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THE CATIONIC POLYMERIZATION
OF KETENE ACETALS

by

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The work described in this thesis was carried out by the Author under the supervision of Dr. P. H. Plesch. Some of the experimental work in Chapter 3, was carried out by Dr. G. R. Cliff, under the supervision of the Author, and this is indicated in the text.

ABSTRACT

This work has been divided into two sections:

SECTION A (Chapters 1-5)

This section is concerned with the preparation and cationic polymerization of various ketene acetals $CH_2:C(OR^1)OR^2$. Four ketene acetals have been synthesized (two of which are new compounds) and their polymerizability has been investigated under homogeneous and heterogeneous conditions, in bulk and in solution, between ca. +50° and -100°. The monomers studied comprise (KA1) $R^1=R^2 = C_2H_4OMe$; (KA2) $R^1=R^2= Et$; (KA3) $R^1=Me$, $R^2=Et$; (KA4) $R^1=Et$, $R^2=i\text{-}Pr$.

Most of the reaction products formed in solution were viscous pale yellow fluids or sticky red solids; whereas those formed in bulk with solid, sparsely soluble initiators were white waxes or powders. For all systems for which solubility of product permitted DP determinations, the highest DPs (ca. 20) were found from bulk polymerization with solid $CdCl_2$. With a wide range of soluble initiators in different solvents over a wide range of concentrations DPs greater than about 8 were exceptional.

It is suggested that there are at least four chain-breaking reactions involving the growing dialkoxycarbenium ion $\sim CH_2.\overset{+}{C}(OR)_2$ and evidence is presented which accounts for the high rate of chain-breaking compared with that of other olefinic monomers.

SECTION B (Chapters 6-8)

This section is concerned with the properties of poly-ketene acetals.

Acid hydrolysis of the polymers yields the corresponding poly-1,3-diketones, $(-CH_2CO-)_n$ and various derivatives of both the keto and enol forms of these have been prepared.

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SECTION A: THE POLYMERIZATION OF KETENE ACETALS

SECTION B: PROPERTIES OF THE POLYMERS

Symbols and abbreviations used in this Thesis

m_o - initial concentration of monomer

m_∞ - final concentration of monomer

m - concentration of monomer

c_o - concentration of nominal initiator

$[P_n^+]$ - concentration of active species

c - concentration of true initiator

$[S]$ - concentration of solvent

$[A]$ - concentration of co-initiator

V_p - rate of propagation

V_b - rate of chain-breaking

k_p - rate-constant of propagation

k_m - rate-constant of transfer with monomer

k_c - rate-constant of chain-breaking by initiator*

k_a - rate-constant of chain-breaking by co-initiator

J - rate of unidentified chain-breaking reactions

k_1 - first-order rate-constant

k_2 - second-order rate-constant

E_m - activation energy for transfer with monomer

E_p - activation energy for propagation

PPY - percentage by weight of the product which was insoluble in pentane

Conversion - $100\ (m_o - m_\infty)/m_o$

M_n - number-average molecular weight

DP - number-average degree of polymerization. Except where indicated in the text the DP values refer to the polymer insoluble in pentane

I.P. - induction period

A^- - anion

MtX_{n+1}^- - complex anion derived from metal halide MtX_n

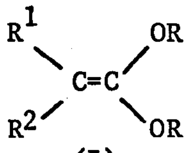
* or by a species whose concentration is proportional to that of the initiator.

SECTION A: THE POLYMERIZATION OF KETENE ACETALS

CHAPTER 1: INTRODUCTION

1.1 Ketene Acetals

Ketene acetals are 1,1-dialkoxy-substituted olefins having the general structure I:



(I)

The name "ketene acetal" is derived from the fact that they bear the same structural relationship to the ketenes that acetals and ketals bear to aldehydes and ketones.

The preparation, properties and reactions of ketene acetals were reviewed comprehensively in 1949 by McElvain.[1] More recently, this class of compounds has been reviewed by Owen[2] (1954), by Oda and Tamai[3] (1961) and by Swetkin[4] (1970)

1.2 Polymerization

The first workers to report that ketene acetals could be polymerized were Beyerstedt and McElvain[5] in 1936. During distillation of ketene diethyl acetal the polymer appeared as a thin white deposit on the walls of the apparatus, and was also observed as a semi-solid gum that separated from distilled samples after a few days. These authors thought that heat caused the polymerization, but it was later shown[15] that the monomer could be heated at 190-240° for six hours in new Pyrex tubes without any perceptible polymerization. It was concluded,[15] that the polymeriztion observed by Beyerstedt and McElvain was caused by the acidity of the glass surfaces of their apparatus. Indeed, if the interior of the apparatus was washed with an aqueous alkali solution (after the use of a chromic acid-sulphuric acid cleaning mixture), the formation of polymer during the distillation of ketene acetal was scarcely noticeable.

In addition to its inability to polymerize thermally, ketene diethyl acetal was found to be stable to sunlight, and to benzoyl peroxide,[15] thus showing its reluctance to be polymerized via a free radical mechanism. Initiators of the cationic type which were found to polymerize ketene diethyl acetal were "in order of increasing effectiveness"[15] the chlorides of nickel, cobalt, cadmium, zinc, iron and aluminium. Presumably this order was derived from the time required to produce an immobile gel. McElvain et al[15] carried out additional experiments on the polymerization of ketene diethyl acetal by cadmium chloride. They found that the addition of 6 mg of cadmium chloride to 10g of the monomer gave a 55% conversion of monomer to polymer. It was assumed that the only chain-breaking reaction was by reaction with alcohol, leading exclusively to $(-OR)_3$ end groups. On this basis number average molecular weights were calculated by measurement of the amount of carbon dioxide evolved on the hydrolytic decarboxylation of the polymer and the values reported were in the range 2600-2700. The assumption of complete chain stopping by alcohol is erroneous, since reaction of a growing chain with a molecule of alcohol will probably be a transfer, not a termination reaction. This should therefore limit the molecular weight but not the conversion. Furthermore, the complete conversion of ketene diethyl acetal to polymeric material is possible if sufficiently pure materials are used. It seems likely that the low conversions reported by McElvain were due to residual moisture in the system killing the active centres, since no precautions were taken to exclude the atmosphere from the polymerizing mixtures. The absence of side reactions was indicated[15] by the presence of only two components.

in the system after polymerization, viz. polymer and monomer.

Lal[6] investigated the polymerization of ketene diethyl acetal and ketene di-n-butyl acetal with cadmium chloride at room temperature, in bulk and in heptane solution. Although the reactions were carried out in nitrogen-flushed bottles and the heptane was distilled off phosphorus pentoxide before use, no details of the drying of the monomers or the initiator are given. The polymerizations were allowed to proceed to "high" conversions. The bulk polymerization of ketene diethyl acetal (0.1% w/w of initiator to monomer) yielded a powdery polymer which was only soluble in σ-dichlorobenzene at 140°. When the monomer was polymerized in heptane solution a similar polymer was produced plus a small amount of a soluble oil. When ketene di-n-butyl acetal was polymerized in bulk and in heptane it yielded a powdery material which was soluble in pentane, chloroform and carbon tetrachloride; the reduced inherent viscosity in heptane was 5.2 dl $g.^{-1}$

An interesting paper describing the polymerization of ketene diethyl acetal with organic π-electron acceptors was published by Noguchi and Kambara.[7] These authors used highly purified materials under vacuum and polymerized ketene diethyl acetal with tetracyanoethylene and with 7,7,8,8-tetracyanoquinodimethane in toluene solution at -78°. No rates or conversions are cited, but the yields of polymer insoluble in methanol produced by reacting the monomer with 0.5 mole % of each initiator were 42.6% and 22.8% respectively. These authors determined what they call "molecular weights" of the polymers by the McElvain method,[15] with the assumption that one polymer molecule would produce one molecule of carbon dioxide when hydrolyzed. In view of their seemingly rigorous purification techniques and the advances which have been made in the understanding of chain-breaking reactions in ionic polymerizations during the twenty five years since McElvain's work was published, this facile assumption cannot be justified. Noguchi and Kambara also reported that ketene diethyl acetal can be polymerized readily with $CdCl_2.2.5H_2O$, $SnCl_4$, $EtAlCl_2$, and Et_3Al/H_2O giving pure white polymers; no further information is given. The above paper is of little value as a scientific document to the worker who is interested in the detailed chemistry and kinetics of ionic reactions. It may however, be useful in the field of organic synthesis. In this context it should be noted that sterically hindered non-polymerizable ketene acetals such as tetramethoxyethylene[8] and dimethyl ketene dimethyl acetal[4] give only cyclobutane derivatives when treated with tetracyanoethylene.

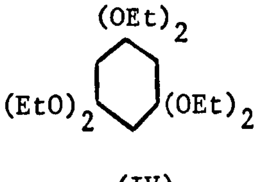
When bulk ketene diethyl acetal was treated with "large" amounts of $CdCl_2$[15] (26 mg initiator to 10g of monomer) the reaction was very vigorous and highly exothermic. The polymer so obtained was a soft gel from which small amounts of the linear dimer (II) and trimer (III), plus the cyclic trimer (IV) could be isolated.

$CH_3C(OEt)_2CH{:}C(OEt)_2$

(II)

$CH_3C(OEt)_2CH_2C(OEt)_2CH{:}C(OEt)_2$

(III)



(IV)

The yield of the cyclic trimer fraction could be materially increased by treating the monomer with hydrogen fluoride in dilute solution,[9] the optimium conditions being $m_o = 8.45 \times 10^{-2}$ M, $[HF] = 4.91 \times 10^{-3}$ M, in diethyl ether as solvent.

The bulk polymerizations of ketene di(2-methoxyethyl) acetal and of ketene di(3,4-dihydro-2H-pyran-2-methyl) acetal with cadmium chloride are reported in the patent literature.[11] No data on the kinetics or the chemistry of the polymerization process are presented.

Highly substituted ketene acetals have been reported as being unpolymerizable,[9,15] presumably for steric reasons. For example, chloroketene diethylacetal is recovered unchanged after being heated with $CdCl_2$ at 110° for 70 h. and dimethylketene diethylacetal can be distilled from aluminium chloride.

The results of polymerization studies are summarized in Table 1.

The polymerization of cyclic ketene acetals (2-methylene-1, 3-dioxolans) has been studied by several groups of workers[13,30] and has been found to be complicated by concurrent vinyl addition polymerization and ring opening.

1.3 Co-polymerization

Lal[6] co-polymerized an equimolar mixture of ketene diethyl acetal and ketene di-n-butyl acetal in heptane with $CdCl_2$ at room temperature. The author tentatively suggested, on the basis of solubility measurements and X-ray diffraction data, that there was sufficient evidence to point to the formation of a co-polymer.

The incorporation of small amounts of ketene diethyl acetal into a recipe for the cationic polymerization of isobutene has been reported by Brannen and Wuellner.[68] The one example cited in this patent comprises the bulk polymerization of a 10:1 mole ratio of isobutene to ketene diethyl acetal with BF_3 gas to about 20% conversion. By this procedure a co-polymer of molecular weight 8 x 10^4 is claimed to have been produced which is useful as a viscosity index improver in lubricating oils.

TABLE 1

The polymerization of ketene acetals

Monomer	Initiators	Temp. /deg	Polymerizability	Nature of Product	Ref.
Ketene diethyl acetal	Chloride of Ba,Hg,Ca,Ni,Co,Cd,Zn, Fe,Al	"Room"	+	Red, brown or white powder	6,15
	Tetracyanoethylene	-78	+	White powder	7
	7,7,8,8,-Tetracyanoquinodimethane	-78	+	Brown powder	7
	HF	"Room"	+	Liquid dimer and trimer	9
	$SnCl_4$,$EtAlCl_2$,$AlEt_3/H_2O$		+	White powder	7
Chloroketene acetals	Chloride of Cd,Co,Fe.	110	-		5,14
	$BF_3/BF_3.Et_2O$	"High"	?	Mobile red oil	15
Ketene di-n-butyl acetal	$CdCl_2$	"Room"	+	Fibrous, brittle solid	6
Ketene diphenyl acetal	HBr, benzoyl bromide	up to 150	+	"Brown viscous polymer"	33
Ketene di-(2-methoxyethyl) acetal	$CdCl_2$	"Room"	+	White solid	11
Dimethylketene dimethyl acetal	$AlCl_3$	195	-		14
Ketene di-(3,4,-dihydro-2H-pyran-2-methyl acetal)	$CdCl_2$	"Room"	+	Yellow wax	11

Kuryla[11] claimed to have produced a water-soluble co-polymer from the bulk co-polymerization of ketene di(2-methoxyethyl) acetal and ethyl vinyl ether with $CdCl_2$. It is however, difficult to envisage the structure as a co-polymer on the basis of the values quoted for the elemental analysis of the reaction product (Found: C, 52.48; H, 8.68. Calc. for the ketene acetal: C, 54.5; H, 9.16. Calc. for ethyl vinyl ether: C, 66.7; H, 11.1).

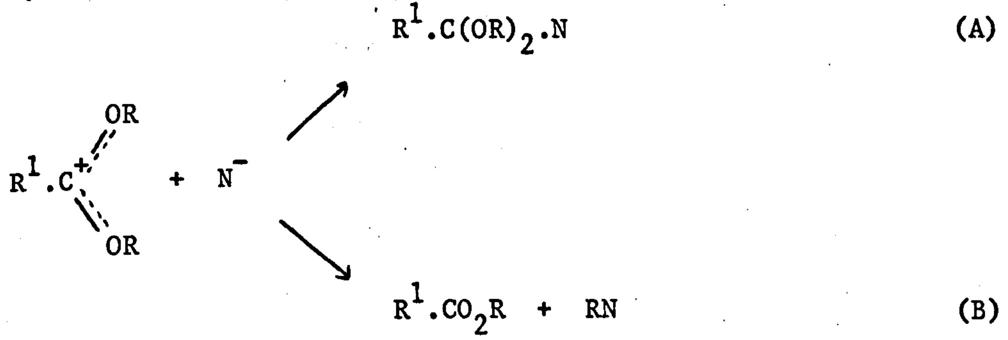
1.4 Scope of this work

One of the major stumbling blocks for the scientist in his inexorable pursuit of knowledge, is the failure of workers to report (often through no fault of their own) the results of experiments which failed to yield the expected positive results. Thus, I feel sure that several groups of workers must have studied the polymerization of ketene acetals and abandoned the topic after failing to obtain polymers of high molecular weight.

When this project was initiated, the object was "to prepare selected ketene acetal monomers, to study their polymerization under controlled conditions, and to characterize the polymers with regard to their chemical, physical, mechanical and thermal properties."

At first sight ketene acetals seem obvious candidates to produce polymers by a cationic mechanism. If a compound is to be polymerized cationically by catalytic amounts of initiators the reaction site must be the most basic point in the molecule. Most oxygen atoms are more basic than isolated double bonds, for example, the carbonyl oxygen of a vinyl ester is more basic than the vinyl group and it captures cations to give a resonance-stabilized ion which does not involve the double bond. However, ketene acetals are undoubtedly highly polar because of the mesomeric effect of the alkoxy groups and the highly nucleophilic character of the carbon 2 has been utilized in many organic syntheses.[12] Ketene acetals have obvious similarities to 1,1 disubstituted monomers such as isobutene, and to alkyl vinyl ethers, both of which can be polymerized to high polymers. Models of linear head-to-tail polymers of ketene acetals show that a considerable amount of free rotation of the polymer molecule is possible (in contrast to polyisobutene where it is impossible to construct a model). Assuming that the enthalpy and entropy of polymerization are of the same order of magnitude as those for the polymerization of isobutene, and taking values of $\Delta H^{o}_{ss} = 54$ kJ^{-1} mol^{-1}, $\Delta S^{o}_{ss} = 125$ JK^{-1} mol^{-1}, the ceiling temperature T_c is calculated as 160° for a 1 M solution of the monomer and 103° for a 0.1 M solution, so that there appear to be no thermodynamic reasons why ketene acetals should not be polymerizable at or below room temperature. It must be emphasised that T_c is characteristic of the monomer-polymer relationship only and is quite independent of reaction mechanisms.

In choosing monomers for study I was not discouraged by the fact that several ketene acetals have been reported to be unpolymerizable, because most of the results in the literature have been obtained by organic chemists who have tried to induce some kind of polymerization by the action of heat, whereas, we now know that the formation of high polymers by a cationic mechanism is favoured by low temperatures. Furthermore, the probable cations formed from ketene acetals, viz. dialkoxycarbenium ions, are well known in the field of organic chemistry and have been shown to be capable of reacting in two main ways:[57]



Reaction (A) usually has a lower activation energy than reaction (B) because of the considerable bond-breaking and reorganisation which must take place in (B). The ester formed by route (B) is however, stabilized by resonance and is normally found to have a higher thermodynamic stability than the addition product.[57] At low temperature the rate of reaction (A) increases[57] and this reaction is also favoured when the nucleophile is strong. The relative rates of the two reactions will also be affected by the polarity of the solvent, but it is difficult to predict the effect of solvent polarity without some knowledge of the polarities of the respective transition states.

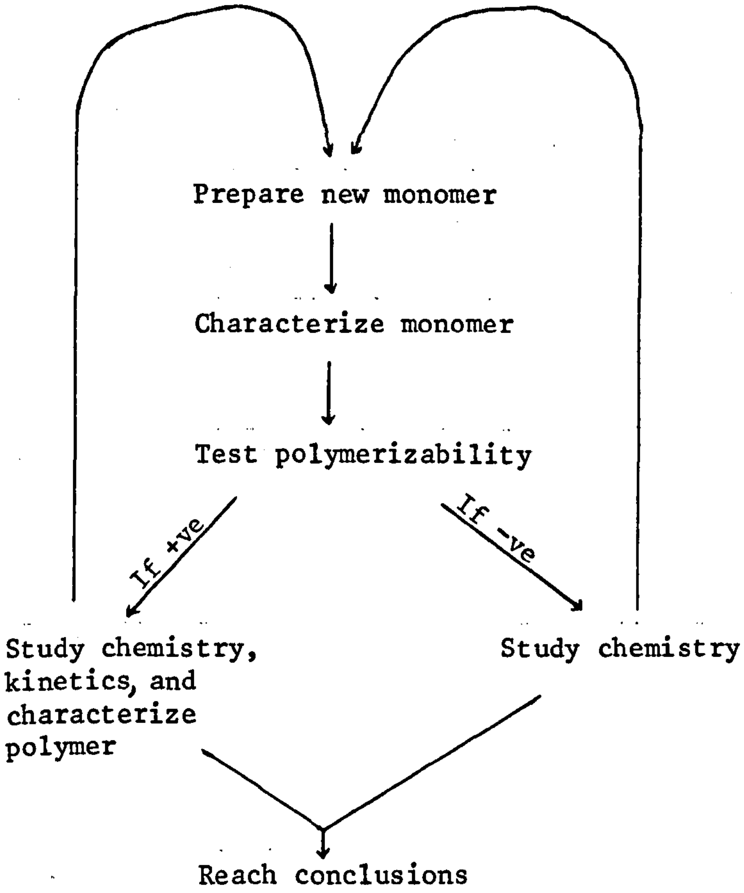
Thus it seemed likely that ketene acetals, which have strong nucleophilic properties, would react with the dialkoxycarbenium ion by reaction (A), i.e. a propagation reaction, at sufficiently low temperatures and in a suitable solvent. An argument similar to the one above may be put forward for the reactions of monoalkoxycarbenium ions (derived from vinyl ethers) with nucleophiles. In this case it is well known that in the polymerization of vinyl ethers, the predominant reaction is progation by a reaction analogous to reaction (A).

A proposed flow-chart for the research programme is shown in Figure 1. However, as usual, actual developments were different because although propagation does occur to some extent, we found that chain-breaking reactions are so important in the cationic polymerization of ketene acetals that we were unable to produce high polymers by a homogeneous mechanism.

We were able, however, to show that transfer reactions involving the monomer are the dominant chain-breaking reactions in the polymerization of ketene acetals, and a quantitative estimate of the rates of these reactions has been obtained.

FIGURE 1

Flow chart for the polymerization of ketene acetals.



CHAPTER 2: TECHNIQUES AND APPARATUS

General techniques are described here; a more detailed explanation of some techniques can be found in other sections of this thesis.

2.1 Introduction

For any serious study of cationic polymerization the exclusion of the atmosphere from the reaction mixture is essential. This requisite demands the use of inert atmosphere techniques or of a high vacuum system. It is sometimes found that the level of impurities in an inert-atmosphere system does not affect the reaction. Once this fact is established, (not assumed!) the obvious advantage of the inert-atmosphere system over the vacuum line, viz. increased flexibility, can be exploited to its full potential.

In this work, I began by manipulating reagents under a dry nitrogen atmosphere and attempted polymerizations in nitrogen-flushed, stoppered test tubes. When the use of more sophisticated inert-atmosphere techniques did not assist me in producing polymers of high molecular weight, I resorted to a high vacuum system in order to eliminate, or at least mitigate, the effect of chain-stopping impurities.

2.2 Dry Nitrogen techniques

Solids were handled in a conventional dry box under a positive pressure of nitrogen. For the dosing of liquids, glass syringes fitted with stainless-steel needles were used. Nitrogen was dried by passing it through a Pyrex glass coil immersed in liquid nitrogen and then straight into the apparatus via an all-glass delivery tube (a gas bubbler was introduced between the coil and the apparatus when required for some experiments, in order to saturate the nitrogen with solvent vapour).

2.3 Dosing of solvents and reagents under high vacuum

Volatile compounds were measured by distillation into precision burettes. Non-volatile liquids were dosed by a gravity feed via precision burettes.

2.4 Dilatometry

Dilatometers of standard design were prepared from Pyrex glass.

For sampling experiments the dilatometer in Figure 2 was used. This arrangement allowed the apparatus to be filled under vacuum and samples to be taken with a syringe against a flow of dry nitrogen.

The change of meniscus level in the dilatometer capillary was followed by a cathetometer. In several of the polymerizations a reference dilatometer, containing monomer and solvent only, was placed in the thermostat bath alongside the reaction dilatometer and the reference meniscus level was noted after each cathetometer reading. This method eliminated any errors resulting from slight temperature variations during a run.

2.5 Calorimetry

Reactions which were too fast to be studied by dilatometry or by sampling techniques were carried out in an adiabatic calorimeter (Figure 3) similar to that described by Plesch.[25] The flanged reaction vessel R is a pseudo-Dewar vessel with a side arm connecting R to the vacuum line. The flanged head H carried a mercury-seal stirrer S and four B14 sockets, for admission of solvent, monomer and initiator solution; and serving as inlets and outlets for dry nitrogen, the fourth socket carrying a copper-constantan thermocouple. The flange and taps were lubricated with Apiezon L grease.

FIGURE 2

Sampling dilatometer

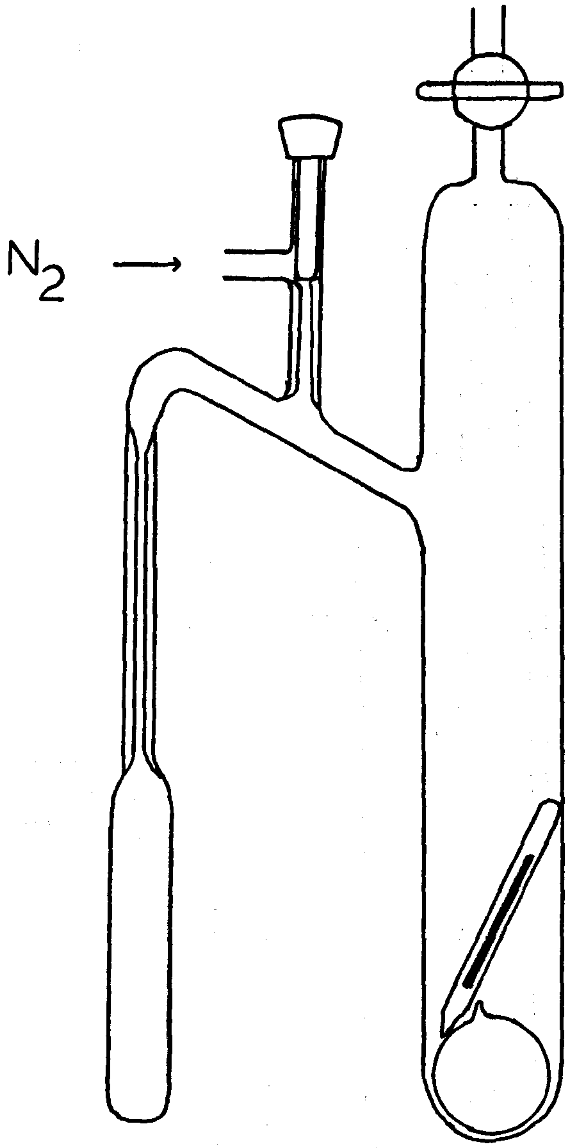
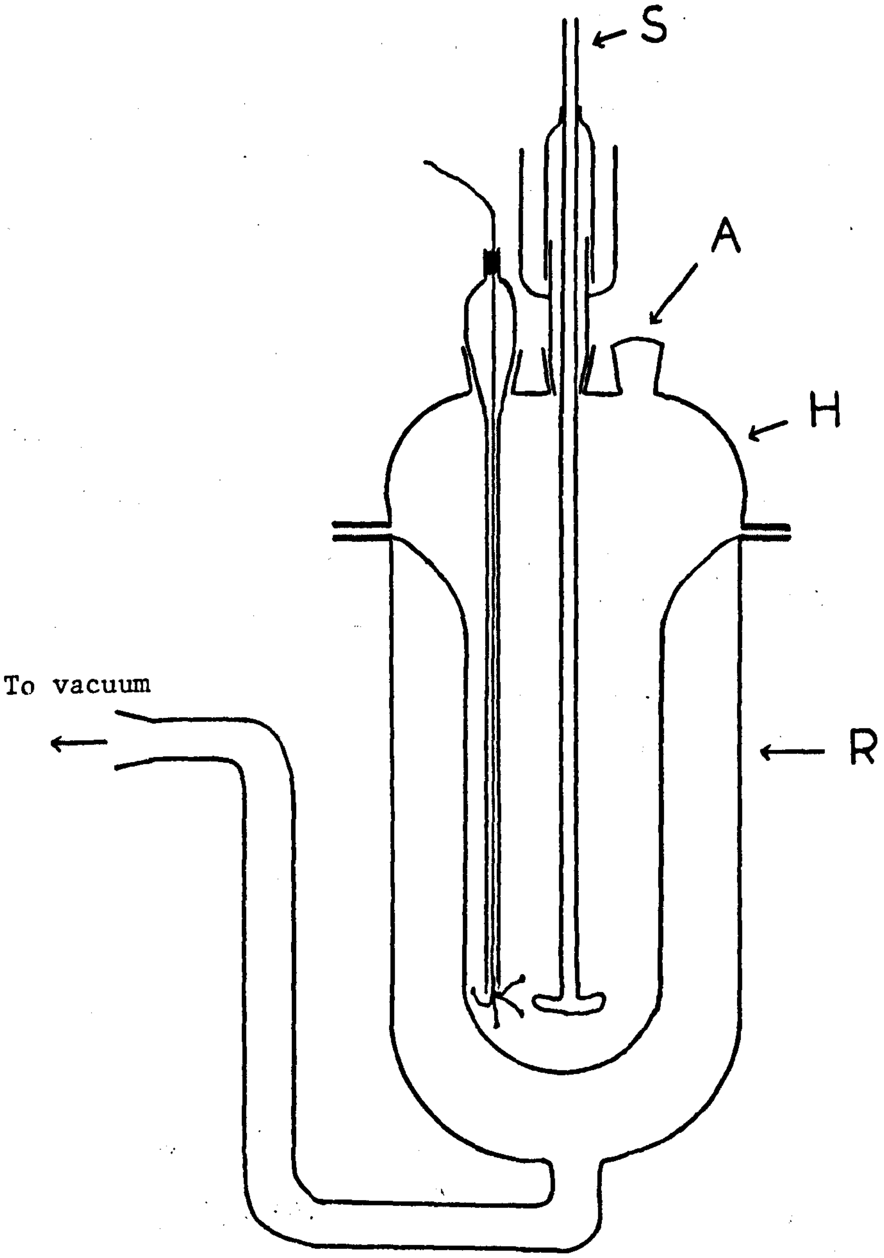


FIGURE 3

Adiabatic calorimeter.



The reaction vessel was purged with dry nitrogen for approximately 1½ hrs. Then the solvent and monomer were syringed in through the self-sealing rubber septum A. A Dewar of liquid nitrogen was placed around the reaction vessel and when a temperature was reached which was about 5° above the temperature at which it was desired to carry out the reaction the Dewar space of the reaction vessel was evacuated. When the desired reaction temperature was reached the initiator solution was syringed in and the temperature rise was followed by means of the thermocouple. When the reaction had subsided, as indicated by a constant cooling rate, the initiator was de-activated (for killing agents see section 2.7 of this thesis), and the contents of the reaction vessel were allowed to come to room temperature before opening the vessel and working up the products.

2.6 Calibration and operation of the thermocouple

The copper-constantan thermocouple, constructed as described by Longworth,[26] had 4 pairs of junctions. One end was kept in melting ice and the other was placed in the thermocouple pocket of the reaction vessel. The thermocouple was calibrated by measuring the freezing points of distilled water, CCl_4, $CHCl_3$ and CH_2Cl_2. A 25° thermostat bath was used as a reference for calibration above room temperature.

2.7 Product isolation

When the reactions were deemed to be complete, the initiator was de-activated, generally by the addition of triethylamine or of methanol.

In the early part of the work the reaction products were poured slowly into an excess of stirred pentane. After standing for a short time the solids were filtered off with a sintered glass crucible, followed by washing with cold pentane and were then dried to constant weight on the vacuum line. The filtrates were evaporated down to recover the pentane-soluble, low molecular weight products. It soon became apparent that the fraction of oligomers obtained in the form of viscous liquids was often comparable to the amount of precipitatable polymer, thus rendering the precipitation procedure both inefficient and time consuming.

Consequently, the products from most of the reactions were isolated by freeze-drying under vacuum, although precipitation in pentane of a sample of the reaction mixture was often used as a rough measure of the success of a polymerization run.

2.8 Molecular weight measurements

The number-average molecular weights of the products were determined by means of a Mechrolab Vapour Pressure Osmometer model 301A, fitted with a non-aqueous probe and thermostatted at 37°. The solvent used for all the measurements was chloroform.

All degrees of polymerization quoted in this thesis are therefore number average values.

2.9 Differential scanning calorimetry

Experiments on the thermal behaviour of the polymers were carried out with a Perkin Elmer DSC 1B instrument which was calibrated with a standard sample of Indium metal.

2.10 X-ray diffraction

To obtain an estimate of the degree of crystallinity of the polymers, X-ray powder diffraction patterns were obtained with a Phillips machine type pw 1009/25.

2.11 Infra-red spectroscopy

The I.R. spectra of the reactants and products were taken with a Perkin Elmer 257 grating spectrophotometer.

2.12 Visible-U.V. spectroscopy

The spectra taken in this work were recorded either on a Beckmann DB recording spectrometer or on a Unicam S.P.800, with a vacuum spectroscopic device[27] or with standard silica cells.

2.13 Proton magnetic resonance spectroscopy

A Perkin Elmer Model R10, 60 mc spectrometer equipped with a probe thermostatted at 35° was used throughout this work. Spectra were run in CCl_4 or $CDCl_3$ using tetramethyl silane as an internal standard.

2.14 Gas-Liquid Chromatography

All chromatograms were run on a Perkin Elmer F-11, fitted with a dual column analyser, a flame-ionization detector, and two 3m. silicone oil SE-30/Chromasorb P 100-120 mesh columns. The instrument operation and sample preparation were as described in the Perkin Elmer manual.

CHAPTER 3: REAGENTS AND RECIPES

3.1 Monomers

Ketene acetals are not available commercially, but several procedures have been described for their preparation.[1,10] For this work a rapid and efficient method was required. The dehydrobromination of α-bromoacetals[15] seemed attractive because several of the precursors are available commercially, and the reaction is reported to give high yields. This preparative procedure was used whenever it was applicable.

The preparation of ketene acetals by the one-step addition of vinylidene chloride to a sodium alcoholate[10] seemed promising, but unfortunately, this reaction only proceeds when the alcoholate possesses an electron-donating atom in the position beta or gamma to the alcoholate oxygen atom. This precludes the formation of ketene dialkyl acetals by this route.

3.1.1. Ketene diphenyl acetal ($CH_2{:}C(OC_6H_5)_2$)

The preparation of ketene diphenyl acetal was attempted by a single-step synthesis involving nucleophilic substitution of the chlorine atoms in vinylidene chloride by phenyl groups from sodium phenoxide:-

$$CH_2{:}CCl_2 + 2C_6H_5.\overset{-}{O}\overset{+}{Na} \xrightarrow[\text{solvent}]{\text{inert}} CH_2{:}C(OC_6H_5)_2 + 2NaCl$$

Several attempts were made to prepare this monomer with either dimethoxyethane or diglyme as the solvents. A typical recipe is as follows:- To a solution of phenol (94 g, 1 mol) in dimethoxyethane (500 g) was added, with stirring, potassium metal (39.1 g, 1 g-atom) at a temperature of 70 to 80°. The potassium was dissolved over a period of five hours under nitrogen, the disappearance of the phenol being followed by g.l.c. analysis of the reaction mixture. Vinylidene chloride (96 g, 1 mol) was then added slowly, with stirring, under nitrogen. Potassium chloride was precipitated, and the colour of the reaction mixture changed from colourless to dark brown.

The rate of disappearance of the phenoxide was followed by adding a sample of the reaction mixture to an excess of iodomethane and analysing for anisole by g.l.c. After the reaction was complete the reaction mixture was filtered and gave a dark brown filtrate and tan potassium chloride. G.l.c. analysis of the filtrate showed that several products had been formed. It was difficult to obtain single products pure enough to analyse by pm.r. spectroscopy. After futile attempts to separate the components by derivative formation (e.g picrates for aromatics), and by preparative g.l.c., a pure main product (b.p. 73-75^o/0.1mm) was isolated by (a) removing traces of phenol with 15% sodium hydroxide solution in a continuous extraction apparatus, followed by (b) careful re-fractionation of the products from four preparations. This product was identified as the mono-phenoxy substituted vinylidene chloride, $CH_2:CCl.OC_6H_5$. No other products could be obtained in sufficient purity to be analysed. This preparative procedure was therefore abandoned.

