THE STUDY OF A NOVEL ZIEGLER CATALYST FOR THE POLYMERISATION OF OLEFINS

DAVID GEORGE BOUCHER

A thesis submitted for the Degree of
Doctor of Philosophy in the Faculty of
Science and Engineering.

Chemistry Department
July 1977

Text cut off in original

ACKNOWLEDGEMENTS

I wish to thank the University of Birmingham for the provision of the grant to support this work. I am grateful to Professor R N Haward, Dr I W Parsons and Dr J N Hay for their valuable discussions and helpful advice. I am indebted to Mr S W Hawley of R.A.P.R.A. for the gel permeation chromatography results and to Mrs L A Price for her assistance and encouragement. I should also like to thank Mrs J Finn and Mrs B Curtis for typing the manuscript and Mrs E Postings for her assistance with the initial draft. Lastly, I must thank my parents for their perseverance and encouragement during the writing of this thesis.

SYNOPSIS

The reactivity of a novel magnesium alkyl reduced Ziegler catalyst system, has been studied in the preparation of various homopolymers and copolymers. Many of the earlier experiments were based upon the use of ethylene monomer as the major component of the polymerisation system. In the later sections, the work mainly concerns the formation of styrene polymers although acetylene and 4-methylpent-1-ene have also been used as the monomers.

A method for graft copolymerisation using the magnesium reduced Ziegler catalyst was studied based upon a technique developed by Greber and Egle. This technique involved the generation of a polymeric dialkyl aluminium precurser which the earlier authors had reported to be capable of initiating polymerisation in a titanium tetrachloride based Ziegler system. However, under the conditions employed in this work such polymeric substrates could not be developed with the ability to act as cocatalyst for a magnesium reduced titanium trichloride system.

Negligible yields of polymer were obtained from the catalyst when a modification of the Greber and Egle technique was used, although previous experiments had shown that the magnesium reduced catalyst system had a high level of activity for ethylene when used with a trialkyl aluminium cocatalyst. The evidence of several experiments suggested that this technique will not provide an efficient route for the synthesis of graft copolymers of ethylene.

An alternative study was undertaken into the activity of the magnesium reduced catalyst in its reaction with other unsaturated monomers. The three alternative monomers used were styrene, acetylene and 4-methylpent-1-ene. In the case of acetylene a polymeric material was generated using this catalyst system. The material appeared to be polyacetylene but proved difficult to handle and characterize. Several samples were prepared using mixtures of ethylene and acetylene but these copolymerised materials were similarly intractable. Low activity and very poor yields were observed when the system was used to polymerise 4-methylpent-1-ene and 4-methylpent-1-ene/styrene mixtures.

The magnesium reduced titanium trichloride catalyst was effective when applied to styrene polymerisation although the activity which the catalyst exhibited was low and proved inferior to that of a conventional aluminium triethyl reduced system. In addition, it was found that a major fraction of the polystyrene produced was readily soluble when extracted with methyl ethyl ketone and so further investigations into the tacticity of the material were undertaken, based largely on spectroscopic studies and an investigation of the crystallisation properties.

The polymer molecular weight and the reaction rate were studied as a function of catalyst, monomer, and cocatalyst concentration, temperature and time. The number average molecular weight, M_n, was estimated from gel permeation chromatography measurements. These results were used to obtain values for the concentration of active polymerisation sites, propagation rate constant and the lifetime of the growing polymer chain. A determination of the overall apparent activation energy of the reaction was made giving a value of 64 ± 30 kJ. This study suggested that the differences between the magnesium reduced catalyst system and conventional Ziegler catalysts can be attributed to the increased disorder in the catalyst particles caused by this novel preparative technique.

CONTENTS

PAGE NUMBER

CHAPTER ONE: ADDITION POLYMERS

SECTION FOUR

CHAPTER TWO; GRAFTED BLOCK COPOLYMER EXPERIMENTS

CHAPTER THREE: STYRENE POLYMERISATION EXPERIMENTS

CHAPTER 1

SECTION 1 - INTRODUCTION

It is only in comparatively recent times that man has investigated the chemical nature of polymers, although they have always been important natural materials, e.g. cellulose, proteins, nucleic acids and enzymes. It is now possible to manufacture many new polymeric materials by the development of suitable chemical reactions and the commercial exploitation of such processes has led to synthetic plastics becoming a familiar part of our contemporary life-style.

1.1. - POLYMERS AND COPOLYMERS

A polymer is defined as being a substance, the molecules of which are made up of many repeating units, the monomers, which are generally small molecules, but may be atoms. The polymer molecule by convention consists of in excess of 100 - 200 such units and is thus of molecular weight ~10,000. A copolymer is defined (1,2) as a polymer consisting of a heterogeneous combination of two or more different repeating units.

Many commercial symethetic polymers are homopolymeric, consisting of relatively linear chains of identical monomer units - e.g. poly(vinyl chloride), polyethylene, polypropylene - as represented below:-

$$- M_1 - M_1 - M_1 - M_1 - M_1 - M_1 - M_1 - M_1 - M_1 - M_1 - M_1 -$$

In contrast, natural polymers are generally copolymers with complicated heterogeneous combinations which, in many cases, involve several different monomer units. Synthetic copolymers normally possess a simpler structure consisting of only a few types of monomer units, e.g. 2 or 3 types, combined together either in a random fashion or in simple arrangements. The three main sorts of synthetic copolymer are outlined below:-

A) A random copolymer

$$- M_1 - M_1 - M_2 - M_1 - M_2 - M_2 - M_1 - M_1 - M_1 - M_1 - M_2 -$$

B) A regular copolymer (e.g. an alternating copolymer)

$$- M_1 - M_2 - M_1 - M_2 - M_1 - M_2 - M_1 - M_2 - M_1 - M_2 - M_1 -$$

Further factors, such as the degree of branching within the molecule and the composition differences between the main chain and side chains, which govern the nature of a copolymer, produce two additional sub-divisions:-

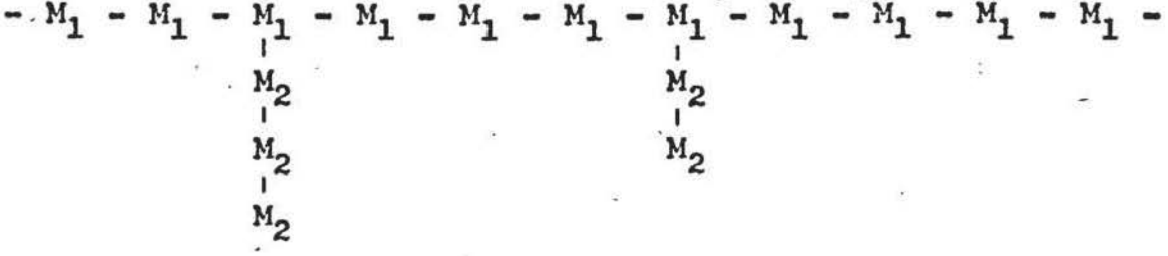
1. Linear block Copolymer:

A linear polymer molecule with two or more uninterrupted sequences of homopolymeric species, e.g. -

$$- M_1 - M_1 - M_1 - M_1 - M_1 - M_1 - M_2 - M_2 - M_2 - M_2 - M_2 - M_2$$

2. Grafted block copolymer:

A branched polymer molecule with a backbone of one polymeric species attached to which are one or more side chains of another polymeric species, e.g. -



$$\begin{array}{ccccccccccccccccccccccc}
- & M_1 & - & M_1 & - & M_1 & - & M_1 & - & M_1 & - & M_1 & - & M_1 & - & M_1 & - & M_1 & - & M_1 & - & M_1 & - \\
 & & & & & | & & & & & & & & | & & & & & & & & & \\
 & & & & & M_2 & & & & & & & & M_2 & & & & & & & & & \\
 & & & & & | & & & & & & & & | & & & & & & & & & \\
 & & & & & M_2 & & & & & & & & M_2 & & & & & & & & & \\
 & & & & & | & & & & & & & & & & & & & & & & & \\
 & & & & & M_2 & & & & & & & & & & & & & & & & &
\end{array}$$

Further sub-division of the main types occurs if branching within the homopolymeric segments (possibly due to transfer or combination reactions, e.g. cross-linking) takes place, and also in cases where the segments forming the 'blocks' are copolymeric rather than homopolymeric.

The tacticity of monomer sequences can also be regarded as a factor for classification, e.g. "stereoblock" copolymers, poly ((iso) styrene - g - (a) styrene) and in the case of polymers derived from diolefins the inclusion of cis and trans (Z and E) nomenclature for the arrangement of the geometrical isomers must also be considered.

1.2. - COPOLYMER NOMENCLATURE

The nomenclature (1,2) used for the classification of the copolymers outlined above, is exemplified in the following list:-

Homopolymers

- polyethylene
- polystyrene
- poly (vinyl acetate)

Copolymers

Random:	poly (butadiene-co-styrene) Note: the first monomer of the pair is the predominant proportion of the copolymer composition.
Alternating:	poly (styrene-alt-maleic anhydride)
Block:	poly (styrene-b-methyl methacrylate)
Graft:	poly (ethylene-g-acrylomitrile) Note: the first monomer of the pair forms the backbone chain of the copolymer.

Complex examples:

poly (styrene-g-butadiene-co-styrene)

poly (methyl methacrylate-b-styrene-co-butadiene)

poly (butadiene-co-styrene-g-styrene-co-butadiene)

e.g. The last copolymer listed above represents a random copolymer with a high proportion of styrene to butadiene grafted onto a rubber with a low proportion of styrene to butadiene.

The prefixes (br) and (c.l) can be used to indicate branching and cross-linking respectively, and tacticity can be accommodated using the prefixes (iso) - for isotacticity, (syndio) - for syndiotacticity and (a) - for atacticity. If the prefix is placed before the "poly" it can be used to indicate that the feature is present in all segments, e.g. (c.l) poly (styrene-g-butadiene), poly (iso) styrene-b-(syndio styrene).

1.3. - TACTICITY OF POLYMERS

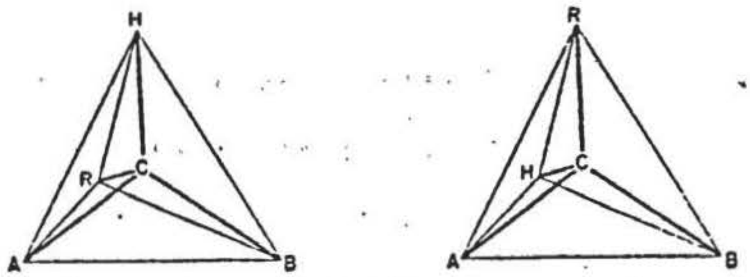
The tacticity of a polymer is a further possible variable in its structure which arises when a carbon atom of the backbone chain is attached to two different side groups. The simplest case is vinyl polymers of the form $-(CH_2-CRR')_n-$ where alternate carbon atoms are chiral, i.e. asymmetric centres, as they are attached to four different atoms or groups. Thus, at such a chiral centre, two possible configurations exist (3), known as R, the right handed, and S, the left handed, mirror images of each other. Polymers which contain a random arrangement of these two configurations are known as atactic polymers, whilst those with regular arrangements are tactic polymers. If there is a continuous repetition of the same type of configuration (e.g. R) the arrangement is known as isotactic, whilst alternation of the two types is called syndiotactic, as illustrated in Figure 1.

SECTION 2 - HISTORICAL BACKGROUND

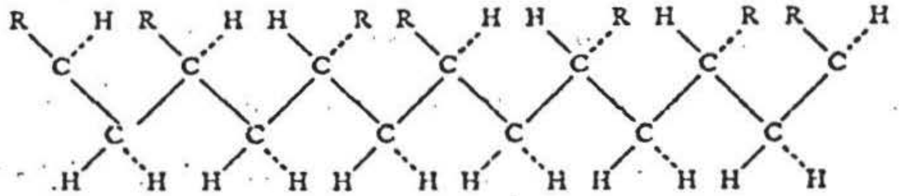
Natural rubber and cellulose have been processed as commercial materials since the 19th century but it is only since the beginning of this century that the development of most of the contemporary synthetic polymers has taken place. Several polymers which were merely laboratory curiosities before 1930 found important applications during the 1939-1945 war and the demands of the war effort intensified their development as new materials. Styrene-butadiene rubbers, polystyrene, polyethylene, polymethylmethacrylate and polyvinylchloride were all introduced commercially as new synthetic materials during the nineteen thirties and forties.

The earliest record of the material we know as polystyrene occurs around the 1840's, when it was observed by Simon (4) and also Blyth and Hoffman(5). By 1866 Berthelot (6) had discovered the technique of solution polymerisation and that the reaction was affected by certain catalytic agents. However, much of the early

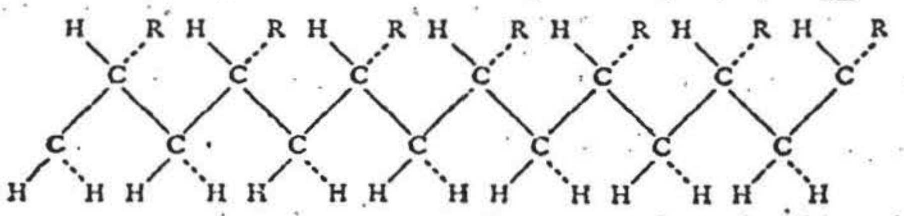
Figure 1



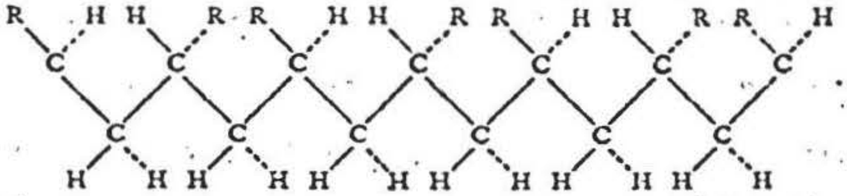
The two possible configurations at an an asymmetric carbon atom.



Atactic



Isotactic



Syndiotactic

Illustrations of the arrangement of substituents in the various forms of tacticity.

~dddddddd~	Isotactic	Tactic
~llllllll~	Isotactic	
~dldldldl~	Syndiotactic	
~dddldlld~		Atactic

The various stereoisomers can be illustrated in the manner shown above with the configurations arbitrarily designated right handed(d-) and left handed(l-)(with no implication as to the direction of any optical rotation).

Representations of polymer tacticity.

Diagrams illustrating polymer tacticity.

study of styrene polymerisation was contributed by the efforts of Ostromislensky (7) between 1910 - 1920, and also the later work of Staudinger (8). Following the recognition of polystyrene as a useful synthetic material, the concentrated effort of many research workers led to its commercial production and the subsequent needs and demands of the 1939 - 1945 war accelerated its development into a very successful commercial product.

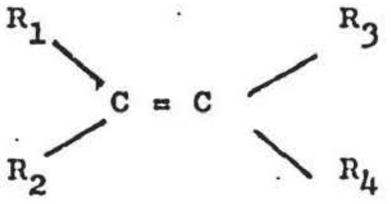
Polyethylene was first observed by Pechmann (9) in 1898 and subsequently prepared by several methods (10) in the 1920's. It was not until the 1930's that commercial interest was attracted by the discovery, by Fawcett and Gibson (11), which involved a high pressure reaction. Further research led to a patent on the process by Imperial Chemical Industries Limited (12) in 1937, and by 1942 the Company had a full scale continuous plant in operation. The next important step forward was some twenty years later, in the development of low pressure synthesis processes.

The first of these syntheses for the low pressure polymerisation of ethylene was discovered by K Ziegler (13) in 1954. This became the starting point from which many other olefin polymerisation processes, using a catalyst precipitated by the reaction of transition metal salts and metal alkyls, were developed. It was followed in 1955 by the discovery of an alternative method by the Phillips Petroleum Company (14) which employs a preformed transition metal oxide catalyst supported on silica.

These processes had an important difference from the high pressure technique, in that the polymer produced was essentially linear chain material, in contrast to that produced by the latter, which was highly branched. An even more significant result is the ability of such catalysts to regulate the stereochemistry of higher α-olefin polymers. After the Ziegler discovery, intensive investigations were carried out by Natta on a wide range of monomers including propylene, styrene, 4-methylpentene and but-1-ene (15). The use of this type of catalyst for steric control of propagation sequences enabled the synthesis of highly isotactic polymers (16), in particular the preparation of isotactic polypropylene both in the laboratory and on a commercial scale. This polymer, in contrast to its atactic counterpart, proved to be a useful and saleable material.

SECTION 3 - α- OLEFIN ADDITION POLYMERISATIONS

A vinyl monomer is a substance whose general formula is indicated below:-



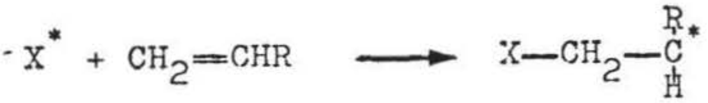
where the groups R_1 - R_4 are either hydrogen or a substituent. In general, very few tetra-substituted monomers readily produce high polymers; however, fluorine atoms are exceptional, due to their small size, and materials such as polytetrafluoroethylene and polychlorotrifluoroethylene are useful polymers. Quite a few compounds in which $R_1 = R_2 = H$ with two substituents are readily polymerisable and a few of the type $R_1 = R_3 = H$ are also easily polymerised. The bulk of the compounds of this type which will form polymers are the monosubstituted ethylenes ($R_1 = R_2 = R_3 = H$).

The addition polymerisation of a typical α-unsaturated monomer may be represented simply in the following equation:-

$$n\left(CH_2{=}C\begin{smallmatrix}R\\H\end{smallmatrix}\right) \longrightarrow \left[CH_2-\overset{R}{\underset{H}{C}}\right]_n$$

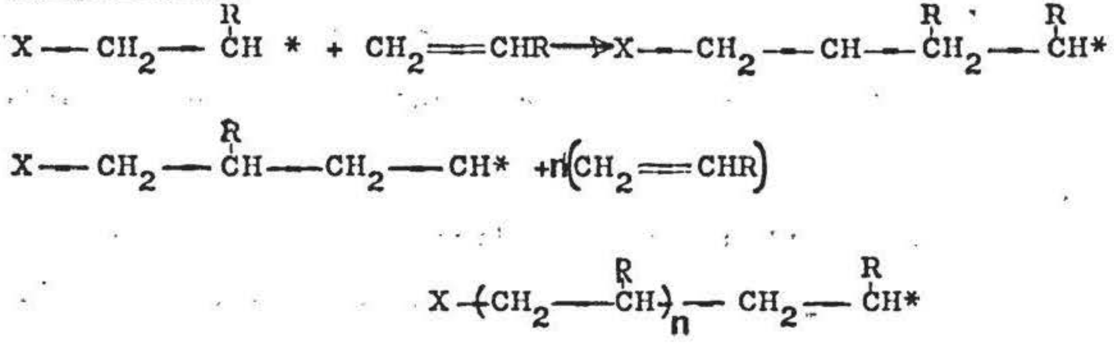
The mechanism for the reaction is far more complex than this over-simplified equation indicates, as there are several possible types of reaction in a vinyl polymerisation. Nevertheless, in general, all the types can be considered to have three basic mechanistic steps:-

(1) Initiation



$$X^* + CH_2{=}CHR \longrightarrow X-CH_2-\overset{R}{\underset{H}{C}}{}^*$$

(2) Propagation

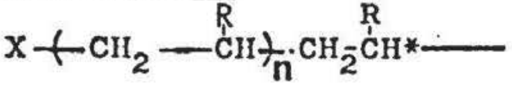


$$X-CH_2-\overset{R}{C}H^{*} + CH_2{=}CHR \rightarrow X-CH_2-CH-\overset{R}{C}H_2-\overset{R}{C}H^{*}$$

$$X-CH_2-\overset{R}{C}H-CH_2-CH^{*} + n(CH_2{=}CHR)$$

$$X(-CH_2-\overset{R}{C}H-)_n-CH_2-\overset{R}{C}H^{*}$$

(3) Termination



$$X(-CH_2-\overset{R}{C}H-)_n\cdot CH_2\overset{R}{C}H^{*}\longrightarrow$$ inactive polymer chain.

These three steps differ in detail depending upon the class of initiation involved in the reaction. The initiator may be one of at least four types, and determines the character of the active centre,

These types are: 1) the free radical centre (17)
2) the cationic centre (18)
3) the anionic centre (19)
4) the co-ordination catalyst active centre (20).

In general terms, the role of the initiator is to start the growth of a particular chain by becoming part of it. Growth is then continued at an active site in which the initiator no longer plays a part. A catalytic centre is usually responsible for starting the growth of many chains and may well participate in the addition of each monomer unit ; i.e. the catalyst is literally the active site or an integral part of it.

Most monomers are only readily polymerised by one or two of the catalyst/initiator types and normally this will not be with equal effectiveness in terms of the scale of reaction and the molecular weight of the polymer. From a consideration of the steric and electronic structure of the monomer it is often possible to estimate its susceptibility to each type of initiation. Generally, polymerisation is less likely for sterically hindered vinyl or diene compounds and enhanced by the electronic effects of substituents which provide resonance stabilisation of the active centre, whether it is an ion or a radical. Table I shows the effect of the various initiators upon various vinyl monomers. Certain monomers may be polymerised by more than one technique if either the radical and one or both of the ionic type active centres can be stabilised, e.g. styrene, iso-butylene and N-vinylcarbazole.

In addition to a consideration of the initiation step, it must be remembered that for polymerisation to occur, the subsequent propagation step must occur much more readily than any termination process. There are characteristic termination reactions for the four types of vinyl polymerisation initiation/propagation mechanisms. The free radical termination mechanism is either the bringing together of two radicals, which destroys the growing centres to give 'dead' polymer molecules, or merely a transfer of the active centre to some other molecule from the growing chain to give a 'dead' molecule (see Figure 2). When the transfer of an active centre takes place, the radical centre may transfer to an atom of a monomer, solvent,

TABLE I

Susceptability of various monomers towards initiator techniques.

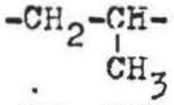
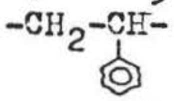
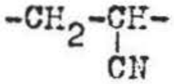
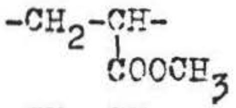
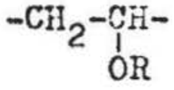
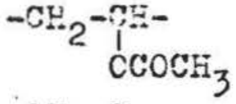
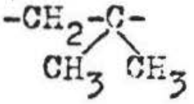
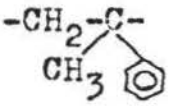
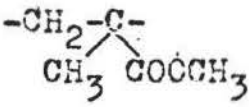
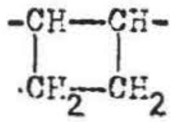
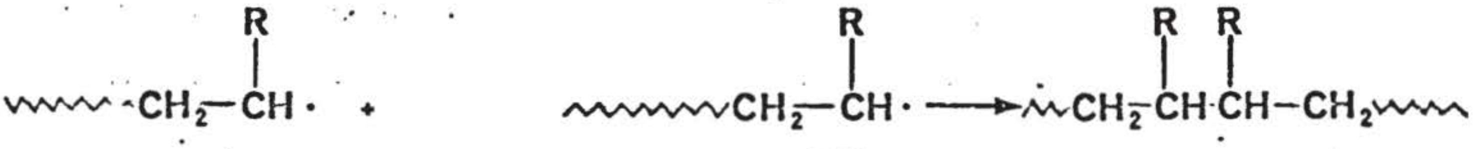
Monomer	Polymer	Initiator			
		Radical	Anionic	Cationic	Ziegler-Natta
Ethylene	$-CH_2-CH_2-$	x	-	-	x
Propylene	 $-CH_2-\underset{CH_3}{\underset{\vert}{CH}}-$	-	-	-	x
Styrene		x	x	x	x
Vinyl chloride	$-CH_2-CHCl-$	x	-	-	-
Acrylonitrile	 $-CH_2-\underset{CN}{\underset{\vert}{CH}}-$	x	x	-	-
Methacrylate	 $-CH_2-\underset{COOCH_3}{\underset{\vert}{CH}}-$	x	x	-	-
Alkylvinylether	 $-CH_2-\underset{OR}{\underset{\vert}{CH}}-$	-	-	x	-
Vinyl Acetate	 $-CH_2-\underset{CCOCH_3}{\underset{\vert}{CH}}-$	x	-	-	-
Isobutene	 $-CH_2-\underset{CH_3\ \ CH_3}{C}-$	-	-	x	-
α-methylstyrene		-	x	x	-
Vinylidene chloride	$-CH_2-CCl_2-$	x	-	-	-
Methylmethacrylate	 $-CH_2-\underset{CH_3\ \ COOCH_3}{C}-$	x	x	-	-
Cyclobutene		-	-	-	x

Figure 2

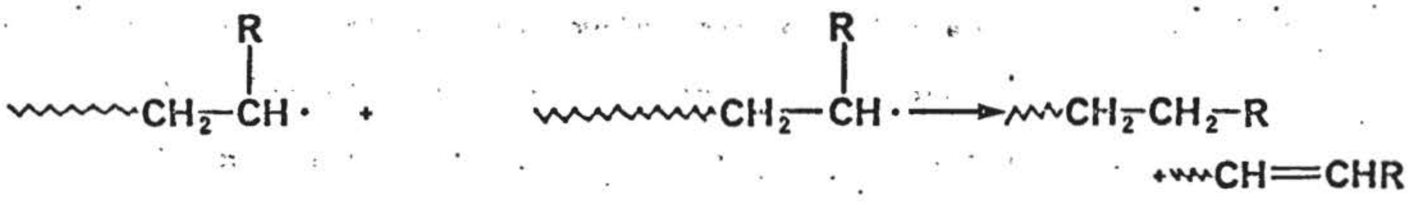
Free Radical Termination Mechanisms

A) Combination of two radicals.



