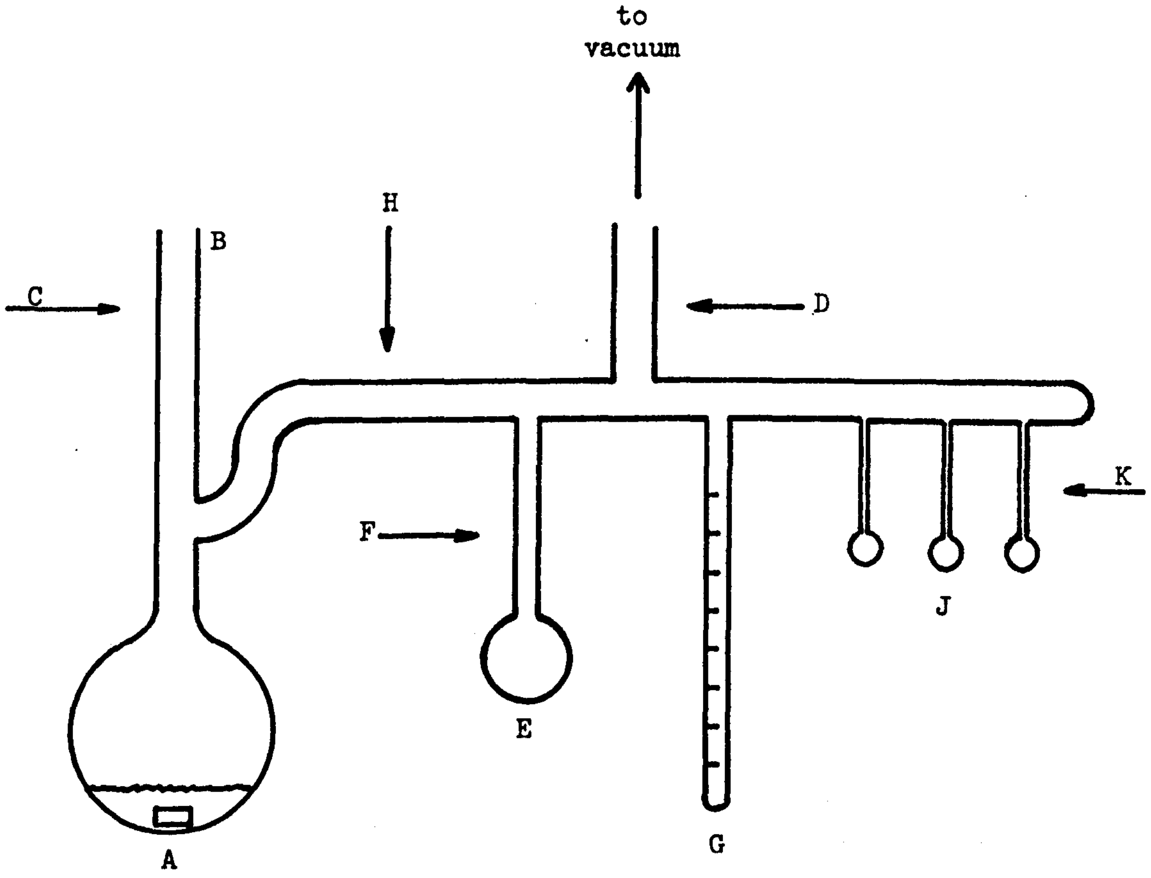
The acid phials were diluted with CH_2Cl_2 by means of the tipping device, Fig. II,2. The procedure was as published(1).

1,b,ii: Trifluoromethanesulphonic acid, (triflic acid)

This acid was supplied to us in two different forms: as the barium salt(4) and as the free acid(5). The salt was used as supplied. The vacuum line arrangement shown in Fig. II,3, was built to vacuum distil out the free acid from a $(CF_3SO_3)_2$ Ba - conc. H_2SO_4 mixture. The procedure was as follows: The salt and an excess of conc. H_2SO_4 were placed into A and the neck of the flask was stoppered at B. While the mixture was stirred magnetically the line was put under vacuum. After thoroughly degassing the mixture, the neck of flask A was fused off at C. The line was pumped for one further hour while keeping the mixture in A at 0^o. Then the line was fused off at D. The mixture was warmed with a hair-dryer and stirred for about one hour. While keeping the mixture warm, a small portion of the triflic acid was distilled into E which was fused off at F. A further portion of the acid was distilled into the microburette G and while keeping both G and A at 0^o, the vessel A was separated from the line at H. The

Fig. II,3

The vacuum line arrangement for the preparation of pure CF_3SO_3H phials.



triflic acid in G was then distilled into the phials J which were fused off at K. The acid which was supplied as the free acid, was distilled into phials by the procedure described above. The acid phials were diluted with CH_2Cl_2 as published(1).

1,c Solvents

1,c,i: Methylene chloride

Commercial methylene chloride supplied by I.C.I. Ltd., was purified as described by Weissberger(16), and dried for at least one day over fused calcium chloride. It was then fractionally distilled through a 4 ft. column charged with nickel turnings. According to the vapour phase chromatogram the middle fraction, approximately 70% of the starting material, was free of any detectable impurity. The solvent was then transferred into the vacuum-line reservoir. Freshly sublimed phosphorus pentoxide was then added, the reservoir was sealed, and the solvent was thoroughly degassed.

Calorimetric(7), dilatometric and spectroscopic(8) experiments were dosed with this solvent as published.

1,c,ii: Chloroform

The commercial product (B.D.H.) was washed with conc. H_2SO_4, then with dilute NaOH, and then with water. It was then refluxed and fractionally distilled. Only the middle fraction (about 80% of initial volume) was collected in a dark bottle containing molecular sieves, type 4A. It was then transferred into the vacuum-line reservoir containing molecular sieves (type 4A) which had been heated at about 200° for one hour under vacuum.

A purity test by GLC showed only a single clean peak. This solvent was dosed by the same procedure as that used for CH_2Cl_2.

1,c,iii: Carbon tetrachloride

This solvent was purified by the same procedure as was used for chloroform. After purification it was kept for two days in a dark bottle containing P_2O_5. It was then transferred, together with the P_2O_5, into the vacuum line reservoir, and thoroughly degassed by repeated freezing and thawing under vacuum. CCl_4 was dosed by the procedure described by Plesch et al.(8).

1,c,iv: Nitroethane

The commercial product (B.D.H., purity not less than 95%) was washed five times with water to remove the alcohols. It was then dried with molecular sieves (type 4A), and refluxed with $NaHSO_3$ for two hours to remove the aldehydes. It was then fractionally distilled through a 60cm Vigreux column with a reflux ratio of about 1:10. The boiling point and the refractive index were compared with the literature(6):

	This work	Literature
b.p.	113.5°/755 torr	114.0°/760 torr
$n_D^{25°}$	1.3903	1.39015

The middle fraction (about 60% of the initial quantity) was transferred into a large conical flask attached to the vacuum line, containing a glass enclosed magnet and chromatographic silica gel which had been previously reactivated by heating it under vacuum at 300°. After thorough degassing and stirring, about 10% was distilled off and discarded. A middle fraction was distilled into another flask (without a drying agent) which was provided with an all-metal BiPl(9) valve. This flask was then fused off from the vacuum line in order to fuse it to the upper end of the dosing burette of the calorimeter metering system. After adequate pumping of the vacuum line the metal tap could be opened to let the solvent flow directly into the burette by gravity.

No impurities could be detected by GLC.

1,c,v: Nitrobenzene

The commercial product (B.D.H.) was purified by fractional crystallization (4 times) followed by fractional distillation at 9 torr (b.p. 87.5°). The slightly yellow middle fraction (about 50% of the initial volume) had $n_D^{25^\circ} = 1.5523$ (lit. $n_D^{20^\circ} = 1.55257$)(6). It was then shaken extensively with molecular sieves (type 4A) and decanted into a conical flask attached to the vacuum line, containing a glass enclosed magnet and chromatographic silica gel, which had been previously activated by heating under vacuum at 300°. From this stage onward the procedure was the same as that used for nitroethane. This solvent was also dosed in the same manner as nitroethane.

The chromatogram of a test portion showed that the only impurity in this solvent (a very small peak) was m-dinitrobenzene. This impurity is most probably responsible for the slight yellow colour of the nitrobenzene. No other impurities could be detected.

1,d, Scavengers

1,d,i Ethanol

Two batches of anhydrous ethanol from the same source were used. The first one was fractionally distilled, discarding generous head and tail portions, and then transferred to a flask attached to the vacuum line. After thoroughly degassing it, the ethanol was dosed into phials as published(10). In two separate calorimetric experiments one such phial was crushed in a styrene/CH_2Cl_2 solution. This resulted in a temperature rise of about 2^o in 1.0 minutes. From the amount of heat liberated we concluded that a catalytic reaction must have occurred. Having looked at the various impurities which are thought to be normally present in ethanol, it appeared reasonable to check on the possible peroxide content. Therefore, a second batch of anhydrous ethanol was refluxed for 3 hours over CaH_2. It was then fractionally distilled, and transferred to the vacuum line. Phials were made as before, and two of them were broken, successively, into a styrene/CH_2Cl_2 solution. Neither phial produced a rise in the temperature. Hence, we conclude that the first two phials contained most probably a peroxide which initiated a short-lived radical polymerisation. The first batch of alcohol was then tested for peroxides. Both the iodine test and the perchromic acid test gave negative results, showing that the concentration of the suspected peroxides must have been extremely low.

The alcohol used in the calorimetric experiments of Chapter III,2,b, was that of the second batch.

1,d,ii Triethylamine

Et_3N contained in a phial left behind in this laboratory by a previous worker, had been purified as published(11). It was diluted with CH_2Cl_2 in the tipping device by the published procedure(1).

PART 2 : Apparatus and Procedure

a, Calorimetry

Reactions which were considered to be too fast to be followed conveniently by dilatometry ($t_{\frac{1}{2}} \lesssim 25$ min.), were carried out in the adiabatic calorimeter. The apparatus and the operational procedure has been described by Biddulph and Plesch(7).

The platinum resistance thermometer (T) was connected to one of the arms of a conventional Wheatstone bridge (Fig. II,4). The resistances R_1 and R_2 consisted of two decade boxes each, one of 0-100 ohms and one of 0-10 ohms. The "Decade" variable (D) consisted of three decade boxes: 0-100 ohms, 0-10 ohm, and 0-1 ohm. These were connected in series with the compensating lead (C). The external resistance R_x was one decade box of 0-100 ohms. The constant EMF source was provided by a 2 volt accumulator. The out-of-balance current through T was followed with one of the pens of a two-pen recorder (Rikadenki Kogyo Co. Ltd., Japan).

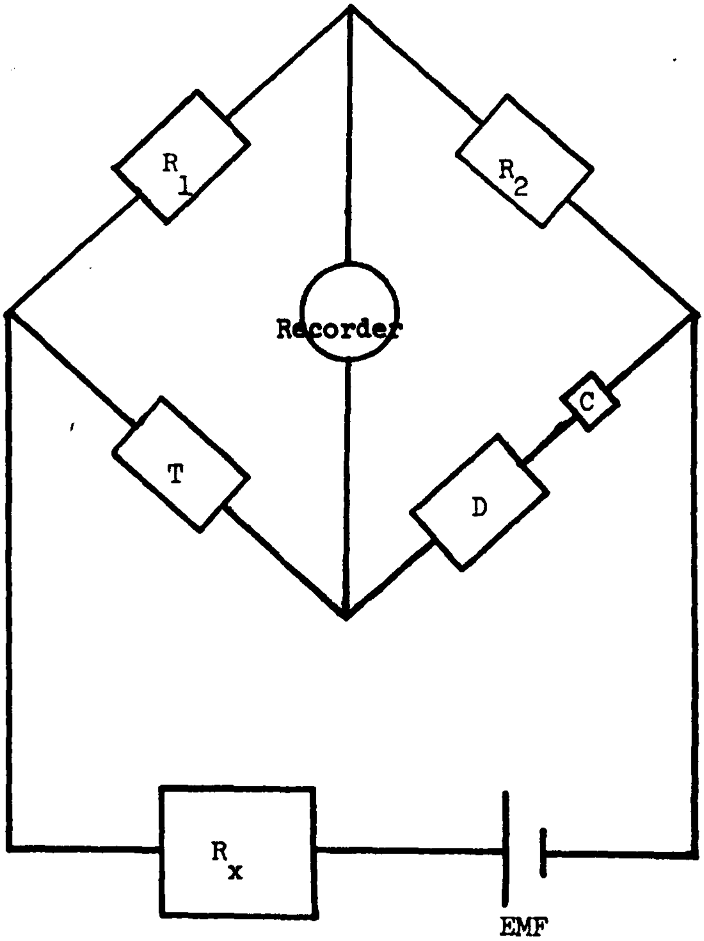
Since for a given EMF and R_x, the highest sensitivity of a conventional Wheatstone bridge is achieved when

$$R_1 = R_2 = R_D + R_C = R_T,$$

I set $R_1 = R_2 = 23$ ohms because this was approximately the resistance

Fig. II,4

The Wheatstone bridge



of T measured at ice-water temperature. Usually $R_x = 0$. If the amount of styrene to be polymerised was expected to result in more than a full-scale deflection on the recording paper, I used $R_x = 10$ ohms.

The thermometer T was calibrated by measuring its resistance at the known freezing points of purified solvents.

b. Conductivity

In calorimetric experiments, the conductivity was followed continuously by means of two platinum electrodes (cell constant $A = 2.70 \times 10^{-2}$ cm^{-1}) fitted to the calorimeter. These electrodes have been described by Gandini, Giusti, Plesch, and Westermann(8). The cell constants, A, reported in this thesis were computed by Fuoss's method(12).

In dilatometric experiments, the conductivity was followed continuously by means of the electrodes fitted to the dilatometer (see following section, Fig. II,6) which was used for the electric field studies reported under Chapter III,2,c.

The electrodes of the calorimeter were connected to a Chandos Linear Conductivity meter which in turn was connected to the other pen of the two-pen Rikadenki recorder mentioned in the previous section. The Chandos instrument was also used for measuring the conductivity of experiment EMs 243 (Chapter III,6), which was carried out in the dilatometer with the two platinum electrodes, see following section.

The conductivities measured during a dilatometric experiment with an applied electric field were measured as follows: The circuit is shown in Fig. II,5. While the electric field was being applied to the reaction solution, a voltage V was measured across a known resistance r (44 ohms ± 5%) put in series with the electrical high tension (EHT) circuit. This voltage was recorded continuously by the Rikadenki recorder.

Let i : current through EHT circuit (a variable)
R : resistance of solution in dilatometer (a variable)
E : applied potential (for a given experiment, a constant)
A : cell constant (0.500 cm^{-1})
K : conductivity

then $V = ir$ and $E = i(R+r)$.

Since r is negligible with respect to the resistance of the reacting solution,

$$E = iR.$$

Hence $$V = Er/R.$$

Since $$K = A/R,$$

then $$K = AV/Er.$$

Thus, since A, E and r are known constants, K is directly proportional to the voltage V being recorded.

c, Dilatometry

The design of the dilatometer used for the electric field experiments (Chapter III,2,c) is shown in Fig. II,6. It is fused to the accessories used for dosing the reagents, as published(8). The

Fig. II,5

The electric circuit for the electric field experiments.

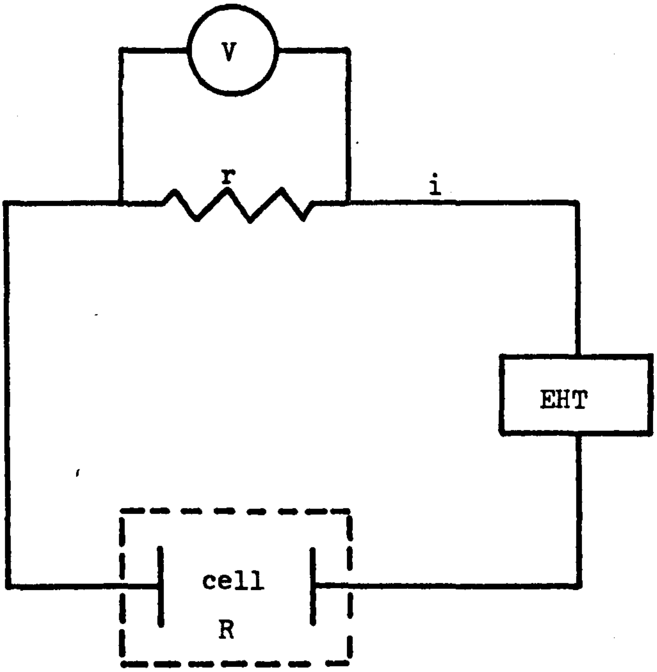
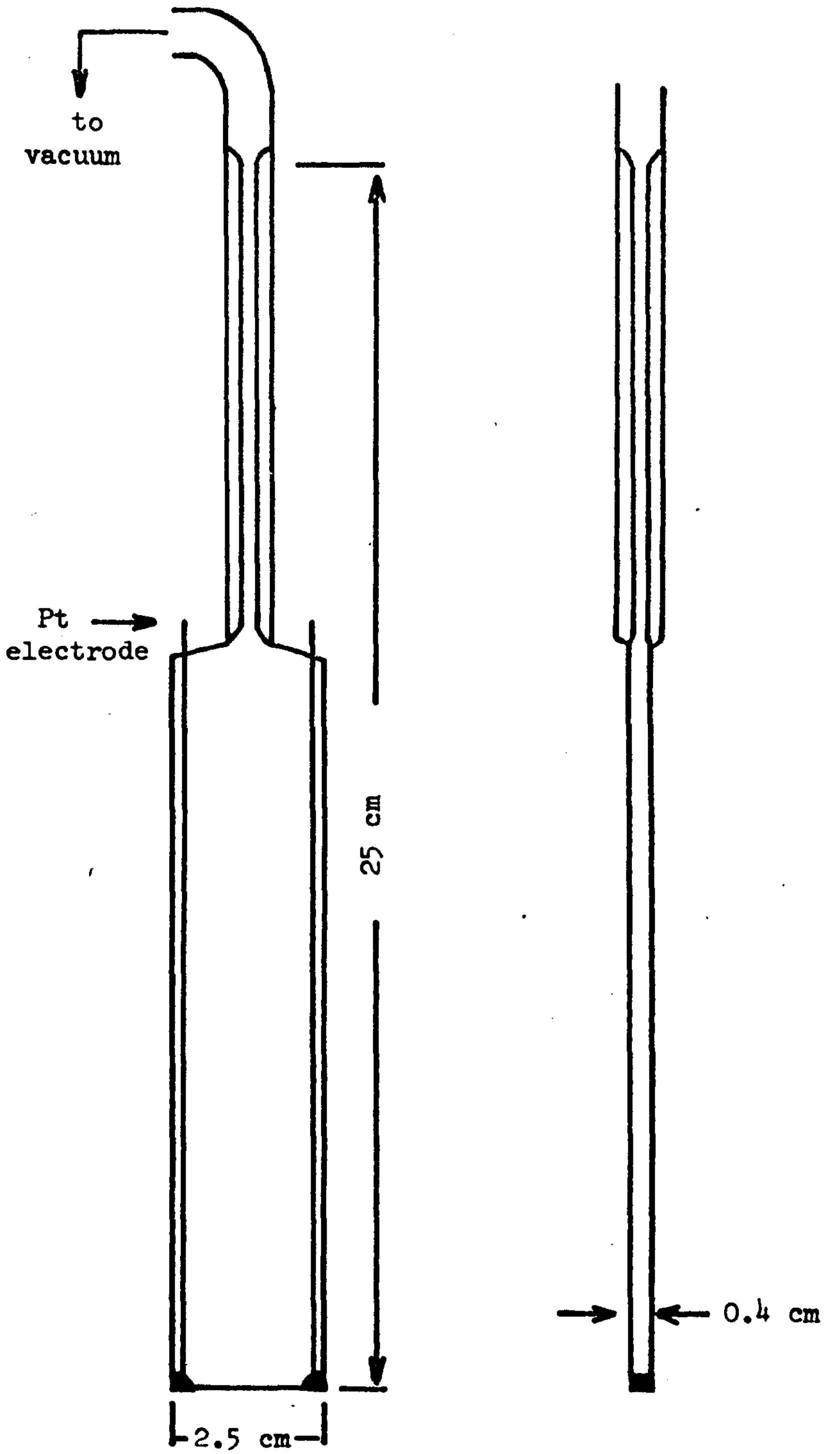


Fig. II,6

The dilatometer for the electric field experiments.



flat design of this dilatometer achieves a very fast heat exchange between the reaction solution and the liquid of the bath. When a solution containing ions (from reaction products) was heated electrically, the meniscus in the capillary rose very slowly, and fell almost instantaneously when the current was turned off.

d, Spectroscopy

d,i Visible - U.V.

The spectra reported in this thesis were taken with a Beckman DB recording spectrophotometer. A special light-tight lid, allowing a large amount of free space above the cell holder of the instrument, was used for large-size devices such as is shown in Fig. II,7. This device was used for measuring the spectra of reacting solutions in the presence of an electric field. The cell was of silica, path-length 1 cm. The procedure for dosing the reagents into A was as published(8).

d,ii Infrared

The I R spectra of the polymers were taken with a Perkin-Elmer 257 Grating Spectrophotometer.

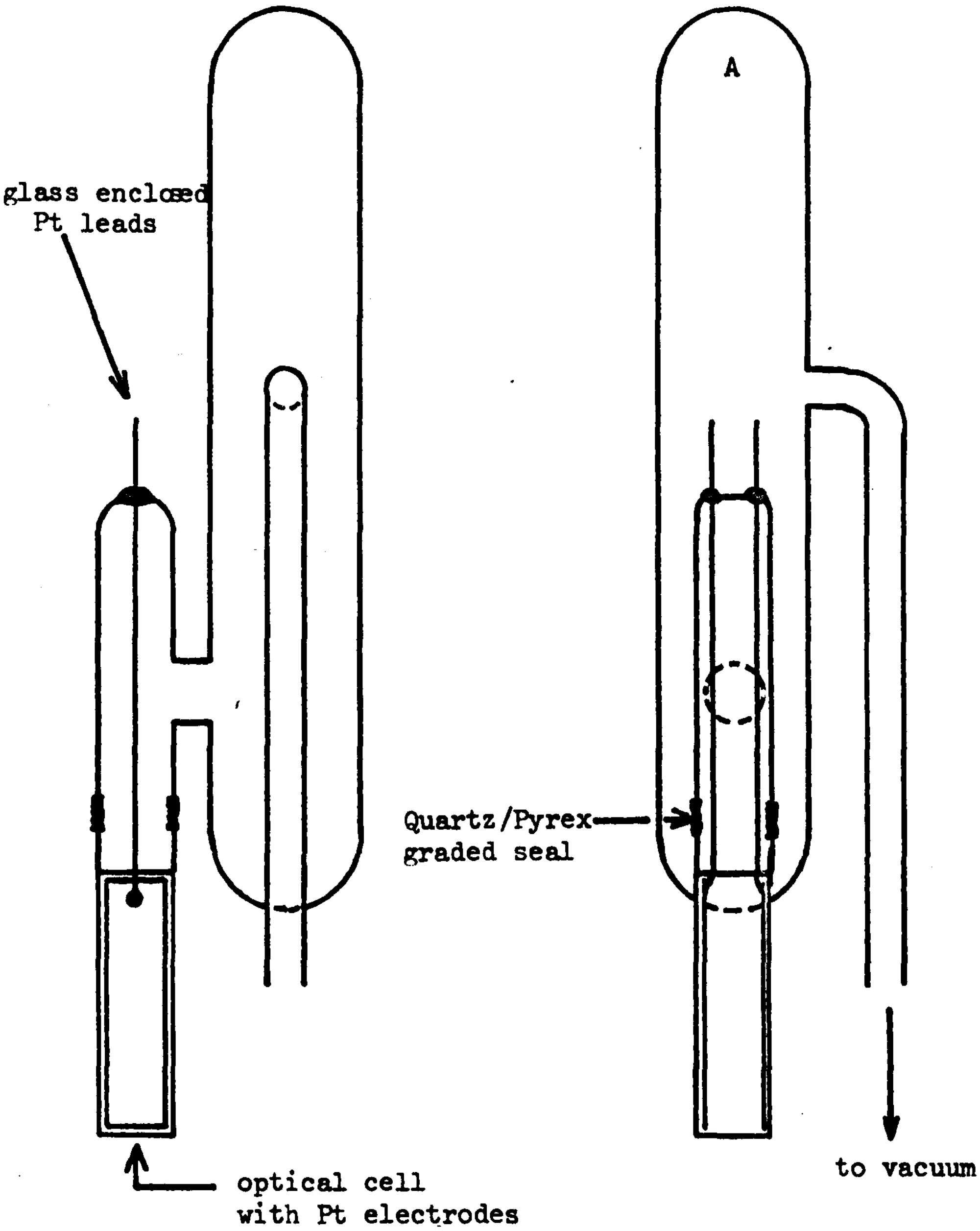
Transparent films of polymers were prepared directly on a NaCl disc by evaporating to dryness a concentrated solution of the polymer in CH_2Cl_2.

e, Electrical High Tension Equipment (EHT)

The potential gradients used in the electric field studies (Chapter III,2,c,) were supplied by a stable d.c. High Voltage Power

Fig. II,7

The optical cell arrangement for the electric field experiments.



Unit of Type 1112A, Serial No. 5, made by Dynatron Radio Ltd., of Maidenhead. This unit is capable of sustaining a maximum of 1 mA without a drop in the voltage.

The circuit to which the EHT equipment was connected is shown in Fig. II,5 of the conductivity section b.

f, Molecular weight determinations

The molecular weights were determined with a Mecrolab Vapour Pressure Osmometer Model 301A. The calibration curve was constructed with Ph_3CH, as a standard, in CCl_4 at 37°. For values of M_n ranging between 400 and 3000 the reproducibility was ±20 units.

g, Isolation of polymers

When a polymerisation was deemed complete, the content of the reaction vessel was poured into a large volume of methanol, containing some 0.880 ammonia to neutralize the catalyst. The precipitated polymer was then filtered off and dried to constant weight at 50° in a vacuum oven. Evaporation under reduced pressure of the filtrate yielded the soluble oligomers. For molecular weight determinations, the two fractions were dissolved together in CCl_4. If there was no precipitable polymer, all the solvent (except when the reaction solvent was $EtNO_2$ or $PhNO_2$) was evaporated off under reduced pressure and the product was weighed. Polymers made in $EtNO_2$ and $PhNO_2$ were isolated by steam distillation, followed by extraction of the polymers with CCl_4.

h, Vapour phase chromatography

All solvents were analysed on a Perkin-Elmer F-11. This instrument was fitted with a 3m silicone oil SE-30/chromosorb P, 100-120 mesh, column.

The reaction products of the experiments carried out in $EtNO_2$ were analysed with a Pye Model 64 instrument, fitted with a 2m 5% silicone oil/chromosorb P column.

Both instruments had a flame ionization detector.

i, C, H, N microanalysis

Polymers made in $EtNO_2$ and $PhNO_2$ were analysed by a F & M, Model 185, instrument.

It was found that, presumably because of the very high carbon content of the polymers, the determination of the C and H content of a polystyrene made with $HClO_4$ in CH_2Cl_2 (with naphthalene as the standard) gave, in the first determination C% + H% = 100.06%, and in the second determination C% + H% = 103.00%. In both determinations however, C%/H% = 12.06 (calc. value 11.92). It was felt that since there was more uncertainty about the degree of purity of the polystyrene made in CH_2Cl_2 than about that of the naphthalene, the latter was the standard used for all the C, H, N determinations on the polymers made in $EtNO_2$ and $PhNO_2$.

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CHAPTER III

THE POLYMERISATION OF STYRENE BY PERCHLORIC ACID

1. INTRODUCTION

As described in the introduction of this thesis the main reasons which aroused suspicion about the ionic mechanism postulated by Reilly and Pepper were the unusually low rate constant of propagation, the unexpectedly high activation energy and the absence of an effect by water on the kinetics of this system.

Gandini and Plesch, though they confirmed Reilly and Pepper's results, have subsequently shown that the polymerisation of styrene by $HClO_4$ in CH_2Cl_2 could be interpreted better in terms of their pseudocationic mechanism which assumes an ester as the propagating species. The ester chain carrier was postulated by virtue of the absence of conductance and colour during polymerisation. It is important to note here that the view that the propagating species is an ester and the description of a non-ionic mechanism are two different issues which, though related, should not be interchanged. One thing is to prove or disprove the non-ionic nature of the propagation mechanism, the other is to see whether the chain carrier is a covalent ester or some other strongly polar active centre.

Since the appearance of the evidence which led to the birth of the pseudocationic mechanism, it has been argued that the lack of a 'killing' effect by water can possibly be due to the very low solubility of water in methylene chloride and the freezing out of the water when the experiments are carried out below zero degrees. In view of the very low concentrations of water used (10^{-3} - 10^{-2}M) I don't believe that these arguments carry much weight. However, since there is considerable uncertainty as to the exact dosing of such small quantities of water in an all-glass vacuum line (even though pretreated with trimethylchlorosilane) it was thought reasonable to use ethanol instead. These experiments have been done in methylene chloride only, and their results will be given in the section "The reaction in methylene chloride". Some reactions under the same heading, were carried out in the presence of triethylamine. Although the use of both these traditional ion scavengers has shed little light on the exact nature of the propagating species, it has given us useful information about the predominantly non-ionic character of the styrene/$HClO_4$/CH_2Cl_2 reaction system.

Sakurada, Ise et al.,(1) have made an extensive study of the ionic polymerisation of various olefinic monomers in the presence of an electric field. Their results indicate that in most of their systems the electric field increases the rate of polymerisation although in some systems they found no effect. For those reactions in which the rates were increased by the electric field, the effect was explained in terms of the increased dissociation of ion-pairs (the second Wien(2) effect), on the reasonable assumption that free ions propagate faster than ion-pairs(3). The absence of an electric field effect in some reactions was explained on the supposition that in these the degree of dissociation of the propagating ion-pairs is so small that the electric field cannot contribute to an increase of the concentration of free ions, i.e. the ion-pairs are too "firm". Generally they found that the effect of an electric field increases as the dielectric constant (DC) of the solvent increases. Yet, they have also found a system (styrene/BF_3 etherate) where there is no electric field effect in toluene (DC_0o:2.44), a definite electric field effect in 1,2-dichloroethane (DC_{20}o: 10.65), and no electric field effect in nitrobenzene (DC_{25}o: 34.82). The lack of an electric field effect in nitrobenzene is explained on the supposition that the degree of dissociation of the ion-pairs is so high (i.e. the concentration of ion-pairs so low) that the electric field cannot increase the concentration of free ions to any important extent. The lack of an electric field effect in the system styrene/I_2/nitrobenzene has been attributed to the same reason.

As a result of the electric field experiments with anionic polymerisations Sakurada, Ise et al.,(4) have proposed an alternative to the second Wien effect. They have found that the free ion rate constant of the styrene/n-butyl-lithium/benzene-tetrahydrofuran system increases with increasing potential gradient, the increase being less pronounced the lower the amount of THF. This phenomenon has been attributed to a free ion desolvation process. The electric field is supposed to remove the THF molecules which solvate the free ions, thus making the free ion become more accessible to monomer.

According to Giusti and Andruzzi(5) the polymerisation of styrene, catalyzed by iodine, occurs via Plesch's pseudocationic mechanism. Hence they conclude that in this system one should not expect an effect of an applied electric field, as in fact was shown by Sakurada, Ise, et al.(6). They have also found an additional system (acenaphthylene/I_2/1,2-dichloroethane)(7) which was not influenced by the application of an electric field, and have thus concluded that their propagation mechanism agrees best with the non-ionic pseudocationic mechanism.

The polymerisation of the system β-methyl-p-methoxystyrene (anethole)/BF_3 Et_2O/1,2 dichloroethane(8) was found to be faster in the presence of an electric field, the effect being ascribed to an ion-pair stabilization process. Recently, however, Giusti et al.(9), in a study of the anethole/iodine system, observed that upon inverting the polarity of the electric field at short regular intervals the polymerisations which, under continuous application of an electric field showed an acceleration effect, failed to exhibit any acceleration. When the inversion of polarity was carried out at longer time intervals the reaction rate was found to be intermediate, between the rates in the absence, and continuous presence, of an electric field. In their attempt to account for these observations, Giusti et al., set out to investigate the concentrations of active species near the anodic and cathodic zones. Their preliminary results substantiate their belief that the accelerations observed under the continuous application of an electric field are due to local variations of the concentrations of the chain carriers.

Since Gandini and Plesch have postulated that the styrene/$HClO_4$ polymerisation in methylene chloride is pseudocationic we should not find an increase in the rate of polymerisation if we carried out this reaction in the presence of an electric field. In order to test this prediction I have carried out several polymerisations in the presence of an electric field. The kinetics of the polymerisation was followed by the high vacuum dilatometric technique, the dilatometer being fitted with two parallel platinum electrodes (Fig. II,6). As will be shown in the discussion of the results, the observed increase of the rate of polymerisation cannot be interpreted to give a clear-cut answer to our problem, namely, what is the propagating species.

It is generally accepted that polymerisations that proceed by an ionic mechanism occur faster the higher the dielectric constant of the medium. In fact this observation has been used by Brown and Mathieson(10) to substantiate the ionic nature of their polymerisations of styrene catalysed by di- and trichloroacetic acids. The results of Pepper,(11) and George and Wechsler(12) on the polymerisations of styrene by $SnCl_4$ in mixed solvents also support the widely held belief that the measured rate constant of ionic polymerisations increases with increasing the dielectric constant of the medium.

The rate of the polymerisation of styrene by perchloric acid, carried out in a mixture of ethylene dichloride and carbon tetrachloride, was also shown(13) to increase with an increase in the ethylene dichloride content. The major drawback to the above examples is that these experiments were all carried out in mixed solvents where the extent and nature of solvation of the reactive centres is very uncertain, i.e. on the molecular scale the mixed solvent is not homogeneous by virtue of the different polarity and geometry of the individual solvent molecules. If the 'mixed solvent' procedure is used to demonstrate the ionic nature of a polymerisation as indeed Reilly and Pepper did, it should be possible to test the validity of their kinetic conclusion by carrying out the same reaction in different inert solvents of varying polarity. As simple as this may appear, the choice of solvents turns out to be extremely limited. The solvent must be inert to the perchloric acid, and given styrene as the monomer, the solvent should be less basic, which excludes all oxygen-and most nitrogen-containing solvents. Not only must the solvent be inert but it also needs to be a good solvent for the catalyst, the monomer, and the polymer. The choice of solvent is restricted further by the requirement that it should have a wide liquid range so that the reactions can be carried out over as wide a temperature range as possible. Guided by these requirements I have carried out several experiments in carbon tetrachloride, chloroform, nitroethane and nitrobenzene. The results and their discussions will be described in this chapter under the subsections 3, 4, 5 and 6.

2.a. THE REACTION IN METHYLENE CHLORIDE

In order to acquire the skill of handling the adiabatic calorimeter, I carried out several 'normal' experiments which consisted of crushing a dilute perchloric acid phial into a styrene/methylene chloride solution, and recording the resulting temperature change of the solution as a function of time. In some cases a two-pen recorder has been used to follow simultaneously the temperature and the conductance of the polymerising solution. Several reactions were also followed by the high vacuum dilatometric technique, and their kinetic results will be reported together with the results of the calorimetric experiments. The experimental set-ups and procedures have been described in Chapter II under sections 2a, 2b, and 2c.

A summary of the results is given in Table III,1.

Having mastered the art of running the adiabatic calorimeter it became evident that the polymerisation of styrene by perchloric acid is not strictly of first-order with respect to the concentration of the monomer as was reported by Reilly and Pepper(13), and Gandini and Plesch(14). This consistent observation was confirmed by the subsequent high vacuum dilatometric experiments. Although the conversion time-curve does not reveal a strikingly different behaviour from first-order kinetics, the first-order plots i.e. log m_t vs. time, clearly show a curvature

Table III,1

The polymerisation of styrene by perchloric acid at 0°. Summary of calorimetric and dilatometric results

EMs	$[C_8H_8]$ (M)	$[HClO_4]^+$ (10^4M)	k' (10^3sec^{-1})	$k'/[HClO_4]$ ($M^{-1}sec^{-1}$)	K^x (10^8mho-cm^{-1})	DP	yield (%)
12C	0.331	19.8g	2.76	1.35	7.7	13.8	60
2C	0.336	12.1g	1.85	1.52	-	-	100
1C	0.335	10.3g	1.67	1.61	-	-	100
15C	0.335	10.2w	2.20	2.60	6.5	14.1	100
27D	0.319	17.1g	2.10	1.23	-	12.3	100
24D	0.326	11.0g	1.31	1.19	-	19.0	100
23D	0.322	11.0g	1.38	1.26	-	17.7	100
21D	0.342	10.5g	1.36	1.30	-	17.6	100
217D	0.336	4.66g	0.61	1.30	-	21.5	100
216D	0.337	4.53g	0.63	1.39	-	20.2	100
215D	0.342	4.15g	0.61	1.47	-	-	100

Continued overleaf. . . . . . .

Table III,1 (continued)

EMs	$[C_8H_8]$ (M)	$[HClO_4]$[+] (10^4M)	k' (10^3sec^{-1})	$k'/[HClO_4]$ ($M^{-1}sec^{-1}$)	K[x] (10^8mho-cm^{-1})	DP	yield (%)
220D	0.343	3.77g	0.44	1.15	-	32.3	100
218D	0.354	2.62g	0.32	1.23	-	20.2	100
219D	0.337	2.27g	0.25	1.11	-	17.3	100
225D	0.332	4.19m	1.27	3.03	-	20.6	100
221D	0.346	4.18b	1.16	2.78	-	19.9	100
222D	0.340	4.17b	0.98	2.34	2.8	26.7	100
223D	0.335	3.11b	0.95	3.05	1.4	22.8	100
224D	0.340	3.11b	0.84	2.70	1.6	23.1	100
229D	0.338	2.20m	0.52	2.36	1.8	17.0	100
230D	0.335	2.19m	0.50	2.29	2.6	21.8	100
227D	0.345	0.79m	0.14	1.83	2.3	20.4	100
228D	0.348	0.78m	0.14	1.84	1.0	24.4	100

[+] The letters denote the different sources of the perchloric acid:

g = Gandini, w = Westermann, b = Bertoli, m = Mathias

[x] The conductances of experiments EMs 12C and 15C were measured with the Chandos Linear Conductivity meter (Ch. II,2,b); all others were measured with the E.H.T. equipment (Ch. II,2,e).

[*] Reaction to which ethanol has been added after the first half-life.

indicative of an acceleration (Fig. III,1). This acceleration only becomes evident at, or sometime after, the first half-life. Hence, the first-order rate constants which are reported in Table III,1 are those which correspond to the slopes of the initial rectilinear portion of the first-order plots. As long as I had stabilized the calorimeter to a constant temperature (as opposed to a constant precooling curve) the first-order plot resulting from the subsequent experiment revealed this acceleration. However, if I stabilized the temperature to a slight precooling curve the first-order plot shows the following features: a straight line up to about 61% conversion, then a very slight acceleration followed by a deceleration (Fig. III,2). The overall curve looks almost completely like a straight line up to 97% conversion. The first-order rate constant obtained from the slope of this line is nearly the same as that obtained by just taking the slope of the initial straight line which resulted up to 61% conversion. Upon retracing the conversion-time curve (A) of this experiment and superimposing it onto an equivalent experiment but without a precooling curve (B) one can deduce by difference the fate of the precooling temperature trace (C), (Fig. III,3).

The first-order rate constants, as tabulated on Table III,1, are linearly proportional to the initial acid concentration. However, taking into consideration the different sources of the

Fig. III,1

The polymerisation of styrene by $HClO_4$ in CH_2Cl_2 at 0°.

First-order plots of typical calorimetric and dilatometric reactions.