3.1.2 Ketene di (2-methoxyethyl) acetal, $CH_2:C(OCH_2CH_2OMe)_2$

Ketene di (2-methoxyethyl) acetal (KA1) was prepared essentially according to the procedure described by Kuryla,[10] which comprises the slow addition of vinylidene chloride to the sodium alcoholate of 2-methoxyethanol in an inert solvent:

$$2\,MeOCH_2CH_2.O^-Na^+ + CH_2{:}CCl_2 \longrightarrow \underset{(KA1)}{CH_2{:}C(OCH_2CH_2OMe)_2} + 2NaCl$$

Three solvents were tried for the reaction, viz. diethylene glycol dimethyl ether, toluene, and xylene. Xylene was found to be the most suitable solvent with regard to minimising the yield of by-products, and ease of purification of the ketene acetal. The synthesis was carried out as follows: To a solution of 2-methoxyethanol (608 g, 8.00 mol) in xylene (300 g) was added, with stirring, sodium metal (184 g, 8 g-atom) at a temperature of 100-120°. The sodium was dissolved over a period of four hours under nitrogen. Much of the sodium alcoholate crystallised out if the solution was allowed to cool; failure to maintain an oxygen-free atmosphere led to a progressive darkening of the initially colourless solution. The disappearance of the 2-methoxyethanol was followed by g.l.c. analysis of the reaction mixture. When all the sodium had dissolved, 450 g (4.6 mol) of vinylidene chloride was added slowly with stirring, under nitrogen. The temperature of the reaction mixture rose from 100° to 150°, sodium chloride was precipitated, and the colour of the reaction mixture changed from colourless to dark brown. After the reaction was complete (signalled by the termination of the exotherm) the reaction mixture was filtered and gave a dark-brown filtrate and tan sodium chloride. The filtrate was fractionated through a 35 cm Vigreux column at a reflux ratio of 15:1 and yielded (KA1) as the high boiling fraction; b.p. 78-80°/1 mm (lit.[10] 78-80°/2 mm), $n_D^{25} = 1.4417$, $d_4^{25} = 1.013$ g ml^{-1} Glc. analysis showed the monomer to be more than 95% pure.

The monomer shows a very strong sharp absorption at 1640 cm^{-1}, characteristic of the $:CH_2$ group, and the p.m.r spectrum confirms the ketene acetal structure. The ultraviolet spectrum in methylene dichloride shows a strong absorption maximum at 238 nm.

Drying and dosing:

It was found that KAl is very sensitive to traces of acid. Insoluble white polymer is formed quite rapidly when KAl is collected in acid-washed Pyrex vessels. However, the rate of polymerization can be minimized by collecting the monomer over anhydrous potassium carbonate in alkali washed containers. Consequently all the apparatus in this work which came into contact with ketene acetals was washed with dilute aqueous sodium hydroxide solution before rinsing it with water and drying.

The drying of monomers for cationic polymerization presents special problems since most of the common drying agents either are active polymerization initiators or form initiators by reaction with water. The attempted drying of KAl with activated molecular sieves led to a very rapid polymerization.

Metal hydrides are popular drying agents in cationic polymerization and have been used extensively in this laboratory for the drying of styrene[28] and cyclic ethers.[29] KAl remains fairly clear and mobile when stored over calcium hydride, so the drying and dosing of KAl on the vacuum line was attempted in the apparatus shown in Figure 4. The freshly-distilled monomer was run into the storage flask A of the evacuated apparatus, which was then sealed off at the constriction. After standing over freshly-ground CaH_2 for 2 days the monomer was degassed by several freeze-pump-melt cycles. The cold finger of condenser C was then filled with liquid nitrogen and the monomer was distilled into the precision burette B. After the monomer had warmed up to room temperature the required amount was run into the polymerization vessel via Rotaflo tap T1. The monomer remaining in the burette was run back into A via Rotaflo tap T2, to prevent any polymerization on the walls of the burette during storage. Because of the low volatility of KAl it was necessary to heat vessel A during the distillation. This procedure led to a rapid polymerization of the monomer, manifested by the deposition of a white solid in flask A and along the whole distillation path. After 3 such distillations the contents of flask A became highly viscous and further distillation became impossible. This technique gives yields of dry monomers which are uneconomically low. The use of $LiAlH_4$, sodium dihydro-bis[2-methoxyethoxy] aluminate or barium oxide in this procedure led to similar results. A trap-to-trap distillation of the monomer on the vacuum line also led to polymerization. These results seem to indicate that dry KAl is very easily polymerized. It is interesting to note that cyclic ketene acetals (2-methylene-1,3-dioxolanes) are found to polymerize spontaneously during their preparation,[30] the rate and conversion being related symbatically to the degree of purity of the monomers.

In order to reduce the amount of polymer formed during the dosing of KAl, it seemed useful to avoid distillation during the dosing procedure. Two techniques were developed to overcome this problem. In the first of these, the freshly distilled monomer was collected over a finely-ground mixture of CaH_2 and anhydrous K_2CO_3, then it was degassed under vacuum, and it was finally distributed into break-seal ampoules via the vacuum distribution device shown in Figure 5. The contents of the

FIGURE 4

Apparatus for the dosing of KAl by distillation.

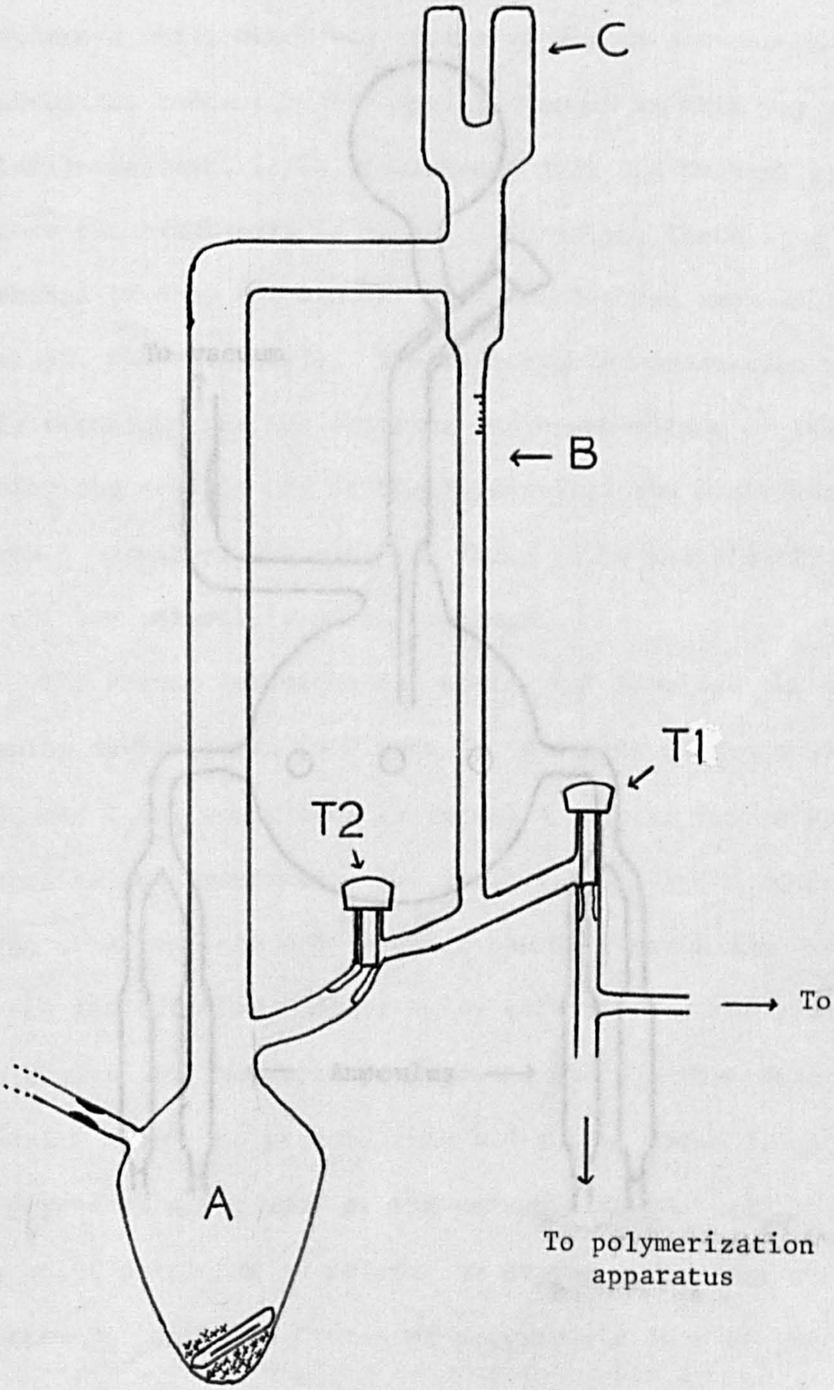
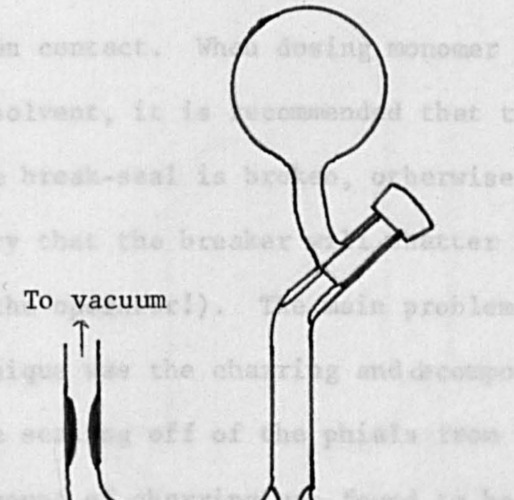


FIGURE 5

Distribution device for filling monomer ampoules.



ampoules were determined by the mid-point method[34] and were then frozen in liquid nitrogen and stored in the freezing compartment of a refrigerator. Ampoules prepared in this way were fused onto a polymerization apparatus which was then evacuated and filled with solvent and an initiator phial, Figure 6. The contents of the ampoule were then thawed and the break-seal was broken by pulling a glass enclosed magnet upwards by means of a solenoid coil, which was activated for an instant only by a push-button contact. When dosing monomer in this way into a volatile solvent, it is recommended that the solvent be frozen before the break-seal is broken, otherwise, there is a high probability that the breaker will shatter the ampoule (and perhaps, the operator!). The main problem associated with this technique was the charring and decomposition of the monomer during the sealing off of the phials from the distribution device. A small amount of charring was found to be unavoidable because of the low volatility of the monomer.

The second technique for dosing KAl involved the use of the tipping device shown in Figure 7. A finely ground mixture of CaH_2 and K_2CO_3 was placed in vessel B and the device was then assembled and evacuated. The freshly-distilled monomer in flask A was then run into B by opening tap T; flask A was then sealed off at the constriction. After being stirred over the drying mixture for 2 days, the monomer was degassed and was then dosed by pivoting vessel B about the greased cone-and-socket joint J. A small plug of degreased glass wool at the entrance to the drip tube prevented any solid particles of polymer or drying agent from entering the burette P. Although traces of polymer did form on the walls of the burette after several weeks, this proved to be the most convenient and economical method of handling KAl under vacuum.

FIGURE 6

Polymerization apparatus fitted with monomer ampoule.

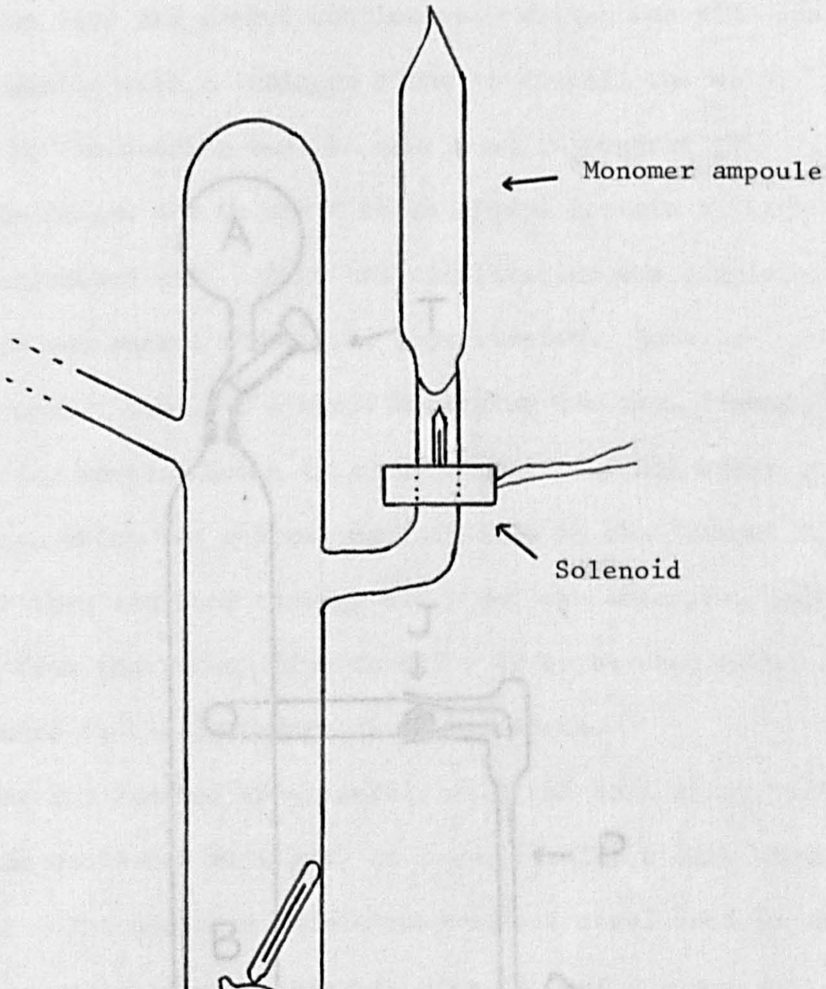
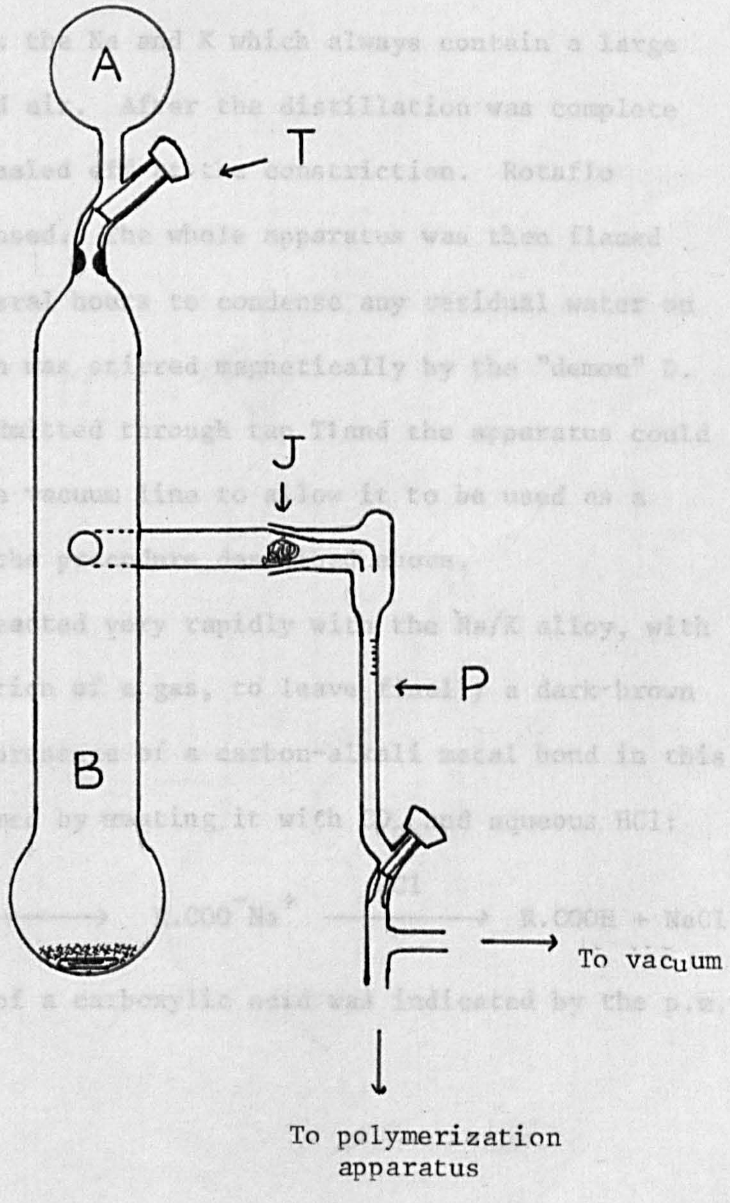


FIGURE 7

Tipping device for the drying and dosing of KAl.



In the later stages of this work an attempt was made to produce ultra-dry KAl by drip feeding the monomer from the tipping device on to freshly distilled sodium potassium alloy. This was done by mounting the apparatus shown in Figure 8 vertically below the tipping device. Freshly-cut pieces of a mixture of Na and K (70% w/w K) were placed in the side arm S which was then sealed off at P. The apparatus was opened to the vacuum line and pumped continuously whilst the side-arm was heated gently with a luminous flame to distill the alloy into flask F; the pumping must be continued throughout this operation to de-gas the Na and K which always contain a large volume of entrained air. After the distillation was complete the side arm was sealed off at the constriction. Rotaflo tap T1 was then closed. The whole apparatus was then flamed cautiously for several hours to condense any residual water on to the alloy, which was stirred magnetically by the "demon" D. Monomer was then admitted through tap T1 and the apparatus could be removed from the vacuum line to allow it to be used as a tipping device by the procedure described above.

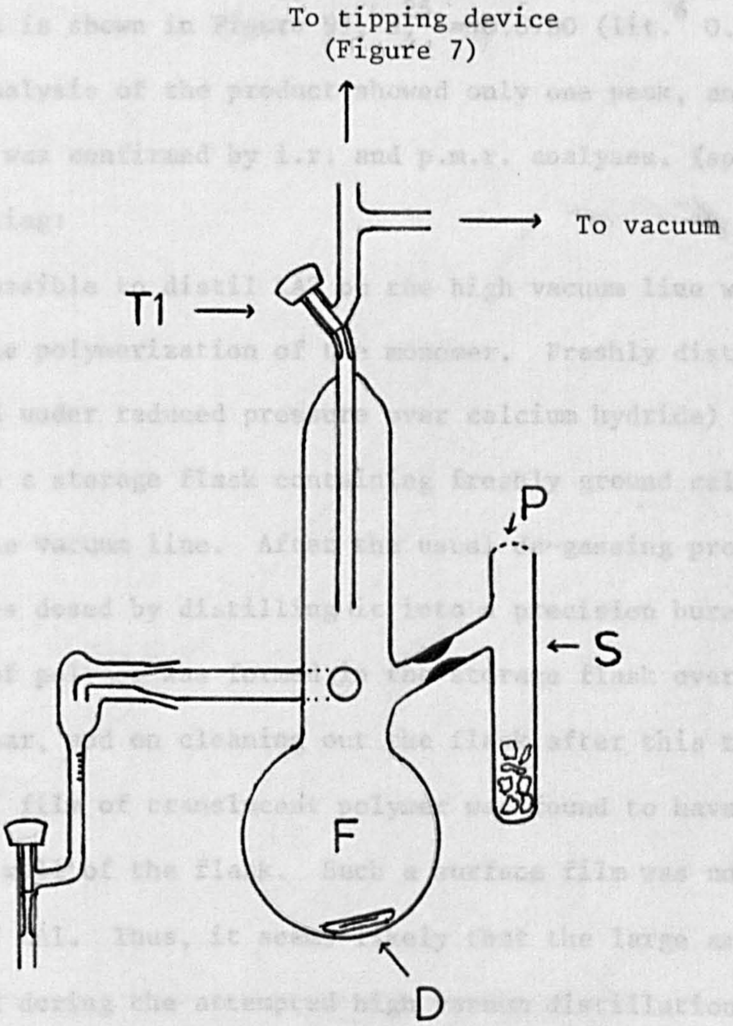
However KAl reacted very rapidly with the Na/K alloy, with considerable evolution of a gas, to leave finally a dark-brown viscous oil. The presence of a carbon-alkali metal bond in this mixture was confirmed by treating it with CO_2 and aqueous HCl:

$$\mathrm{R.C{-}Na + CO_2 \longrightarrow R.COO^{-}Na^{+} \xrightarrow{HCl} R.COOH + NaCl}$$

The presence of a carboxylic acid was indicated by the p.m.r. spectrum.

FIGURE 8

Apparatus for drying KA1 with Na/K alloy.



3.1.3 Ketene diethyl acetal $CH_2C(OEt)_2$

Ketene diethyl acetal (KA2) was prepared by the dehydrobromination[16] of bromoacetaldehyde diethylacetal (Koch-Light) with potassium t-butoxide in t-butanol to give (in 70% yield) a colourless liquid; b.p 94-96°/300 mm. This material was refluxed over calcium hydride for one hour and then fractionated through a 36 cm Vigreux column at a reflux ratio of 10:1, rejecting generous head and tail fractions, and was collected and stored under reduced pressure over freshly-ground calcium hydride.

The pure compound is a liquid; b.p 75-76°/135mm, (a vapour-pressure curve constructed from literature values and values from this work is shown in Figure 9), d_4^{25} = 0.8780 (lit.[6] 0.8777)

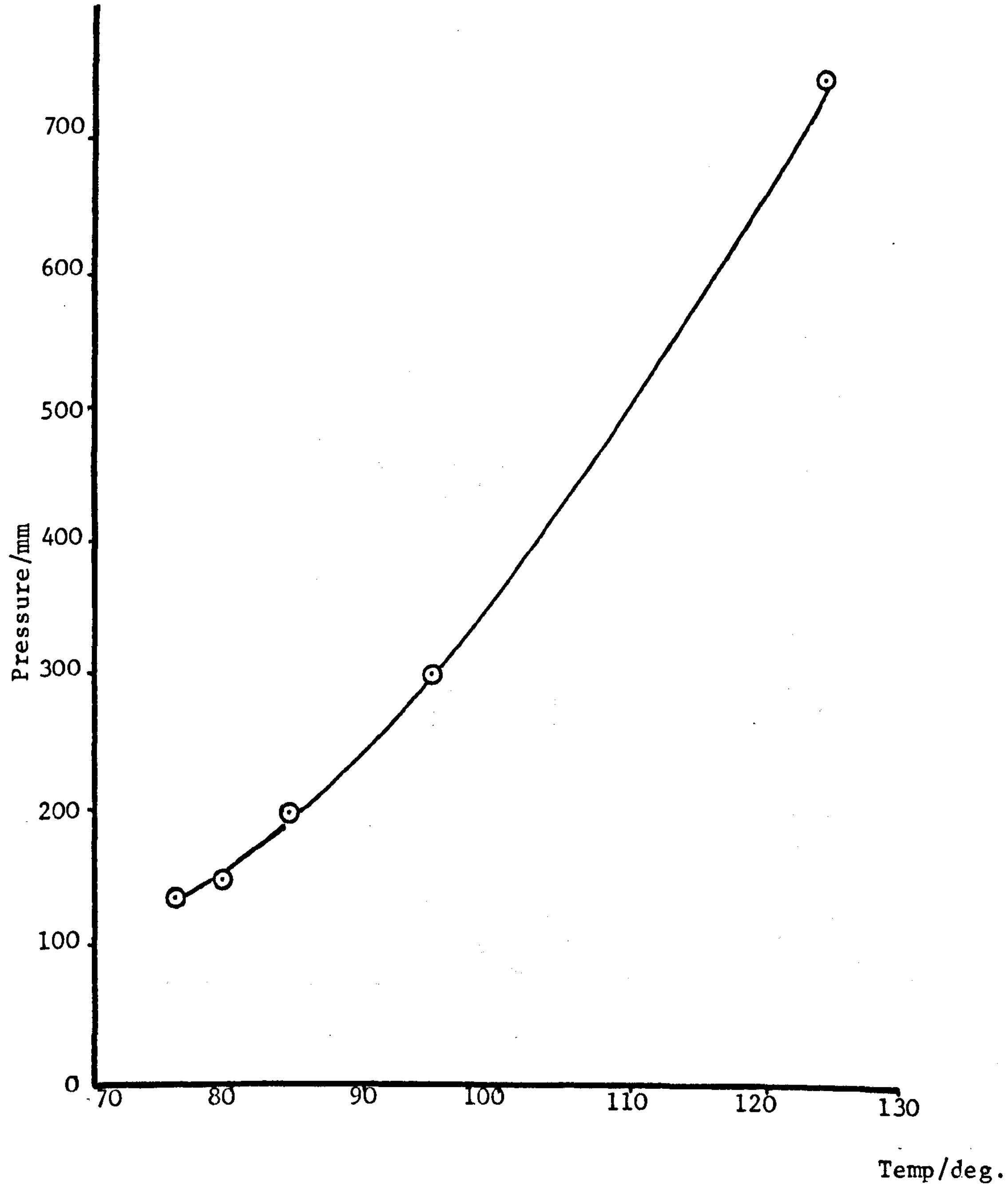
G.l.c. analysis of the product showed only one peak, and the KA2 structure was confirmed by i.r. and p.m.r. analyses. (spectrum 1)

Drying and dosing:

It was possible to distil KA2 on the high vacuum line without any appreciable polymerization of the monomer. Freshly distilled KA2 (collected under reduced pressure over calcium hydride) was distilled into a storage flask containing freshly ground calcium hydride, on the vacuum line. After the usual de-gassing procedure the monomer was dosed by distilling it into a precision burette. Only a trace of polymer was formed in the storage flask over a period of a year, and on cleaning out the flask after this time a thin, coherent film of translucent polymer was found to have formed on the wall of the flask. Such a surface film was not found in the case of KA1. Thus, it seems likely that the large amount of polymer formed during the attempted high vacuum distillation of KA1 is due (at least partly) to a surface reaction between the monomer

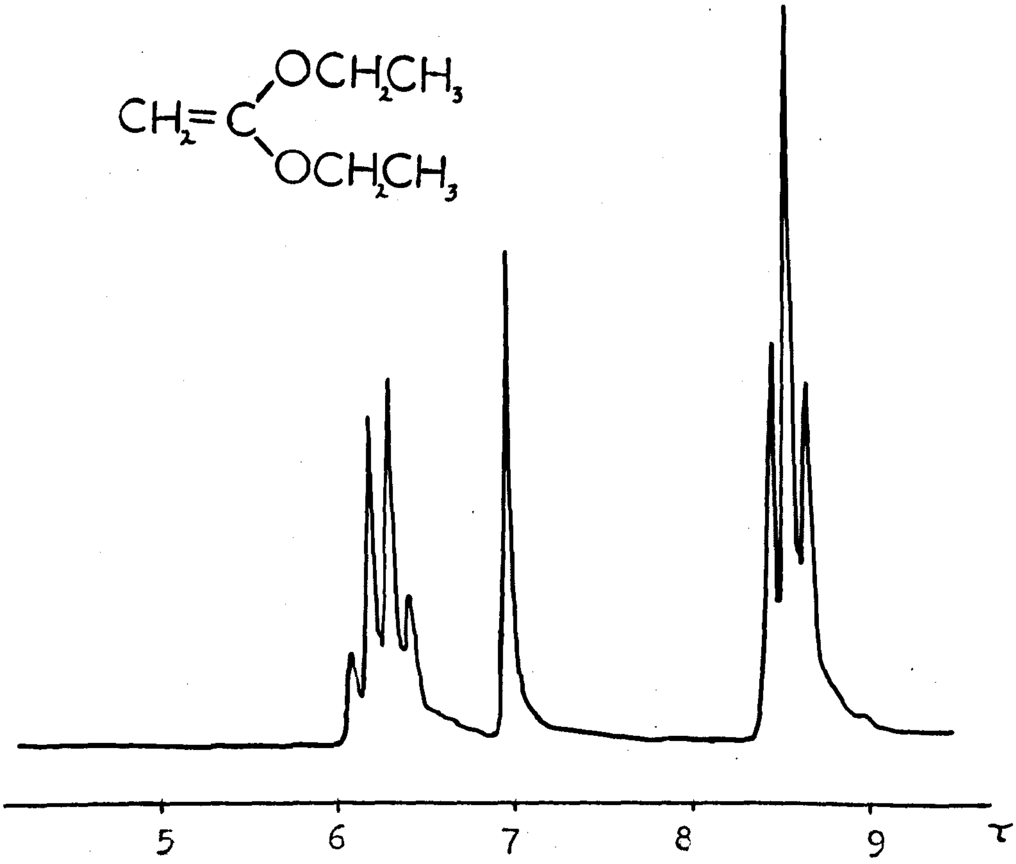
FIGURE 9

Vapour pressure curve for KA2.



SPECTRUM 1

The p.m.r. spectrum of KA2



and some initiating species present on the walls of the glass, and to the inability of KA1 to form a protective polymeric film.

3.1.4 Ketene ethyl methyl acetal $CH_2{:}C(OMe)OEt$ (experimental work carried out by Dr. G. R. Cliff)

The preparation of ketene acetals by the dehydrobromination of α-bromoacetals has been exploited by Baldwin and Walker[31] to produce mixed phenyl ketene dialkyl acetals. The following route was envisaged for the preparation of ketene ethyl methyl acetal (KA3):

$$CH_2{:}CH.OEt + Br_2 \longrightarrow \underset{\text{(I)}}{Br.CH_2.CHBr.OEt}$$

$$\text{(I)} + Na^+\ \bar{O}.Me \longrightarrow \underset{\text{(II)}}{Br.CH_2(OMe)OEt} + NaBr$$

$$\text{(II)} + K^+\ \bar{O}Bu^t \longrightarrow \underset{\text{(KA3)}}{CH_2{:}C(OMe)OEt} + KBr + Bu^tOH$$

Bromoacetaldehyde ethyl methyl acetal was prepared according to the procedure described by Baldwin and Walker[31] for the preparation of α-bromophenylacetaldehyde mixed acetals. The dehydrobromination reaction was carried out according to the procedure described[16] for the preparation of KA2 from bromoacetal.

Procedure:

To prepare the bromoacetal (II) a solution of ethyl vinyl ether (564 g, 7.84 mol) in 2 litres of dry diethyl ether was cooled to -30° in a Drikold/acetone bath. To this solution 404 ml (7.84 mol) of bromine was added, with stirring, at such a rate that the temperature remained below -25°; this required 2½ hrs. The addition of bromine was stopped when a faint permanent yellow colour became apparent. The colour was then destroyed by back-titrating with ethyl vinyl ether.

To the resulting solution of ethyl 1,2-dibromoethyl ether (I), maintained at -30°, was added, with stirring, a solution of one equivalent of sodium methoxide in 2 litres of methanol. The rate of addition was regulated to keep the temperature below -30°, but when the addition was complete the reaction mixture was allowed to warm to room temperature and was stirred overnight.

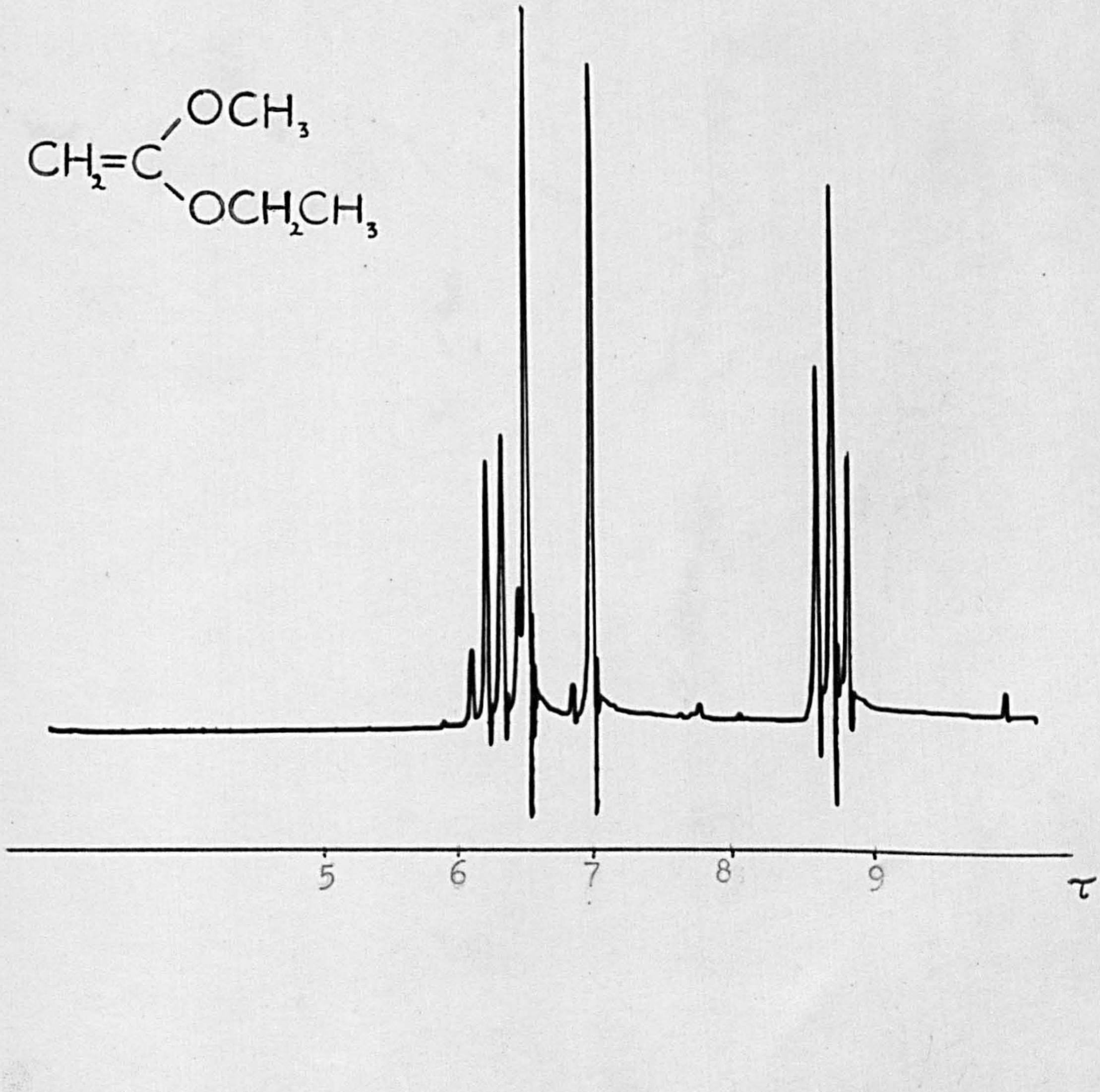
The reaction mixture was then poured into 1 litre of 20% w/v aqueous potassium carbonate solution, contained in a 5 litre separating funnel. The organic layer was separated, the aqueous layer was extracted once with 400 ml. of diethyl ether, and the combined organic layers were dried over anhydrous potassium carbonate. The organic layer was then concentrated by distilling it through a 50 cm column packed with glass helices. Heating was supplied by a steam bath and all material which boiled below 80° was collected and discarded. The residue was found by g.l.c. and p.m.r. to be pure (II) in 84% yield.

The dehydrobromination of (II) to KA3 was accomplished, following the procedure described by McElvain and Kundinger[16] for the dehydrobromination of bromoacetal. KA3 (55% yield) was collected under reduced pressure over anhydrous potassium carbonate (b.p. 58-60°/195 mm). The i.r. and p.m.r. (spectrum 2) spectra confirm the KA3 structure.

It was apparent that this preparative procedure suffered from two major disadvantages, viz. the tedious removal of a large volume of t-butanol during the final distillation, and, since the ketene acetal was the highest boiling material in the system, a significant amount of the acetal was lost in the residual potassium bromide and in the distillation column. Modifications to the procedure were therefore considered and these were directed

SPECTRUM 2

The p.m.r. spectrum of KA3



towards finding an alternative strong base derived from a non-volatile conjugate acid, and finding a suitable, inert high boiling solvent to act as a 'chaser' to the ketene acetal.

The most promising base appeared to be potassium 2,6-di-t-butyl phenolate. This has been reported[32] to be similar in basic strength to t-butoxide, and has the advantage that 2,6-di-t-butylphenol has a very high boiling point. However, no ketene acetal could be isolated from the reaction between potassium 2,6-di-t-butylphenolate and bromoacetaldehyde ethyl methyl acetal. This reaction was not investigated further.