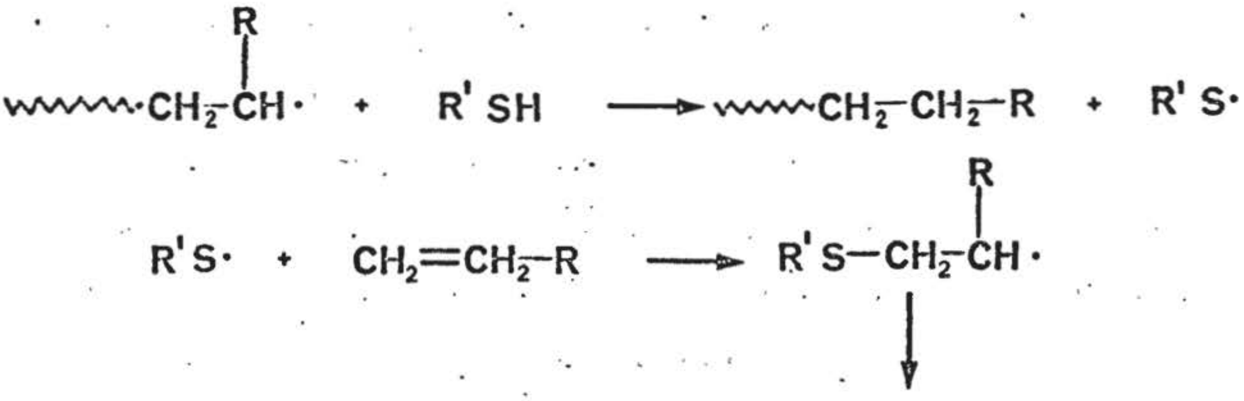
$$\sim\!\sim CH_2-\overset{R}{\overset{|}{C}}H\cdot + \sim\!\sim CH_2-\overset{R}{\overset{|}{C}}H\cdot \longrightarrow \sim\!\sim CH_2-\overset{R}{\overset{|}{C}}H-\overset{R}{\overset{|}{C}}H-CH_2\sim\!\sim$$

B) Disproportionation of two radicals.



$$\sim\!\sim CH_2-\overset{R}{\overset{|}{C}}H\cdot + \sim\!\sim CH_2-\overset{R}{\overset{|}{C}}H\cdot \longrightarrow \sim\!\sim CH_2-CH_2-R + \sim\!\sim CH=CHR$$

C) Chain transfer.



$$\sim\!\sim CH_2-\overset{R}{\overset{|}{C}}H\cdot + R'SH \longrightarrow \sim\!\sim CH_2-CH_2-R + R'S\cdot$$

$$R'S\cdot + CH_2=CH_2-R \longrightarrow R'S-CH_2-\overset{R}{\overset{|}{C}}H\cdot$$

Continuing propagation.

In addition to added transfer agents, in certain instances monomer, solvent and dead polymer chains may act as chain transfer agents.

dead polymer chain, or an added transfer agent molecule. Although this reaction terminates an individual molecular chain, the kinetic chain growth may continue by reaction of this new radical with further monomer.

The principal anionic termination reaction is the abstraction of a relatively acidic hydrogen. This results in the creation of a new anion but the overall process is a chain transfer only if this reinitiates further monomer (See Figure 3). In the absence of impurities or built-in transfer and/or termination processes, the 'living' chain end of an anionic polymerisation has a remarkably long life-time, allowing for further addition of more or different monomers with continuing propagation.

The carbonium ion of a cationic mechanism may be terminated in one of three ways, via an elimination or by reaction with an anion, or alternatively it may undergo a transfer step similar to that found in radical mechanisms. These reactions are illustrated in Figure 4.

For Ziegler (co-ordination) systems, the termination processes are less well defined but individual chain growth may be terminated by one of several postulated transfer reactions of which Figure 5A) and 5B) are typical examples. The termination of the active centre, i.e. true kinetic termination, generally arises from a reaction with an acidic compound (see Figure 5C)).

As Table I illustrates, the range of monomers polymerised by these four types of mechanism is so wide that it is difficult to adequately summarise the individual

Figure 3

Anionic Termination Mechanisms.

The presence of impurities in an anionic system such as alcohol molecules causes a termination reaction as shown below for the polymerisation of formaldehyde, although subsequently reinitiation may occur.

Termination

$$\sim\sim\sim\sim\sim\sim CH_2O^{\ominus} + ROH \longrightarrow \sim\sim\sim\sim\sim\sim CH_2OH + RO^{\ominus}$$

Reinitiation

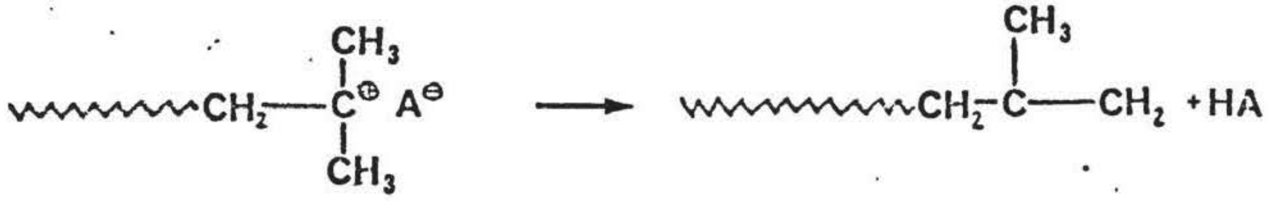
$$RO^{\ominus} + CH_2O \longrightarrow RO{-}CH_2O^{\ominus}$$

Under very vigorous reaction conditions the above termination reaction may occur as an internal hydride elimination forming a vinyl end group in a similar reaction to that shown for cationic polymerisation.

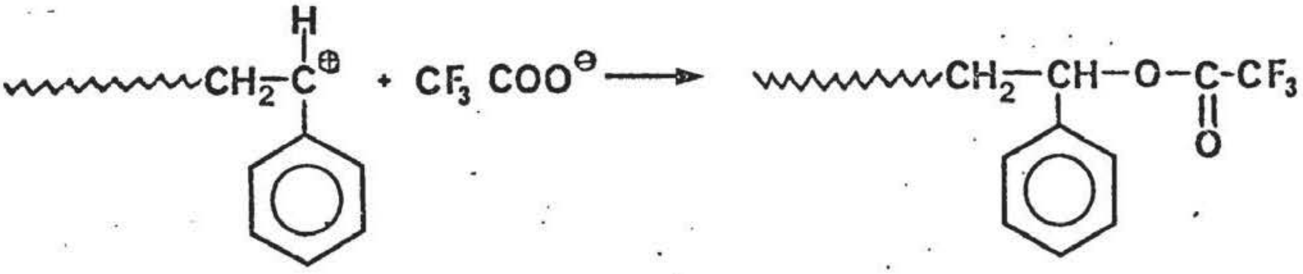
Figure 4

Cationic Termination Mechanisms.

A) Elimination



B) Reaction with an anion



C) Chain transfer

(Normally to monomer but may also be to other transfer agents. E.g. dead polymer chains.)

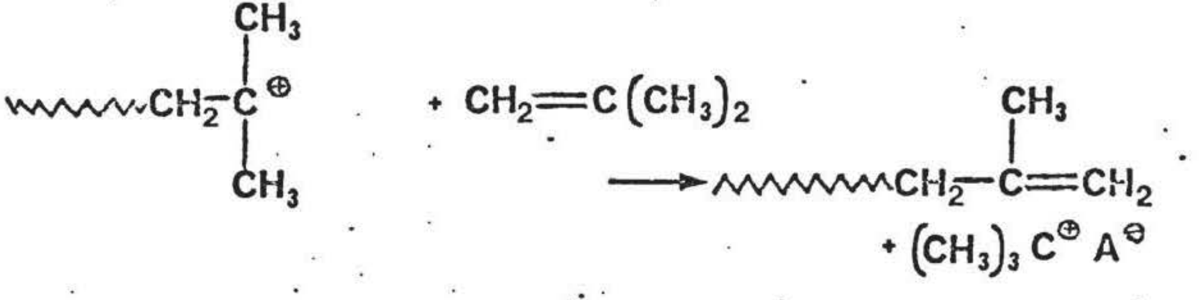
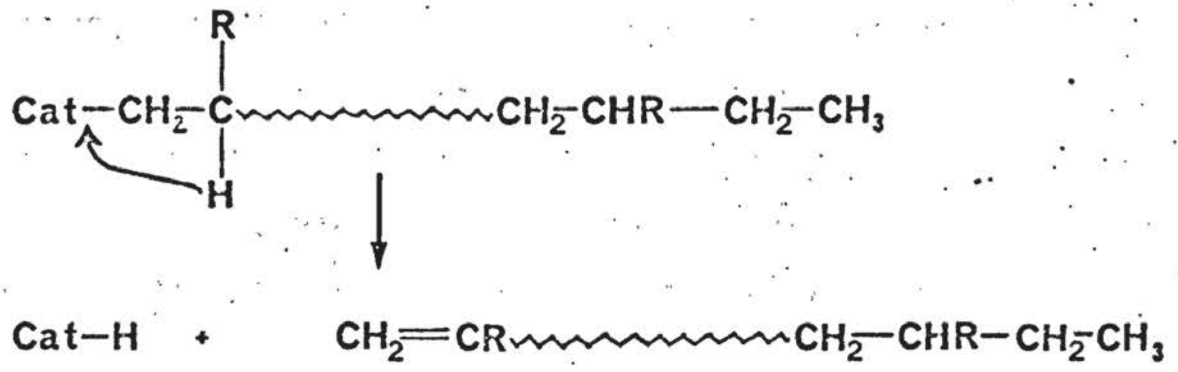


Figure 5

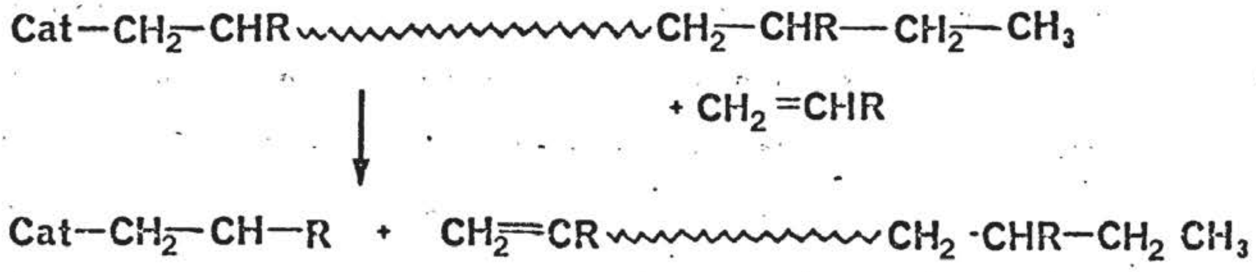
Ziegler system Termination Mechanisms.

A) Internal hydride transfer.

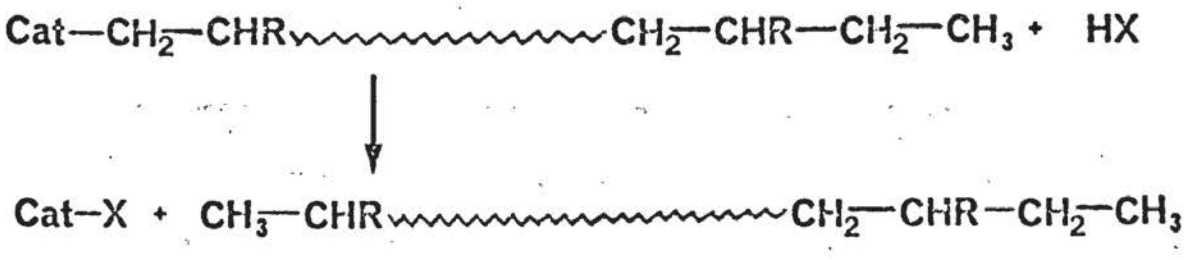


B) Transfer to monomer.

(Similar transfer may occur with metal alkyl, or alkyl group or with added agents such as hydrogen)



C) Termination by acidic species.



techniques by which these various active centres are generated and the typical conditions of the polymerisations. However, details of these aspects of the various systems may be found in the literature as follows:-
Free Radical Polymerisation, Bamford et at (17); Cationic Polymerisation, Plesch (18); Anionic Polymerisation, Szwarc (19); Ziegler systems, Reich and Schindler (20).

SECTION 4.1. - ZIEGLER CATALYST SYSTEMS

Ethylene and most higher α-olefins, which require high temperatures and pressures for free radical polymerisation, react readily at room temperature and pressure using Ziegler catalysts. These catalysts are typically obtained by mixing together a metal alkyl or aryl of Groups I - IV of the Periodic Table with a compound (generally the halide) of a transition metal of Groups IV - VIII. Thus, there are numerous possible permutations of catalyst and many have been cited in the literature, although in general the most useful combinations have been obtained from titanium or vanadium chlorides and aluminium trialkyls or dialkylchlorides. These catalysts normally produce polymer of a high molecular weight and with a linear, stereoregular structure which confers enhanced crystalline properties over the material produced by a radical mechanism.

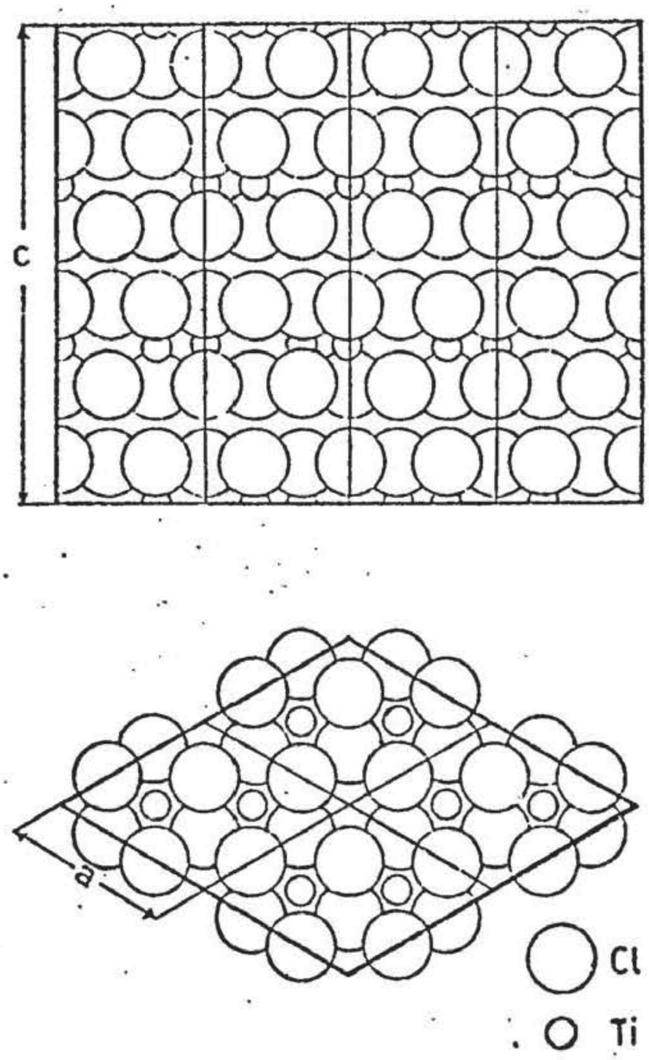
Much of the early development of Ziegler catalysts was by research workers in European countries where several industrial plants now exist for the production of materials such as high density linear polyethylene, isotactic polypropylene, poly-4-methylpent-1-ene, polybut-1-ene and polybutadienes.. The original discovery of this type of catalyst is credited to K Ziegler and his research school at the Max Planck Institute, Mülhein. However, in earlier work, M Fischer (21) refers to ethylene polymerisation by a catalyst mixture of a similar nature (aluminium, aluminium chloride, and titanium tetrachloride) and several British and US patents which stem from the investigations in 1949 of Roedel (22), Pease et al of the Du Pont Company also cite combinations of this type. Likewise, Herman and Nelson (23) report a styrene polymerisation in 1953 using a catalyst which would now be considered as a Ziegler system. In the middle nineteen fifties, after the Ziegler discovery, intensive work was carried out concurrently by K Ziegler and G Natta, the latter concentrating on the polymerisation of higher α-olefins (24), especially with respect to the preparation of stereoregular polymers (25). The extensive research carried out by these workers was recognised in 1963 with the award of the Nobel Prize in Chemistry jointly to K Ziegler and G Natta. Their accounts of the development of the work can be found in their Nobel addresses (26, 27).

A Ziegler catalyst is usually formed by bringing together in an inert atmosphere, a transition metal compound in which the transition metal is in a valency state below its normal maximum (e.g. titanium (111), chloride, vanadium (111) chloride) and an organometallic compound (e.g. aluminium triethyl, aluminium diethyl chloride). The former is generally though to be a 'true' catalytic compound. The technique of reduction is extremely important, often being the most important single factor in deciding the activity of the catalyst. The latter acts principally as an activator, alkylating the catalytic surface, and also as a scavenger for minor traces of any catalyst poisons.

In conventional Ziegler polymerisations, a slurry of titanium (111) chloride is preformed by reduction using an aluminium trialkyl or aluminium dialkyl halide (usually R=ethyl) in a dry, oxygen-free inert hydrocarbon solvent (e.g. heptane, iso-octane) under a nitrogen atmosphere. The catalyst efficiency varies with the nature and the crystal structure of the catalyst particles and therefore particular care is necessary over the reduction conditions, and so elaborate techniques have often been developed to achieve optimum results. When carried out below 70°C such reduction produces the β - crystal modification of titanium (111) chloride (28, 29) which, although a very active α-olefin polymerisation catalyst, has the poorest stereoregulating properties of the four known modifications. This β-form of titanium (111) chloride has, also, a crystal structure considerably different from the three other forms, consisting of threads of linear macromolecules of titanium tri-chloride, shown pictorially in Figure 6.

Enhanced isotactic stereospecificity, especially for propylene, may be conferred on such a catalyst by a heat treatment cycle, heating the catalyst above 150°C (28, 30, 31), which converts it to the γ- modification. A further alternative crystalline modification is α-titanium (111) chloride, which is also capable of this higher degree of

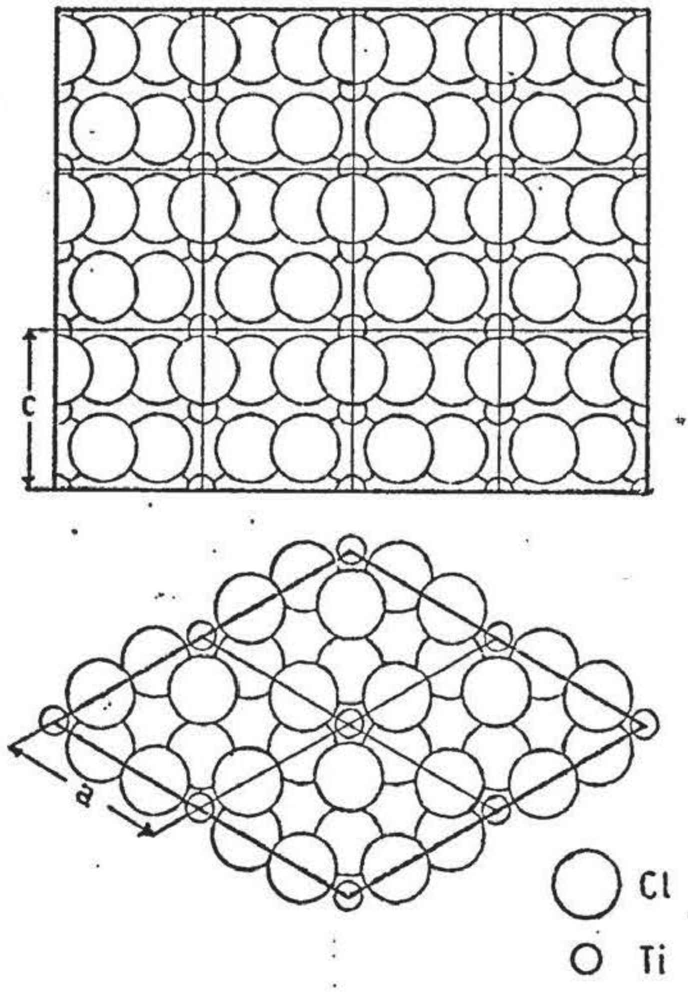
Figure 6



Structural model of the α-modification of $TiCl_3$.
The X-ray spectrum can be interpreted on the basis of a layer lattice, which can originate from the hexagonal close-packing of the chlorine atoms, in which the titanium atoms are arranged in layers, placed at every second layer of the chlorine atoms. The elementary unit cell of this modification has constants of : $a=b=6.12Å, c=17.50Å, \gamma=120°$.
$(1Å=10^{-10} m.)$

The crystal structures of the various modifications of titanium (III) chloride.

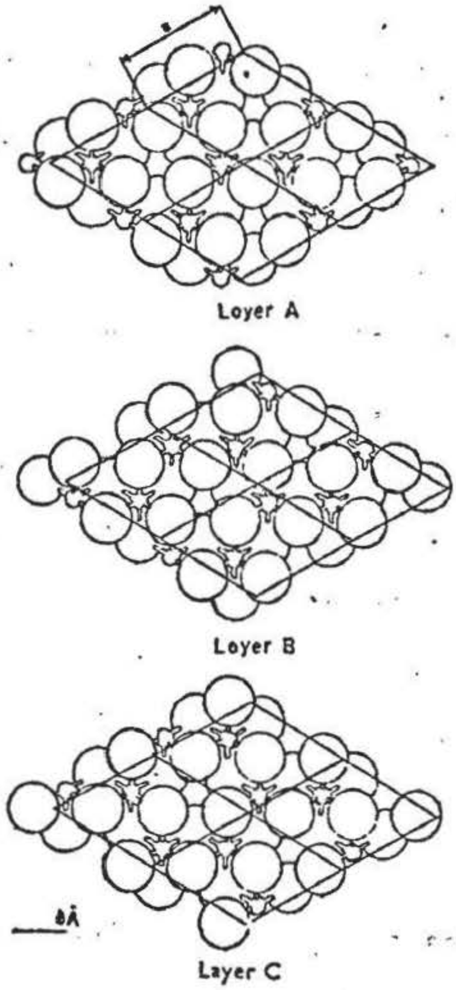
Figure 6



Structural model of the β-modification of $TiCl_3$.
The X-ray spectrum can be interpreted on the basis of a hexagonal close-packing of the chlorine atoms ,in which the $TiCl_3$ molecules are gathered in rows that are parallel to the three-fold axis.The coordination of the halogen atoms around the titanium is still octahedral,but the way in which the titanium atoms are arranged among themselves is completely different.The spectrum yields a hexagonal unit cell,having constants : a=6.27Å ; c=5.82Å.

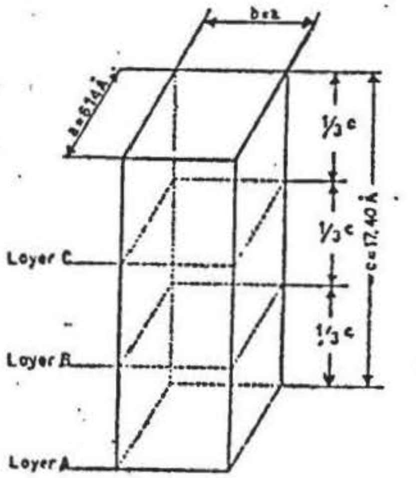
The crystal structures of the various modifications of titanium (III) chloride.

Figure 6



Distribution of the titanium atoms(small balls);and of the chlorine atoms in consecutive structural layers of the unit cell of γ-$TiCl_3$.

From the X-ray powder spectrum,the hexagonal unit cell has the following constants: a=b=6.14Å; c=17.40Å ; γ=120°,and contains six monomeric units $TiCl_3$.



Unit cell of γ-$TiCl_3$.The layers,as shown above,repeat along the c-axis,thus determining a cubic close packing of the chlorine atoms.