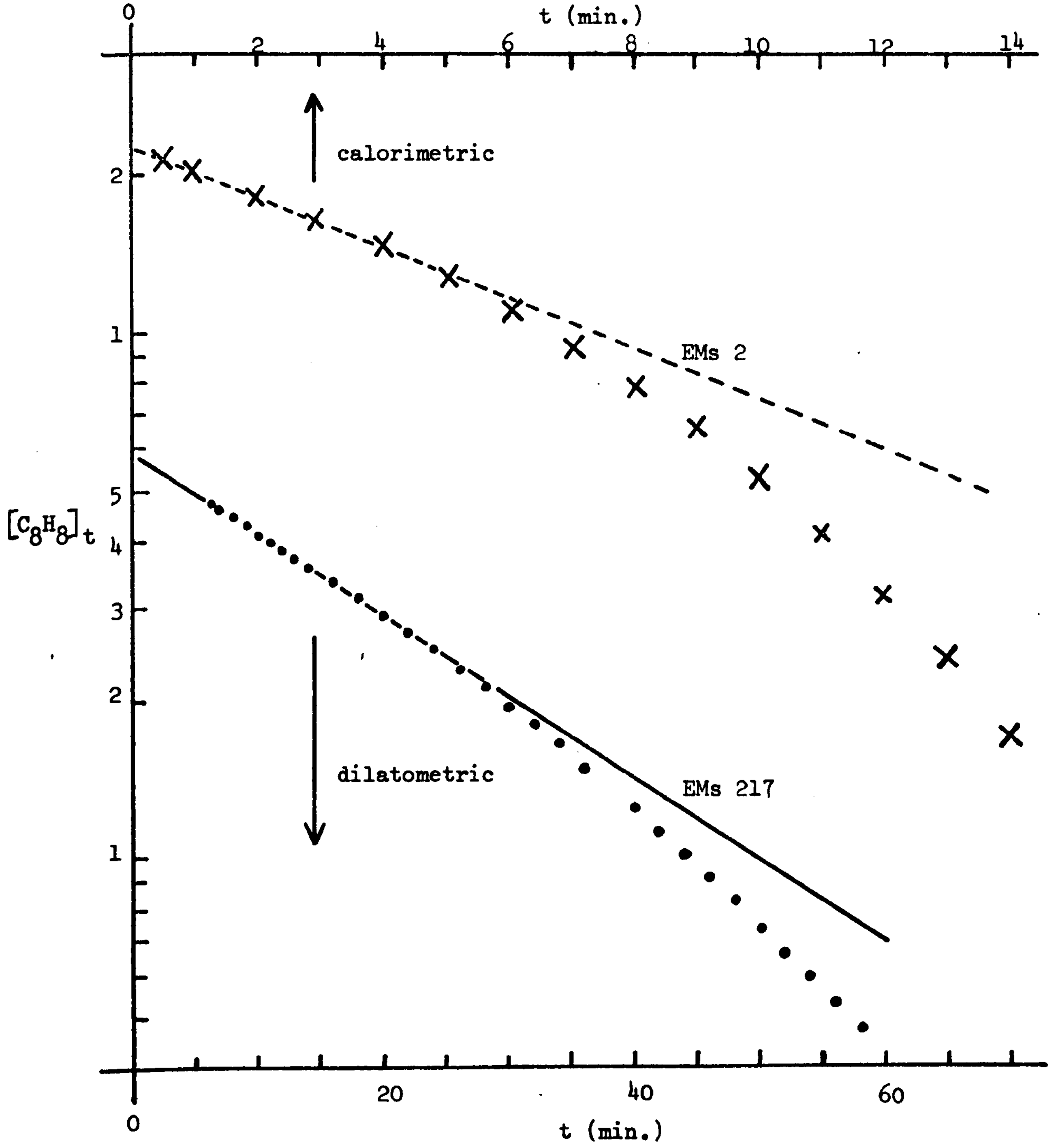


Fig. III,2

The polymerisation of styrene by $HClO_4$ in CH_2Cl_2 at 0°.

Comparison of the first-order plots of two calorimetric experiments.

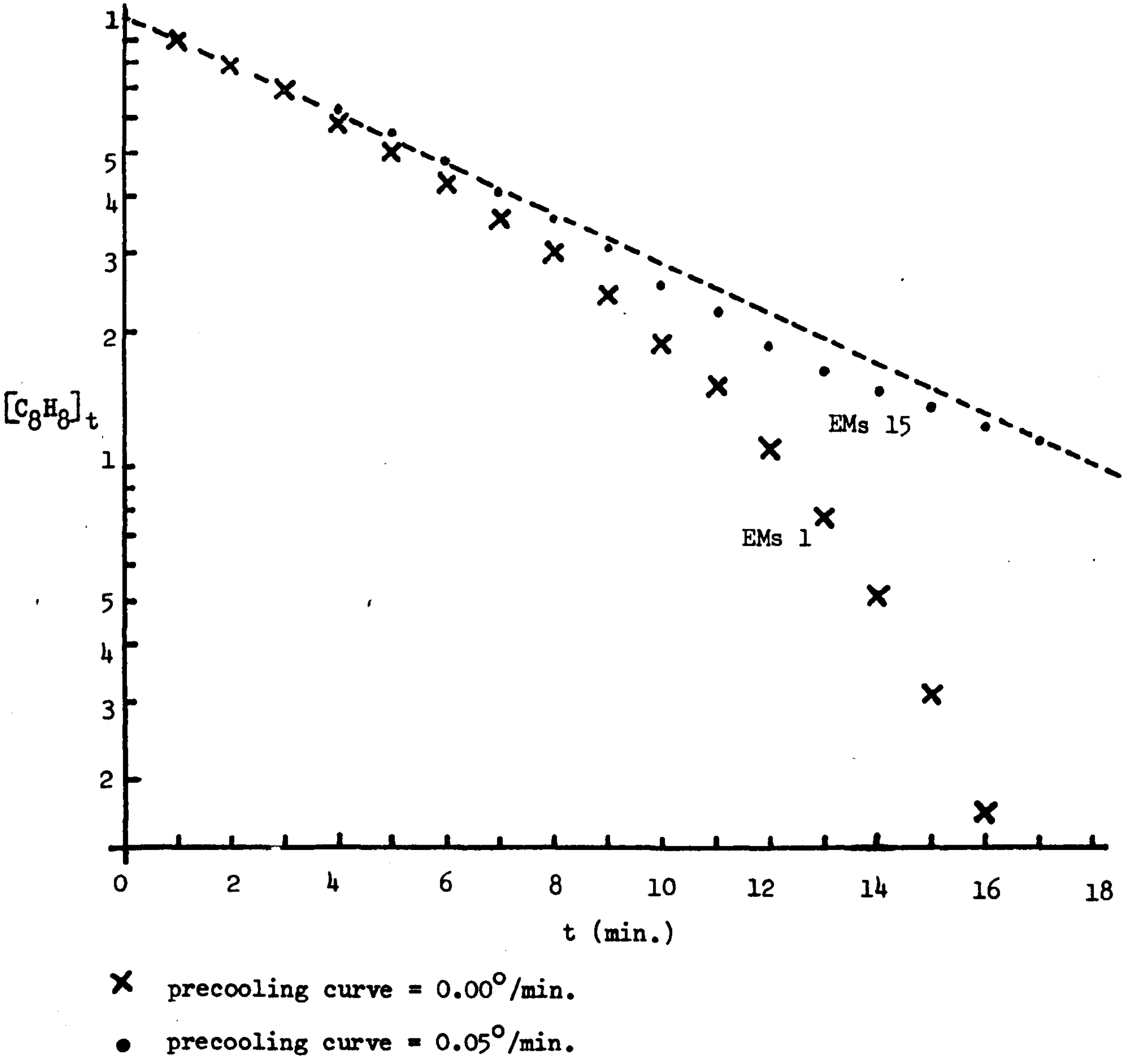
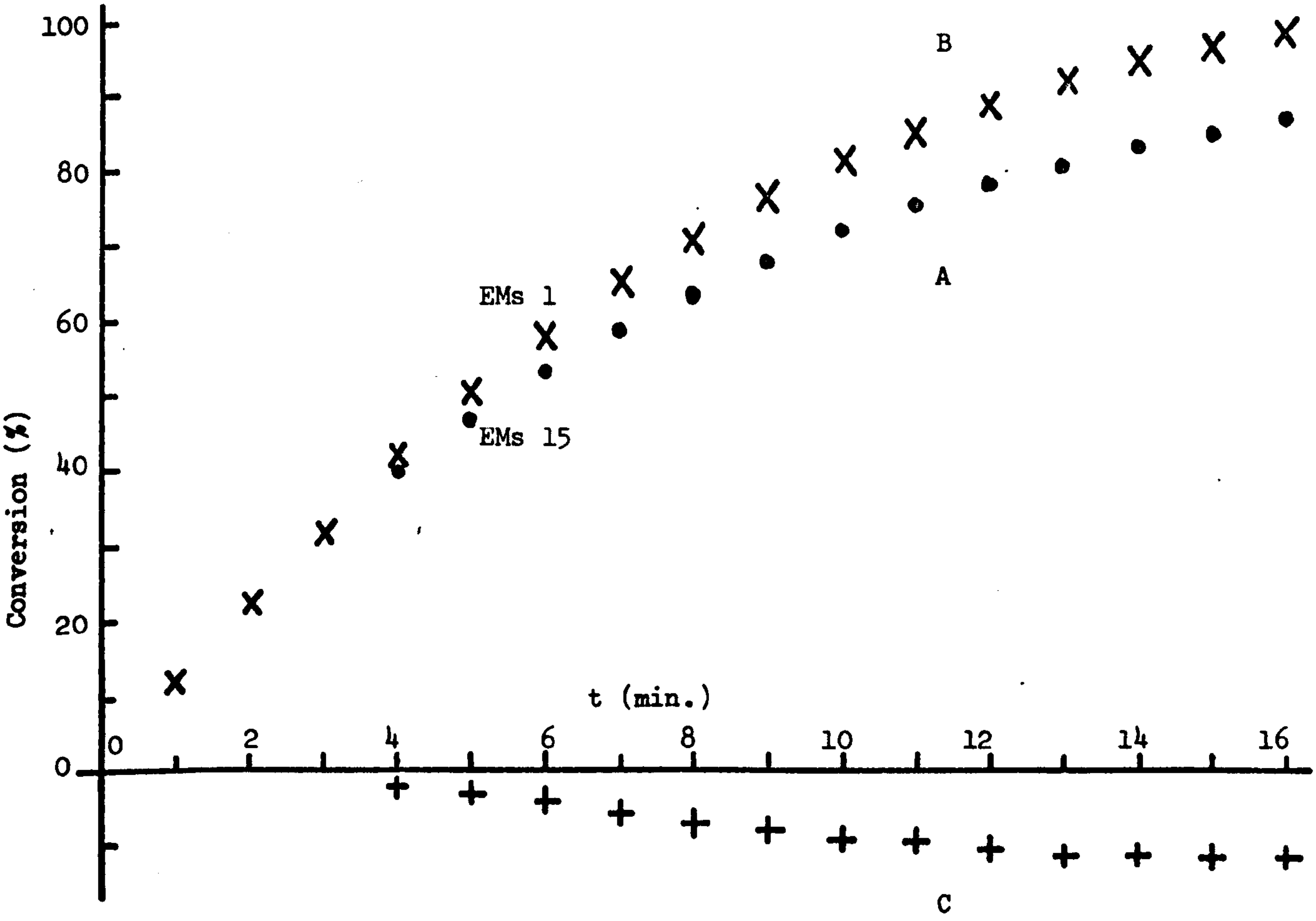


Fig. III,3

The polymerisation of styrene by $HClO_4$ in CH_2Cl_2 at 0°.

Comparison of the conversion-time plots of two calorimetric experiments, one with and one without a precooling curve.



perchloric acid, one obtains two sets of first-order rate constants each of which gives a different slope on the k' vs. $[HClO_4]_o$ plot, Fig. III,4. The slopes, which according to the kinetic rate expression

$$R_p = k_2[HClO_4]_o \, [M] = k'[M]$$

give the second order rate constant k_2, are 1.26 M^{-1} sec^{-1} and 3.05 M^{-1} sec^{-1} respectively.

An order analysis (plot of the logarithm of the instantaneous rate against the logarithm of the monomer concentration) of a normal calorimetric experiment (EMs 15) shows that the order of the reaction with respect to the monomer concentration is less than one. The order analysis of two dilatometric experiments, EMs 217 and EMs 225, also gave reaction orders less than one, Table III,2.

The specific conductance, K, tabulated in Table III,1 is that which was measured between about 15 seconds after the catalyst was added to the styrene/methylene chloride solution, and the first half-life of the reaction. During this period the conductance remained constant and was approximately equivalent to the conductance of the styrene/methylene chloride solution alone, $K_0o \approx 6.4 \times 10^{-8}$ mho cm^{-1}. The reaction solution remained completely colourless. At, or shortly after the first half-life, the conductance rose slowly at first, and when the reaction was almost over, it rose quickly to

Fig. III,4

The polymerisation of styrene by $HClO_4$ in CH_2Cl_2 at 0°. The acid dependence of the first-order rate constant.

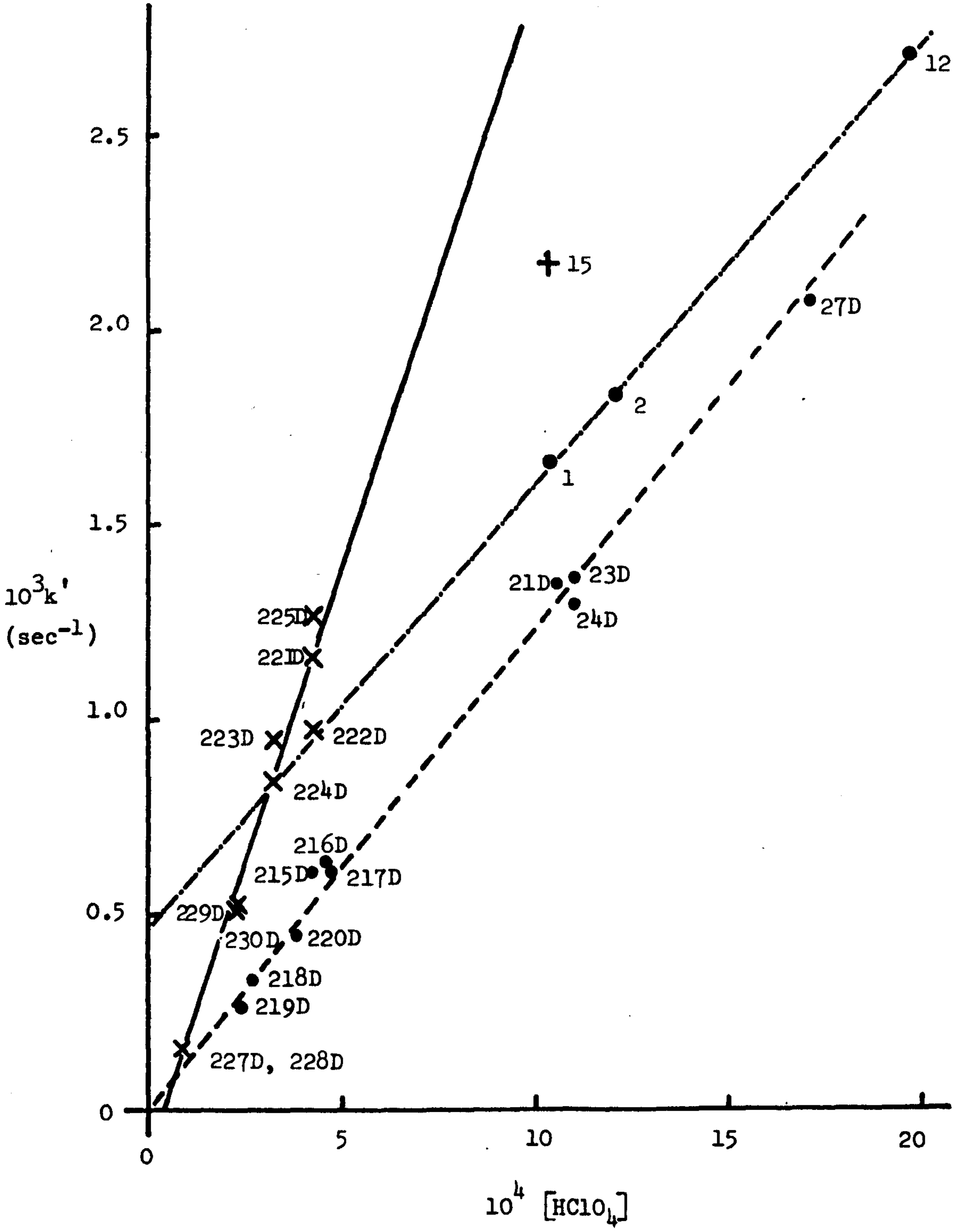


Table III,2

The results of an order analysis of three typical reactions at 0°.

EMs	$[C_8H_8]$ (M)	$[HClO_4]$ (10^4M)	Order
15C	0.335	10.2	0.58
225D	0.332	4.19	0.79
217D	0.336	4.66*	0.84

*The concentration of the acid should be divided by 2, see text.

a plateau. At this stage, the reaction solution was yellow. If the reaction mixture was left unattended the conductance would start decreasing very slowly.

Of the above results, the first item which needs clarification is the internal disagreement between the two second-order rate constants. Evidently, according to the Table III,1 and the Fig. III,4, all the experiments whose catalyst originated from a stock left in our laboratory by A. Gandini are on the line which yields the $k_2 = 1.26\ M^{-1}\ sec^{-1}$. All the rest of the experiments (except experiment EMs 15) give the line whose slope is $3.05\ M^{-1}\ sec^{-1}$. The source of the catalyst for these latter experiments were from a stock left over by V. Bertoli, and from my own perchloric acid extractions, the method of which is described in Chapter II,1,b,i. The catalyst for the experiment EMs 15 was again from another source, P.H. Westermann.

It will be found that if we moved all the experimental points, which make up the line of $k_2 = 1.26\ M^{-1}\ sec^{-1}$ toward the left by taking $[HClO_4]_0/2$, the points will all be in line with $k_2 = 3.05\ M^{-1}\ sec^{-1}$. According to Gandini and Plesch(15) the second order rate constant at 0^o is $2.66\ M^{-1}\ sec^{-1}$. This agrees well with the result previously obtained by Pepper and Reilly(13) in the 1,2 dichloroethane/carbon tetrachloride solvent system. Interpolation for solutions of equivalent dielectric constants gave $k_2 = 2.6\ M^{-1}\ sec^{-1}$.

In view of the fact that, regardless of the source of the catalyst all my reactions were qualitatively similar, and guided by the previously established k_2's, we will assume that the catalyst concentrations of those reactions which make for the $k_2 = 1.26 \ M^{-1} \sec^{-1}$ were in error by a factor of about 2.

As a result of the accelerations which I observed in all of my experiments, a comparison of my k_2 with that found by other investigators becomes somewhat meaningless. It is conceivable that my reactions started accelerating even before the first half-life of the reaction was over, so that, having taken the slopes of what appeared to be a rectilinear portion of the first-order plots, my internal rate constants (k') came out consistently higher than expected for a $k_2 = 2.66 \ M^{-1} \sec^{-1}$. In any case, a higher value of k_2 is an encouraging sign since, upon extrapolation of the forthcoming arguments, k_2 should in fact be even higher.

Both groups of investigators, Reilly and Pepper as well as Gandini and Plesch, have found their first-order plots to be rectilinear up to almost total conversion of the monomer. Hence, an explanation is due as to why they have not found the accelerating feature of this reaction. Initially I thought that the curvatures which I observed on the first-order plots meant that the usefulness of the calorimetric technique is limited to half-lives of about four to five minutes. Although any information obtained from reactions of longer half-lives should be considered with due care, the calorimetric technique still gives quite good results as far as I can judge by the fact that the accelerations are very gradual.

For the purpose of a kinetic study, one of the major factors which determines the success of the calorimetric technique, is the attainment of a stable initial temperature which enables one to assume a stable temperature baseline. To this end I have placed much effort in stabilizing the temperature not just to a constant precooling rate but to a constant temperature. This constant temperature requirement becomes the more important and critical the longer the half-life of the reaction. As long as I had stabilized the calorimeter to a constant temperature (as opposed to a constant precooling rate) the first-order plot resulting from the subsequent experiment revealed the gradual curvature indicative of an acceleration. As has been stated previously, this gradual curvature was much less pronounced when I stabilized the temperature of the calorimeter to a constant precooling rate. In view of the fact that Gandini has worked with much steeper precooling curves than I did, this has (in the absence of any other reasons) hidden the acceleration effect which Gandini thus never saw.

Since the non-first-order nature of the reaction has been confirmed by high vacuum dilatometry, why did Reilly not detect this acceleration? As will be seen from subsequent discussions, the propagating species which is responsible for the observed increase in the rate of consumption of monomer is only present at very low concentrations and appears to be very susceptible to impurities.

Hence, it seems that this species which is generated during the reaction cannot survive in an "open" dilatometric system. In fact, that impurities (not necessarily only water) are present even in our vacuum systems seems to be shown by the fact that the plot of the first-order rate constants vs. initial acid concentration (Fig. III,4) shows an intercept on the acid concentration axis. This intercept gives us an idea of the amount of the residual impurities in our system. Thus, unless the level of impurity is decreased to such a degree that whatever amount of impurity is still left in the system is very soon consumed by, say, a propagating species, any higher level of impurity as might be expected in an "open" system will give results consistent with the previously observed first-order behaviour. On the assumption that the polymerisation reaction follows the general form of

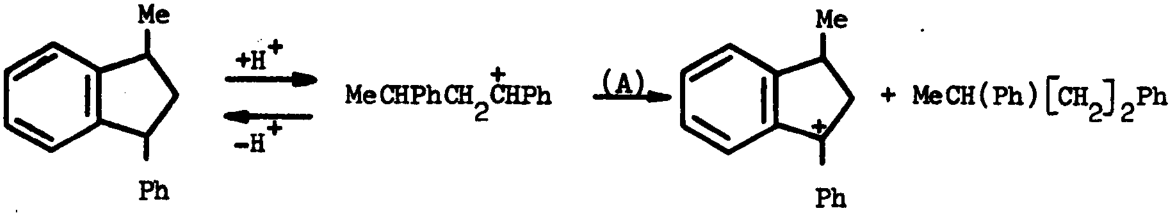
$$\text{Rate} = k\, m^n$$

I have made an order analysis (plot of log $(\text{rate})_t$ vs. log m_t) on three typical reactions, the results of which are tabulated in Table III,2. Although, in the light of our new interpretation of this system, this order analysis is not really justified, it helps to substantiate the effect of impurities on the kinetics of this system. With decreasing initial perchloric acid concentration the "order" of the reaction increases, i.e. the reaction approaches first-order kinetics since decreasing the initial acid concentration results in an increase in the relative concentration of impurities.

The most important factors which contributed to the birth of Plesch's pseudocationic polymerisation came from the combination of calorimetric, spectroscopic, and conductimetric studies of the styrene/$HClO_4/CH_2Cl_2$ system(14). It was found that in the course of the polymerisation the reaction solution remained colourless. When the polymerisation ceased, the solutions became yellow and the visible spectrum showed an absorption at about $\lambda = 424$ nm. The spectroscopic studies revealed that upon scanning the polymerising solutions at constant wavelength ($\lambda = 424$ nm), the D_{424} never exceeded 0.0087 (experimental error for D = 0.000) until near the end of the polymerisation at which time D_{424} increased following a second-order curve. The conductimetric results showed that while polymerisation proceeds (here the styrene was added to a $HClO_4/CH_2Cl_2$ solution) the conductance of the reacting solution remained at a level characteristic of the acid solution alone. Near the end of the polymerisation, the conductance rose in a manner closely resembling the corresponding increase in the D_{424} of the spectroscopic experiments. Although at the time the absorptions observed at the end of the reactions were thought to be due to the secondary polystyryl cation, the real origin of the absorption at 424nm was later ascribed to the poly(styryl)indanyl ion(16). The development of these findings as well as the details of the last ionogenic reaction were presented in the introduction of this thesis. Suffice it to say here, the absence of a conductance during the polymerisations studied by Gandini and Plesch is in obvious disagreement with my conductance results.

As has been previously described, at or after the first half-life of my polymerisations the conductance rises, if only very slowly at first, and reaches a maximum at the end of the polymerisation. The disagreement between the observations made by Gandini and myself lies in my detecting a rise of conductance <u>during</u> the polymerisations. Since the rise of conductance between the first half-life and the near total consumption of the monomer is only very small, and since no correlation could be found between the conductance rise and the conversion, one cannot conclude that the observed increase of conductance is directly related to propagating free ions. However, in view of the fact that the increase in conductance is in accord with the continued increase observed in the reaction rate, it is reasonable to assume that the two phenomena are a function of each other.

In a detailed spectroscopic study of the carbonium ions derived from aromatic olefins, Bertoli and Plesch(17) have found that when styrene, 1,3-diphenylbut-1-ene or 1-methyl-3-phenylindane react with a large excess of perchloric acid in methylene chloride their U.V. spectra are the same showing two maxima at 308 and 420 nm ($D_{420} > D_{308}$). These peaks have been attributed to the 1,3-diphenylindanyl cation. The same investigators have also shown that under the above conditions as well as under the conditions of polymerisation, the formation of the indanyl ion is always preceeded by the formation of the 1,3-diphenylindane. The direct ionisation of the indane occurs only in the presence of a large excess of acid. It was suggested that it occurs via a ring opening of the indane (A) forming the 1,3-diphenyl-n-butyl ion (B) which in turn abstracts a hydride ion from another indane molecule giving the 1,3-diphenylindanyl cation (C) and 1,3-diphenyl-n-butane, i.e.



(A) (B) (C)

The 1,3-diphenyl-n-butyl ion has in fact been identified by Bertoli and Plesch(17a).

It appears that in the light of the above results the acceleration which I observed in my polymerisation reactions could be explained in the above terms provided one abandons the prerequisite that the indanyl ion is formed only when a large excess of acid is present in the system. This prerequisite is obviously not found while the polymerisation proceeds. However, indane end groups are formed during the polymerisation(18), although very slowly, and the increase of the conductance is undeniable. Hence, it is conceivable that the conductance is due to the appearance of a very low concentration of indanyl ions and thus necessarily also due to the intermediate oligostyryl ions by which the indanyl ions are formed. In view of the very high reactivity of free ions such as the secondary oligostyryl ion, only a very small concentration of these would be needed to make themselves evident in the kinetics in terms of the observed acceleration. In the light of all my results, the observed accelerations are most probably due to the species (B) which is generated in the course of the reaction.

The appearance of the ion (B) during the polymerisation could possibly come also from the direct dissociation of an ester. Once it is formed it can lead to the formation of indanyl ions via a hydride abstraction. Since this process requires the presence of the polystyrylindane, whose formation during the polymerisation is slow, it could lead to a gradual increase of the concentration of (B) and hence to a gradual increase in the rate of polymerisation. As one would expect from an ionic propagating species, it is very susceptible to impurities, and in the presence of these, the overall polymerisation reaction behaves like a normal first-order reaction. Also, in view of Pepper's(19) finding, that the polymerisation reaction at 0^o is partially suppressible by the addition of a perchlorate salt, the nature of the suppressible propagating species must be ionic and in equilibrium with some other non-ionic species. Most likely, this non-ionic species is the propagating ester of Gandini and Plesch.

2.b. THE POLYMERISATION OF THE SYSTEM STYRENE/$HClO_4$/CH_2Cl_2 IN THE PRESENCE OF ETHANOL AND TRIETHYLAMINE

As has been stated in the introduction of this thesis, the attacks made on Gandini and Plesch's pseudocationic theory required further work to elucidate the nature of the propagating species. It was already known that small quantities of water had no appreciable effect on the rate of consumption of monomer. However, because of the alleged insolubility and freezing out of the water in the methylene chloride, which would thus loose its carbonium ion "killing" ability, I set out to study the effect of ethanol on the kinetics of this system. In all but one of these experiments the alcohol has been added to the styrene methylene chloride mixture before adding the perchloric acid catalyst. This method was dictated by the belief that adding the alocohol to the already polymerising system would result in a too high local concentration of alcohol in the mixture at the moment of crushing the phial. On the other hand, adding first the alcohol and then the catalyst introduces some uncertainties as to the effect of alcohol on the initiation reaction of the perchloric acid with styrene. In view of the results, the sequence of addition of the alcohol is indeed extremely critical.

The results obtained at 0° and -70° are different in many important respects and they will therefore be presented separately.

Experiments at 0°, Table III,3:

Although in these experiments the ratio of the alcohol to the initial acid concentration was always above one, those experiments in which the acid was added after the alcohol did give polymerisations. However, the reaction traces were not first-order curves and the reactions were very much slower than they would have been in the absence of alcohol.

According to the reaction trace of experiment EMs 7 (over 24 seconds) the yield of the polymer should have been 6% whereas the actual polymer collected corresponded to a yield of 39%. The molecular weight of this polymer (DP = 24.7) was 'normal' with respect to equivalent reactions in the absence of alcohol. The reaction EMs 16 is a repetition of EMs 7 except that it was intentionally killed immediately after the initial fast reaction. The yield of the much lower molecular weight product (DP = 3.4) was 21%. The reaction EMs 8, similar to reaction EMs 7 in monomer and acid concentration, was left to proceed and also showed that the polymerisation was not inhibited by the alcohol. Hence, it appears that the yield of the recovered polymer depends on the length of time one allows the slow polymerisation to proceed. This conclusion is also borne out by the experiments carried out at -70°.

Upon adding the alcohol 5 minutes after the acid (i.e. while the polymerisation is proceeding normally, EMs 12) the reaction is killed, and the yield of the recovered polymer (60%) corresponds

Table III,3

The polymerisation of styrene in the presence of ethanol+.

Experiment at 0°

EMs	$[C_8H_8]$ (M)	$[HClO_4]$ (10^3M)	$[EtOH]$ (10^3M)	$\frac{[EtOH]}{[HClO_4]}$	K_{max} (10^7mho-cm^{-1})	yield* (time) (%) (min.)	DP
7	0.331	1.34	5.88	4.4	3.81	39(~24)	24.7
16	0.335	1.36	6.03	4.2	3.99	21(0.8)	~3.4
8	0.331	1.40	2.93	2.1	2.20	90(~33)	21.6
12	0.331	1.98	5.88	3.0	0.75a 4.06b	60(85)	13.8
				Experiments at -70°			
9	0.166	10.3	11.8	1.14	V. High	100(220)	44.2
13	0.168	14.2	5.9	0.42	V. High	82(19)	29.2
14	0.169	14.9	11.9	0.80	V. High	93(~59)	41.9

+In all experiments except EMs 12 the EtOH was added before the $HClO_4$.

*The yields of these reactions in the absence of alcohol are 100%.

a At time of addition of $HClO_4$ to C_8H_8/CH_2Cl_2

b At time of addition of EtOH to $C_8H_8/HClO_4/CH_2Cl_2$

to that expected on the basis of the reaction trace even though the reaction mixture was left undisturbed for 85 minutes ($t_{1/2}$ = 4.2 min.). The conductance in all the above reactions was followed continuously. This conductance appeared as soon as the perchloric acid was released into the reaction mixture. The conductance of the reaction mixture EMs 12 was initially, i.e. before the alcohol was added, the same as that of the solvent and acid alone, but it increased immediately when the alcohol phial was crushed. All the reaction mixtures, including that of EMs 12 after the alcohol was added, had a higher conductance than when the polymerisation proceeds without alcohol in the system. The temperature and conductance traces of these experiments are shown on Fig. III,5.

The qualitative behaviour of the conductance curves have helped us in the interpretation of these results. But the only quantitatively meaningful information from these conductance measurements came from the initial conductance maxima at the instant the acid phial was crushed into the reaction mixture. These maxima are tabulated, in terms of the conductivity K, in Table III,3. The plot of the K_{max}, normalized to unit initial acid concentration, against $[EtOH]/[HClO_4]$ gave a straight line as shown on Fig. III,6.

Experiments at -70°, Table III,3:

As pointed out previously, the polymerisation of styrene, in the absence of any alcohol, proceeds by two stages, the fast ionic first stage (Stage I) followed by the slow pseudocationic

Fig. III,5

The polymerisation of styrene by $HClO_4$ in CH_2Cl_2 at 0°.

The effect of alcohol

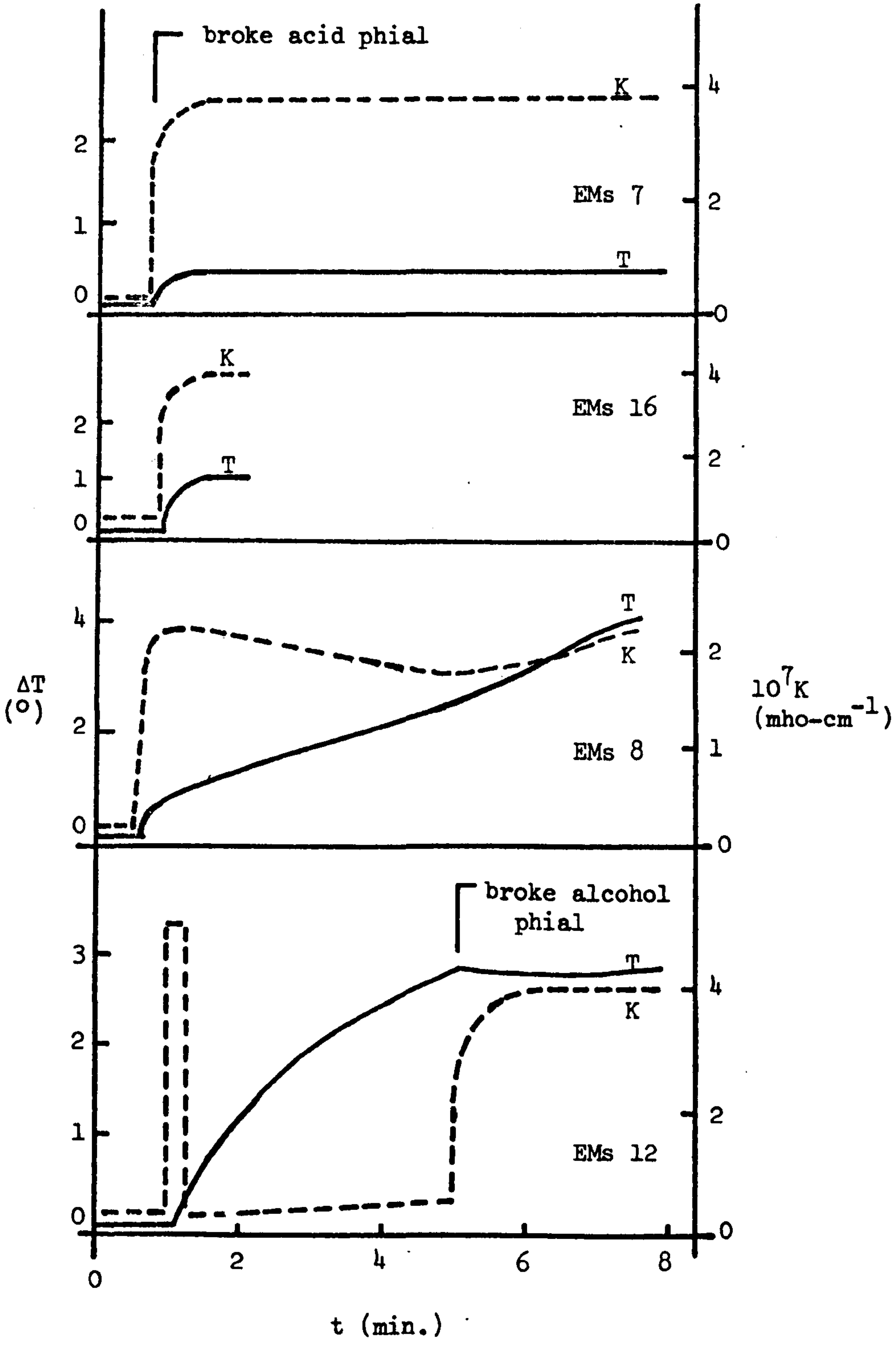
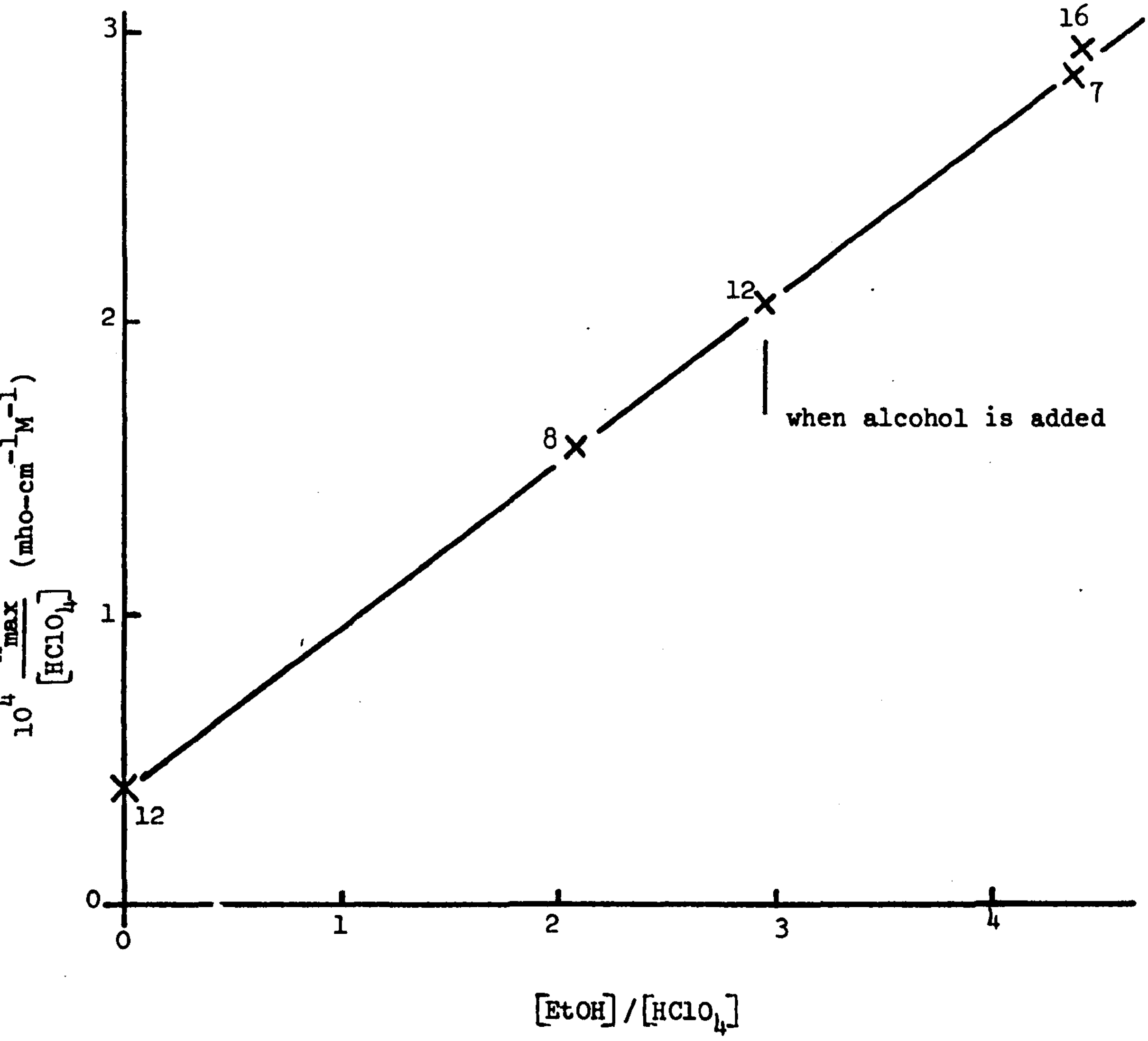


Fig. III,6

The polymerisation of styrene by $HClO_4$ in CH_2Cl_2 at 0°.

The effect of alcohol on the conductivity.



Stage II. Hence, these experiments had the dual purpose of testing the effect of alcohol on Stage I, and on Stage II. In all these experiments, the alcohol was added before the perchloric acid. Provided that the ratio of the alcohol to acid concentration is below one, the rate of the Stage I appears to decrease with increasing alcohol concentration. However, in terms of the monomer consumed, it still seems to be the predominant stage. If the [alcohol]/[acid] ratio is above one (EMs 9), the Stage I disappears almost completely but the Stage II, though it becomes very slow, still persists. The reaction was left running for a long time (220 min.) and the recovered polymer corresponded to 100% conversion. Hence, here again, as with the experiments at 0°, given enough time for the reaction to proceed, the reaction will go to completion. The non-ionic propagating species appears to be quite insensitive to alcohol.

The DP of the polymers produced in the presence of alcohol are about the same as those produced in its absence. If anything, the molecular weights seem to be slightly higher in the alcohol experiments. This can be expected, since in the absence of alcohol, the first interaction of perchloric acid and styrene, which is always accompanied by a very temporary presence of a yellow colour, is presumably an oligmerisation reaction. This follows from the observation made by Bertoli and Plesch(17b) that styrene in the presence of an excess of perchloric acid (which is expected in my experiments when the acid phial is broken into the reaction mixture) forms the linear dimer (1,3-diphenylbut-1-ene) and subsequently the cyclic dimer (1-methyl-3-phenylindane) of styrene. The yellow flash comes from the 1-methyl-3-phenylindanyl ion which is formed, as has been described previously, by a hydride abstraction mechanism. That this mechanism is possible even in the presence of alcohol, is substantiated by the appearance of the yellow colour (from the 1-(poly)styryl-3-phenylindanyl cation) at the end of the reactions EMs 9 at -70°, and EMs 8 at 0°, even though the [alcohol]/[acid] ratio was above one. Since the alcohol might at least partially inhibit the oligomerisation the molecular weights might be expected to be higher in these experiments than in those without alcohol.