A consideration of the properties of several other bases revealed that none were as suitable as potassium t-butoxide, and further modifications were directed towards improving the reaction procedure using this base.

The most satisfactory procedure proved to be the reaction between a suspension of solid potassium t-butoxide in xylene and the bromoacetaldehyde acetal. In this way the amount of t-butanol to be removed was limited to two equivalents ($KOBu^t$ unless baked at high temperature, contains one molecule Bu^tOH of crystallization). Xylene was chosen as a 'chaser' solvent solely on the grounds that it is cheap, high boiling, solvent, traces of which, if present in the ketene acetal, would not be detrimental. The reaction with the solid butoxide proved unsuitable for large-scale preparations because of the difficulty in controlling the exothermic dehydrobromination reaction.

Dosing under vacuum:

The KA3 was re-distilled over calcium hydride, under nitrogen, at a reflux ratio of 20:1. Large head and tail fractions were rejected and the material boiling at 108 to 108.5°/755 mm. was collected over CaH_2. The monomer was then distilled into a flask on the high vacuum line containing well-baked barium oxide. After being stirred overnight, the KA3 was degassed and distilled into a flask containing Na/K alloy (prepared as described in the dosing procedure for KA1). The monomer and alloy were allowed to stand for a short time only, as considerable reaction was observed to occur and a pale-yellow colour was produced. After the usual degassing procedure the KA3 was quickly distilled into a storage flask containing freshly prepared barium oxide. The monomer was dosed by distilling it into a burette.

KA3 seems to be similar to KA2 in its behaviour towards drying agents, only traces of polymer being formed over long storage periods.

3.1.5 Ketene ethyl isopropyl acetal $CH_2{:}C(OPr^i)OEt$ (experimental work by Dr. G. R. Cliff)

Ketene ethyl isopropyl acetal was prepared and dosed in an analogous way to KA3, the only difference being the substitution of isopropanol for methanol in the preparation of the bromoacetal. The KA4 after purification had b.p. 74-79°/125 mm. The structure of KA4 was confirmed by its p.m.r. spectrum (spectrum3).

3.1.6 Ketene ethyl 2-methoxyethyl acetal $CH_2{:}C(OCH_2CH_2OMe)OEt$ (experimental work by Dr. G. R. Cliff)

A procedure for the preparation of ketene ethyl 2-methoxyethyl acetal (KA5) has been described in the patent literature.[11] This procedure involves the simultaneous bromination and dehydrobromination of ethyl vinyl ether and reaction of the 1-bromo-2-ethoxyethylene so produced with sodium 2-methoxy-ethoxide:

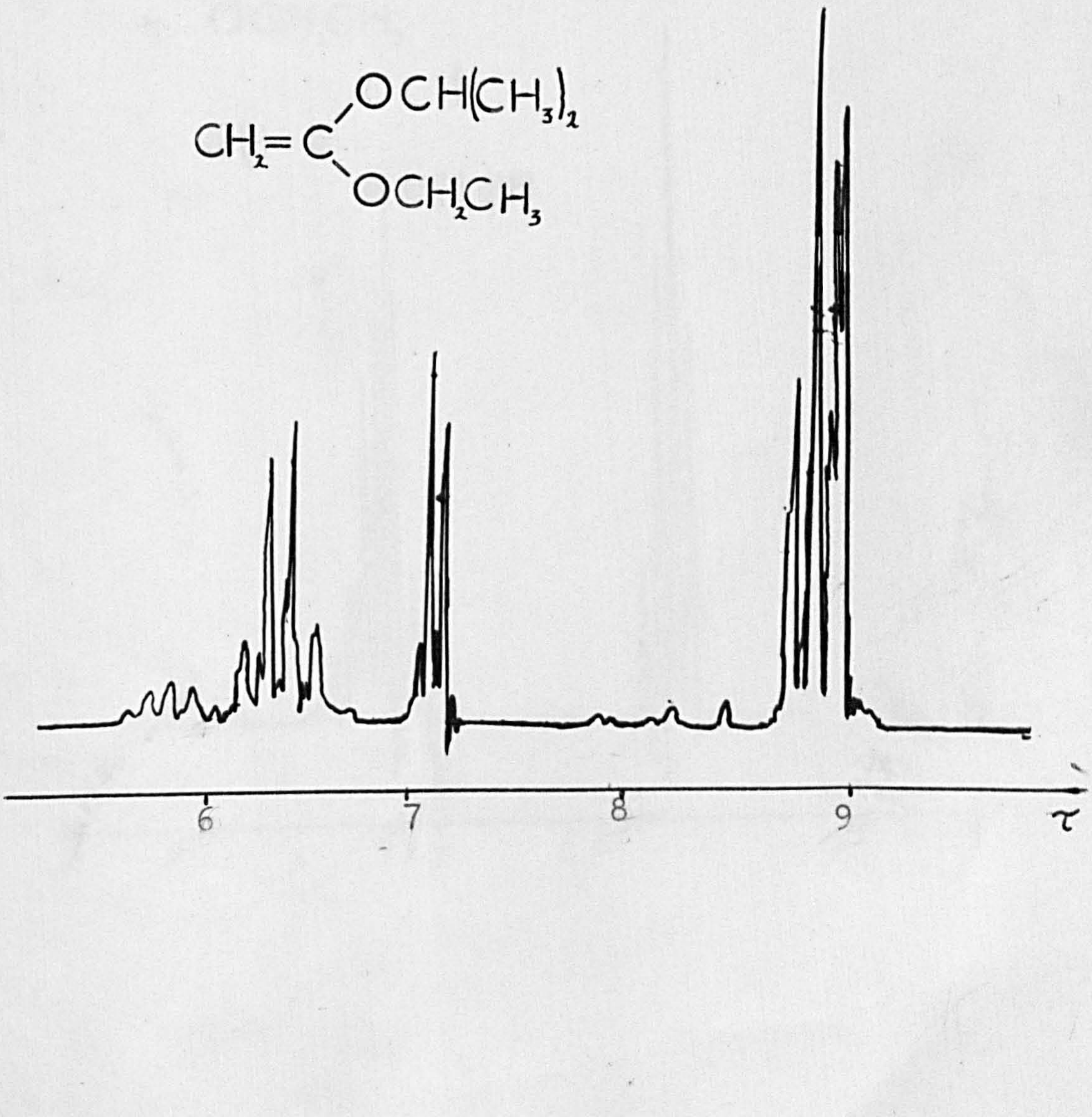
$$CH_2{:}CH.OEt \xrightarrow[-HBr]{Br_2} Br.CH{:}CH.OEt$$

$$Br.CH{:}CH.OEt + Na^+\bar{O}CH_2CH_2OMe \longrightarrow CH_2{:}C(OCH_2CH_2OMe)OEt + NaBr$$

(KA5)

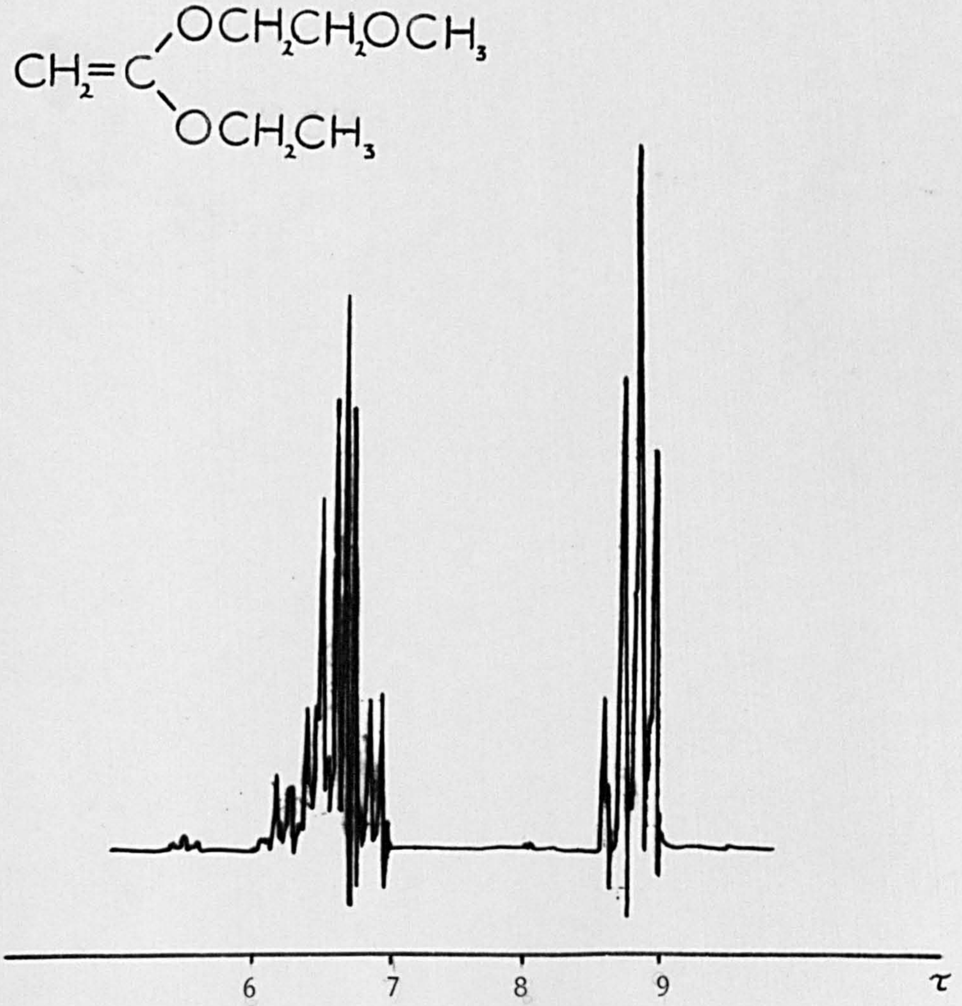
SPECTRUM 3

The p.m.r. spectrum of KA4



SPECTRUM 4

The p.m.r. spectrum of the product from the attempted preparation of KA5.



This reaction procedure yielded a mixture of products (b.p. 95-105°/2.5 mm) which could not be separated completely by distillation. The p.m.r. spectrum (spectrum 4) of the mixture was complex and difficult to interpret but showed the presence of KA5. This preparative procedure was abandoned.

3.1.7 Ketene ethyl phenyl acetal $CH_2:C(OPh)OEt$ (experimental work by Dr. G. R. Cliff)

Two preparative routes to this monomer were considered:

$$\begin{tikzcd}
\text{A)}\ CH_2:CH.OEt + Br_2 \arrow[r] & Br.CH_2CHBr.OEt \arrow[dr] & \\
 & & Br.CH_2CH(OPh)OEt \arrow[dd, "-HBr"] \\
\text{B)}\ CH_2:CH.OPh + Br_2 \arrow[r] & Br.CH_2CHBrOPh \arrow[ur] & \\
 & & CH_2:C(OPh)OEt
\end{tikzcd}$$

A synthesis of ketene diphenyl acetal by a procedure analogous to route B has been reported by McElvain and Fajardo-Pinzon,[33] but because it was impossible to obtain large quantities of phenyl vinyl ether, synthesis by route A was investigated. Bromoacetaldehyde ethyl phenyl acetal prepared by route A was a yellow liquid which, on being concentrated and left standing in the air for a few minutes, polymerized very violently and exothermically to leave what is best described as an "expanded carbon foam". This preparative procedure was abandoned.

3.2 Solvents

3.2.1 Methylene dichloride CH_2Cl_2

The Honeywill & Stein Ltd., "pure" product was purified as described by Maryott et al.[18] Preliminary drying was carried out over calcium chloride. The solvent was then refluxed over phosphorus pentoxide for several hours and then fractionated through a 160 cm column fitted with nickel gauze rings at a reflux ratio of 10:1. The main fraction of constant refractive index was collected under dry nitrogen in dark Winchester bottles b.p.40°/ 760 mm (lit.[17] 39.95/760 mm).

The solvent was then transferred into a 5 litre reservoir on the vacuum line. Freshly-ground calcium hydride was then added, the reservoir was then closed with a mercury seal and the solvent degassed and refluxed for several days. The dosing of methylene dichloride under high vacuum has been described.[19]

3.2.2 Toluene $C_6H_5.CH_3$

This solvent was available in the laboratory in a flask on the high vacuum line (stored over calcium hydride).

3.2.3 Chloroform $CHCl_3$ and carbon tetrachloride CCl_4

These solvents (Hopkins & Williams Ltd.) were purified as described for methylene dichloride. They were refluxed over calcium hydride for several hours and then distilled through a 36 cm Vigreux column.

3.2.4 Petroleum ether (100-120°)

The commercial product (Hopkin and Williams Ltd.) was shaken with concentrated sulphuric acid, separated, washed with aqueous sodium carbonate solution and then with water. After preliminary drying over calcium chloride, the solvent was refluxed over sodium and then distilled through a 36 cm. Vigreux column. The fraction boiling above 100° was collected and transferred into a flask on the high vacuum line. It was found that material purified in this way still contained sufficient aromatic material to produce a visible reaction with stannic chloride. Aromatic-free material was obtained by stirring the acid-washed solvent over aqueous acid potassium permanganate for several hours, followed by distillation from aluminium chloride. After washing this material with aqueous sodium carbonate solution and then with water, it was dried with, and distilled from, sodium as described above.

3.2.5 Other solvents

Solvents for preliminary polymerization experiments, precipitation of polymers etc. were used without further purification.

3.3 Initiators

3.3.1 Anhydrous cadmium chloride $CdCl_2$

Anhydrous cadmium chloride (Hopkin and Williams Ltd) was finely ground and was then heated at 100° in a vacuum oven for several hours. The material was handled and dosed by standard techniques under dry nitrogen or under high vacuum.

3.3.2 Cadmium chloride-ether complexes

The possibility of preparing soluble addition complexes of cadmium chloride was investigated by reacting[20] the halide with 1,3-dioxane and with tetrahydrofuran, under reflux. The products thus formed were found to be insoluble in both ketene acetals and in methylene dichloride.

3.3.3 Anhydrous mercuric chloride $HgCl_2$

The May and Baker "pure" material was used without further purification. It was dried and dosed like cadmium chloride.

A saturated solution of mercuric chloride in methylene dichloride was prepared under vacuum and was found to be 1.52×10^{-2} molar by a gravimetric analysis. This solution was diluted and dosed into phials, by standard techniques.[21]

3.3.4 Boron trifluoride etherate $BF_3.Et_2O$

The commercial product (B.D.H. Ltd) was used without further purification.

3.3.5 Stannic chloride $SnCl_4$

Stannic chloride was purified on the high vacuum line in the apparatus shown in Figure 9(a). The apparatus was evacuated over-night with periodic flaming. Phosphorus pentoxide was sublimed into flasks A and C by gentle heating of the material in the side-arms which were then sealed off at the constrictions. Flasks A and C were then isolated by closing their respective Rotaflo taps. The vacuum in Flask A was then let down with dry nitrogen, and stannic chloride (B.D.H. Ltd) was syringed in through the greased tap G. Flask A was re-evacuated and tap G sealed off at the constriction. The stannic chloride was degassed several times and was stirred over-night. It was then distilled into Flask C after sealing off a generous head fraction in Flask B. After stirring over-night and after further degassing, the break-seal BS was broken and the dry stannic chloride was distilled into break-seal ampoules, which were sealed off and stored in the dark. Stannic chloride purified by this technique has remained completely colourless and transparent for over a year. Phials were filled with solutions of stannic chloride in methylene dichloride and in 100-120° petroleum ether by using a tipping device as described.[21]

3.3.6 Titanium tetrachloride $TiCl_4$

Phials of this material in methylene dichloride were available in the laboratory, having been prepared by Panton.

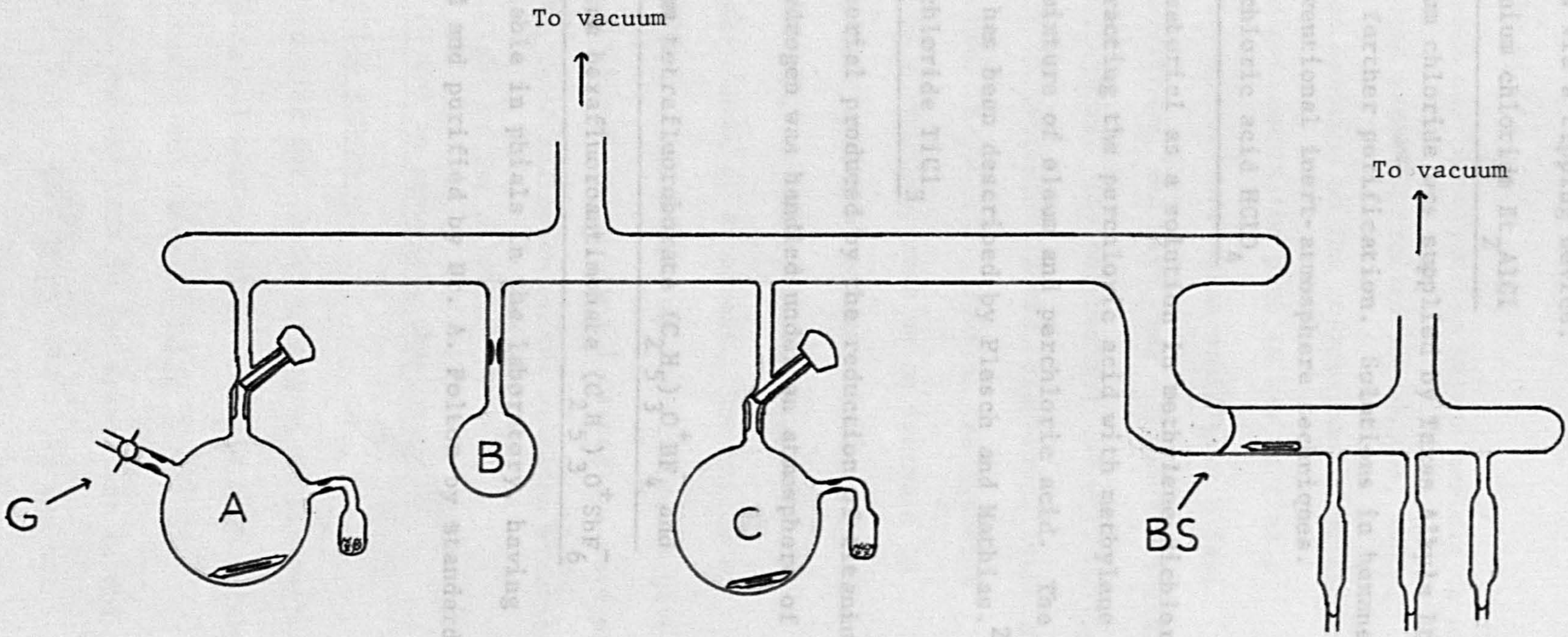
Only phials whose contents were completely colourless and transparent were used for polymerization experiments.

3.3.7 Ethyl aluminium dichloride $EtAlCl_2$

A solution of $EtAlCl_2$ in octane obtained from Shell and stored in break-seal ampoules was freed from octane by vacuum distillation. The solid compound was fractionated in vacuo three times and gave finally a snowy-white crystalline product. This material was distilled into a break-seal ampoule and was diluted with cyclohexane

FIGURE 9(a)

Apparatus for the purification of $SnCl_4$.



and dosed into phials via a tipping device.[21]

3.3.8 Diethyl aluminium chloride Et_2AlCl

Diethyl aluminium chloride was supplied by Texas Alkyls Ltd., and was used without further purification. Solutions in hexane were prepared by conventional inert-atmosphere techniques.

3.3.9 Anhydrous perchloric acid $HClO_4$

Phials of this material as a solution in methylene dichloride were prepared by extracting the perchloric acid with methylene dichloride out of a mixture of oleum and perchloric acid. The method of extraction has been described by Plesch and Mathias.[24]

3.3.10 Titanium trichloride $TiCl_3$

The Stauffer material produced by the reduction of titanium tetrachloride with hydrogen was handled under an atmosphere of dry nitrogen.

3.3.11 Triethyloxonium tetrafluoroborate $(C_2H_5)_3O^+BF_4^-$ and triethyloxonium hexafluoroantimonate $(C_2H_5)_3O^+SbF_6^-$

These were available in phials in the laboratory, having been freshly prepared and purified by Dr. A. Polton by standard procedures.[22,23]

CHAPTER 4: RESULTS AND DISCUSSION

4.1 The polymerization of KAl

The aim of this work was to polymerize ketene acetals to high molecular weight products under controlled conditions, and to study the chemistry and kinetics of the polymerization process.

For the kinetic measurements the problem was to find a combination of initiator and solvent which would give a fast and homogeneous polymerization, and with that aim several initiators and solvents were investigated. The polymerizations were carried out at room temperature in nitrogen-flushed, stoppered, test-tubes. The results are summarized in Table 2. Most of the reaction mixtures showed signs of a reaction, such as an increase in temperature and/or the development of colour, within a few minutes of adding the initiator. On the basis of these experiments methylene dichloride was chosen as a solvent. The choice of initiator was more difficult, since most of the initiators gave at least some polymer. Consequently, several initiators were used in order to investigate their influence on the reaction kinetics and on the molecular weight of the polymer.

4.1.1 Polymerization of KAl in methylene dichloride

4.1.1.1 Boron trifluoride etherate

Experiments were carried out, under nitrogen, to see whether $BF_3.Et_2O$ could be used to polymerize KAl in CH_2Cl_2 to high molecular weight polymer. The results are shown in Table 3.

The highest DP achieved was 12.2 in the experiment in which $m_o = 1.89$ M and $c_o = 1.33 \times 10^{-2}$ M at -100^o. It was not possible to use higher monomer concentrations at low temperatures because of the high freezing point of the monomer. The results indicate that the molecular weight is limited by one or more transfer or termination reactions.

4.1.1.2 Triethyloxonium tetrafluoroborate

In order to reduce the possibility of chain-breaking by impurities, experiments were carried out in vacuum dilatometers with highly purified materials. The results are shown in Table 4. No contraction was observable, but in fact a small dilation was observed. However, on adding the initiator in experiments 22 and 26 the apparatus became quite warm. This suggested that the reactions were very fast and that they were probably complete before the dilatometer had reached temperature equilibrium.

The reaction mixtures were highly coloured. A yellow colour was formed initially which changed to dark red as the reaction proceeded. The rate of darkening of the colour increased with increasing concentrations of monomer and initiator. The red solution exhibited absorption maxima at 227, 266 and 348 nm and had a long absorption 'tail' extending into the visible region. The i.r spectra of the products showed a strong absorption at 1740 cm^{-1}, characteristic of the carbonyl group.

The results show that the reactions are probably very fast and they indicate that the chain-breaking reactions may be an inherent property of the system.

4.1.1.3 Anhydrous perchloric acid

The interaction between KA1 and anhydrous perchloric acid was studied in vacuum dilatometers. Table 5 shows the results. The mixtures turned cherry red immediately on breaking the initiator phial and a dilation was observed. The U.V.-visible spectra of the mixtures were identical to those of the $Et_3O^+BF_4^-$

TABLE 2

Exploratory experiments on the polymerization of KAl; $m_o = 0.1$ to 2.0 M, $c_o = 10^{-4}$ to 10^{-2} M

Initiator	Solvent	Solubility* of initiator	Polymerizability*	Solubility* of polymer
$CdCl_2$	-	-	+	-
	Methylene dichloride	-	+	+
	Toluene	-	+	+
	Hexane	-	+	-
$HgCl_2$	-	-	+	-
	Methylene dichloride	-	+	+
	Chlorobenzene	+	+	+
$SnBr_4$	-	-	+	-
	Methylene dichloride	+	+	+
$SnCl_4$	-	+	+	-
	Methylene dichloride	+	+	+
	Hexane	+	+	-
	Diethyl ether	+	+	-
$TiCl_4$	-	+	+	-
	Methylene dichloride	+	+	+
	Toluene	+	+	+
Et_2AlCl	Hexane	+	-	
$EtAlCl_2$	Methylene dichloride	+	-	
$MgCl_2$	Hexane	-	+	-
	Methylene dichloride	-	+	+

Table 2 contd.

Initiator	Solvent	Solubility* of initiator	Polymerizability*	Solubility* of polymer
H_2SO_4	-	+	+	-
	Methylene dichloride	+	-	
$HClO_4$	-	+	-	
	Methylene dichloride	+	-	
	Hexane	+	-	
$Et_3O^+BF_4^-$	-	-	+	-
	Methylene dichloride	+	+	+
$Et_3O^+SbF_6^-$	-	-	+	-
	Methylene dichloride	+	+	+
BF_3Et_2O	-	-	+	-
	Methylene dichloride	+	+	+
	Chlorobenzene	+	-	
	Nitrobenzene	+	-	
	Hexane	?	+	-
	Pentane	?	+	-
	Petroleum ether	?	+	-
	Ethyl acetate	+	-	
	1,3 dioxane	+	-	
$C_7H_7^+BF_4^-$	-	-	+	
	Methylene dichloride	+	+	+
	Hexane	-	+	-
$C(NO_2)_4$	-	+	+	-
	Methylene dichloride	+	+	-
	Hexane	+	+	-

---

* A(+) sign indicates that the initiator was soluble in the solvent; a precipitate was formed on pouring the reaction mixture into pentane; the polymer was soluble in the solvent.

TABLE 3

The polymerization of KA1 with $BF_3.Et_2O$ in CH_2Cl_2.

Expt. No.	m_o /M	c_o $/10^2$ M	Temp. /deg.	Conversion /%	PPY /%	DP
2(a)	1.42	1.0	20	95	0	-
2(b)	1.42	1.0	0	95	0	-
2(c)	1.42	1.0	-78	95	28	4.25
95(a)	1.89	1.33	-100	100	26.5	12.2
95(b)	1.14	0.8	-100	100	37.5	8.9
96(a)	0.19	1.33	0	100	0	-
96(b)	0.19	1.33	-78	100	0	-
96(c)	0.19	1.33	-100	100	0	-
96(d)	0.19	0.01	-100	100	0	-

TABLE 4

The polymerization of KAl by $Et_3O^+BF_4^-$ at 25° in methylene dichloride

Expt. No.	m_o /M	c_o /10^2 M	Conversion /%	DP*
21	0.61	1.02	100	2
22	1.89	7.13	100	1.7
26	1.92	0.27	100	-

* The reaction products which were viscous liquids were freeze-dried under vacuum.

TABLE 5

The interaction between KAl and anhydrous $HClO_4$ in CH_2Cl_2

Expt. No.	m_o /M	c_o /10^2 M	Temp. /deg.	Conversion /%	DP*
23	1.74	7.8	25	100	3.1
25	1.58	0.65	-53	100	2.3
50†	5.68	0.65	25	not determined	

† Bulk monomer

* DP of freeze-dried products

initiated reaction mixtures. The products were red liquids which absorbed strongly at 1740cm^{-1}, and at 3460cm^{-1}.

The interaction between acids and ketene acetals has been reviewed by McElvain.[1] When a ketene acetal is added to a solution of an acid it is quantitatively de-alkylated to the normal ester and the alkyl ester of the acid:

$$CH_2{:}C(OR)_2 \; + \; HX \; \longrightarrow \; CH_3.COOR \; + \; RX$$

If, however, the acid is added to the ketene acetal (as it was in this work) there is a secondary reaction, which involves the addition of the acid across two molecules of the ketene acetal:

$$2\ CH_2{:}C(OR)_2 \; + \; HX \; \longrightarrow \; CH_3.C(OR)_2.CH_2.C(OR)_2.X \; \longrightarrow$$

$$\longrightarrow \; CH_3C(OR){:}CH.COOR \; + \; ROH \; + \; RX$$

G.l.c. analysis of the reaction products indicated the presence of (at least) four components. The results can therefore be explained tentatively by regarding the interaction between KA1 and $HClO_4$ as consisting of two concurrent competitive reactions: polymerization and addition.

4.1.1.4 Stannic halides

Stannic halides are used extensively as initiators for cationic polymerizations. In this work experiments were carried out under nitrogen and under vacuum at different temperatures. The results are summarized in Table 6. The conversion curves in Figure 10 were constructed by monitoring the amount of residual monomer in the reacting mixtures by means of g.l.c.

TABLE 6

The polymerization of KA1 under nitrogen by stannic halides in CH_2Cl_2.

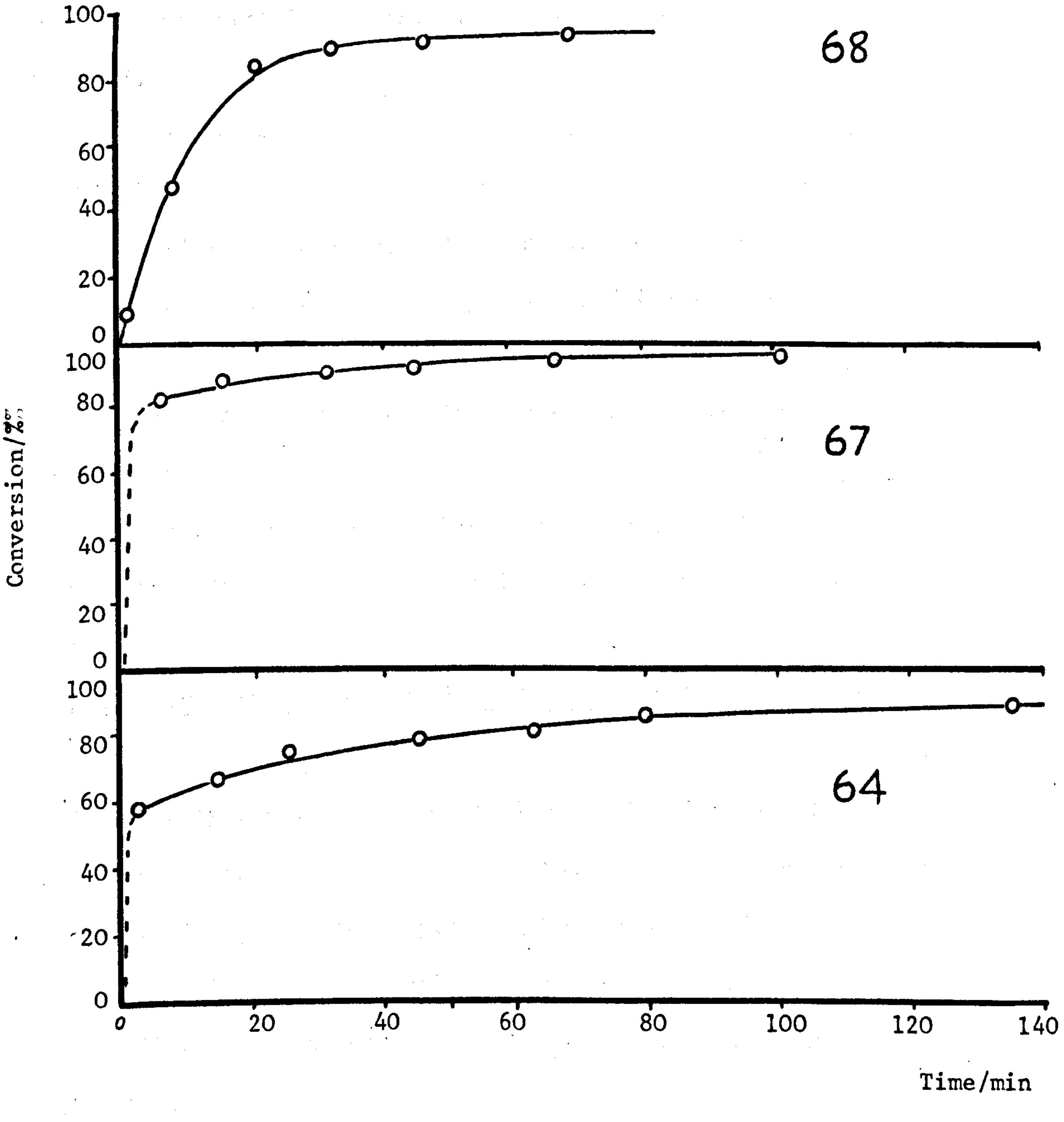
Expt. No	Nature of initiator	m_o /M	c_o /10^3 M	Temp. /deg.	Conversion /%	PPY /%	DP
63†	$SnCl_4$	0.29	13.6	-60	87	21	*
67	$SnCl_4$	0.79	26.2	-55	95	8	*
68	$SnCl_4$	0.30	7.5	-80	96	30	*
64	$SnBr_4$	1.57	3.4	20	90	5	1.9
65	$SnBr_4$	2.68	7.1	-50	94	10	1.9
66	$SnBr_4$	3.79	7.5	0	90	16	3.7

† Experiment carried out under vacuum.

* The DPs in expts. 63, 67, 68 could not be determined because the products were insoluble in all common organic solvents.

FIGURE 10

Conversion curves for the polymerization of KAl by $SnCl_4$ in CH_2Cl_2.



These plots show that the reactions are too fast to be followed by dilatometry. The reacting mixtures showed some interesting colour affects. At room temperature and at 0^o a deep-red colour was developed on adding the initiator to the monomer solution; this colour gradually faded and finally a pale-yellow solution was left. At low temperatures the reaction mixtures were colourless, but a permanent colouration could be induced by warming them up to about -20^o.

4.1.1.5 Other initiators and solvents

The results obtained from the interaction of KAl with several potential initiators in various solvents are shown in Table 7.

Since high conversions were always achieved, it seemed highly improbable that the observed low molecular weights were caused by the destruction of the active species.

The results indicate that polymer of "high" molecular weight can be obtained by means of a precipitation polymerization, i.e in solvents from which the polymer precipitates in the course of the reaction.

Benzoyl peroxide or azo-bis isobutyronitrile did not polymerize KAl either in bulk or in solution at room temperature. (18 to 20^o).

4.1.2 Polymerization of KAl in 100-120^o petroleum ether by stannic chloride.

The polymerizations were carried out in nitrogen-flushed test tubes. Table 8 shows the results. The reactions were very fast and always went to completion, but no attempt was made to follow the kinetics. The colour of the reacting mixtures varied from yellow to red depending on the concentrations of monomer and initiator.

TABLE 7

The polymerization of KA1 under vacuum - the effect of initiator and solvent

Nature of initiator	m_o /M	c_o /10^3 M	Solvent	Temp. /deg.	Conversion /%	PPY /%	DP
$EtAlCl_2$	0.7 to 1.2	0.1 to 8	Methylene dichloride	25	80 to 85	5	
$C_7H_7^+BF_4^-$	0.5 to 1.9	1 to 10	Methylene dichloride	-100 to 25	100	trace	
$C(NO_2)_4$	0.5 to 4.5	9 to 100	Methylene dichloride	20	100	trace	
$C(NO_2)_4$	0.63	28	Hexane	25	100	83	
$TiCl_4$	1.0 to 2.5	1.6 to 2.2	Hexane	-70 to 0	90 to 95	trace	
$TiCl_4$	1.57	0.69	Toluene	-40	90	10	
$HgCl_2$	2.0 to 3.5	0.07 to 30	Chlorobenzene	0 to 25	90	10 to 20	2 to 3
$SnCl_4$	1.14	8.6	100-120° pet. ether	25	100	60	6.4
$SnCl_4$	1.14	8.6	Toluene	25	95	10	

TABLE 8

The polymerization of KA1 in 100-120^{o} petroleum ether by stannic chloride.