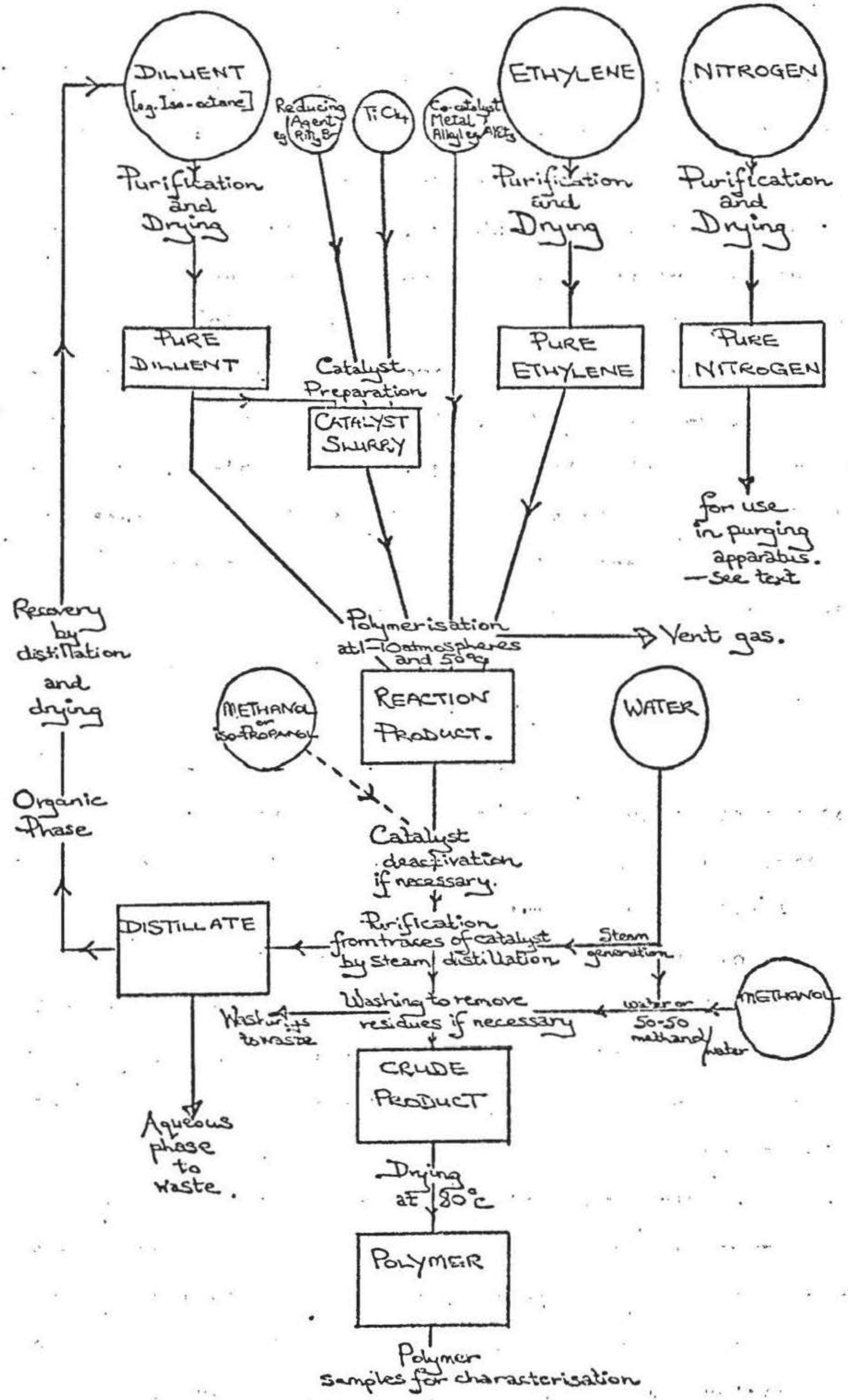
stereoregulation. This latter variety results from the reduction of titanium (IV) chloride with hydrogen or aluminium at high temperatures (32, 33). Finally, a third form with similar properties is the δ- form, which can be obtained by prolonged grinding of either α- or γ- forms (34). All these three forms, α-, γ- and δ- titanium (III) chloride are purple in colour, whereas the β- form has a brown colour. These forms of titanium (III) chloride, which are formed by reduction of titanium (IV) chloride with an aluminium alkyl reducing agent, are normally found to be a solid solution of aluminium chloride (35). This is supported by observations (34) that samples of varying aluminium content have essentially undetectable differences in X-ray spectral intensities and that no indications of a superstructure can be found.

The α-, γ- and δ- forms of titanium (III) chloride all have a similar crystal structure. In the α- form it is a cadmium iodide type structure consisting of hexagonally close packed chloride ions with titanium atoms distributed in the interstitial spaces between alternate layers of chloride ions (see Figure 6). Similar layer structures can be found in the other two modifications, γ- titanium (III) chloride differs from the α- form only in that the chloride ions are in a cubic close packed array. The δ- form has a less ordered layer structure, with a degree of alternation between the cubic and hexagonal packing. This may be observed in the X-ray powder spectrum which indicates an essentially disordered structure (34) although some characteristics of the α- and γ- layer structures may be found. The similarity of the crystal structure of the α-, γ - and δ - forms is reflected in the results obtained when each is used as a component of a Ziegler catalyst. Although each of them exhibits greater stereospecificity than the β- form, it appears to be achieved at the expense of the rate of polymerisation.

All the four types of structure found in titanium (III) chloride contain octahedrally co-ordinated titanium ions and similar layer lattice structures containing octahedrally co-ordinated metal atoms are found in titanium (II) chloride (36), and also vandaium and chromium trichlorides, all of which are active Ziegler catalysts. In contrast, inactive compounds such as titanium (IV) chloride and titanium (IV) alkoxides contain tetrahedrally co-ordinated titanium ions. Thus, for stereospecific polymerisation, the presence of this octahedral configuration in a Ziegler catalyst may be regarded as being of as great importance as any specific valency state.

In a polymerisation reaction, the titanium catalyst is used in conjunction with a cocatalyst, normally either aluminium trialkyl or dialkyl-chloride. The reaction is generally carried out in diluent medium (a hydro-carbon, e.g. heptane, iso-octane) and the product forms as a solution or a particulate slurry. Figure 7, a typical application of a Ziegler catalyst system, illustrates schematically the steps involved in the industrial polymerisation of ethylene by a slurry process. This particular reaction is generally

Figure 7



A general scheme for the Ziegler polymerisation of Ethylene.

carried out at 0.1 - 1.0 MNm^{-2} (1-10 atmospheres) using a catalyst suspended in a monomer solvent chosen to be a poor solvent for the polymer, which thus forms as a solid on the catalyst particles, producing a slurry of the material. The reaction temperature, usually less than 100°C, (~ 50-80°C), ensures that polymer solubility remains low and in industrial situations the excess solvent and monomer may be recovered and re-cycled. Before work-up, if the product contains a high proportion of catalyst, it may be necessary to deactivate it by treatment with alcohol or water. In such ases, it may also be necessary to wash out catalyst residues (de-ash) with acid and water or by steam stripping, before proceeding with drying.

SECTION 4.2. - THE MECHANISM OF ZIEGLER CATALYSTS

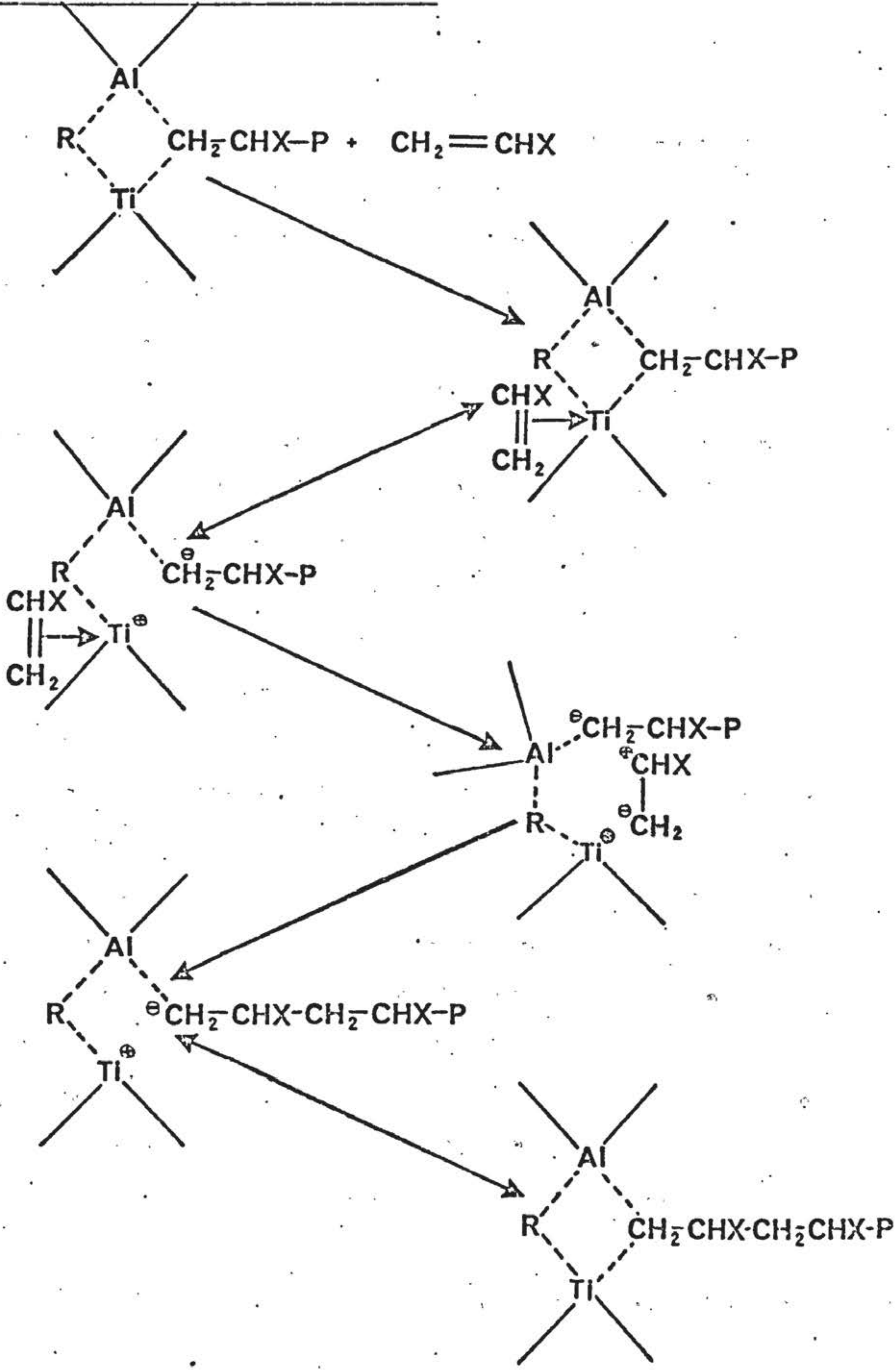
Many aspects of the mechanism of Ziegler catalysts have been described as a result of recent investigations. However, the mechanism of these immensely complicated systems, is still not conclusively and fully explained. Two major groups of theories exist, those employing a bimetallic and those employing a monometallic mechanism. In the bimetallic mechanisms, the presence of two metals in the catalyst combination is considered to be essential. In the monometallic mechanisms, however, only one metal atom (the transition metal) is necessary for polymerisation. In the case of bimetallic mechanisms, the propagation step employs two metal atoms which may be the same or different elements, whereas a monometallic mechanism involves growth about only one metal centre.

One of the early mechanisms proposed by Natta (37) in 1960, is a cogent example of the bimetallic mechanism which provides a simple explanation for the creation of isotactic polymers and is outlined in Figure 8. More recently, this type of mechanism has lost favour, as later evidence has not apparently supported it (38). An increasing amount of the recent evidence and opinion has favoured the monometallic theories. This type of mechanism was proposed as early as 1956 by Nenitzescu (39) and found support from the later experimental evidence of Carol and Carrick (40). A more elaborate model including a description of the olefin co-ordination using molecular orbital treatment was developed by Cossee (41) in 1962) and this still forms the backbone of many current proposals.

The active site in the monometallic mechanisms is the transition metal atom (e.g. Ti) and a second metal atom (e.g. Al) is not directly involved. In such cases, an active catalyst species (e.g. Ti-Et) is formed by the alkylation of the reduced metal compound (e.g. titanium (111) chloride) by the second catalyst component (e.g. aluminium triethyl). This type of mechanism is supported by the experimental evidence of several important polymerisation parameters (e.g. copolymerisation reactivity (40), propagation rate constants (42) in presence and absence of metal alkyls) which can be related only to the properties of the transition metal and not to those of the other metal present.

Figure 8

The Natta Bimetallic Mechanism.

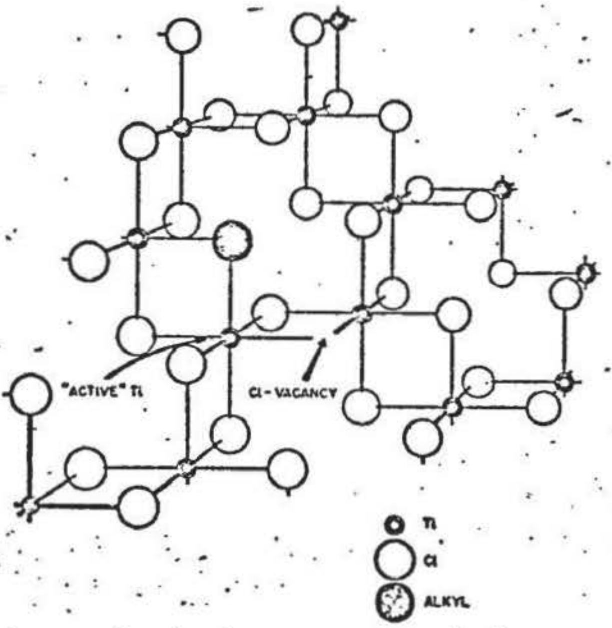


The active centre proposed in the Cossee (41, 43) model essentially consists of an octahedrally co-ordinated transition element, with empty or nearly empty t_{2g} orbitals, which has in its co-ordination sphere one alkyl group positioned cis to one vacant position through a $p\pi - d\pi$ (dihapto) bond. The mechanism shown in Figure 4 will thereby be facilitated as this co-ordination step also appears to weaken the transition metal - carbon bond to the alkyl. The mechanism supposes that the active centre is formed due to the interaction of a chlorine vacancy on the titanium (III) chloride surface with an alkyl aluminium. Such vacancies were proposed by Arlman to exist on the crystal edges to ensure its electro-neutrality. The result of this reaction is the replacement of one of the chlorine atoms on a Ti centre by an alkyl group and the retention of a ligand vacancy (see Figure 9). This generates the active centre, providing a Ti-C σ-bond and the facility for monomer co-ordination to the Ti. Propagation is due to the adsorption of a monomer unit, which forms a Ti bond to the Ti centre and is subsequently inserted into the Ti-C bond via a four membered ring transition state (see Figure 9). The overall thermodynamic drive for a vinyl polymerisation arises from the relief of strain in going from the unsaturated sp^2 hybrid C-atom configuration, to the saturated sp^3 form, but this process is an activated one and the activation barrier has to be reduced by a catalyst. Cossee postulates that, as a result of the availability of the d-orbitals, the alkyl

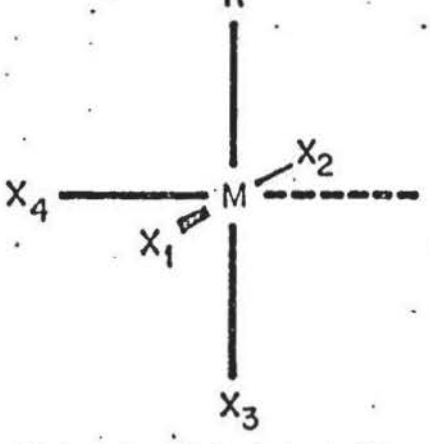
Figure 9

The Cossee Monometallic Mechanism.

A) Mechanism for the propagation step as proposed by Cossee.



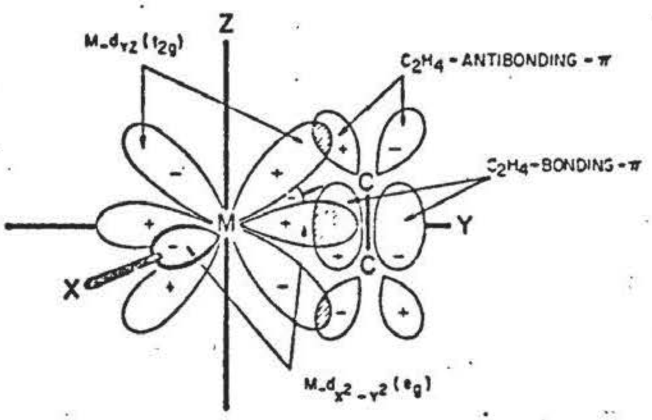
B) One layer of the crystal structure of α-$TiCl_3$ showing the Ti-alkyl bond and the chlorine vacancy forming the 'active' centre in the surface.



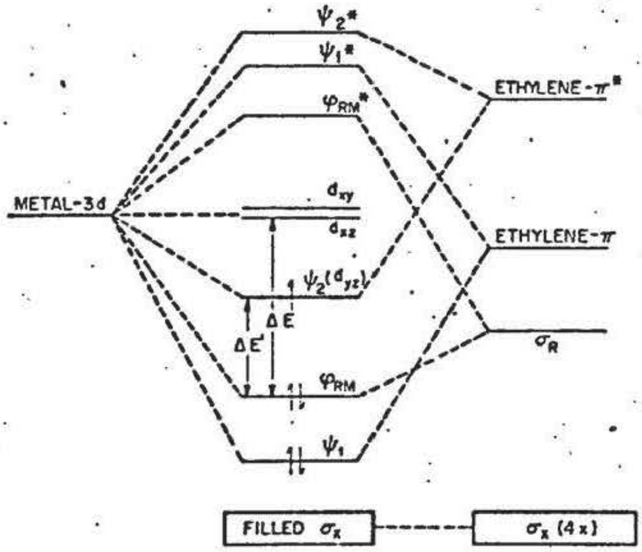
C) The configuration supposed to be the active centre in a Ziegler catalyst. (M= Transition metal ion; R= Alkyl group(growing polymer chain), X_1 - X_4= Anions.)

Diagrams illustrating the Cossee Mechanism (J).

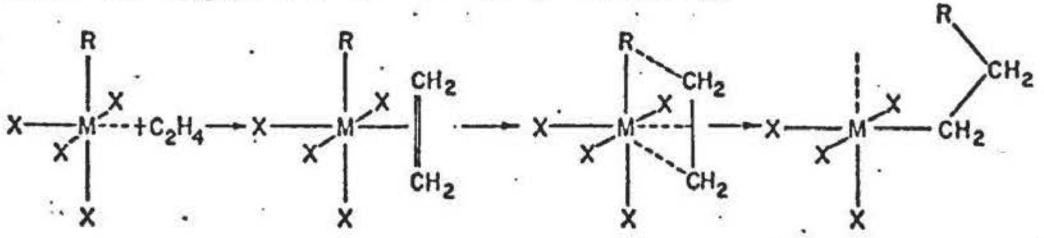
Figure 9



D) A schematic picture showing the spatial arrangement of the relevant orbitals in a π-bond between a transition metal and ethylene.



E) The molecular orbital energy diagram for the octahedral complex R Ti Cl_4 (C_2H_4). (For reasons of simplicity 4s and 4p orbitals are not taken into account and the Ti-Cl bond is supposed to be 100% ionic.)



F) The complete mechanism sequence proposed by Cossee.

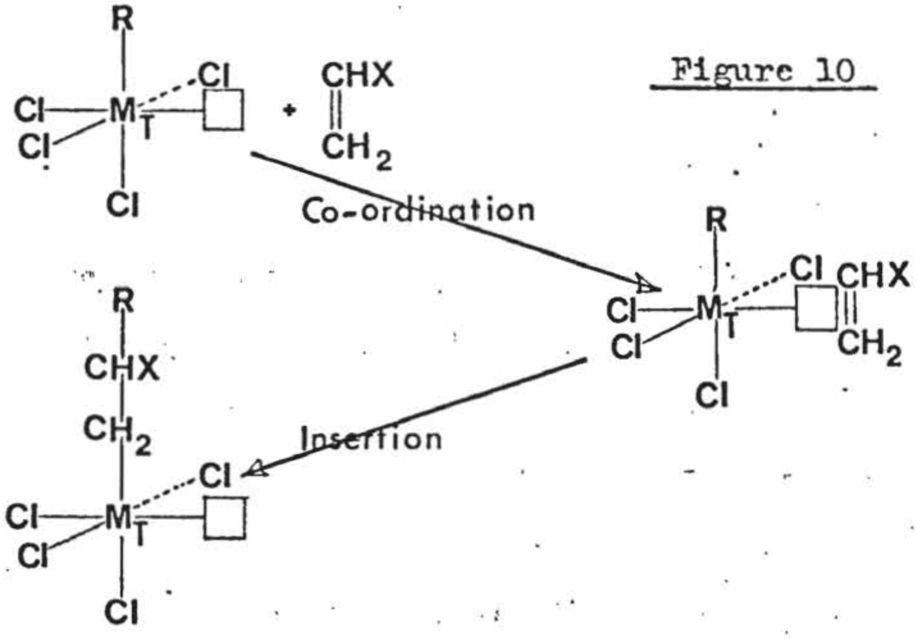
Diagrams illustrating the Cossee Mechanism (II).

group migrates, using a combination of p and d orbitals all along its reaction path, which allows it to remain relatively strong bonded to the active centre and gives the reaction a low activation energy (see 4-membered ring transition state, Figure 9). This he describes in terms of a molecular orbital diagram (see Figure 9). In the uncomplexed condition, the energy Δ E must be obtained to weaken the Ti-C bond (i.e. transfer an electron from the bonding orbital into the metal 3 d orbitals) and as catalysts may be stored for long periods without decomposition, ΔE is large enough to maintain the bond intact in the absence of olefin. However, when an olefin is co-ordinated to the complex, a new energy level $d_{(yz)}$ is formed by mixing metal d orbitals and ethylene antibonding orbitals ("back donation"). This new level is lower than that of the original metal 3 d orbitals and the energy, $\Delta E'$, required to excite an electron is less than ΔE, therefore more readily obtained. This lowering of the energy gap makes the Ti-C bond more susceptible to homolysis.

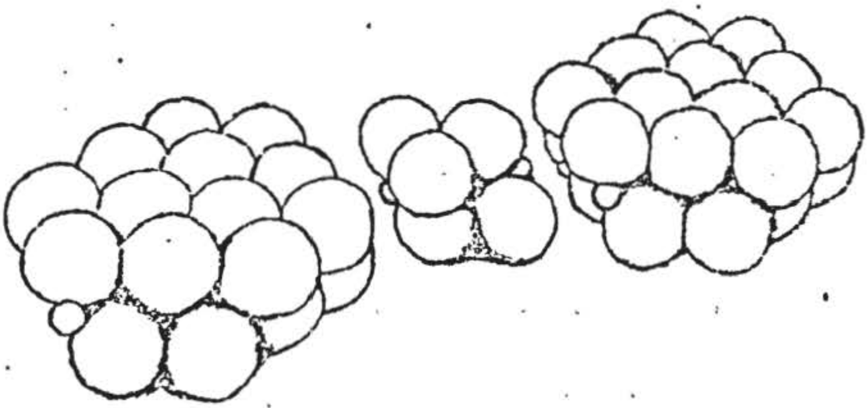
It should be noted that in the mechanism proposed by Cossee the growing chain and the vacant position change place during propagation, which would give rise to a syndiotactic polymer. In order to account for isotactic polymerisation, Cossee proposed that the alkyl group returned to its original position before a further monomer unit was complexed. It was considered that such an alkyl shift would be aided by the presence of the $d_{(yz)}$ orbital, similarly to its migration in the propagation step.

Subsequent developments of the Cossee mechanism have questioned the occurrence of the complexation step and the final migration back step of the vacant position. Boor has put forward a concept (44) originating with Tennett, that the mechanism is a <u>cis</u>-four-centre addition without prior co-ordination. They suggest co-ordination would increase activation energy as the ground state is more stabilised than the transition state, so that a complex formation would lower the rate of insertion. The Boor model postulates a highly polarisable metal-carbon bond, and the driving force of the mechanism is transfer of an electron around the four centre system (see Figure 10). This achieves a thermodynamically favourable conversion of the unsaturated C=C bond into a saturated one whilst retaining the metal-carbon σ-bond. In place of the Cossee complexation step, this mechanism only requires the approach of the olefin to the active centre and the lengthening of the M-C bond by polarisation resulting in a direct insertion of the olefin into that bond. The advantage of this model is that the position of the ligands around the Ti centre remains the same, which eliminates the requirement for the final vacant position migration step of the Cossee mechanism in order to achieve isotacticity. This model also has the advantage of accommodating a number of catalysts with d^4 and d^5 electronic systems which have been found to polymerise ethylene and propylene, and which violate the d^0 and d^3 requirements of the original Cossee model.

Figure 10



The Boor expression of the Cossee mechanism for Ziegler catalysis.



Oblique view of two $Ti_8\ Cl_{24}$ units separated by $Al_2\ Cl_6$.

The Buls and Higgins concept of an eight Titanium atom active centre moiety.

Recent proposals by Buls and Higgins (45) modify the Cossee mechanism by considering that the process is not a surface phenomenon but that the whole Ti content of the activated catalyst is actively involved. Using their experimental data from the $TiCl_3/AlEt_2Cl$ system, they conclude the basic structure in the unactivated catalyst is a $Ti_8\ Cl_{24}$ molecule containing $Al_2\ Cl_6$ present in solid solution. They postulate that the eight Ti atoms are arranged in a planar p-xylene like skeleton (see Figure 10), giving an overall structure with regularly spaced cavities into which monomer and alkyl may diffuse. The cocatalyst addition causes alkylation of the exposed titanium atoms producing active centres each with two vacant ligand positions but otherwise similar to those proposed by Cossee. The configuration of these vacancies within the alkylated Ti_8Cl_{24} unit is such that they are mirror images of each other and a co-ordination/insertion process as already outlined by Cossee, results in isotacticity. Although the mechanism provides a plausible explanation in the context of the studied system, it is difficult to accept generally as it appears contrary to much photographic evidence supporting crystal edge and defect polymer growth.

Theoretical investigations have attempted to describe in greater detail the tentative orbital sequences proposed for the active titanium site. The essentially qualitative scheme constructed by Cossee has been recently discussed quantitatively in terms of the electronic structures and energy levels of the intermediate complexes by Armstrong, Perkins and Steward (46). They do not find it necessary to postulate that a vacancy exists on the titanium at some point but rather that the complex in which an alkyl group lies between two octahedral sites has the lower energy and a mechanism in which an incoming ethylene displaces this on co-ordination is shown to be possible.

SECTION 4.3. - MAGNESIUM REDUCED CATALYSTS

The Ziegler catalyst used in the present work is a preformed titanium (111) chloride prepared by alkyl magnesium reduction and activated using an aluminium trialkyl. The technique for preparing the catalyst was originally developed by Shell Research Company Limited (47,48) but the modified technique (49,49A) adopted in our earlier ethylene polymerisations was used throughout the present work. This system has also been found to be active in the polymerisation of propylene (50) and investigations into its use with this monomer are currently being carried out. Duck, et al (51) have also investigated a similar Ziegler catalyst for the polymerisation of ethylene and propylene. In their case the titanium (111) chloride was prepared by the reduction of titanium IV chloride with a magnesium alkyl chloride carried out by ball milling in the presence or absence of a support.

A three component system, titanium IV chloride, an aluminium alkyl and diphenylmagnesium has been studied by

Radenkov _et_ _al_ (52). In this system, the highest yields were obtained when the diphenyl magnesium was added as the final catalyst component. At atmospheric pressure, the polymerisation of ethylene proceeded at a constant rate of ~250 g C_2H_4/g $TiCl_4$/min for a long period, when carried out at 6 Kg/cm^2 pressure very high rates were produced but these died rapidly after a few minutes, then tended towards zero rate.