The Experiments with Triethylamine at 0°, Table III,4

Not wanting to interfere with the initiation step of the polymerisation I carried out several experiments with triethylamine as the scavenger, adding it at or before completion of the first half-life. Provided that $[Et_3N] < [HClO_4]$, the addition of the base to the polymerising mixture resulted in a slowing down of the reaction. This lower rate was that expected from $[HClO_4]_f = [HClO_4]_o - [Et_3N]$. If $[Et_3N]/[HClO_4] \geq 1$, the reaction stopped. In every experiment, the conductance rose sharply when the base was added, and remained high. The results of these experiments are analogous to the result of the alcohol experiment EMs 12; hence, they are expected to be consistent with any explanation proposed for the experiment EMs 12.

Table III,4

Experiments on the polymerisation of styrene in CH_2Cl_2 with triethylamine^{+} at 0°.

EMs	$[C_8H_8]$ (M)	$[HClO_4]_o$ (10^3M)	$[Et_3N]$ (10^3M)	$\frac{[Et_3N]}{[HClO_4]_o}$	yield* (time) (%) (min.)	DP
64	0.330	4.80	1.32	0.28	100(11)	15.9
60	0.330	5.05	2.78	0.55	100(28)	15.5
63	0.338	11.75	10.60	0.90	20(4)	17.0
59	0.340	1.80	2.70	1.50	10(6)	17.6

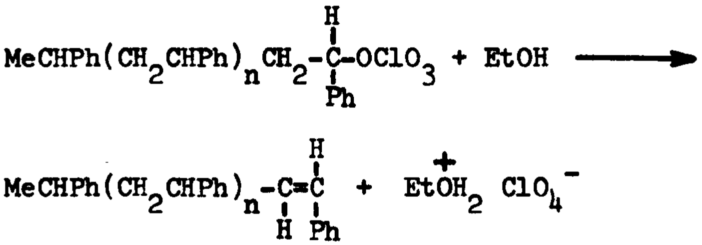
$^{+}$The Et_3N has always been added after the $HClO_4$.

*The yields of these reactions in the absence of Et_3N are 100%.

Discussion of the Experiments with Alcohol

On the basis of the above results it is obvious that the effect of alcohol on the polymerisation of styrene depends on the sequence of addition of the alcohol to the reaction mixture. Consequently, it becomes necessary to postulate two reaction schemes: one to account for the observations made on experiment EMs 12 and the experiments in which triethylamine was used as the 'scavenger', and the other to account for all the reactions in which the alcohol was added before the acid.

The first reaction scheme, A, is:



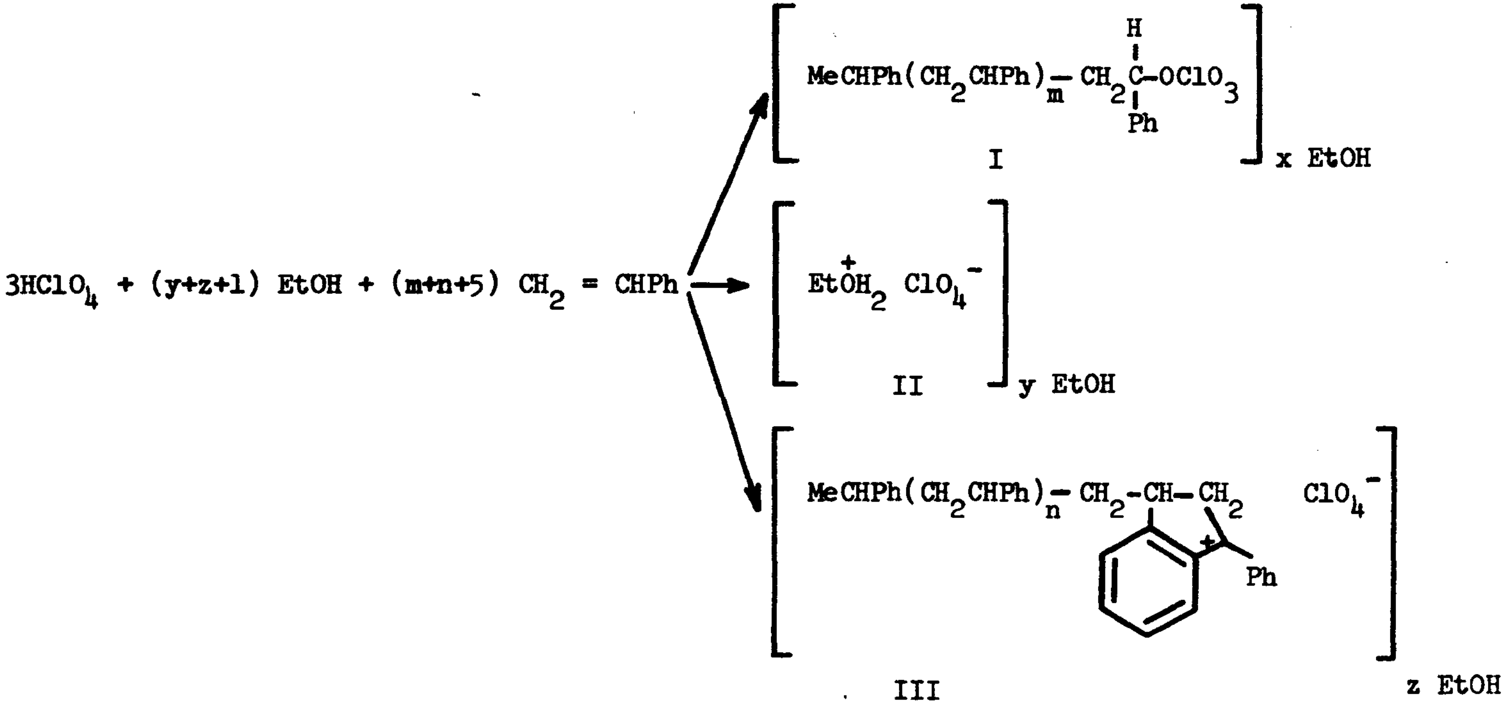
$$\mathrm{MeCHPh(CH_2CHPh)_nCH_2{-}\underset{Ph}{\overset{H}{C}}{-}OClO_3} + \mathrm{EtOH} \longrightarrow$$

$$\mathrm{MeCHPh(CH_2CHPh)_n{-}\underset{H}{C}{=}\underset{Ph}{\overset{H}{C}}} + \mathrm{Et\overset{+}{O}H_2\ ClO_4^-}$$

It accounts for the observations made on the experiments where the alcohol (or triethylamine) is added after the acid, i.e., while the polymerisation proceeds. In these experiments the reaction stops completely if $[\mathrm{EtOH}]; [\mathrm{Et_3N}] > [\mathrm{HClO_4}]$. If $[\mathrm{EtOH}]; [\mathrm{Et_3N}] < [\mathrm{HClO_4}]$ the alcohol is completely consumed and the remaining chain carriers continue to react normally. The second reaction scheme, B, is shown in Fig. III,7. Upon adding the perchloric acid to the styrene/ CH_2Cl_2/EtOH system the acid reacts with both the styrene and the alcohol. The polymerisation does start and goes to completion, but it is slower than an equivalent reaction without alcohol, hence some of the acid must have formed propagating species and the rest must somehow have been inactivated. As soon as the acid is added to the

Fig. III,7

Scheme B: The perchloric acid is added to a mixture of styrene, ethanol and methylene chloride.



$y > z \gg x = 0$

system the conductance increases sharply and remains high, which indicates that there are free ions present. Although we have no direct evidence, the most likely cations formed are $Et\overset{+}{O}H_2$ (II) and possibly some indanyl ions (III) (yellow flash). Since the polymerisation continues in the presence of excess of ethanol, and the very reactive styryl ion would, if present, certainly react to completion with this, we conclude that the propagating species must be the ester (I). We conclude further that the unprotonated alcohol is bound mainly to the ethyloxonium ions (II), and to some extent to the indanyl end group ions (III). This follows from the reaction scheme A which shows that if the alcohol were not bound to these ionic species it would react with the ester (I) and the polymerisation would stop. Hence in scheme B, $x = 0$. Since the ester competes unsuccessfully against the ions for the alcohol, it can continue to react in the normal way. Furthermore, the observation that the indanyl ions appear at the end of experiment EMs 8 and EMs 9 is strong evidence that the alcohol is bound in such a way that it is not free to interact with that cation. The fact that polymerisation occurs supports Plesch's(20) belief that the formation of the propagating species, the ester, is extremely fast. The rate of formation of the ester must be approximately the same as the rate of interaction of the acid with the ethanol.

Since at low temperature the Stage I is exceedingly fast, and the Stage II very slow, the alcohol in these experiments (see Table III,3) has always been added before the acid. Hence these results are to be interpreted by scheme B, which applies irrespective of the reaction temperature. At low temperature the fast Stage I is affected in a manner consistent with its interpretation as a true cationic polymerisation$^{(21,19)}$. The carbonium ions react with the alcohol forming $R\overset{+}{O}HEtClO_4^-$ and in the presence of the triethylamine, forming $R\text{-}\overset{+}{N}\text{-}Et_3\ ClO_4^-$. However, the slower reaction Stage II continues to full conversion, as in the reactions at higher temperature, in accordance to scheme B.

Pepper$^{(22)}$ et al. have reported that the reaction at -97° (in which only Stage I seems to occur) goes to limited conversion, i.e. that no further reaction occurs, the yield of the polymer increasing with increasing initial catalyst concentration. They have also observed that if the temperature is raised, a stopped reaction of this type will resume polymerisation at the rate expected for Stage II at that temperature. This phenomenon has been called by Pepper a true termination, which is reversible when the temperature is > - 80°. Further work by Pepper$^{(19)}$ et al. has shown that the addition of an inert salt ($n\text{-}Bu_4\overset{+}{N}ClO_4^-$) strongly reduces the yield of Stage I and also slows down Stage II. The extrapolation of a conversion vs. $[salt]^{-\frac{1}{2}}$ plot to 'infinite' salt concentration, shows that the conversion due to Stage I is, within experimental error completely suppressible. However, the effect of the salt on the rate of Stage II is only partial. The rate constant is reduced to a limiting value, $k_{(lim)}$, which amounts to about 20% of the value of the rate constant obtained in salt free polymerisations. Hence, the conclusion drawn from these observations is that Stage I is a polymerisation carried "virtually entirely" by free ions and that Stage II is a polymerisation due to free ions and non-suppressible chain carriers which Pepper believes to be ion-pairs.

It appears that though the stage I is carried predominantly by free ions, the other propagating species, not evident in Stage I, are not ion-pairs, but non-ionic chain carriers which for the purpose of the argument will be regarded as the ester. Were this second propagating species an ion-pair, increasing the temperature, after the Stage I is over, should not have resulted in a polymerisation whose rate is equal to that of Stage II at that temperature. Pepper's hypothesis for the Stage II is, that the monomer is consumed by the propagation of free ions and ion-pairs, these being in equilibrium with each other and with a 'dead' covalent ester. If the argument for the explanation of the Stage II is that an increase of the dielectric constant of the reaction medium shifts the equilibrium of propagating ion-pairs toward propagating free ions, thus giving a higher rate of polymerisation, then an increase in the rate, due to an increase in the temperature in the low temperature experiments, cannot be attributed to the same kind of equilibrium shift since an increase of the temperature decreases the dissociation of ion-pairs.

Since a propagating free ion is expected to be very much more reactive than a propagating ion-pair(3) (i.e. E_a free ions << E_a ion-pairs) it seems improbable that an increase of the polymerisation rate due to an increase in the contribution of the ion-pairs (by raising the temperature) and the concurrent increase in their rate-constant, can outweigh the decrease of the rate of polymerisation due to a lowering of the concentration of free ions by the same temperature rise.

I have shown by means of the alcohol experiments (scheme A), that the ester is formed extremely rapidly. At low temperature the formation of these esters is slower since the recombination of the initial styryl cation with the perchlorate anion to form the ester, is slowed down by virtue of the higher dielectric constant of the medium at that low temperature. Thus at the very low temperatures the free ions survive long enough to propagate quickly and convert a large part of the monomer before recombination of the ions occurs to form the ester. Since these esters are very slow in propagating at -97°, the reactions <u>seem</u> to be over before all the monomer is consumed. That the reactions only <u>seem</u> to be over may be substantiated by the observation that occasionally the reactions at -97° were found to go on "creeping"(23). Increasing the initial perchloric acid concentration increases the concentration of the transient styryl cations, hence the conversion in Stage I is higher, the higher the acid concentration, and the concentration of the 'dormant' esters is equally increased. It is under these conditions (in which one may assume that $[\text{ester}] = [HClO_4]_o$), that I would expect that the rate of the subsequent reaction, when the temperature of a -97° experiment is raised, would be the same as that of a Stage II reaction at that higher temperature.

Thus, in view of my interpretation of the 'revived' polymerisation it becomes unnecessary to postulate a true reversible termination. I believe that the observed 'revival' of the polymerisation is not due to a change of concentration of a chain carrier but that it is due to an increase in the rate of polymerisation of the same propagating species which was unobservably slow at -97° and has become evidently faster as the temperature is raised.

The suppression of Stage I by the $n\text{-}Bu_4N^+ClO_4^-$ salt is consistent with the expected increased rate of ion recombination to form the ester.

In view of our new interpretation of the Stage II (Chapter III,2,a), the partial suppression of this stage by the perchlorate salt is most probably due to the total removal of the oligostyryl ions by ester formation and the $k_{(\text{lim})}$, as reported by Pepper, is therefore more likely the rate constant of the ester, rather than that of the ion-pair.

2.c. DILATOMETRIC AND SPECTROSCOPIC EXPERIMENTS IN THE PRESENCE OF AN ELECTRIC FIELD

In an attempt to ascertain the nature of the propagating species, Gandini and Plesch(14) have found that upon adding styrene to a $HClO_4/CH_2Cl_2$ solution the conductance during the ensueing polymerisation remained the same as that of the acid solution alone ($K << 10^{-7}$ mho-cm^{-1}). Having confirmed that the conductance of this system is exceedingly low, it was reasonable to believe that, if this conductance were due to ions in equilibrium with ion-pairs, these ion-pairs would most probably behave like any ordinary weak electrolyte. Wien(2) in 1927 found that the conductance of a weak electrolyte is increased by an electric field and concluded that this effect must be due to an increase in the degree of dissociation (α) of the weak electrolyte, forming more free ions. On the basis of this observation and its theoretical interpretation by Onsager(24), Sakurada, Ise et al.(1), have made an extensive study of the polymerisation of various olefinic monomers, hoping to elucidate the nature of the propagating species which in most cases was thought to be ionic. Their results have been presented in the introduction of this chapter. Therefore, since some (or all) of the ions responsible for the low conductance in the polymerising system styrene/$HClO_4/CH_2Cl_2$ might be propagating carbonium ions, it was hoped that the effect of an electric field on the system might throw some light on the nature of the propagating species. At the time, most of Ise's results seemed to be consistent with the ion-pair dissociation hypothesis. Since then, an explanation in terms of a free ion desolvation effect has been favoured, at least for some of their systems. Both these hypotheses will be discussed in the light of my results.

Procedure and Results

Except for the spectroscopic experiments, all the kinetic results were obtained by carrying out the reaction in the dilatometer described in Chapter II,2,c.

The applied potentials (A.P.) across the electrodes produced the following potential gradients (P.G.):

A.P.	P.G.
1000V	0.55Kv/cm
2000V	1.10Kv/cm
3000V	1.65Kv/cm

All the reactions were carried out at 0°. The procedure was as follows: First, the electric field was applied to the styrene/CH_2Cl_2 solution alone, to remove any electrolysable impurities. Since this part of the procedure did not seem to make a difference in the kinetic results it was later discontinued.

Having started the reaction, and after obtaining a few cathetometer readings with the field off, I turned the field on and continued to take readings at one minute intervals. These were continued up to at least the first half-life of the reaction. The intervals were than increased as the reaction approached its asymptotic end. In all but one experiment the field was applied continuously until it became obvious from the dilatometric readings and the conductance, that the reaction mixture was being heated and that excessive electrolysis was imminent.

All the reactions to which the electric field was applied revealed an increase of the reaction rate, the magnitude of this increase depending on the acid concentration as well as on the intensity of the electric field (Table III,5). The only reasonable way in which I could measure these increases in reaction rate was by making the usual first-order plot, taking the slope of the line before the field was applied (k'_o) and comparing it with the slope (k'_E) of a "best" line drawn through the points obtained within five minutes after the field was turned on. A typical example of this procedure is shown on Fig. III,8. The ratio of the 'rate-constants' thus obtained (k'_E/k'_o) is plotted against the initial acid concentration and shown on Fig. III,9. It is important to note that the ratio of the 'rate-constants' noted on the figure only represents the extent to which the reaction rate has increased during the first five minutes since the electric field was turned on. Since the effect of the electric field is actually a continuous acceleration, the rate of the reaction near the end of it is several times higher (approximately 18 x at 1.10Kv/cm, and 5x at 0.55Kv/cm) than the rate in the absence of the electric field. Since k'_E is fairly constant within a period of about 5 minutes one can obtain several k'_Es for different 5-minute intervals. A plot of log k'_E vs. t gives us a better picture of the

Table III,5

The polymerisation of styrene by $HClO_4$ in CH_2Cl_2 in the presence and absence of an electric field.

EMs	$[C_8H_8]$ (M)	$[HClO_4]$ (10^4M)	k'_o (10^3 sec^{-1})	k'_E (10^3 sec^{-1})	k'_E/k'_o	P.G. (Kv cm^{-1})	DP
228	0.348	0.78	0.14	0.21	1.47	1.10	24.0
227	0.345	0.79	0.14	0.25	1.71	1.65	21.4
230	0.335	2.19	0.50	1.00	1.98	1.10	21.6
229	0.338	2.20	0.52	0.77	1.49	1.65	18.0
224	0.340	3.11	0.84	1.62	1.93	0.55	23.0
223	0.335	3.11	0.95	1.97	2.07	1.10	22.8
222	0.332	4.17	0.98	1.32	1.34	1.65	26.0

Fig. III,8

The polymerisation of styrene by $HClO_4$ in CH_2Cl_2 at 0°.

First-order plot of a typical reaction in the presence and absence of an electric field.

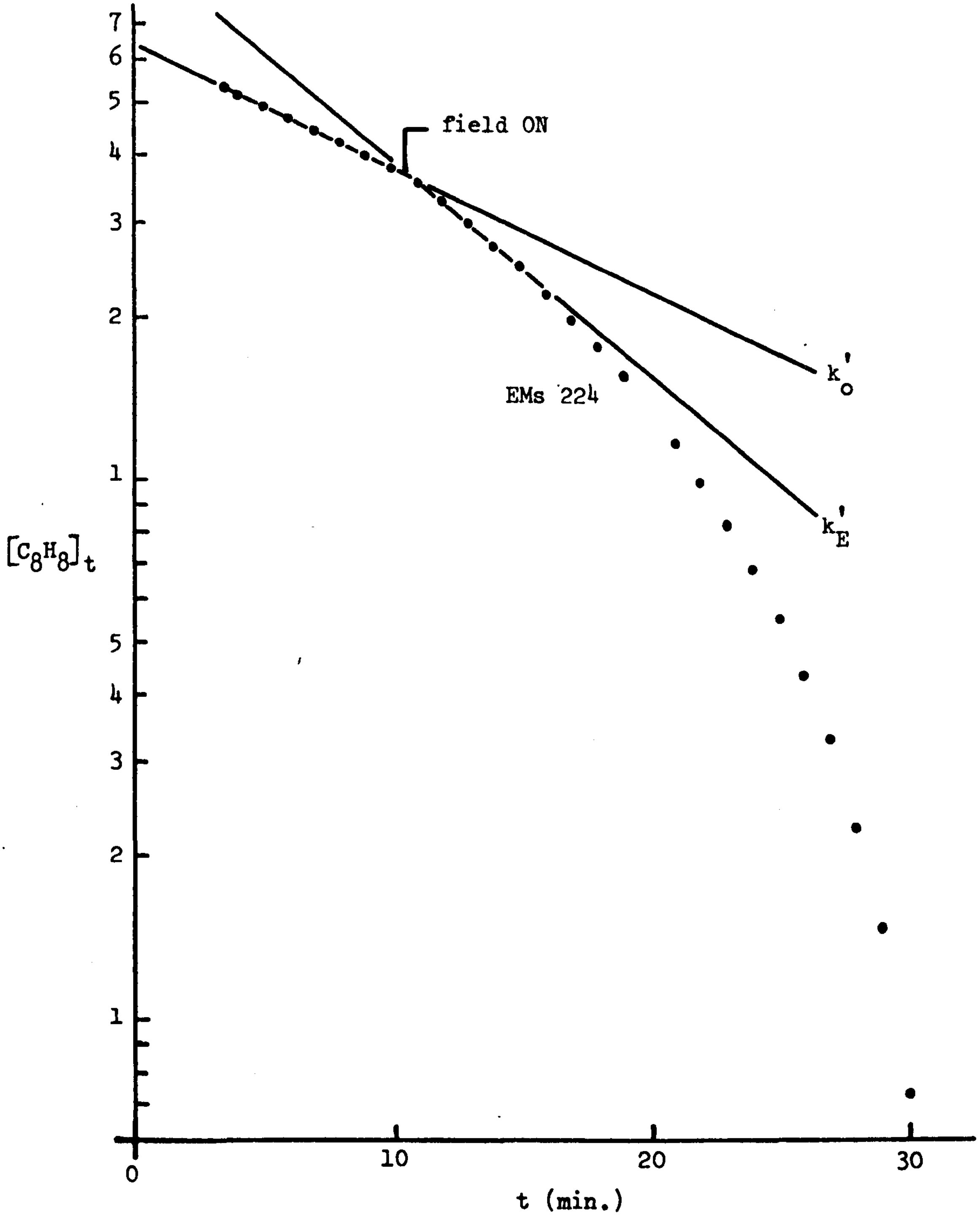
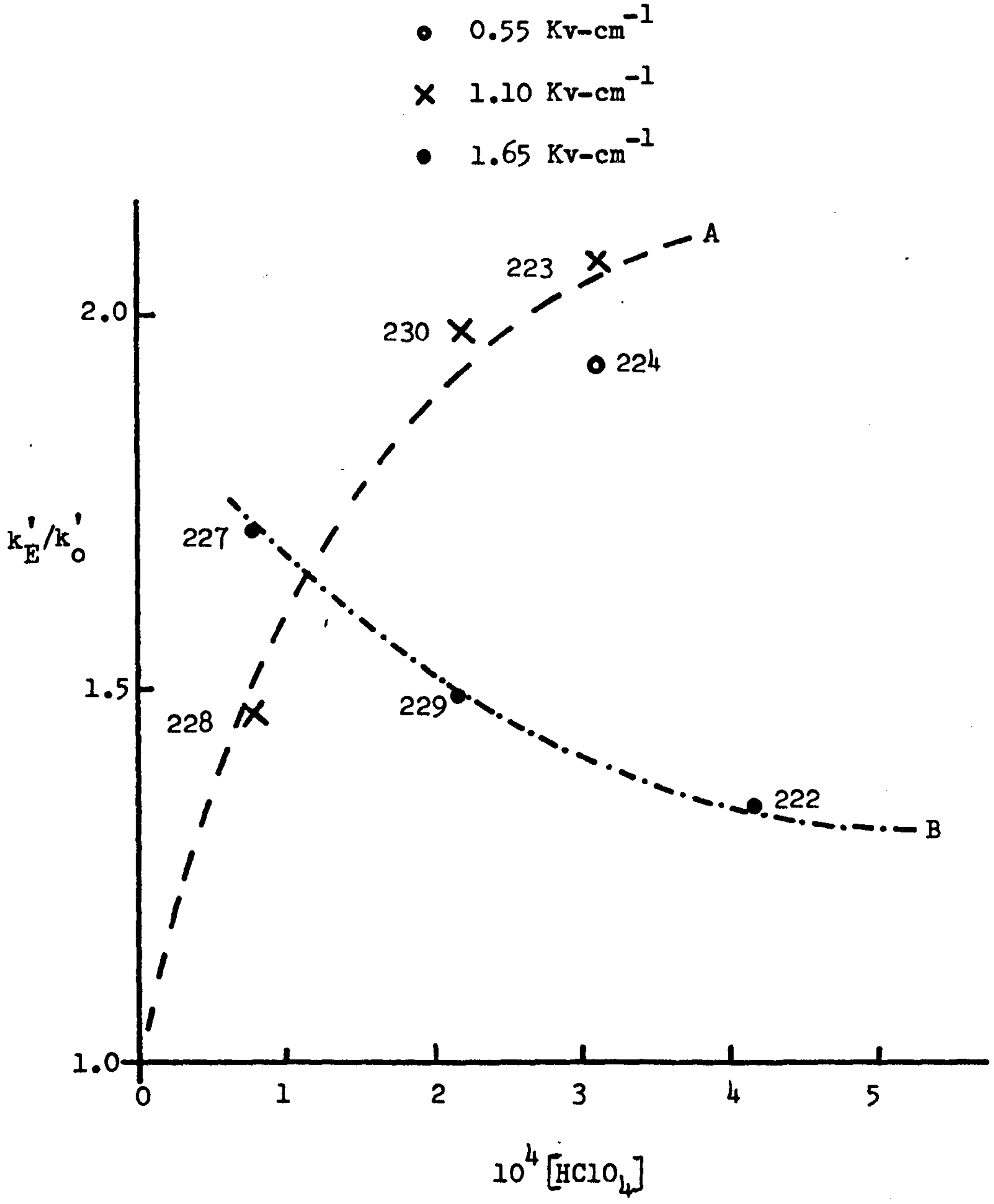


Fig. III,9

The polymerisation of styrene by $HClO_4$ in CH_2Cl_2 at 0°. The $HClO_4$ dependence of k_E'/k_o'



degree of acceleration due to the electric field (Fig. III,10).

Provided that the P.G. was 0.55Kv/cm or 1.10Kv/cm, the conductance in these experiments behaved in the same way as it did in reactions in the calorimeter, i.e. it increased very slowly. At the moment of turning the field on, the conductance shot up sharply, but it then decreased and levelled off rapidly to the low conductance exhibited by the solvent and acid alone (Fig. III,11). Throughout the reaction the conductance rose slightly and increased more and more rapidly until a bubble appeared in the dilatometer.

With a P.G. = 1.65Kv/cm one can observe the reaction accelerating, but very soon the reaction mixture warms up, because of Joule heating, and a bubble appears in the dilatometer. This effect, which is only evident at P.G. = 1.65Kv/cm, increases with the initial acid concentration and makes the determination of k'_E increasingly more unreliable. This probably accounts for the decrease of k'_E/k'_o with initial acid concentration (Fig. III,9, Curve B).

It is conceivable that the curvature observed on the Fig. III,9 for the experiments at 0.55Kv/cm is due to an increasing Joule heating effect with increasing initial acid concentration. However, these effects appear to be negligible in comparison to the accelerations observed. The flat dilatometer of Fig. II,6 proved to be extremely efficient in its heat exchange. Provided that the initial acid concentration was sufficiently high the application of an electric field never prevented the formation of the indanyl ions

Fig. III,10

The polymerisation of styrene by $HClO_4$ in CH_2Cl_2 at 0°.
The time dependence on log k_E'.

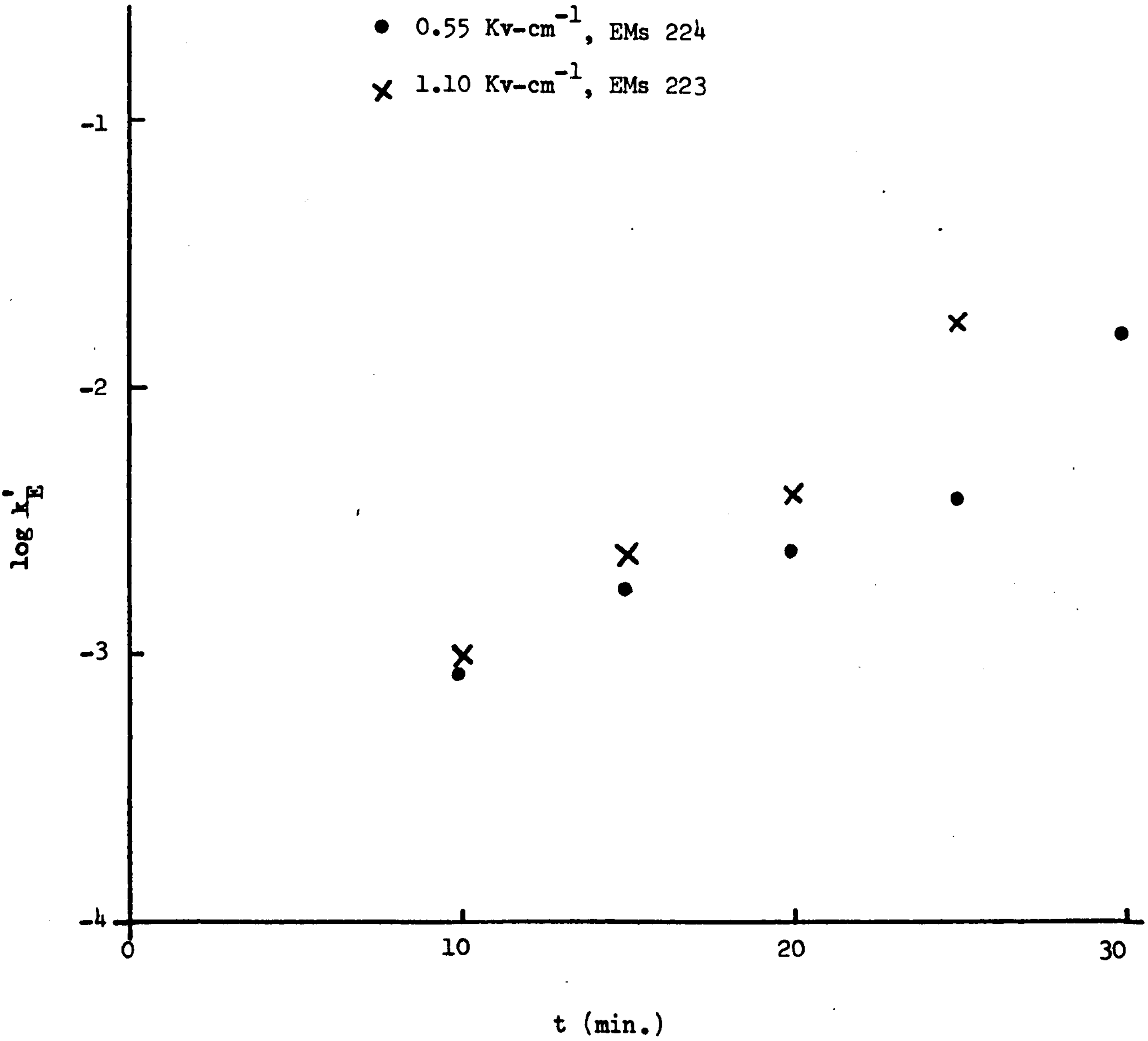
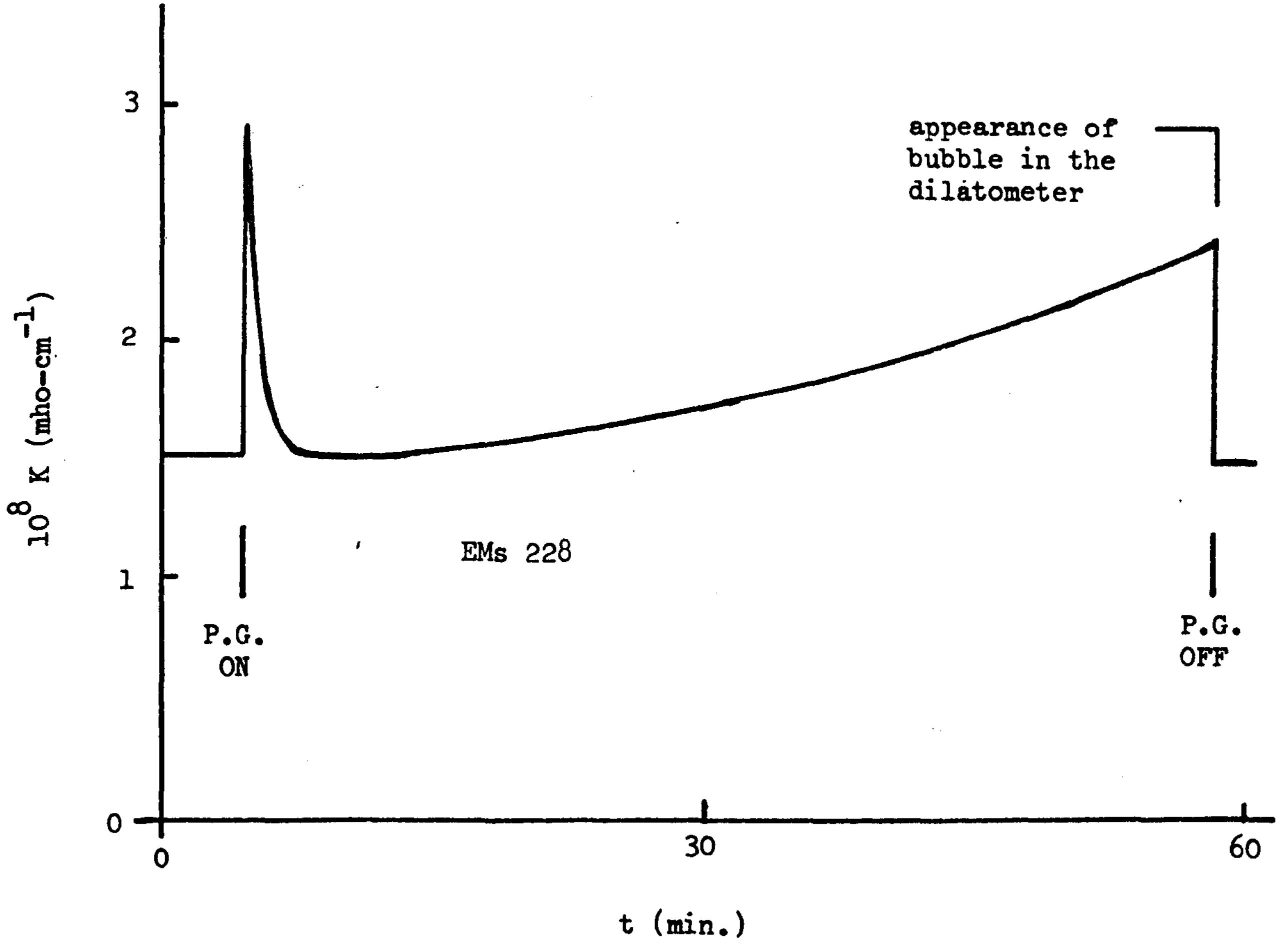


Fig. III,11

The polymerisation of styrene by $HClO_4$ in CH_2Cl_2 at 0°. The behaviour of the conductivity during the application of an electric field.



(yellow colour) at the end of the reaction (Fig. III,12). Continued application of the electric field on the final yellow reaction mixtures rendered them colourless. However, the conductance of the solution although decreasing slightly, still remained high. Thus it appeared that some other ionic species exists at the end of the reaction which is not coloured. Therefore I carried out several reactions, in the presence of an electric field, using the spectroscopic cell shown in Fig. II,7 . These reactions were carried out at 2°.

The first spectroscopic experiment was an intentionally slow reaction which according to the dilatometric evidence should have been influenced by the electric field, Table III,6. Although the indanyl peak in the visible never appeared because of the low concentration of acid used, application of the electric field at 3.54Kv/cm during the reaction soon produced two peaks in the U.V. region. The absorption maxima of these two peaks were at 331 nm and 349 nm with $D_{331} \gtrsim D_{349}$, Fig. III,13. A repetition of this experiment, with a higher acid concentration and a lower electric field intensity (EMs 413, P.G. 2.36Kv/cm), again showed the appearance of these two peaks. In this as well as in the previous experiment, the absorbances of these peaks at first increased with time but soon (within the first half-life of the polymerisation) reached a steady value. In order to make sure that these peaks really appear only when an electric field is applied I repeated the above experiment (P.G. 2.36Kv/cm), applying the field only after

Fig. III,12

The polymerisation of styrene by $HClO_4$ in CH_2Cl_2 at 0°.

Behaviour of the conductivity during the application of an electric field.

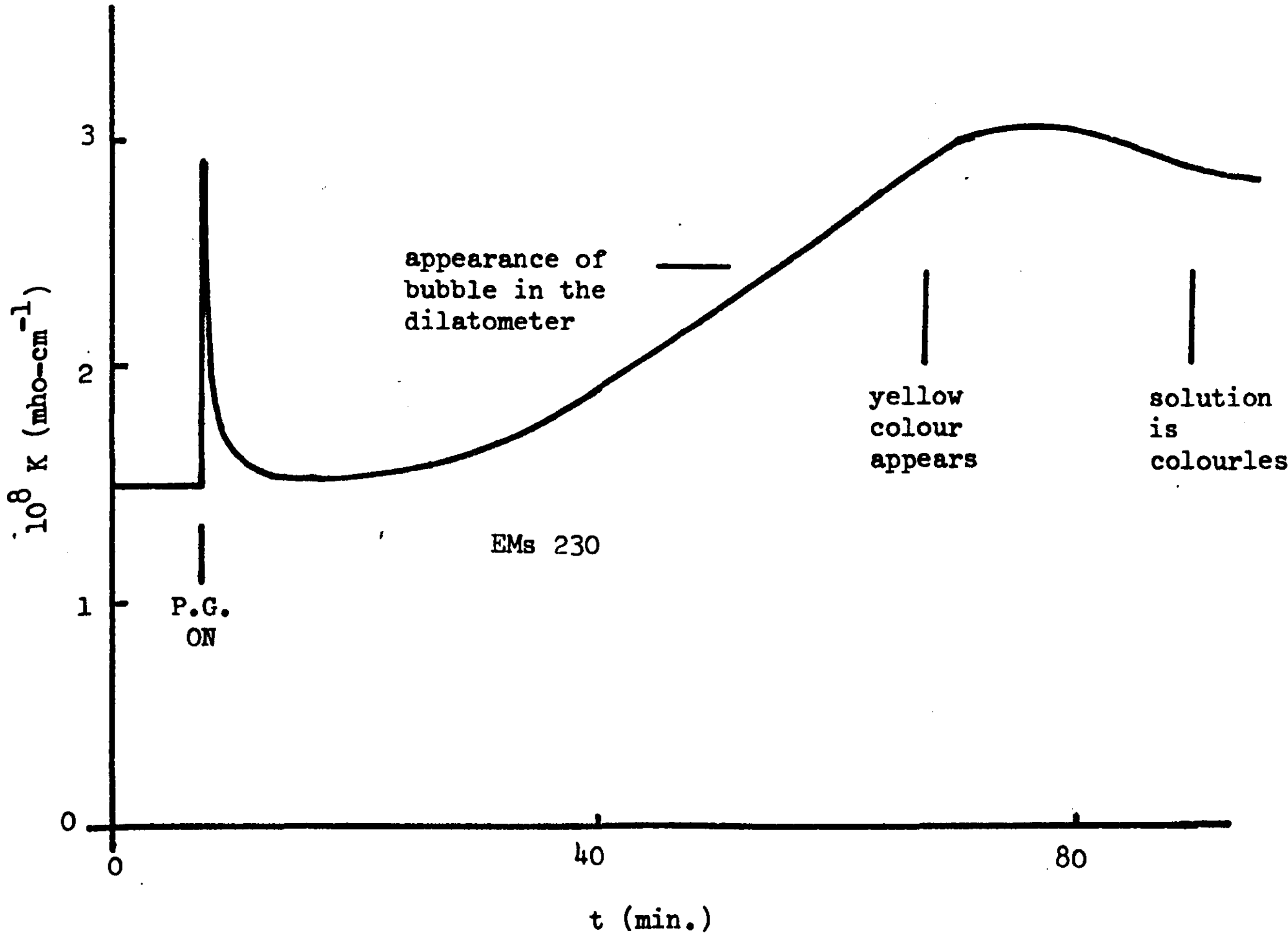


Table III,6

The polymerisation of styrene by $HClO_4$ in CH_2Cl_2 at 2°.