Expt. No.	m_o /M	c_o /10^3 M	Temp. /deg.	PPY /%	DP*
104(a)	1.14	8.6	20-22	60	4.4
104(b)	0.28	8.6	20-22	39	3.0
104(c)	0.11	8.6	20-22	19	2.3
105(a)	1.14	8.6	0	73	4.7
105(b)	0.28	8.6	0	58	4.0
105(c)	0.11	8.6	0	28	2.5
105(d)	5.68	8.6	0	89	17.3
108(a)	1.67	8.6	20	73	4.8
108(b)	1.67	0.86	20	51	4.5
108(c)	1.67	0.086	20	59	10.2
108(d)	1.67	86	20	70	4.6
108(e)	1.67	0.30	20	50	6.1

* DP of freeze-dried products

The DPs of the polymers were high enough to enable quantitative measurements on the effect of m_o and c_o on the molecular weights to be carried out. One object of molecular weight studies is to identify all the chain-breaking reactions and to measure their rate-constants. The relevant measurements yield the ratios of the chain-breaking rate-constants to k_p. The method of obtaining these ratios is by the use of the Mayo equation.

Figure 11 shows the first Mayo plots (1/DP against $1/m_o$). From these plots the values of k_m/k_p and X/k_p were calculated by means of the equation:[35]

$$\frac{1}{DP} = \frac{k_m}{k_p} + \frac{1}{k_p m_o} (k_t + k_c c + k_a[A] + k_s[S] + J)$$

X is the coefficient of $1/k_p m_o$ and the symbols in ( ) have the following significance:

k_t is the rate-constant for unimolecular termination

c, [A] and [S] are the concentrations of initiator, co-initiator, and solvent respectively.

J is a term which accounts for all other possible, as yet unidentified, chain-breaking reactions.

Although the above equation is strictly only valid for the "instantaneous" DP, approximate values for the chain-breaking coefficients may be calculated from it. The calculated values from Figure 11 are $k_m/k_p = 0.19$ and $X/k_p = 2.9 \times 10^{-2}$ M at 20-22°, and 1.7×10^{-2} and 2.7×10^{-3} M at 0°. Since at the largest value of m_o (1.69 M) $X/k_p m_o \approx 0.0145$, the rate of chain-breaking by reactions with monomer is 0.19/0.0145 = 13 times greater than that due to all other chain-breaking reactions together. This is

FIGURE 11

The first Mayo plot for the degree of polymerization measured at complete conversion. System: KAl/$SnCl_4$/pet. ether, $c_o = 8.6 \times 10^{-3}$ M

⊙ 20°

● 0°

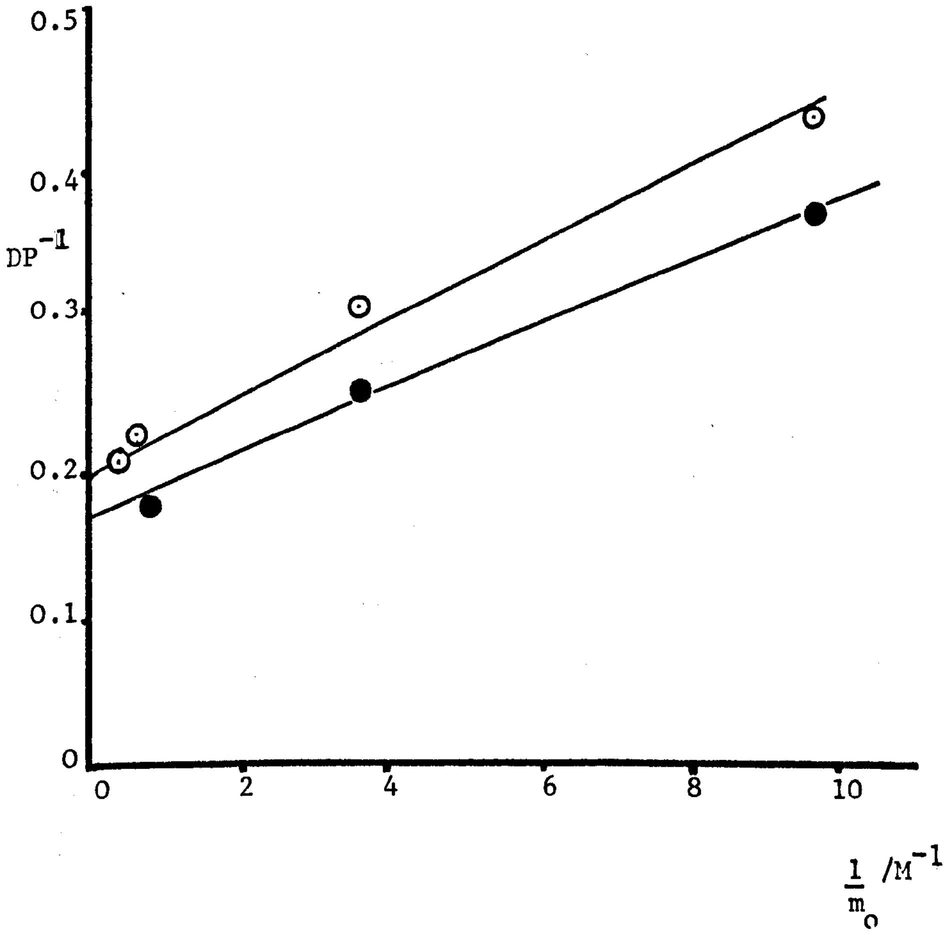
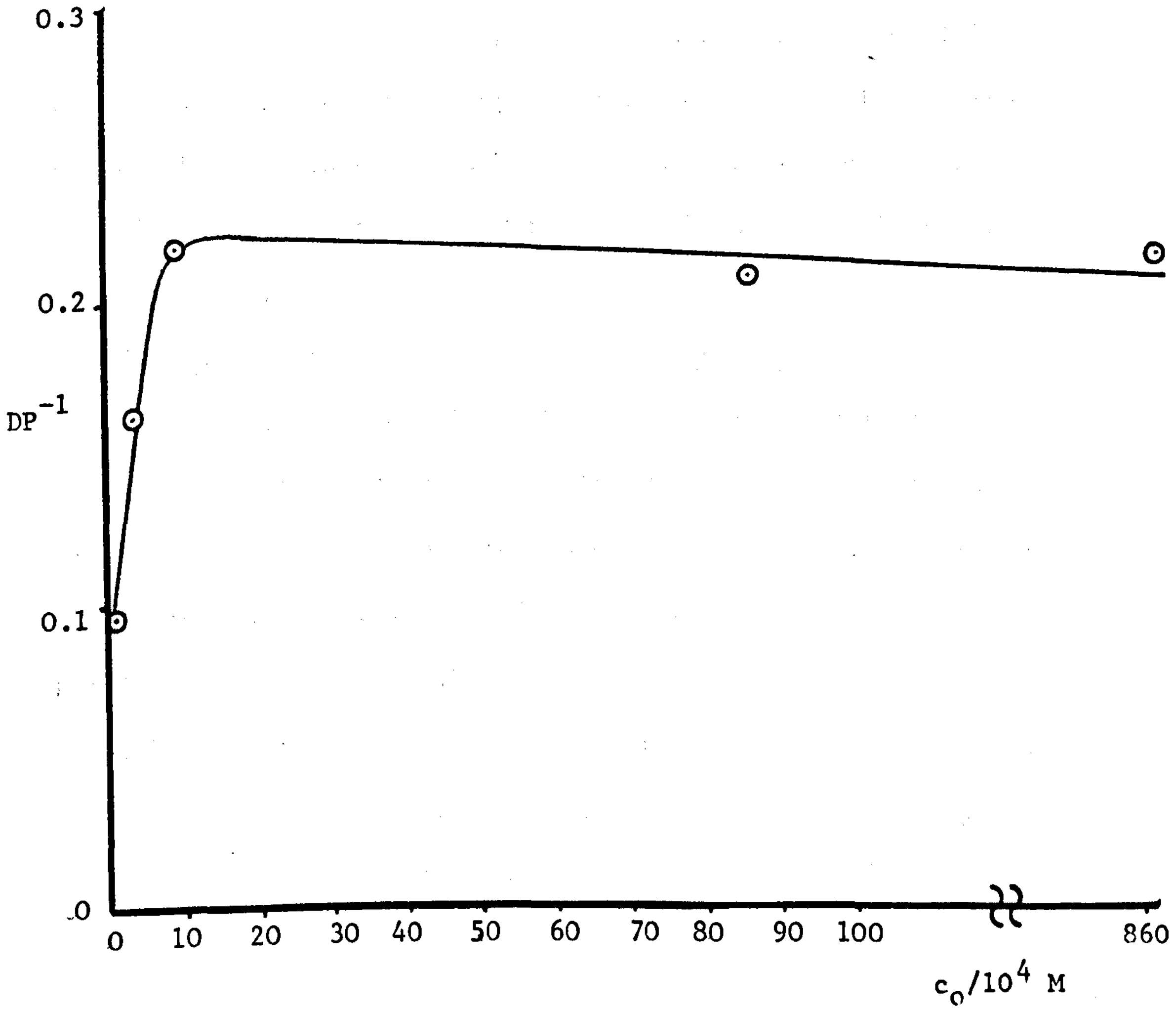


FIGURE 12

The second Mayo plot for the degree of polymerization measured at complete conversion. System: $KAl/SnCl_4/$ pet. ether at 20°, $m_0 = 1.67$ M



not unexpected, since monomer transfer reactions have been shown to be the principal chain-breaking reactions in many cationic polymerizations. The influence of temperature on the transfer reactions involving the monomer is reflected in the intercepts of the first Mayo plots. Since these are the same (within experimental error) we conclude that $E_m - E_p \approx 0$. The apparent linearity of the first Mayo plots at least for $m_o > 0.517$ indicates that propagation is a second order reaction:[35]

$$V_p = k_p \, m[P_n^+]$$

The second Mayo plot in Figure 12 shows that chain-breaking reactions with the initiator are important in this system. It also shows the expected result that the formation of high polymer is favoured by a combination of high m_o and low c_o. It has been found that in many systems[40] the DP goes through a minimum or falls to a constant level as the concentration of one of the reagents is increased. The plot in Figure 12 may be explained by there being present in the system a reagent, which itself may or may not be a chain-breaker, but forms a (more effective) chain-breaking reagent with another reagent, which itself is not a chain-breaker.[40]

4.1.3. The heterogeneous polymerization of KAl

The interaction of KAl with sparingly-soluble initiators (Table 9) was found to produce polymer with a molecular weight higher than that obtained from homogeneous systems. The polymerizations were carried out in nitrogen-flushed screw-capped bottles with stirring. The optimum conditions for the formation of high polymer were high m_o and low temperature. In an unstirred bulk polymerization the polymer around the initiator was yellow to red. The colour could be destroyed by the addition of

TABLE 9

The heterogeneous polymerization of KA1

Initiator		Monomer	Solvent		Temp.	Conversion	PPY	DP
Nature	Quantity/g	Quantity/g	Nature	Quantity/ml	/deg.	/%	/%	
$CdCl_2$	0.001	5.0	-	-	20	73	59	22.7
	0.001	2.39	-	-	20	-	32	18.5
	0.01	10.0	-	-	20	100	20	3.5
	0.001	6.0	Methylene dichloride	5.05	25	67	10	2.2
	0.001	5.1	Methylene dichloride	5.0	-80	10	5	-
	0.001	2.0	Methylene dichloride	2.0	-35	20	5	-
	0.001	5.0	Toluene	5.0	-80	20	10	16.0
$HgCl_2$	0.001	5.0	-	-	20	76	36	11.8
	0.1	3.5	Methylene dichloride	6.5	25	40	23	2.0
$C_7H_7^+BF_4^-$	0.001	2.0	-	-	20	100	100	-
	0.001	2.0	Hexane	16		70	30	-

triethylamine and the polymers were white waxes or powders. The essentially heterogeneous nature of these polymerizations was confirmed by filtering a reacting mixture through a No.3 glass sinter, whereupon the rate of polymerization was reduced drastically, but not to zero. It was suspected that many of the polymerizations of bulk monomer with other initiators, e.g. $SnBr_4$, $BF_3.Et_2O$, were in fact heterogeneous, but this idea was difficult to test because of the rapidity of the polymerization and the insolubility of the polymer in the monomer.

A Ziegler-Natta catalyst, viz. $TiCl_3$ and Et_2AlCl, did not polymerize KA1 in hexane.

4.2 The polymerization of KA2

Ketene diethyl acetal was not a very promising monomer for a serious academic study because of the insolubility of its polymer in all common organic solvents. However, it is very easy to prepare and purify, and a comparison of its polymerizability with that of KA1 was expected to give some insight into the polymerization mechanism.

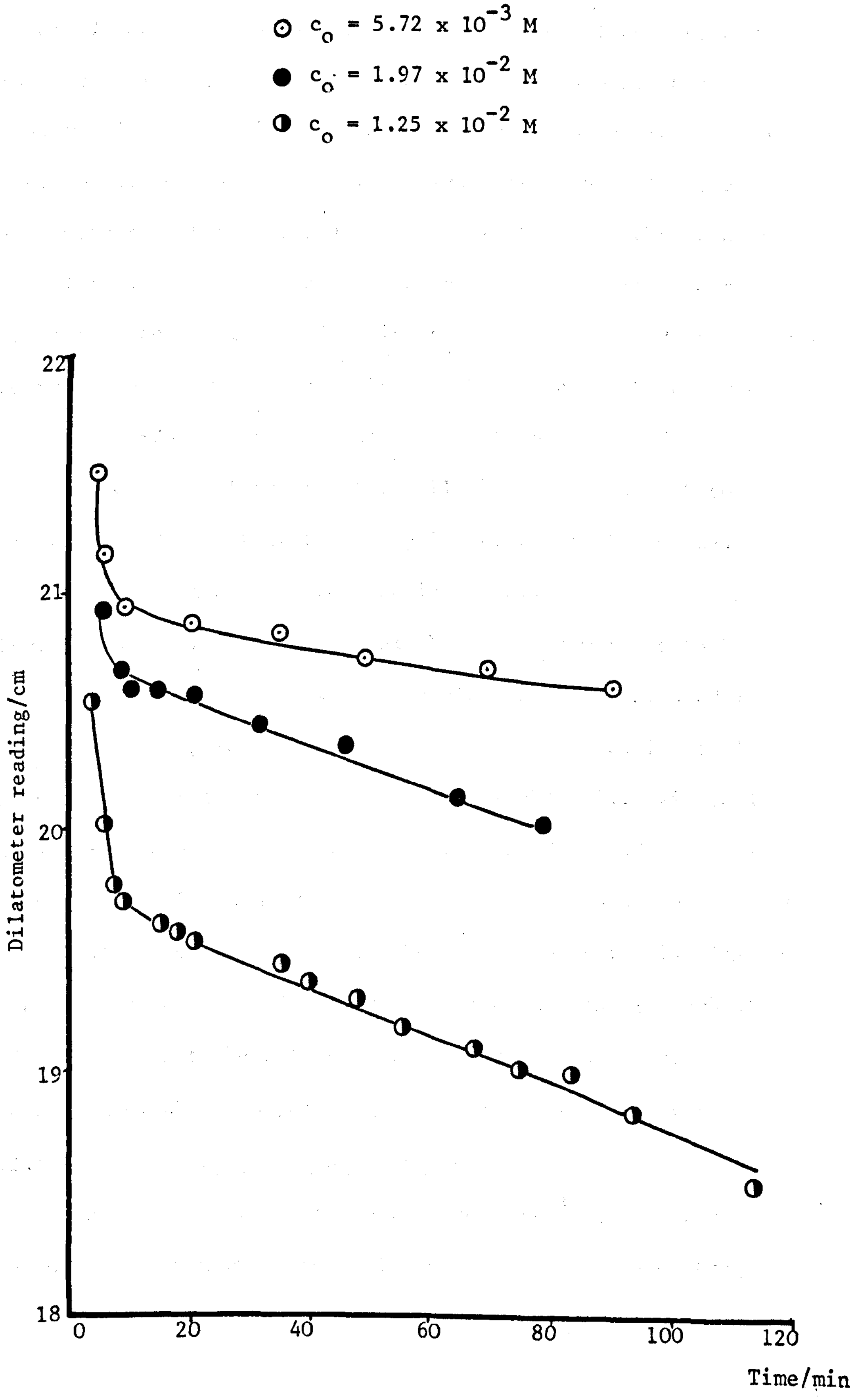
4.2.1 The polymerization of KA2 in methylene dichloride

4.2.1.1 Stannic chloride

Most of the work on KA2 was carried out with $SnCl_4$ as the initiator in order to be able to compare the results directly with those obtained with KA1. All the experiments were carried out in vacuum dilatometers with highly purified materials. Figure 13 shows the dilatometric contractions. The initial dilatometer reading could not be determined because observations of the reference dilatometer showed that about 10 minutes was required for the contents to come to temperature equilibrium.

FIGURE 13

The conversion curves for the polymerization of KA2 by $SnCl_4$ in CH_2Cl_2 at -60^o - effect of c_o; m_o = 0.33 M.



The reaction mixtures were colourless throughout the polymerizations, although traces of yellow polymer were formed on the walls of the part of the apparatus which protruded from the low-temperature bath. Towards the end of the polymerizations some turbidity was developed and finally the contents of the dilatometer were transformed into a white solid. As a consequence of this the final reading of the dilatometer could not be determined because of distortion of the meniscus. It was necessary to transfer the contents of the dilatometer to the side-arm of the apparatus for killing. This required the apparatus to be warmed to room temperature to lower the viscosity of the products and to increase the vapour pressure of the solvent. The products turned red above about -20° and the colour could not be destroyed completely by either of the killing agents. All the reactions went to completion and the products were pale yellow sticky solids.

One reaction was carried out in the dilatometer shown in Figure 1 which allowed samples of the reacting mixture to be taken at regular intervals. The samples were precipitated in pentane and the percentage of the product which was insoluble was noted, together with the conversion (Table 10). Figure 14 shows a simultaneous plot of dilatometer reading and conversion against time. The results show that the reactions are too fast to be followed by dilatometry. The conversion curve is similar to that obtained with KA1 under similar conditions (Figure 10) and suggests that the nature of the reaction changes at a conversion of about 60%, although the PPY remains almost constant.

4.2.1.2 Other initiators and solvents

A few exploratory experiments were carried out to compare the polymerization characteristics of KA2 with those of KA1.

TABLE 10

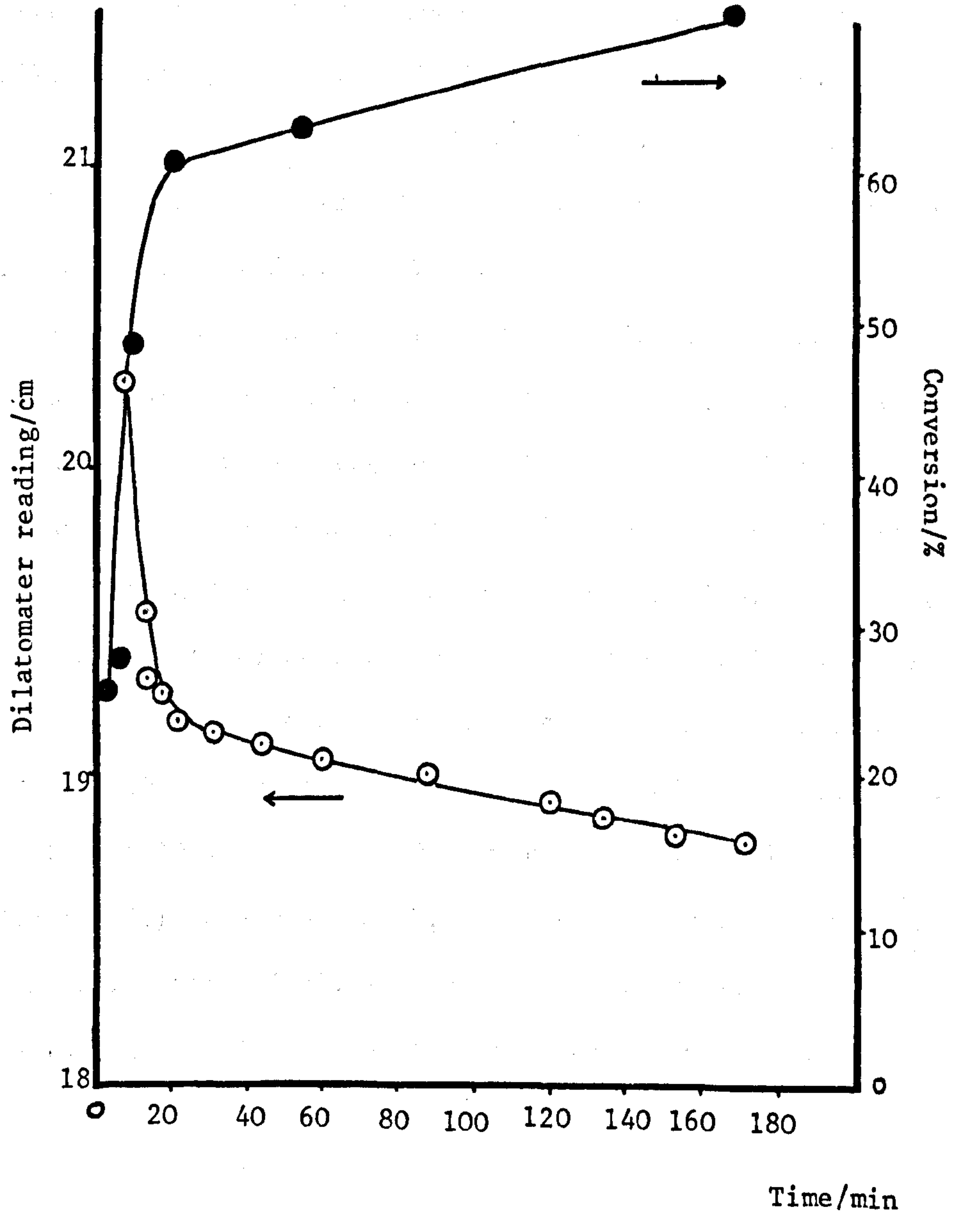
The polymerization of KA2 by $SnCl_4$ in CH_2Cl_2 at -80° —— sampling experiments; $m_o = 0.33$ M, $c_o = 1.25 \times 10^{-2}$ M.

(see Figure 14)

Time /min	Dilatometer reading /cm	Conversion /%	PPY /%
0.5	-	26.9	52
3	-	29.2	57
8	20.253	46.9	
9	19.610		
11	19.412		
13	19.384		
18	19.285	60.3	
27	19.218		
44	19.089		
59	19.031	62.0	54
93	18.960		
117	18.890		
133	18.834		
148	18.750		
169	18.742	69.0	
∞	-	100.0	55

FIGURE 14

The polymerization of KA2 in CH_2Cl_2 by $SnCl_4$ at -80°, $m_o = 0.33$ M, $c_o = 1.25 \times 10^{-2}$ M.



With $EtAlCl_2$ in methylene dichloride at room temperature (c_o = .05 to 1.0 x 10^{-2} M, m_o = 1.05 M) the yield of solid polymer amounted to 10%. Tetranitromethane in hexane (c_o = 1.57 x 10^{-3}, m_o = 0.76 M) gave a yield of 26%. With insoluble initiators like $CdCl_2$ the addition of 0.002g of the initiator to 1.3g of the monomer gave 80% of solid polymer, but the PPY was halved if the monomer was diluted with 3 mls of methylene dichloride.

4.3 The polymerization of KA3

The polymerization of ketene ethyl methyl acetal has not been reported. This monomer seemed very suitable for a quantitative study of its polymerizability because it does not suffer from either of the disadvantages of KA1 or KA2; KA3 is quite volatile and its polymer is soluble in organic solvents. A series of experiments was carried out with highly purified materials in the adiabatic calorimeter according to the procedure described in section 2.5, and Table 11 shows the results.

Figure 15 shows the temperature/time plots. The polymerizations were characterized by an inhibition period, an acceleration and a first-order phase (Figures 16-18). The fact that the reactions did not go to completion during this first-order phase, but eventually did reach it by a very slow reaction, is consistent with the observations that the polymerization of KA1 and KA2 also took place in two quite distinct stages. If a polymerization of KA3 was allowed to continue after the end of the exotherm, a conversion of 100% was attained eventually. Figure 19 shows that the first-order rate-constant k_1 increases linearily with m_o^2. The 'induction period' (I.P.) was determined by drawing a tangent to the inflexion point on the temperature/time plots and

TABLE 11

The polymerization of KA3 by $SnCl_4$ in 100-120° pet. ether - adiabatic calorimetry.

Expt. No.	m_o /M	c_o /10^2 M	Temp. /deg.	Conversion /%	DP	I.P. /s	k_1 /10^2 s^{-1}
121	1.69	1.06	0	72.5	3.8	17.5	9.72
124	0.845	1.06	0	73.8	4.7	32	2.62
126	0.28	1.06	0	73.0	4.1	200	0.119
122	1.69	1.06	-70	0*	-	-	-
123	1.69	1.06	-40	0*	-	-	-
128†	0.28	1.06	0	0*	-	-	-

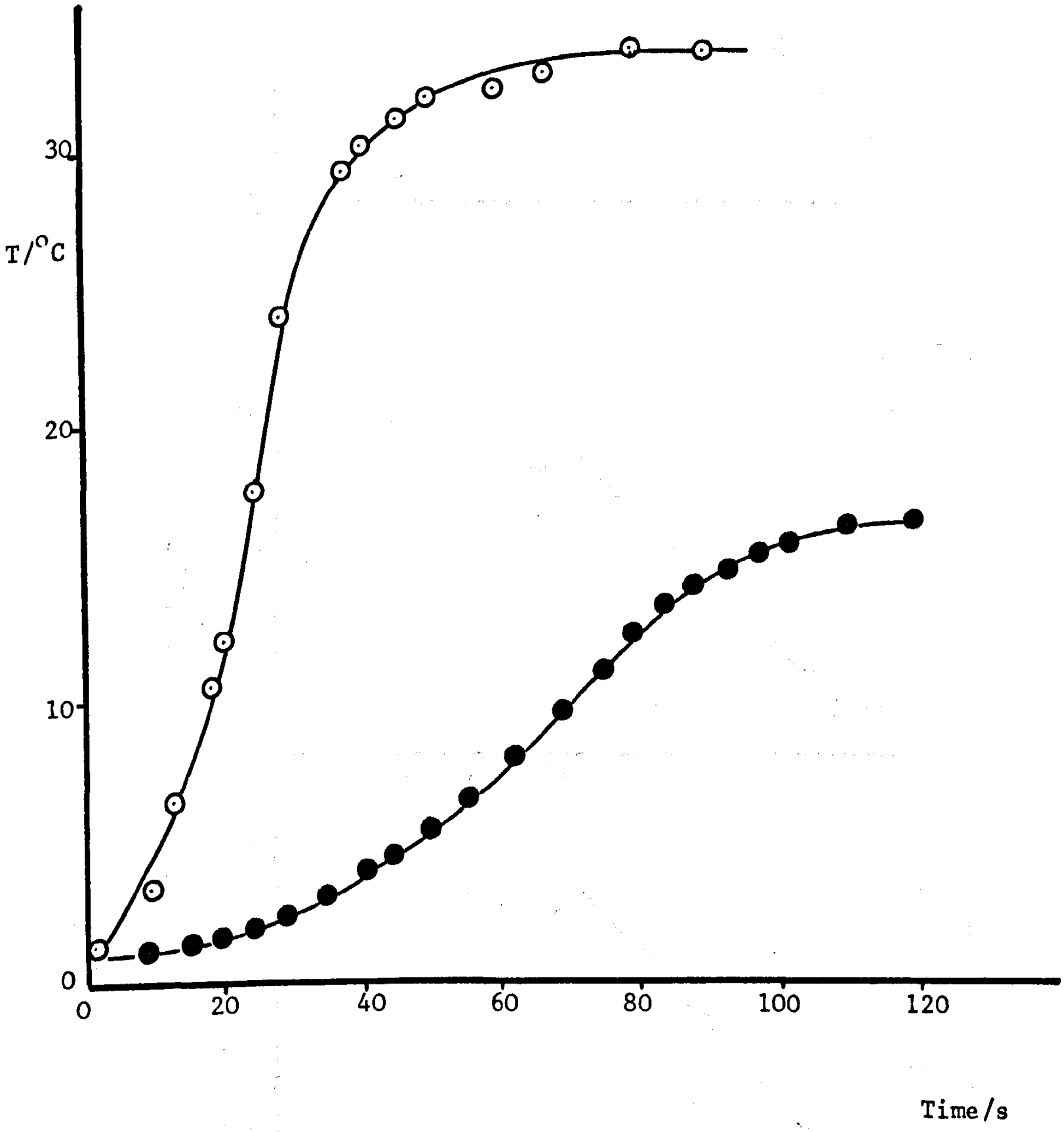
* No temperature rise observable in 20 mins

† Conducted in the presence of t-butanol, [t-BuOH] = 4.5×10^{-3} M.

FIGURE 15

Typical temperature/time plots for the polymerization of KA3 by $SnCl_4$ in pet. ether, $c_o = 1.06 \times 10^{-2}$ M

⊙ $m_o = 1.69$ M
● $m_o = 0.845$ M



FIGURES 16-18

First-order plots for the polymerization of KA3 by $SnCl_4$ in pet. ether.

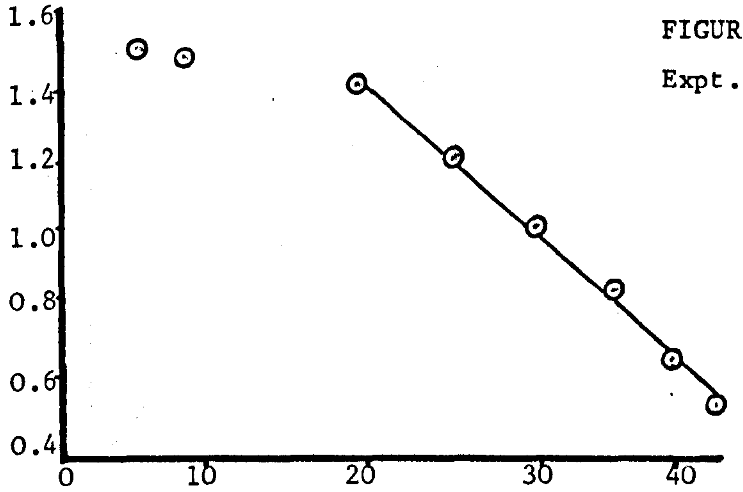


FIGURE 16
Expt. 121

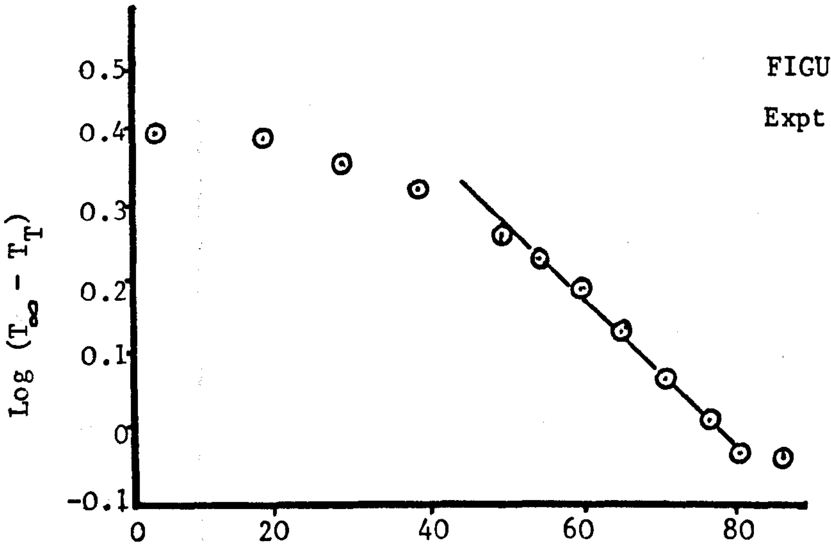


FIGURE 17
Expt. 124

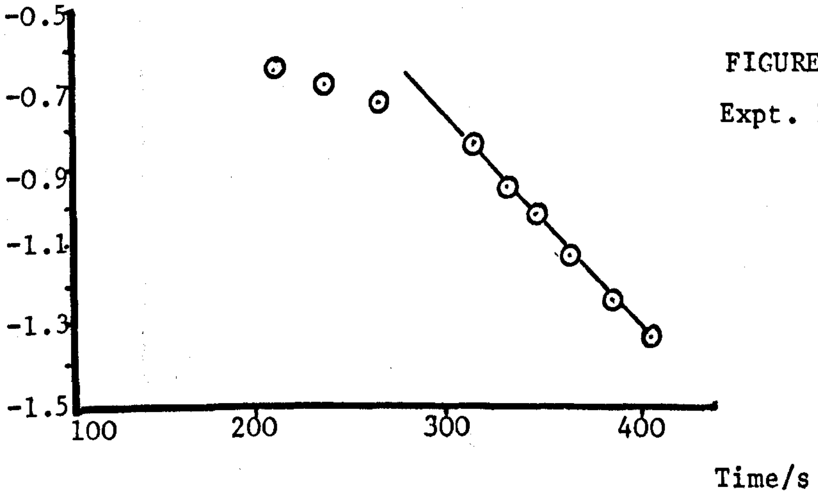


FIGURE 18
Expt. 126

FIGURE 19

The influence of m_o on k_1.