---oOo---

CHAPTER 2

GRAFTED BLOCK COPOLYMER EXPERIMENTS

SECTION 1 - INTRODUCTION

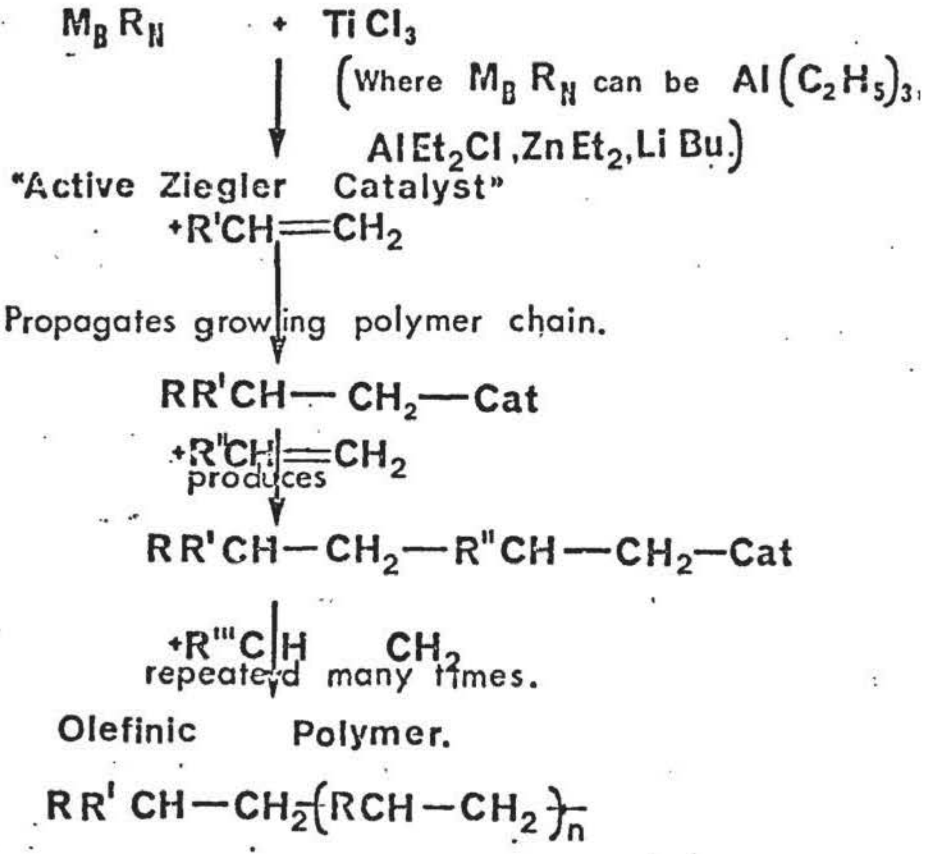
Previous work using a magnesium reduced catalyst for the polymerisation of ethylene (48,49) demonstrated that it was extremely active, capable of producing in excess of fifty kilogrammes of polymer per gramme of $TiCl_3$. It was therefore proposed to use this catalyst to prepare graft copolymer materials by the synthesis of suitable polymeric cocatalysts for use in the subsequent Ziegler catalysed olefin polymerisation. There is currently evidence (43, 53,54) to show that an alkyl group present in the organometallic compound used as a cocatalyst in a Ziegler system is normally incorporated as the first unit of the growing polymer chain. If this alkyl group can be replaced by a polymer chain whilst still retaining the initiating properties of the compound, the technique may be used as a general synthetic route to block copolymers.

1.1. - THEORETICAL CONSIDERATIONS

A general scheme for the preparation of an active Ziegler catalyst using titanium trichloride and its use for an olefin polymerisation is shown in Figure 11. In order to produce copolymers by such a system it was necessary to introduce segments of another macromolecular species into the scheme. This appears possible at two points:

A) At the catalyst activation stage; by substitution of a preformed macromolecular chain P into the metal alkyl cocatalyst M_BR_N to produce a species $M_BR_{N-1}P$. Theoretically this would yield polymers with R and with P end groups

Figure 11



A general scheme for the preparation of active Ziegler catalysts using titanium trichloride (e.g. homopolymer of the form:

as in the Figure 11 scheme and also copolymer of the form:

B) At the chain propagation stage by the substitution of alternative α-olefins. This may be accomplished by either of two techniques:

i) Firstly the α-olefin may be more than one type of monomer, this can be achieved by using mixed monomer feeds producing random copolymers or by sequential feeding of alternate monomers which is said to produce a more 'blocky' type of arrangement within the copolymer. (e.g. As for Figure 11 but where $R' \neq R''$ giving copolymers of the types:

a) $-R''CH-CH_2-R'CH-CH_2-R''CH-CH_2-R''CH-CH_2-R''CH-CH_2-R'$
$CH-CH_2-R'CH-CH_2-$

Random copolymers.

b) $-R'CH-CH_2-R'CH-CH_2$ ...... $R'CH-CH_2-R''CH-CH_2-R''$
$CH-CH_2-R''CH-CH_2$ ...... $R''CH-CH_2-$

Block copolymer.

Both these particular schemes have already been well studied for various catalyst systems. The former technique has found a limited commercial application as a method for the modification of the physical properties of a polyolefin. For instance, in low pressure techniques especially the Phillips process, ethylene with properties closer to the high pressure products than the straightforward low pressure polymer.

ii) Secondly, the olefin could be a polymeric species in which case a graft or block copolymer may be formed. (e.g. As in Figure 11, except $R^{/}$ = P where P = polymer chain). This produces copolymers of the form: $RPCH\text{-}CH_2\text{-}R^{//}CH\text{-}CH_2\text{-}R^{//}CH\text{-}CH_2\text{-}(R^{//}CH\text{-}CH_2\text{-})_n$. The present work has concentrated on investigating methods A) and B)ii) as synthetic routes to copolymers.

Organometallic Synthesis

As outlined earlier an active Ziegler catalyst can be prepared using a metal alkyl of the general formula M_BR_N. Typical examples of such alkyls are aluminium triethyl, aluminium diethyl chloride, zinc diethyl, and lithium butyl. Various techniques were studied with the intention of producing modified macromolecular metal alkyls of the general formula $M_BR_{N-1}P$, where P is a polymer chain. Preparative investigations into the synthesis of such compounds were centred around two points:

i) The Group III alkyls (especially aluminium compounds as these generate very active Ziegler catalysts).

ii) The Group I alkyls (especially lithium, as here there is less likelihood of homopolymer formation when the sole alkyl group has been substituted for by a polymer group.

The Group I organometallic compounds containing lithium may be prepared by two types of reaction either directly or by exchange reactions (55,56,57). The latter involve the conversion of a readily prepared lithium derivative into the desired lithium derivative. Such exchange reactions are generally of three types:

A). Metal - metal exchange

e.g.

$$\begin{array}{lcl} Ph.Li & + & Ph_3Sn - CH_2-CH = CH_2 \\ & \downarrow & \\ Ph_4Sn & + & Li.CH_2.CH = CH_2 \end{array}$$

B). Metal - halogen exchange

e.g.

$$\begin{array}{lcl} BuLi & + & p\text{-}Br.C_6H_4.NMe_2 \\ & \downarrow & \\ BuBr & + & p\text{-}Li.C_6H_4.NMe_2 \end{array}$$

C). Metal - hydrogen exchange

e.g.

$$\begin{array}{lcl} PhLi & + & PhC = CH \\ & \downarrow & \\ C_6H_6 & + & PhC = CLi \end{array}$$

Although these methods provide better routes (i.e. higher yields) to many organolithium compounds than the direct methods, in this work such syntheses were inappropriate in many instances. A requirement of the exchange method is generally for an excess of the lithium reagent to be used and in the metal-metal exchange a further metal alkyl (eg. Ph_4Sn). is generated. Neither of these situations is desirable as efficient separation of the alkyls is difficult without decomposition and if these alternative alkyls are present in the subsequent polymerisation reaction they will cause interference and/or poisoning of the catalyst. The method of preparation involving a direct route also has limitations. The reaction between lithium and another organometallic compound (if an alternative polymeric organometallic were available) similarly creates undesirable side products which may be difficult to exclude. Thus there remain these routes in which Lithium metal reacts directly with an alkyl halide or alkane substrate and it is with these that investigations were initially carried out.

Greater practical difficulty is associated with the obtaining of Group III organometallic compounds, containing aluminium on a laboratory scale. These highly reactive materials may be directly synthesised only by the following methods (58):

i) From another organometallic compound, e.g. R_2Hg.
ii) From an alkyl halide, e.g. RX.
iii) From an olefinic compound, e.g. $RCH = CH_2$.

Method i) can only be realised if a suitable alternative polymeric metal compound (e.g. polymeric mercury compound) is available and providing that its reaction side product (e.g. mercury) does not interfere at the polymerisation stage. Method iii), the direct synthesis of alkyls from an olefin and aluminium which is the current industrial method of synthesis:-

$$\begin{array}{l} 2Al \;+\; 3H_2 \;+\; 6\;(RCH \;=\; CH_2) \\ \quad\quad\;\downarrow \\ 2Al\;.\;(CH_2CHR)_3 \end{array}$$

also proves unsuitable as the necessary special equipment for a high pressure, high temperature reaction generating highly reactive products of this type was not available. However, an indirect variation of the reaction as has been previously employed by Greber and Egle (59) was used. In this instance the preparation of a polymeric aluminium was carried out using an unsaturated polybutadiene substrate and diethyl aluminium hydride:

$$Et_2AlH + RCH = CH_2$$
$$\downarrow$$
$$Et_2AlCH_2CH_2R$$

where R is the polybutadiene substrate.

Method ii) was also investigated to find out whether it could be suitable for the synthesis of polymeric metal alkyls from saturated substrates. In this case a halogenated polystyrene was reacted with aluminium metal and also with an aluminium - magnesium alloy in order to produce alkyl aluminium compounds.

1.2. - EXPERIMENTAL CONSIDERATIONS

The initial step in the synthesis consisted of the preparation of an organometallic polymeric initiator which was then used for a Ziegler catalysed ethylene polymerisation to produce a copolymer. Experiments of a similar nature were reported by Greber and Egle in 1963 (59) who proposed that a macromolecular Ziegler catalyst was formed by the addition of a dialkyl aluminium hydrides to an unsaturated macromolecule (a styrene - butadiene copolymer containing pendant vinyl groups) and treatment of the product with titanium (IV) chloride. The subsequent use of this catalyst for ethylene polymerisation apparently yielded a copolymeric material. The present experiments study the use of a saturated substrate, polystyrene, and an unsaturated substrate, polybutadiene (with a high pendant vinyl content ($\sim$60%), on to which it was attempted to graft a polyethylene chain.

The majority of the experiments were concentrated on the preparation of macromolecular aluminium alkyls of a similar type to those of Greber and Egle, as the aluminium compounds appear to be the most effective alkylating agents for the Ziegler systems (60,61). However, certain experiments involving lithium and magnesium alkyls were also undertaken.

The two main synthetic routes used with the two substrates are illustrated by Figure 12. The reaction products of these metallation experiments were tested for activity as initiators in an ethylene polymerisation. In order to make comparative estimations of the activity of these catalyst systems control experiments were first carried out using a conventional aluminium triethyl cocatalysed homopolymerisation. These results were compared with those previously obtained for this system as a check on the reproducibility. The reaction products from the copolymerisation experiments were subjected to a fractionation procedure in order to separate and characterise the copolymer content.

SECTION 2 - EXPERIMENTAL PROCEDURE

PREPARATION OF MACROMOLECULAR METAL ALKYLS FOR USE AS CO-CATALYSTS

2.1. - HALOGENATION EXPERIMENTS

Initial experiments investigating the preparation of macromolecular metal alkyls were carried out using a polystyrene starting material. As outlined earlier, this material was usually halogenated first and subsequently subjected to a metallation reaction. In earlier instances a direct metallation was employed. The polystyrene material used throughout these experiments was Shell Carinex polystyrene

H.R. grade: IV; 0.7 - 0.8 (M.wt.~100,000 - 120,000), which was used without further purification.

1. <u>Preparation of Poly(p-iodo)styrene</u>

Poly (p-iodo) styrene was prepared by the method of Braun (62). Polystyrene (5.2 gms, 0.05 mole*) was dissolved in nitrobenzene (150 cm^3) and a mixture of I_2 (5.1 gms, 0.04 mole) and $H\ 10_3$ (1.9 gms, 0.01 mole) were added, together with CCl_4 (5 cm^3) which was used to wash the sublimed iodine back into the reaction mixture. Finally, the mixture was completed by the addition of 1 : 1 H_2SO_4 (10 cm^3) and then refluxed under vigorous agitation, and maintained at 90°C for 36 hours. After being allowed to cool, the entire reaction mixture was run dropwise into 2 dm^3 of CH_3OH saturated with SO_2. During this addition, the mixture was vigorously stirred. The poly (p-iodo) styrene was recovered by filtration and washed well with CH_3OH. The precipitate was dried in a vacuum oven at 50°C and then subjected to elemental analysis, I.R and N.M.R. spectroscopy.

Yield : 10.3 gms of poly (p-iodo) styrene (90%)

Elemental Analysis: C: 45.8% H: 3.3% I: 52.5% (95% Iodination)

Similar results were obtained when the experiment was repeated on a larger scale using 52 gms of polystyrene (0.5 moles). A partially iodinated material was also prepared using the same technique with 13 gms of polystyrene (0.125 moles) and 0.46 gms of iodine (0.0036 moles).

Elemental Analysis: C: 89.1% H: 7.4% I: 3.1% (6% Iodination)

NOTE:* Throughout the text the quantities of polymer used are expressed as moles of the monomer unit present.

Figure 12

Saturated backbone (polystyrene)

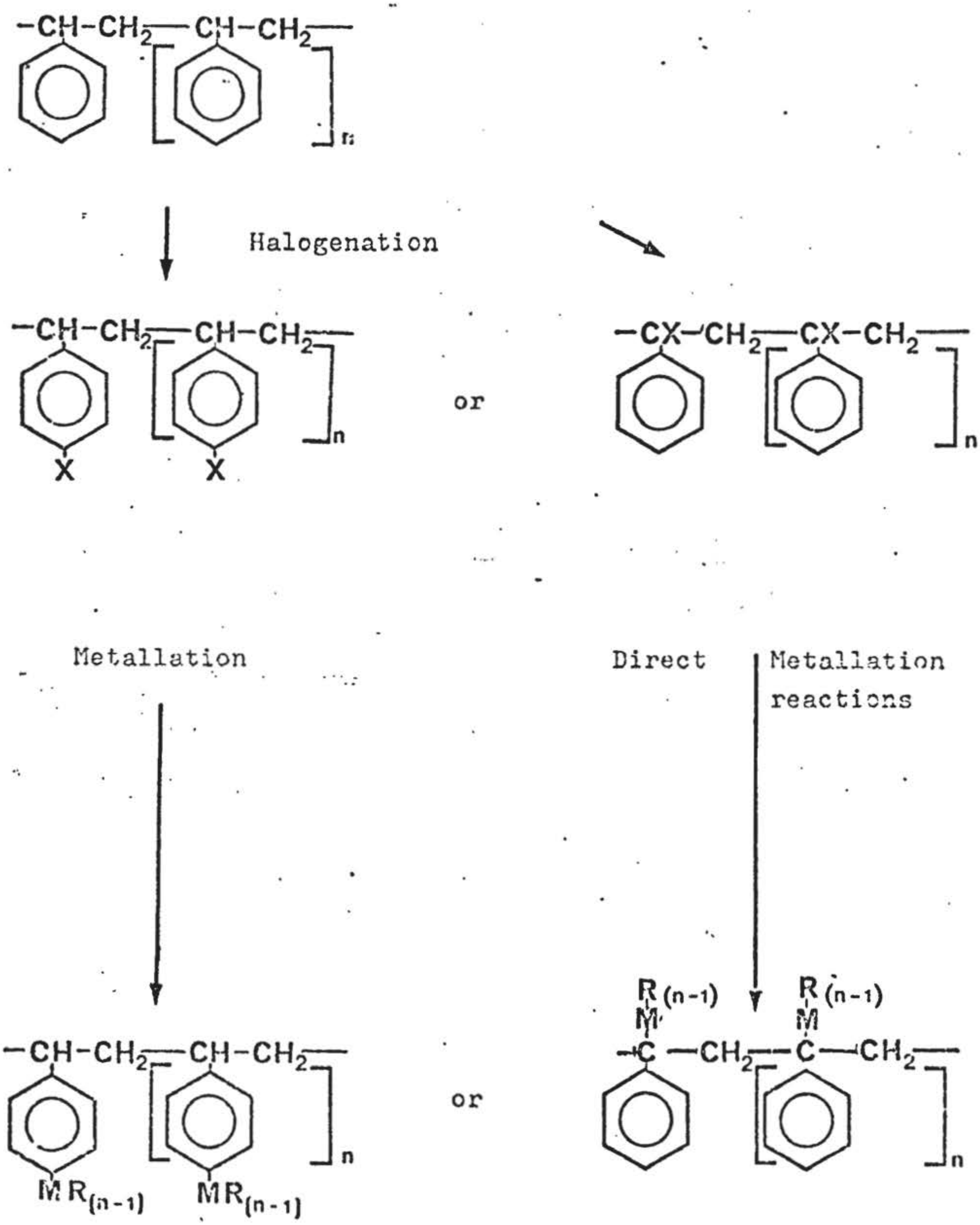
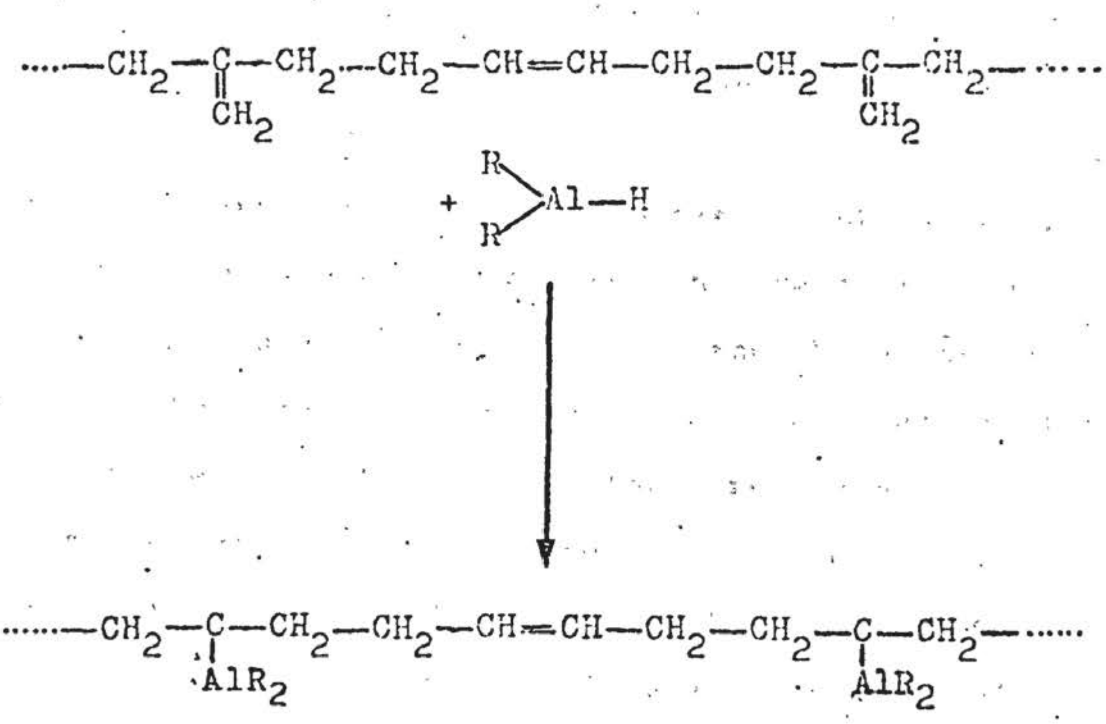


Figure 12

Unsaturated backbone (polybutadiene)



$$\cdots\!-CH_2-\underset{\underset{CH_2}{\|}}{C}-CH_2-CH_2-CH=CH-CH_2-CH_2-\underset{\underset{CH_2}{\|}}{C}-CH_2-\cdots$$

$$+\ R_2Al-H$$

$$\cdots\!-CH_2-\underset{\underset{AlR_2}{|}}{C}-CH_2-CH_2-CH=CH-CH_2-CH_2-\underset{\underset{AlR_2}{|}}{C}-CH_2-\cdots$$

2. Preparation of Poly(p-bromo)styrene

Poly (p-bromo) styrene was prepared by the method of Bachmann, Hellman *et al* (63). Br_2 (26 cm^3(80 gms), 0.5 moles) was added dropwise over four hours to a solution of polystyrene (52 gms, 0.5 moles) dissolved in CCl_4 (250 cm^3) in which was suspended Fe powder (2 gms, 0.036 mole) catalyst. The mixture was contained in a three necked flask fitted with a reflux condenser, mechanical stirrer and dropping funnel. The reaction was run at room temperature and the apparatus shielded from the light. After the bromine had been completely added the mixture was left standing for three days before the product was precipitated by dropwise addition to a vigorously stirred solution of SO_2 in CH_3OH. After filtration and washing with CH_3OH the precipitate was dried in a vacuum oven at 50°C.

Yield	: 90.6 gms of poly (p-bromo) styrene (99%)
Elemental Analysis:	C: 52.8% H: 4.0% Br: 41.2% (94% Bromination)

3. Preparation of Poly(α-bromo)styrene

Polystyrene (10.4 gms, 0.1 mole) was dissolved in CCl_4 (300 cm^3) and maintained at 60 - 70°C whilst Br_2 (2.6 cm^3 (8 gms), 0.1 moles) dissolved in CCl_4 (50 cm^3) was added dropwise. The reaction was carried out in a magnetically stirred three necked flask fitted with reflux condenser, dropping funnel and thermometer pocket. The apparatus was illuminated by a 60 cm, 20 watt fluorescent strip light for the duration of the reaction. Agitation and heating of the mixture were continued for two hours after the addition of the bromine was complete. When cool, the mixture was precipitated and worked up as in preparation 2.

Yield : 9.8 gms (54%)

Elemental Analysis: C: 77.3% H: 6.0% Br: 16.7%

(38% Bromination)

The experiment was repeated on a 0.5 moles scale using 51.6 gms of polystyrene (0.49 moles) and Br_2 (13 cm^3(40 gms) 0.05 moles), with the following results:-

Yield : 89.4 gms (65%)

Elemental Analysis: C: 30.0% H: 6.3% Br: 13.7%

(31% Bromination)

A partially brominated sample was prepared on the 0.1 mole scale, using only 0.06 cm^3 (0.19 gms) of Br_2 (0.0023 moles).

Yield : 10.2 gms

Elemental Analysis: C: 91.7% H: 7.8% Br: 0.5%

(1% Bromination)

4. Preparation of Poly(p-bromoethyl)styrene (Friedel-Craft (64))

Polystyrene (20.8 gms, 0.2 moles) was dissolved in nitrobenzene (600 cm^3) in a three necked 1 dm^3 flask fitted with a reflux condenser, mechanical stirrer and thermometer pocket. $BrCH_2CH_2OH$ (8.5 cm^3 (15 gms), 0.12 mole) and conc. H_2SO_4 (100 cm^3) were added, and the mixture was heated at 70°C for 4½ hours. After cooling, the entire reaction mixture was poured into ice water. The product was recovered by filtration and dried (vacuum oven at 50°C). The crude product proved impossible to dissolve in toluene for further purification, and so it was concluded that crosslinking of the polymeric material had taken place.

2.2. - METALLATION EXPERIMENTS

i) - ORGANOLITHIUM AND ORGANOMAGNESIUM COMPOUNDS

5. Preparation of Lithiated Polystyrene from Poly(p-bromo) Styrene and Lithium Metal

Poly (p-bromo) styrene (5.7 gm, 0.03 moles) from preparation 2 was dissolved in 50 cm^3 of fresh distilled (off $LiAlH_4$) tetrahydrofuran (T.H.F.) and added to lithium shot (0.7 gms, 0.1 moles) suspended in T.H.F. (25 cm^3). The mixture was contained in a magnetically stirred three necked flask, fitted with nitrogen inlet, reflux condenser with while oil bubbler and dropping funnel. The apparatus had been oven dried over night at 140°C and flushed out with dry nitrogen before use.

Prior to the addition of the brominated polymer, the lithium surface was cleaned by the addition of a few drops of ethylene dibromide. After all the brominated polymer solution had been added, the mixture was refluxed over night, then allowed to cool to room temperature under the nitrogen atmosphere. In order to determine the degree of lithiation subsequent experiments were carried out in which the substituted lithium was replaced with a stable group which could be readily detected analytically (see preparations 7 and 8).

6. Preparation of Poly(trimethylsilyl)styrene

A 20 cm^3 (0.008 moles) aliquot of the reaction mixture from the above experiment was reacted with $(CH_3)_3SiCl$ (1.0 cm^3, 0.85 gms, 0.011 moles) in a dry flask under a nitrogen atmosphere. After standing for several hours to ensure complete reaction, the polystyrene was recovered by precipitation into methanol, filtration and drying under vacuum at 50°C. The product was subjected to elemental analysis and N.M.R. spectroscopy.