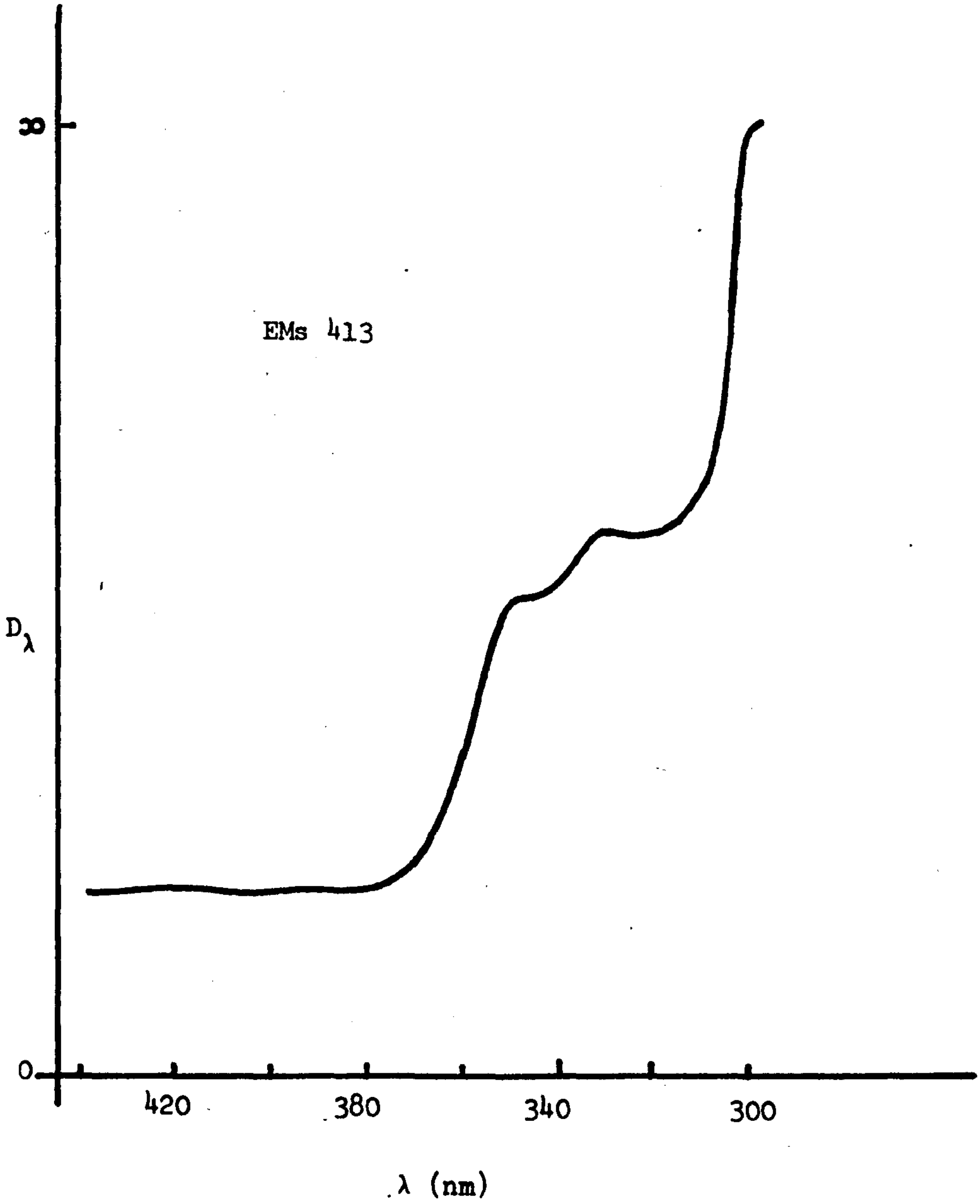
The spectroscopic experiments in the presence of an electric field.

EMs	$[C_8H_8]$ (M)	$[HClO_4]$ (10^4M)	P.G. (Kv cm^{-1})
412	0.350	0.90	3.54
414	0.325	1.49	2.36*
413	0.346	1.67	2.36

*The field was applied only after 75% of the monomer had been consumed.

Fig. III,13

The polymerisation of styrene by $HClO_4$ in CH_2Cl_2 at 0°. U.V. spectrum of the reacting solution in the presence of an electric field.



about 75% of the monomer had been consumed. The two peaks did not appear at any stage of the reaction until the field was applied. When the field was applied there was a broad absorption in the U.V. range with shoulders at about 330 nm and 350 nm. Upon pouring the reaction solution into alcohol the mixture was slightly fluorescent. However, the U.V.-Vis. spectrum of a solution of re-dissolved polymer failed to show any absorption between 300 nm and 700 nm. The absorptions below 300 nm were at: 294 nm, 285 nm (shoulder), and 273 nm. This spectrum is shown on Fig. III,14, trace A. The trace B is the spectrum of a re-dissolved polymer made in the absence of an electric field.

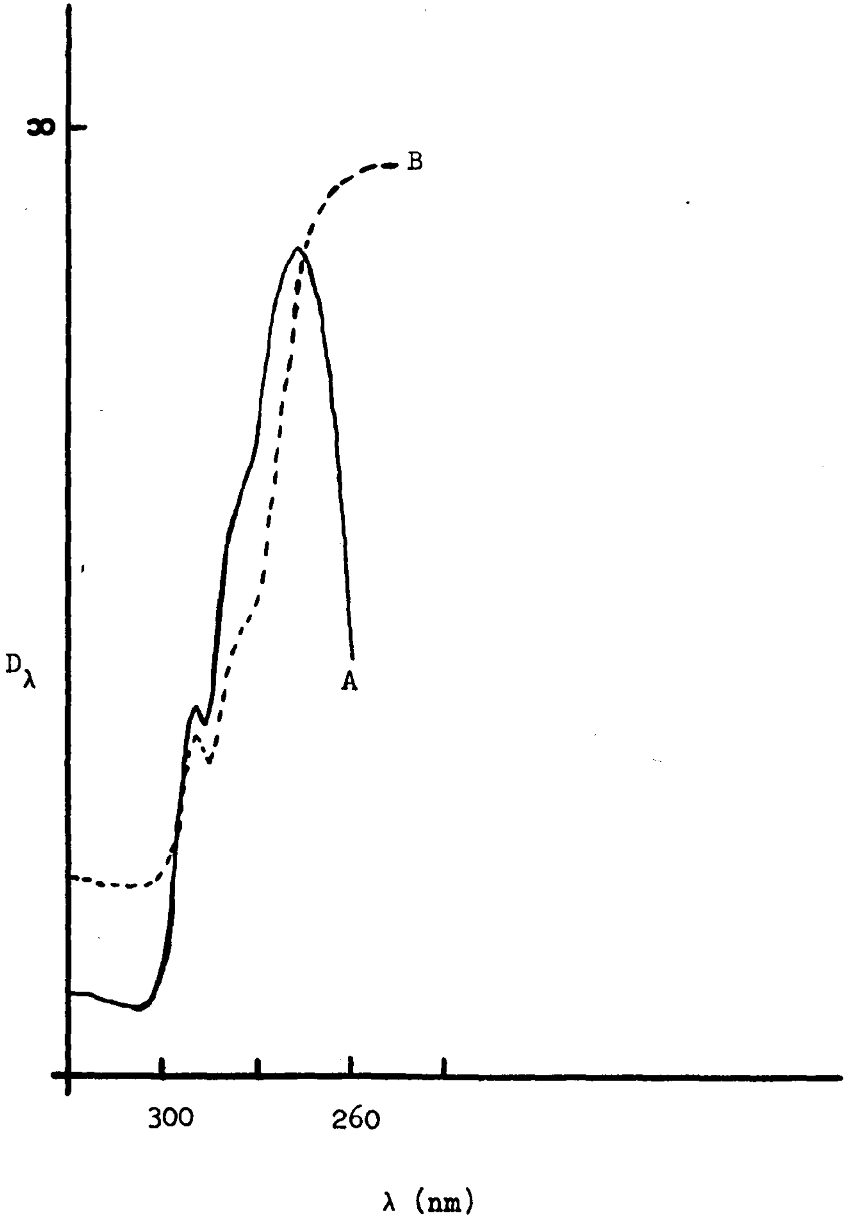
There was no difference in the I.R. spectra of polymers made in the presence and absence of an applied electric field. The DP of the polymers are not significantly different from those of polymers made in the absence of the electric field.

In view of the above experiments the appearance of the two absorption peaks at 331 nm and 349 nm is clearly a direct consequence of the electric field. The species producing these peaks, however, cannot be polystyryl ions. On the basis of the extinction coefficient found for the 315 nm peak of 1,3-diphenyl-n-butyl ion(17) ($\epsilon \sim 10^4$), the extinction coefficient of the polystyryl ion is expected to be of the same order of magnitude. Thus, if the two peaks were due to polystyryl ions their concentration would be approximately 5×10^{-5} M. If we take the propagation rate constant due to free ions(25) as 10^6 M^{-1} sec^{-1}, the first-order rate constant would be

Fig. III,14

The polymerisation of styrene by $HClO_4$ in CH_2Cl_2 at 0°.

The U.V. spectra of two redissolved polymers made in the presence (A), and absence (B) of an electric field.



50 sec^{-1}. Hence, half of the monomer would have been consumed in 0.01 second, i.e. the reaction would have been over long before the time I scanned the spectrum.

The fact that the products, in ethanol, are fluorescent indicates that at least some of the polymers are polyunsaturated, as has been found previously by Gandini and Plesch(26). These investigators found that their reaction mixtures also exhibited fluorescence, and reported absorptions at 390 nm and 410 nm. By analogy to the double-peak absorption of diphenylpolyenes, Gandini and Plesch attributed their absorption peaks to oligomers containing two to three conjugated double bonds. The compound $Ph(CH=CH)_2Ph$ absorbs at 334 nm, and 352 nm(27). Hence, the two peaks (331 nm and 349 nm) which appear in the presence of the electric field are most probably due to oligomers with two conjugated double bonds along the backbone of the chain. Since neither we nor anyone else has ever seen these peaks before in the absence of an electric field, it seems that their appearance is enhanced by the application of an electric field.

According to Gandini and Plesch(26) the polyunsaturations are formed by proton abstractions from allylic ions ($\lambda \approx 450$ nm) by some more basic species such as a conjugated system. Furthermore, the peaks at 390 nm and 410 nm only appeared several hours after the polymerisation was over, and were preceeded by the strong absorption peak at 450 nm. Although I have not observed any absorption at 450nm, it is conceivable that my system did nevertheless contain a very low concentration of allylic ions. This seems to follow from my observation that the fluorescence only appeared after the reaction products had been poured into alcohol. Presumably the alcohol has abstracted a proton from the allylic ions forming polyunsaturated polymers which are responsible for the fluorescence.

The spectra of two redissolved polymers failed to show the peaks expected of polyunsaturated oligomers. This is most probably because the polymers were exposed to air and light which may have resulted in the oxidation of most double bonds. The absorptions seen below 300 nm are of the type associated with the unsaturated (294 nm), and cyclic (273 nm) dimers of styrene.

In order to make at least a reasonable guess as to the reason for the accelerations, one needs to consider first the proposals (see introduction to present chapter) made by Sakurada, Ise et al.(1). These proposals are: (a) the increased rate of polymerisation is due to an increase in the dissociation of ion-pairs by the electric field, (b) in some cases, the increased rate of polymerisation is due to a desolvation of the free ion which results in an increased accessibility of the free ion to the monomer.

The dissociation of propagating ion-pairs into propagating free ions requires the separation of the two charges. If the ion-pairs are, say, contact ion-pairs the strength of the electric field which will oppose the separation will be of the order of 10^6-10^7 volts /cm. An externally applied electric field of 1000 volts/cm would be considerably reduced by the presence of the dielectric medium so that the internal electric field, i.e. the electric field which a dipole experiences by virtue of being surrounded by other dipoles, in the vicinity of an ion-pair may remain virtually unchanged. Hence, it is difficult to conceive that an externally applied electric field of about 1000 volts/cm could contribute significantly to the dissociation of these ions. Nevertheless, since the equilibrium constant for the dissociation of the ion-pairs is logarithmically related to the free energy of this dissociation, a slight change in the free energy could result in a change in the dissociation constant sufficiently large to make itself evident in the rate of polymerisation.

Whether or not Ise's free ion desolvation hypothesis is applicable to our system cannot be decided at this stage. Since in a polar reaction medium such as ours, free ions are expected to be strongly solvated it is hard to imagine a desolvation process which results in an increased accessibility of the cation to monomer without also favouring, at least to some extent, its accessibility to the anion which should result in a decreased reactivity of the active species. One does not know where the balance of the two counteracting effects lies, but since the rate of polymerisation increases in the presence of the field, the increased accessibility of the cation seems to outweigh the increased recombination of ions. Since Ise's desolvation hypothesis stems from the fact that the increase in the polymerisation rate comes from a change in the propagation rate constant of the free ions, it seems also possible that the electric field increases the rate constant by increasing the rate (and efficiency?) of encounters between the free ions and the styrene, i.e. by increasing the parameter A of the Arrhenius relationship

$$k = Ae^{-\frac{E_a}{RT}}$$

In the absence of enough sufficiently accurate information about the electric field effects on our polymerising system, we cannot tell whether the increase of the rate by the field is due to an increased dissociation of the esters or due to an effect on the rate constant of propagation of the free ions.

There is another possibility which could account for the acceleration of the reaction of styrene/$HClO_4$/CH_2Cl_2 by an electric field. It is reasonable to assume that in the presence of an electric field the distortion polarisation of the dipoles in the system is very much smaller than the orientation polarisation, though even this polarisation is necessarily small since thermal collisions would tend to disorient the dipoles. The electric field exerts a torque on each dipole to orient it in the field. The stronger the field, the greater the tendency to alignment will be, which in turn increases the induced polarisation. This preferential alignment can conceivably result in an increased dipole-dipole interaction between the propagating species and the solvent molecules, which may be regarded as an increased solvation of the propagating species. This increase in solvation is expected to be greater with the polystyryl ions than with the propagating esters. Since the ions are in equilibrium with the esters, the electric field - induced increase in degree of solvation of the ions would provide the driving force for augmenting the dissociation of the esters. That is to say, the electric field, rather than desolvating the propagating species (Ise's hypothesis), increases the solvation of the propagating species and thus stabilises the ions and induces a corresponding shift in the prevailing equilibria. This idea is not intended to be compatible with the dissociation hypothesis of Ise, which is based on an increase of dissociation of ion-pairs as a direct consequence of the electric field - ion-pair interaction, i.e. pulling the ions apart.

As has been mentioned previously Giusti et al(8) have found that the system anethole/BF_3Et_2O/1,2-dichloroethane polymerises faster in the presence of an electric field. Since the order of the reaction with respect to the catalyst changes from two in the absence of the field, to one in the presence of a field (0.5Kv/cm), the effect is ascribed to an ion-pair stabilisation by the electric field by increasing the dielectric constant of the medium. In fact, it has been found(28,29) that the dielectric constant of 1,2-dichlorethane is increased by an electric field because the field increases the proportion of the gauche-conformation.

In our system of styrene/$HClO_4$/CH_2Cl_2 the increase in the rate of polymerisation by the electric field is most probably not due to an increase in the dielectric constant of the medium. This follows from the observations made by Kautzsch(30) who observed that the dielectric constant of chloroform decreases with an increase in the externally applied electric field. It is found that, provided the distortion polarization is negligible with respect to the orientation polarization, this decrease is extremely small (ΔD for low dielectric constants is of the order of $10^{-4} - 10^{-6}$) even at very high potential gradients (P.G. > 10^4V/cm). Since it is unlikely that the distortion polarization of CH_2Cl_2 would be significantly different from that of $CHCl_3$, the change of the dielectric constant of CH_2Cl_2 is not expected to be significantly greater than that for $CHCl_3$. Hence, the increase in the rate of polymerisation of our system styrene/$HClO_4$/CH_2Cl_2 by an electric field cannot be attributed to an increase in the dielectric constant of the medium, as could be argued by Giusti for the anethole/BF_3Et_2O/1,2-dichloroethane system.

The proposed explanations so far only account for the observation that the rate of polymerisation increases in the presence of an electric field. However, as can be seen from my results (Fig. III,8) the increase in the rate of polymerisation increases with time, i.e. there is an acceleration.

Ise, et al.(31) have shown that the rate of polymerisation of the styrene/BF_3Et_2O/1,2-dichloroethane system increases in the presence of an electric field. Their first-order plot with respect to monomer is only linear to about ten minutes after starting the reaction. Beyond this time the plot appears to show an acceleration. The linear portion of the plot is taken as the initial rate of polymerisation under the influence of the electric field. Their subsequent results are all shown in terms of these initial rates, and no further mention is made of the acceleration. Furthermore, throughout the electric field investigations made by Ise et al. the authors only mention the initial rates of polymerisation in the presence of the electric field and correlate these to other parameters. Hence it is not clear whether or not systems other than those mentioned above, showed a continuous acceleration of the polymerisations. No one else seems to have observed a continuous acceleration in the reactions under an electric field.

The acceleration by the electric field which I observed in our system of styrene/$HClO_4/CH_2Cl_2$ may arise as a consequence of the electric field effect on several equilibria, such that there is a continued increase in the concentration of some chain carrier. Furthermore, there may be some electrolysable "impurity" which is slowly consumed by both propagating species and electrolysis, but which in the absence of the electric field is consumed by the propagating species only. The impurity may have come from the catalyst phial since in most of my experiments the electric field was also applied to the styrene/CH_2Cl_2 solution alone before the polymerisation was started. This should have removed the electrolysable impurities.

Though there appears to be no polymerisation when the electric field is applied to the styrene/CH_2Cl_2 solution alone, the presence of some species during the polymerisation may help the formation of an electrolytically initiated propagating species. If the concentration of this necessary species is gradually increasing (e.g. indanyl ions) the overall rate of polymerisation under the electric field may increase continuously with time.

The finding by Giusti et al.(9), that a periodic reversal of the fields polarity cancels the increase of rate seen when the field is not reversed (Ch. III,1), will need further tests before one can find a satisfactory explanation for the field accelerated reactions. Apparently, the electric field can create a sufficiently high concentration gradient of active species to make the rate of polymerisation in the anodic zone significantly different from that in the cathodic zone. Maybe vigorous stirring of the reaction mixture will help to prevent the formation of the concentration gradient, though then the reaction could not be followed by dilatometry.

Comment by P.H. Plesch on Section 3 of Chapter III, p.77, of Ph.D. Thesis of E. Mathias.

The results with CCl_4 are at present inexplicable. It is known that $HClO_4$ is highly soluble in this solvent which has been used to measure the IR/Raman spectra of the acid.

Also, S.D. Hamann at C.S.I.R.O., Melbourne, has done kinetic measurements on the system styrene-$HClO_4$-CCl_4, which are in course of publication.

Thus the results reported here should be treated with scepticism until the matter is resolved.

December, 1970

3. THE REACTION IN CARBON TETRACHLORIDE

If the polymerisation of the styrene/$HClO_4$/CH_2Cl_2 system occurs by means of three types of propagating species, i.e. free-ions, ion-pairs, and esters, and assuming that these species are in equilibrium with each other, it is reasonable to expect an increase in the relative concentration of the ester as one decreases the dielectric constant of the reaction medium. It was felt that if one could find a medium in which the ester is the only propagating species, a detailed study of that system should reveal much-needed information about the actual structure and chemical behaviour of the ester.

Preliminary work by Reilly and Pepper$^{(13)}$ showed that the polymerisation of styrene by perchloric acid in carbon tetrachloride is a very slow reaction. At 25°, and with $[HClO_4] = 5 \times 10^{-2}$ M, the reaction took about 10 hours to go to 90% conversion. Since the reaction was followed by a dilatometric technique the temperature of 25° presented the problem of solvent distilling in and out of the capillary. Furthermore, Reilly and Pepper felt that higher concentrations of the acid would make the system increasingly irrelevant for the kind of comparisons for which the rate study was to be used. Hence, guided by the above information I set out to do some dilatometric experiments in CCl_4 at 0°. I decided first to make acid phials of a concentration of about 2×10^{-2} M with CCl_4 as solvent which upon further dilution in the dilatometric device would result in an approximate concentration of 2 x 10^{-3} M.

In the process of preparing the appropriate catalyst phials I found that the perchloric acid is not soluble in CCl_4. The $HClO_4/CCl_4$ mixture looked cloudy. Only after leaving the mixture standing for three days did the cloudiness disappear. Upon tipping the clear solution into the phials (see Fig.II,2) the wall of the conical flask, which was in direct contact with the liquid phase for those three days, appeared completely covered with minute droplets. Having fused off the phials, I opened the conical flask which resulted in the formation of very dense fumes. Addition of methyl red indicator to the flask showed that the content of the flask was definitely acidic.

Nevertheless, in spite of the surprising insolubility of the acid in the carbon tetrachloride, I carried out four dilatometric experiments adding to the styrene/CCl_4 solution a phial in which the acid was dissolved in methylene chloride, Table III,7. When the acid phial was broken, no colour was visible nor did any colour appear during the experiment.

None of the four experiments gave any polymer. When in one experiment (EMs 239) the contents of the dilatometer were poured into alcohol, a very slight fluorescence was visible which indicated that some oligomerisation must have occurred, presumably at the stage when the acid phial was crushed into the styrene/CCl_4 solution.

Table III,7

Conditions of the styrene/$HClO_4$ experiments in CCl_4 at 0°.

EMs	$[C_8H_8]$ (M)	$[HClO_4]$ (10^4M)
244	0.334	50.0
240	0.337	33.7
239	0.346	30.1
241	0.352	0.38

One experiment (EMs 244) was left undisturbed for two days, but from that too no polymer could be recovered and the U.V. spectrum showed that the concentration of the styrene was the same as that calculated from the initial dosing into the dilatometer.

The results clearly indicated that carbon tetrachloride is not an adequate solvent for the polymerisation of styrene by perchloric acid. The fact that I could not observe a polymerisation is evidently in disagreement with the polymerisation, if only very slow, seen by Reilly and Pepper. There appear to be only two differences between Reilly and Pepper's technique, and ours. Whereas we dose our materials under high vacuum conditions, Reilly and Pepper dose theirs in the air by taking special precautions: drying tubes, and nitrogen purging. The other difference between our techniques is the fact that the $HClO_4$ used in our experiments came from a stock of $HClO_4/CH_2Cl_2$ phials whereas the $HClO_4$ used in Pepper's experiments came from a stock of $HClO_4$ in 1,2-dichloroethane. Hence one possible explanation for the difference in our results is that the 1,2-dichloroethane may be an even better solvent for the acid than CH_2Cl_2 thus imparting a greater solubility of the acid in the $(CHCl)_2/CCl_4$ mixture than in the CH_2Cl_2/CCl_4 mixture.

I find it unlikely that the difference in the dosing technique could account for the difference in our findings. If the dosing technique were responsible, I would have expected that no polymerisation would have taken place by Pepper's technique (rather than by our technique) since in the "open" system the perchloric acid is more likely to be hydrated by residual moisture of the system, and the hydrate is most probably as insoluble in 1,2-dichloroethane as it is in methylene chloride.

4. THE REACTION IN NITROETHANE

Reilly and Pepper(32) have reported that with solvent mixtures of nitroethane and 1,2-dichloroethane, the polymerisation of styrene by $HClO_4$ becomes increasingly complex as the percentage of the nitroethane is increased. The reaction rate at first increases with increasing nitroethane content (up to about 40%) although the increase is less than that expected on the basis of their results with the 1,2-dichloroethane/carbon tetrachloride solvent system. Above 40% of nitroethane the reaction becomes increasingly inhibited, giving limited yields and deviating from first-order kinetics. In view of the fact that nitro-solvents are generally regarded to be good solvents for cationic polymerisations, the above observations are very surprising indeed.

According to Gandini(33) the polymerisation of styrene by $HClO_4$ in nitromethane is not homogeneous (the polymer of DP = 4 is not soluble), is very fast, and goes to 100% conversion. The reaction solutions remained colourless at all times and hence were regarded as non-ionic. The same observations were made with two experiments in nitroethane, except that in this solvent the polymer is soluble.

Since just as little is known about Pepper's ionic propagating species as there is about Plesch's non-ionic one, the polymerisation of styrene by $HClO_4$ in nitroethane alone looked like a promising system for the study of the ionic propagating species. The reactions which I carried out were all done in the adiabatic calorimeter. The quantitative results of these experiments are summarized in Table III,8. The procedure consisted of dosing the styrene and the solvent into the calorimeter and, after stabilizing the temperature to 0^o, crushing the catalyst phial into the mixture. Three runs were carried out by this method.

Two more reactions were carried out by the 'reverse addition' method, i.e. the catalyst was added to the solvent first, and then the monomer was added.

The reactions in which the acid was added to the monomer in nitroethane were fast ($t_{1/2}$ about 20-30 sec.) and the solution remained colourless at all times. However, as soon as the acid was added, the conductance rose sharply and remained high throughout the course of the reaction. The reaction asymptote of the conversion vs. time plots always reached a value higher than corresponded to 100% conversion. The reactions were neither first nor second-order with respect to the monomer. A typical reaction curve is shown on Fig. III,15, trace A.

The 'reverse addition' experiments revealed that the perchloric acid reacts catalytically with the solvent, Fig. III,16. Upon adding the styrene to the catalyst-solvent mixture (EMs 23) a

Table III,8

The polymerisation of styrene by perchloric acid in nitroethane

(initial temperature 0°)

EMs	$[C_8H_8]$ (M)	$[HClO_4]$ (10^3M)	Final reaction temp. (°C) Calc.[2]	Final reaction temp. (°C) Measured	K $(10^4 mho\text{-}cm^{-1})$	Recovered yield (%)	DP
22	0.171	7.71	4.25	10.36	1.15	109	14.2
21	0.251	6.62	6.22	11.12	1.06	112	19.5
20	0.251	4.01	6.22	9.20	0.14	113	19.2
23[1]	0.195	-3.8	4.82	4.92	1.04*	109	16.7
24[1]	0.140	0.26	3.47	0.68	0.15*	1	-

[1] Reverse addition experiments

[2] Calculated temperature increase expected for 100% conversion

*When acid is added to the $EtNO_2$. No further increase in conductivity when styrene was added.

Fig. III,15

The polymerisation of styrene by $HClO_4$ in $EtNO_2$ at 0°.

Typical reaction traces.

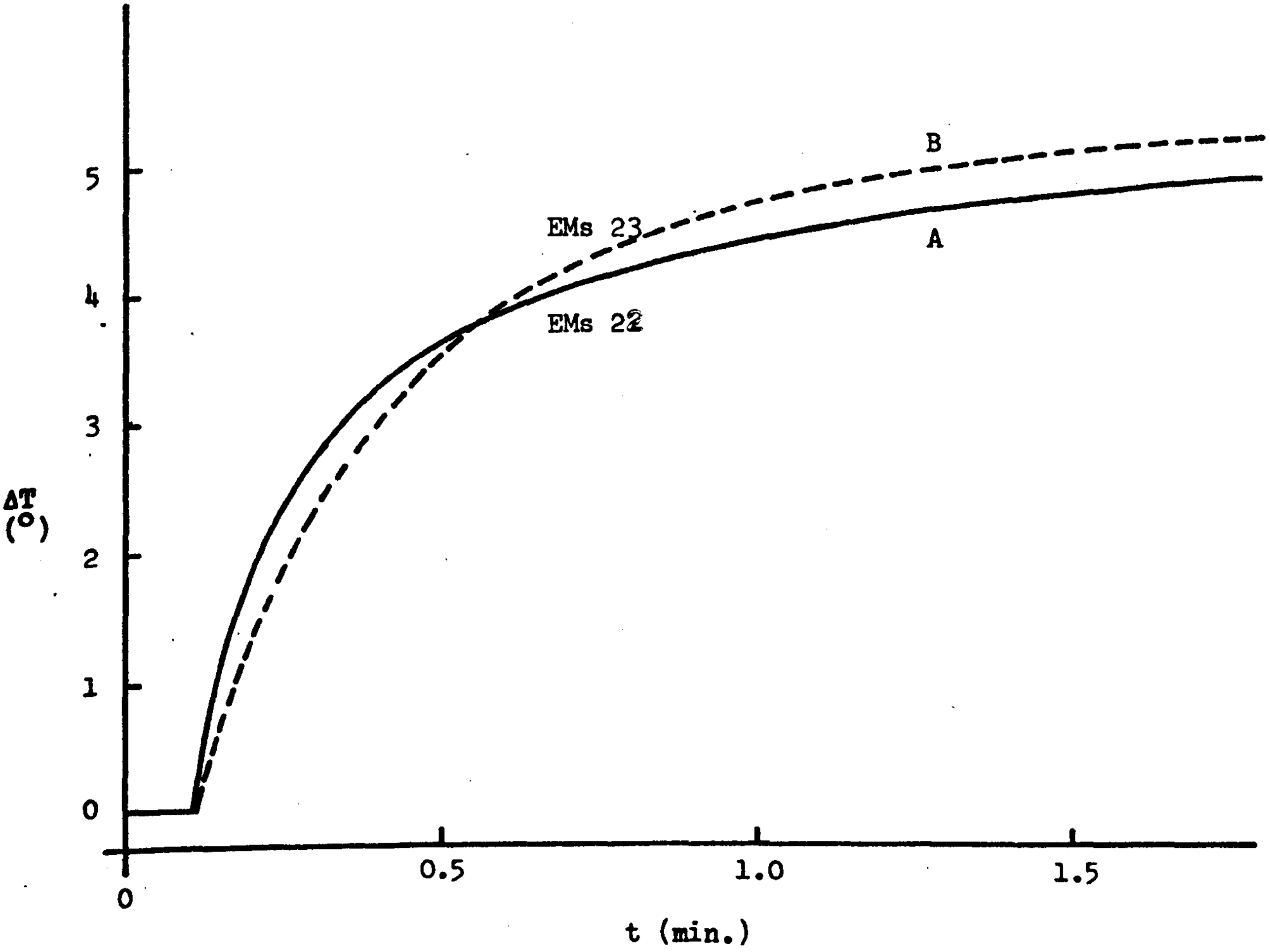
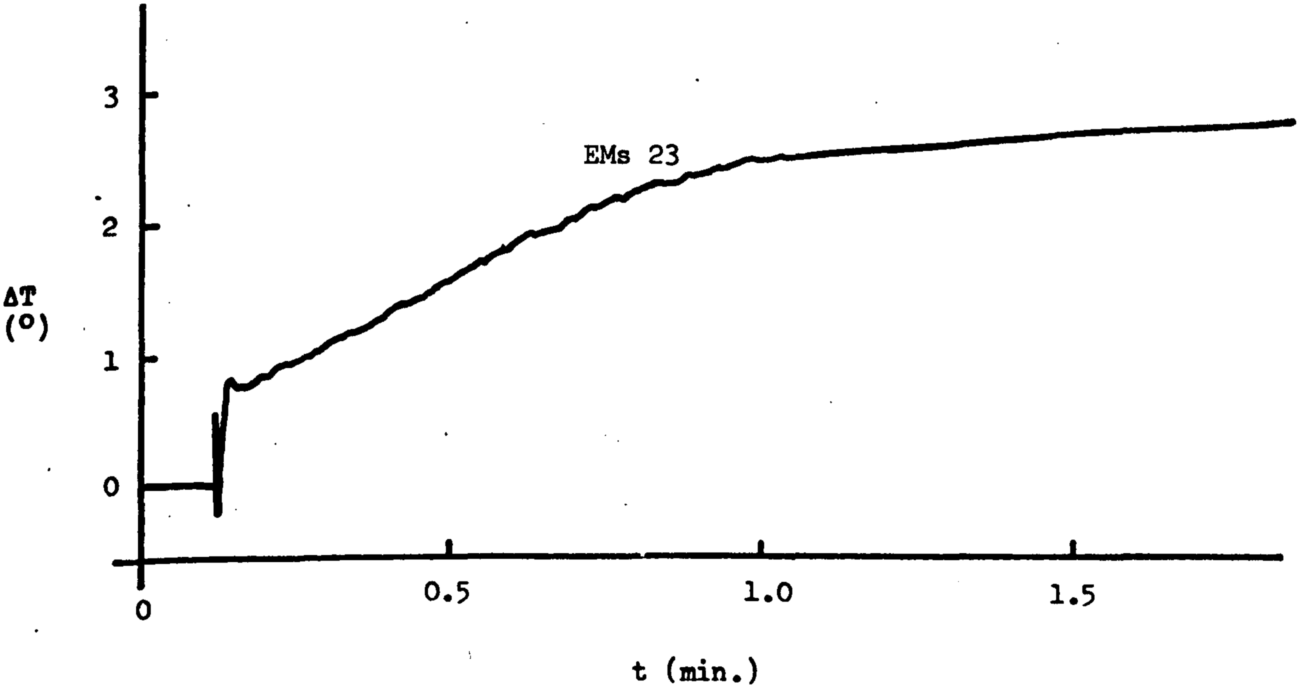


Fig. III,16

The polymerisation of styrene by $HClO_4$ in $EtNO_2$ at 0°.

The reaction trace following the addition of $HClO_4$ to $EtNO_2$.



fast polymerisation occurred, and the reaction asymptote reached the height expected for 100% conversion. However, also this reaction was not of first-order with respect to the monomer, Fig. III,15, trace B. When the reaction was over, 10 ml of the reaction mixture was distilled out for analysis. The index of refraction of the distillate was in very good agreement with that reported by Weissberger(34), i.e.:

Obs. $n_D^{25} = 1.3903$, lit. $n_D^{25} = 1.39015$

The NMR spectrum was identical to the NMR spectrum of the 'standard' nitroethane.

The I.R. of the distillate differed from that of 'standard' nitroethane only in a sharp peak at 746 cm^{-1}. The experiment EMs 24 also showed a reaction of the acid with the solvent but addition of the styrene only resulted in a limited yield.

The infrared spectra of all the polymers produced were identical to those of polymers made in methylene chloride. However, a carbon, hydrogen, nitrogen microanalysis of the polymers showed that the percentages of carbon and hydrogen did not add up to 100%. According to the microanalysis report there is definitely no nitrogen in the polymers. The results are shown in Table III,9.

All the polymers dissolved only very slowly in acetone, methylene chloride, and carbon tetrachloride. The best solvent seemed to be benzene.

Table III,9

C, H, N Microanalysis Results of Styrene Polymers Made in Nitroethane.[1]

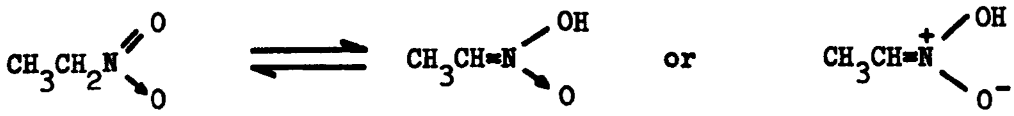
	Calculated			Experimental			
EMs	C%	H%	C%/H%	C%	H%	C%/H%	C%+H%
20	92.26	7.74	11.92	83.9	6.91	12.14	90.8
21	92.26	7.74	11.92	85.8	7.08	12.12	92.9
22	92.26	7.74	11.92	86.6	7.32	11.84	93.9
23[2]	92.26	7.74	11.92	84.8	7.19	11.8	92.0

[1] The standard was naphthalene (see also Chapter II,2,i).

[2] Reverse addition experiment.

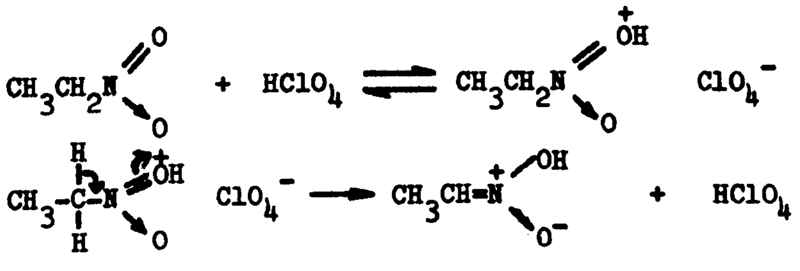
Since the polymerisations in nitroethane were unexpectedly complicated by side reactions no further reactions were carried out in this solvent.

The most reasonable explanation for the reaction of the acid with the nitroethane seems to come from the fact that primary nitroparafins can exist in tautomeric forms,(35) for example:



The tautomeric form on the right is called the nitronic acid, or the aci-form of the true nitro form on the left.

Since the formation of the aci-form can be catalysed by acids(35,36) it is likely that in the presence of the perchloric acid the nitroethane is protonated, and in turn forms the aci-form, i.e.



The protonation of the nitroethane seems to be borne out by the observed high conductance of the reaction mixtures. $EtNO_2H^+ ClO_4^-$ is expected to be a weaker acid than $HClO_4$; and, since the polymerisation of styrene in nitroethane is slower than one would expect on the basis of the dielectric constant of the medium, we conclude that the slowness of this polymerisation is probably due to a slow initiation by $EtNO_2H^+ ClO_4^-$.

According to the infrared spectra and the C, H, N analysis of the polymers, they did not contain nitrogen. The reason for the 6-10% which are missing from the sum of the carbon and hydrogen percentages remains obscure. Since one atom of oxygen in a polymer of $\bar{M}_n = 1600$ would give us 1% of oxygen by weight, the 6-10% which needs to be accounted for cannot be present in the polymer as end-groups. In view of the low molecular weight of the polymers, if the oxygen were along the backbone of the polymer, the infrared spectra should have given some indication of this.

I believe that, in view of the much better agreement between the experimental carbon-hydrogen ratios and the theoretical ratio, the discrepancies in the C% + H% values arise from some instrumental peculiarity. In fact, it is known that the C, H, N microanalyses becomes increasingly less reliable when the carbon content of a sample is very high. Results of samples with a carbon percentage above about 80 cannot be regarded as entirely conclusive.

The rather slow solubility of the polymers in acetone, methylene chloride, or carbon tetrachloride appears to indicate that the polymers are structurally somewhat different from those made in methylene chloride.

5. THE REACTION IN NITROBENZENE

According to Reilly and Pepper(32) the polymerisation of styrene by perchloric acid in nitrobenzene/1,2-dichloroethane is a fast reaction provided that the nitrobenzene content did not exceed 30%. As the proportion of nitrobenzene is increased beyond this, the reaction rate becomes increasingly inhibited, and there is no polymerisation with 70% of nitrobenzene. This inhibiting effect was most surprising, and it was thought worthwhile to carry out some polymerisations in nitrobenzene alone.

The procedure was the same as that used for the experiments in nitroethane, Chapter III,4. The results are summarised in Table III,10. Because of the high freezing point of the nitrobenzene, all the reactions were carried out at 6°.

The reverse addition experiment (EMs 25) showed that the perchloric acid reacts with the solvent. As soon as the acid phial was broken, the conductance rose and remained steady. This was accompanied by the appearance of an orange-pink colour. When the styrene was added, an S-shaped reaction trace was obtained, Fig. III,17. The conductance at first decreased slightly but soon went up to its original value. The colour of the solution changed to a more redish pink.

Since the reaction of the acid with the solvent was far less pronounced than with nitroethane, five more reactions were carried out by adding first the monomer to the solvent and then the catalyst. When the acid was added, polymerisation occurred, the

Table III,10

The polymerisation of styrene by perchloric acid in nitrobenzene

(initial temperature 6°)

EMs	$[C_8H_8]$ (M)	$[HClO_4]$ (10^3M)	k' ($10^2 sec^{-1}$)	K ($10^5 mho-cm^{-1}$)	Recovered yield (%)	DP
30	0.058	8.96	1.84	3.79	94	13.2
25+	0.120	7.07	3.97*	3.36	67	25.9
27	0.127	9.04	2.99	3.92	101	13.0
26	0.130	7.09	2.01	3.52	97	16.1
28	0.131	10.9	3.44	4.22	97	13.7
29	0.337	9.04	5.99	4.06	104	17.2

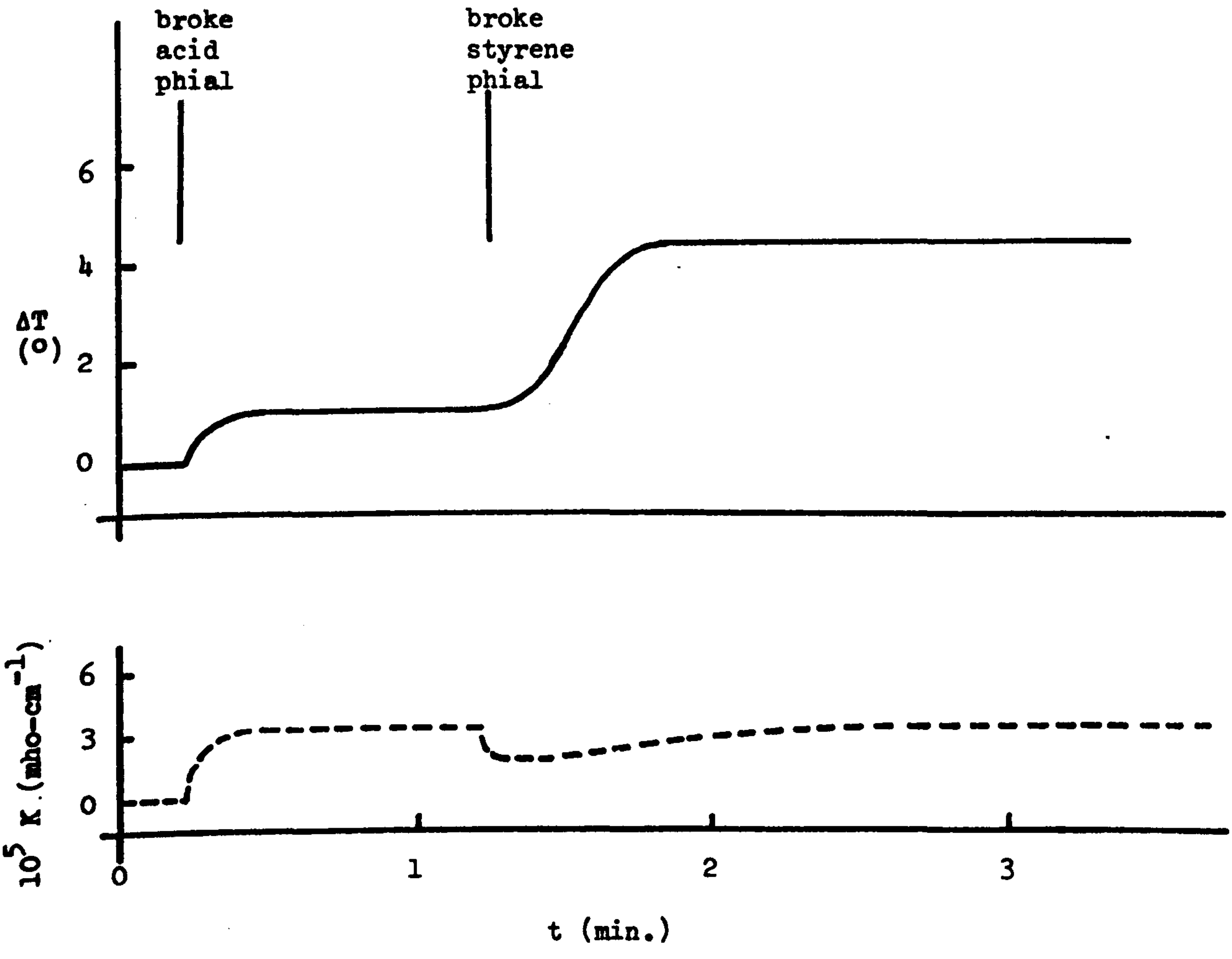
+ Reverse addition experiment.