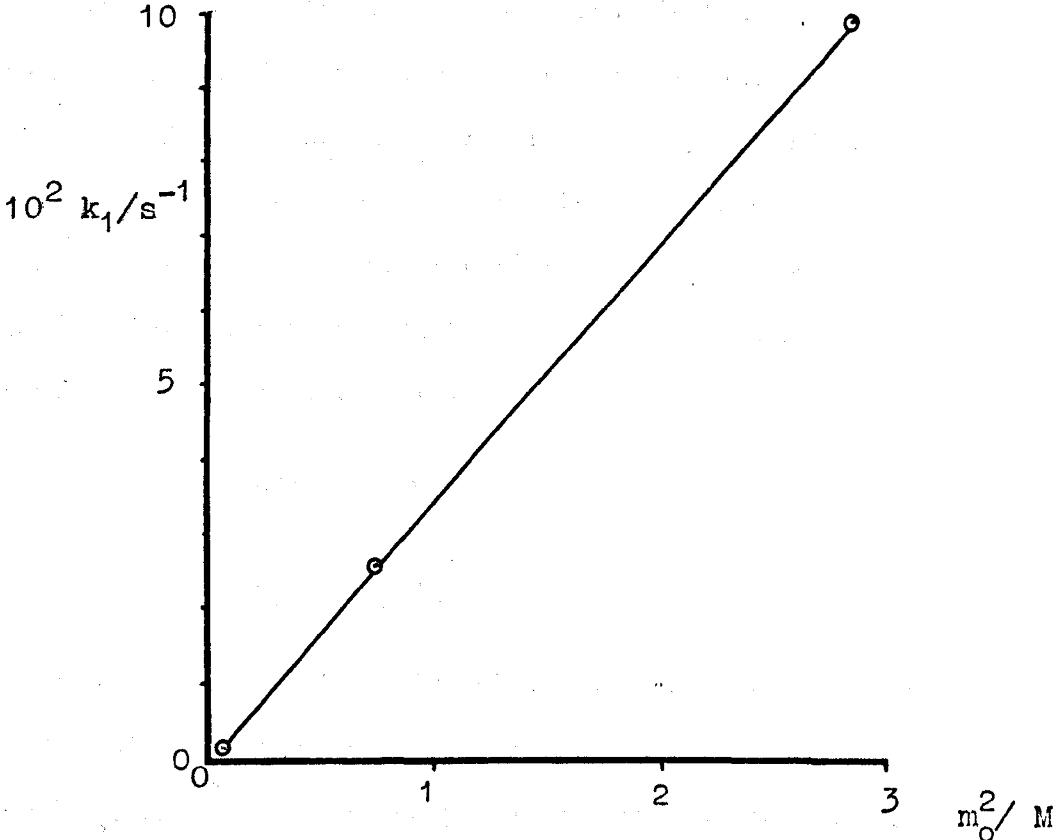
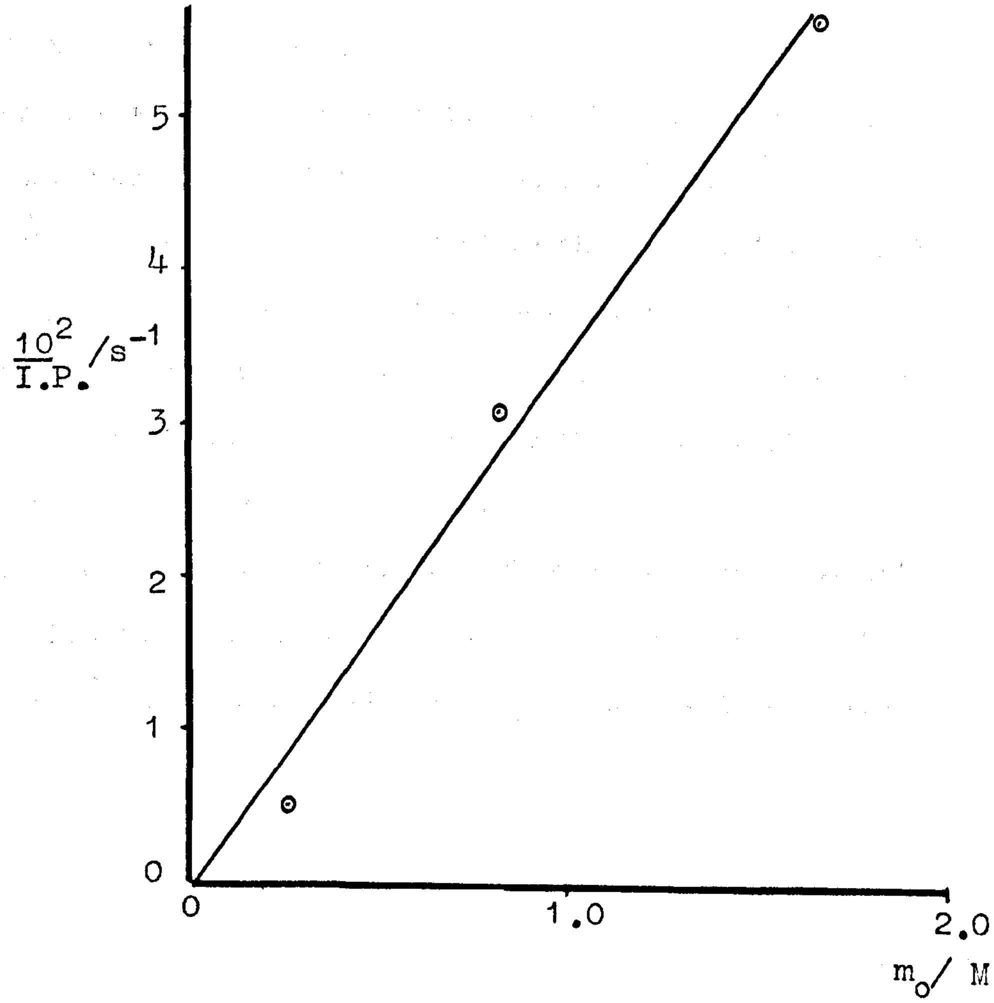


FIGURE 20

The influence of m_o on I.P.



extrapolating it to intersect the abscissa. Figure 20 shows that the reciprocal of the induction period plotted against m_o gives a straight line passing through the origin.

The dependence of k_1 on m_o^2 and induction periods have been observed frequently in cationic polymerizations (e.g. refs. 35-37). From the present results it follows that between the inflexion point and the asymptote of the first-order phase the rate-equation is:

$$- d\,m/dt = k_1 m$$

$$\text{and } k_1 = k_2 m_o^2$$

There are several possible explanations for the above features. Since the values of k_1 were determined over a very wide range of m_o, the concurrent change in polarity of the reaction medium may have affected the rate. Also the presence of a co-initiator in the monomer would account for both the increase in k_1 and the decrease in I.P. with increasing m_o. Apart from water, the most probable co-initiator likely to be present in the monomer was t-butanol in trace amounts. However, the addition of a small amount of t-butanol to the monomer (expt. 128) rendered the initiator completely inactive. In addition to showing that t-butanol was not an active co-initiator when present in these quantities, this result indicated that wastage of initiator occurs by some other process.

Further investigations in the calorimeter, such as a variation of the initiator concentration, were not carried out because the reaction products, which were either sticky orange solids or red oils, had very low molecular weights (Table 11 and Figure 21). The adiabatic technique is not very useful for the study of such systems because the heat of reaction for each of the first ca. 5 oligomerisation steps probably decreases towards an asymptotic value, as for α-methyl styrene.

The induction period in the calorimeter experiments was found to be increased drastically by lowering the initial temperature. This was probably partly caused by the insolubility of the monomer at low temperatures. Several experiments were carried out at temperatures down to -100° in both $100-120^{\circ}$ petroleum ether and in methylene dichloride, but, although the polymerizations became slow enough to be followed dilatometrically, the maximum DP achieved was only 5.5.

The polymerization of 1.78g of KA3 by 0.01g of $CdCl_2$ in 7.0g of refluxing benzene gave the conversion curve shown in Figure 22, but the DP of the polymer was only 4.3.

4.4 Copolymerization

Copolymerization studies are often very useful in elucidating problems in reaction mechanism. In particular, for well-behaved systems, it should be possible to measure the absolute rate-constants for a monomer by copolymerizing it with another monomer for which the corresponding rate-constants are known. Unfortunately, the full potential of this technique has not yet been realised because of the difficulties inherent in the study of cationic polymerizations.

Copolymerization is also often useful in improving the properties of homopolymers. For example, the incorporation of isobutyl vinyl ether in a copolymer system is likely to confer the following improvements in major properties: higher flexibility, better tack,

FIGURE 21

The influence of m_o on DP for expts. 121, 124 and 126.

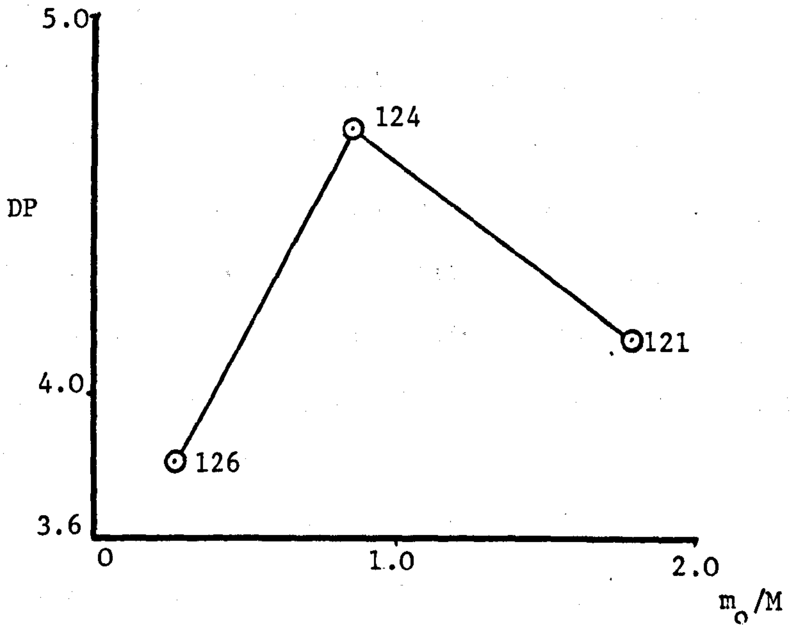
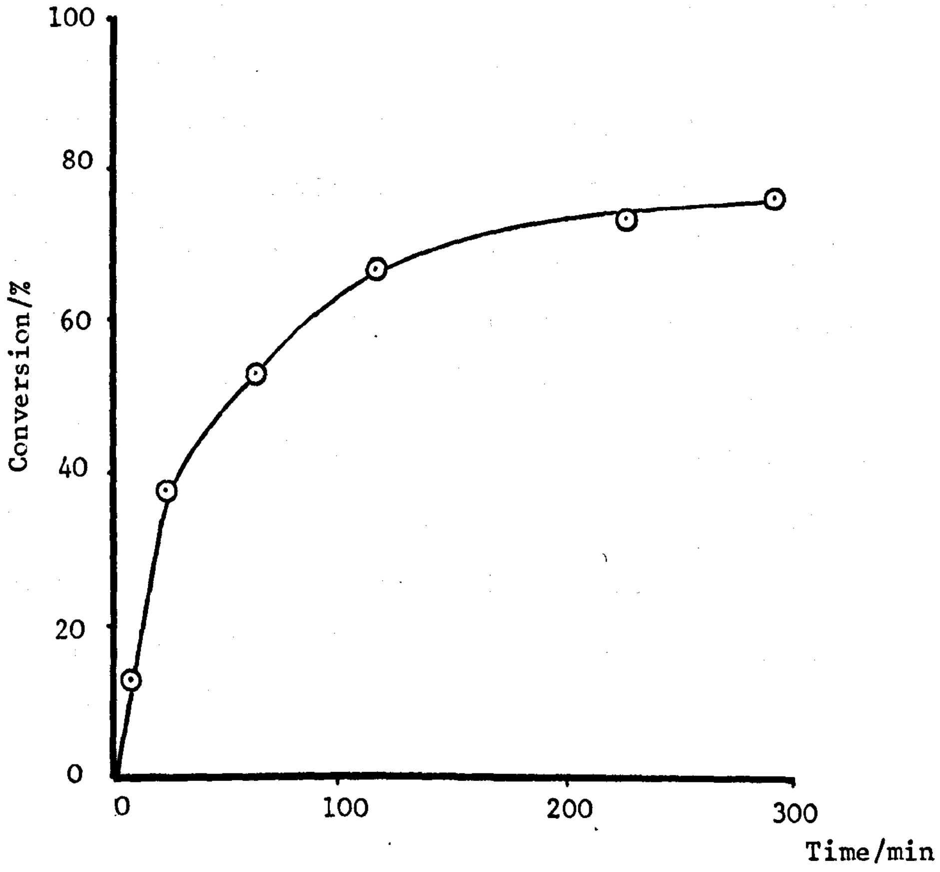


Figure 22

The conversion curve for the polymerization of KAl by $CdCl_2$ in boiling benzene.



and greater adhesion. The classic case of cationic copolymerization is of course, the incorporation of a small number of isoprene units into polyisobutene; the resulting points of unsaturation are then potential sites for vulcanization.

In the case of ketene acetals, the incorporation of these monomers in a copolymer, followed by the hydrolysis of the acetal groups, should produce a material having pendent oxo groups extending from the backbone of the copolymer. These chemically reactive groups permit the addition of functional groups to produce copolymers having multifunctional properties and are of course also potential sites for vulcanization.

4.4.1 The copolymerization of KA1 and KA2

A few experiments were carried out to see whether KA1 and KA2 could be copolymerized. If the observed insolubility of poly-KA2 was in fact caused by its high degree of crystallinity then the presence of KA1 units would be expected to remove the regular structure of poly-KA2 and thus reduce its tendency to crystallize. The results are shown in Table 12. It was found that solid polymer could only be obtained by copolymerizing the monomers with the insoluble initiator $CdCl_2$. The infra-red spectra of the products from experiments 84 and 88 are shown in Figure 23 together with the spectra of the homopolymers. The 3,000 cm^{-1} region of the spectrum can be used to obtain a qualitative measure of the copolymer composition. Making the following assignments:[39] 2970 cm^{-1} and 2880 cm^{-1} (CH_3 vibrations), 2925 cm^{-1} (CH_2 vibrations) and 2820 cm^{-1} (OCH_3 vibrations) the spectra show that the product from experiment 88 contains the higher fraction of $-OCH_3$ groups. The p.m.r. spectrum of the polymer from experiment 88 indicated the presence of two types of methyl groups.

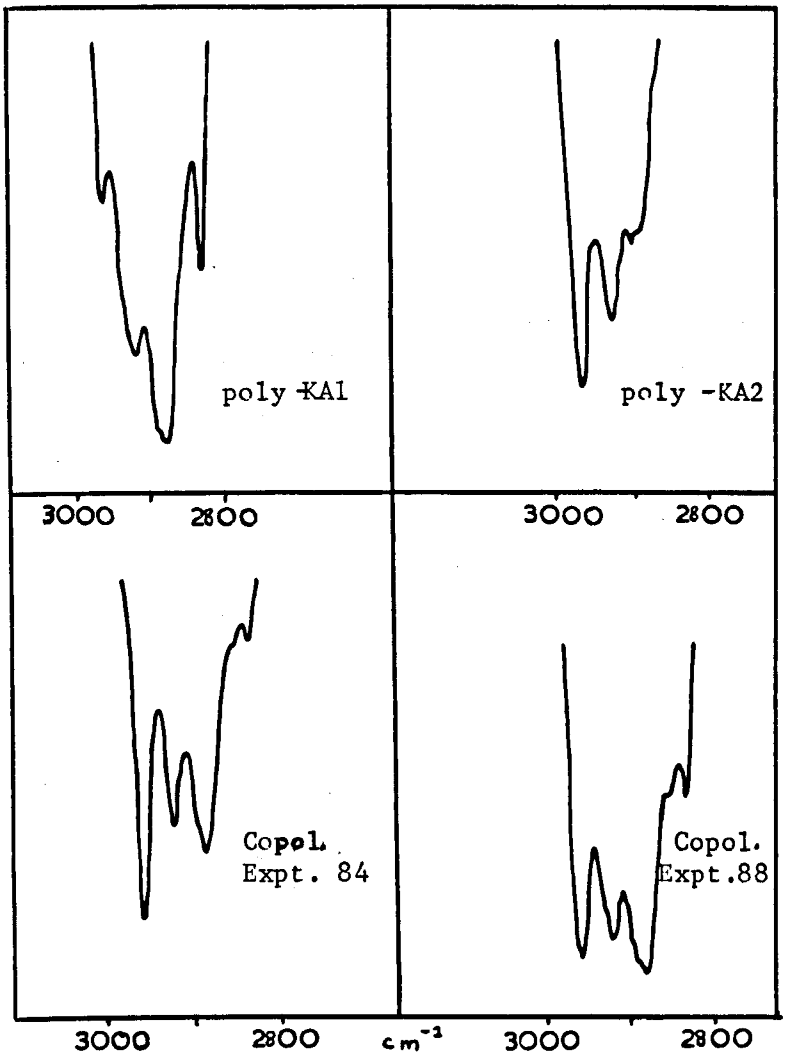
TABLE 12

The copolymerization of KA1 and KA2

Expt. No.	Initiator	KA1 m_o /M	KA2 m_o /M	Solvent	Temp. /deg.	Nature of product	10^3 M_n
69	1.42×10^{-2} M $SnCl_4$	0.28	0.37	Methylene dichloride	0	Yellow viscous liquid	-
84	3×10^{-3} M $SnCl_4$	0.28	0.28	Methylene dichloride	-60	Yellow sticky solid	-
88	.01g $CdCl_2$	3.23	3.23	-	0	Pale yellow wax	3.32
89	.01g $CdCl_2$	3.23	3.23	-	-20	Pale yellow wax	2.61

FIGURE 23

The i.r. spectra of the homopolymers and the copolymers of KA1 and KA2.



Although the polymers were not fractionated, further evidence of the formation of a copolymer, rather than a mixture of the two homopolymers, was provided by the fact that the products were found to be completely soluble in methylene dichloride and in chloroform even at -60°.

4.4.2 Copolymerization of KAl with vinyl ethers

The attempted copolymerization in bulk of an equimolar mixture of KAl and ethyl vinyl ether by $CdCl_2$ at room temperature gave a white solid which had an i.r. spectrum identical to that of poly-KAl. A similar result was obtained with isobutyl vinyl ether. These results lend credence to the idea that the polymerization of KAl by $CdCl_2$ is a heterogeneous process; vinyl ethers cannot be polymerized by cadmium chloride.

The interaction of mixtures of KAl and ethyl vinyl ether with stannic chloride at temperatures down to -60° gave products which were low molecular weight viscous liquids.

4.4.3 Copolymerization of KAl with N-vinyl carbazole

Mercuric chloride is known to polymerize N-vinyl carbazole (NVC). However, the addition of 0.001g of $HgCl_2$ to a solution of 5g of NVC in 5g of KAl at 18° gave an off-white powdery solid which was shown to be poly-KAl by its i.r. spectrum.

An equimolar mixture of KAl and NVC (m_o = 0.56 M) was polymerized by $BF_3.Et_2O$ ($c_o = 1 \times 10^{-3}$ M) in 100-120° petroleum ether under nitrogen at 20°. After the reaction was complete, the product, which was a pale yellow wax, was poured into pentane and the solids were filtered off. The solid product had M_n = 794 and was shown to contain 19.2%w/w of NVC by its U.V. spectrum in chloroform.[39]

4.4.4 The attempted copolymerization of KA2 and isobutene

The addition of $SnCl_4$ to a mixture of isobutene and KA2 in methylene dichloride, under vacuum at -78^o, transformed the reactants, over a period of several hours into a translucent white solid from which a sticky red solid (yield 5%) was isolated by freeze drying. The range of reactant concentrations tried was $[isobutene] = 0.4$ to 3.9 M, $[KA2] = 0.04$ to 0.623 M, $c_o = 1.34 \times 10^{-3}$ to 2.98×10^{-2} M. The products were not investigated further.

4.4.5 The attempted copolymerization of KA1 and methyl methacrylate

Monomers which cannot be homopolymerized by free-radical initiators will often add to the radicals derived from other monomers to form copolymers.

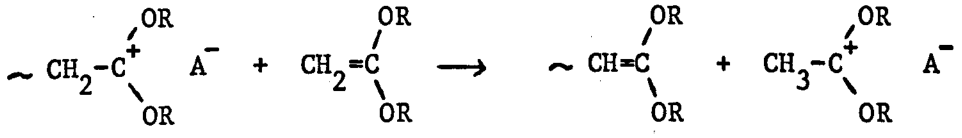
To 1.7g of an equimolar mixture of KA1 and methyl methacrylate (MMA) was added 1.5×10^{-2}g of benzoyl peroxide. The mixture was maintained at 60^o for two days and the resulting yellow viscous solution was poured into pentane to give 0.6g of a white granular precipitate, which was shown to be poly-MMA by its i.r. spectrum. This result shows that MMA is much more reactive than KA1 towards the MMA radical or that KA1 is completely unreactive towards this radical.

4.5 End-group analysis and reaction characteristics

Since only materials with low molecular weights were produced by soluble initiators, experiments were directed towards an investigation of the chemistry of the polymerization and the nature of the products.

4.5.1 Infra-red spectroscopy

There are some difficulties associated with the search for end-groups in poly-ketene acetals. The spectra of ketene acetals have not been studied in any detail although the effect of there being two oxygen atoms in conjugation with the olefinic double bond has been shown to be very important in lowering the frequency of the $:CH_2$ wagging mode.[38] The main differences between the i.r. spectrum of KAl and its polymer (DP = 20) are shown in Table 13. The disappearance of the absorptions associated with the $:CH_2$ group was as expected. The increase in intensity of the peaks at 2880 and 1376 cm^{-1} shows that the production of methyl end-groups by proton transfer from the growing chain to the monomer is important:



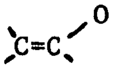
$$\sim CH_2-\underset{OR}{\overset{OR}{C^+}}\ A^- + CH_2=\underset{OR}{\overset{OR}{C}} \longrightarrow \sim CH=\underset{OR}{\overset{OR}{C}} + CH_3-\underset{OR}{\overset{OR}{C^+}}\ A^-$$

The intensity of absorptions associated with the terminal trisubstituted double bond which is produced by this mechanism are very low and hence their absence in the spectrum of a polymer with DP = 20 is not unexpected.

The spectra of several samples of poly-KAl were compared. In particular the spectra of high (DP = 14 to 20) and low (DP = 2 to 4) polymers were analysed carefully. There are several additional peaks present in the spectra of the low polymers which can be ascribed to end-groups. Strong absorptions at 1600 cm^{-1} and 790 cm^{-1} indicate the presence of a trisubstituted double bond. The low frequency of the C=C absorption (1600 cm^{-1}) may be caused by it being conjugated. There was also an OH peak at 3500 cm^{-1} and a very weak absorption at 890 cm^{-1}. The peak at 890 cm^{-1} seemed to be associated with the OH group as its

TABLE 13

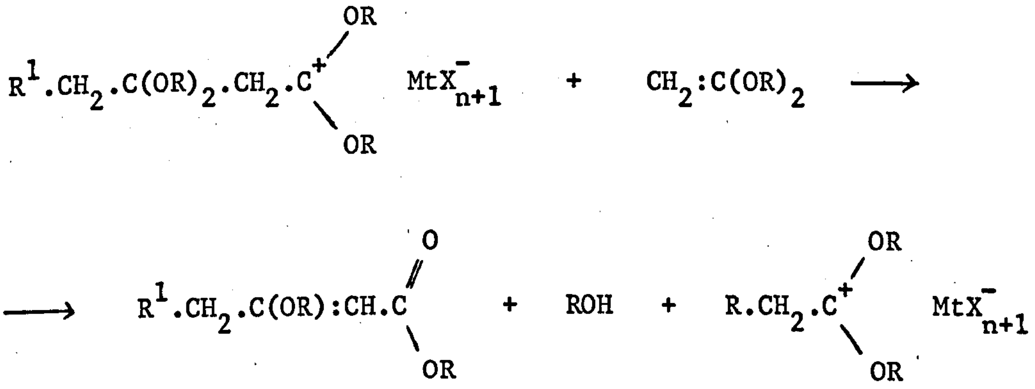
The i.r. spectra of KAl and the polymer formed from the $CdCl_2$ initiated polymerization of KAl at room temperature (the polymer was the fraction insoluble in pentane, DP = 20)

Monomer absorption $/cm^{-1}$	Effect of* polymerization	Assignment
3110w	D	Vinyl CH stretch
2970 2925 2880	Increase in 2880	Alkane C-H stretch, $-CH_2$ and $-CH_3$
2820		$-OCH_3$ stretch
1650 vs	D	Vinyl C=C stretch
1450s	U	asymmetric CH_3 def. and $-CH_2-$def.
1376m	I	symmetric CH_3 def.
1287s	D	 stretch
1200 1130 1098 1055	Peaks at 1200 1155, 1130 vs, 1075	C-O-C-O-C asymmetric stretch
980m	U	
	946	
870m	D	$:CH_2$ twist
850m		
716m	D	$:CH_2$ wag.

vs = very strong
s = strong
m = medium
w = weak

* D, peak disappears; R, intensity of peak is reduced; U, peak unaffected; I, intensity of peak is enhanced.

intensity varied with that of the band at 3500 cm^{-1} and it disappeared in samples with no OH groups. A similar phenomenon has been reported by Jones.[22] A strong absorption at 1740 cm^{-1} indicates the C=O stretching vibration of an ester.



$$\mathrm{R^1.CH_2.C(OR)_2.CH_2.C^+}\begin{matrix}\mathrm{OR}\\ \mathrm{OR}\end{matrix}\quad \mathrm{MtX^-_{n+1}} + \mathrm{CH_2{:}C(OR)_2} \longrightarrow$$

$$\longrightarrow \mathrm{R^1.CH_2.C(OR){:}CH.C}\begin{matrix}\mathrm{O}\\ \mathrm{OR}\end{matrix} + \mathrm{ROH} + \mathrm{R.CH_2.C^+}\begin{matrix}\mathrm{OR}\\ \mathrm{OR}\end{matrix}\quad \mathrm{MtX^-_{n+1}}$$

In addition to acting as a chain-transfer agent, the alcohol formed in this reaction may react with the monomer to produce the corresponding orthoester:

$$\mathrm{CH_2{:}C(OR)_2} + \mathrm{ROH} \longrightarrow \mathrm{CH_2.C(OR)_3}$$

This reaction may be one of the reasons why the polymerizations nearly always went to completion, as measured by the complete disappearance of the monomer. It is impossible to estimate the changes in the i.r. absorption of the ether groups with their changing environment because of the complexity of the spectra in the 1000–1300 cm^{-1} region. A corollary of the fact that additional peaks in the spectra of low polymers are due to end groups is that these peaks should disappear or their intensities should be reduced in the spectra of polymers of higher DP. This was found to be the case except that a strong absorption appeared at 950 cm^{-1} in the spectra of the high polymers. There is no information on absorptions at this frequency for this type of compound and the origin of this peak is not known. There was no evidence in any of the i.r. spectra for the existence of carbon-halogen bonds in the polymers.

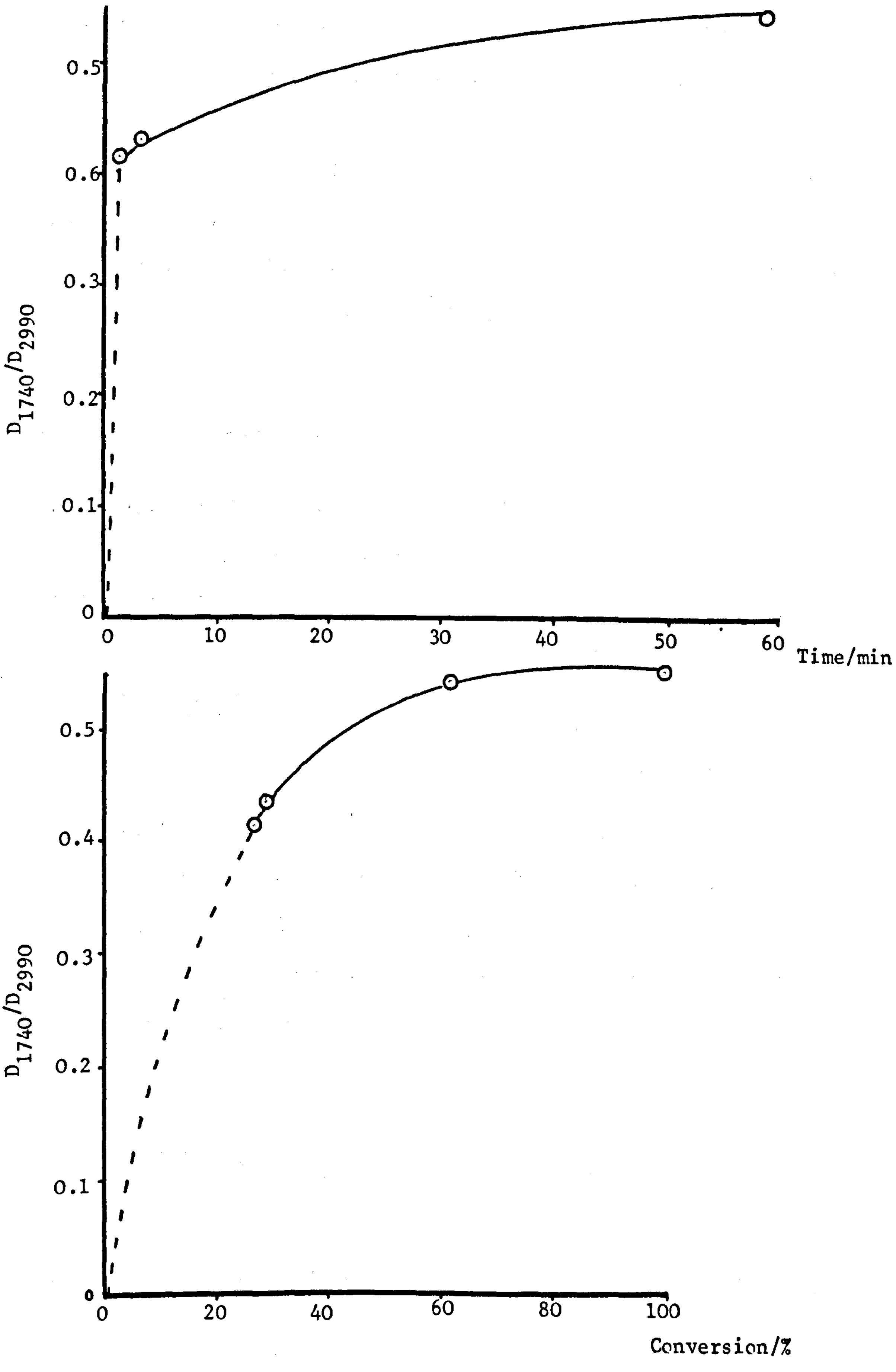
The i.r. spectra of various samples of poly-KA2 showed essentially the same characteristic features as those of poly-KA1, but the resolution of the spectra was poor (because of the insolubility of the polymer) and this precluded a detailed analysis of these spectra. However, one interesting piece of information did emerge from studies on the i.r. spectrum of a polymerizing solution of KA2. In the sampling experiment described in section 4.2.1.1 the optical density of the carbonyl peak at 1740 cm^{-1} was measured as a function of conversion; the C-H stretching absorption at 2990 cm^{-1} was used as an internal thickness standard. Figure 24 shows plots of optical density D against conversion and time. Although the accuracy of the determinations leaves much to be desired, because of the difficulty in obtaining a good spectrum, it is interesting to note that the concentration of C=O groups increases during the course of the reaction.

4.5.2 P.m.r. spectroscopy

The spectra of samples of poly-KA1 were taken with 10% solutions in $CDCl_3$, with TMS as the internal standard, and were compared with the spectrum of the monomer. The monomer gave three peaks at 6.34, 6.74 and 7.0τ in a ratio of 4:3:1 (spectrum 5). These are ascribed to the 2 protons in the vinyl group, the 6 protons in the methoxyl groups, and the 8 methylene protons respectively. The peak at 6.34τ was a quadruplet and the other two peaks were singlets.

FIGURE 24

I.r. determination of concentration of C=O groups. System: KA2/$SnCl_4$/CH_2Cl_2 at -80°.