Yield of polymer : 1.7 gms (116%)

Elemental Analysis: C: 50.6% H: 3.8%

7. Preparation of Poly(p-iodo)styrene

A 20 cm^3 (0.008 moles) aliquot of the reaction mixture as in the experiment above was reacted with I_2 (1.5 gms, 0.012 moles) in a dry flask under a nitrogen atmosphere. After standing for several hours to ensure complete reaction, the polystyrene was recovered by precipitation in CH_3OH, filtration, and drying under vacuum at 50°C. The product was subjected to elemental analysis:-

Yield of Polymer : 1.7 gms (89%)

Elemental Analysis: C: 50.5% H: 3.7% I: 0% Br: 44.0%

8. Preparation of a Poly(lithio)styrene Initiated Copolymer

Preparation 6 was repeated on a doubled scale reacting poly(p-bromo) styrene (11.5 gms, 0.063 moles) dissolved in T.H.F. (200 cm^3) with lithium shot suspended in T.H.F. (150 cm^3). A 150 cm^3 portion of the solution from this reaction was subsequently used as co-catalyst in a high pressure ethylene polymerisation using 1500 cm^3 of toluene solvent, a $TiCl_3$ catalyst (1 mM concentration) and temperature of 80°C. Negligible polymerisation of ethylene occurred. See later results of experiments E/2, E/8 and SE/1.

9. Preparation of a Polystyryl Grignard Reagent

The conventional method (65) for the preparation of a

Grignard reagent was employed in this experiment. Magnesium powder (1.70 gms, 0.070 moles) was vigorously stirred under a nitrogen atmosphere at 130°C for two hours in a magnotically stirred three necked flask fitted with a nitrogen inlet, reflux condenser, with a white oil bubbler and a dropping funnel. The apparatus was oven dried over night at 130° and flushed with dry nitrogen before use. After slight cooling, a solution of poly(p-bromo) styrene, (10 gms, 0.055 moles) in freshly distilled T.H.F. (100 cm^3) was added dropwise to the Mg. The mixture was allowed to reflux during the addition and this was continued for a further two hours after all the bromide had been added. At this point, further T.H.F. (150 cm^3) was added to the reaction mixture, which was then refluxed for a further two hours before it was allowed to cool under a nitrogen atmosphere. The strength of the Grignard solution was estimated by reacting a 10 cm^3 aliquot with 1M HCl (20 cm^3) then back titrating the excess HCl with 1M NaOH using phenolphthlein indicator. A hydrolysed sample of the reaction mixture was recovered and subjected to elemental analysis. 19.95cm^3 of 1M NaOH were required, therefore Strength of Grignard Solution: 5×10^{-3} M

Elemental Analysis: C: 50.4% H: 3.9% Br: 46.1%

10. Preparation of Lithiated Polystyrene from Poly(p-iodo) Styrene and Lithium Metal

This experiment was carried out with the same technique as used for preparation 6 except that poly (p-iodo) styrene (73 gms, 0.03 moles) dissolved in tetrahydrofuran T.H.F. (200 cm^3) was added to lithium (14 gms, 0.20 moles) suspended in T.H.F. (100 cm^3). Elemental analysis was carried out on a hydrolysed aliquot of the reaction mixture after it had been worked up.

Elemental Analysis: C: 46.5% H: 3.5% I: 51.5:

11. Preparation of Lithiated Polystyrene from Poly(α -bromo) Styrene and Lithium Metal

This experiment was also carried out using the technique described in preparation 6. Poly(α -bromo)styrene (5.8 gms, 0.032 moles) was dissolved in T.H.F. (100 cm^3) and added to lithium (0.07 gms, 0.10 moles) together with sodium (0.05 gms) suspended in T.H.F. (50 cm^3). Elemental analysis was carried out on a hydrolysed aliquot of the reaction mixture after it had been filtered and dried in the usual way.

Elemental Analysis: C: 79.1% H: 6.3% Br: 14.7%

12. Preparation of Polystyryl Grignard Reagent using an "Activated Magnesium" Technique

An alternative Grignard preparation was carried out using an activated form of magnesium. This was produced by the method of Rieke and Bales (66) which prepares very reactive magnesium in situ using a $MgCl_2$-K-T.H.F.-KI mixture. Freshly cut potassium (2.48 gms, 0.064 moles), anhydrous $MgCl_2$ (3.37 gms, 0.035 moles), oven-dried KI (2.64 gms, 0.016 moles) and 80 cm^3 T.H.F. (freshly distilled off $LiAlH_4$) were placed in a dry 250 cm^3 three necked flask, which had been flushed out with a nitrogen atmosphere. The flask was magnetically stirred and fitted with a dropping funnel, nitrogen inlet, condenser and white oil bubbler.

The mixture was vigorously stirred and heated to reflux for 2 to 3 hours, producing a viscous black mixture. Before poly(α-bromo)styrene (2.9 gms, 0.016 moles) dissolved in T.H.F. (70 cm^3) was added, the mixture was cooled to room temperature over 30 minutes. Upon completion of the addition of the bromide, the mixture was returned to reflux for a further 90 minutes then allowed to cool to room temperature under the nitrogen atmosphere. Aliquots of the mixture were titrated as in preparation 10. 19.95cm^3 of 1H NaOH were required, therefore Strength of Grignard solution:- 0.005 M.

13. Preparation of Lithiated Polystyrene using N-Butyl Lithium

As an alternative to the direct metallation methods, the exchange reaction technique was also used to prepare lithiated polystyrene. Methods using exchange reactions normally with n-butyl lithium have been devised by several workers, namely Braun (62,67), Leavitt and Maternas (68) and Huglin (69). The method used here is basically that used by Braun. The n-butyl lithium used for this preparation was a commercial product, a 21% solution in n-hexane supplied by Courturch Chemicals Limited. Before use, its activity was determined by the technique of Eppley and Dixon (70) in which the n-butyl lithium is titrated against a standard solution of benzoic acid in monoglyme. This estimation is carried out under scrupulously dry inert conditions, using a triphenylmethane indicator.

14.0 cm^3 of a 2.2 M solution of lithium butyl (0.031 moles) in n-hexane were diluted with dry benzene (65 cm^3) in a dry 250 cm^3 three necked flask. The flask was equipped with magnetic stirrer bar, and also a nitrogen inlet and while oil bubbler which provided a nitrogen atmoshphere. Poly(p-iodo)styrene (0.81 gms, 0.0035 moles) dissolved in benzene (65 cm^3) was added dropwise from a tap funnel over a period of 1 - 2 hours to the vigorously stirred mixture at room temperature. Upon the completion of the addition, the mixture was stirred for a further 10 minutes. Dry n-hexane (100 cm^3) was added to the mixture to induce precipitation of the polystyrene. After leaving the mixture to settle for a few hours, the bulk of the supernatant liquor was decanted off and the precipitate was washed twice with 100 cm^3 portions of dry n-hexane to remove as much of the excess butyl lithium as possible. Finally, the washed poly(p-lithio)styrene was redissolved in toluene (35 cm^3) and used <u>in lieu</u> of a magnesium alkyl as the reducing agent for the preparation of a titanium chloride slurry by the usual technique. (See polymerisation number SE/1).

ii) - ORGANOALUMINIUM COMPOUNDS

Two methods were used for the preparation of the aluminium organometallic compounds. The first method utilises the addition reaction used by Greber and Egle (59) in their experiments.

$$RCH{=\!=}CH_2 + Al\ Et_2\ H \longrightarrow RCH_2 - CH_2 - Al\ et_2$$

where R = polymer chain.

The unsaturated polymer substrate employed was a high vinyl polybutadiene rubber, and as a commercial source of diethylaluminiumhydride in the United Kingdom could not be located, it proved necessary to prepare this material for use in the above reaction.

14. Purification of Polybutadiene Rubber

The polybutadiene material was obtained from the International Synthetic Rubber Company Limited, Southampton, and is manufactured under the trade name "Intolene 50". The particular grade used had a high vinyl content with about 60% of the butadiene in the 1,2 configuration. As supplied, the material contained a significant proportion ($\sim$ 30%) of extender oil which was removed by dissolving the material in an 80 : 20 mixture of n-hexane/cyclohexane solvents and reprecipitating the rubber in a large excess of n-butanol. The rubber precipitate was filtered off, immediately washed with methanol and dried in a vacuum oven at 50°C. This purification procedure was then repeated to obtain the starting material for the subsequent experiments.

15. Preparation of Diethylaluminium Hydride

The method of Ziegler et al (71) employing sodium hydride and diethylaluminiumchloride was used for this preparation. Before use, the activity of the sodium hydride was determined by reaction with ethanol, followed by titration of the sodium ethoxide produced against 1M HCl using bromocresol purple indicator. 17.7 gms of the ($\sim$50%) sodium hydride dispersion in oil (0.40 moles) was added to a dry 250 cm^3 three necked flask flushed out with N_2. The flask was magnetically stirred and fitted with a nitrogen inlet, septum cap, and a condenser which could be connected either to the vacuum system or a white oil bubbler. After the addition of the sodium hydride the apparatus was evacuated and warmed gently for two hours. It was then allowed to cool and filled with nitrogen.

Benzene (45 cm^3) and diethyl ether (52 cm^3) (both having been dried using calcium chloride then sodium wire) were added to the sodium hydride. Diethyl aluminium chloride (55 cm^3, 0.44 moles) was added continuously, dropwise, to the mixture over a period of 7 - 8 hours from a syringe through the serum cap whilst the temperature was maintained at 47°C. Upon completing the addition, the mixture was left standing overnight. The solvent was then stripped off under vacuum and the product recovered by distillation at 65 - 75°C at a vacuum of 0.7 mm Hg. **

Yield: 30 cm^3 (25 gms) of diethylaluminium hydride

16. Preparation of an Aluminium Polybutadiene Compound Using Diethyl Aluminium Hydride

The method of Greber and Egle was used for the preparation of aluminium metallated samples of polybutadiene which were introduced into an ethylene polymerisation system. Preparation of these compounds was either carried out in the polymerisation reactor prior to the ethylene polymerisation or in the apparatus as used for the organoliothium preparations, in which case a measured aliquot of the polymer solution was transferred to the reactor. Dry iso-octane or toluene was used as the solvent for these experiments of which the following is a typical example.

NOTE; ** Reference 55, Chapter III, Page 340, also Annalen <u>589</u>, 91 (1954). (b.p. 65 - 70°C at 0.7 mm Hg).

(0.7 mm Hg=93Nm^{-2})

The purified polybutadiene (5.25 gms, 0.097 moles) was dissolved in iso-octane* in the reactor and stirred at 85°C. Diethyl aluminiumhydride (6.0 cm^3 (4.9 gms), 0.05 moles) was added to the mixture, which was then left stirring for three hours before starting the ethylene polymerisation. To ensure maximum reaction, it was preferred to leave the mixture overnight at a minimum of 50°C before use. Details of these polymerisations, experiment numbers BE/1, BE/2, BE/3 and BE/4, are given later in the text.

17. Preparation of a Polystyrene Aluminium Compound from Amalgamated Aluminium

The preparation of $Et_3Al_2I_3$ by this type of reaction, was first reported by Hallwachs and Schafarik (72) in 1859, but the method used in this preparation is similar to that used by Grosse and Mavity (73). In this experiment the aluminium was activated by amalgamation using the technique of Wislicenus and Kaufmann (74). Aluminium turnings were firstly etched by the addition of dilute sodium hydroxide and shaking the mixture until hydrogen was evolved. The sodium hydroxide solution was then decanted off and the turnings washed with water. They were then treated with 0.5% mercuric chloride solution for 1 - 2 minutes. After decanting this solution off, the entire process was repeated. When the mercuric chloride solution had been decanted off for the second time the turnings were washed with portions of water, then dry ethanol, then dry ether, before their immediate use.

NOTE: * In other cases toluene was also used as an alternative.

About 5 gms of the aluminium turnings prepared as above were placed in the three necked flask apparatus as described previously for metal alkyl preparation. Poly(α -brome)styrene (9.2 gms, 0.05 moles) dissolved in toluene (100 cm^3) was added to the turnings and after the addition of a crystal of iodine the mixture was brought to reflux. After refluxing overnight, the mixture was allowed to cool and an aliquot of the supernatant solution was used as initiator in a polymerisation experiment, SE/2.

18. Preparation of Polystyrene Aluminium Compound Using a Magnesium Aluminium Alloy

The preparation was carried out using the technique of Grosse and Mavity (73). The apparatus used was as for preparation 17. 4.32 gms of magnalium turnings (an alloy of 30% Mg and 70% Al) together with poly(α -bromo)styrene (9.2 gms, 0.05 moles) was placed in the flask and dissolved in 100 cm^3 of toluene. The procedure then followed that of preparation 17. See polymerisation number SE/3.

2.3. - EXPERIMENTS TO PREPARE AN UNSATURATED POLYSTYRENE SUBSTRATE

The following three step procedure was adopted in order to synthesise a vinyl substituted polystyrene.

19. Preparation of Poly(p-chloromethyl)styrene using a Frieder Crafts Reaction

The method of Kockelbergh and Smets (75) was used for the preparation of poly(p-chloromethyl)styrene. This required the use of chloromethyl methyl ether which was prepared by the Gilman and Blatt procedure (76). A mixture of 438 cm^3 (350 gms) of methanol (10.9 moles) and 900 gms of technical formalin solution containing 252 gms of formaldehyde (8.4 moles) in a 2 dm^3 flask were reacted with a stream of hydrogen chloride gas supplied from a cylinder. The ether was salted out of the aqueous phase with $CaCl_2$ and separated off. The product was dried over $CaCl_2$ before further use. 15 gms of polystyrene (0.14 moles) were dissolved in 300 cm^3 of carbon disulphide and the mixture cooled in an ice bath to 0°C. After 30 cm^3 (32.1 gms) of chloromethyl methyl ether (0.40 moles) had been added, 7.5 gms of anhydrous aluminium chloride were, over a period of two hours, gradually added to the vigorously stirred mixture. 120 cm^3 of dioxane was added to the reaction after a further four hours, and the polymer was then precipitated by pouring the mixture into methanol. The product was filtered off, washed well with portions of water, then methanol and finally vacuum dried at 50°C.

Yield:	19.2 g (87.3%)
Elemental Analysis:	C: 79.5% H: 6.9% Cl: 13.6%
	(59% Chloromethylation)

20. Preparation of the Triphenyl Phosphonium Salt of Poly(p-chloromethyl)Styrene

11.0 gms (0.072 moles) of poly(p-chloromethyl)styrene were placed in a flask together with 23.6 gms of triphenyl phosphine (0.09 moles) in dimethylformamide (700 cm^3) and the mixture stirred under reflux for three hours. When cool the precipitate was filtered off, washed with benzene and dried *in vacuo* at 50°C

Yield : 25.4 g (93%)

Elemental Analysis: C: 76.6% H: 6.9% P: 4.3% Cl: 6.0%
(53% Phosphorylation)

21. Preparation of Poly(p-vinyl)styrene

12.9 gms of the phosphonium salt (0.034 moles) from preparation 20 were suspended in a mixture of 160 cm^3 of toluene and 200 cm^3 of anhydrous ethanol. 100 cm^3 of a saturated solution of formaldehyde in ethanol were added to the mixture, followed by 150 cm^3 of a 0.3 M solution of lithium ethoxide (0.043 moles) (prepared by the addition of 2.0 gms of lithium wire to 1 dm^3 of anhydrous ethanol). The mixture was stirred well, then allowed to stand. The precipitation of the product was assisted by the addition of 250 cm^3 of water and the refrigeration of the mixture overnight. The precipitate was recovered by filtration, washed with ethanol and dried *in vacuo* at 50°C. A purified sample was prepared by reprecipitation. It was found that a considerable amount of the material was insoluble in toluene, which suggests that cross linking of the polystyrene had occurred.

Yield : 5.2 gms of reaction product (1.6%)
0.1 gms of toluene soluble material (2%)

Elemental Analysis of the toluene soluble material : C: 64.3% H: 7.7%

Theoretical figures for poly(p-vinyl) styrene : C: 92.3% H: 7.7%

2.4. - POLYMERISATION EXPERIMENTS

Ethylene polymerisation experiments were carried out using the technique employed for previous work (48,49) (see also Figures 7, 13, 14). The technique, apparatus and materials were as employed previously with the following exceptions. In these experiments the gas supply systems were reconstructed entirely from metal, the pipework and catalyst columns being chiefly copper or stainless steel connected using "Wade" brass fittings. Nylon tubing was used to a very limited extent, only for essential flexible connections, especially in the couplings connected to the glassware, as in the solvent supply system. The gas supply system incorporated an additional drying column containing molecular sieve type 3A and the solvent supply system incorporated one containing molecular sieve type 5A. All sieve pellets used for these experiments were 1/16 in. diameter. The drying agent for the solvent distillation was sodium-potassium alloy in preference to lithium aluminiumhydride, since its activity could be relied upon providing liquid metal was visible.

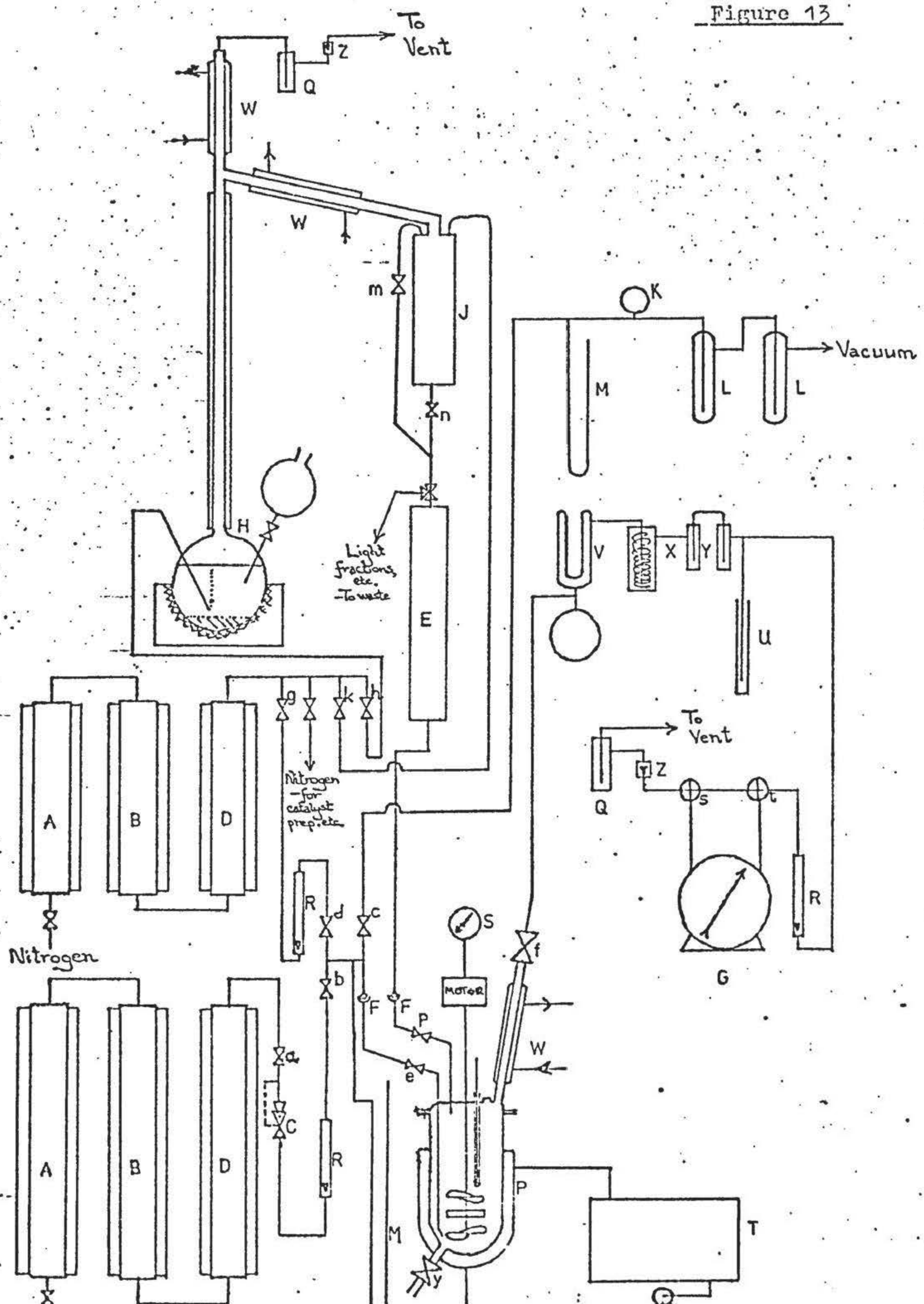
22. Ethylene Homopolymerisations

A series of 11 experiments were conducted initially to test out the activity of the rebuilt apparatus for preparing ethylene polymers. Results were obtained using aluminium triethyl and compared with previous figures in order to obtain a system with high catalyst activity. Control experiments, where alternative metal alkyls were employed, were carried out in order that comparable activity results could

KEY TO Figure 13

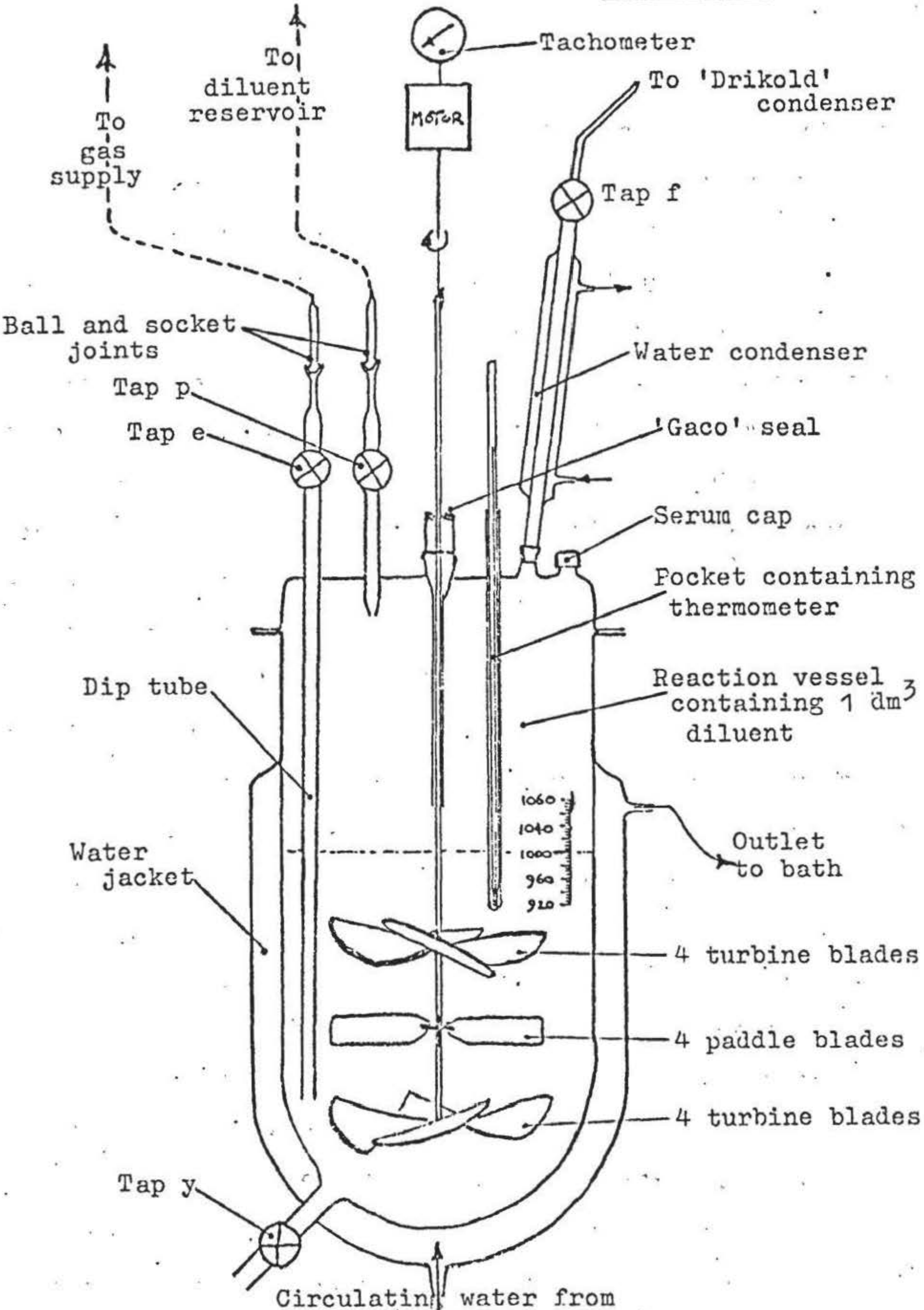
A. B.A.S.F. R3-11 catalyst column maintained at 135°C
B. Linde molecular sieve, type 3A, (1/16" pellets) column
C. Constant differential flow controller
D. Linde molecular sieve, type 4A, (1/16" pellets) column
E. Linde molecular sieve, type 5A, (1/16" pellets) column
F. Ball and socket couplings
G. Wet type gas meter
H. Solvent still
J. Distilled solvent reservoir
K. McLeod vacuum gauge
L. Liquid air cooled vapour trap
M. Manometer
P. Polymerisation reactor
Q. Drechsel bottle vapour trap
R. Rotameter
S. Stirrer tachometer
T. Thermostat bath with circulating pump
U. Mercury pressure relief tube
V. "Drikold" condenser
W. Water condenser
X. Drechsel bottle vapour trap filled with glass wool
Y. White oil bubbler
Z. Non-return valve

Figure 13



THE APPARATUS USED FOR THE ATMOSPHERIC PRESSURE α-OLEFIN POLYMERISATIONS

Figure 14



The reaction vessel used for the atmospheric pressure Ethylene polymerisations.

be used to ascertain "activator" efficiency. Metal alkyls used for this work included lithium butyl, aluminium diethylchloride and aluminium diethyl hydride.

23. Ethylene Polybutadiene Copolymerisations

A series of four experiments were carried out using co-catalyst preparations in which polybutadiene rubber was reacted in order to form an alkylating material. Samples from certain of these experiments were fractionated for evidence of copolymerisation. Details of the results of these tests are given later in the text.

24. Ethylene Polystyrene Copolymerisations

A series of three experiments using polystyrene based catalyst materials was also carried out. These employed the materials cited in the earlier preparations (numbers 13, 16, 17). Characterisation of one of the copolymer samples was attempted and the results are given later.