* For last part of reaction after inflection point.

Fig. III,17

The polymerisation of styrene by $HClO_4$ in $PhNO_2$ at 6°.

The reaction and conductivity trace of the experiment EMs 25.



reaction mixtures immediately became orange-yellow, and the conductance rose to a steady value.

The reaction mixtures of experiments EMs 25 and 26 were analysed by GLC. Nitrobenzene was the only peak shown on the chromatograms, which also indicated that the reactions had gone to completion.

All the polymers dissolved much less readily in acetone, methylene chloride, or carbon tetrachloride than those made in methylene chloride. The best solvent for these polymers appeared to be benzene.

The infrared spectra of the polymers were identical to those of polymers made in methylene chloride. A carbon, hydrogen, nitrogen microanalysis of the polymers showed that the percentage of carbon and hydrogen add up to more than 100%. However, like the C, H, N results for the polymers made in nitroethane, the C%/H% ratio is again in good agreement with the calculated value. The results are tabulated in Table III,11. According to the microanalysis report there was no nitrogen in the polymers.

Except for the reverse addition experiment, EMs 25, all the conversion-time traces appeared to follow a first-order behaviour. However, the first-order plots for these reactions showed an initial curvature after which the plots gave a straight line, Fig. III,18. The first-order constants, k', are listed in Table III,10. Clearly, the k' are also a function of the initial monomer concentration and

Table III,11

C, H, N Microanalysis Results of Styrene Polymers Made in Nitrobenzene[1]

	Calculated			Experimental			
EMs	C%	H%	C%/H%	C%	H%	C%/H%	C%+H%
25[2]	92.26	7.74	11.92	95.2	8.18	11.64	103.4
26	92.26	7.74	11.92	94.9	8.11	11.70	103.0
27	92.26	7.74	11.92	95.7	8.23	11.63	103.9
28	92.26	7.74	11.92	95.5	8.33	11.46	103.8
29	92.26	7.74	11.92	95.4	8.24	11.58	103.9
30	92.26	7.74	11.92	93.1	8.06	11.55	101.2

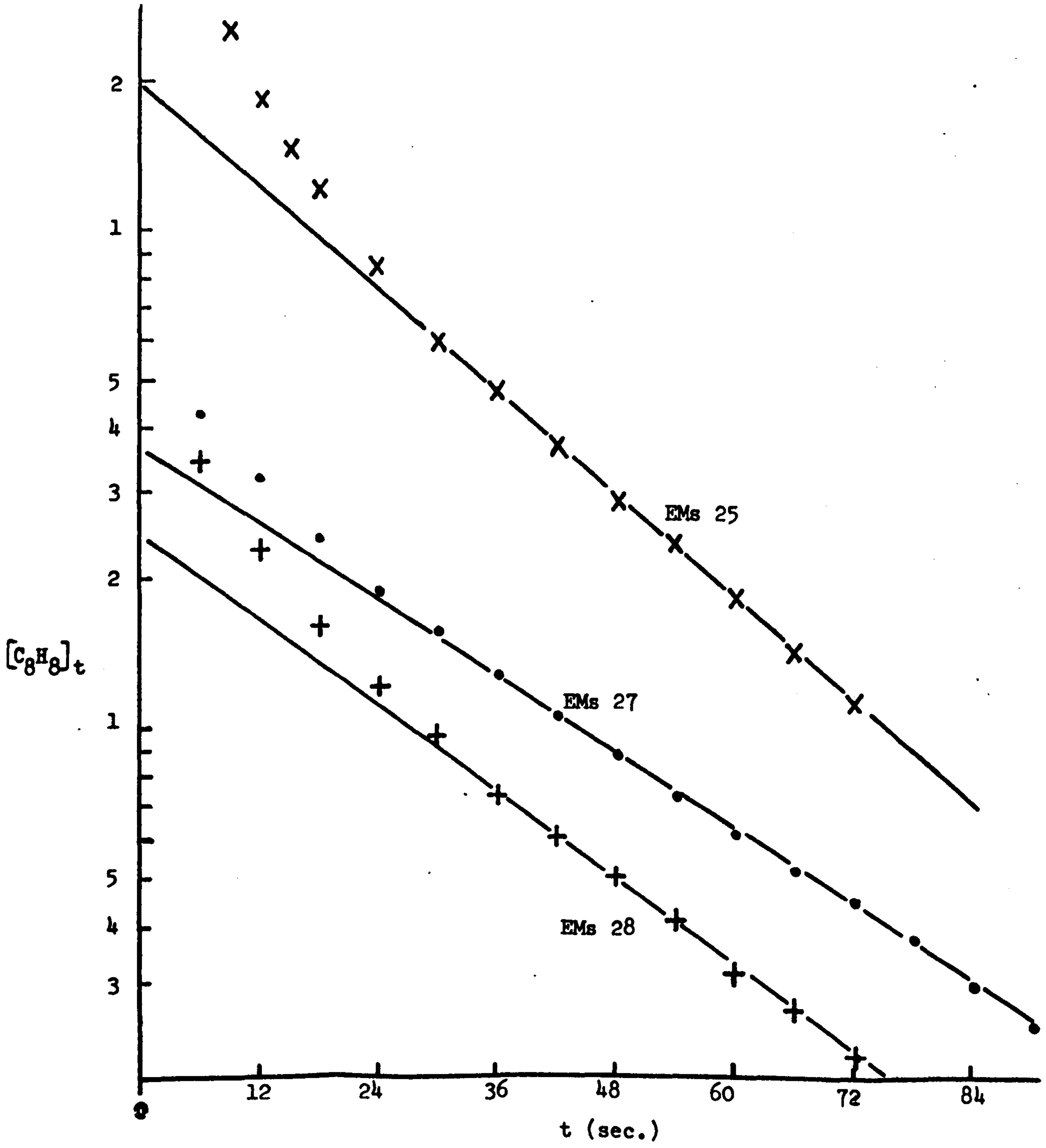
[1] The standard was naphthalene (see also Chapter II,2,i)

[2] Reverse addition experiment.

Fig. III,18

The polymerisation of styrene by $HClO_4$ in $PhNO_2$ at 6°.

Typical first-order plots



hence the overall reaction is not of first-order with respect to monomer.

In view of the complex nature of the reaction and its inapplicability to our original purpose, we stopped the experiments with nitrobenzene.

It is difficult to imagine why nitrobenzene, mixed with 1,2-dichloroethane, inhibits the polymerisation whereas, in pure $PhNO_2$, the reaction is fast and goes to completion. It is clear that the reaction is slower than one would expect from dielectric constant considerations alone. However, since the perchloric acid interacts with the solvent one cannot tell what the concentration of the propagating species is. Based on my argument below, the concentration of the propagating species is probably very low.

The reaction of the perchloric acid with the solvent can be thought of as being a direct protonation of the nitro group:

$$PhNO_2 + HClO_4 \rightleftharpoons PhNO_2H^+ \; ClO_4^-$$

If styrene is added to the above system, as has been done in experiment EMs 25, a competition for the proton of the perchloric acid would shift the above equilibrium to the left. This follows from the reaction and conductance trace of experiment EMs 25, Fig. III,17, where upon adding the styrene the conductance at first decreases slightly and then returns to its original value. Since the decrease of the conductance is only slight the concentration of the propagating species appears to be only a small fraction of the original catalyst concentration. However, since the propagating species itself may be ionic, and the equilibrium concentration of the perchloric acid in the equilibrium shown above is not known, the results cannot supply a quantitative support of my conclusion.

Although the C, H, N results are peculiar in that the C% + H% is higher than 100%, it appears that since the C%/H% ratio is in good agreement with the theoretical value, the polymer most probably consists only of carbon and hydrogen. The IR spectra of the polymers help to support this conclusion.

Since the polymers made in nitrobenzene do not appear to dissolve as readily as those made in methylene chloride, it seems that the polymers, like those made in nitroethane, are structurally somewhat different from those made in methylene chloride.

6. THE REACTION IN CHLOROFORM

Since no polymerisation occurred when perchloric acid was added to styrene in CCl_4 solution, chloroform was chosen as another possible solvent which might meet all the solvent requirements stated in the introduction of this Chapter. Although chloroform, alone and mixed with other solvents, has been used before as a medium for cationic polymerisations, it has never been used with $HClO_4$ as the catalyst.

Since the low dielectric constant of chloroform was expected to give us a slow polymerisation, the reactions were initially followed by dilatometry. The kinetic features of these reactions were internally consistent.

In order to cover as wide a range of acid concentrations as possible, several reactions were also followed by adiabatic calorimetry. Although the results obtained by this technique were also internally consistent, at first they did not seem to behave in accordance with the previous dilatometric experiments. We believe, however, that we have found the link between the two sets of results. Hence, the results of these two sets of experiments will be presented separately but they will be discussed together.

The dilatometric experiments at 0^o

The experimental procedure was as described in Chapter II, 2,c.

Upon crushing the catalyst phial into the styrene/$CHCl_3$ solution, a slight yellow flash was visible. The polymerisation which followed was of first-order and the reacting mixture remained colourless until, quite suddenly, the solution started to turn yellow and a new first-order reaction started; the yellow gradually became more intense. The time up to the appearance of the yellow colour was the longer, the lower the initial acid concentration. This sequence of events is best illustrated in Fig. III,19, which is typical of all the experiments carried out in the dilatometer. The two first-order rate constants calculated from the two parts of the first-order plots, are tabulated in Table III,12 as k'_{II} and k'_{III}, for the initial slow polymerisation II and the subsequent fast reaction III, respectively. Both these first-order rate-constants are linearly dependent on the initial acid concentration, Fig. III,20 and Fig. III,21. The slopes of these lines give $k_{II} = 1.63M^{-1}\ sec^{-1}$ and $k_{III} = 18.7M^{-1}\ sec^{-1}$. The intercepts of these plots give us an estimate of the concentration of $HClO_4$ which has been inactivated either by impurities or by a side-reaction of the acid with the solvent; they are for the k'_{II} plot $x_2 = 6 \times 10^{-5}M$, for the k'_{III} plot $x_3 = 1.6 \times 10^{-4}M$.* Thus, k_{II} and k_{III} are the first-order rate-constants per unit of "effective" acid concentration, i.e. $k_{II} = k'_{II}/([HClO_4]-x_2)$ and $k_{III} = k'_{III}/([HClO_4]-x_3)$. Hence, it follows that

$$-\frac{d[C_8H_8]}{dt} = k_{II}\ ([HClO_4]-x_2)\ [C_8H_8] = k'_{II}\ [C_8H_8]$$

---

*The uncertainties in x_2 and x_3 are such that the difference between them is not significant.

Fig. III,19

The polymerisation of styrene by $HClO_4$ in $CHCl_3$ at 0°.

A typical first-order plot of a dilatometric experiment.

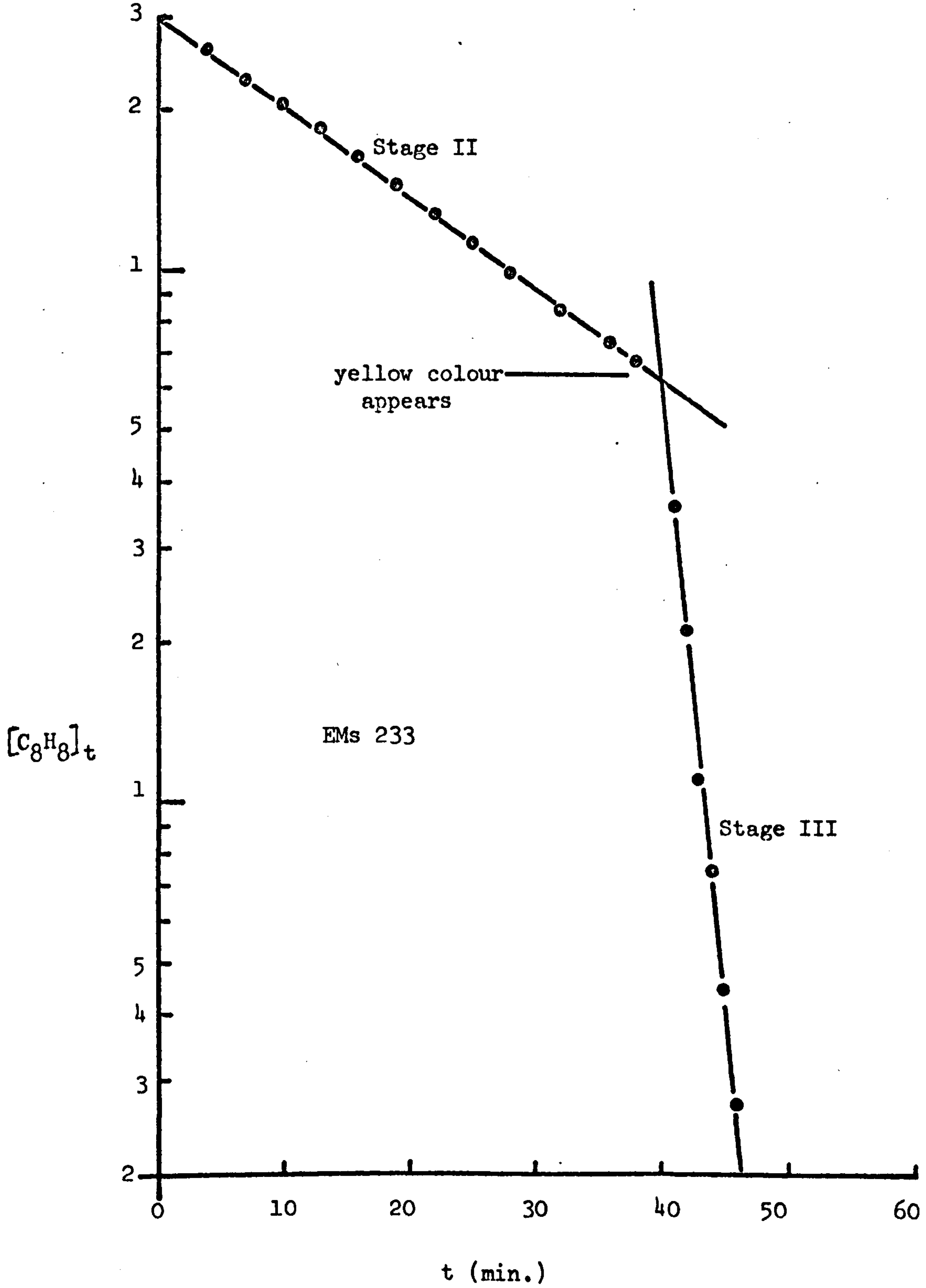


Table III,12

The polymerisation of styrene by $HClO_4$ in $CHCl_3$

Dilatometric experiments at 0°.

EMs	$[C_8H_8]_o$ (M)	$[HClO_4]_o$ (10^4M)	k'_{II} (10^4 sec^{-1})	k'_{III} (10^3 sec^{-1})	t' (min)	$[C_8H_8]_{t'}$ (10^2M)	yield[+] (%)	DP
242	0.333	1.30	1.37	-	230	-	100	7.0
234	0.350	2.25	2.67	1.24	109	6.4	100	6.4
235	0.356	3.23	4.16	3.11	69	6.3	100	6.2
233	0.349	4.46	6.58	9.21	40	7.2	100	6.4
236	0.350	4.52	6.70	5.49	41	6.5	100	5.9
237	0.354	5.57	8.36	7.72	31	7.3	100	5.7
245[x]	0.126	86.80	6.05	-	-	-	100	3.4

[+] The reaction was 'killed' when no more contraction occurred in the dilatometer.

[x] Approximate calorimetric conditions.

Conductimetric[*] (at 0°) and Spectroscopic[†] (at 2°) experiments

243[*]	0.352	4.53	- -	- -	41	5.80	100	6.1
417[†]	0.329	2.57	- -	- -	23	-	-	-

Fig. III,20

The polymerisation of styrene by $HClO_4$ in $CHCl_3$ at 0°.

The acid concentration dependence of k'_{II}

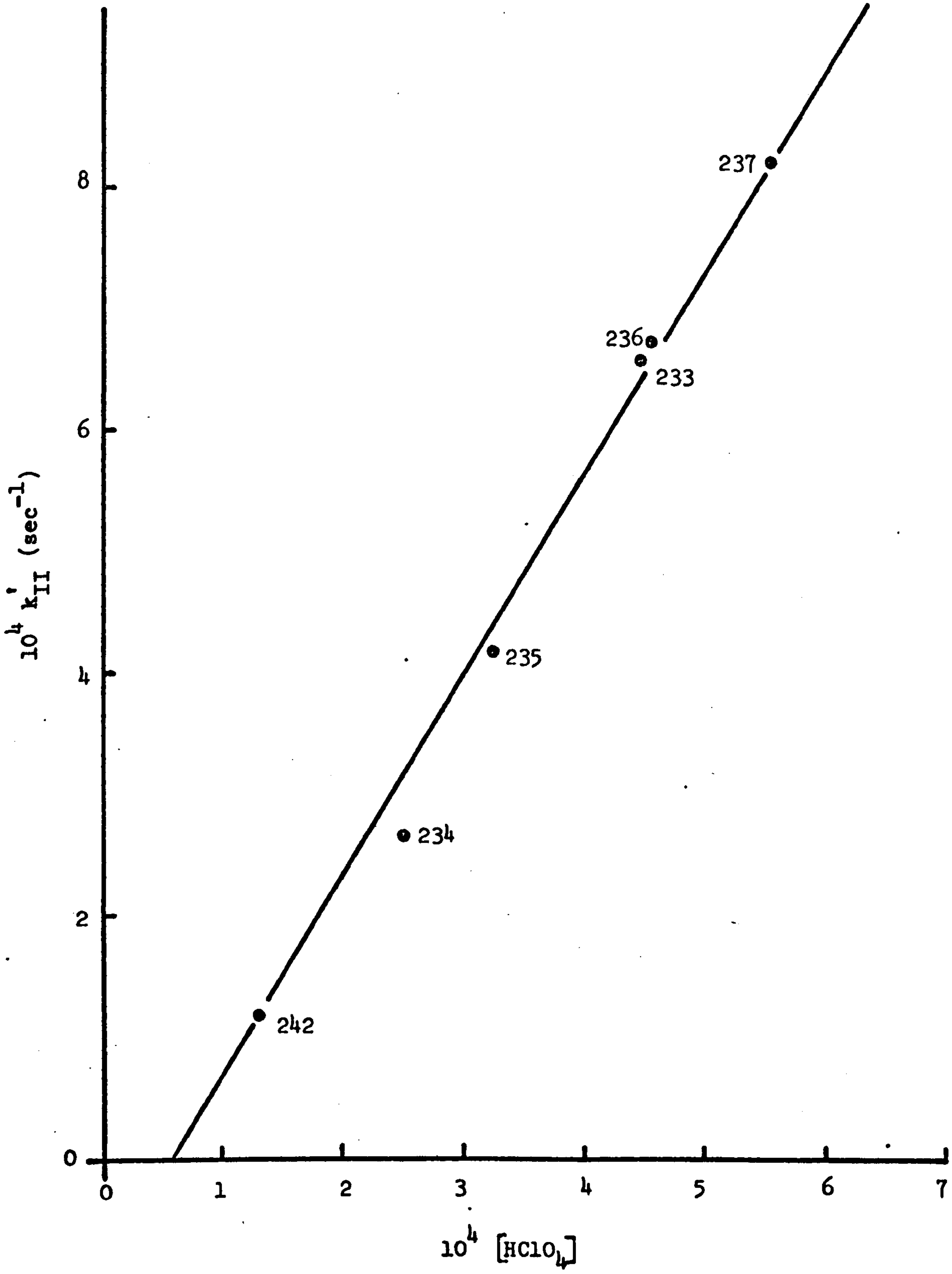
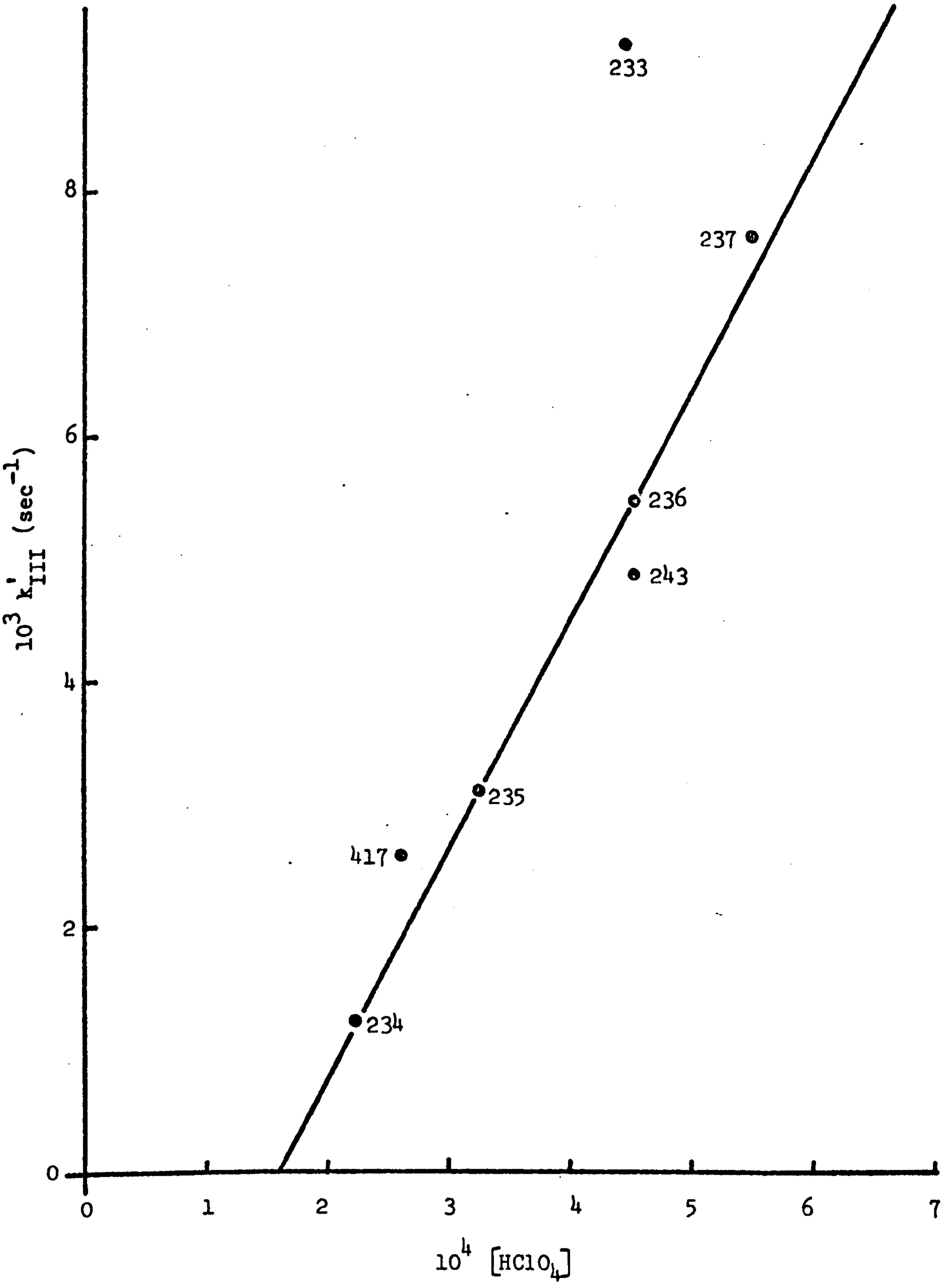


Fig. III,21

The polymerisation of styrene by $HClO_4$ in $CHCl_3$ at 0°. The acid concentration dependence of k'_{III}



and

$$-\frac{d[C_8H_8]}{dt} = k_{III}\,([HClO_4]-x_3)\,[C_8H_8] = k'_{III}\,[C_8H_8]$$

The time interval from the moment of starting the polymerisation to the moment of appearance of the reaction III, shall be called the "latency period", t'. The amount of unpolymerised styrene left at t', per unit initial acid concentration will be denoted by n. The dependence of 1/n on the initial acid concentration is shown in Fig. III,22. Since this plot gives us a straight line it follows that the styrene concentration at t' is ~~a~~ constant.

The reaction III was also followed conductimetrically and spectroscopically. The results of these experiments are included in Table III,12 because the reaction conditions are the same as those in the dilatometric experiments. The conductance trace is shown in Fig. III,23.

Since the colour of the final solution was yellow, I followed this latter stage spectroscopically by repeatedly scanning at timed intervals from 500nm to 400nm. At first only a broad peak at 420nm appeared. Another peak appeared later on at about 440nm. Three hours after crushing the catalyst phial the spectrum showed predominantly peaks at 450nm and at 308nm. This sequence of spectra is shown in Fig. III,24. The absorptions can be ascribed to the same ionic species which have been found in the styrene/$HClO_4$/CH_2Cl_2 system. The origin of these species has been described in the

Fig. III,22

The polymerisation of styrene by $HClO_4$ in $CHCl_3$ at 0°.

The acid dependence of 1/n.

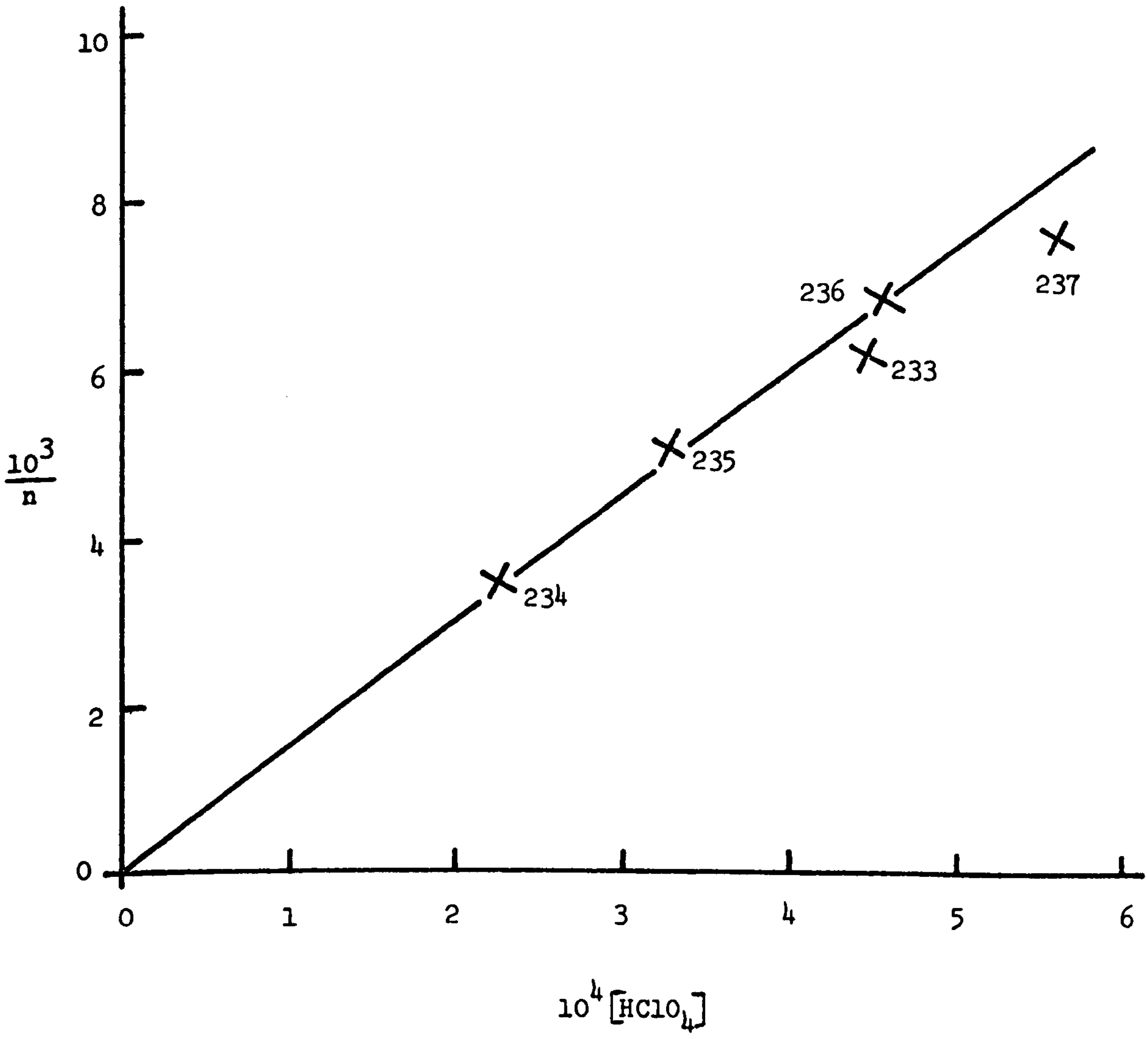


Fig. III,23

The polymerisation of styrene by $HClO_4$ in $CHCl_3$ at 0°.

The conductivity trace arising from stage III

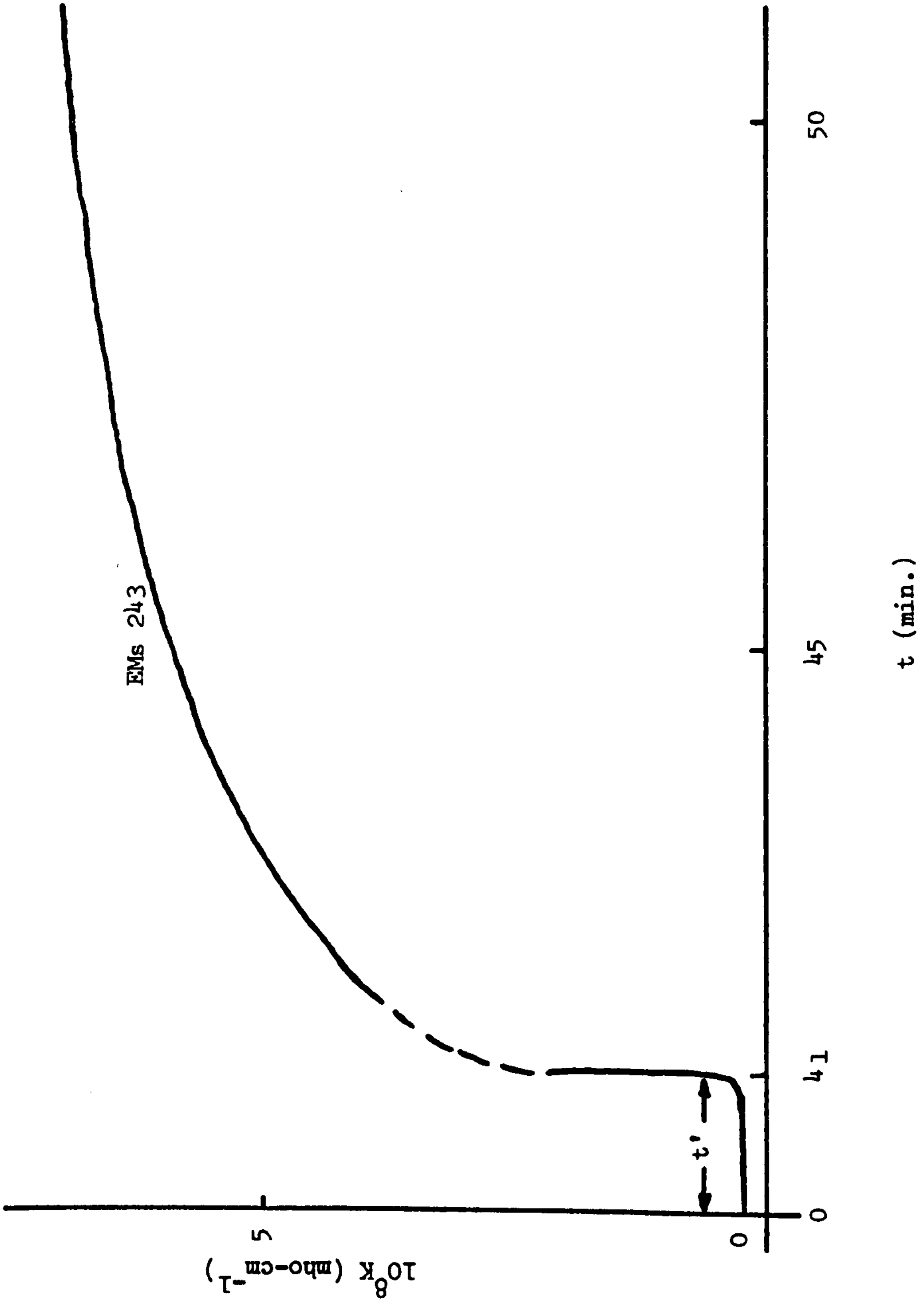


Fig. III,24 (opposite)

The sequence of spectra arising from experiment EMs 417.

Times after starting the polymerisation.

A : 37 min.

B : 42 min.

C : 48 min.

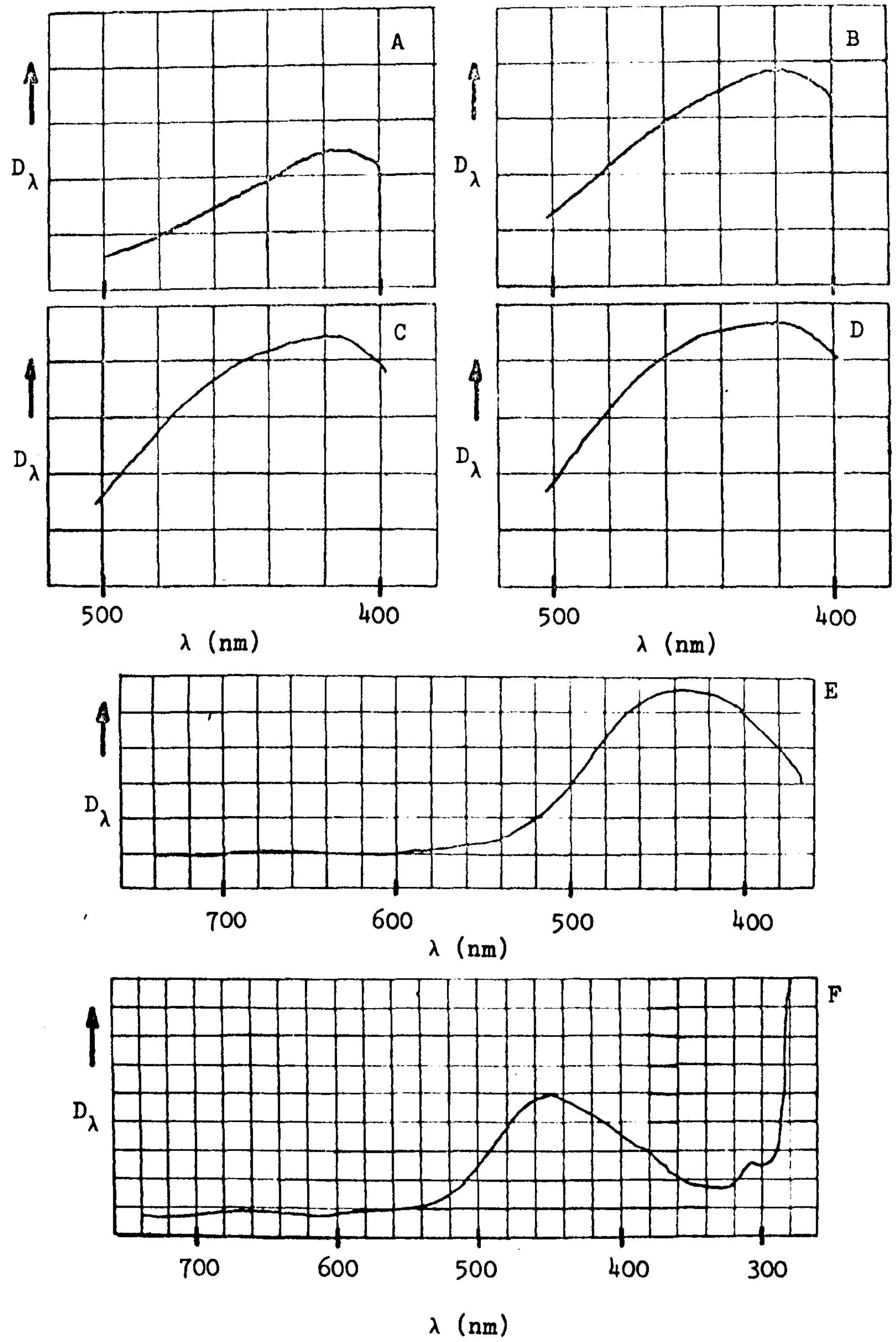
D : 54 min.

E : 68 min.

F : 3 hrs.

Fig. III,24

The polymerisation of styrene by $HClO_4$ in $CHCl_3$ at 2°. The spectra arising from experiment EMs 417.



introduction of this thesis. The peaks at 420nm and 308nm are due to the indanyl ions and the peak, which at first appears as a shoulder at 440nm but which, when by itself, is at 450nm, is due to the allylic ions. The presence of the latter ions is further confirmed by the fluorescence of the reaction products when they are poured into alcohol. As mentioned in this chapter under Part 2c, the fluorescence is due to polyunsaturated polymers which are formed by a proton abstraction from the allylic ions by some more basic species.

The polymers are of low molecular weight. Except for a strong peak at 1740 cm^{-1}, their I.R. spectra were identical to those of polymers made in CH_2Cl_2. Treatment of the polymer with bromine water left the peak at 1740 cm^{-1} unchanged. The spectrum after the Br_2-H_2O treatment did show, however, the disappearance of two peaks at 965 cm^{-1} and 745 cm^{-1}, and the appearance of a small peak at 660 cm^{-1}. No major change was noticeable between 1600 cm^{-1} and 1700 cm^{-1}. Hence, the peak at 1740 cm^{-1} is most probably due to a carbonyl group. Presumably this could be formed by oxidation of a double bond end-group. The peaks at 965 cm^{-1} and 745 cm^{-1} show that at least some polymers have unsaturation of the type $CHR_1 = CHR_2$. The peak at 660 cm^{-1} is due to the C-Br bond formed when the polymers are subjected to the bromine water treatment.

The calorimetric experiments

The experimental procedure was as described in Chapter II,2,a.

A typical reaction trace is given by the polymerisation of the first portion of styrene in experiment EMs 33, Fig. III,25. The reaction traces of all the experiments listed in Table III,13, failed to reach a final stable temperature, i.e. the reaction trace kept on creeping upward. Nevertheless, except for the experiment EMs 70, the reactions were stopped shortly after it became clear that the temperature trace was not about to level off.

A first-order plot of two typical reactions is shown in Fig. III,26. Clearly the lines have a strong curvature between what appear to be two rectilinear portions. The rate-constants corresponding to the slopes of the initial and final rectilinear portions of the lines are listed in Table III,13 as k_I' and k_{II}' respectively. The dependence of k_I' and k_{II}' on the initial acid concentration is shown in Fig. III,27, and Fig. III,28 respectively. The slope of the line in Fig. III,28 is given by the slope of the line obtained from the k_{II}' vs. $[HClO_4]$ plot of the dilatometric experiments, Fig. III,20. As will be shown in the later discussion, the combined dilatometric and calorimetric results seem to indicate that the k_{II}' obtained dilatometrically is also the k_{II}' obtained calorimetrically.

The conductance trace in Fig. III,25 is also typical of the reactions at 0°. Although there was no sharp increase of the

Fig. III,25

The polymerisation of styrene by $HClO_4$ in $CHCl_3$ at 0°.