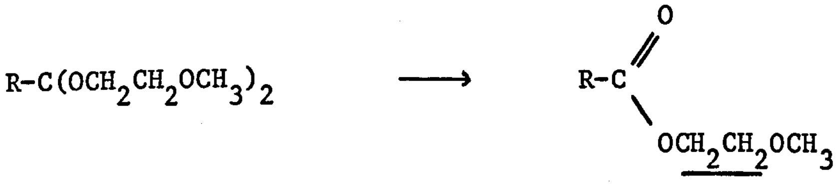


This is in complete agreement with the structure of KA1.[10] A polymer of DP=20 which had been precipitated in pentane gave three peaks, which were not resolved, at 6.4 and 6.74 and 7.3τ in a ratio of 4:3:1 (spectrum 6). The peak at 7.3τ can be ascribed to the protons of a methylene group between two acetal groups. This spectrum suggests that the product is a linear head-to-tail addition polymer of KA1. A low polymer (DP=3.1) gave a very complex spectrum. In addition to the peaks described above there were complex peaks centred at 5.2, 6.0 and 7.85τ, and a singlet at 6.7τ . (Spectrum 7)

The peaks at 5.2τ may be ascribed to the α proton of an α,β unsaturated ester:

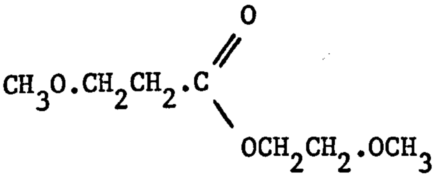
$$\sim \mathrm{CR{:}CH.CO_2R}$$

The multiplet at 6.0τ is in agreement with the expected chemical shift for the adjacent methylene protons when the acetal group of KA1 (or poly-KA1) is converted into its normal ester:



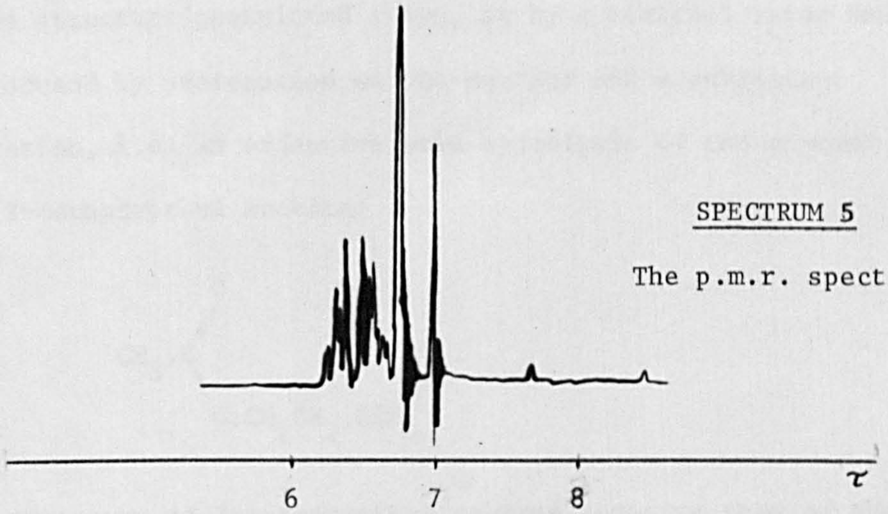
$$\mathrm{R{-}C(OCH_2CH_2OCH_3)_2} \longrightarrow \mathrm{R{-}C({=}O)OCH_2CH_2OCH_3}$$

The de-shielding effect of the carbonyl group shifts the resonance downfield. The singlets at 6.70τ and 6.74τ show that there are probably 2 non-equivalent methoxyl groups in the sample. The presence of the methoxyethyl ester of 4-methoxybutanoic acid will explain this observation:



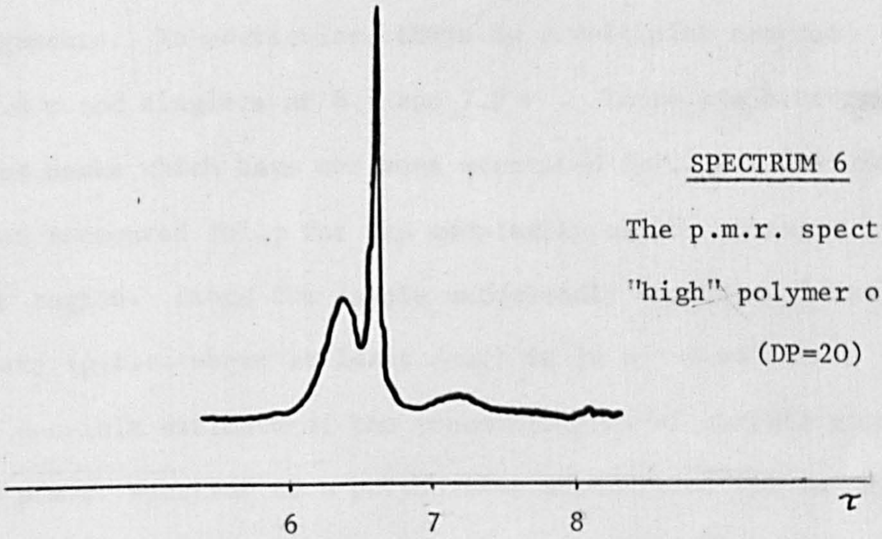
$$\mathrm{CH_3O.CH_2CH_2.C({=}O)OCH_2CH_2.OCH_3}$$

The two methoxyl groups in this structure are in different chemical



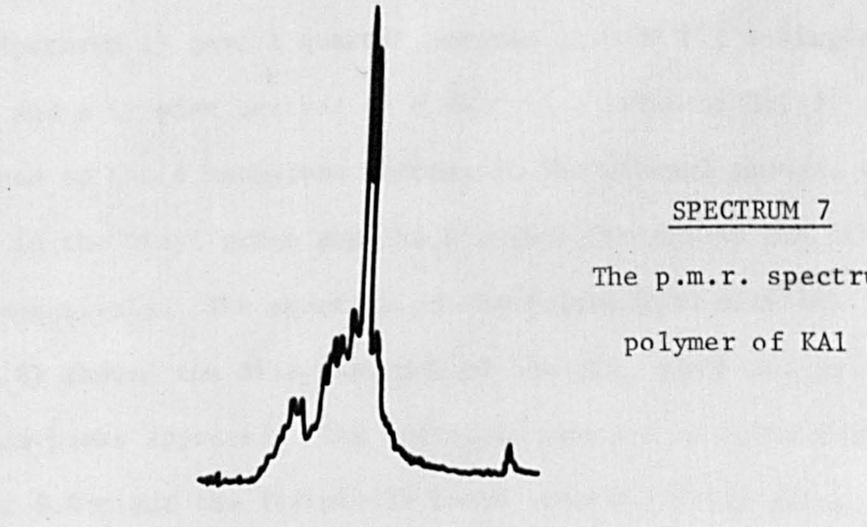
SPECTRUM 5

The p.m.r. spectrum of KA1



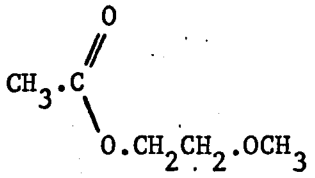
SPECTRUM 6

The p.m.r. spectrum of a "high" polymer of KA1 (DP=20)



SPECTRUM 7

The p.m.r. spectrum of a low polymer of KA1 (DP=3.1) environments from each other and from the acetal methoxyl groups in the polymer, because of the de-shielding effect of the carbonyl group. The peak at 7.85 τ may be caused either by the presence of a methylene group adjacent to the carbonyl group of an ester as in the structure postulated above, or by a terminal ester methyl group produced by protonation of the monomer and a subsequent de-alkylation, i.e. an effective acid hydrolysis of the monomer to give 2-methoxyethyl acetate:

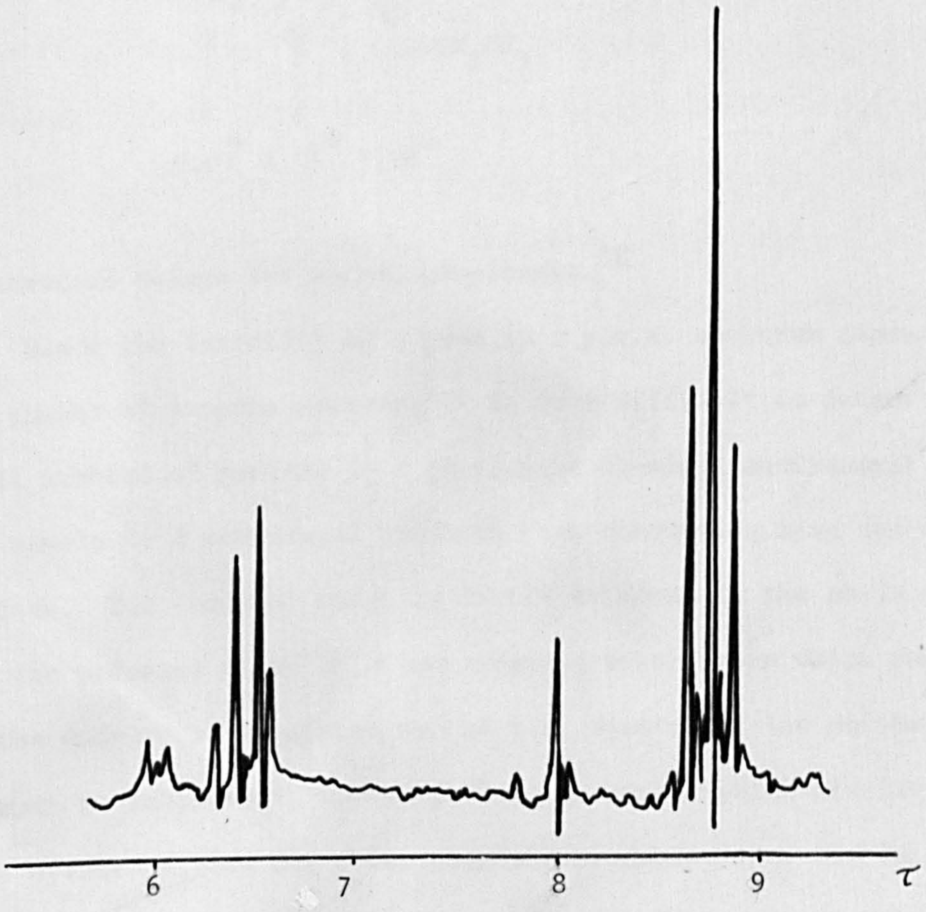


The spectrum of 2-methoxyethyl acetate suoports some of the above arguments. In particular, there is a multiplet centred around 6.0 τ and singlets at 6.7 and 7.9 τ . There are however, still some peaks which have not been accounted for. For instance, I have not accounted fully for the complexity of the spectrum in the 6-7 τ region. Since the sample undoubtedly consists of a mixture of products (g.l.c. shows at least four) it is not possible to obtain a sensible estimate of the concentrations of certain groups.

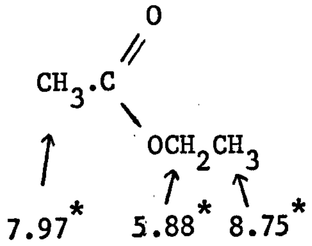
The p.m.r. spectrum of a polymerized solution of KA2 in CH_2Cl_2 initiated by $SnCl_4$ was compared with that of the monomer. The monomer (spectrum 1) gave a quartet centred at 6.28 τ , a singlet at 7.04 τ and a triplet centred at 8.74 τ in a ratio of 2:1:3. These are ascribed to the 4 methylene protons in the ethoxyl groups, the 2 protons in the vinyl group and the 6 methyl protons in the ethoxyl groups respectively. The spectrum of the polymerized solution (spectrum 8) showed the disappearance of the $:CH_2$ group and in addition, several new peaks appeared. The multiplet centred around 6 τ the singlet at 8.0 τ and the (triplet?) peaks near 8.7 τ may all be

SPECTRUM 8

The p.m.r. spectrum of a polymerized solution of KA2.

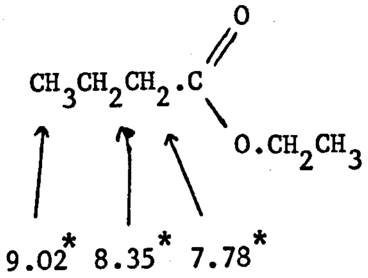


accounted for by the presence of ethyl acetate in the product:



* Literature values.[42]

Attack of an ethyl cation on KA2, followed by a dealkylation, would give ethyl propionate. Although there is no definite evidence for this compound in the spectrum, its presence is suggested by the small peaks at 7.8 and 8.1τ .



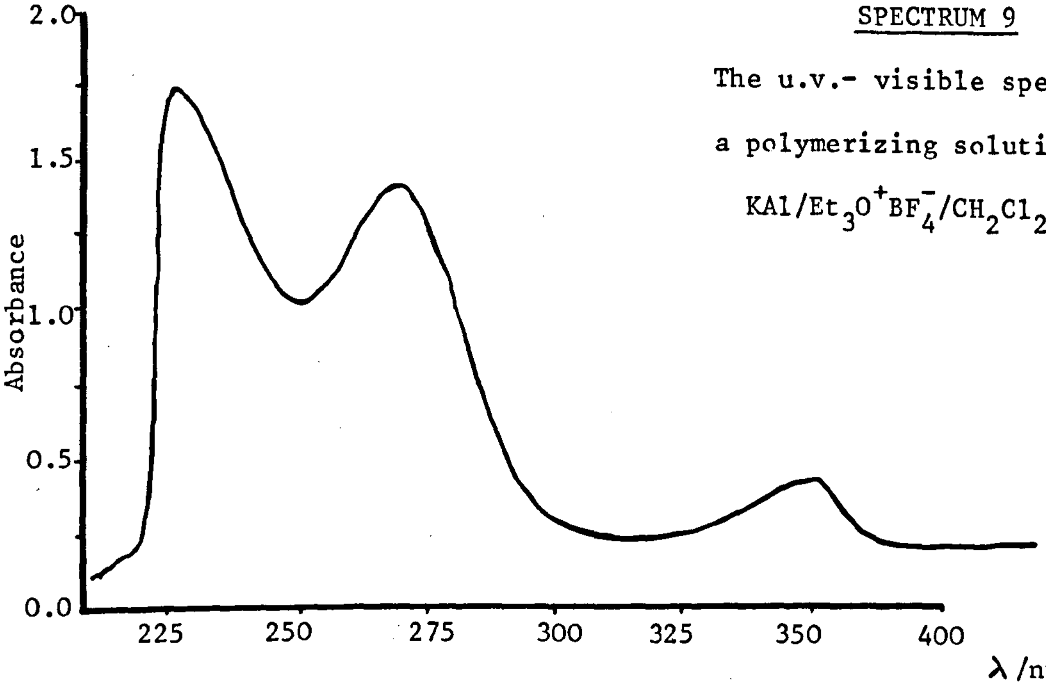
*Literature values for methyl propionate.[42]

Since the intensity of a peak in a p.m.r. spectrum depends on the number of protons present, it is very difficult to detect small numbers of protons in a particular chemical environment when the sample is a mixture of products each containing many non-equivalent protons. For example, there is little evidence in the above spectra for the presence of an α,β unsaturated ester group which was one of the end-groups suggested by the i.r. spectra of low polymers of KA1. It must be remembered, however, that the proton which distinguishes this structure from the other possible products, viz. the CH proton, is only one of fifteen protons in this end-group. In a polymer of DP = 3.4 with methyl and α,β unsaturated ester end-groups the CH proton is only 1 in 60.

4.5.3 U.V.- visible spectroscopy

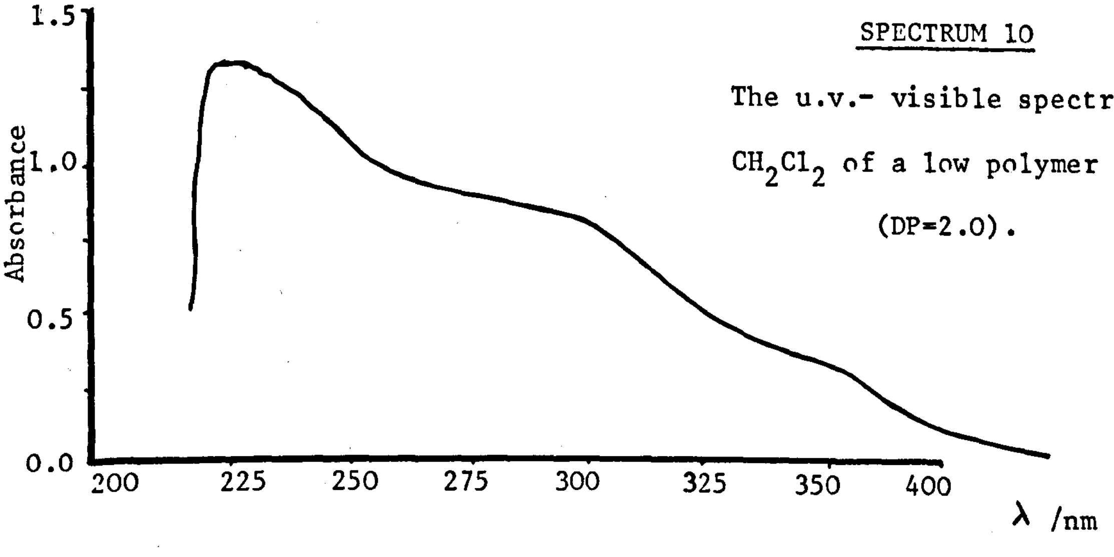
The U.V.- visible spectra of a polymerizing mixture and of the polymers was expected to give some information on the structure of the reaction products. The spectra are not complicated by the presence of the propagating species, since the probable ions, viz. dialkoxy carbenium ions, do not absorb above 200 nm.[41] The spectrum of a polymerizing solution of KA1 in methylene dichloride initiated by $Et_3O^+BF_4^-$ is shown in spectrum 9. The monomer has an absorption maximum at 238 nm in methylene dichloride. The maxima in the polymerizing solution are difficult to explain. The $\pi \rightarrow \pi^*$ transition of the carbonyl chromophore of an ester is usually observed in the 200-220 nm region, while that of an α,β - unsaturated ester is at 200-270 nm depending on the nature of the β-substituents. In addition, unsaturated esters have a weak $n \rightarrow n^*$ absorption in the 275-330 nm region. The spectra in this work may be influenced by complex interactions between the initiator and the monomer and/or the products. Although there is no published information on complex formation with ketene acetals, complexes between olefins and Lewis acids are well known.[45,46] Also, the formation of complexes of esters with Lewis acids has been studied in detail. For example, stannic chloride forms 1:1 complexes with esters such as ethyl acetate and ethyl propionate.[47] Complex formation in the present work was suggested by the characteristic colours of the reacting mixtures at or slightly below room temperature, which were absent at low temperatures.

The spectrum of a low polymer of KA1 in CH_2Cl_2 (DP=2.0) showed a very broad absorption, with a maximum at 235 nm, and a long tail with several shoulders extending to 400 nm. (Spectrum 10) A high polymer (DP=20) gave a similar spectrum but the maximum was shifted to around 253 nm. (Spectrum 11) This bathochromic shift is difficult to explain but it may be caused by differing extents of conjugation



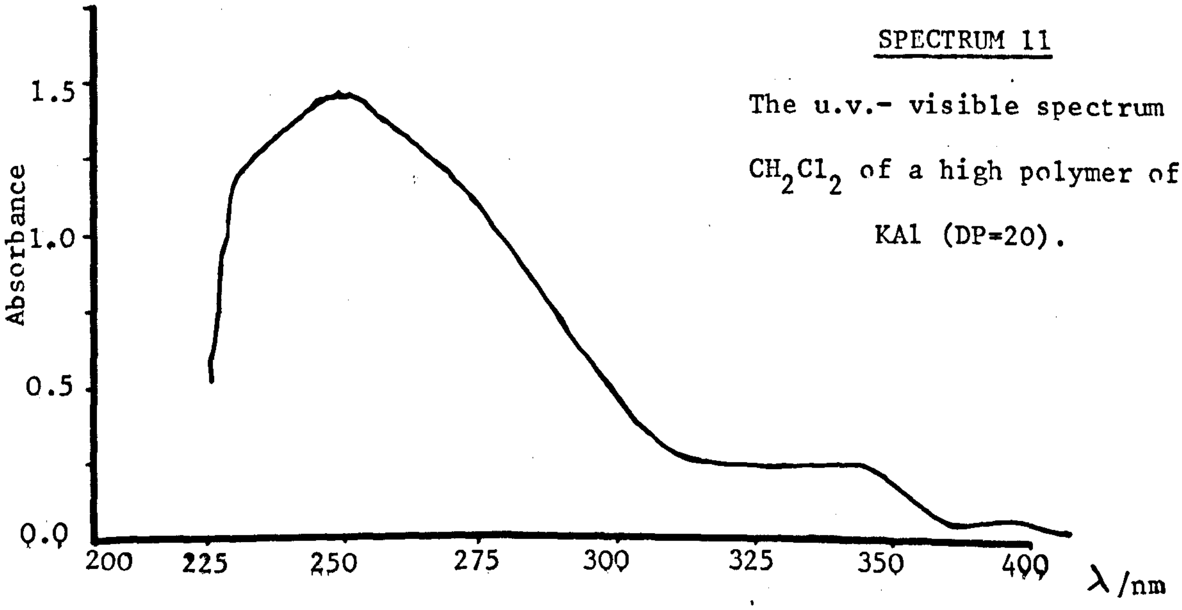
SPECTRUM 9

The u.v.- visible spectrum of a polymerizing solution. System: $KAl/Et_3O^+BF_4^-/CH_2Cl_2$ at 20°.



SPECTRUM 10

The u.v.- visible spectrum in CH_2Cl_2 of a low polymer of KAl (DP=2.0).



SPECTRUM 11

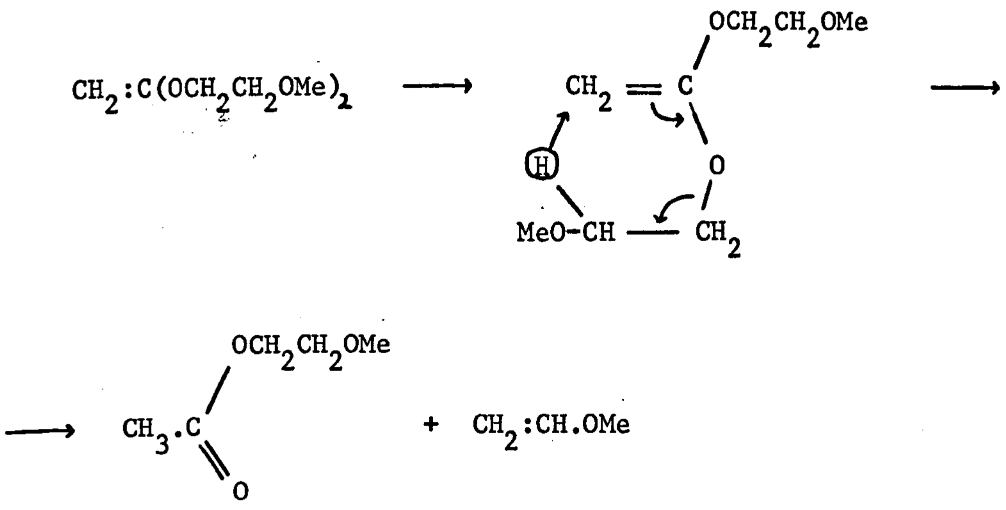
The u.v.- visible spectrum in CH_2Cl_2 of a high polymer of KAl (DP=20).

of the double bonds which are present in the polymers.

Thus, in the absence of detailed information on the chemistry of ketene acetals, U.V. and visible spectra are not very useful in helping to elucidate the chemistry of the polymerization.

4.5.4 Gas-liquid chromatography

G.l.c. of the monomers and their reaction products was complicated by their tendency to decompose on heating. The chromatography of KA1 was particularly difficult, because the high column temperature which was necessary to obtain good resolution led to the appearance of 2 new peaks, with shorter retention times than the monomer. The products were not identified but they were possibly methyl vinyl ether and 2-methoxyethyl acetate, formed by the intramolecular thermal rearrangement of the monomer:



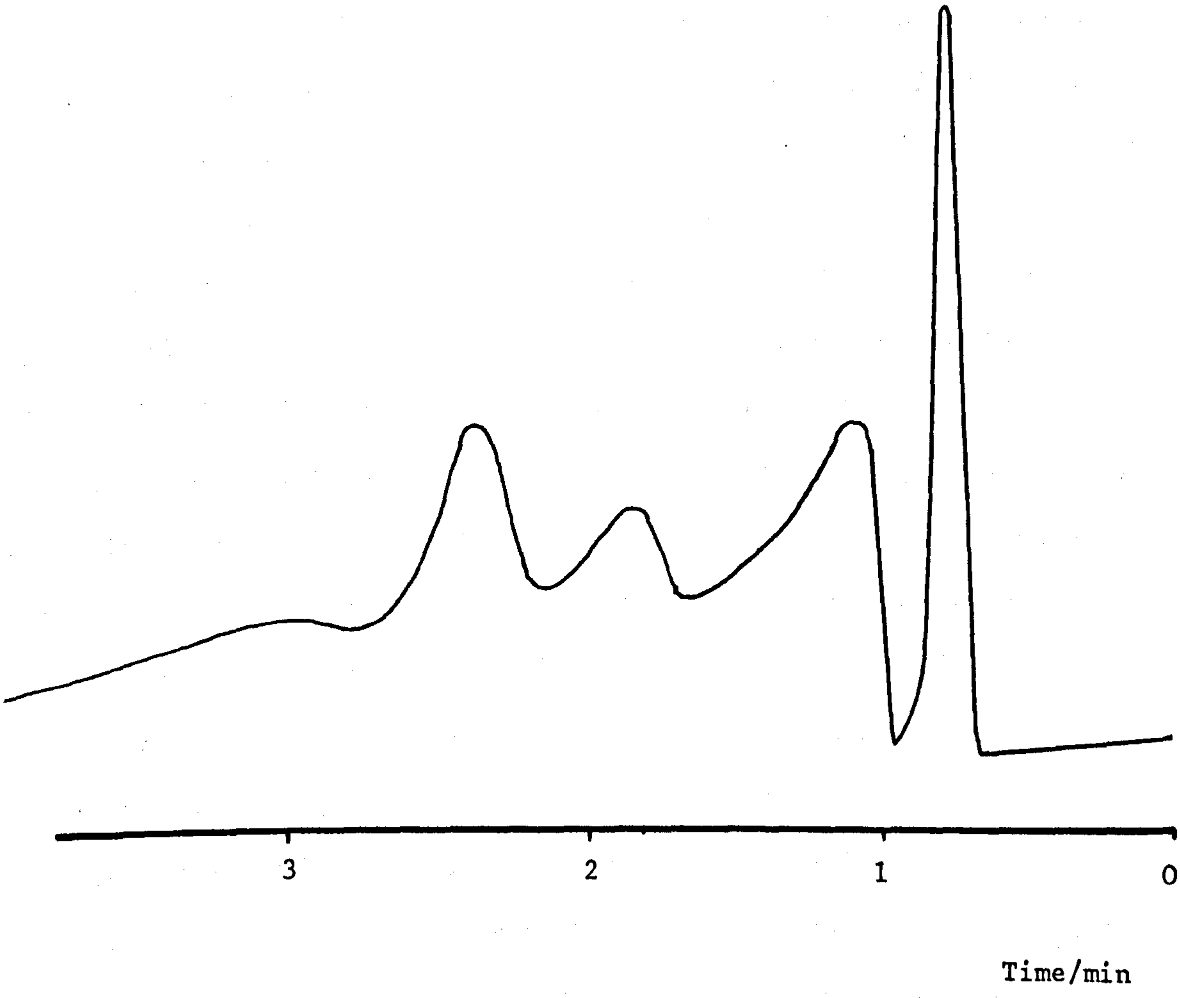
This reaction mechanism will also explain the formation of ethyl acetate and ethylene from the pyrolysis of KA2.[1]

The chromatogram of a low polymer (DP=2.0) indicated the presence of at least five major components (Figure 25) with retention times of 45, 65, 107, 140, and 180 s respectively. There were also two broad minor peaks with retention times of 5 and 8 minutes respectively. This shows that, during the polymerization

FIGURE 25

G.l.c. of a low polymer of KA1 (DP = 2.0)

Column temperature = 130°



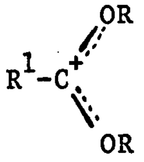
of ketene acetals, several products are formed in addition to high polymer.

A methylene dichloride solution of high polymer (DP=20) which had been precipitated in pentane gave only the solvent peak.

4.6 Discussion

4.6.1 Initiation

The addition of a cation at the carbon 2 of a ketene acetal produces a dialkoxycarbenium ion:



(I)

It is well known that initiators of the cationic type do interact with ketene acetals to give a dialkoxycarbenium ion as the primary product. For example, HCl and iodine react with ketene acetals via a dialkoxycarbenium ion intermediate.[57,63] In the present work a wide range of initiators has been used; each one of these presents us with the problem whether that particular initiator can react by some form of 'direct' initiation or whether it needs a co-initiator to produce the ions. (I do not intend to discuss the systems in which polymerization is believed to occur without the participation of ions, viz. pseudo-cationic polymerizations.[35]) It is well established that carboxonium or carbenium salts like $Ph_3C^+SbCl_6^-$ and $Et_3O^+BF_4^-$ are capable of initiating a polymerization directly without the intervention of a co-initiator.[35] However, with some other cationic initiators, particularly metal halides, no generalizations can be made about the initiation process except to say that in some systems a co-initiator is necessary whereas in others, apparently similar, it is not.

Although reasonable efforts were made in the present work, to remove impurities, there is no information on the role of a co-initiator (if any) in the systems under consideration. Furthermore, common co-initiators such as water can also hydrolyze ketene acetals and the fate of the water will be determined by the relative basicities of the initiator and of the monomer.

It is not possible to apply thermochemical arguments to the interaction between cations and ketene acetals because the relevant thermodynamic parameters are not available.

Concerning the rate of initiation, one possible explanation for the accelerating part of the sigmoidal conversion curves obtained in the calorimetric work with KA3 and $SnCl_4$ (Chapter 4) is that initiation is slow. The increase in the induction period as the temperature is lowered and as m_o is decreased, supports this idea, although an alternative explanation is that the nominal initiator is in equilibrium with the true initiator, and its reaction with the monomer shifts the equilibrium towards the formation of more of the true initiator. One example of this could be initiation by cations formed by self-ionisation of a metal halide:

$$\begin{tikzcd}
2\,\mathrm{MtX}_{n+1} \arrow[r, rightleftharpoons] & \mathrm{MtX}_{n-1}^{+} + \mathrm{MtX}_{n+1}^{-} \arrow[d, "P_1"] \\
& \mathrm{MtX}_{n-1}\text{-}P_1^{+}
\end{tikzcd}$$

Thus the concentration of growing species increases during the polymerization. The first-order plots obtained from the KA3/$SnCl_4$/pet. ether system (Chapter 4) suggest that after the inflexion point the concentration of active species becomes constant.

4.6.2. Propagation and chain-breaking

It is generally accepted that many olefin polymerizations proceed through carbenium ion chain-carriers, and in these reactions the propagation consists simply of the successive additions of a carbenium ion to the double-bond of the monomer.

Since the condition for the formation of high polymers is that the propagation reaction must be faster than all other reactions of the growing species, it is evident that special conditions are required for the formation of high polymers by cationic polymerization. The general conditions which must be satisfied are:

(a) Extreme purity to reduce the total rate of adventitious chain-breaking reactions.

(b) Low temperature to reduce the rate of inherent chain-breaking reactions.

In the present work we have been unable to produce high polymers under homogeneous conditions. From the molecular weight measurements and the spectroscopic experiments in Chapter 4, the following conclusions concerning the propagation and chain-breaking reactions in homogeneous systems have been reached:

1) The initiator, or a species whose concentration is proportional to that of the initiator, is involved in the chain-breaking reactions (Figure 12).

2) Transfer reactions involving the monomer are the dominant chain-breaking reactions (Figure 11).

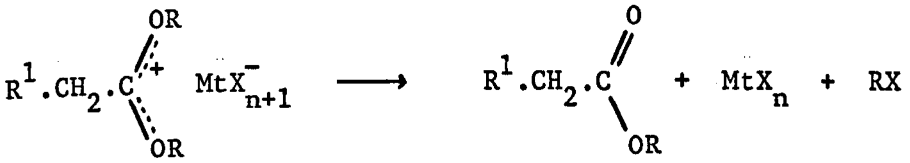
3) The molecular weights of the polymers are only affected slightly by changing the nature of the solvent.

4) The relative rates of propagation and chain-breaking are almost unaffected by temperature, and $E_m - E_p \approx 0$.

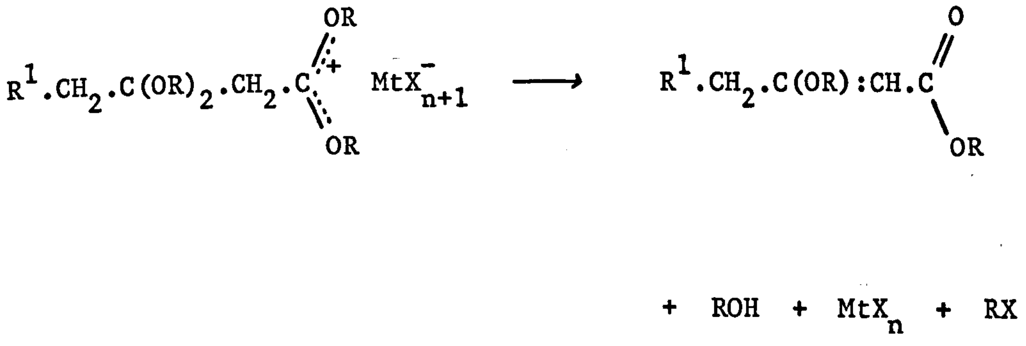
5) At least two types of unsaturated groups are present in the low polymers.

6) The systems under consideration are very complex and the above problems have been found to be inextricably interrelated.

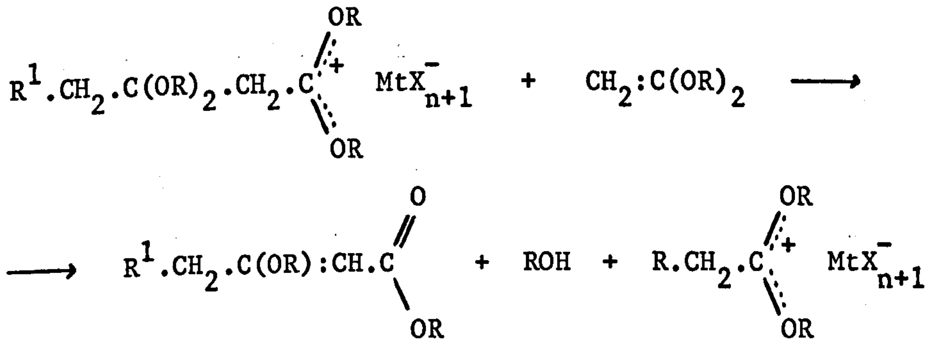
Once one realises that the number of possible chain-breaking reactions is at least four, (not counting reactions with solvent and impurities) one can understand why the total rate of chain-breaking is so much greater than with other olefinic monomers. I propose to discuss the propagation and chain-breaking reactions in the polymerization of ketene acetals by reference to the following reactions:



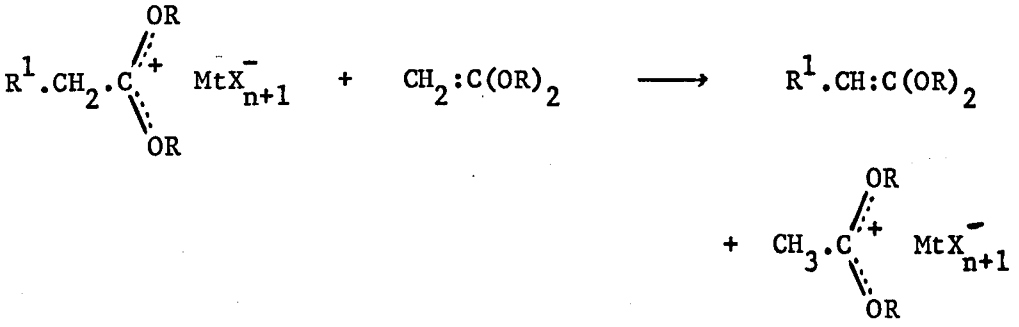
$$R^1.CH_2.\overset{+}{C}(OR)_2\ \ MtX^-_{n+1} \longrightarrow R^1.CH_2.C(=O)OR + MtX_n + RX \qquad (1)$$



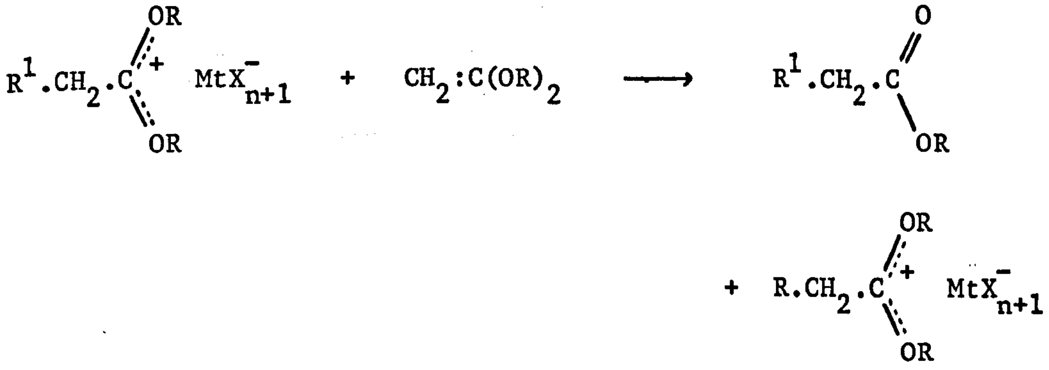
$$R^1.CH_2.C(OR)_2.CH_2.\overset{+}{C}(OR)_2\ \ MtX^-_{n+1} \longrightarrow R^1.CH_2.C(OR){:}CH.C(=O)OR + ROH + MtX_n + RX \qquad (2)$$



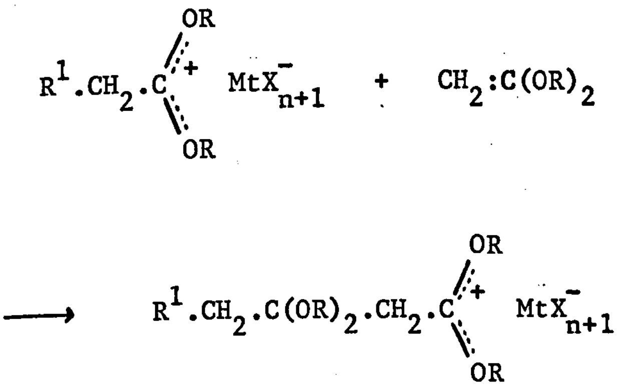
$$R^1.CH_2.C(OR)_2.CH_2.\overset{+}{C}(OR)_2\ \ MtX^-_{n+1} + CH_2{:}C(OR)_2 \longrightarrow R^1.CH_2.C(OR){:}CH.C(=O)OR + ROH + R.CH_2.\overset{+}{C}(OR)_2\ \ MtX^-_{n+1} \qquad (3)$$



(4)



(5)

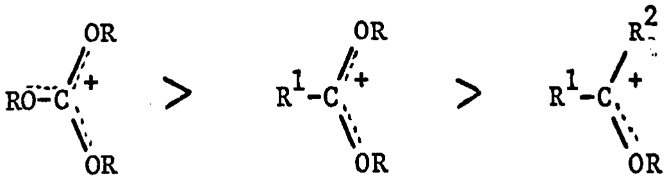


(6)

Reactions (1)-(5) are chain-breaking reactions, (6) is propagation. Reactions (3), (4) and (5) are transfer reactionswhile (1) and (2) may be either transfer or termination reactions depending on the nature and the reactivity of the metal halide MtX_n which is generated.