25. Characterisation of the Copolymer Materials

The first stage of characterisation of the copolymeric materials was fractionation of the crude polymer using solvent extraction techniques. The following method was employed: A weighed sample of the crude material was placed in a 500 cm^3 flask and refluxed for 20 hours with a solvent, then the mixture was filtered whilst still hot. The filtrate was evaporated to dryness, usually on a rotary evaporator* and both that and the residue dried *in vacuo* at 50°C. After

---

NOTE: * High boiling point solvents were vacuum distilled to low bulk and then the polymer precipitated in methanol and the precipitate recovered by filtration.

reweighing, the residue was treated with a different solvent in the same way.

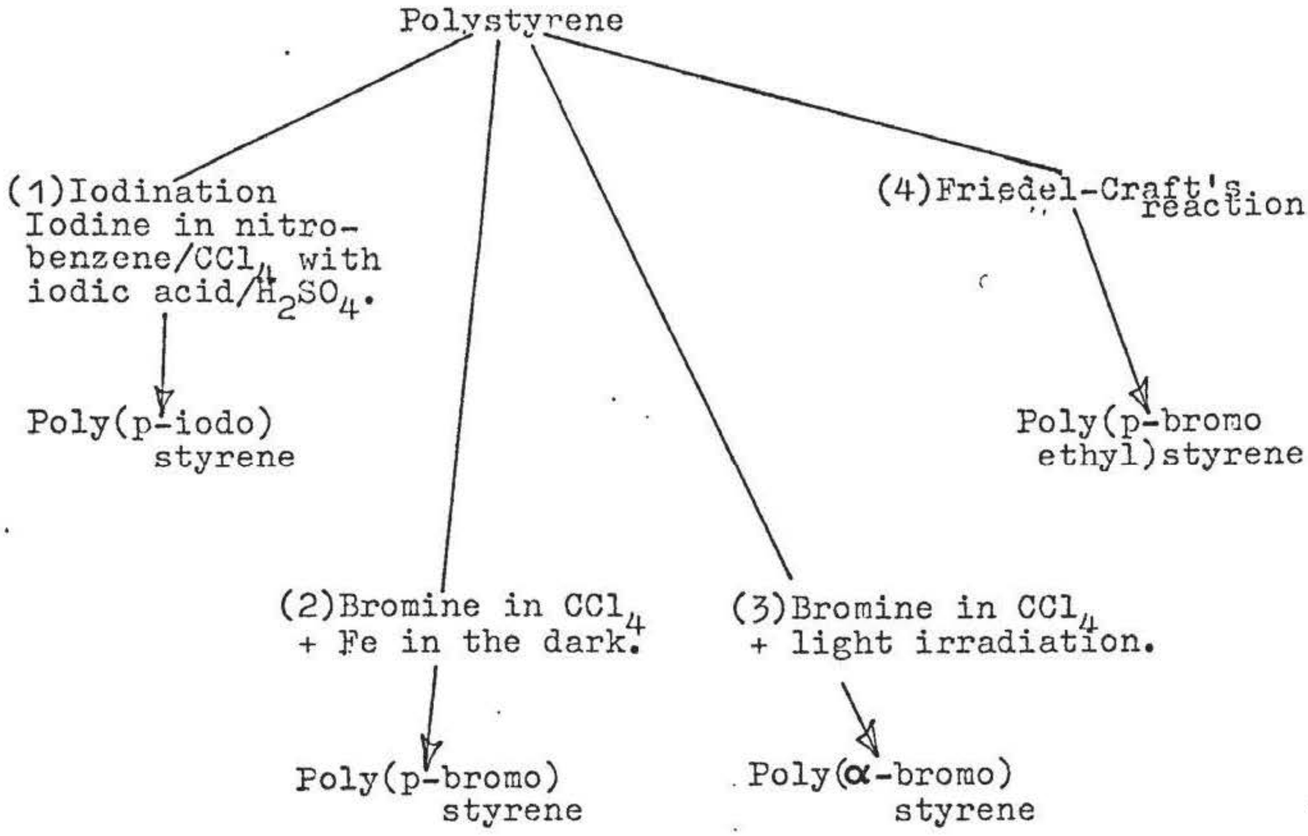
The butadiene - containing materials were treated with benzene, trichloroethylene, cyclohexane, iso-amyl acetate, tetralin and decalin in that order. The styrene - containing materials were similarly treated with the following sequence of solvents; toluene, xylene, tetralin and decalin. Where possible, samples of the fractionated materials were cast into films and subjected to infra-red spectroscopy. If sufficient material was available, an intrinsic viscosity determination was made, using the method given in reference 49, page 39.

SECTION 3 - RESULTS AND DISCUSSION

The initial experiments were concentrated on the preparation of the macromelecular organo-metallic compounds as only very limited ethylene polymerisation facilities were available at this stage. Whilst investigating these reactions, the reconstruction of the ethylene polymerisation apparatus was also undertaken incorporating all modifications thought necessary from the previous work. The first preparations were the halogenation experiments summarised by the scheme overleaf . In general, these reactions were successful in providing precursors for the later organometallic syntheses.

Preparations 1 to 3 were readily effected with a useful yield of the various poly(halo)-styrene compounds. The p-iodo-material was prepared by an established route which gave a 90% recovery and an estimated 95% halogenation according to

HALOGENATION EXPERIMENTS

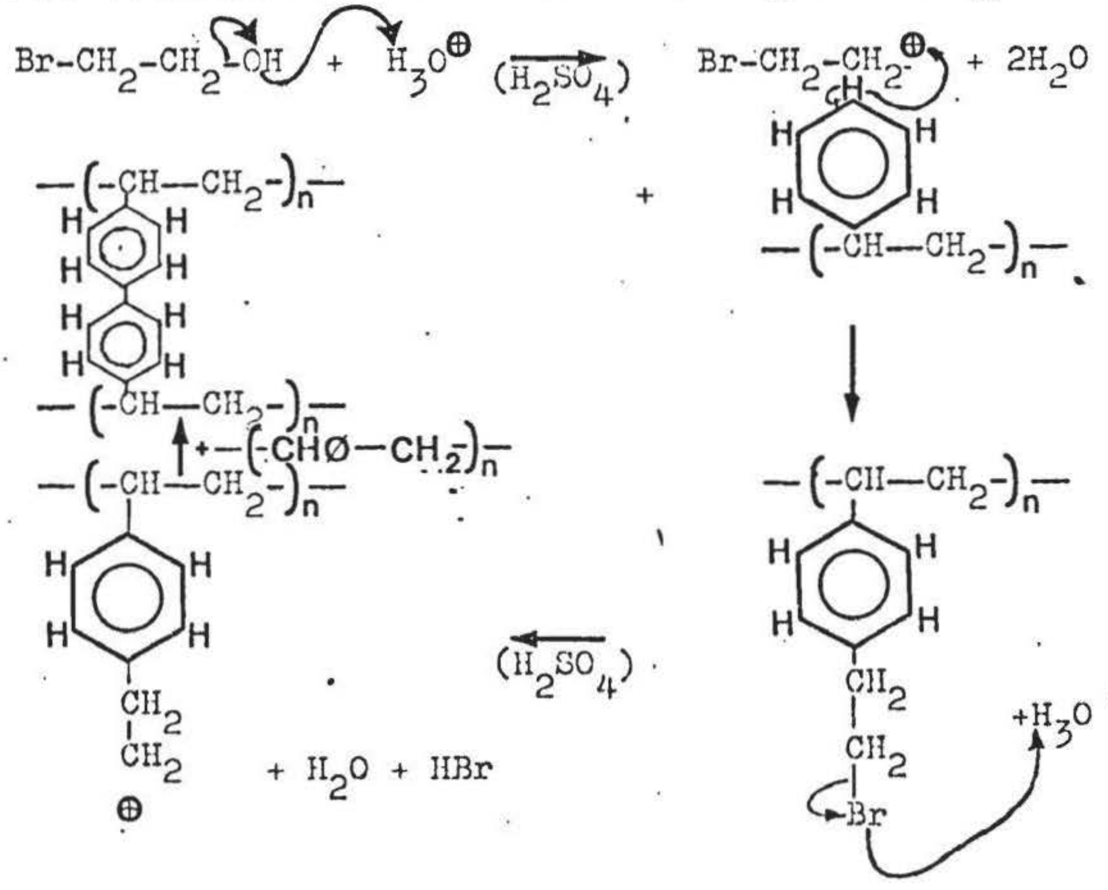


Direct lithiation experiments were carried out on all the above polyhalostyrenes. Poly(α-and p-bromo) styrenes were used for Grignard preparations and the poly(p-iodo)styrene was used in an "alkyl exchange reaction" type lithiation.

the elemental analysis. N.M.R. and I.R. spectra were obtained for the poly(p-iodo)styrene. The I.R. spectrum confirmed the para substitution showing strengthening of the peak at 840 cm^{-1} in relation to those found at 700 and 750 cm^{-1}. The 1600 cm^{-1} absorption of a polystyrene film is greatly reduced in the nujol mull of the poly(p-iodo) styrene and the absorptions at 1490 and 1450 cm^{-1} are found at the lower values of 1470 and 1400 cm^{-1} respectively. The N.M.R. spectrum was consistent with para-substitution. The p-bromo material was also prepared by an established method and gave a high recovery (99%) and good conversion (94% bromination). The I.R. spectrum is similar to that found for the p-iodo derivative. A peak at 820 cm^{-1} confirms para-substitution, and slightly larger movement of the 1490 and 1450 cm^{-1} bands is found this time to 1450 and 1370 cm^{-1} respectively. A similar N.M.R. spectrum to that found in the p-iodo experiment also confirms para-substitution has taken place.

The method used in preparation 3 for the α-bromination of polystyrene was a novel technique which gave acceptable results. A yield of 65% was achieved and elemental analysis on two preparations gave brominations of 38% and 31%. The I.R. spectrum does not contain any disubstitution bands but only a peak at 695 cm^{-1} with side peak at 730 cm^{-1} from the monosubstituted phenyl ring of the styrene. The mid spectrum peaks are found at 1450 and 1370 cm^{-1}. The N.M.R. spectrum found for the product was consistent with α- bromination. In the preparations attempting partial halogenation a usefully iodinated material was produced containing 6% iodination but the ∝-brominated material with only 1% bromination was considered of less practical value.

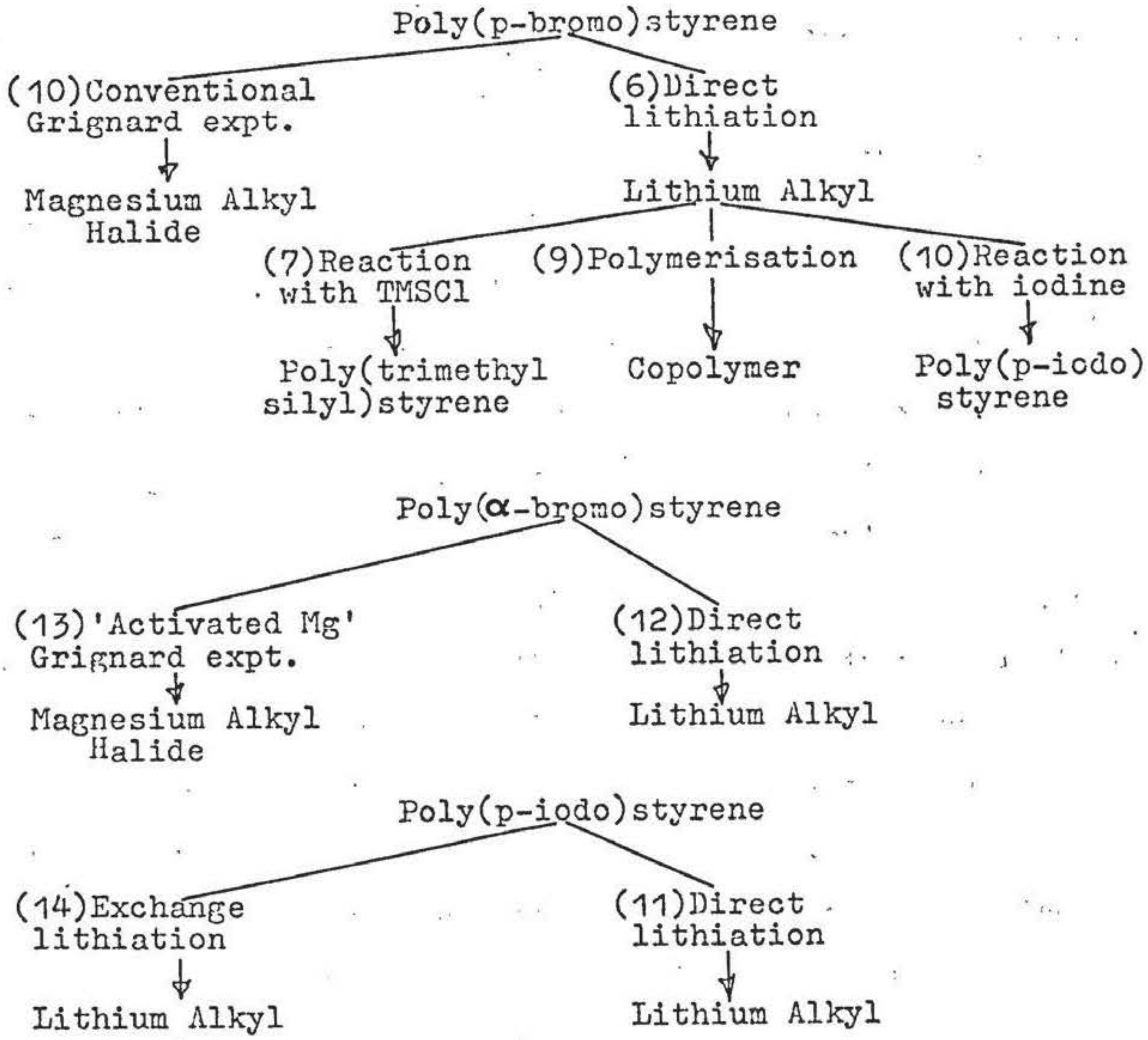
In order to obtain a polyhalostyrene derivative which has no sterically bulky groups immediately adjacent to the halogen atom, unlike those mentioned above, e.g. aryl group or polymer chain, a preparation of bromoethyl polystyrene was undertaken. However, the attempt to substitute a large alkyl function into the para-position of the phenyl nucleus as in preparation 4 was a failure. The resulting product was highly crosslinked and no soluble material could be recovered from the reaction mixture. The use of the acid catalysed Friedel-Crafts method with the 2-bromo-ethanol proved unsuitable, probably owing to further carbonium ion formation involving the halogen atom.



METALLATION EXPERIMENTS

Organolithium and Organomagnesium Compounds

As outlined earlier in the text, the halogenated polystyrenes were used in experiments for the preparation of metal alkyls as shown in the diagram below:-



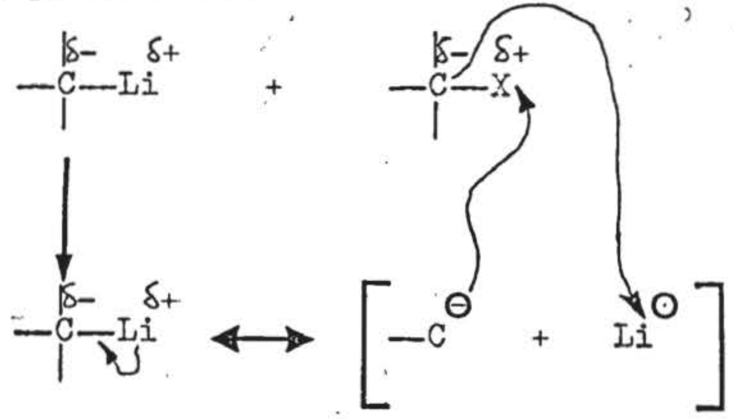
The scheme shows a summary of the lithium and magnesium metallation experiments which were generally found to give very poor results. None of the direct methods, preparations 5, 10 and 11, were successful.

The direct lithiation of poly(p-bromo)styrene, preparation 5, was qualitatively monitored by preparations 6, 7 and 8. The effect of preparation 6, the replacement of Li functions by $Si(CH)_3$ was monitored spectrascopically. The I.R. spectrum does not show a characteristic peak for CH_3-Si which should be present ~ 1250 cm^{-1}. The N.M.R. spectrum does not show the peaks (the characteristic chemical shift) which would be anticipated from the $(CH_3)_3Si$ group. These results imply that negligible lithiation of the material has been achieved and is confirmed by the elemental analysis of preparation 7. The determination of the percentages of bromine and iodine present in a product sample gave these results:- C: 50.5% H: 3.7% I: 0.0% Br: 44.0%, which shows that the lithiation of the material was insufficient to be detected by this method. The polymerisation attempt using material from preparation 5 as cocatalyst was also unsuccessful, a minimal quantity of polymer being prepared.

The Grignard syntheses, preparations 9 and 12, failed to work using the polymeric alkyl halide substrates. The titration results for aliquots from each of the preparations were at the error limit for the burette readings and it was concluded that no detectable reaction had taken place.

Additional lithiation experiments using p-iodo and α-bromo substituted polymers, preparations 10 and 11, were also failures. These showed that activation of the substrate using an alternative halogen and alkyl rather than aryl type substitution had no effect. Overall, the results confirm that direct synthesis of lithio-substituted styrene polymer using poly(p-bromo)styrene and lithium metal does not take place. The metallic lithium does not appear to be a sufficiently powerful reagent to react with a polymer substrate. An exchange reaction seems, therefore, indicated.

Exchange reaction:



In the exchange reaction the polarisation of the Li-C bond leading to attack by the alkyl group is sufficient to drive the reaction whereas in the case of metallic Li this is absent.

Thus, the only lithiation technique which produced a high yield was the butyl lithium exchange reaction, preparation 13, but this method enountered practical difficulties regarding the use of its product for polymerisation experiments. Although this reaction proved a much more effective synthetic route, the technique employed requires an excess of lithium reagent and therefore in this instance its application was limited because of the impracticality of recovering the lithiopolystyrene product from the excess reagent. However, partial recovery proved possible by precipitation of some of the polymeric material and separation of this from the bulk of the reaction mixture.

A quantitative estimation of the activity of the butyl lithium solution was made by the Eppley and Dixon method (70), using the following reactions:-

A) Titration reaction:

$$BuLi + C_6H_5COOH \rightarrow C_6H_5COOLi + BuH\uparrow$$

B) End Point reaction:

$$BuLi + (C_6H_5)_3CH \rightarrow (C_6H_5)_3C\,Li \text{ (red colour)} + BuH\uparrow$$

In the absence of DMSO a white ppt. rather than a red colour change is observed.

The titration reaction (see Equation A) is carried out in a dimethylsulphoxide/monoglyme/hydrocarbon solvent using triphenylmethane as indicator (see Equation B).

The n-butyl lithium exchange reaction proceeded smoothly as found by earlier authors (62, 68) using this method. The washing procedure devised for preparation 13 appears effective and the lithiated polymer recovered was used to reduce titanium tetrachloride, producing the slurry employed in polymerisation experiment SE/1 (see later).

At this stage the organolithium was used as a catalyst reducing agent rather than a cocatalyst as the early homopolymerisation results showed that even the short chain lithium butyl was not effective as a cocatalyst for this magnesium reduced Ziegler system.

The purification of the polybutadiene rubber, preparation 14, proved to be a difficult practical problem. The material was only soluble in hydrocarbons and required considerable effort to produce a solution, as it did not even readily dissolve in these. The optimum solvent appeared to an 80/20 n-hexane/cyclohexane mixture in which the rubber dissolved after vigorous stirring and gentle heating. Any excessive heating was found readily to crosslink the material, producing a solvent swollen gel. The aluminium organometallic compounds were prepared by two routes, firstly the addition reaction as used by Greber and Egle:

$R.CH = CH_2 + AlEt_2H \rightarrow R.CH_2CH_2AlEt_2$

where R = polymer chain.

Secondly, preparations involving the use of the parent metal directly. The resultant product is an alkyl metal halide.

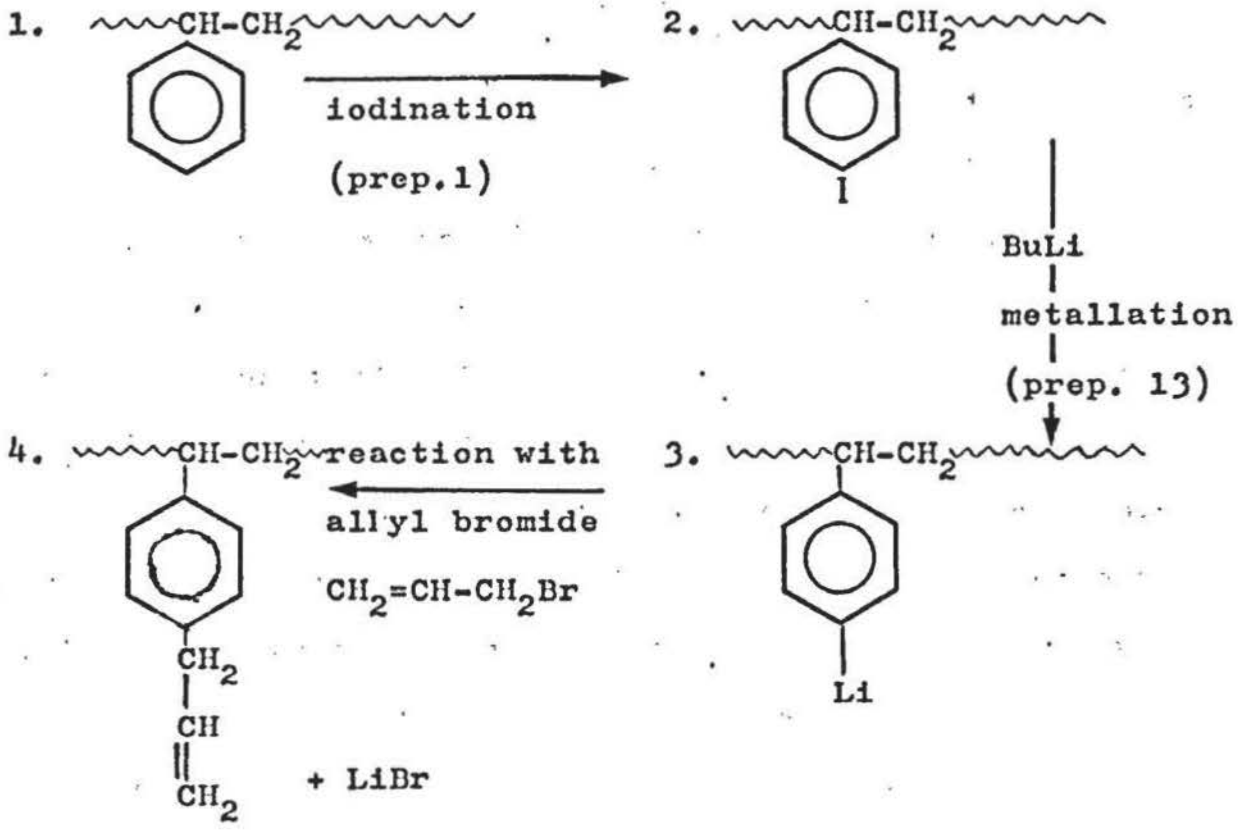
I) $3RX + 2Al \rightarrow R_2Al\ X + RAl\ X_2$

An alternative direct method using aluminium magnesium alloy gives a product essentially free from the undesirable dihalide side-product.

II) $(2Al + Mg) + R.X \rightarrow 2R_2AlX + MgX_2$.

The most convenient way of ascertaining the reactivity of the macro-molecular organoaluminium compounds which were prepared was by their direct use as cocatalysts for ethylene polymerisation. Aliquots of the reaction product from experiments as described in preparation 16 were used for the cocatalyst in polymerisation experiments BE/1, BE/2, and BE/3. Polymerisation BE/4 used a catalyst consisting of a $TiCl_3$ slurry made using an aliquot of a similar reaction product as the reducing agent and a cocatalyst of aluminium triethyl. The reaction product from preparation 17 was used as cocatalyst for polymerisation SE/2 and an aliquot from preparation 18 was used similarly in polymerisation SE/3. The results for these polymerisations will be found in a later section of the text.

An investigation of reactions involving an olefinic double bond and aluminium alkyls in polymers containing a polystyrene backbone was also proposed. In order to do this it was necessary to synthesise a vinyl substituted polystyrene polymer. The synthetic route given in diagram p.71 was adopted. This technique failed in so far as the bulk of the material produced was cross-linked by the end of the reaction sequence. However, this does serve to illustrate a basic prerequisite of the techniques which must be used in the organic chemistry of polymers. The synthetic route used should be kept to a minimum of stages. In conventional organic chemistry the products of side reactions can be removed at each stage of the synthesis by purification techniques. In polymer organic chemistry, undesirable side products are incorporated into the same polymer chain as the required functions and the two are, therefore, inseparable. This will often lead to cross-linking at other stages of the synthesis, and only a relatively small degree of crosslinking is required for the formation of insoluble gels. Alternatively, a solubility problem may exist solely because of the variety of functions, including undesirable ones, present in the polymer. The following synthesis is proposed as an alternative for the formation of vinyl containing polystyrenes, and offers the possibility of substituting longer alkyl side chains.



Both of the early stages may be carried out with high yields and little interference from side reactions. The novel step in the reaction is the last stage where the lithiated polymer reacts with an alpha bromo-omega unsaturated alkane (e.g. alkyl bromide, 17-octadecanoic bromide, $CH_2=CH(CH_2)_{14}.CH_2CH_2Br$) and eliminates lithium bromide forming a vinyl substituted polystyrene material. Interference with this reaction may occur if the substituted ethylene reagent preferentially polymerises in the presence of the lithiated polymer. Polymerisation has been shown to take place with non-halogen containing olefinic monomers (77), e.g. methyl methacrylate, acrylonitrile, styrene and isoprene. An alternative proposal is that a vinyl lithium reagent can be used with a halogenated polymer, e.g. poly(p-chloromethyl)styrene, or poly(p-bromo)styrene, and a similar elimination of lithium halide carried out.