Typical reaction and conductivity trace (first temperature rise) and the trace of a 2nd-addition experiment (second temperature rise)

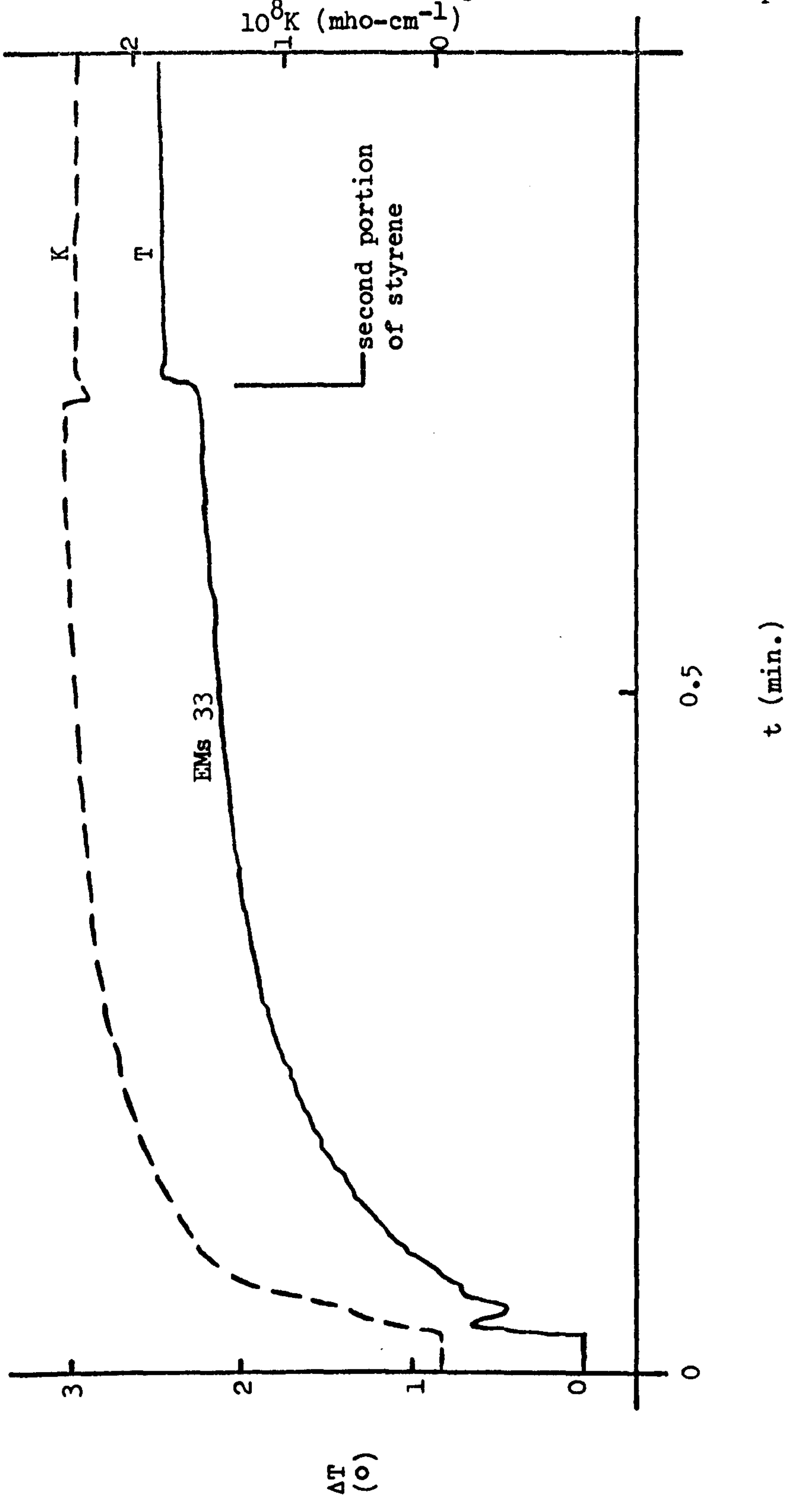


Table III,13

The polymerisation of styrene by $HClO_4$ in $CHCl_3$.

Calorimetric experiments at 0°

EMs	$[C_8H_8]$ (M)	$[HClO_4]$ (10^3M)	k'_I (10^2 sec^{-1})	k'_{II} (10^2 sec^{-1})	K (10^8 mho-cm^{-1})	yield (%)	(time) (min.)	DP
69	0.501	7.07	-	0.41	1.35	48	(14)	4.6
70[*]	0.403	0.67	-	-	very low	96	(80)	5.7
34[+]	0.354	7.09	8.09	1.20	2.70	50	(12)	4.4
33[+]	0.135	7.07	4.98	2.29	2.70	62	(10)	3.5
67	0.134	3.84	5.44	-	0.54	37	(4)	3.4
65	0.133	8.66	3.87	0.93	2.70	71	(12)	3.1
31	0.131	14.00	4.26	1.23	5.89	93	(4)	3.3
32	0.131	10.00	5.63	1.58	2.70	100	(>11)	3.4
41[†]	0.080	2.00	(4.14)	(4.14)	-	21	(4)	2.8
66	0.052	7.07	5.04	2.92	2.92	30	(3)	2.1

[*] Approximate dilatometric conditions

[+] Second addition of styrene experiments

[†] Reverse addition experiment

Fig. III,26

The polymerisation of styrene by $HClO_4$ in $CHCl_3$ at 0°.
Typical first-order plots of two calorimetric experiments.

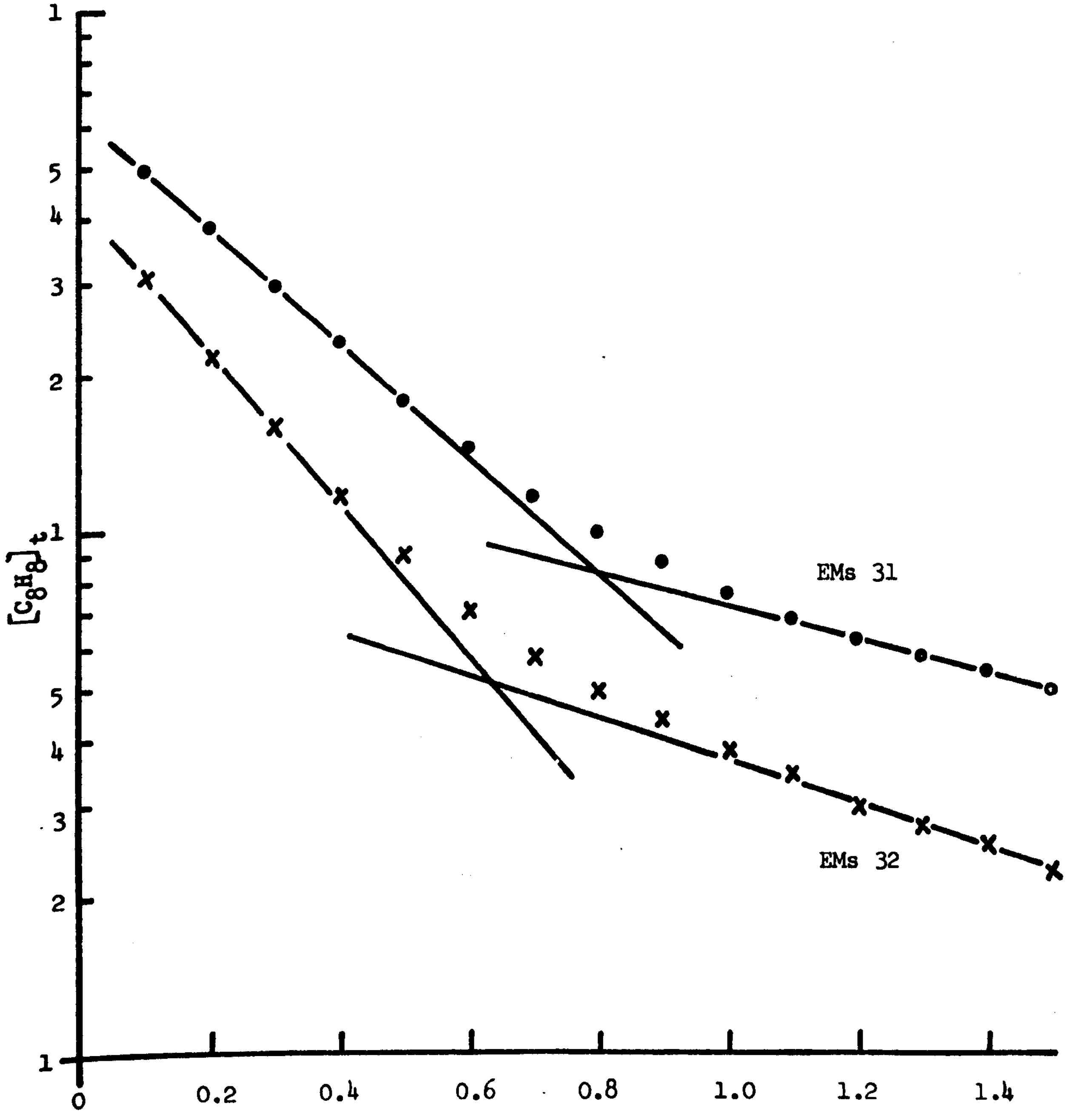


Fig. III,27

The polymerisation of styrene by $HClO_4$ in $CHCl_3$ at 0°, -30°, and -60°.

The acid concentration dependence of k'_I

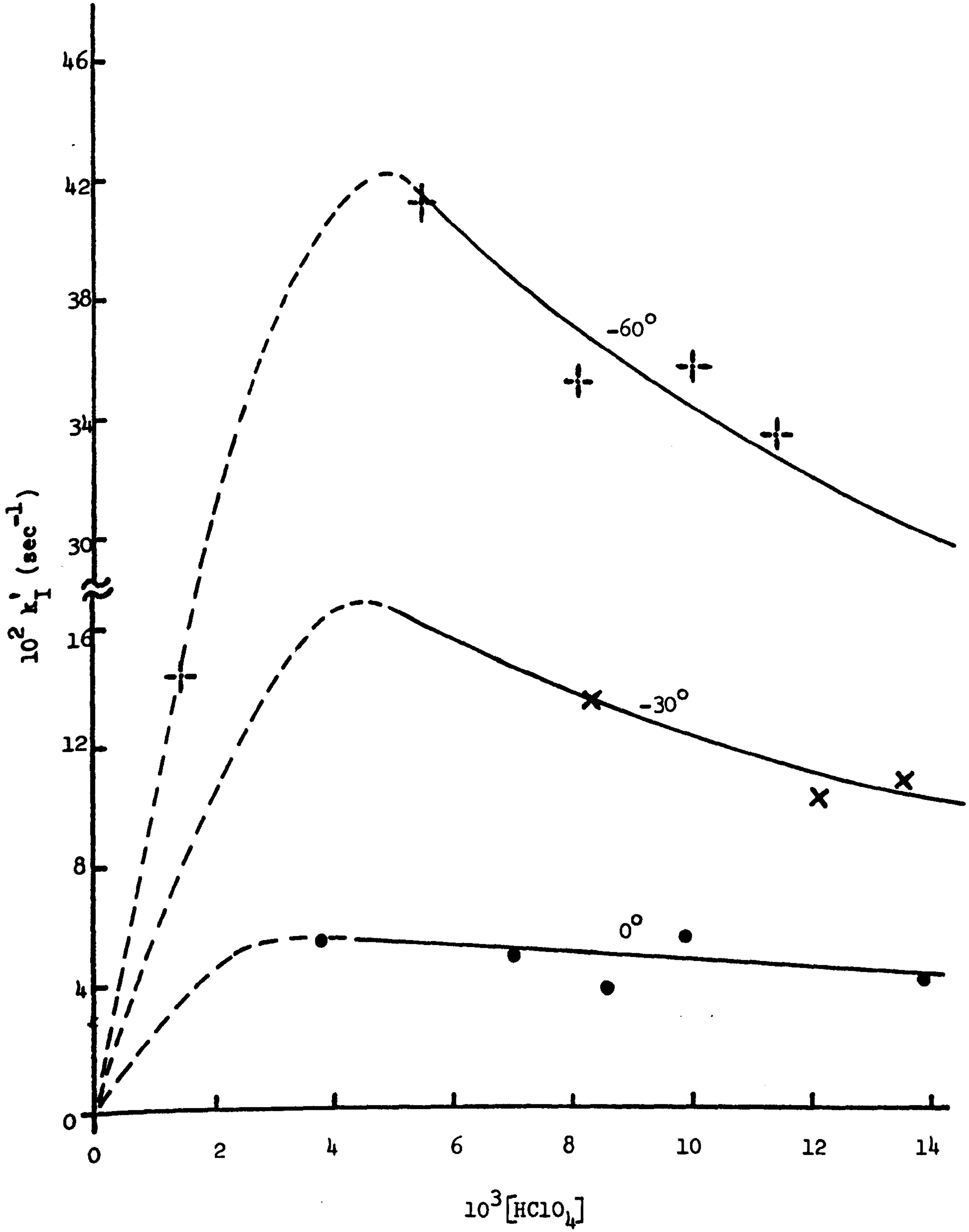
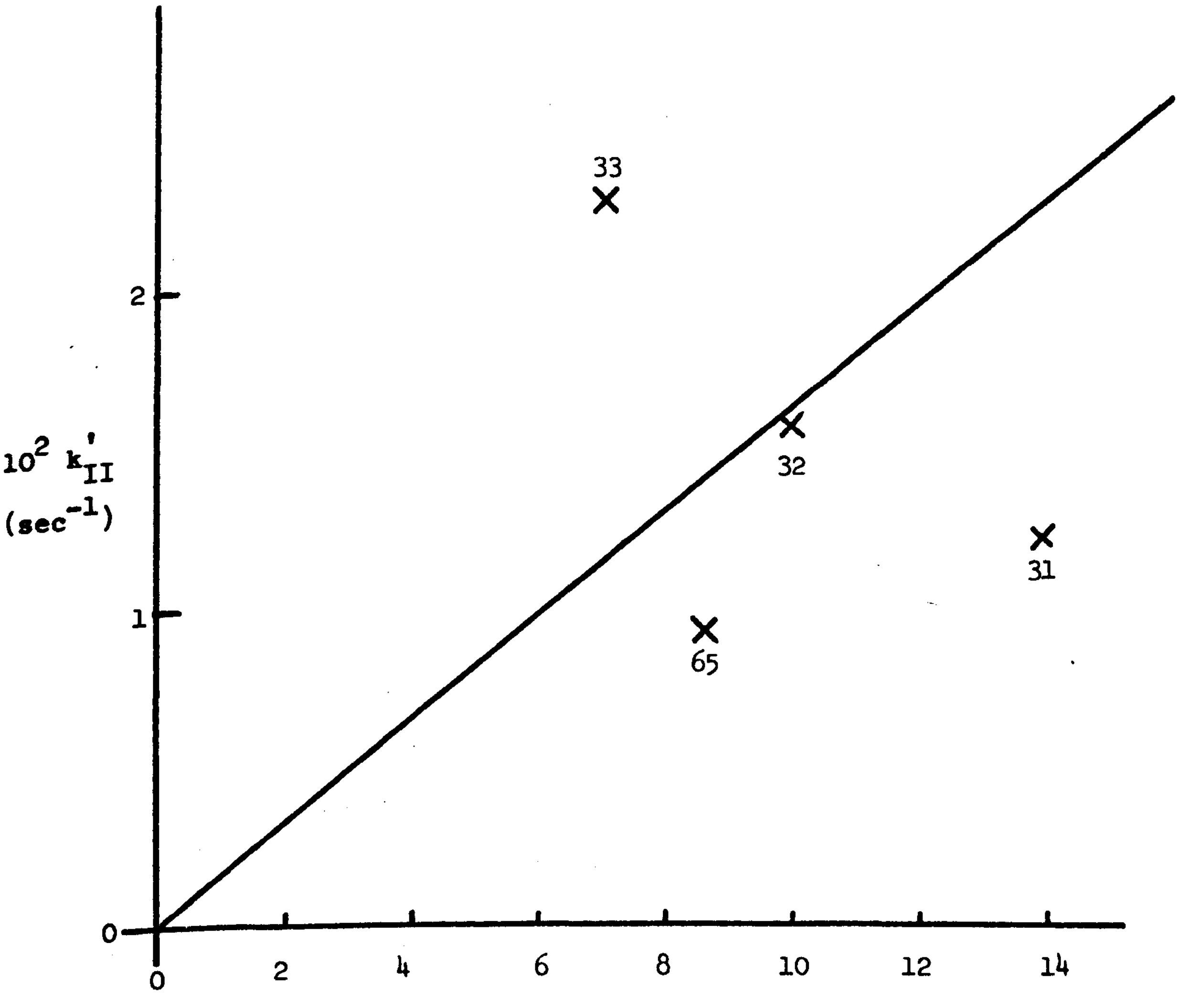


Fig. III,28

The polymerisation of styrene by $HClO_4$ in $CHCl_3$ at 0°.

The acid concentration dependence of k'_{II}.



$10^3\ [HClO_4]$

conductance when the acid phial was crushed, a light yellow flash was visible and the colour persisted throughout the polymerisation. The conductance levelled off to an approximately constant value, the magnitude of which is tabulated, in terms of the conductivity K, in Table III,13.

When the reaction vessel was opened after each experiment the reaction mixture smelt of styrene, which showed that the polymerisations had not gone to completion. The limited yields were clearly at variance with the complete conversions observed in the dilatometric experiments. Hence experiment EMs 70 was carried out to see if, given enough time, the reaction would go to completion. The reacting mixture was left undisturbed for 80 minutes, while the temperature of the calorimeter was kept as nearly at 0° as possible. After 80 minutes I had expected the appearance of the deep yellow colour observed at the end of the dilatometric experiments. Since the reaction should have been nearly over in 80 minutes, I opened the calorimeter. In the process of doing so the expected deep yellow colour appeared. The recovered 96% of polymer was short of the expected 100%, probably because the last reaction stage was partly inhibited by the presence of the moisture which got into the calorimeter when it was opened.

Two second addition experiments were carried out, i.e. a second portion of styrene was added, when the polymerisation of the first portion of styrene seemed to be over. In the experiment EMs 34 the second addition of styrene failed to have any effect on the temperature trace, as well as on the conductance trace. The effect of the second addition in experiment EMs 33 is shown in Fig. III,25.

Fig. III,29 shows the visible-U.V. spectra of a small sample of the reaction mixture of experiment EMs 32 before and after 'killing' the reaction with $NH_4OH/EtOH$. The major portion of the reaction mixture was 'killed' right after the sample was taken for the U.V. spectra. Since the spectrum A is somewhat featureless, not much can be concluded from it, except that the reaction mixture contains allylic ions (λ = 460nm) and indanyl ions (λ = 415nm). The reaction products, when poured into ethanol exhibited slight fluorescence, which is due to the polyunsaturated polymers formed from the polymeric allylic ions.

One "reverse addition" experiment was carried out, EMs 41. Upon adding the acid to the $CHCl_3$ a reaction occurred. Since, on the basis of the temperature rise the heat given off by the reaction is approximately 400 kcal. per mole of perchloric acid, the reaction is most probably a catalytic one. There was no change in the initial background conductance ($K = 8.0 \times 10^{-9}$ mho-cm^{-1}) and no colour was visible in the $CHCl_3/HClO_4$ solution. Subsequent addition of styrene to this solution resulted in only a small and slow temperature increase. This sequence of events is shown in Fig. III,30. Since the acid appeared to react with the $CHCl_3$, a plot was made of the temperature increase, as recorded by the instrument, vs. the final amount of styrene polymerised, based on the yields of polymers.

Fig. III,29

The polymerisation of styrene by $HClO_4$ in $CHCl_3$ at 0°. The visible - U.V. spectra of the reaction solution of experiment EMs 32, before (A) and after (B) addition of $NH_4OH/EtOH$.

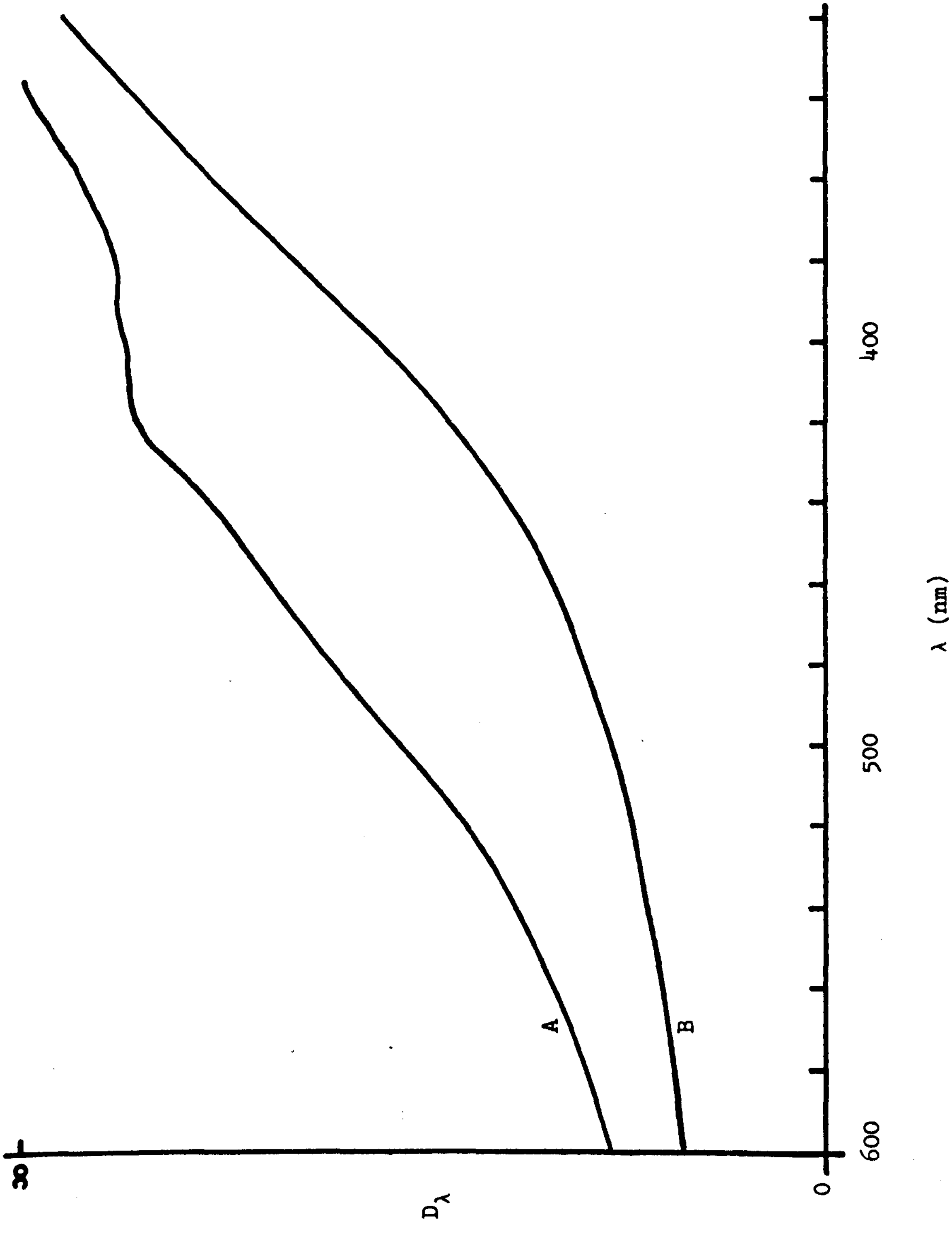
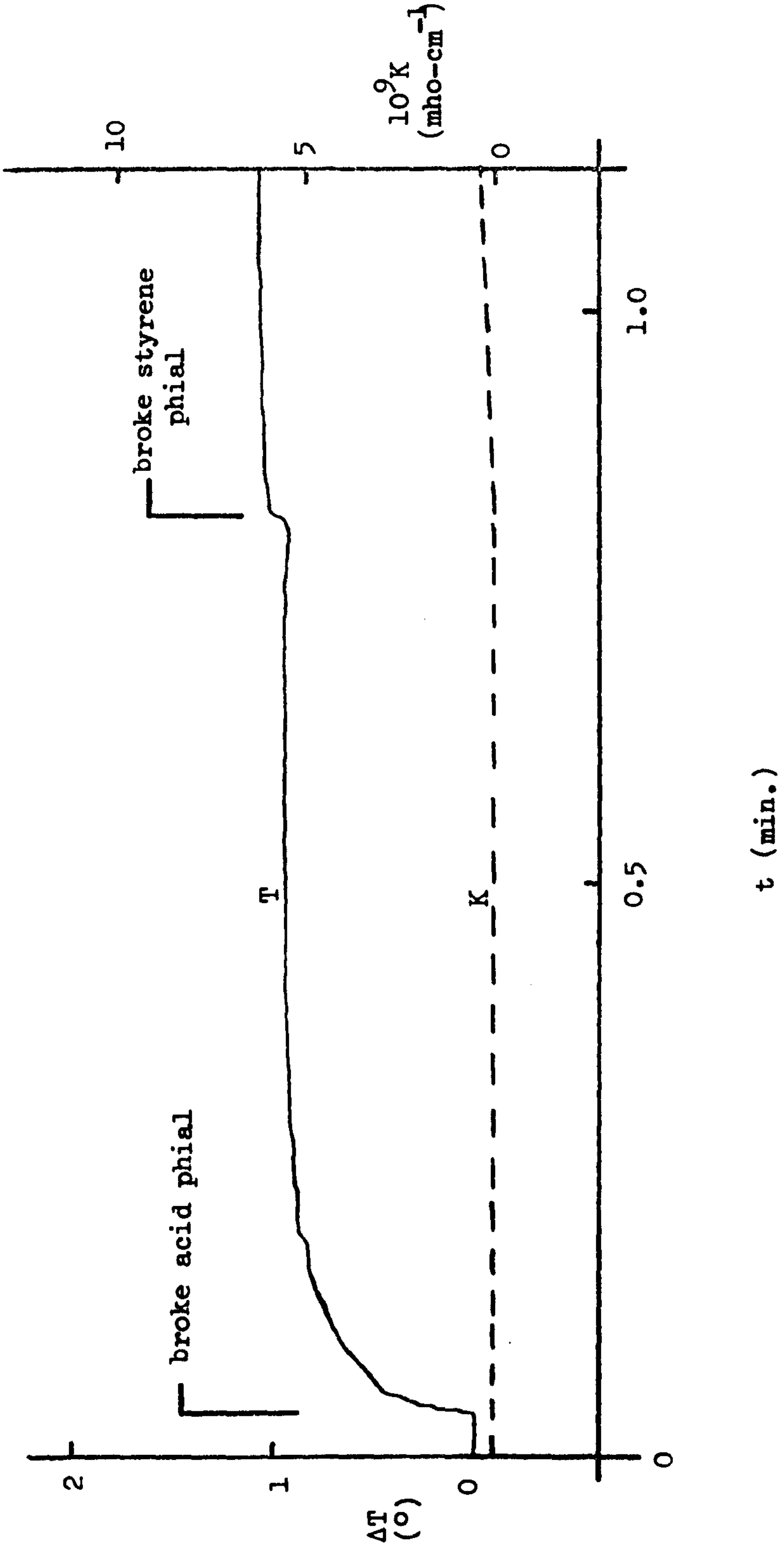


Fig. III,30

The polymerisation of styrene by $HClO_4$ in $CHCl_3$ at 0°.
The reaction and conductivity trace of experiment EMs 41.



This plot is shown in Fig. III,31. The intercept, as obtained by the most reasonable line in this plot, probably indicates the temperature increase of the reaction mixture due to the reaction of the acid with the solvent.

The experimental conditions of polymerisations carried out at -30° and -60° are shown in Table III,14.

A typical reaction trace of an experiment at -30° is shown in Fig. III,32. Its first-order plot is given in Fig. III,33. The k_{I}' obtained from the first-order plot is only intended to be used as an approximate guide for judging the rate of the first stage of the reaction. There is most probably also considerable error involved in the evaluation of k_{II}'. For reasons of comparison the dependence of k_{I}' on the acid concentration is included in Fig. III,27. Although the temperature trace of the reaction at -30° eventually levelled off to a constant value, the conductance trace kept rising all the time. Contrary to the initial conductance behaviour of the reactions at 0° (see Fig. III,25) the initial conductance at -30° increases very sharply.

The reactions at -60° seem to be over in a very short time. When the acid phial was crushed into the styrene/$CHCl_3$ solution the temperature rose quickly to a steady value. The conductance also rose sharply, but as soon as the reaction was over it returned to its pre-reaction value ($K = 8.0 \times 10^{-9}$ mho-cm^{-1}). A typical reaction trace is given by the experiment EMs 38, Fig. III,34. Its first-order plot, together with that of experiment EMs 39, is shown on

Fig. III,31

The polymerisation of styrene by $HClO_4$ in $CHCl_3$ at 0°. The plot of ΔT vs. the amount of styrene polymerised.

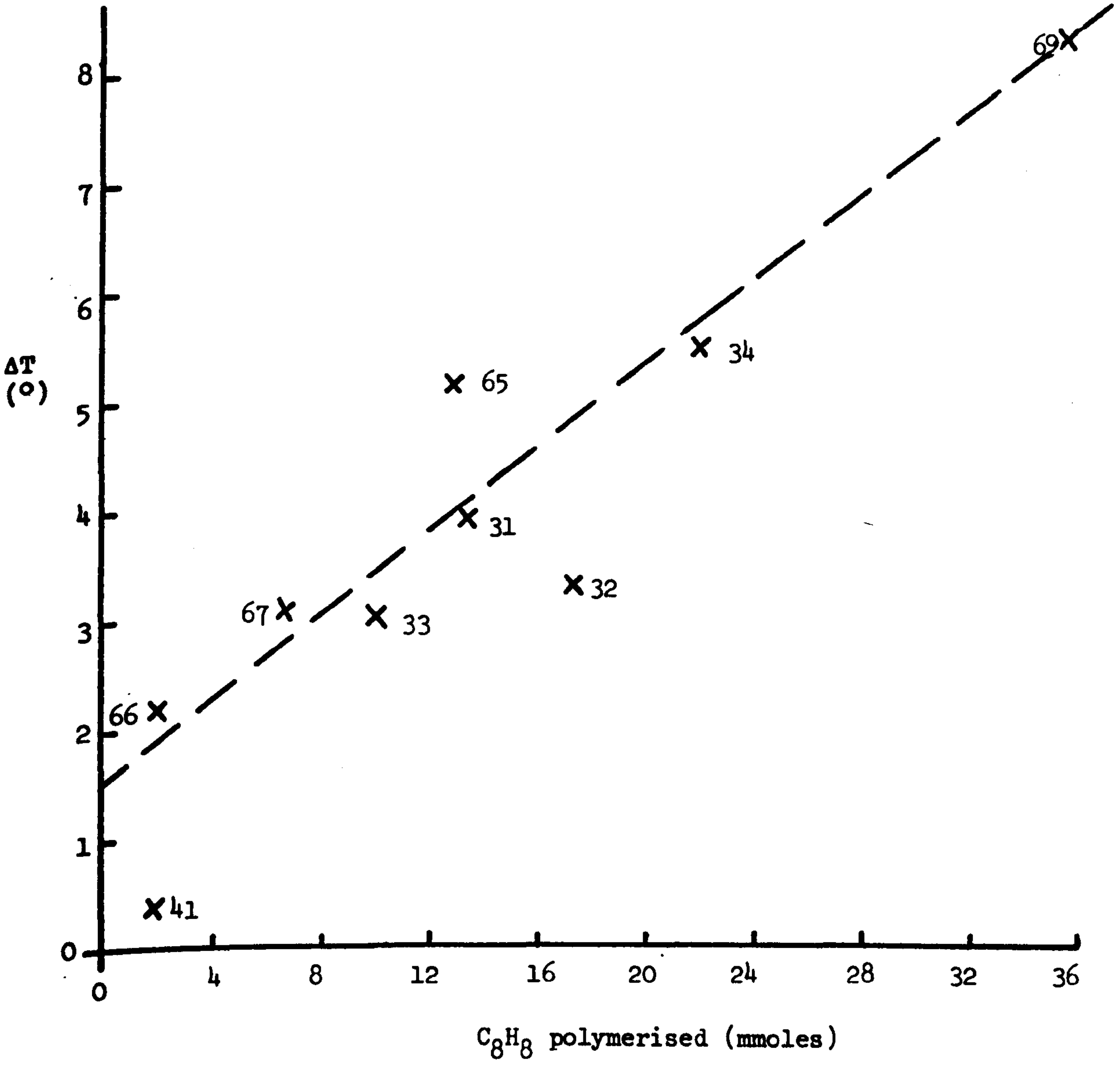


Table III,14

The polymerisation of styrene by $HClO_4$ in $CHCl_3$.

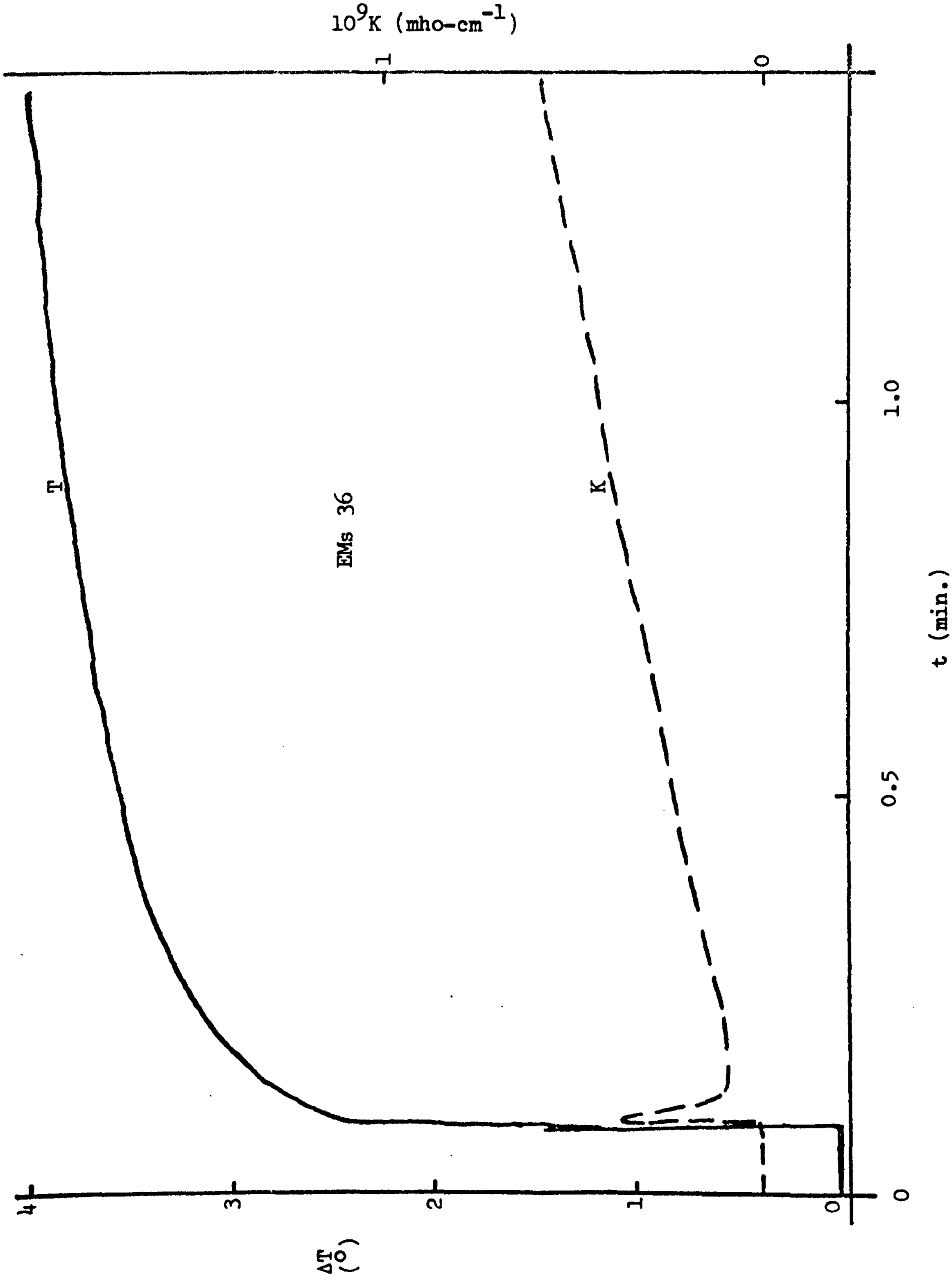
Calorimetric experiments at -30°

EMs	$[C_8H_8]$ (M)	$[HClO_4]$ (10^3M)	k'_I (10^2 sec^{-1})	k'_{II} (10^2 sec^{-1})	K (10^8 $mho\text{-}cm^{-1}$)	yield (%)	(time) (min.)	DP
37	0.132	8.34	13.5	1.72	-	53?	(33)	-
36	0.130	12.20	10.2	1.69	-	64?	(12)	2.5
35	0.129	13.60	10.8	1.29	(2.48)	80?	(12)	-
Calorimetric experiments at -60°								
43	0.391	10.10	35.7		very low	20	(1.8)	3.0
42	0.261	5.52	41.2		very low	10	(0.7)	4.0
39	0.130	8.13	35.2		very low	23	(33)	10.8
68	0.130	1.43	14.5		very low	3	(3)	4.4
38	0.129	11.50	33.4		very low	29	(2.3)	7.2

Fig. III,32

The polymerisation of styrene by $HClO_4$ in $CHCl_3$ at -30°.

Typical reaction and conductivity trace.



<u>Fig. III,33</u>

The polymerisation of styrene by $HClO_4$ in $CHCl_3$ at -30°.

The first-order plot of experiment EMs 36.

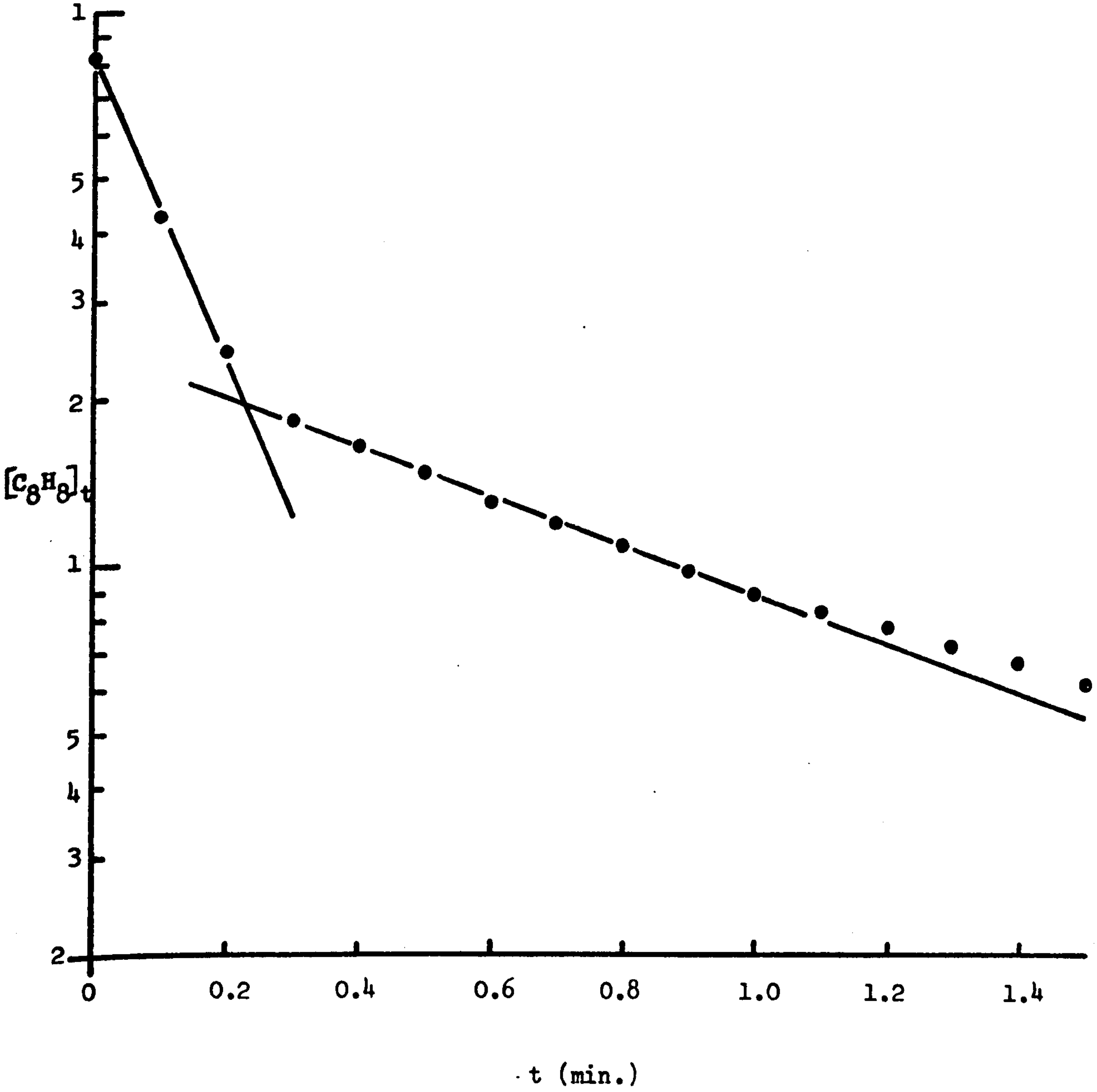


Fig. III,34

The polymerisation of styrene by $HClO_4$ in $CHCl_3$ at -60°.