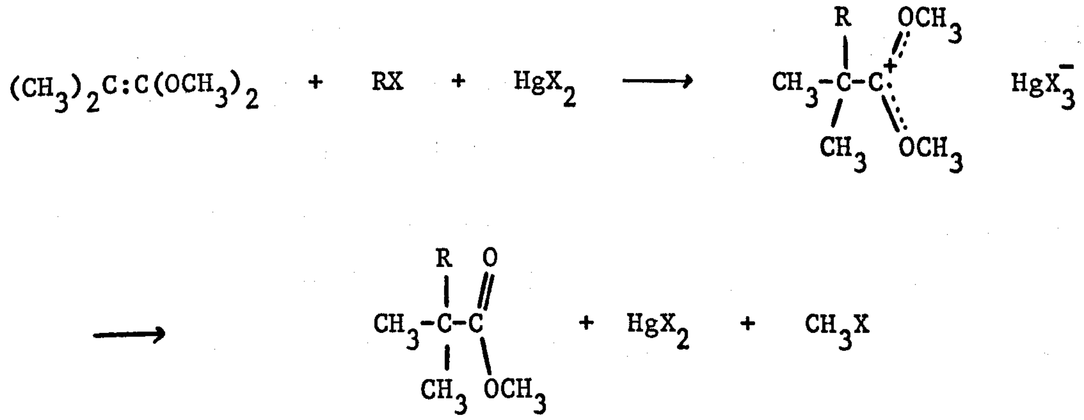
Reactions (1) and (2) are in agreement with the second Mayo plot in Figure 12 which shows that the DP decreases to a constant value as c_o is increased, thus suggesting that the initiator is involved in the chain-breaking reactions. Chapter 4 contains evidence that dealkylation of the growing ion together with an intramolecular loss of alcohol gives an α,β- unsaturated ester group, (reactions (2) and (3)) and the alcohol resulting from this reaction can add to the monomer to give an orthoester.

It is well known that the chemistry of dialkoxycarbenium ions is complicated by the fact that they decompose in solution by reaction (1). Cations are more stable, i.e. are lower in energy, the more highly the positive charge is delocalized (this of course is the driving force for the isomerization of carbenium ions). Alkoxycarbenium ions have a diffuse charge because the charge is distributed over at least two centres. It has been shown by mass spectrometry[43] that in the gaseous state the stability of tertiary alkoxycarbenium ions decreases in the sequence:

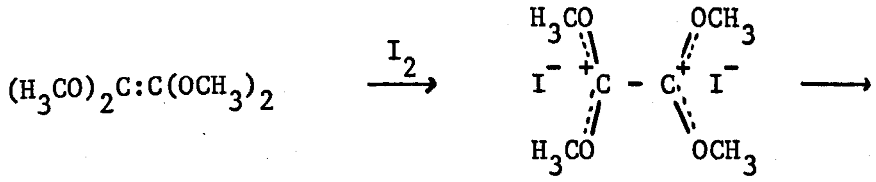


The term stability must, however, be used with caution! An ion may indeed have considerable stabilization energy and be intrinsically stable with respect to its decomposition. It may however, be very unstable from the chemical point of view because of a low activation energy for the various reactions in which it can participate.

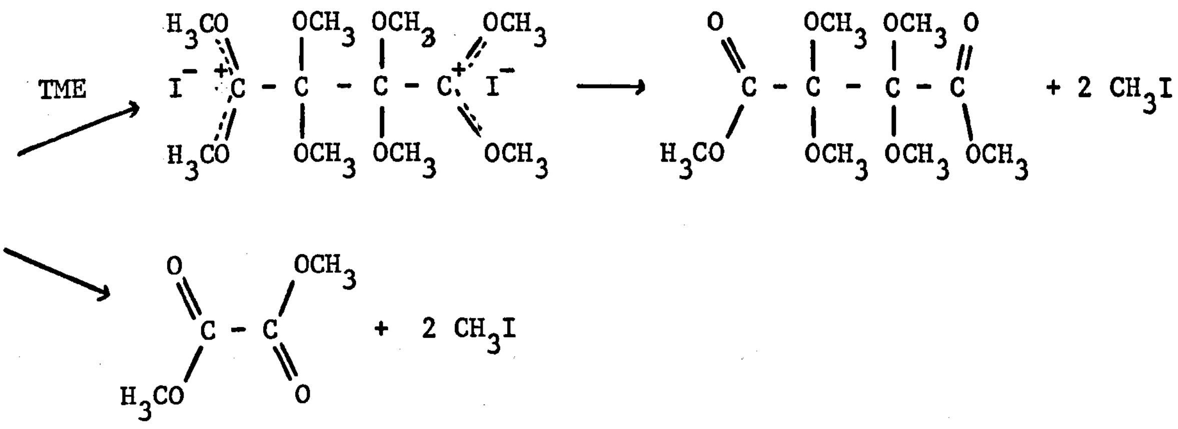
Cations in solution are always accompanied by an equal number of anions and the interaction between them to form inactive species is one of the termination reactions in cationic polymerization. In practice it has been found that the hexafluoroantimonate and the tetrafluoroborate anions produce the most stable dialkoxycarbenium salts. Temperature is also important with regard to stability as is shown by the fact that dimethoxyethyl bromide $CH_3.C^+(OCH_3)_2\ Br^-$ is stable in SO_2 below -30°, but at higher temperatures it decomposes by reaction (1) to give methyl acetate and methyl bromide.[44] A similar decomposition has been reported by McElvain and Aldridge[49] in the alkylation of ketene acetals by alkyl halides:



More recently this reaction has been re-investigated with trityl bromide as the alkyl halide.[50] An example which is more closely related to the present work is provided by the mechanism which has been proposed[63] for the oxidation of tetramethoxyethylene by iodine:



(TME)



This mechanism shows that there is concurrent dimerization (reaction (6)) and decomposition.

An interesting nexus between the present problem and other polymerization systems is provided by a study of the chemistry of cyclic dialkoxycarbenium ions which are well known as reaction intermediates in the polymerization of cyclic acetals such as 1,3-dioxolan. Kubisa and Penczek[51] have shown that dioxolenium hexachloroantimonate decomposes in solution, forming β-chloroethylformate and $SbCl_5$:

$$SbCl_6^- \rightleftharpoons ClCH_2CH_2OCHO + SbCl_5 \qquad (7)$$

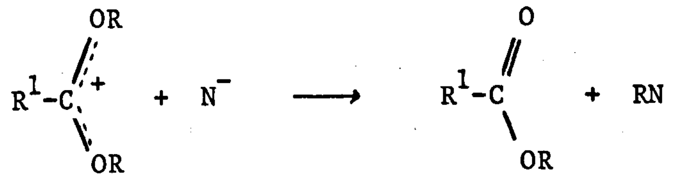
(II)

Thus, it seems plausible that a similar decomposition of the growing ion $R^1.\overset{+}{C}(OR)_2$, which is clearly closely related to ion (II), may be one of the chain-breaking reactions during the polymerization of ketene acetals.

However, because high yields were always obtained in the present work, and no carbon-halogen bonds could be detected in the products, the decomposition reactions (1) and (2) are considered to be of minor importance compared with other chain-breaking reactions to be discussed below.

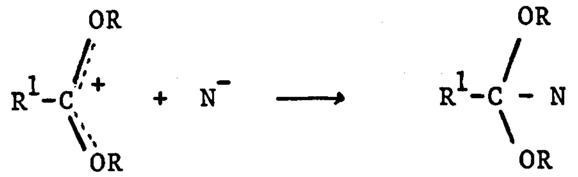
The first Mayo-plots in Figure 11 show that transfer reactions involving the monomer are the dominant chain-breaking reactions in the polymerization of ketene acetals.

Spectroscopic evidence has been presented (Chapter 4) for the production of an unsaturated end-group. It is reasonable to suppose that this occurs by the transfer of a proton from the growing ion to the monomer (reaction 4). This type of transfer reaction is widely assumed to be the dominant chain-breaking step in the polymerization of alkyl vinyl ethers. I have suggested tentatively in Chapter 4 that one of the most important transfer reactions involving the monomer is one in which the dialkoxycarbenium ion is dealkylated and the monomer alkylated (reactions (3) and (5)). In the extreme case, i.e. where no propagation or other side-reactions occur, reaction (5) would be equivalentto the conversion of a ketene acetal to a saturated ester. These reactions will explain the increase in concentration of ester carbonyl groups which was observed during the sampling experiment (Figure 24). Further evidence in support of reactions (3) and (5) is provided by the fact that dialkoxycarbenium ions are among the strongest alkylating agents known,[56] being even stronger than trialkyloxonium salts. For example, they can alkylate ethers smoothly to trialkyloxonium salts, while the reverse reaction (alkylation of carboxylic esters with trialkyloxonium salts) is impossible.[56] A review of the more important alkylations has been published.[57] The reaction between dialkoxycarbenium ions and nucleophiles (N^-) can be generalized to consist of two competitive reactions, viz. dealkylation of the ion by a reaction analogous to reaction (1):



(8)

and addition of the nucleophile at the carbenium centre of the ion:



(9)

The chain propagation reaction in the polymerization of ketene acetals is equivalent to reaction (9) when the nucleophile is a monomer molecule (reaction (6)). The positive charge in dialkoxycarbenium ions is delocalized considerably, compared with for example, simple alkyl cations and oxonium ions, (from primitive electrostatic considerations one can conclude that diffuseness of charge is in some respects equivalent to an increase in ion size). The low charge density on the carbenium ion centre of the ions is manifested by the fact that, in general, only very strong nucleophiles are added at this point. Thus, the fact that some polymer was produced in this work is further evidence of the highly polar nature of ketene acetals.

The most unexpected feature of this work was that we failed to produce high polymer even at very low temperatures (down to -100°) where the transfer reactions might be expected to become less important because of their expected high activation energies. This was partly caused by the insolubility of the monomer at low temperatures which precluded the use of concentrated solutions. However, the first Mayo plots in Figure 11 show that $E_m - E_p \approx 0$. It was expected that the propagation reaction (reaction (6)) would have a lower activation energy than the dealkylation reactions (reactions (3) and (5)) and would thus become progressively more important as the temperature was lowered. The reasons why the DP is found to be almost independent of temperature are obviously related to the great chemical complexity of the systems under consideration and are not fully understood.

The slightly higher molecular weights obtained in the precipitation polymerization of KAl in aliphatic hydrocarbons is contrary to the usual trend in cationic polymerizations where molecular weights are usually found to increase in solvents of higher polarity. There is little information in the literature regarding the effect of solvent on the distribution of primary products during the reactions of dialkoxycarbenium ions, but this work shows that the propagation reaction is favoured by a medium of low polarity and workers in the future will no doubt establish whether this is a general phenomenon for this type of reaction.

It was reported in Chapter 4 that the highest molecular weights were found in bulk polymerizations with sparsely soluble initiators. Because the rates of reactions in heterogeneous systems are often determined by the rates of diffusion, absorption, and desorption, rather than by chemical factors, we cannot give a sensible chemical explanation for this effect. However, I suggest tentatively that the anion in these initiators (presuming they are ionic!) may be stabilized in the crystal lattice and its participation in any transfer or termination processes is therefore much less rapid.

CHAPTER 5: CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

The work described above has proved to be insufficient for a definitive solution of all the problems encountered. However, a more systematic study on these problems would have required a much larger amount of work and it has been my intention throughout to adhere closely to the original aims of the research.

As far as we can gather, this work has been the first serious attempt to study the polymerization of ketene acetals. It has been shown that low polymers of ketene acetals are produced in homogeneous systems because of inherent chain-breaking reactions, and it seems unlikely that ketene acetals can be polymerized to give polymers with molecular weights comparable to those from other olefinic monomers.

The chemistry of the systems under consideration is, however, very interesting and on the basis of the present results the following suggestions can be made:

1) The dialkoxycarbenium ion derived from a monomer such as ketene diphenyl acetal is expected to be more stable towards dealkylation because of the increased strength of the O-Ph bond compared with simple O-R bonds. Thus, although the monomer is itself less polar than other ketene acetals (because of the electron-acceptor properties of the aromatic groups) the increased stability of the growing ion may favour propagation.

2) A study of the conductivity of the reacting solutions both during and after polymerization may provide insight into the nature and concentration of the active species.

3) The complete characterization of the many by-products and a study of the kinetics of their formation should help one to deduce and to separate the factors which are important in determining the molecular weight of the polymers.

4) Some brave chemist may be tempted to study the polymerization of ketene acetals with sparsely soluble initiators. Although this type of system is likely to be intrinsically more difficult than the corresponding homogeneous systems it is at least made attractive by the fact that "high" polymers are produced.

SECTION B: PROPERTIES OF THE POLYMERS

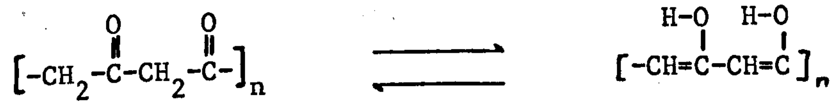
CHAPTER 6: INTRODUCTION

The first systematic investigation of the properties of polyketene acetals was carried out by McElvain et al.[15] These workers reported that poly-KA2 was a white solid which was insoluble in all common organic solvents, although the monomer and aromatic hydrocarbons produced a noticeable swelling.

McElvain postulated that the observed insolubility was caused by the cross-linking of the linear polymer chains by an intermolecular loss of alcohol. The insolubility was disputed by Lal[6] who reported that the polymer was soluble in o-dichlorobenzene at 140°. He published X-ray diffraction data to show that the insolubility in common organic solvents was in fact due to its high degree of crystallinity. However, Noguchi and Kambara[7] found that their poly-KA2 was insoluble even in o-dichlorobenezene at 140°. There are no data on the influence of molecular weight on the solubility of any poly-ketene acetal. The molecular weight, and hence the tendency towards insolubility, is expected to be related symbatically to the degree of purity of the polymerization system. The rigour of the purification and handling techniques is in the order McElvain < Lal < Noguchi and Kambara. However, McElvain stated that "the polymer is insoluble in all organic solvents" without referring to temperature and it is quite possible that his poly-KA2 would have been soluble in o-dichlorobenzene at 140°. It would then appear that the insoluble polymer made by Noguchi and Kambara had a higher molecular weight than the other two polymers because of the high degree of purity of their polymerization system.

Poly-KA2 was shown to be fairly stable to heat[15], no decomposition being observed when it was heated at 200° (0.5 mm) for 1½ hrs. When the polymer was heated at 250°, a rapid decomposition took place and ethyl alcohol amounting to 27% of the weight of the original polymer was obtained. The remaining material was an acetone-soluble, viscous, red tar. Lal[6] found that poly-KA2 decomposed to a red oil at 226° in air and at 275° under vacuum or in silicone oil; presumably Lal failed to observe a crystalline melting point. The polymer of KA1, prepared with $CdCl_2$ as the initiator, was found to melt at 200-210°.[11]

Poly-ketene acetals are stable to alkali but are extremely sensitive to acids.[15] When allowed to stand in the air for 24 hrs poly-KA2 slowly turns to a brownish-red powder.[15] Dilute aqueous acids hydrolyse the polymer to a reddish-black oil. The colour and alkali-solubility of this product indicate a poly-1,3-diketone in an enolic, and hence highly conjugated, tautomeric form:



$$[-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-]_n \rightleftharpoons [-CH=\overset{\overset{H-O}{|}}{C}-CH=\overset{\overset{H-O}{|}}{C}]_n$$

An unsuccessful attempt to obtain such a poly-1,3-diketone from poly-vinylidene chloride has been reported.[58] Poly-1,3-diketones have previously been produced by the oxidation of poly-vinyl alcohol,[59] and by the action of boron trifluoride on ketene and diketene.[60]

Although the sensitivity of poly-ketene acetals to acids restricts severely their potential as polymeric materials,it does however offer exciting synthetic possibilities because a distinctly novel feature of the poly-1,3-diketone is the possibility of reacting the pendent oxo or hydroxyl groups, or the enolic double bonds, with suitable reagents to produce new polymers. A reagent which is reactive towards any one of these functional groups will shift the keto-enol equilibrium so as to permit complete reaction of one form or the other.

CHAPTER 7: CHEMICAL REACTIONS ON THE POLYMERS

On standing in the laboratory air, poly-KA1 turns slowly into a reddish-brown tacky solid, and this change is accompanied by the appearance of a strong sharp absorption peak at 1740 cm^{-1}.

Most of the reactions described here were carried out on poly-KA1, but the only difference between polymers of different ketene acetals should be in their ease of hydrolysis, because steric factors are known to be important in determining the position of the chemical equilibria in the acid-catalysed hydrolysis of acetals.

7.1 Hydrolysis of poly-KA1

The preparation of a poly-1,3-diketone comprises the addition of dilute aqueous acid to a solution or a suspension of a poly-ketene acetal. The choice of solvent for the reaction is severely restricted by the insolubility of many poly-ketene acetals. It has been found that chlorinated hydrocarbons, such as chloroform or carbon tetrachloride, are the most suitable solvents for poly-KA1. The temperature at which the reaction is carried out is not very critical, but it is desirable to avoid high temperatures (say, more than 100°) in order to reduce thermal scission of the polymers.

The process of producing poly-1,3-diketones is advantageously conducted by dissolving the poly-ketene acetal in a chlorinated hydrocarbon solvent, adding excess of dilute aqueous acid, and stirring the resulting two-phase mixture vigorously. The hydrolysis is accompanied by a change in colour of the reaction mixture from colourless to red. A typical recipe is as follows: To a 25 ml screw-capped bottle was added 1g of poly-KA1 (M_n = 1900), dissolved in 8 mls of carbon tetrachloride, and 6 mls of N sulphuric acid. The mixture was stirred vigorously for 17 hours at room temperature and under a nitrogen atmosphere. There was formed a dark-orange swollen gel in the carbon tetrachloride layer. This gel and the carbon tetrachloride solution were poured into diethyl ether and thus yielded a red tacky solid (M_n = 400) which gave the following analysis:

Analysis: Found: C, 60.7; H, 5.71. Calculated for (C_2H_2O): C, 57.14; H, 4.76.

The high hydrogen content of the polymer indicated that the conversion of poly-ketene acetal to polyketone was incomplete. The high carbon content suggested the possibility of inter-molecular loss of water to produce a cross-linked structure. On exposure to the air the polyketone turned slowly to a black tar which was analysed as follows: C, 57.7; H, 8.02. This analysis suggested that the polymer was being partially oxidized.

The infra-red spectrum showed strong bands at 1720, 1670 and 1610 cm^{-1} indicating C=O, and a weak broad band centred at 3400 cm^{-1} characteristic of -OH. The visible and u.v. spectrum of an aqueous alkali solution showed an increasing absorption with decreasing wavelength, with only a few indistinct shoulders. The product was partly soluble in alcohols and exhibited an absorption maximum at 280 nm in methanol, and 310 nm in ethylene glycol.

The properties of the polyketone (PK1) were compared with those quoted for the alleged poly-1,3-diketone (PK2) prepared by Japanese workers from the polymerization of ketene and diketene.[60] These authors reported a light-brown powder which was soluble in aqueous alkali, acetone and m-cresol, but insoluble in ether, ethanol and carbon tetrachloride. The infra-red spectra of the two products are very similar, but lack of detail in the Japanese paper prevents a critical comparison. An ethylene glycol solution of PK2 showed maximum absorption at 250 nm with ε ca. 60,000. In contrast PK1 was sparingly soluble in the above solvent and had an absorption maximum at 310 nm. This bathochromic shift shows that the average number of conjugated end groups is probably greater in PK1 than in PK2.

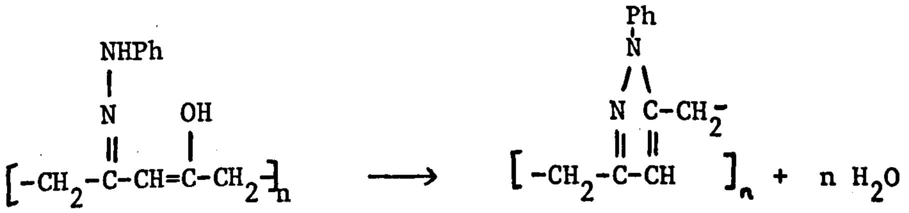
7.2 Derivatives of the poly-1,3-diketone

7.2.1 2,4 dinitrophenyl hydrazone

Preparation of the 2,4 dinitrophenylhydrazone (DNP) of the polyketone, by carrying out the acid hydrolysis of the poly-KA1 in the presence of Brady's reagent, gave an orange-brown product (m.p. 135-140°) which in alkali solution had an absorption maximum at 430 nm, which is characteristic of the DNP's of aliphatic ketones.

7.2.2 Phenylhydrazone

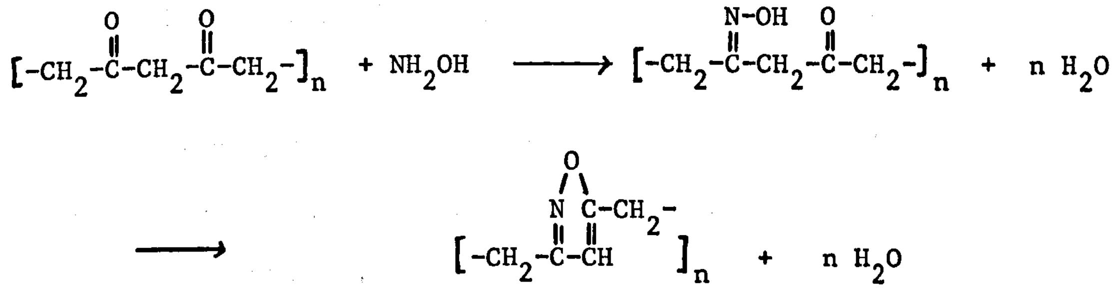
The preparation of the phenylhydrazone of the polyketone was attempted by neutralizing a hydrolyzed solution of poly-KA1 (M_n = 2400) and then adding an excess of phenylhydrazine. The mixture was stirred at room temperature for 24 hrs and gave a dark-brown tacky solid (M_n = 1720). The product of the reaction between PK2 and phenylhydrazine showed strong absorptions in the 1600-1500 cm^{-1} region, which were attributed to the -C=C-C=N- system in a pyrazole ring:-[60]



The product from PK1 also absorbed at 1600-1500 cm^{-1} but the complexity of the spectrum did not allow a distinction to be made between phenylhydrazone and pyrazole.

7.2.3 Reaction between the polyketone and hydroxylamine

The condensation reaction between hydroxylamine and the carbonyl group of a ketone is used frequently to prepare oximes; it has also been used to convert polyketones into polyamides via the oxime and a Beckmann rearrangement.[61] However, the reaction of a 1,3-diketone with hydroxylamine is the method most widely used for the synthesis of isoxazoles - the monoxime of the diketone loses a molecule of water and rearranges to form the isoxazole. Thus our poly-1,3-diketone should yield a polyisoxazole:



$$[-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-]_n + NH_2OH \longrightarrow [-CH_2-\overset{\overset{N-OH}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-]_n + n\,H_2O$$

This reaction was attempted by adding slowly a hot solution (60°) of poly-KAl in dimethoxyethane to a hot solution (60°) of hydroxylamine hydrochloride in a sodium acetate-acetic acid buffer solution (pH = 5). The stirred reaction mixture was kept at 60-70° for 16 hrs and was then poured into cold-water to precipitate the product. After filtration and washing of the residue with cold-water a dark-yellow solid was isolated.

Analysis found: C, 48.20; H, 3.95; N, 13.40. Calculated for oxime (C_2H_3NO): C, 42.10; H, 5.26; N, 24.56. Calculated for isoxazole (C_4H_3NO): C, 59.20; H, 3.70; N, 17.28.

The carbon and nitrogen analyses indicated that approximately 50% of the carbonyl groups had been converted into oximes. However, the infra-red spectrum showed almost complete disappearance of the C=O absorption at 1720 cm^{-1}. Thus it appeared that this material consisted of a mixture of isoxazole and ketene oxime units.

Heating the yellow solid with aqueous alkali or with pyridine for several hours failed to alter the elemental analysis (monoximes of β-dicarbonyl compounds can often be converted into isoxozoles by treatment with a base). It should be noted that in a reaction between neighbouring groups in a polymer chain, the stoichiometric limit of the reaction cannot be reached. Random coupling of pairs of neighbouring groups will occasionally leave single groups isolated between neighbours which have reacted. Thus, the maximum conversion of our poly-1,3-diketone to a polyisoxazole can be estimated by the statistical treatment of Flory,[67] who derived an expression for the average number of isolated substituents per molecule, for any chain length. However, the molecular weight of the product was not determined because it was only soluble in solvents such as pyridine and dimethyl formamide, which are not suitable for osmometry.

Differential scanning calorimetry of the product (Figure 26) showed a m.p. 155-190° followed by vapourization at higher temperatures.

7.2.4 Reduction

A very useful reaction for characterising the poly-1,3-diketone is its reduction to poly-vinyl alcohol. Reduction may be accomplished by reacting the polyketone with sodium borohydride or other specific reducing agents.

Procedure:

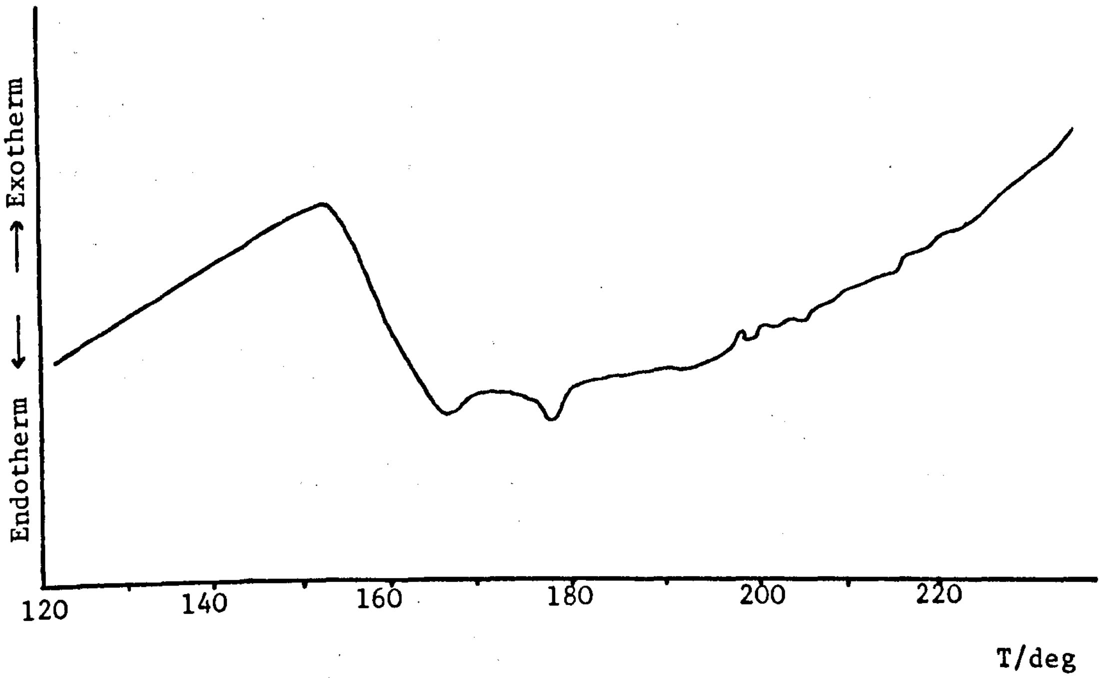
A solution of poly-1,3-diketone in chloroform was prepared. This solution was neutralised with dilute aqueous sodium hydroxide, and an excess of aqueous sodium borohydride solution was added. The mixture was stirred vigorously at room temperature for 30 hours and yielded a very pale yellow chloroform layer. When this solution was poured into pentane, it yielded a white fibrous solid, which was soluble

FIGURE 26

Differential scanning thermogram of polyisoxazole.

Range: 8

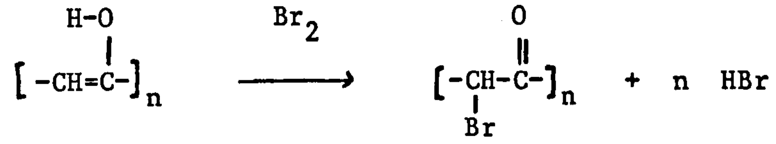
Heating rate: 16° min^{-1}



in hot water and was identified as poly-vinyl alcohol by its infra-red spectrum.

7.2.5 Bromination

By repeating the hydrolysis at room temperature with a polymer of M_n = 2000, in the presence of excess of bromine a yellow powder was isolated (M_n = 1900). The i.r. spectrum of this material indicated that it contained an α-bromoketone and also some unsubstituted units:

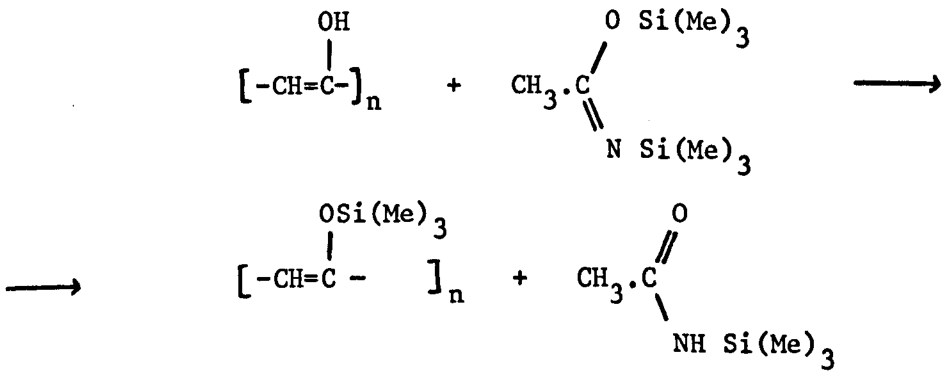


$$[-CH=\overset{H-O}{\overset{|}{C}}-]_n \xrightarrow{Br_2} [-\underset{Br}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-]_n + n\ HBr$$

Analysis: Found: C, 25.5; H, 1.77. Calculated for α-bromoketone (C_2HOBr): C, 19.83; H, 0.083. Calculated for poly-1,3-diketone (C_2H_2O): C, 57.14; H, 4.76. The incomplete conversion is also indicated by the aerobic degradation of the yellow powder to produce a black tar, similar to that from the poly-1,3-diketone.

7.2.6 Silylation

The following reaction was envisaged for the interaction between the poly-1,3-diketone and bis-trimethylsilyl acetamide (BSA):



$$[-CH=\overset{OH}{\overset{|}{C}}-]_n + CH_3.C\begin{matrix}\diagup O\ Si(Me)_3\\ \diagdown\!\!\diagdown N\ Si(Me)_3\end{matrix} \longrightarrow$$

$$\longrightarrow [-CH=\overset{OSi(Me)_3}{\overset{|}{C}}-\ ]_n + CH_3.C\begin{matrix}\diagup\!\!\diagup O\\ \diagdown NH\ Si(Me)_3\end{matrix}$$

However, the addition of BSA to a solution of the poly-1,3-diketone (M_n = 191) in chloroform gave a sticky black tar (M_n = 246) which was soluble in acetone. It was evident from the molecular weight that some chain-scission had occurred and the product was not investigated further.

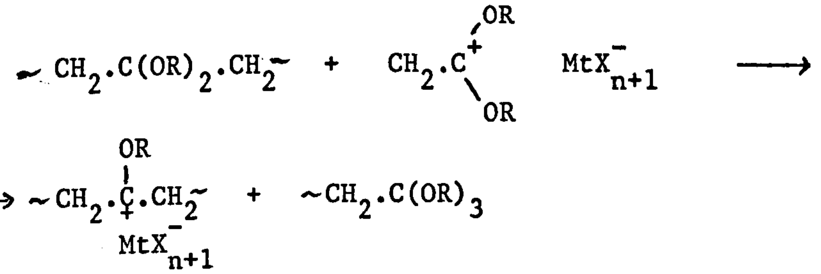
7.3 The hydrolysis of poly-KA2 and poly-KA3

Poly-KA2 decomposed much more slowly in air than poly-KA1. The acid hydrolysis was difficult because of the insolubility of the polymer. However, the polymer suspended in chloroform, was hydrolyzed by dilute acid at room temperature, as described for poly-KA1. The red solid obtained had a similar u.v. and visible absorption spectrum to that of hydrolyzed poly-KA1, but the broad absorption centred at about 3400 cm^{-1}, (characteristic of hydrogen bonded -OH stretching) which was observed for hydrolyzed poly-KA1, was significantly reduced. The hydrolysis of poly-KA3 dissolved in benzene gave a polyketone identical to that produced from poly-KA1.

It is obvious that many more reactions could have been carried out on the poly-1,3-diketone in order to find a product which is suitable for commercial application. The industrial supervisor has suggested two possible applications of the products to date:
a) The poly-1,3-diketone may be useful as a chelating agent for the removal of metallic ions from solutions; b) the polyisoxazole is a potential reagent for the insolubilization of enzymes - special polymers for this purpose are very expensive.

CHAPTER 8: OTHER PROPERTIES OF THE POLYMERS

The "high" polymer of KA1 is soluble in chlorinated hydrocarbons, in aromatic solvents, and in hot dimethoxyethane, but it is insoluble in most other common organic solvents. The polymer isolated by cooling a solution in dimethoxyethane slowly from 60° to room temperature, had a low degree of crystallinity, as determined from an X-ray diffraction powder diagram. In contrast to poly-KA1, poly-KA2 was found to be insoluble in all common organic solvents. It is difficult to explain why poly-ketene acetals are difficult to dissolve; crystallinity can only be partly responsible because the published X-ray diffraction patterns[6] and those taken in this work show that the polymers have a low degree of crystallinity. If intermolecular cross-linking of the polymer chains is responsible for the insolubility, it is not necessary to postulate a mechanism that involves the intermolecular loss of alcohol,[15] because the following explanation seems plausible: The growing ion may abstract an alkoxy group from the polymer chain to give an orthoester end-group and a polymeric tertiary carbenium ion:



$$\sim CH_2.C(OR)_2.CH_2\sim \;+\; CH_2.\overset{+}{C}\begin{smallmatrix}OR\\ OR\end{smallmatrix} \quad MtX^-_{n+1} \longrightarrow$$

$$\longrightarrow \sim CH_2.\underset{MtX^-_{n+1}}{\underset{+}{\overset{OR}{C}}}.CH_2\sim \;+\; \sim CH_2.C(OR)_3$$

If this ion can take part in propagation a 3-dimensional network will be formed eventually which could account for the observed insolubility.

All "high" polymers of the ketene acetals are white powdery solids. Poly-KA1 had a m.p. 200-210° and when the white polymer was heated to 100° for eight hours under vacuum, it became brown, but no volatile products could be isolated.

APPENDIX 1: THE EFFECT OF THE ANION ON THE DP IN CATIONIC POLYMERIZATION

THE EFFECT OF THE ANION ON THE DP IN CATIONIC POLYMERIZATION

There are many papers which purport to record the effect of the anion on the DP of the polymer formed in cationic polymerization. Plesch[35] has shown that in solvents of ε greater than ca. 10, ion-pairs are largely irrelevant as far as propagation is concerned. There is however, evidence that in systems where propagation is predominantly by free ions, the nature of the initiator, which determines essentially the nature of the anion, can influence the DP of the polymer.