Initial ethylene homopolymerisations were carried out in order to test the system and ascertain the activity of the titanium chloride catalyst, (see experiments E/1 - E/7). The early experiments E/1 - E/5 (see table 1) showed that the activity of the system was not as high as was to be expected from previous work (35, 36). In order to improve the activity, extra precautions were taken. After the first polymerisations E/1 - E/3, the gas supplies were double checked for gas leaks and all ground glass joints in the solvent system regreased. A new $TiCl_3$ catalyst slurry was prepared and fresh aluminium alkyl used for experiments E/4 and E/5 but no improvement in activity has been made. The reduced activity was suspected to arise from either of two sources. Firstly, the solvent was recylced material from the earlier work which had used freshly supplied commercial material. Secondly, the dodecyl bromide used in the catalyst preparation was technical grade material and not that supplied by BDH Limited. In order to overcome any problems arising from these causes, the solvent was initially washed with three portions (10% by volume) of concentrated sulphuric acid.

This was followed by washing with acid potassium permanganate and then water. The solvent was dried with anhydrous calcium chloride then sodium wire before its distillation as normal. The dodecyl bromide was washed with portions of concentrated hydrochloric acid, water, sodium bicarbonate and finally water, before standing it over anhydrous calcium chloride. Before use the bromide was vacuum distilled. These precautions resulted in the preparation of a catalyst with an approximately 50% increased activity. The increase in activity of this catalyst to approximately 75% of that used previously (48, 49) was considered to make it acceptable for the comparative work.

Four further homopolymerisations were carried out to estimate the efficiency of various metal alkyls as cocatalyst initiators. The results are shown in Table 2 ⊛ for aluminium diethyl chloride, aluminium diethyl hydride and lithium butyl. The two alternative aluminium alkyls gave markedly reduced yields in comparison with aluminium triethyl, and the lithium butyl gave negligible yield. As a result of the poor reactivity of the lithium alkyl in experiments E/2 and E/8, it was decided to concentrate on the preparation of macromolecular aluminiums rather than lithiums.

Four copolymerisation experiments were carried out with the polybutadiene backbone and three with the polystyrene backbone. Details of these experiments are also given in Table 2. ⊛ In experiments BE/1 and BE/3, a polybutadiene organometallic was used as the cocatalyst compound, and in BE/4 as the reducing agent for the $TiCl_3$ slurry. Experiments SE/2 and SE/3 used polystyrene organometallics as cocatalysts. SE/1

⊛ See p.69 for Table 2.

employed a $TiCl_3$ catalyst prepared by reduction using a polystyryl lithium compound. The monomer absorption rate versus time was calculated from experimental observations using a programme written for an ICL 1906A Computer, and a graphical output produced using the graph plotting (GHOST) routines which are available in the system (GEORGE 4) implemented in Birmingham.

The results of the fractionation experiments, preparation 25, are given in TableIII.+ The IR spectra for samples of the fractions are shown in part II , the spectroscopic section, Appendix . The fractionation of the ethylene-polybutadiene materials was very disappointing. The reaction product proved practically insoluble in low boiling point solvents. When subjected to higher boiling point solvents the poly-butadiene rubber component was obviously becoming increasingly crosslinked, forming an insoluble gelled material. However, small quantities of material were recovered and analysis of this material attempted. Here again, results were somewhat disappointing. In cases where only a very small fraction had been recovered, the casting of a viable film for IR analysis often proved to be impossible. In films where an adequate spectrum could be traced, there was insufficient difference in absorption peaks to show conclusively that a copolymer had been formed. Interference in the spectra by absorption from silicone grease contamination was found in the 625-1300 wave-number region. Absorptions were generally present in the 3000 and 1600-1800 wave -number regions. Fractionation of the ethylene-polystyrene materials

+ See p.70 for Table III.

was an easier process experimentally; however, even in this case some of the material present at the later stages appeared to be forming a gel residue and some degradation of material was also taking place. IR spectra of these samples were similar to those found for the polybutadiene materials.

The fraction soluble in tetralin from experiment BE/2 was extracted with toluene to remove the silicone grease impurity. An estimate of the molecular weight of this fraction was then made by a single-point viscosity determination. Assuming the relationship as cited for polyethylene in reference 35 holds for this material, the intrinsic viscosity was 4.45 dl/g and the estimated number average molecular weight was 1.7×10^5.

SECTION 4 - SUMMARY AND FUTURE DEVELOPMENTS

The results obtained in this section of the work, have shown that the probability of using macromolecular organometallics in order to generate an active Ziegler catalyst system for the production of graft copolymers is low. The reactions which can be employed for the preparation of such organometallics without degrading the substrate are mainly inefficient. The polymeric compounds produced have shown a low activity when used as co-catalysts with the magnesium reduced catalyst and a poor efficiency as reducing agents, c.f. magnesium alkyl halides for $TiCl_4$ reduction.

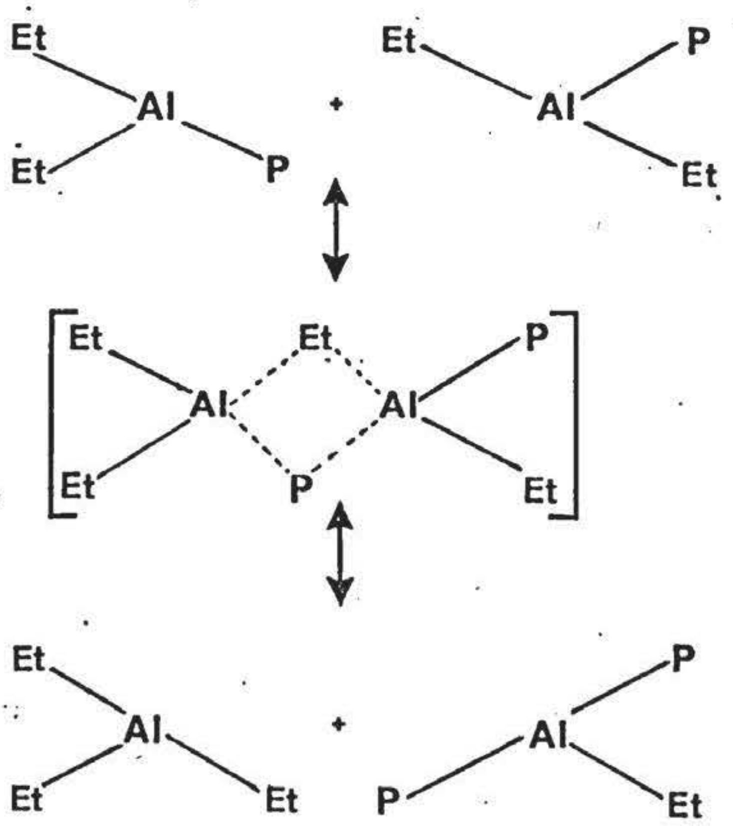
The early preparations showed that polystyrene polymers can be readily substituted with halogen atoms in the main chain or the phenyl ring. Subsequent experiments proved that these polymers can only be successfully lithiated by exchange type reactions. A further development of this work might be to react a lithiated polymer material produced in this way with an α-halo, Ω-unsaturated alkane. The product of such a reaction could be either a styrene-(alkyl halide substituted) ethylene copolymer initiated by the lithium function, if polymerisation occurs, or a styrene substituted with a terminal vinyl side chain if a simple lithium - bromine exchange reaction occurs.

The latter compound could be used for further investigations. Firstly, it can be subjected to the Greber and Egle style reaction with aluminium diethyl hydride. Any product of the reaction might be suitable as a cocatalyst and/or a reducing agent for the titanium catalyst. Alternatively, it could be used as a monomer for copolymerisation with ethylene in an attempt to form a random Ziegler copolymer using the conventional techniques.

However, the results found in the current work do not substantiate the obvious inference which can be made from the Greber and Egle copolymerisation experiment. This is that a macromolecular organometallic compound reduces $TiCl_4$, alkylates the catalyst surface and propagates a growing polymer chain after the role generally proposed for aluminium triethyl in a Ziegler catalysis. An alternative proposal might be that in the system used by Greber and Egle, the combination of polymeric alkyl and ethylene in the reaction mixture may have generated aluminium triethyl either by a displacement reaction

(78) or an abstraction/addition process.

i) Displacement Reaction:



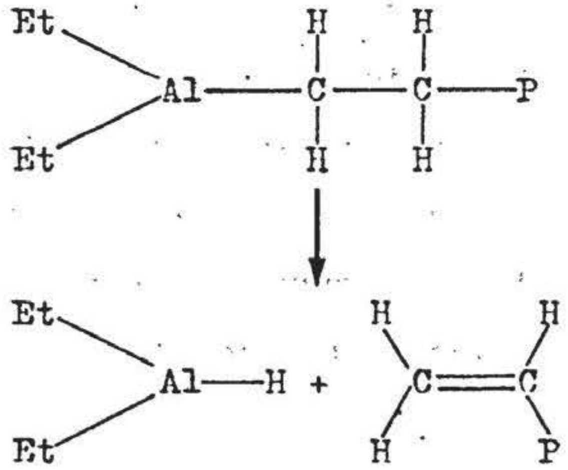
P = Polymeric Alkyl.

For the case of the displacement reaction it may be postulated that the formation of a dimeric bridged aluminium alkyl intermediate can occur, which may by displacement generate aluminium triethyl and a dipolymeric aluminium ethyl species. Dimeric bridged species of a similar type have been postulated by Hoffman (79) although there is no direct evidence for the stable existence of dimers with unlike alkyl bridges. However, such species might only have a very transitory existence, and would therefore prove difficult to isolate.

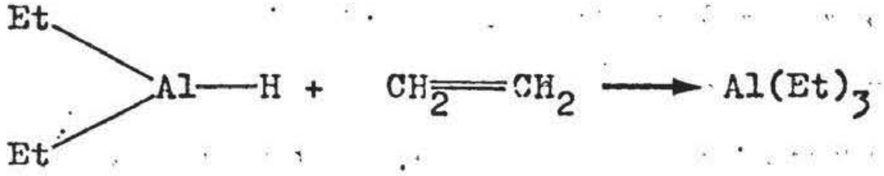
ii) Abstraction/Addition Reactions:

Aluminium alkyls are susceptible to hydrogen abstraction (80) which in the case of the polymeric alkyl species, may regenerate the vinyl polymer and the aluminium diethyl hydride. The latter, in the presence of ethylene, would be converted to aluminium triethyl by an addition reaction.

a)βHydrogen Abstration



b) Addition Reaction



An exchange process using this abstration/addition mechanism accounts for the equilibrium established in aluminium triisobutyl (15).

e.g. $(i\text{-Bu})_3Al \longrightarrow (i\text{-Bu})_2AlH + CH_2 = C(CH_3)_2$

If aluminium triethyl is generated by either of these processes, it will reduce $TiCl_3$ and form an active Ziegler catalyst system which can generate copolymers by reacting with polymeric vinyl groups, e.g. incorporation of regenerated $CH_2 = CHP$

species, or any unreacted vinyl groups where these are present in the graft substrate material. The in situ reduction of $TiCl_4$ by Greber and Egle in their system may have promoted such reactions as postulated above, whilst the use of a preformed $TiCl_3$ in our experiments may account for the poor activity. Such a mechanism as proposed above might be elucidated by experiments using radiolabelled ethylene in a mixture with a macromolecular aluminium alkyl and monitoring whether any radioactivity is incorporated into the metal alkyl.

Overall, the preparation of graft copolymers by this type of synthetic route does not seem very practical. The Ziegler catalyst system is very sensitive to a wide range of poisons, especially oxygen and water. The synthetic preparations necessary to produce the precursors required for this work increase the opportunities for introducing such poisons. In particular in this work, undesirable functions (oxygen containing, etc) may be incorporated into the substrate polymer during the synthetic steps. These will be impossible to remove entirely and will reduce its effectiveness as a cocatalyst or reducing agent. An alternative method of preparation of this type of graft copolymer may be envisaged, however, employing the type of reaction which is normally associated with catalyst poisoning. This will limit the copolymer to a two block system only. The technique depends upon quenching and active Ziegler polymerisation with a suitably activated backbone on to which the growing ethylene chains become grafted. Unfortunately, the main termination reaction for Ziegler polymerisations is normally a hydrogen abstration, e.g:-

$(Cat)\text{-}CH_2CH_2P + ,eOH$

$(Cat)\text{-}OMe + CH_3CH_2P$

Thus the activated polymer species must be more reactive than an abstractable hydrogen atom. Such a technique would nevertheless remove the extra complication of preventing contamination of the Ziegler system by the grafting substrate as encountered in the present work.

---oOo---

TABLE 2

Experiment No.	Activator	Activator conctn. (mM)	Catalyst	Catalyst conctn. (mM)	Duration of Reaction (mins)	Temp. °C	Yield (gms)	Specific Activity (kg/g $TiCl_3$ 1 hour/ atoms)	% Activity c.f.1973 Results
E/1	$AlEt_3$	0.5	$MgR-TiCl_3$	0.01	180	50	43.7	9.4	45%
E/2	BuLi	2.2	$MgR-TiCl_3$	0.01	60	50	0.07	-	-
E/3	$AlEt_3$	1.1	$MgR-TiCl_3$	0.01	60	50	27.5	-	-
E/4	$AlEt_3$	3.7	$MgR-TiCl_3$	0.02	180	50	70.3	7.7	46%
E/5	$AlEt_3$	1.8	$MgR-TiCl_3$	0.02	186	50	75.0	8.1	48%
E/6	$AlEt_3$	0.7	$MgR-TiCl_3$	0.02	180	50	117.5	12.7	76%
E/7	$AlEt_3$	0.7	$MgR-TiCl_3$	0.02	180	50	107.8	11.6	70%
E/8	BuLi	4.4	$MgR-TiCl_3$	0.02	195	50 80	0.3	-	-
E/9	$Et_2Al\ H+ALEt_3$	1.9	$MgR-TiCl_3$	0.02	60+15	50	12.4	-	-
E/10	Et_2AlCl	1.6	$MgR-TiCl_3$	0.02	127	50 80	38.1	-	-
E/11	Et_2AlH	2.3	$MgR-TiCl_3$	0.02	180	80	8.9	1.0	6%
BE/1	(Al-Polybut.)	56 +	$MgR-TiCl_3$	0.05	180	80	8.3++	-	-
BE/2	(Al-Polybut.)	28 +	$MgR-TiCl_3$	0.05	180	80	4.9++	-	-
BE/3	(Al-Polybut.)	28 +	$MgR-TiCl_3$	0.05	180	80	-	-	-
BE/4	$AlEt_3$	0.7	(Al-Polybut)R-$TiCl_3$	2.0 +	180	50	—	-	-
SE/1	$AlEt_3$	1.5	(Bu-Li-Polysty.) R-$TiCl_3$	0.2 +	180	50	1.8++	-	-
SE/2	(Al-Polystyr)	25 +	$MgR-TiCl_3$	0.1	180	80	-	-	-
SE/3	(Mg/Al-Polysty)	35 +	$MgR-TiCl_3$	1.4	180	80	-	-	-

\+ Based on estimated yield of ethylenic material.

++ Assumes 100% conversion to alkyl.

The Magnesium alkyl reducing reagent used throughout these experiments was dodecyl magnesium bromide.

TABLE III

FRACTIONATION OF REACTION MATERIAL

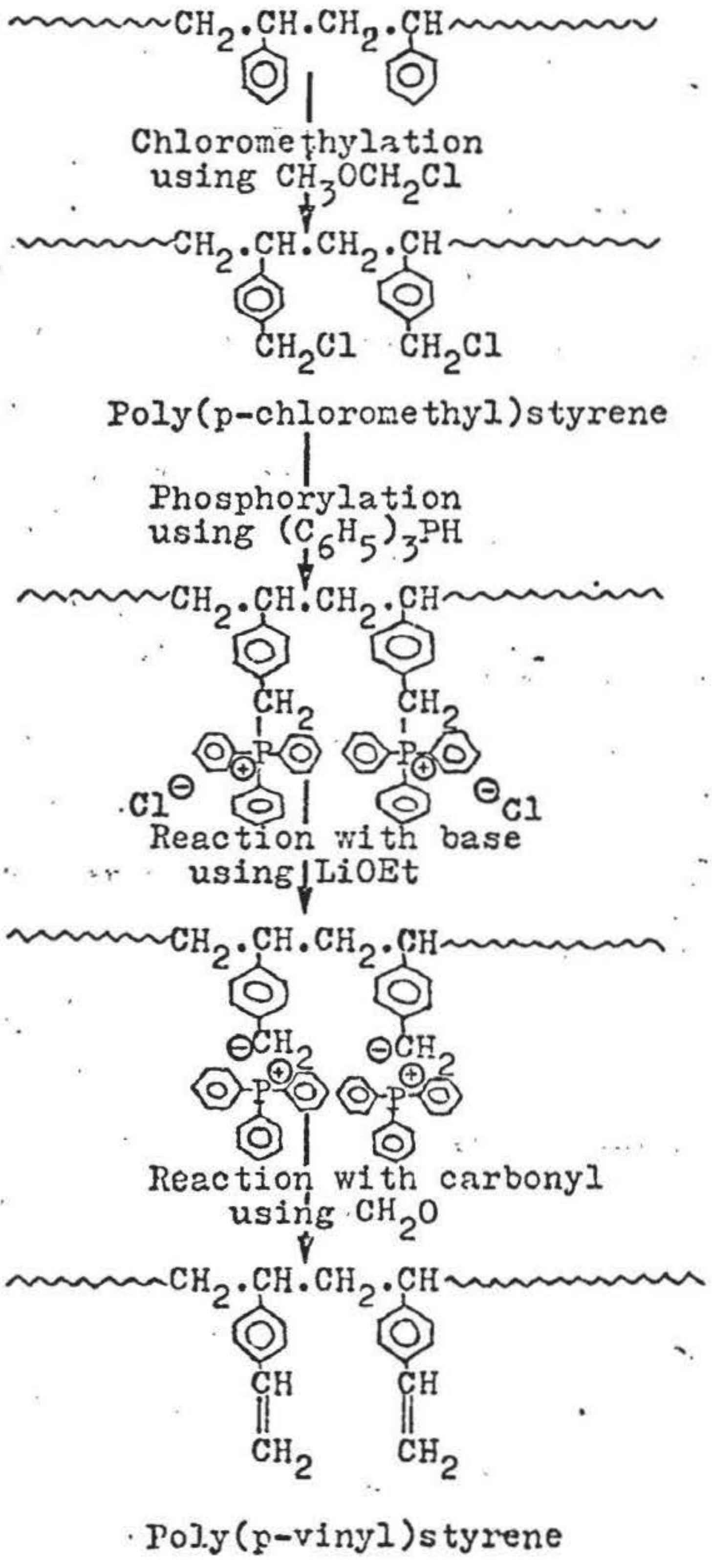
Run Number	BE/1	BE/2	SE/1
Dry Weight of material soluble in hot solvent			
Crude material	13.6 g	9.9 g	1.8 g
Iso-octane	-	0.8 g	0.4 g
Benzene	0.6 g	0.6 g	-
Trichloroethylene	0.3 g	0.3 g	-
Cyclohexane	0.1 g	0.1 g	-
Iso-amyl acetate	0.8 g	1.0 g	-
Toluene	-	-	0.2 g
Xylene	-	-	0.1 g
Tetralin	0.4 g	0.3 g	0.1 g
Decalin	1.6 g	1.2 g	0.4 g
Insoluble Residue	8.9 g	5.3 g	0.2 g

The tetralin fraction from experiment BE/2 was extracted with toluene to remove any silicone grease present. A viscometry determination was carried out on the sample after the toluene extraction and additional IR films were cast an analysed.

Viscometry results found for this sample:

$$\eta = 4.45$$

$$M_n \sim 1.7 \times 10^5$$



The synthetic route for the preparation of vinylated polystyrene

CHAPTER 3

STYRENE POLYMERISATION EXPERIMENTS

SECTION 1 - INTRODUCTION

In the light of the lack of progress with the preparation of graft copolymers using the magnesium reduced catalyst system, attention was transferred to the investigation of the activity of this catalyst in the polymerisation of alternative α-olefins. Current experiments by K Gardner at Birmingham, have already shown that the use of this catalyst for propylene polymerisation produces a mixture of atactic and isotactic polypropylenes (50). It was therefore proposed to investigate the activity of the catalyst towards the more bulkily substituted monomer styrene. Another alternative monomer acetylene was also studied concurrently with the initial styrene experiments. Details of those experiments will be found in Chapter 4.

1.1. - THEORETICAL CONSIDERATIONS

Several authors have previously reported results for the polymerisation of styrene using a variety of Ziegler catalysts. One of the first examples of styrene polymerisation by organotitanium compounds is the work of Herman and Nelson (23) using a Grignard reduced titanate mixture. However, this work was carried out before the existence of Ziegler catalysis was widely recognised and the author's contemporary conclusions attributed the catalytic activity of the titanium to a radical mechanism caused by the generation of phenyl radicals through the decomposition of Ti-C bonds. The use of either titanium IV chloride or titanium III chloride/aluminium triethyl systems for styrene polymerisation(81) is reported in the early studies (24) of Natta. He also appreciated the stereoregulating properties of these catalysts and a fairly comprehensive characterisation of the isotactic polystyrene which he produced is given in subsequent papers(82,83). There are several reports of investigations by other authors into the catalytic activity of titanium IV chloride based systems towards styrene monomer. Authors reporting studies of such systems include Overberger <u>et</u> <u>al</u>, (84), Kern <u>et</u> <u>al</u> (85), and Murahashi <u>et</u> <u>al</u> (86). The further study of titanium III chloride based systems has been reported by Burnett and Tait (87), who investigated the kinetics of the stereospecific polymerisation of styrene using an α-$TiCl_3$-alkylaluminium (or alkylaluminium halide) catalyst system. The titanium III chloride/aluminium trithyl and α- vanadium III chloride/aluminium triethyl systems have also been employed by Otto and Parravano for the study of the Ziegler polymerisation of styrene (88).

Prior to the present kinetic experiments, an initial experiment had been carried out to ascertain whether the magnesium reduced catalyst was active for styrene polymerisation. The apparatus described in Chapter 2 for the ethylene experiments was used, and the results obtained are reported in Table III. When the material produced by this experiment was examined, a portion was found to be toluene insoluble when subjected to solvent extraction, indicating that a quantity of isotactic material had been produced. Further study of the reaction and its kinetics was undertaken, and a dilatometric procedure for monitoring the reaction rates was chosen. Observation of the rates by this means is possible due to the volume change occurring on polymerisation. The relationship between the volume contraction and the degree of conversion can be expected in terms of a function relating to the density of the polymer ρp and that of the monomer ρm respectively:-

$$\% \text{ Conversion} = \frac{\rho p \,.\, \% \text{ contraction} \,.\, \text{constant}}{(\rho_p - \rho_m)}$$

$= C \,.\, \%$ contraction, where C is constant for the given system at a given temperature.

A derivation of this relationship may be obtained by consideration of the measurements involved in the volume change taking place in the dilatometer and the capillary.

Now, as Change in volume in dilatometer capillary

$$= \pi r^2 dh \text{ .... } (1)$$

Where r = radius of capillary

dh = height change during time, dt.

If x, is the mass of polymer produced during time, dt, then also - Change in volume,

$$= \frac{1}{\rho m} - \left\{\frac{1-x}{\rho m} + \frac{x}{\rho p}\right\} \text{ .... } (2)$$

Where ρm and ρp = the density of the monomer and polymer respectively.

By combining (1) and (2) -

$$dh = \frac{x(\rho p - \rho m)}{\pi r^2 .\, \rho m \,.\, \rho p} \text{ .... } (3)$$

As - Conversion, $d(P) = \frac{x - 100}{V \rho m}$

Where V = the initial volume of styrene monomer in the system,

by substitution in (3) -

$$dh = \frac{V \cdot \rho_m \cdot 100\ (\rho_p - \rho_m)\ d(P)}{\pi . r^2 \cdot \rho_m \cdot \rho_p}$$

$$d(P) = \frac{\pi .\ r^2 . \rho_p \cdot dh}{V \cdot 100 \cdot (\rho_p - \rho_m)}$$

$$= \frac{k \cdot \rho_p \cdot dh}{(\rho_p - \rho_m)} \quad \text{Where } k = \frac{\pi r^2}{100.V}$$

$$= C \cdot dh$$

Similarly an expression for the rate of polymerisation may be derived as follows:-

Rate of polymerisation = Rp, moles min.$^{-1}$

$$= \frac{x}{M.W. \cdot dt}$$

by substitution of x from (3) above -

$$= \frac{dh}{dt} \cdot \frac{\pi r^2}{M.W.} \left(\frac{\rho_m\ \rho_p}{\rho_p - \rho_m}\right)$$

$$\text{then } Rp = \frac{dh}{dt} \cdot \frac{\pi r^2 . \rho_m \rho_p}{M.W.\ (\rho_p - \rho_m)} \text{ moles min.}^{-1}$$

$$\text{or} = \frac{dh}{dt} \cdot \frac{\pi r^2 . \rho_m . 10^4}{M.W. . F . V . 6} \text{ moles litre}^{-1}\ \text{sec}^{-1}$$

Where $\frac{dh}{dt}$ = Rate of contraction, cm min.$^{-1}$

πr^2 = Cross sectional area of capillary, cm^2

M.W. = Molecular weight of monomer

ρ_m. = Density of monomer, gm.cm^{-3}

ρ_p. = Density of polymer, gm.cm^{-3}

$F = \frac{(\rho_p - \rho_m).100}{\rho_p}$

= the percentage contraction for 100% conversion of monomer to polymer

V = Total volume of reagents, cm^3

Hence, as $\frac{\pi r^2 \cdot \rho_m \rho_p}{M.W.(\rho_p - \rho_m)}$ can be considered a constant for the given system at a given temperature, then -

$$Rp \propto \frac{dh}{dt}\,,$$ the rate of contraction.