Typical reaction and conductivity trace.

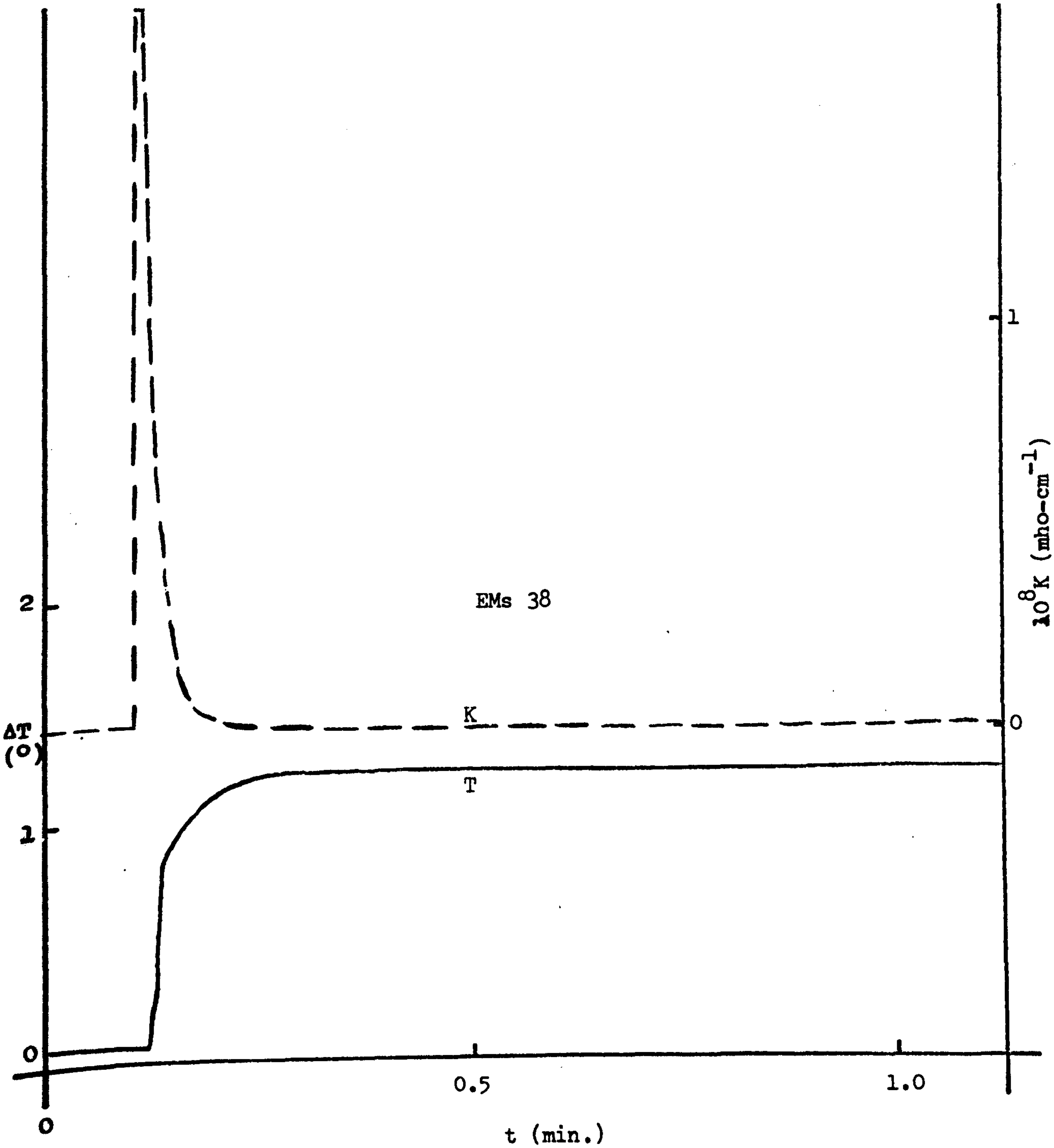


Fig. III,35. I have assumed that, on the basis of its magnitude, the first-order rate constant as obtained from this plot is the k'_{I} (as opposed to k'_{II}), and for the purpose of comparison, its dependence on the acid concentration is included in Fig. III,27.

For all the experiments at -60°, the calculated yields, from the temperature rise, always agreed with the yield of the recovered products.

The experiment EMs 39 was left undisturbed for 33 minutes but the yield did not exceed that expected on the basis of the initial temperature rise.

The I.R. spectra of the polymers made in the calorimeter were identical to those of polymers made in the dilatometer.

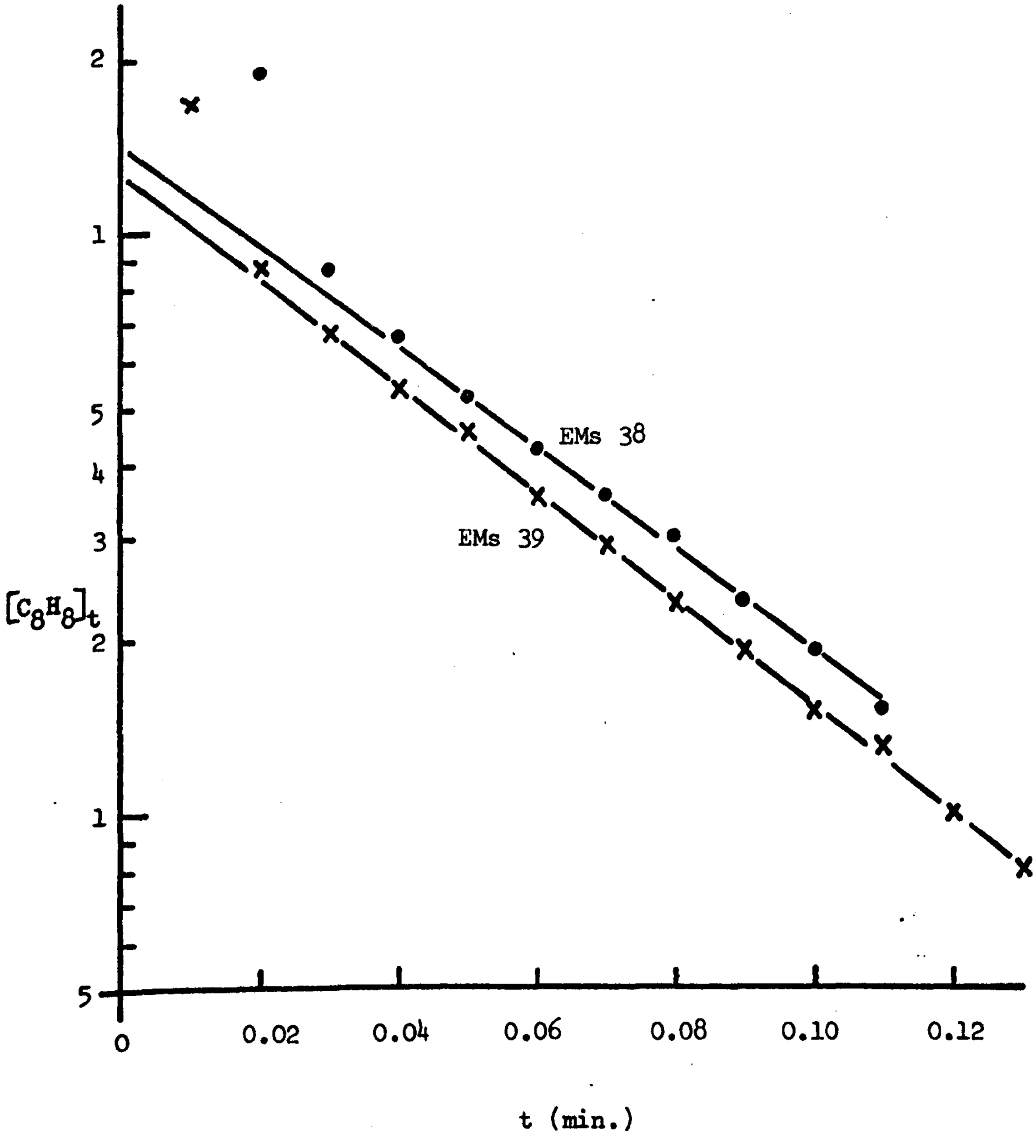
Discussion

The system styrene/$HClO_4$/$CHCl_3$ does not fulfill the requirements for which it was intended, namely as a system in which one might be able to learn more about the polymerising ester which we believe is at least one of the propagating species in the styrene/$HClO_4$/CH_2Cl_2 system. At first, however, having started with the dilatometric experiments, the kinetics of the styrene/$HClO_4$/$CHCl_3$ system looked somewhat promising. The polymerisation occurred while the solution was colourless until, suddenly, it turned yellow and the rest of the monomer was consumed. The rate of the polymerisation which occurred in the absence of the colour followed first-order kinetics so that the problem of a continuous acceleration, as we found in the styrene

Fig. III,35

The polymerisation of styrene by $HClO_4$ in $CHCl_3$ at -60°.

Typical first-order plots.



$/HClO_4/CH_2Cl_2$ system, did not seem to prevail when chloroform was the solvent. Although the appearance of the yellow colour was at a surprisingly early stage of the polymerisation, it was not entirely unexpected. The perchloric acid polymerisation of styrene in CH_2Cl_2, between 22° and -19°, was also found to end with the appearance of a yellow colour(26). This colour was later found to be due to the appearance of indanyl ions(16).

In studying the styrene/$HClO_4/CH_2Cl_2$ system, Gandini and Plesch(26) found that the appearance of the ions, measured spectroscopically and conductimetrically at room temperature, was perfectly reproducible and always occurred when the ratio $n = [C_8H_8]/[HClO_4]$ had fallen to 4.

On the basis of my results in $CHCl_3$ (see Fig. III,22), n for this system is far greater than four, and the styrene concentration at t' (end of the latency period, start of stage III) is not proportional to $[HClO_4]_o$. Hence, the processes which operate during the latency period in $CHCl_3$ appear to be quite different from those in CH_2Cl_2.

From our dilatometric results in $CHCl_3$ we find that a plot of the initial acid concentration against $1/t'$ is a straight line (of positive slope) which intercepts the acid concentration axis at $x = 1.1 \times 10^{-4}$ M. This intercept is close to the intercept x_2 given by the line in Fig. III,20, and is a measure of the amount of acid consumed by some impurity, probably residual water. The equation of the line gives

$$t' = F/([HClO_4]_o - x)$$

where F is a constant. This suggests that there is some process of second-order with respect to the acid concentration. This process may involve the propagating species reacting with themselves which would lead to their consumption. Once this process reaches a certain stage, ions are formed and the remaining monomer is quickly consumed.

In view of the complexities of the reaction in chloroform one cannot be sure of the validity of a comparison between the rate-constant of propagation (?) k_2 measured in CH_2Cl_2 and the rate-constant k_{II} (dilatometric) measured in chloroform. On the basis of the dielectric constant dependence of k_2 in mixed solvents(13), k_2 in $CHCl_3$ at 0° should have been equal to 2.2×10^{-2} M^{-1} sec^{-1}. This is considerably lower than the k_{II} (dilatometric) = 1.63 M^{-1} sec^{-1}. The k_2 in CH_2Cl_2 at 0° is 3.05 M^{-1} sec^{-1} (Chapter III,2,a). Hence, if we are comparing like with like, it appears that the polymerisation of styrene by $HClO_4$ is not as dependent on the dielectric constant of the solvent as is implied by the measurement of k_2 in mixed solvents. This may be expected if the propagating species are non-ionic.

An obvious extension of the dilatometric experiments was to increase the acid concentration and hence follow the polymerisation by the adiabatic calorimetry technique.

As was stated in the presentation of the results, the $HClO_4$ reacts with $CHCl_3$. Initially it appeared to us that this reaction did not occur in the presence of styrene. This impression was given by the plot of Fig. III,31 which, after a few experiments (EMs: 31, 32, 33, 34, 41), seemed to be a straight line through the origin. However, subsequent experiments showed that, although the scatter of the points is considerable, the best curve through them is a straight line with an intercept on the ΔT axis. Thus it appears that the reaction of the acid with the solvent still takes place even in the presence of styrene. Probably the degree of scatter depends on the relative rates of the acid-solvent reaction and of the polymerisation reaction. Some of the scatter however, may also be due to the different extents of oligomerisation in the different experiments. We have found that the D.P. of the polymers obtained, especially those made in the calorimeter, are very low. The heat of dimerisation and trimerisation of styrene is known to be higher than that of polymerisation once the D.P. ≥ 10. Since the different reactions in the calorimeter gave different degrees of oligomerisation, the overall temperature rise would not represent correctly the amount of polymer produced. Since for the experiments at -60° all the calculated yields agree with the yields of recovered polymers, it seems that the reaction of the acid with the solvent at this temperature is slow.

Contrary to the complete conversions obtained in the dilatometric experiments, excepting the experiments EMs 32 and EMs 70, the yields obtained in the calorimeter were always less than 100%, but increased with increasing acid concentrations. The experiment EMs 32, being left undisturbed for a longer time than experiment EMs 31, went to 100% conversion in spite of the fact that the initial acid concentration of EMs 32 was lower than that of EMs 31. The dilatometric experiment EMs 245, in which the concentrations were the same as those used in the calorimeter, as well as the calorimetric experiment EMs 70, with concentrations as used in the dilatometer, also gave a 100% yield of polymer. Hence, we conclude that all the reactions carried out in the calorimeter would have gone to completion if they had been left undisturbed for a long time.

The fast reaction I observed in the calorimetric experiment appears to be due to the simultaneous reaction of the acid with the monomer and the solvent. Accordingly a first-order plot of this reaction stage is not meaningful. Nevertheless, first-order plots have been made as some means of measuring the different rates of this stage as we change the reaction conditions. It seems that on the basis of the plot of Fig. III,27, the reaction I, which appears at all the temperatures used with the calorimeter, becomes slower with increasing acid concentration. However, at the low end of the acid concentration range, the rate of stage I seems to decrease again, as is indicated by the experiment EMs 68 at -60°.

We know that, even in the presence of styrene, the $HClO_4$ also reacts with the solvent. As we increase the acid concentration we may also increase the reaction rate of the acid with the solvent. If the increase of the rate of the reaction of acid with solvent is greater than the increase in the rate of the reaction of acid with styrene, less perchloric acid will be available for the monomer and hence the overall rate of stage I decreases with increasing acid concentration. The stage II in the calorimetric reactions should also be affected by this initial consumption of catalyst. This is not readily evident from the k'_{II} measured from the calorimetric reactions, but it seems to be indicated by the dilatometric experiment EMs 245 in which a high acid concentration (as in the calorimeter) was used. The k'_{II} for this reaction is unusually low. If the initial acid concentration is low the rate of the reaction of the acid with the solvent is slow, there is, relative to the case where the initial acid concentration is high, more acid available to react with the monomer, and thus the k'_{I} increases at first with increasing acid concentration. One further point which is given by the plot of Fig. III,27 is that the stage I reaction seems to be ionic, since decreasing the temperature, increased its rate. The initial sharp increase of the conductances, especially at -30° and -60°, substantiates this conclusion, although the conductance cannot be entirely due to oligostyryl ions.

During the stage II of the calorimetric experiments we should again have the situation in which a process of second-order is operative. It seems that since the second addition of styrene (experiments EMs 33 and 34) did not result in a corresponding increase in the rate of polymerisation, the polymerisation before the second addition of styrene involved a termination. Hence it is possible that the process which is second-order in acid leads to a continuously decreasing concentration of active centres. If so, the decrease of the concentration of active centres would be about 100 times slower in the dilatometric experiments which would explain why the dilatometric stage II appeared to follow first-order kinetics in spite of the termination reaction.

The slow reaction which occurs in the calorimeter, and which eventually may lead to complete conversion, is almost certainly the corresponding slow polymerisation stage II which is observed in the dilatometer. This is indicated by the line in Fig. III,28 which shows the acid dependence of the dilatometric k'_{II}, onto which the k'_{II} values from the calorimetric experiments, seem to fall. One needs to keep in mind that the k'_{II} (calorimetric) may carry a considerable error since that stage of the reaction is far too slow for reliable kinetic measurements to be made by the calorimetric technique.

On the basis of the combined dilatometric and calorimetric results and their discussions, one can summarize the kinetic behaviour of the polymerisation at 0^{o} as consisting of three stages: Stage I: two simultaneous reactions of the acid with the solvent and with the monomer. These reactions are followed by a Stage II which is a polymerisation of the monomer, the kinetics of which seems to indicate a simple first-order reaction, although there is some evidence which indicates that the propagation reaction is accompanied by a termination reaction. The polymerisation is apparently propagated by a non-ionic chain carrier, presumably a perchlorate ester. Stage II is followed by Stage III, a fast polymerisation of the remaining monomer, with the simultaneous appearance of the indanyl ions and subsequently of allylic ions. The DP of the polymers from the dilatometric experiments are generally higher than those from the calorimetric runs. This may be due to the high local acid concentration in the calorimetric experiments at the moment the acid phial is broken. This seems to lead to a fair amount of dimers and/or trimers. Hence, since most of the calorimetric experiments were stopped before 100% conversion, and since the initial acid concentration in the dilatometric experiments is low, the ratio of the low to high molecular weight oligomers in the calorimetric experiments is probably greater than in the dilatometric experiments. This appears to be shown by the uniquely low DP of the polymer from the dilatometric experiment EMs 245, in which "calorimetric" concentrations were used, and the distinctly higher DP of the polymer made in the calorimetric experiment EMs 70, in which "dilatometer" concentrations were used.

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IV THE POLYMERISATION OF STYRENE BY TRIFLUOROMETHANESULPHONIC ACID (TRIFLIC ACID)

Probably the greatest problem encountered in truly cationic polymerisations is the attainment of reproducible results, since these reactions are extremely susceptible to trace impurities. The experience gathered from the non-stationary polymerisation of styrene by H_2SO_4(1) led Reilly and Pepper to look for a strong, monoprotic acid which was expected to generate only propagating polystyryl ions. The acid they have chosen was $HClO_4$. It came as a surprise when the polymerisation of styrene by $HClO_4$ in 1,2-dichloroethane was found to be very reproducible, at least in the temperature range of 25° to -30°. The details of this reaction, and the development of the investigations which followed have been described in the introduction of this thesis. Suffice it to say here, the work of Gandini and Plesch has led to the hypothesis that the polymerisation of styrene by $HClO_4$ in CH_2Cl_2 is not ionic, but is propagated by a non-ionic chain carrier, tentatively described as a perchlorate ester(2). In the course of our work, which is the subject of this thesis, we have tried to learn more about the nature of the propagating species. The approach was to change the reaction conditions (solvents), to observe the effect of carbonium ion scavengers on the kinetics of the polymerisation, and to observe the behaviour of the polymerisation in the presence of an electric field. These results have been presented in chapter III of this thesis.

In the absence of a simple clear picture of the polymerisation of styrene by $HClO_4$, it was felt that if we found another strong acid similar to $HClO_4$, but capable of forming a higher concentration of propagating ions than that formed from styrene and $HClO_4$, we should be able to learn more about the properties of these ions. Alternatively, an acid similar in acid strength to $HClO_4$, but which would yield a more stable propagating ester, would serve to facilitate the study of the ester.

The acid chosen was trifluoromethanesulphonic acid (triflic acid). A literature survey showed that this acid had not been used as a catalyst for the polymerisation of styrene. The most common chemical usage of this acid (and its derivatives) was as an alkylating agent in organic syntheses(3). Since this acid is relatively new in the chemistry laboratory, a description of its physical and relevant chemical properties will be given:

Physical properties of triflic acid(4)

Formula	:	CF_3SO_3H
Formula Weight	:	150.02
Physical State	:	Colourless liquid (fumes in moist air)
Odour	:	Strong, pungent
Boiling Point	:	162°C/760 mm Hg 84°C/ 43 mm Hg 54°C/ 8 mm Hg
Density, g/cc	:	1.696/24.5°C
Index of Refraction	:	$n_D^{25°} = 1.325$
Dissociation Constant (in acetic acid)	:	$K = 1.26 \times 10^{-5}$

Relative Acid Strengths:

Measurements of the conductivity of strong acids in acetic acid have shown that trifluoromethanesulphonic acid is the strongest acid known. Acid strenth relative to nitric acid is shown(5).

CF_3SO_3H	427	CH_3SO_3H	17
$HClO_4$	397	HCl	9
HBr	164	CF_3CO_2H	1
H_2SO_4	30	HNO_3	

Triflic acid is a stable, hygroscopic, and mobile liquid which, when exposed to moisture, gives a stable crystalline monohydrate (m.p: 34°, b.p: 96° at 1 torr)(6).

The anhydrous acid can be heated to 400° in absence of air, without appreciable breakdown. Moisture and air decrease the decomposition temperature of the acid(7,8). The acid, when heated with conc. HNO_3 to 150° for 48 hours, does not decompose(9).

The acid is only slightly soluble in benzene and carbon tetrachloride, but is miscible with water in all proportions. It is also soluble in many oxygen-containing liquids such as alcohols, ethers and ketones(8).

The characteristic infra-red absorption bands of the $CF_3SO_3^-$ group are at 7.85μ, 8.5μ, and ca. 9.7μ(6).

Chemical Properties of Triflic acid

The solubility of triflic acid in the oxygen-containing liquids is generally accompanied, or followed, by a reaction of the acid with the solvent. Oxonium compounds are the first products, but often further reactions occur, especially on heating the reaction mixture. For example, the acid reacts with ethanol giving ethyl trifluoromethanesulphonate as the major product and, diethyl ether, ethylene, and a residue. Probably the residue is a polymer of ethylene, since ethylene itself reacts with triflic acid giving the ethyl trifluoromethanesulphonate and a low polymer of ethylene(8).

The reactions of triflic acid are dominated by its very strong acidity. Because of the strong electron - withdrawing effect of the CF_3SO_2 group, alkyl-oxygen fission is facilitated which makes the esters of triflic acid good alkylating agents.

Most of what is known about triflic acid, its derivatives and its reactions with organic compounds is presented in a series of papers by Haszeldine et al.(6,11).

The acid is normally made by the electrolytic method devised by Simons(12). One version of an electrolytic cell is given by Haszeldine et al.(9). Although the electrolytic method of preparing the acid is now the most common one, chemical synthetic methods have also been used, but with much more limited success, e.g.(9).

$$CS_2 \xrightarrow{IF_5} CF_3S_2CF_3 \xrightarrow[h\nu]{Hg} (CF_3S)_2\,Hg \xrightarrow{H_2O_2} CF_3SO_3H$$

and

$$\begin{tikzcd}
& CF_3SCl \arrow[dr, "H_2O_2"] & & \\
CF_3\,S_2\,CF_3 \arrow[ur, "Cl_2", "h\nu"'] \arrow[rr, "Cl_2 - H_2O", "h\nu"'] & & CF_3\,SO_2\,Cl \arrow[r] & CF_3\,SO_3\,H
\end{tikzcd}$$

Often it is most convenient to handle the acid as its barium salt. This liberates the free acid when treated with conc. H_2SO_4. The salt is made as follows(13):

$$CH_3SO_2Cl \xrightarrow[\text{fluorination}]{\text{electrochemical}} CF_3SO_2F \xrightarrow[H_2O]{Ba(OH)_2} (CF_3SO_3)_2Ba$$

Although the barium salt is hygroscopic, it can readily be dehydrated at 100° under vacuum, m.p. > 370°.

We were fortunate in receiving some barium triflate as a gift(14). The vacuum line set-up for preparing the free acid from this is shown in Chapter II,1,b,ii. Furthermore, we received a gift of the free acid(15), which was distilled into phials by the same vacuum line arrangement. Once the phials of pure acid had been made, they needed to be diluted for the contemplated polymerisation reactions.

In the process of making the appropriately dilute acid phials in CH_2Cl_2, it was found that triflic acid reacts with this solvent. Hence, I shall first describe the observations made on the interaction of the acid with CH_2Cl_2 before going into the results of the styrene polymerisations by triflic acid.

The Interaction of the Triflic Acid with CH_2Cl_2

The observations described below are mainly those made while diluting triflic acid derived from the barium salt. The visual observations made (mainly of colour) when diluting the free acid from 3M Co., were the same. However, no chemical tests were made on the phials of acid obtained from this latter source.

All the phials were made under high vacuum conditions.

I intended to make dilute acid phials of approximately 0.3M. These phials will be referred to as of first generation (G-1), Table IV,1.

When a phial of pure triflic acid was crushed into CH_2Cl_2, the acid dissolved immediately. The solution was clear. After 15-20 seconds the solution developed a light yellow colour. The intensity of the yellow colour increased rapidly and after about 1 minute the colour of the solution was deep orange, though it was still transparent enough to see that there was no separation of phases. However, upon cooling the phials with liquid nitrogen, some minute orange (?) crystals appeared. While warming the phials again, two liquid phases were visible: a small quantity (approximately equivalent to the quantity of triflic acid used) of deep orange mobile liquid was on the bottom of the container, and the upper layer (mostly CH_2Cl_2) was orange but less intensely so than at room temperature. The temperature of the mixture must have been below 0°, since at ice-water temperature no separation of phases occurred.

Table IV,1

Preparation of CF_3SO_3H/CH_2Cl_2 phials

Generation of phials	$[CF_3SO_3H]$ (10^2M)	Description
G-1	36	first dilution of acid from barium salt
G-2	36	colourless distillate of G-1
G-3	2.98	dilution of G-2
G-4	0.26	dilution of G-3
g-1	1.85	first dilution of acid from 3M Co.

The reaction went on for about 1 hour, since during this time the orange colour became increasingly intense. After the solution had stood overnight at room temperature, it appeared dark brown and almost completely opaque. However, upon closer observation the colour appeared deep violet-yellow. The yellow tint seemed to be confirmed by the fact that the solution looked only violet when seen through glass-blowing spectacles. The contents of the phials of this generation were subjected to the following tests:

Upon crushing a phial into distilled water its contents fumed heavily, and the deep violet colour disappeared immediately.

Since the triflic acid had been distilled out of sulphuric acid, a phial was tested ($BaCl_2$) for sulphate ions. There was no barium sulphate visible, i.e. no cloudiness in the solution.

A test for fluoride ions (with freshly prepared Alizarin-Zirconium reagent) was negative.

Two tests for chloride ions were made: one was made with $AgNO_3$ directly with the water-G-1 phial solution. This test was negative. Another G-1 phial was taken and the colourless liquid phase was distilled off into a new phial. Since this type of distillation was carried out with several of the G-1 phials, the resulting colourless phials will be regarded as of second generation, i.e. G-2. Upon exposing the deep violet residue (left behind during the above distillation) to air, the colour changed within five minutes to yellow. This yellow residue, which was 0.50% of the weight of the content of the G-1 phial, was subjected to a Lassaigne test. The Na_2S which results in the sodium fusion was removed by boiling the 'fusion' solution with dilute sulphuric acid. The subsequent chloride test (Ag NO_3) was negative. Furthermore, the yellow solid residue was found to crystallize into small bar-like structures. The melting point ranged between 100° to above 360°.

In order to ascertain the acid concentration of the G-1 and G-2 phials, two of the G-1 and one of the G-2 phials were titrated by crushing the phial into excess NaOH and back titrating it with HCl. The concentration of all three phials were within 2% of the concentration calculated on the basis of the amount of triflic acid and CH_2Cl_2 used for making the G-1 phials.

After five days in the refrigerator (0°) the G-2 phials turned light yellow. Dilution of a G-2 phial gave seemingly colourless G-3 phials which, however, after two days in the refrigerator, also turned very light yellow. G-4 phials seemed to remain colourless even after four months in the refrigerator.

The first and only dilution made with pure triflic acid from 3M Co., (g-1) was made keeping the solution temperature as low as practical. The resulting light yellow solutions were kept in a dry-ice box. After one day the yellow colour became more intense. After one month the colour was deep yellow, and apparently remained at the same intensity for the next one month. The phials were then kept at room temperature for two months (to date) during which time their colour turned very light violet.

The phials G-2, G-3, and g-1, which at a temperature below 0° were yellow, turned violet at room temperature. Lowering the temperature to 0° reverted the colour to yellow. The violet colour at room temperature always appeared less intense than the yellow colour at 0°. Figure IV,1 shows the absorption spectrum of a diluted (in CH_2Cl_2) G-1 phial at room temperature.

From the above findings it is clear that triflic acid, when mixed with methylene chloride, reacts with something giving two (?) products which are in equilibrium with each other. It is not clear whether the reaction is with the methylene chloride itself or with some impurity. Judging from the fairly large amount of material left behind, when distilling off the volatile fraction of a G-1 phial, I doubt that the reaction is with an impurity. A plausible reaction of the triflic acid with CH_2Cl_2 is

$$CF_3SO_3H + CH_2Cl_2 \longrightarrow CF_3SO_3CH_2Cl + HCl$$

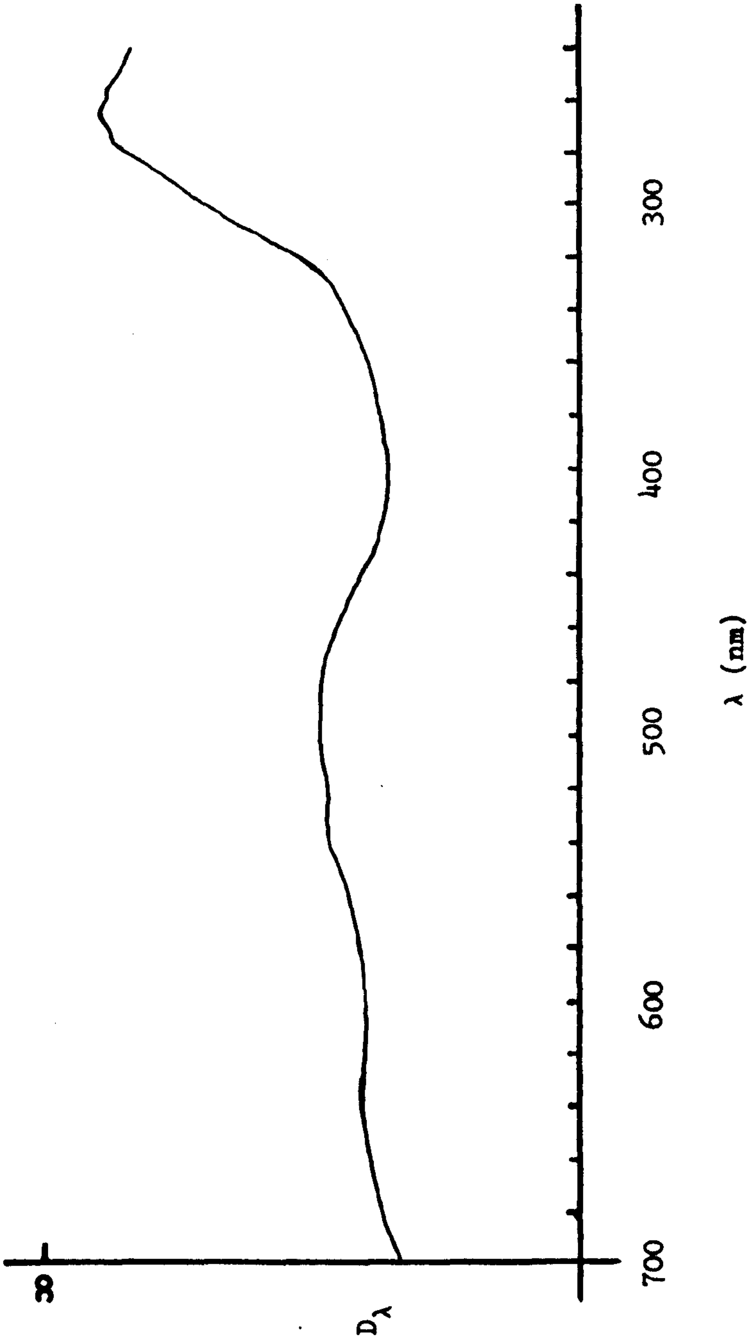
I doubt, however, that $CF_3SO_3CH_2Cl$ would be coloured.

It seems possible that the acid reacts with something in the glass. However, since the pure acid does not become coloured when left in Pyrex glass phials, the methylene chloride may be a necessary ingredient for the formation of the coloured products. Furthermore, since the G-2 phials turned coloured very much more slowly than the G-1 phials, and assuming that the triflic acid added to the G-1 phials is still triflic acid at the time the G-2 phials are made,

Fig. IV,1

The polymerisation of styrene by trifluoromethanesulphonic acid in CH_2Cl_2.

The spectrum of a diluted G-1 phial at room temperature.



a large surface area of new "unconditioned" glass (i.e. glass which has not been exposed previously to the triflic acid) may also be necessary. For the purpose of the distillations of the G-1 phials, the only new glass surface available for the acid to react with was that of the G-2 phial, so that the reaction to form the coloured products may be expected to be slow, and the colour less intense. The acid may possibly coordinate with a metal atom from the glass, forming a complex which is easily electronically excited. Because of the many unknowns about the triflic acid/methylene chloride system, I have been unable to trace the origin of the optical absorptions shown in Fig. IV,1.

Since the G-2 phials appear to have the same amount of titratable acid as the G-1 phials, the acid does not seem to be consumed or inactivated. However, an agreement within 2% between the titrated phials, is too large a discrepancy to make a confident decision as to the possible amount of triflic acid consumed while reacting in the G-1 phials.

Since the major purpose in choosing to work with triflic acid was to learn if and how this acid polymerises styrene, several reactions were carried out in the adiabatic calorimeter. While carrying out these reactions it became apparent that the reason for the somewhat irreproducible nature of the polymerisation was the reaction which the triflic acid undergoes while being stored in the methylene chloride.

The polymerisation reactions

The conditions of the experiments are listed in Table IV,2. The experiment EMs 44 was carried out with a dark violet G-1 phial (see preceeding section for coding of the phials). The polymerisation was very fast and, according to the reaction trace (Fig. IV,2), it went to completion in about 1-2 seconds. The experimental conditions of this experiment were repeated in EMs 45, taking a freshly distilled G-2 phial. Also this polymerisation was very fast, apparently as fast as EMs 44. Both these reactions were too fast for a kinetic analysis. The conductance of both experiments rose sharply when the acid was added to the styrene/CH_2Cl_2 solution. The reacting solution was yellow at all times. All the other experiments listed in Table IV,2, were done using G-3, and g-1 phials.

The shape of the reaction trace given by the polymerisation of the first portion of styrene in experiment EMs 47 (Fig. IV,3), is typical of all the reactions at 0^o. Also, the conductance trace of this experiment is typical for this reaction temperature. Addition of the acid to the styrene/CH_2Cl_2 solution gave a yellow flash. This flash was accompanied by a sudden increase of the conductance, which continued increasing even after the polymerisation was over. Often the sudden sharp increase in conductance resulted in a peak, the intensity of which is tabulated in Table IV,2, as K_{max}.

Table IV.2

Polymerisation of styrene by CF_3SO_3H in CH_2Cl_2*

EMs	$[C_8H_8]$ (M)	$[CF_3SO_3H]$ (10^4M)	Generation of phial	k' (10^2sec^{-1})	k'/$[CF_3SO_3H]$ (10^{-2}M^{-1}sec^{-1})	K_{max} (10^7mho-cm^{-1})	yield (time) (%) (min.)	DP
Experiments at 0°								
44	0.130	39.4	G-1	-	-	-	100 (3)	13.6
45	0.130	39.4	G-2	-	-	30.2	100 (3)	18.6
46	0.130	2.70	G-3	7.2	2.66	0.82	100 (6)	19.6
47+	0.066	2.70	G-3	12.2	4.52	-	100 (3)	12.6
48	0.034	2.70	G-3	12.8	4.74	2.14	100 (8)	15.0
54	0.131	1.73	g-1	1.18	0.68	0.19	86 (10)	8.7
Experiment at -30°								
49	0.122	3.10	g-1	15.3	4.94	2.40	100 (3)	24.7
Experiment at -60°								
50	0.120	2.97	G-3	1.5	0.50	4.02	100 (5)	20.1
53	0.121	2.97	G-3	3.9	1.31	3.26	100 (3)	29.6
57	0.120	2.80	G-3	8.0	2.87	3.52	100 (1)	18.9
Experiment at -90°								
51	0.118	3.29	G-3	-	-	-	100 (4)	27.6
52	0.121	3.29	g-1	0.6	0.18	0.10	100 (4)	36.4

*The acid was added to the styrene/CH_2Cl_2 solution.

+Second styrene addition experiment. The second addition of styrene represented a $[C_8H_8]$ = 0.042M. The k' is that for the first polymerisation. The yield and DP are based on the total monomer used.

Fig. IV,2

The polymerisation of styrene by triflic acid in CH_2Cl_2 at 0°. The reaction and conductivity trace of experiment EMs 44.

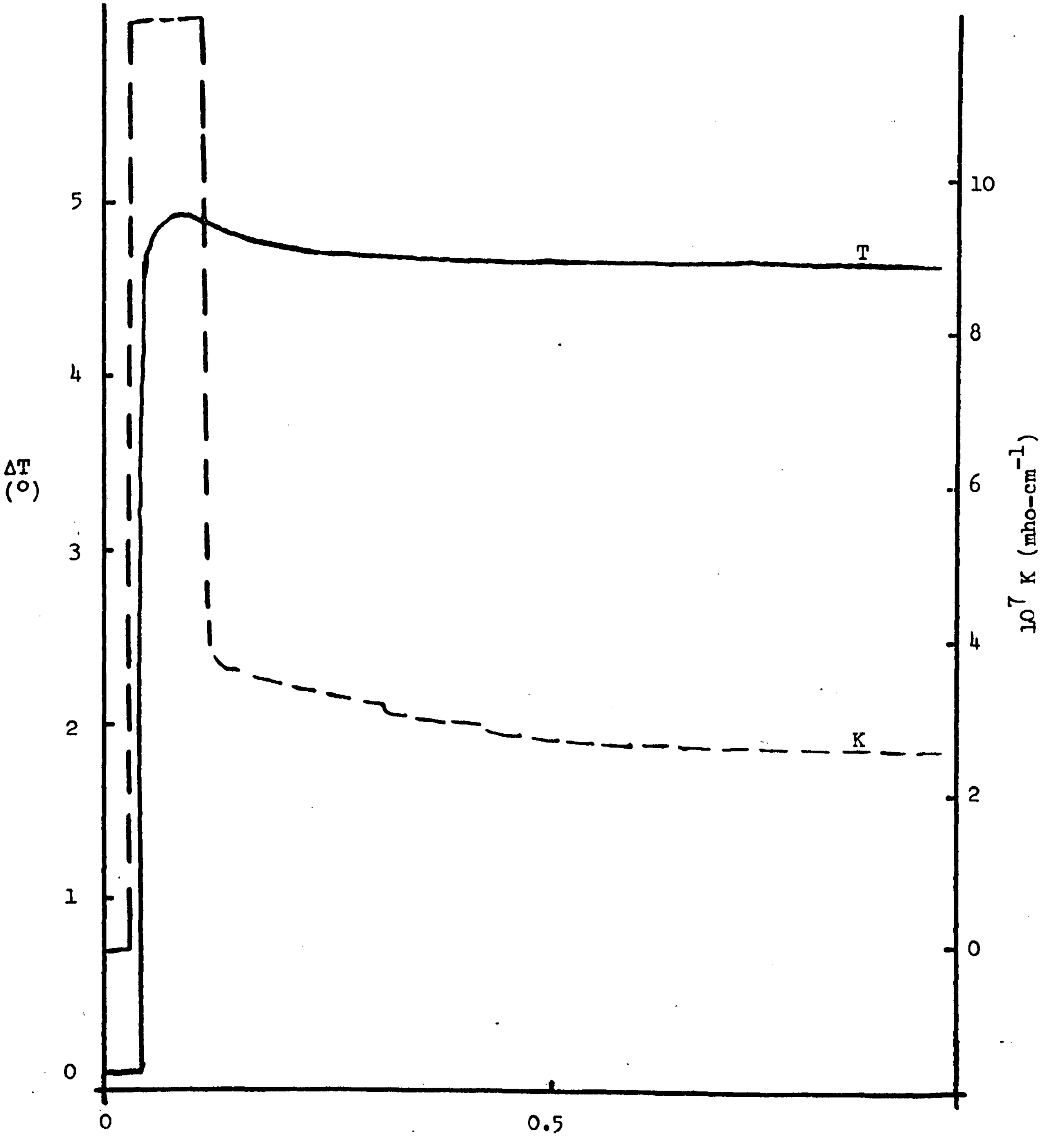
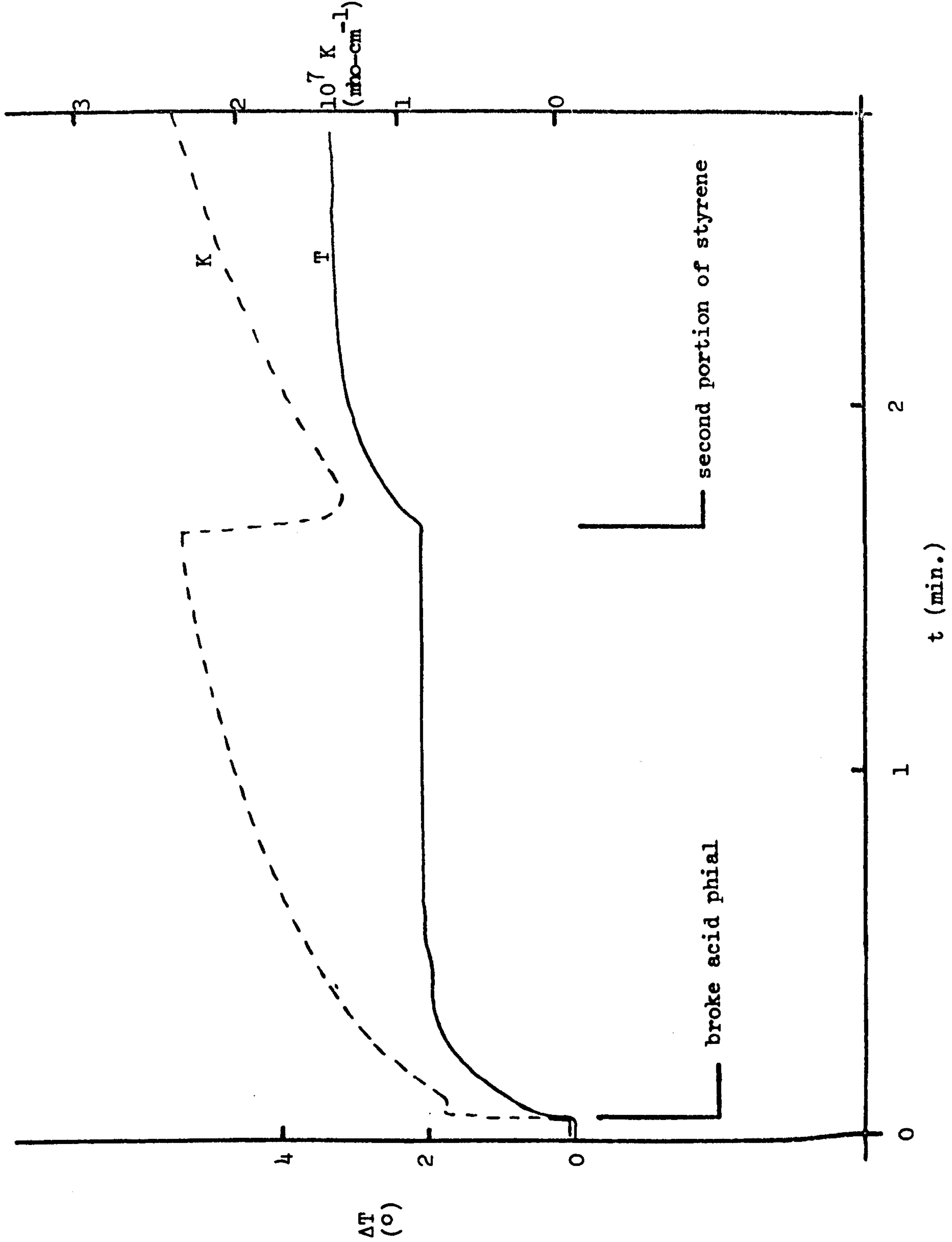


Fig. IV,3

The polymerisation of styrene by triflic acid in CH_2Cl_2 at 0°.