The most important way in which a change of anion could influence the DP is probably through the effect of ion size on the ion-pair dissociation constant K_D:-

$$P^+A^- \rightleftharpoons P^+ + A^- \qquad K_D$$

K_D is related to ion size by the Bjerrum-Fuoss equation:-

$$-\log K_D = A - B/a\varepsilon T$$

where a is the distance of closest approach of the ions, ε is the dielectric constant of the solvent, T is the temperature, and A and B are calculable constants.

Suppose that the probability of chain-breaking is greater when the cation is paired than when it is free; this is not unlikely since there is one type of chain-breaking reaction which is peculiar to the paired cation, viz. unimolecular decomposition of the ion-pair. Furthermore, it is not unreasonable to assume that participation of the anion may be a necessary condition in the transition state of the proton transfer to monomer. Then from the point of view of the DP the time during which an ion is paired is much more important than the free time, and thus a change in that time due to a change of anion, has a much greater effect upon the DP than on the rate.

When developing an equation which describes the dependence of the DP on the reaction variables it has been the usual practice to assume that there is only one propagating species in the system. Equations need to be worked out which take into account the existence of two or more propagating species, the relative concentrations of which are governed by equilibria, and which have different propagation, transfer, and termination rate constants.

Consider the following typical set of reactions, consisting of propagation, monomer transfer, and termination:

$$\begin{array}{lcll}
HP_n^+A^- + P_1 & \longrightarrow & HP_{n+1}^+A^- & k_p^{\pm} \\
HP_n^+ + P_1 & \longrightarrow & HP_{n+1}^+ & k_p^{+} \\
HP_n^+A^- + P_1 & \longrightarrow & P_n + HP_1^+A^- & k_m^{\pm} \\
HP_n^+ + P_1 & \longrightarrow & P_n + HP_1^+ & k_m^{+}
\end{array}$$

$$\left.\begin{array}{lc}
HP_n^+A^- & \longrightarrow \\
HP_n^+ + A^- & \longrightarrow
\end{array}\right\} HP_nA \text{ or } P_n + HA \qquad \begin{array}{l} k_{t1} \\ k_{t2} \end{array}$$

Using the following notation:

m = monomer concentration

k_p^+ = free-ion propagation rate-constant

$k_p^{\pm}$ = ion-pair propagation rate-constant

k_m^+ = free-ion monomer transfer rate-constant

$k_m^{\pm}$ = ion-pair monomer transfer rate-constant

k_{t1} = first-order ion-pair termination rate-constant

k_{t2} = second-order free-ion termination rate-constant

i = free-ion concentration

p = ion-pair concentration

c = $i + p$

K_D = ion-pair dissociation constant

β = $k_p^+ / k_p^\pm$

γ = $k_m^+ / k_m^\pm$

The number-average DP of the "instantaneous" polymer is:

$$DP = \frac{\text{Rate of chain propagation}}{\text{Rate of chain breaking}} = V_p/V_b \qquad (1)$$

In this treatment we ignore unidentified chain-breaking reactions and we assume that there is only one type of cation and of anion. Thus:

$$V_p = k_p^+ \, im + k_p^\pm \, pm = m\,(k_p^+ \, i + k_p^\pm \, p) \qquad (2)$$

$$V_b = m\,(k_m^+ \, i + k_m^\pm \, p) + k_{t1}p + k_{t2}\, i^2 \qquad (3)$$

From equations (1), (2) and (3):

$$\frac{1}{DP} = \frac{m\,(k_m^+ \, i + k_m^\pm \, p)}{m\,(k_p^+ \, i + k_p^\pm \, p)} + \frac{k_{t1}\, p + k_{t2}\, i^2}{m\,(k_p^+ \, i + k_p^\pm \, p)} \qquad (4)$$

Since $\gamma = k_m^+/k_m^\pm$ and $\beta = k_p^+/k_p^\pm$:

and,

$$k_m^+ i + k_m^\pm p = k_m^\pm i \, (\gamma + iK_D^{-1})$$

$$k_p^+ i + k_p^\pm p = k_p^\pm i \, (\beta + iK_D^{-1})$$

Hence,

$$\frac{1}{DP} = \frac{k_m^\pm (\gamma + iK_D^{-1})}{k_p^\pm (\beta + iK_D^{-1})} + \frac{k_{t1}p + k_{t2} i^2}{imk_p^\pm (\beta + iK_D^{-1})} \qquad (5)$$

i and p are related to K_D by the Ostwald dilution law:

$$K_D = \frac{i^2}{p} = \frac{i^2}{c-i} \qquad (6)$$

Solving equation (6) for i and dividing through by K_D:

$$iK_D^{-1} = -\tfrac{1}{2} + (\tfrac{1}{4} + cK_D^{-1})^{\frac{1}{2}}$$

Substituting for iK_D^{-1} in equation (5):

$$\frac{1}{DP} = \frac{k_m^\pm \left[\gamma - \tfrac{1}{2} + (\tfrac{1}{4} + cK_D^{-1})^{\frac{1}{2}}\right]}{k_p^\pm \left[\beta - \tfrac{1}{2} + (\tfrac{1}{4} + cK_D^{-1})^{\frac{1}{2}}\right]}$$

$$+ \frac{1}{m}\left[\frac{-\tfrac{1}{2} K_D + \tfrac{1}{2} (K_D^2 + 4K_D c)^{\frac{1}{2}} (k_{t2} + k_{t1}K_D^{-1})}{k_p^\pm \left[\beta - \tfrac{1}{2} + (\tfrac{1}{4} + cK_D^{-1})^{\frac{1}{2}}\right]}\right] \qquad (7)$$

Equation (7) takes the form of the normal Mayo equation[35] if either free ions or ion-pairs are ignored completely.

There are very few reliable values quoted in the literature for the reaction variables used in equation (7) and the full implications of the ideas and equations suggested here remain to be explored. We are carrying out calculations using a computer, in order to see the effect of the reaction variables, particularly K_D and c, on the slopes and intercepts of the Mayo plots.

APPENDIX 2: REPORT ON C.A.P.S. INDUSTRIAL PERIOD SPENT AT THE INTERNATIONAL SYNTHETIC RUBBER COMPANY, HYTHE, HAMPSHIRE.

CONTENTS

CHAPTER 1: INTRODUCTION

1.1 Co-operative Awards in Pure Science

The Co-operative Awards in Pure Science (C.A.P.S.) scheme is designed to encourage the development of collaboration between universities and industry and in particular to provide an opportunity for graduates working in pure science departments to undertake research of direct interest to industry.

To this aim, Dr P. H. Plesch (Keele University) and Dr E. W. Duck (I.S.R.) on the initiative of the former, agreed to supervise jointly a Ph.D student working on the polymerization of ketene acetals. This report describes the work carried out by the author while in the employment of I.S.R. during the period October to December 1972.

1.2 The Company

I.S.R. was founded in 1956 by a consortium of eight major tyre companies, to construct and operate Britain's first large-scale plant for the manufacture of styrene-butadiene rubber (SBR). At present the company has two manufacturing plants in operation, at Hythe (Hampshire) and at Grangemouth (Scotland). In addition to the production of SBR, which is still the 'bread and butter' of the Company, the range of products is diverse and now includes polybutadiene, acrylonitrile-butadiene-styrene resins, and speciality latices. In 1961 a small Research and Development group was established at Hythe; this grew into one of the leading polymer research and development units in Europe. With the recent world surplus in synthetic rubber and increasing competition from abroad, I.S.R. has followed the lead set by other polymer companies and has pruned its research and development staff severely, thus leaving well-equipped research laboratories to be staffed by the chosen few.

CHAPTER 2: THE CENTRAL TESTING LABORATORIES

A period of four weeks was spent in these well-equipped and very efficient laboratories which act not only as a quality control centre for the plant, but also as an analytical centre within the Research and Development Department. I was able to gain invaluable experience in the practical applications of instruments, some of which had until now been for me merely diagrams or photographs in scientific text books.

2.1 Electron microscopy

The electron microscope is used extensively for the determination of the distribution of particle sizes in rubber latices. I was given the opportunity of preparing a test specimen of SBR latex and of examing it under the microscope.

2.2 Differential scanning calorimetry

A Perkin Elmer DSC 1B instrument was used to study the thermal behaviour of some of my poly-ketene acetals. This instrument is used by I.S.R. to measure second-order transitions in rubbers and now that the company has entered the field of semi-crystalline plastics (viz. polypropylene) it will be useful in the future for the study of their first-order transitions.

2.3 X-ray diffraction

The degree of crystallinity of a polymer is very important with regard to its usefulness as an industrial material. In addition to measuring the degree of crystallinity of some poly-ketene acetals, I prepared moulded samples of polyethylene and polypropylene and studied the effect of varying the rate of cooling (and hence the rate of crystallization) on the appearance of the diffraction patterns. Polypropylene, in particular gives diffraction patterns which are very sensitive to crystallite orientation effects and it is very difficult to study in a quantitative manner.

2.4 Gel Permeation Chromatography (G.P.C.)

The adoption of this technique by the polymer industry has accelerated rapidly over the last few years and it is now invaluable, not merely as a research tool, but also as an accurate method of measuring and monitoring the weight-average molecular weight and the molecular weight distribution of a polymeric material, which are so important in determining its physical and mechanical properties. I was shown how to use the Waters G.P.C. instrument and given the opportunity to inject a sample of polystyrene and to calculate its polydispersity.

2.5 High speed membrane osmometry

A Hewlett Packard 501 osmometer was used to measure the number-average molecular weights of samples of ethylene-propylene rubber. Because of the instability of the instrument and the consequent irreproducibility of the measurements, a considerable amount of 'trouble-shooting' was necessary. During this time I became acquainted with many of the problems which have to be overcome and the skills which are necessary to ensure satisfactory operation of the instrument.

CHAPTER 3: THE RESEARCH AND DEVELOPMENT DEPARTMENT

A period of seven weeks was spent in these laboratories. Even in this short time I was able to appreciate the difficulties and frustrations of the industrial chemist in trying to fulfill his philosophical desires whilst working within the realities of big business.

3.1 The polymerization of propylene

Recently, I.S.R. announced that they would commence the manufacture of polypropylene in 1974 at their Grangemouth plant, with an initial capacity of 40,000 tons per annum. The siting of the plant at Grangemouth is due to there being a readily available supply of propylene and hexane from the adjacent British Petroleum (B.P) refinery, and also due to the fact that I.S.R. had polymerization reactors available at Grangemouth.

Most commercial polypropylenes are produced by reacting propylene with a heterogeneous Ziegler-Natta catalyst, comprising titanium trichloride and diethyl aluminium chloride, at moderately high temperatures and pressures ($80-100^{o}$, 5-10 atmos.) in a hydrocarbon diluent such as hexane. This system yields a polymer of 98% isotacticity.

Badische Anilin-und Soda fabriken (B.A.S.F.) have developed a process for the vapour-phase polymerization of propylene with $TiCl_3$ and triethyl-aluminium, utilizing a fluidized-bed reactor. This process gives a polymer of approximately 70% isotactic material in very high yields which, although it is not suitable for structural applications, is still a very useful material.

I.S.R. have investigated several modified Ziegler-Natta catalyst combinations to produce polypropylene consisting of 60-80% isotactic units. The most satisfactory catalyst to date comprises a mixture of $TiCl_3$, $AlEt_3$ and vanadium oxytrichloride $VOCl_3$. A considerable amount of development work has gone into this system in order to devise a suitable commercial process. Four aspects of this project were studied by the author, viz. polymerization using Et_2AlCl in place of $AlEt_3$, the attempted production of 'living' polypropylene, the measurement of the amount of isotacticity in the polymers, and attempts to increase the isotactic content.

3.1.1 Reagents and recipes

3.1.1.1 Propylene

The commercial material (B.P Ltd) was passed through a column containing a copper-ethanolamine complex and finally through a column containing activated molecular sieves type 4A.

3.1.1.2 Hexane

The commercial material (B.P Ltd) was dried by passing it through a column containing activated molecular sieves.

3.1.1.3 Petroleum ether (100-120°)

This solvent (Carless Ltd) was purified by passing it through a de-aromatization column containing silver nitrate on alumina. It was then refluxed over Na/Pb alloy under nitrogen and distilled from a second portion of Na/Pb alloy to which a small amount of butyl lithium had been added. A middle fraction was collected under nitrogen.

3.1.1.4 Toluene

The Fisons A.R. grade solvent was refluxed over sodium for two hours. It was then fractionated under nitrogen through a 36 cm Vigreux column at a reflux ratio of 10:1 and the fraction boiling at 109-109.5°/1 atm. was collected over activated molecular sieves. The solvent was de-oxygenated by bubbling a stream of dry nitrogen through it for several hours.

3.1.1.5 1-Octene

The B.D.H. material was refluxed over freshly-ground calcium hydride for one hour and was then distilled under nitrogen through a 10 cm. Vigreux column. Generous head and tail fractions were rejected and the middle fraction was collected over activated molecular sieves; b.p. 121-122°/1 atm (lit.[64] 121.3/760 mm).

3.1.1.6 Titanium trichloride

Natta[65] has described the various crystalline modifications of $TiCl_3$, α, β, γ and δ forms. In this work δ $TiCl_3$, which is formed by the prolonged grinding of the α form, was found to form the most active catalyst. Also, $TiCl_3$ formed by the reduction of $TiCl_4$ with aluminium was found to be much more active than the material produced by the hydrogen reduction of $TiCl_4$:

$$3\,TiCl_4 + Al \longrightarrow 3\,TiCl_3 + AlCl_3$$

Stauffer AA grade $TiCl_3$ (AA = "aluminium reduced and activated by grinding") was used without further purification. The handling of this material is discussed in section 3.1.2 of this report.

3.1.1.7 Aluminium alkyls

Triethyl aluminium and diethylaluminium chloride (Texas Alkyls) were used without further purification. Diluted samples were prepared by syringing the pure alkyls into dry hexane under nitrogen through a self-sealing rubber septum.

3.1.1.8 Vanadium oxytrichloride

This material (Murex Ltd) was purified by a trap to trap distillation under reduced pressure (1 mm). The involatile oxidation and hydrolysis products were thus removed to leave a pale-yellow liquid, which was diluted as described for aluminium alkyls.

3.1.1.9 Vanadium oxybisdiethyl phosphate (V.D.E.P.)

A slurry of this material (Copolymer Corp.) was prepared in dry hexane under nitrogen.

3.1.1.10 Stearic Acid and calcium stearate

The commercial materials (B.D.H. Ltd) were used without further purification.

3.1.1.11 Nitrogen

This gas was available in the laboratory 'on tap' having been dried by passing it through two columns of activated molecular sieves.

3.1.2 Techniques and apparatus

3.1.2.1 Preparation of $TiCl_3/VOCl_3$ catalyst slurries

All the catalysts were prepared in ½ pt. crown-capped bottles which were fitted with a self-sealing rubber septum.

Procedure:

An uncapped bottle containing a mixture of three sizes of glass balls was heated in an oven at 150° for several hours, and was then allowed to cool under a stream of dry nitrogen. The bottle was then transferred to a glove box and was dosed with the required amount of $TiCl_3$. After capping the bottle, it was charged with dry hexane directly from the still by means of a syringe needle inserted through the septum. The required amount of $VOCl_3$ was syringed into the bottle, which was then placed on electrically driven rollers and the contents were ball-milled for a measured time. The quantities of the reagents were determined by weighing the bottle before and after each addition.

3.1.2.2 Polymerization

The procedures described below are the "standard" procedures; any deviations from these are indicated in the results section of this report.

3.1.2.2.1 Experiments at atmospheric pressure

The polymerization apparatus was a flanged vessel of about 600 mls capacity. The flanged vessel-head carried four sockets. The central socket was fitted with a stirrer which was lubricated with castor oil. Two of the sockets carried inlets and outlets for nitrogen and propylene. The outlet tube was fitted with a condenser and was protected by a gas washing bottle containing liquid paraffin. The fourth socket carried a thermometer pocket. A Teflon gasket was used as a sealant between the flanges, and the taps were lubricated with silicone grease.

Procedure:

The vessel and all its fittings were dried in an oven at 150° for several hours. The apparatus was assembled whilst hot and was then allowed to cool under a stream of dry nitrogen. The required amount of petroleum ether (500 mls) was dosed into the reaction vessel and a stream of dry nitrogen was allowed to bubble through the solvent for 2 hours. The nitrogen supply was then turned off, the stirrer was started, and the propylene supply was connected. An electrical heating mantle was then placed around the vessel. At between 30-40° the required amounts of aluminium alkyl solution and $TiCl_3/VOCl_3$ slurry were syringed into the vessel (this order of addition is important since some of the aluminium alkyl undoubtedly acts as an impurity scavenger). The vessel and its contents were then heated to 80° and maintained at this temperature for the required reaction time; the propylene addition was continued throughout the polymerization. The uptake of propylene could be checked by turning off the propylene supply momentarily and observing (sucking-back in the gas washing bottle) the partial vacuum created by the polymerization.

After the required reaction time, the catalyst was deactivated by the addition of 5 mls of methanol, containing 10% STAVOX antioxidant. The contents of the reaction vessel were then poured into 2 litres of acetone. After being allowed to stand overnight, the polymer was filtered off and dried to constant weight in a vacuum oven at 60-80°.

3.1.2.2.2 Experiments under pressure

Experiments were carried out in a stainless-steel reaction vessel. The flanged vessel-head carried inlets for nitrogen and propylene and a self-sealing rubber septum for the introduction of catalyst. A vent pipe was fitted to allow the reactor to be de-pressurized. The vessel was fitted with an oil-pressurized Crane-seal stirrer and a stainless steel 'O' ring was clamped between the bolted flanges.

Procedure:

The assembled reactor was heated by means of an external heating jacket to 200° under a stream of dry nitrogen. After being allowed to cool, 3 litres of hexane were poured into the reaction vessel. The stirrer was started and nitrogen was admitted to a pressure of 100 p.s.i.g.; the nitrogen was then vented off to the atmosphere. This process was repeated a further three times. After the final purging with nitrogen the vessel was pressurized to 25 p.s.i.g. with propylene. The pressure was then reduced to 10 p.s.i.g. to allow aluminium alkyl solution and the $TiCl_3/VOCl_3$ slurry to be syringed in through the rubber septum. The reactor was then heated to, and maintained at, 85° and the pressure of propylene was increased to 100-130 p.s.i.g. The decrease in pressure observed in the reaction vessel on shutting off the propylene supply for several minutes, was used as a crude measure of the success or failure of a reaction. At the end of the polymerization the reactor was cooled and dismantled and the contents were poured into rapidly-stirred boiling water; this served to flash off the hexane and to break up the polymer into a finely divided form. The polypropylene was then filtered off and was dried to constant weight in a vacuum oven at 60-80°.

3.1.2.3 Heptane extractions

Representative samples of the polymers were extracted in a Soxhlet apparatus for 4 hours with boiling heptane. The insoluble residue is expressed as the percentage (by weight) remaining of the initial sample.

3.1.2.4 Infra-red spectroscopy

A Unicam SP200 instrument was used to record the spectra of films prepared from the whole polymers by compression moulding at 180°.

3.1.2.5 Intrinsic viscosities

Intrinsic viscosities were measured with a Ubbelodhe viscometer in decalin at 135°. The addition of 0.5% w/w of N-phenyl-2-naphthylamine to the samples served to prevent oxidative degradation.

3.1.3 Results and discussion

3.1.3.1 Polymerization with Et_2AlCl under pressure

The results of these experiments are shown in Table A1. The most obvious feature of these reactions was the very low yields (Y) obtained compared with the corresponding system containing $AlEt_3$, where Y = 35 kg/g Ti. Experiments 1, 2 and 13 show that under these reaction conditions Y is independent of the amount of

TABLE A1

The Polymerization of Propylene with Et_2AlCl and $TiCl_3/VOCl_3$ under pressure.[a]

Expt. No.	Et_2AlCl /mmol	Q[b] /mmol	Propylene pressure /p.s.i.g	Yield of Polymer /g	Y[c] /kg	Deviations from standard procedure
1A	6.0	2.0	110	193	2.01	
1B	6.0	2.0	110	176	8.84	
2A	6.0	1.0	110-115	97	2.02	
2B	6.0	1.0	110-115	109	2.30	
13	6.0	0.5	110-115	51	2.13	
3A	6.0	2.0	115	210	2.19	Catalyst added at 90° under propylene
3B	6.0	2.0	115	261	2.72	ditto.
5	6.0	2.0	110-115	194	2.02	Catalyst added at 85° under nitrogen
6A	6.0	2.0	110-115	205	2.14	Only 1l. hexane used
6B	6.0	2.0	110-115	183	1.91	ditto.
8	3.0	2.0	110	0	0	
9A	6.0	2.0	110-115	276	2.88	$Et_2AlCl/TiCl_3$ catalyst; no $VOCl_3$
9B	6.0	2.0	110-115	248	2.59	
10	6.0	2.0	110	0	0	2g of stearic acid added.
11A	6.0	2.0	110	79	0.82	ditto.
12	6.0	2.0	110-115	0	0	2g of calcium stearate added.

a Volume of hexane 3 litres; reaction temperature 90°
b Quantity of 25:1 $TiCl_3/VOCl_3$; ball-milled for 16 hours.
c Yield of polymer/g Ti in 4 hours.

$TiCl_3/VOCl_3$ (Q). Although only 2 different amounts of Et_2AlCl were used (6 mmol and 3 mmol) it appeared that either the Et_2AlCl was impure or a greater amount of Et_2AlCl was required to react with the $TiCl_3$, since amounts of $AlEt_3$ as low as 0.2 mmol could be used quite successfully.

Because of the limited amount of time available, only the 25:1 mole ratio Ti:V catalyst was used; this has been found to be the optimum mole ratio for the $AlEt_3$ system. Reaction 9 shows that the presence of $VOCl_3$ lowers the yield and reduces the isotacticity of the polymer.

In connection with the studies on the $AlEt_3$ system (see section 3.1.3.2) experiments were carried out to determine whether the catalyst could be added at the reaction temperature. Experiments 3 and 5 show that this procedure can be carried out quite successfully without any detrimental effect on either the yield of polymer or its isotacticity. However, the polymer produced by this procedure consisted of large agglomerated lumps which are not very suitable for use in an injection-moulding machine. The polymerization of propylene in the presence of a small amount of 1-octene (experiment 11) resulted in a reduction in Y of about 70%.

Thus the use of Et_2AlCl in place of $AlEt_3$ gives a significantly lower yield and does not improve the isotacticity of the product. The main advantage of this system is that the catalyst can be added at the reaction temperature.

Chemistry:

The chemistry of the Ziegler-Natta polymerization of propylene has been reviewed many times, but it has not as yet been found possible to elucidate completely the structure of the catalyst sites.

The reaction of aluminium alkyls with transition metal halides can be described as an exchange reaction between alkyl groups and halide ions, followed by reductive dealkylation of the organo-transition metal so formed: e.g.

$$AlEt_3 + TiCl_3 \longrightarrow Et_2AlCl + EtTiCl_2$$

Various mechanisms have been proposed for the Ziegler-Natta polymerizations of α-olefins, including radical, coordinated cationic, and coordinated anionic reactions. The last two involve insertion of a monomer molecule between a metal atom and an alkyl group, and the catalyst sites in these reactions are believed to contain either one or two types of metal atoms, but the available evidence is insufficient to differentiate between mono and bi-metallic catalyst sites. The mechanisms most likely involves an insertion reaction that is based on a coordinated anionic species. The catalyst site contains at least one empty transition-metal orbital for adsorption of the monomer in the form of a complex formed with the π-electrons of the double bond. This adsorption serves both to activate the double bond for the addition reaction and to orient the monomer for stereoregular growth; complexing is a form of cationic attack on the double bond. The monomer adds to a growing polymer chain at a metal-carbon bond present in the catalyst site. Chain transfer occurs with monomer, catalyst components, or by internal hydride transfer. Termination normally occurs by reaction with added compounds (e.g water) or by over-reduction of the catalyst components.

The role of the $VOCl_3$ in the I.S.R. catalyst is not known. $VOCl_3$ plus an aluminium alkyl is known to form a soluble catalyst system, but it will not produce high molecular weight isotactic polymer. Furthermore, analysis has shown that after ball-milling $VOCl_3$ with $TiCl_3$, no vanadium is detectable in solution. Some of the $TiCl_3$ is undoubtedly oxidized but only one mol of Ti for 8 mol of V is found in solution. The most probable modes of action of the $VOCl_3$ are either by its interaction with $TiCl_3$ to form fresh active sites, or by it acting alone as a supported heterogeneous catalyst.

3.1.3.2 Polymerization with $AlEt_3$ at atmospheric pressure

3.1.3.2.1 The $AlEt_3/TiCl_3/VOCl_3$ system

One of the problems associated with this catalyst system, compared with the Et_2AlCl system, is the fact that it is not possible to produce polymer if the catalyst is added at the reaction temperature. The Company management decided that addition of the catalyst at the reaction temperature was desirable, although the author was unable to find out whether there were any basic chemical engineering problems which could not be overcome by operating with a temperature gradient in a continuous flow stirred tank reaction system.

When the catalyst is added to the solvent saturated with propylene at temperatures above about 60^o, the solution turns black and a very low yield of sticky, stringy polymer is formed. Thus it seemed likely that the reduced activity was due to over-reduction of the $TiCl_3$ ($TiCl_2$ is an insoluble black solid.) The possibility of using a vapour-phase polymerization (similar to the B.A.S.F. process) was vetoed by the Managing Director.

Investigations were directed towards stabilizing the catalyst before its introduction into the reaction vessel. Mixtures of $AlEt_3$ and $TiCl_3/VOCl_3$ were prepared in hexane at room temperature and then propylene was bubbled through the mixture until traces of polypropylene could be seen. These catalyst mixtures were then ball-milled for 7 hours. The results of these experiments are shown in Table A2.

It is known that higher olefins can be polymerized by Ziegler-Natta catalysts to yield low molecular weight products. However, the ball-milling of the $TiCl_3/VOCl_3$ with various amounts of 1-octene did not improve its stability at high temperatures. The most successful method of stabilization of the catalyst seems to be to add the catalyst at 80^o to solvent which is saturated with ethylene (ethylene is much more reactive than propylene). The propylene supply may then be connected to give a successful polymerization.

3.1.3.2.2 The $AlEt_3/TiCl_3$/V.D.E.P. system

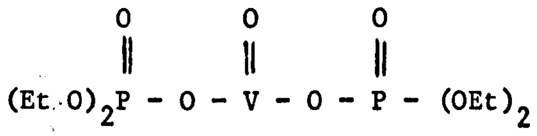
The management suddenly decided that it would be wise to investigate the possibility of increasing the isotactic content of the polypropylene.

One possible reason for the lowering of the isotacticity by $VOCl_3$ is the following reaction:

$$TiCl_3 + VOCl_3 \longrightarrow TiCl_4 + VOCl_2$$

The interaction between $TiCl_4$ and aluminium alkyls yields brown β-$TiCl_3$ which always forms larger amounts of atactic polypropylene than the other three forms of $TiCl_3$.

Vanadium oxybisdiethyl phosphate (V.D.E.P.) is used commercially as a component of a ternary Ziegler-Natta catalyst for the production of ethylene-propylene rubbers.



$$(\mathrm{Et{\cdot}O})_2\overset{\overset{\displaystyle O}{\|}}{P} - O - \overset{\overset{\displaystyle O}{\|}}{V} - O - \overset{\overset{\displaystyle O}{\|}}{P} - (\mathrm{OEt})_2$$

V.D.E.P.

TABLE A2

The addition of $AlEt_3/TiCl_3/VOCl_3$ to the reactor at 80° under atmospheric pressure

Expt. No.	$AlEt_3$ /mmol	Q /mmol	Colour of catalyst mixture	Observations on adding catalyst to reactor
17A	20	5	Black	Mixture turned black - low yield of stringy highly atactic polymer produced.
17B	2.5	5	Violet	
17C	5	5	Brown	

Preliminary results on the polymerization of propylene with the $AlEt_3/TiCl_3$/V.D.E.P. system at atmospheric pressure indicated that the percentage of heptane-insolubles could be increased to 75% (D_{998}/D_{973} = 0.923) without any decrease in yield. However, the intrinsic viscosity of the polymer was only 3.6 dl g^{-1}.

3.1.3.3 Polymer properties

3.1.3.3.1 Appearance of injection-moulded polymer

When the author began this work, the production of polypropylene samples for physical testing purposes by injection-moulding techniques invariably led to highly discoloured products, frequently dark brown, It was suspected that this discolouration was caused by the presence of catalyst residues in the polymer. Since the removal of trace quantities of catalyst residues would be expensive on an industrial scale, methods for removing the discolouration were investigated. It was found that if the finely-divided polymer was mixed intimately with 1% w/w of calcium stearate or stearic acid before the injection moulding, the resulting samples were pure white. Calcium stearate and stearic acid are described in the literature on polymer additives as 'lubricants'.

The possibility of including calcium stearate or stearic acid in the polymerization recipe was investigated. Experiments 10 and 12 (Table A1) show that the presence of these reagents prevents the formation of an active catalyst. However, if 1g of either of these reagents were stirred with the polymer slurry, before working it up, the resulting polymer produced a colourless product when injection moulded. It was of interest to determine whether calcium stearate or stearic acid reacted with the catalyst components to produce a colourless product. Although a comprehensive investigation was not carried out, the interaction between stearic acid and $TiCl_3$ was investigated; this reaction has not been reported in the literature. The reactions were carried out in toluene, under nitrogen. A typical recipe was as follows:- To a slurry of $TiCl_3$ (3.9 g, 25.3 mmol) in 50 mls of toluene was added with stirring, under nitrogen, a solution of stearic acid (22g, 76 mmol) in 50 ml of toluene. The colour of the mixture remained violet and there was no visual indication of a reaction. The mixture was then heated at reflux for 2 hours, whereupon the colour darkened and finally a very dark blue solution was left. When the solvent was removed under reduced pressure there remained a dark blue solid which was not investigated further. If a sample of the solution was allowed to stand in the atmosphere, its colour changed in 5 min. through green and claret, and finally apale brown solid was precipitated from it.

3.1.3.3.2 Degree of crystallinity and isotacticity

Two methods are commonly employed to estimate the amount of stereo-regular material in polypropylene, namely the percentage of material insoluble in boiling heptane[66] and measurement of the intensity of certain absorption peaks in the infra-red.[67] The solubility method is subject to errors due to non-selective dissolution, whilst the i.r. method is probably applicable as a relative means of estimating crystallinity rather than tacticity. Tests were carried out to establish a correlation between the two methods. For this purpose it was necessary to use a 'standard' method for preparing the films for i.r. measurements. Thin films were prepared by hot pressing (3000 p.s.i.g. at 180^o) and they were then annealed in an oven at 170^{o} for 10 minutes. The oven was then switched off to allow the films to cool slowly. Quantitative absorbance measurements were made at 998 cm^{-1} and the 973 cm^{-1} band was used as an internal film thickness calibration. In order to determine the effect of molecular weight on the measurements, the intrinsic viscosities of the polymers were also determined. The results are shown in Table A3 and Figure AI. The D_{998}/D_{973} has been shown to correlate well with the absolute crystallinity of propylenes. It is apparent from the scatter of points in Figure AI that other factors in addition to crystallinity affect the percentage soluble in heptane. The number of intrinsic viscosity determinations is not sufficient to establish a definite relationship between D_{998}/D_{973} and percentage of insolubles at a constant $[\eta]$, but it seems plausible to assume that for any set of samples the increased insolubility which one would expect to accompany high crystallinity may be outweighed by their lower molecular weight.

TABLE A3

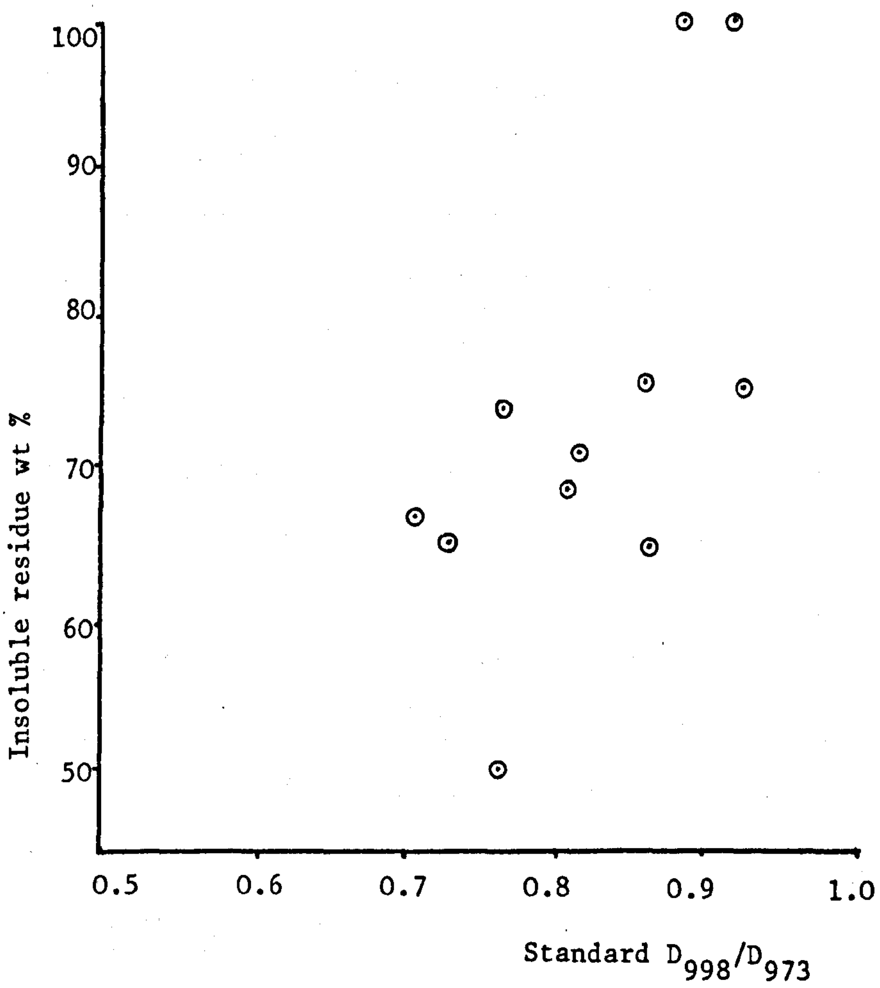
Properties of the Polymers

Sample No.	% heptane insolubles	Standard D_{998}/D_{973}	$[\eta]/\mathrm{dl\ g^{-1}}$	Appearance of dry polymer
1A	65	0.865	-	fine white powder
1B	69	0.812	6.0	ditto.
2A	50	0.758	5.7	ditto.
2A*	100	0.894	5.9	ditto.
3B	82	-	-	sticky translucent lumps
5	65	0.739	7.5	stringy white solid
6A	67	0.725	-	fine white powder
6A*	100	0.919	-	ditto.
9A	71	0.820	-	very fine white powder
9B	76	0.861	-	ditto.

* Residue from Soxhlet extraction

FIGURE A1

Correlation of amount of insoluble residue with i.r absorption at 998 cm^{-1} for polypropylene



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