Typical reaction and conductivity trace (first temperature rise) and the trace of a second-addition experiment (second temperature rise).



Except for the experiment EMs 54, the polymerising solution was always slightly yellow, and the intensity of this colour increased as the reaction trace approached its asymptotic end.

Addition of the second portion of styrene in experiment EMs 47 resulted in a polymerisation accompanied by a slight decrease of the conductance (Fig. IV,3). The yellow colouration of the solution, before the second addition of styrene, decreased considerably in intensity as the second polymerisation proceeded.

Whenever possible, first-order plots (log $[M]_t$ vs. t) were made from the reaction traces. The k's listed in Table IV,2 are derived from the slopes of the initial straight lines given by the first-order plots. The degree of linearity of these plots varied with reaction conditions. This is best seen from the reactions carried out at 0°, Fig. IV,4 and Fig. IV,5. The slope of the line given by the second polymerisation of styrene in experiment EMs 47 gives $k' = 7.68 \times 10^{-2}\ \text{sec}^{-1}$.

The polymerising solutions at -30° and -60° showed the same colour features as those at 0°. For -90°, the calorimeter had to be immersed deeply into the liquid nitrogen Dewar, and since under these conditions the calorimeter becomes extensively covered with frozen moisture from the air, I could not observe the colour of the reacting solutions.

The reaction trace of EMs 49 is shown in Fig. IV,6. Its corresponding first-order plot is shown in Fig. IV,7.

Fig. IV,4

The polymerisation of styrene by triflic acid in CH_2Cl_2 at 0°. Typical first-order plots.

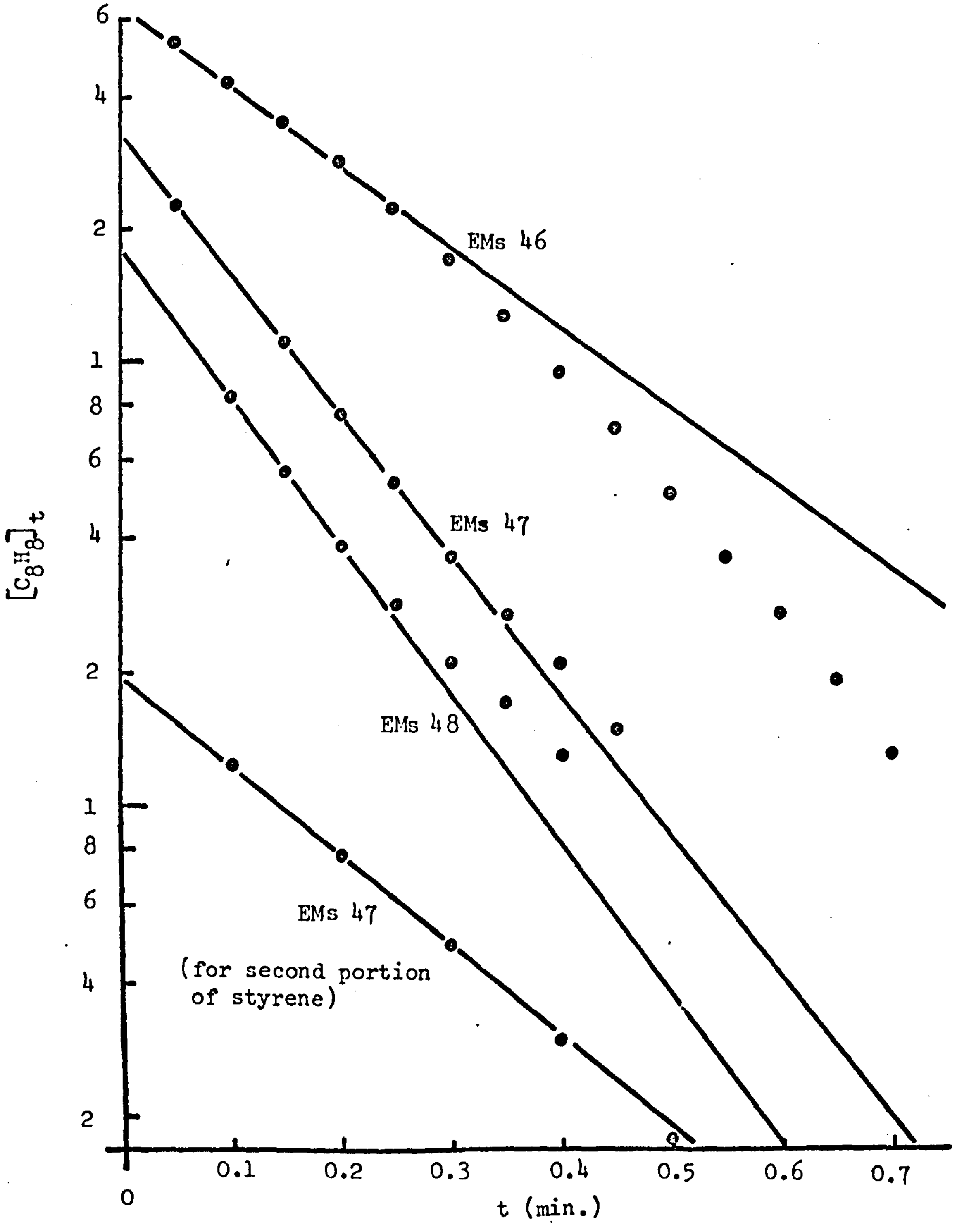


Fig. IV,5

The polymerisation of styrene by triflic acid in CH_2Cl_2 at 0°.

The first-order plot of experiment EMs 54.

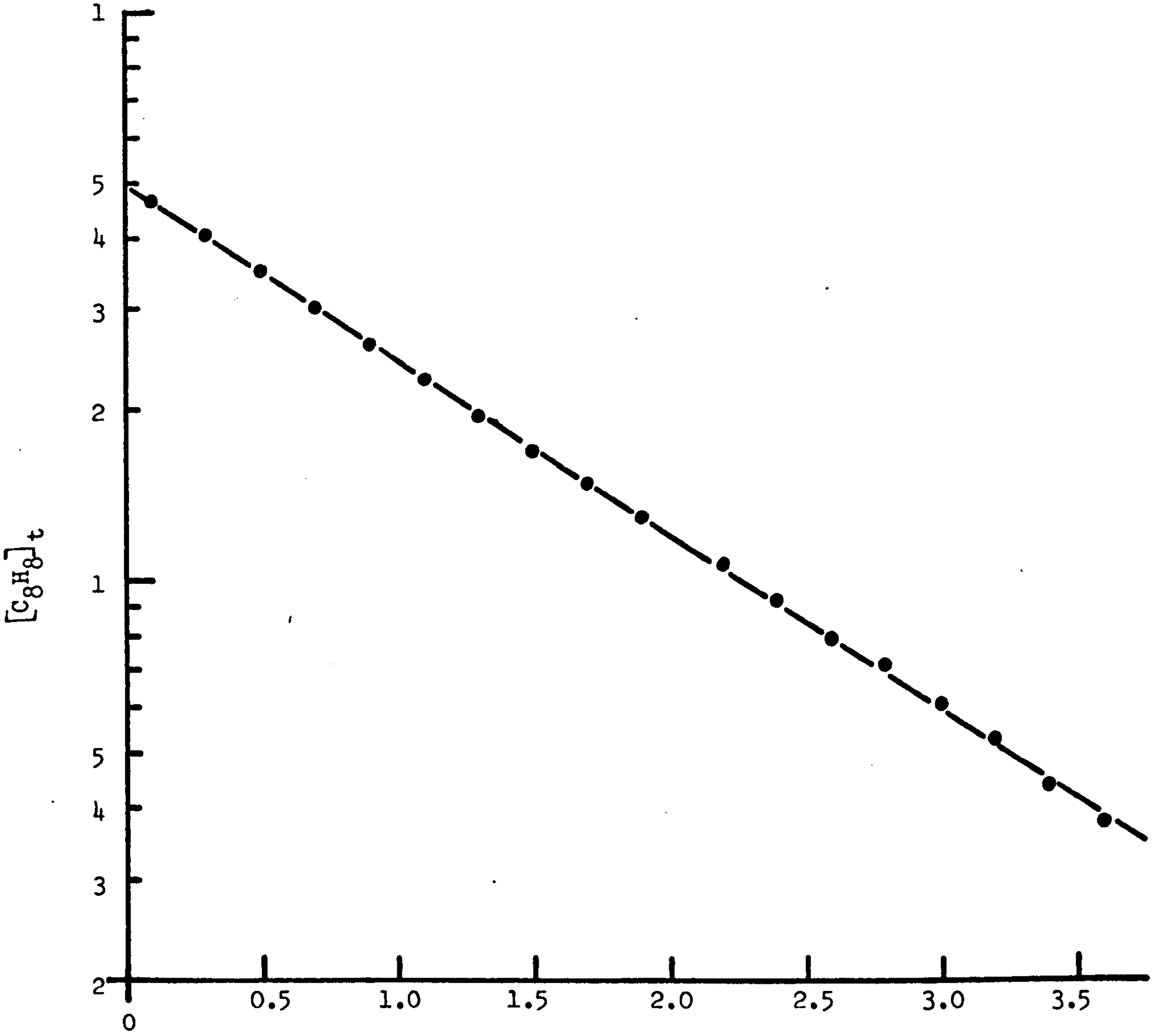


Fig. IV,6

The polymerisation of styrene by triflic acid in CH_2Cl_2 at -30°.

The reaction and conductivity trace of experiment EMs 49.

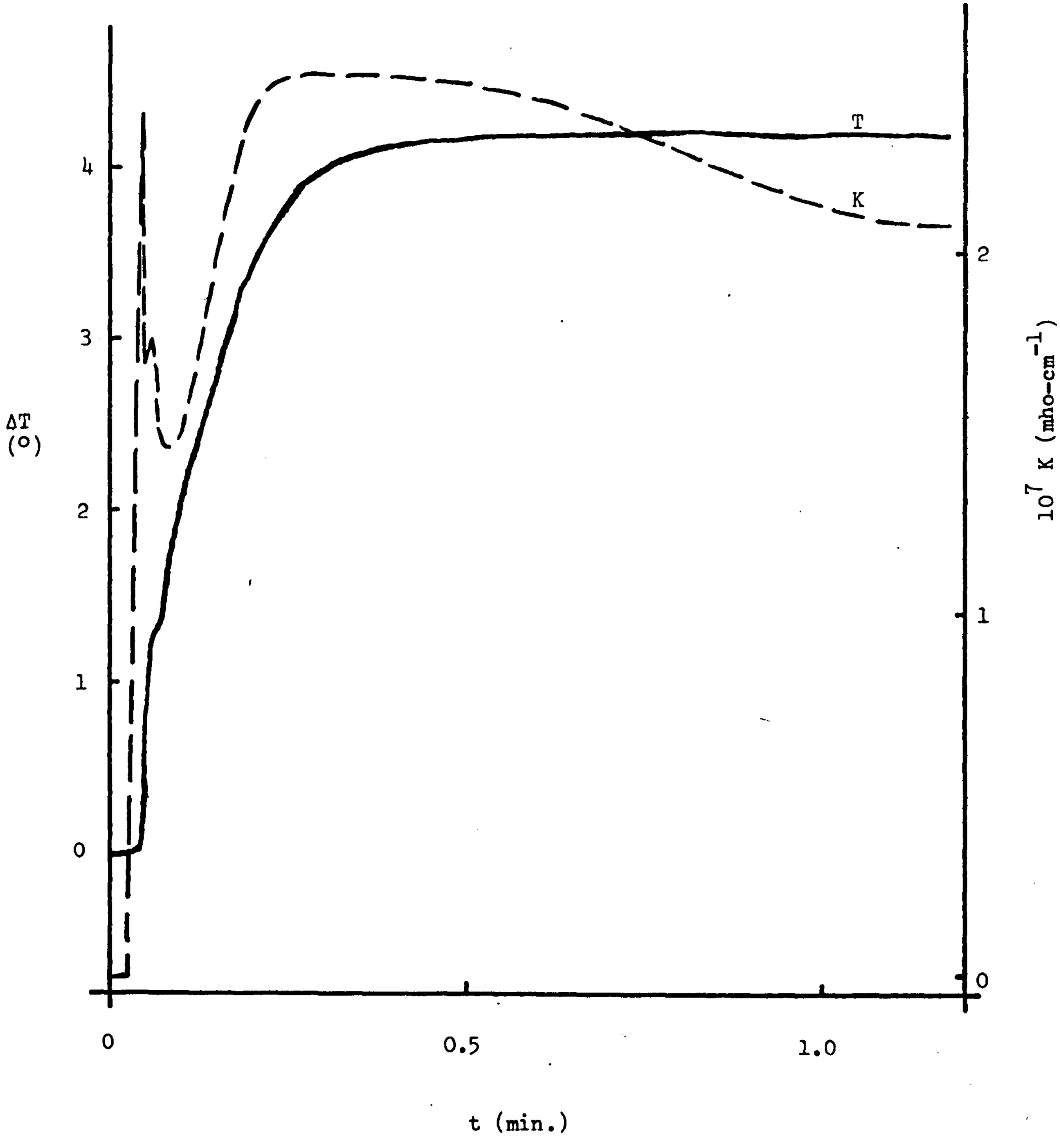
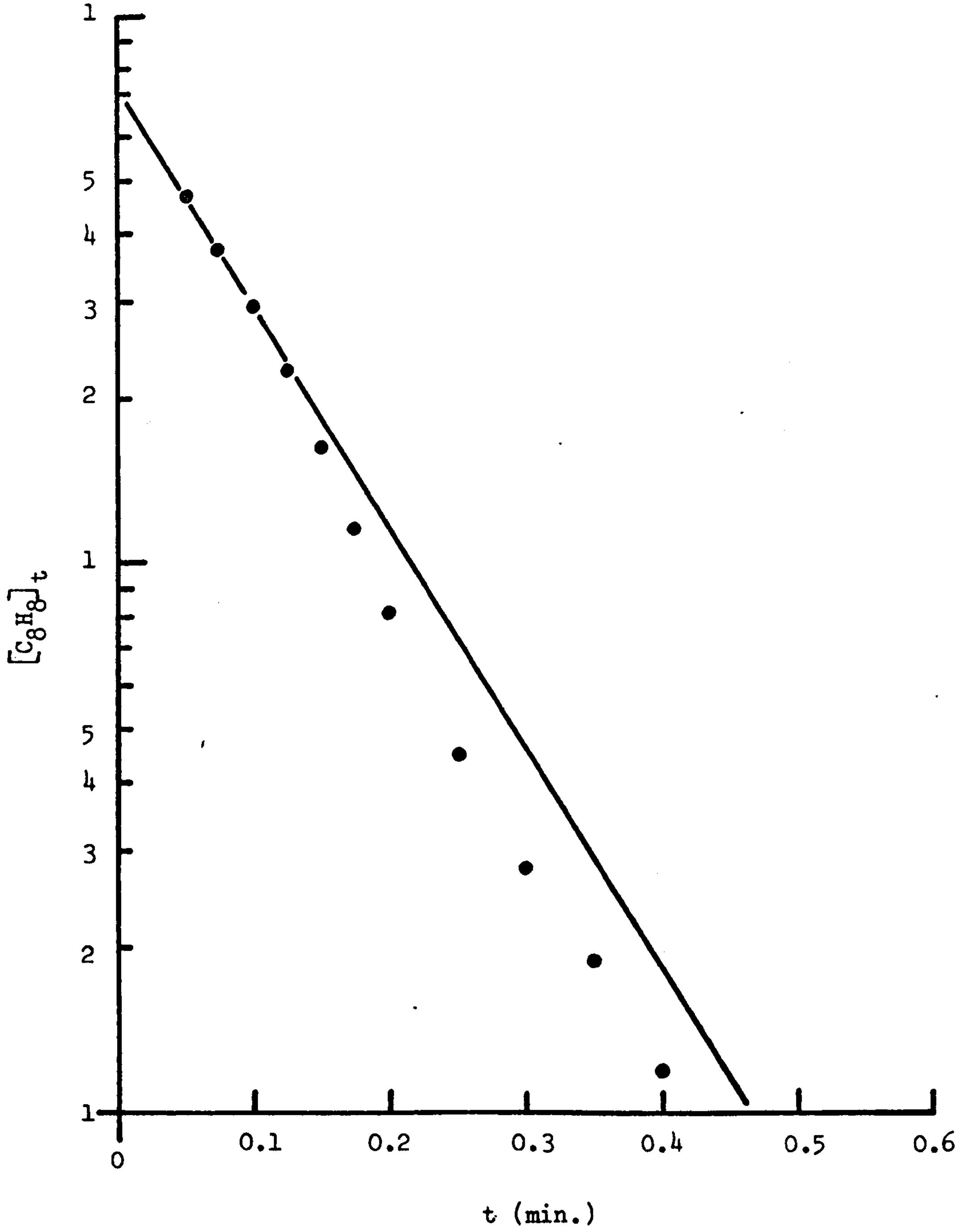


Fig. IV,7

The polymerisation of styrene by triflic acid in CH_2Cl_2 at -30°. The first-order plot for experiment EMs 49.



The reaction traces of the experiment at -60° are shown in Fig. IV,8. Since the experimental conditions of these experiments are nearly identical to each other, their reaction traces show the best example of the effect of "ageing" of the acid phials. The age of the acid phials for the experiments EMs 50, 53, and 57 were 7, 20, and 40 days respectively. The first-order plots for these experiments are shown in Fig. IV,9.

The reaction trace and the first-order plot of EMs 52 are shown in Fig. IV,10 and Fig. IV,11 respectively.

The infra-red spectra of the polymers made with triflic acid were identical to those made with perchloric acid.

In view of the instability of the acid/CH_2Cl_2 solutions, and the complexity of the polymerisations catalysed by these solutions, no further work was done with the triflic acid.

Discussion

Unfortunately, the results of the polymerisations are not consistent enough for us to be able to reach a definite conclusion as to their similarity to the polymerisations catalysed by $HClO_4$. In fact, it is not clear what actually catalyses the polymerisations. Apparently the inconsistencies in the rates of polymerisation are governed by the instability of the acid in the CH_2Cl_2. It seems, however, that some comparisons can be made with the polymerisations catalysed by $HClO_4$ at 0°.

Fig. IV,8

The polymerisation of styrene by triflic acid in CH_2Cl_2 at -60°. The reaction and conductivity traces.

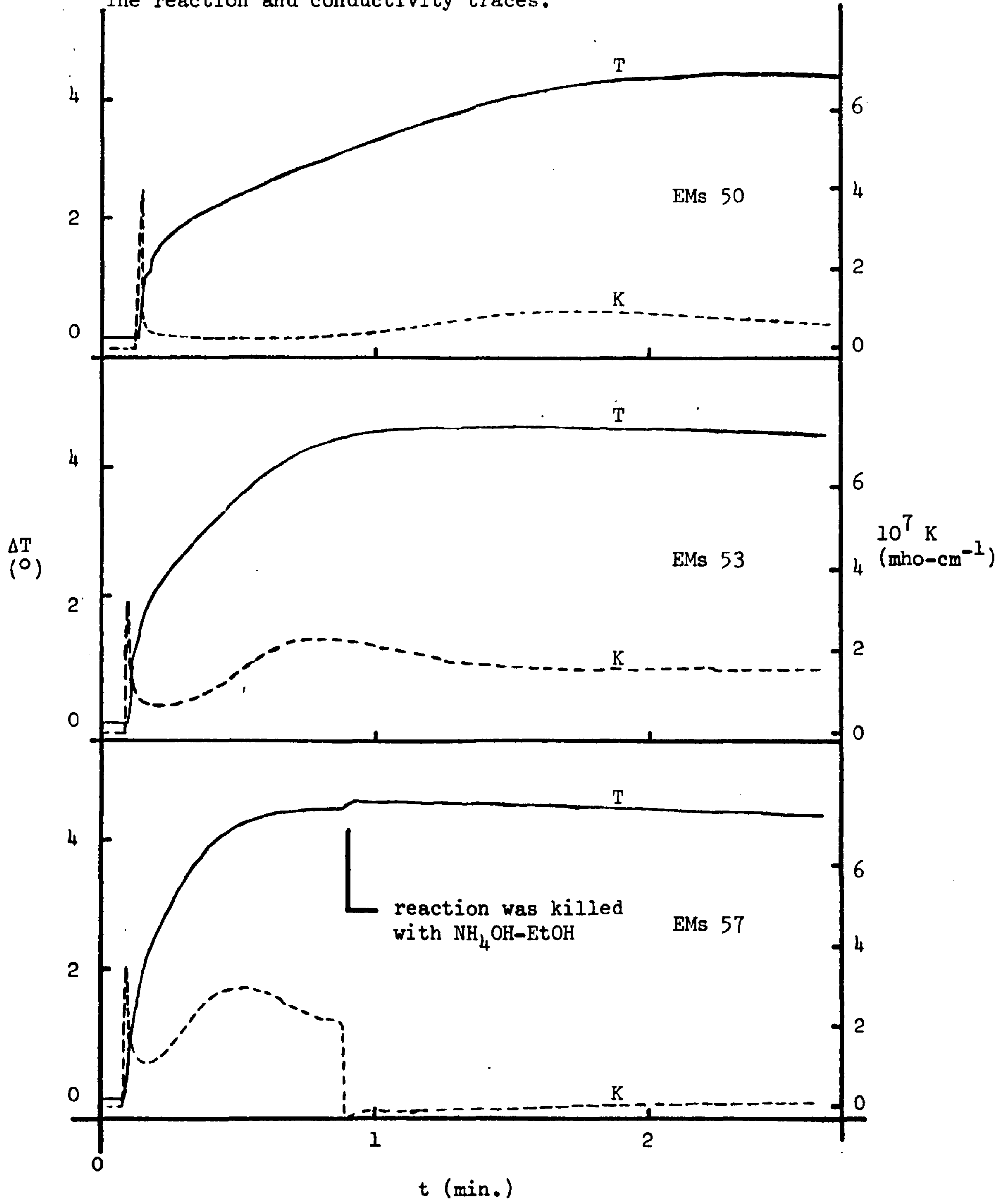


Fig. IV,9

The polymerisation of styrene by triflic acid in CH_2Cl_2 at -60°.

First-order plots

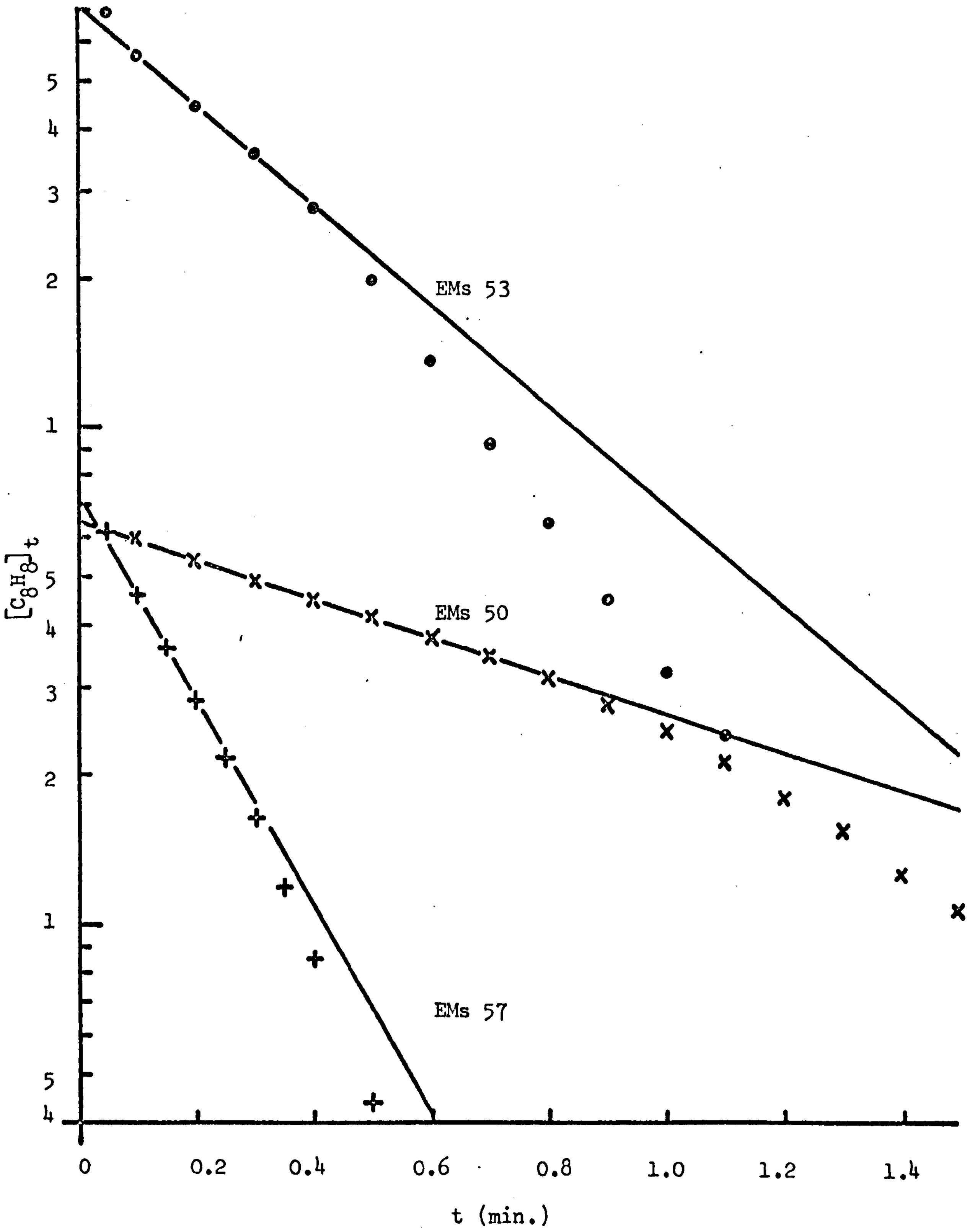


Fig. IV,10

The polymerisation of styrene by triflic acid in CH_2Cl_2 at -90°.

The reaction and conductivity trace of experiment EMs 52.

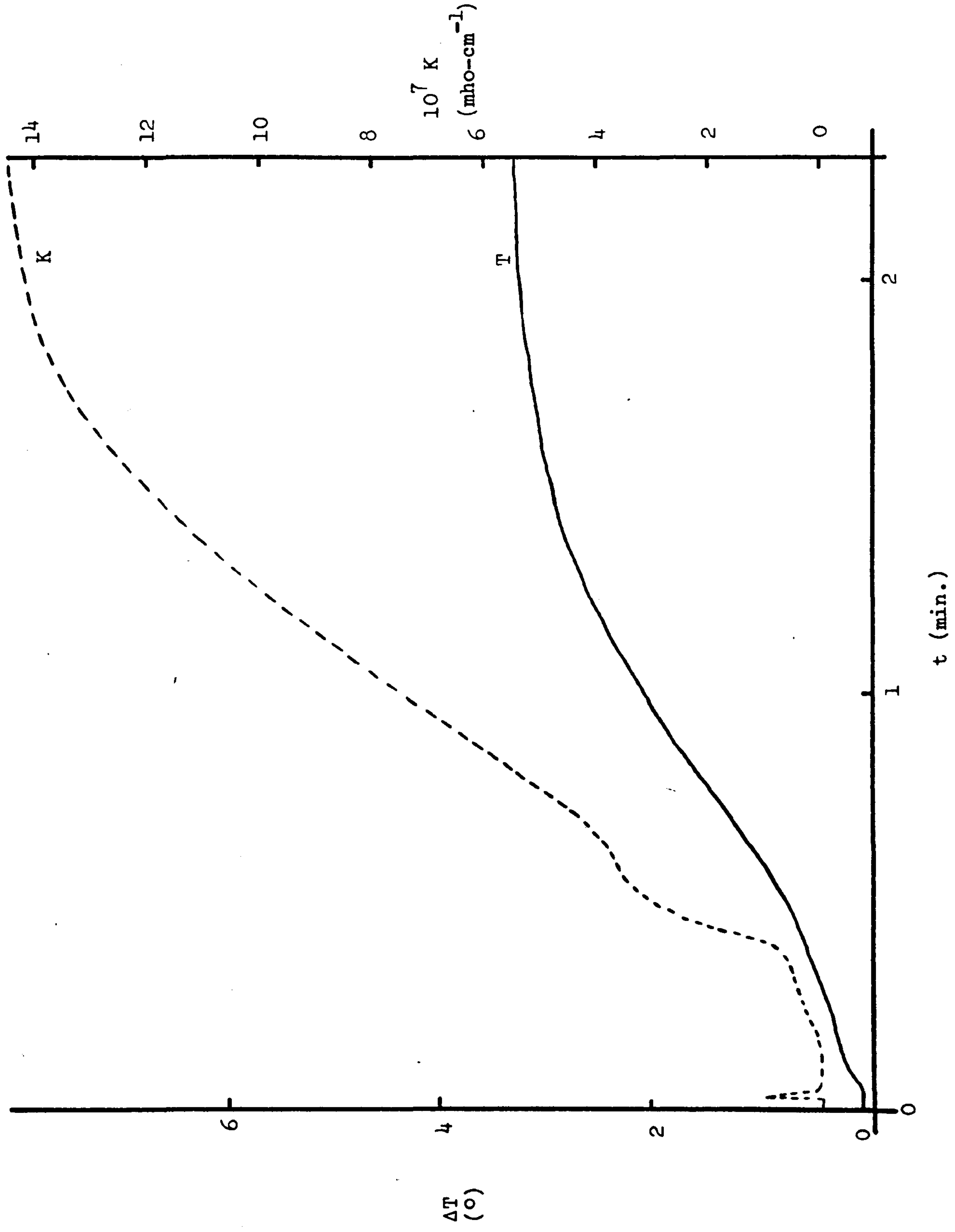
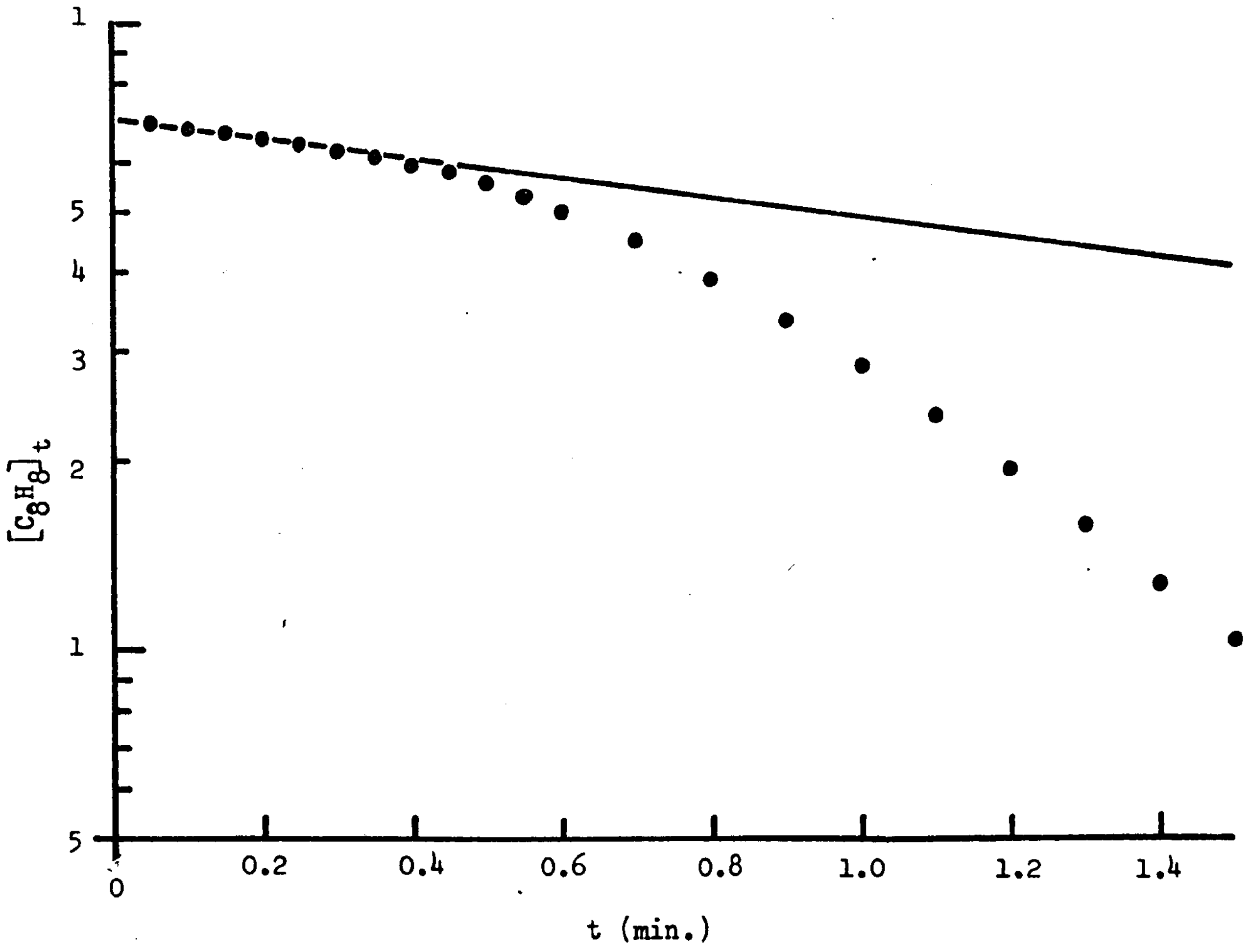


Fig. IV,11

The polymerisation of styrene by triflic acid in CH_2Cl_2 at -90°.
The first-order plot of experiment EMs 52.



The conductances measured during the polymerisations are overall higher than the conductance during the polymerisations with $HClO_4$. Whether or not this conductance has anything to do with the propagating species is not known. Certainly not all of the conductance could be due to polystyryl ions since if it were, the polymerisation would have been over in fractions of a second. Since the conductance was accompanied by the appearance of a yellow colour in the reaction solution, probably most of the conductance is due to the appearance of indanyl ions. This impression may be significant since, if correct, it would mean that, like in the polymerisations catalysed by $HClO_4$, the indanyl ions can be formed during the polymerisation even though there is no excess of acid in the system.

Although the polymerisations go to completion, some of the catalyst seems to become inactivated. This seems to be indicated by the fact that the k' for the polymerisation of the first portion of styrene in experiment EMs 47 is about 1.6 times higher than the k' for the polymerisation of the second portion of styrene. However, since we don't know exactly how much of the initial triflic acid actually participates in the polymerisation, the comparison between the k's may not be a fair one.

The reactions at -60° are mainly interesting in that they show the effect of "ageing" of the catalyst phials: The older the phials, the deeper the intensity of their yellow colour, and the faster the polymerisations which they catalyse. From these observations it almost seems as if the component which is responsible for the yellow colour of the phials is also at least partly responsible for catalysing the polymerisation. The reaction at -90°, however, seems to indicate that the more intense the yellow colour of the catalyst phials (by lowering the temperature from -60° to -90°) the slower the polymerisation. The trace of the reaction at -90° looks somewhat surprising. Contrary to the polymerisations catalysed by $HClO_4$, there is no initial flash-type polymerisation. Since at this temperature the acid solution in the phial was also yellow (as they are at -60°) it seems as if the component in the phial which is responsible for the yellow colour may act as a much weaker acid than one would have expected of pure triflic acid. This does not necessarily contradict the findings at -60°: We know that the intensity of the yellow colour of the acid in the phials increases with time, and with decreasing temperature. At room temperature the phials are violet. Hence, it seems that the experiments at -60° show the effect of time on the absolute concentrations of the yellow and violet components in the phials, whereas the experiment at -90° seems to show that as we decrease the reaction temperature there is a higher concentration of the yellow component, at the expense of the violet one. This argument suggests also that, if the slower reaction at -90° is not just due to a temperature effect on the kinetics of the polymerisation, the violet component in the catalyst phial is a stronger acid than the yellow one. Unfortunately, a test of the above argument really would require that an experiment similar to EMs 52 (at -90°) be made at the same time as an experiment at -60°, for instance a repeat of EMs 53. The experiment EMs 53 was carried out five days after EMs 52, so that a direct comparison between the rate-constants is not meaningful.

The strange behaviour of the conductance traces at -60° also shows a trend with "ageing" of the phials. It looks as if during the polymerisation there is a continuous change in some equilibrium which seems to have something to do with the rate of polymerisation. It could be a change associated with the equilibrium between the yellow and violet components present in the acid phials, and maybe both components can initiate polymerisation.

If, as shown previously, triflic acid reacts with CH_2Cl_2, the polymerisation may also be catalysed by the HCl formed. As mentioned in the introduction of this thesis, HCl has been used to polymerise styrene and was found to give irreproducible results(16).

The molecular weights of the polymers made at 0° (Table IV,2) are slightly lower than those of polymers made by $HClO_4$; for $[C_8H_8] = 0.35M$ and $[HClO_4]_o = 2.6 \times 10^{-4}$ M, DP ≈ 20. Since, according to Pepper et al.(17), the DP of polymers made by $HClO_4$ is almost independent of the initial acid concentration, the difference in the DP's above may arise from the difference of the initial monomer concentrations. The polymers made with H_2SO_4 in 1,2-dichloroethane(18) ($[H_2SO_4]_o$ not given, but assumed constant) at 0° have a DP$\approx$22 which increases as $[C_8H_8]_o$ increases. Furthermore, the DP of these polymers, as well as the DP of polymers made by $HClO_4$, are increased considerably by decreasing the reaction temperature. The molecular weights of the polymers made by triflic acid, however, are not increased markedly by decreasing the reaction temperature. Hence, it seems that the molecular weight of these polymers, like that of the polymers made by $HClO_4$ and H_2SO_4, is also determined by transfer processes, but these have lower activation energies.

The irreproducibility of the DP's listed in Table IV,2 is most probably related to the instability of the triflic acid in CH_2Cl_2.

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