As the initial experiment indicated that a mixture of atactic and isotactic polymers could be expected, it was decided to evaluate C for individual experiments by directly relating the total % contraction to the total % conversion determined by weighing the polymer produced.

1.2. - EXPERIMENTAL CONSIDERATIONS

In order to observe the catalyst system over a wide range of conditions, the scale of these experiments was reduced compared to the ethylene work. A nominal size of 50 - 100 cm^2 capacity was chosen for the dilatometers which meant that the system could be studied over a 1000 - fold range of titanium, aluminium and styrene concentrations. In general, it is difficult to obtain reasonably reproducible results for Ziegler catalysed polymerisations unless scrupulous care is taken in the decontamination of the apparatus and reagents used. Details of the precautions taken for the styrene polymerisation will be given in the experimental section. The samples of polymer obtained in these experiments were subjected to various characterisation procedures, to determine the effect upon the product of the wide variety of conditions which were investigated.

SECTION 2 - EXPERIMENTAL PROCEDURE

2.1. - MATERIALS AND PURIFICATION TECHNIQUES

Styrene

Styrene monomer was obtained from B D H Chemicals Limited, stabilized with 0.001% - 0.002% tert-butyl catechol. This inhibitor was removed by washing twice with 10% sodium hydroxide solution, followed by washing with water until the washings were neutral to red litmus paper (normally three times). After drying over anhydrous calcium chloride, the inhibitor free styrene was allowed to stand over freshly powdered calcium hydride for two days with occasional shaking. The monomer was then fractionately distilled under a nitrogen atmosphere at a reduced pressure (15 mm Hg). The fraction boiling at 38°C was collected over freshly powdered calcium hydride in a storage vessel which was sealed at the reduced pressure and transferred on to the high vacuum system.

4-methylpent-1-ene

4-methylpent-1-ene was also used as a monomer for a few copolymerisation experiments. This was a gift from ICI Plastics Limited, and treated in the same way as the styrene except that molecular sieve type 5A, 1/16" pellets were used as a drying agent in place of calcium hydride. The fraction collected was b.p. 53.5 - 54.5°C at ambient pressure under nitrogen.

Iso-octane

Iso-octane (99% pure grade) was supplied by Phillips Petroleum Limited. The freshly supplied material was dried

(15 mm Hg.=2000Nm^{-2}.)

by refluxing overnight over molten sodium-potassium alloy. The solvent was distilled as in Chapter 2. After fractionation, the middle fraction (b.p. 99 - 100°C) was passed through a column of molecular sieve 5A, 1/16" pellets (1 m. long, 5cm. diam.) before transfer to an evacuated storage reservoir. The solvent was transferred on to the high vacuum system in this whilst remaining under vacuum.

Solvent recovered from previous ethylene polymerisations was also used for some of the initial experiments. Before being treated in the same way as for fresh solvent, this material, which had generally been recovered by steam stripping, was washed three times with concentrated H_2SO_4 (500 cm^3 per 4 dm^3 solvent). This was followed by washing once with a 10% (H_2SO_4) 5% $KMnO_4$ solution. After decanting off the permanganate, the solvent was washed three times with water to remove any pink coloration or grey powder before being dried firstly with calcium chloride then with sodium wire.

The distillation apparatus used for these experiments was the same as that used to distil iso-octane in Chapter 2.

Titanium III Chloride

The titanium chloride was prepared as a slurry in iso-octane by alkyl magnesium halide reduction of titanium IV chloride. This preparation used the technique described in the previous work (49,49A) with ethylene except that the final dilution with 240 cm^3 of osi-octane was not made so that the slurry was in $TiCl_3$ 0.025 M concentration. The magnesium alkyl employed throughout this work was dodecyl magnesium bromide.

Aluminium Alkyls

Aluminium triethyl and Aluminium tri-n-octyl were both obtained from Schering A.G., a specified purity of not $<$ 90% (by decomposition gas analysis). The material was used as supplied by the manufacturer.

Drying Agents

Calcium hydride was obtained from Hopkin and Williams Limited in lump form. The lumps were powered, using a pestle and mortar, in a nitrogen filled dry box, immediately prior to use.

Calcium chloride was obtained from Fisons Chemicals Limited and used as supplied.

Molecular Sieve pellets, manufactured by the Lindo Air Products division of Union Carbide Corporation, were obtained through B D H Chemicals Limited, and used as supplied. Regeneration was carried out when necessary as recommended, using a stream of dry nitrogen at 300°C.

Sodium potassium alloy was made up by heating a 40 : 50 mole % mixture of freshly cut lumps of the two metals under liquid paraffin until a molten alloy was formed. After allowing the mixture to cool, the bulk of the organic liquid was decanted off, taking care not to expose the liquid metal. The alloy was washed several times with dry petroleum ether, then iso-octane, before being poured into the distillation flask under the iso-octane (with great care!). The alloy was maintained by occasionally adding freshly cut lumps of the two metals separately to the distillation flask and then bringing the solvent up to reflux.

Nitrogen

Dry nitrogen gas was supplied from the system described for the ethylene experiments in Chapter 2.

2.2. - APPARATUS AND PROCEDURE FOR STYRENE POLYMERISATIONS

The styrene polymerisations were carried out in vacuum sealed dilatometers of the pattern shown in Figure 15. These consist of a bulb of capacity about 50 cm^3 sealed on to a tube with uniform bore of radius about 0.48 cm. A teflon coated magnetic stirrer bar was placed in the bulb to keep the entire contents of the dilatometer stirred. The dilatometers were filled two at a time using the apparatus shown in Figure 16. Quantities of styrene and iso-octane were purified as outlined above, and the sealed storage reservoirs connected to the filling apparatus at points X and Y. The remaining apparatus, which had been previously dried overnight at 140°C and assembled warm, was evacuated using tap E for 1 hour, flushing once with dried nitrogen after 30 minutes. In addition, whilst under vacuum, these parts of the apparatus which could be appropriately "flamed out" (i.e. all glassware except around teflon seals) were heated with a gentle Bunsen flame. Approximately 100 cm^3 of each of the reagents styrene and iso-octane were freshly distilled under vacuum from flasks R and S into flasks P and Q respectively. The systems were evacuated through taps A and B, and the reagents condensed by immersing the receiving flasks in liquid air. After distillation the styrene and iso-octane

Figure 15

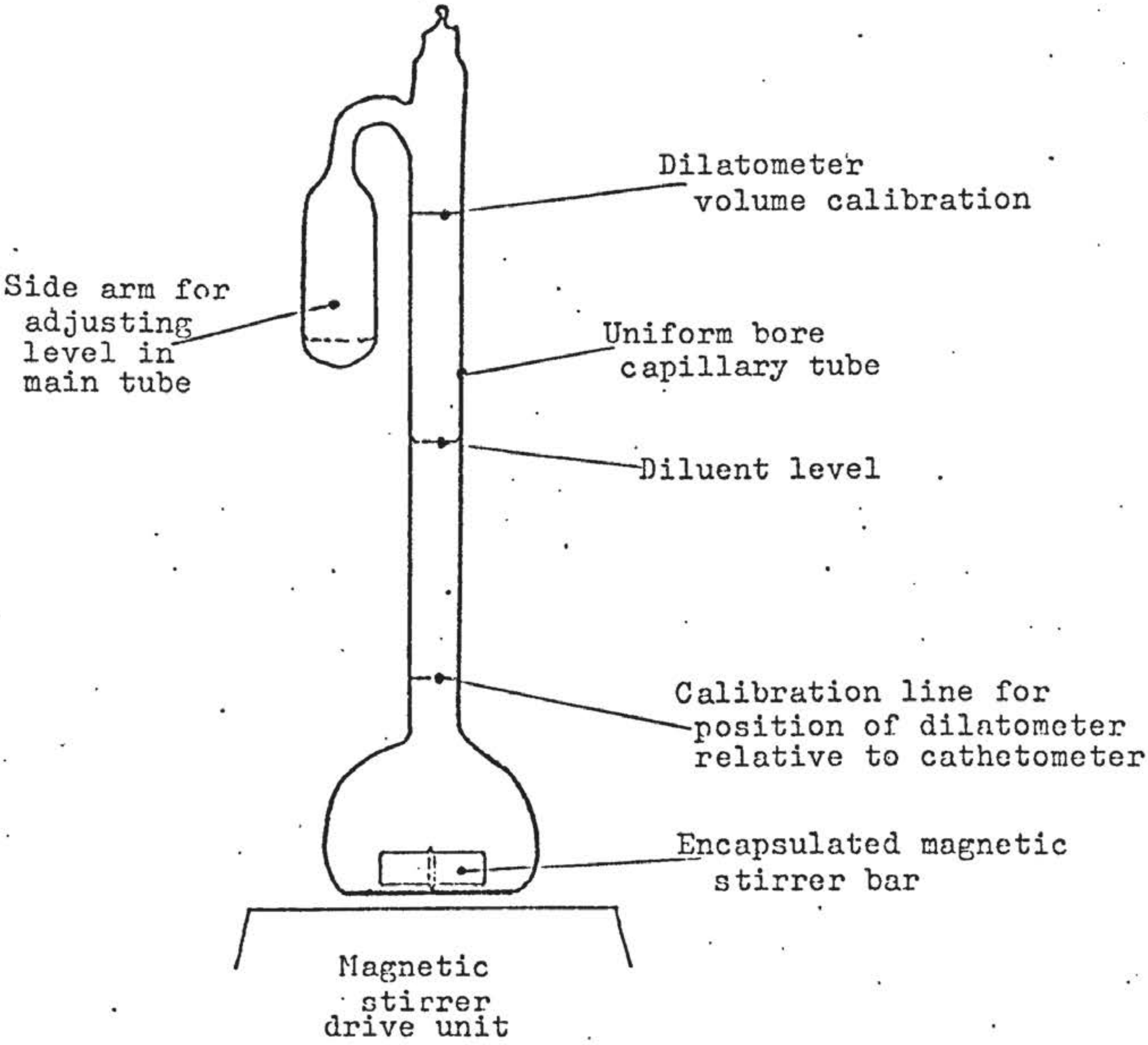


Diagram of the dilatometer used for the Ziegler polymerisations using styrene.

were allowed to warm up to room temperature. Meanwhile, the titanium trichloride catalyst slurry was transferred into the dilatometers under nitrogen by syringe, using the serum caps M and N, the pressure in the lower part of the apparatus having been adjusted to atmospheric using dry nitrogen admitted through tap E. After addition of the catalyst slurry the apparatus was re-evacuated until the bulk of the iso-octane solvent had been removed from the slurry.

Styrene and iso-octane were then drawn into the evacuated burettes C and D, whilst dry nitrogen was being admitted through taps A and B. A measured volume of monomer was then allowed into one of the dilatometers by manipulation of the funnel device F, using a magnet outside the apparatus to move the glass encased bar G. The other dilatometer was meanwhile sealed off by tap K. Aluminium alkyl was next added by syringe under nitrogen through the serum cap. The pressure in the dilatometer was adjusted to atmospheric with dry nitrogen for this step. Finally, iso-octane was added from the burette to make up the dilatometer to the desired volume marked on the stem. The contents of the dilatometer were frozen immediately they were mixed, using a liquid air bath and sealed under vacuum by tap J. The funnel F was then transferred across to the other dilatometer and the filling sequence repeated after opening tap K. Once filled, each dilatometer was degassed by a freezing/thawing cycle and then sealed off under evacuation at point T whilst the contents were frozen.

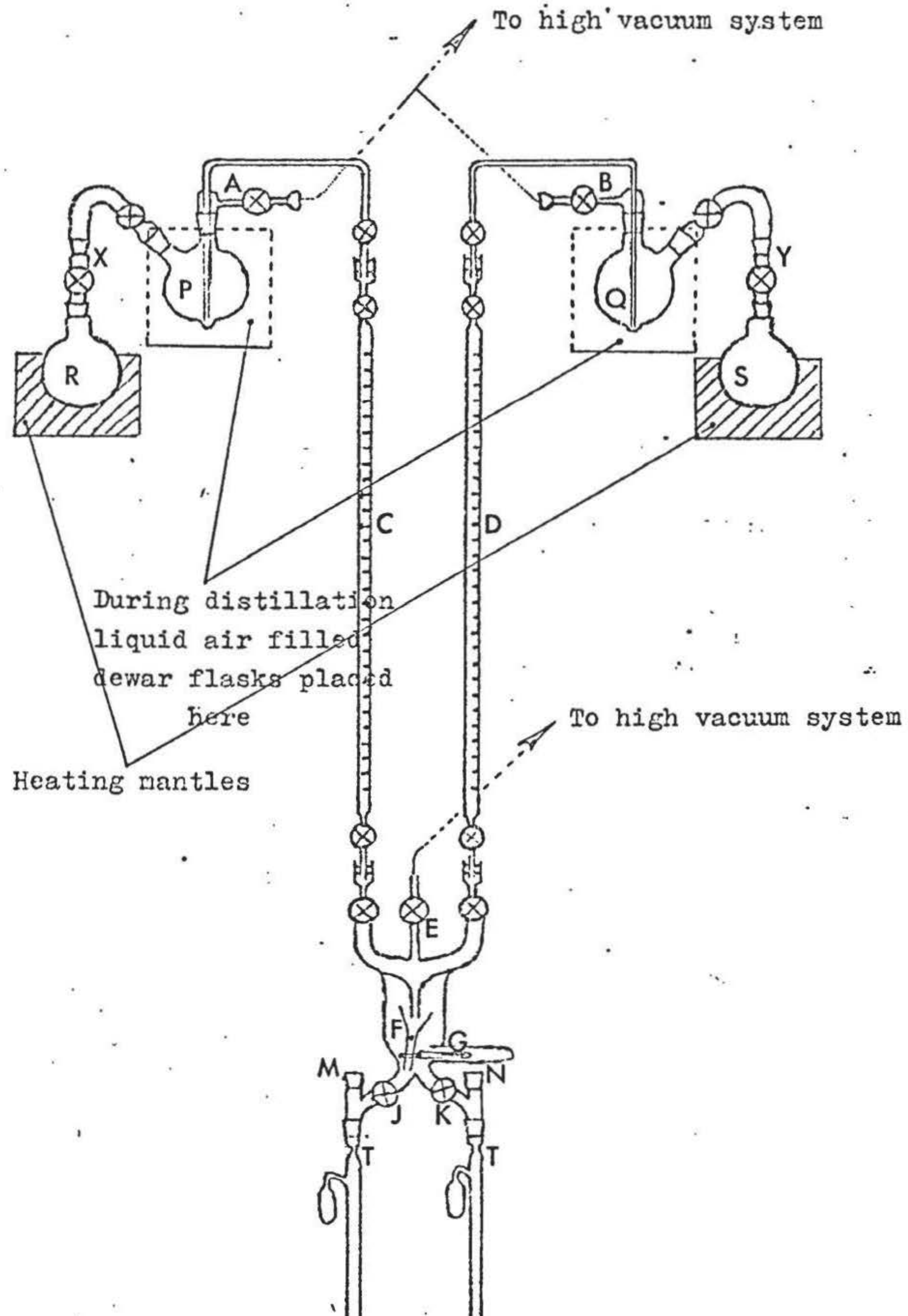


Diagram of the apparatus used for filling the dilatometers.

The sealed dilatometer was rapidly brought to room temperature and then immersed in a thermostat bath normally set at 50°C ± 0.02°C. After the dilatometer had been rigidly clamped on top of a magnetic stirrer unit (see Figure 17), the rate of contraction of the contents was measured by observations of the height of the meniscus using a cathetometer (readings to ± 0.001 cm). During the early part of the reaction these readings were taken at 5 minute intervals, gradually increasing to 30 or 60 minutes towards the finish. The dilatometer was removed from the bath, generally after 24 hours, and immediately immersed in liquid air. When convenient, the vacuum was released by breaking open the top at point T, and after rapidly thawing the contents were poured into 2 dm^3 of vigorously stirred methanol acidified with concentrated hydrochloric acid (20 cm^3). The dilatometer was washed out several times with toluene and finally with methanol to ensure quantitative removal of the polymer. After standing overnight the precipitated polymer was filtered off, using a sintered glass crucible. The crucible was dried <u>in vacuo</u> at 50°C to constant weight. The dry polymer samples were subjected to viscometry or gel permeation chromatography to determine the molecular weight(s). Infra-red and magnetic resonance spectroscopy observations, extraction and crystallisation experiments were carried out in an attempt to obtain data on the structure of the polymer. These are discussed later in the text.

A series of 4 polymerisations were carried out, using

Figure 17

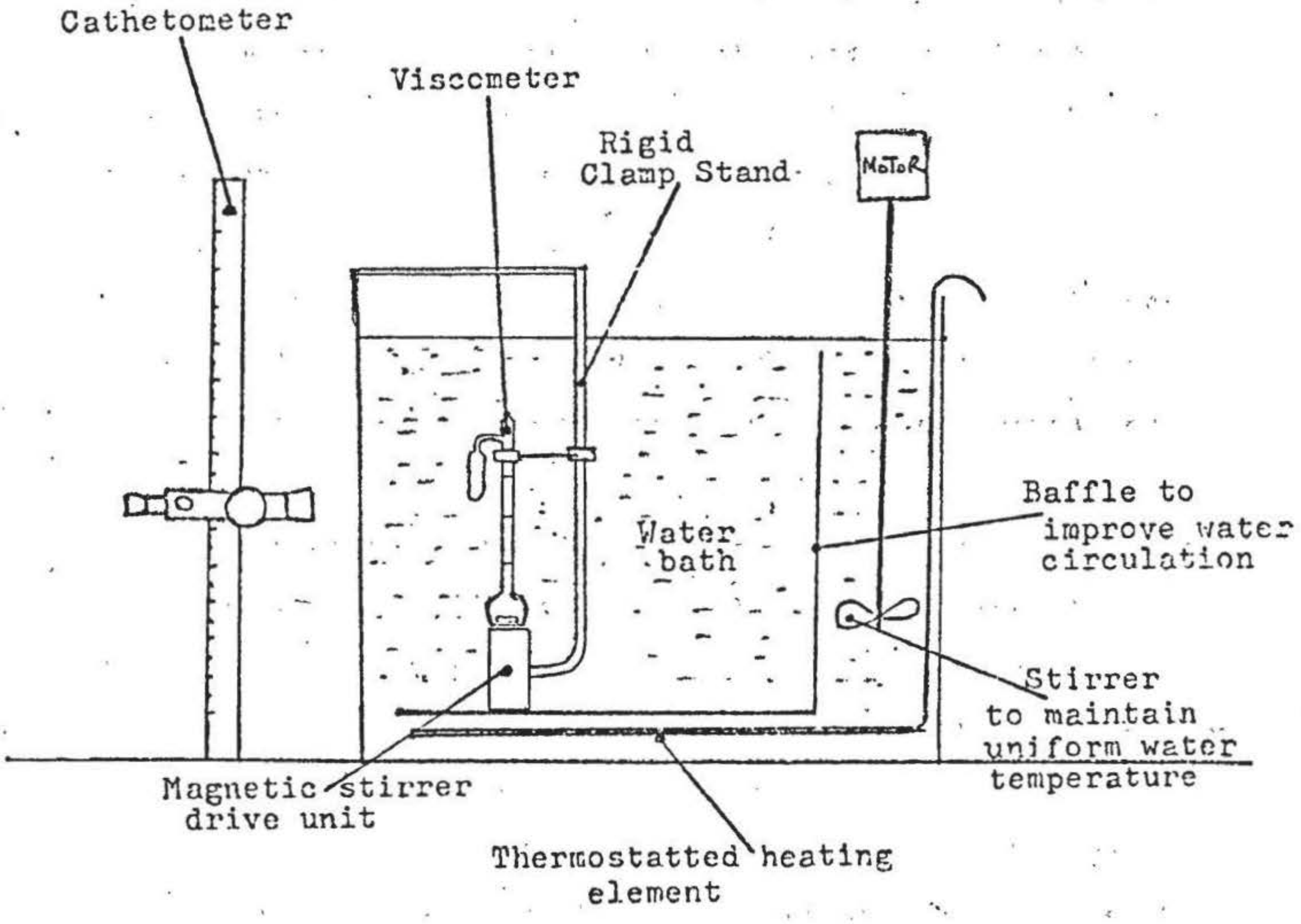


Diagram of the apparatus used for the Ziegler polymerisation of styrene.

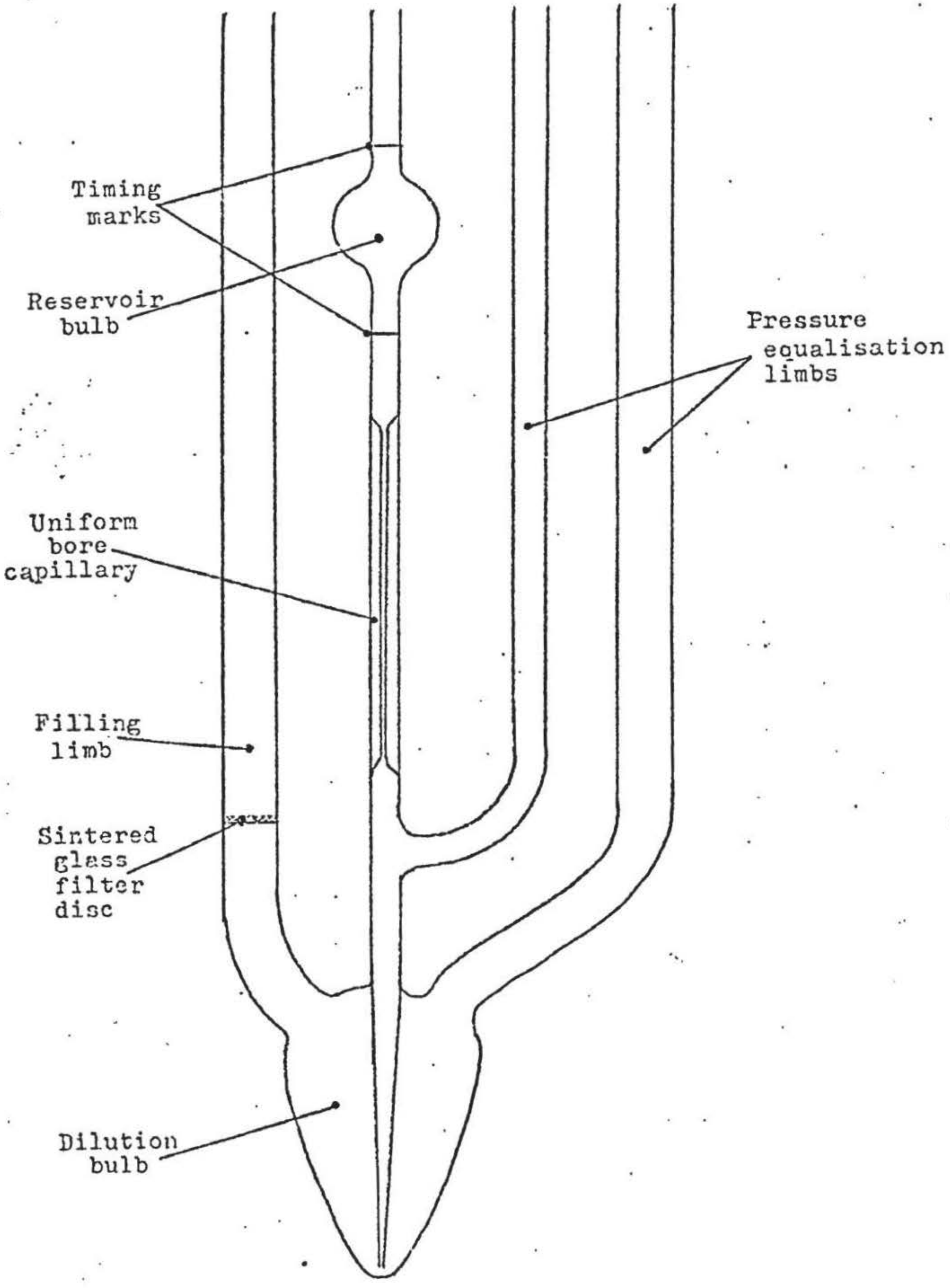
the monomer 4-methylpent-1-ene (4-MP-1). These experiments consisted of one homopolymerisation and three copolymerisations with styrene using different initial monomer feed ratios. The method used for these experiments was identical to the styrene procedure with the exception that freshly distilled 4-MP-1 monomer, which had been collected under a nitrogen atmosphere over molecular sieve type 5A, was added by syringe in the same way as the aluminium alkyl.

2.3. - MOLECULAR WEIGHT DETERMINATION

The initial characterisation of a polymer sample was an estimation of its molecular weight, either by a determination of the intrinsic viscosity or by gel permeation chromatography.

The viscometry method was similar to that used in the previous work, reference 49A, p.39. In this case, for the partially isotactic polystyrene, the solvent used was o-dichlorobenzene and it was possible to use the conventional dilution technique and graphical extrapolation to C_o in place of the single point method used for polyethylene. The viscometer used was of the pattern shown in Figure 18. This was charged with a 15 cm^3 aliquot of 0.5% polymer solution which was prepared by dissolving the powdered polymer in o-dichlorobenzene at 140°C and stirring for 1 hour before allowing it to cool to room temperature. The viscometry observations were carried out at 25 ($\pm$0.05)°C and dilutions made using 2 x 5 cm^3 and 3 x 10 cm^3 aliquots of solvent. The intrinsic viscosity was determined by extrapolation of the functions $\frac{t - t_o}{t_o c}$ and $\mathrm{Log}_e \frac{t/t_o}{c}$ to zero concentration.

Figure 18



Viscometer used for dilution viscometry experiments.

This viscosity average molecular weight M_v was calculated using the relationship, due to Krigbaum (89.):

The gel permeation chromatography was performed by Mr S W Hawley at RAPRA, Shrewsbury. The determinations were made using a set of four columns with pore sizes 700 - 2000 A^o, $1.5\text{-}5\times10^4\ \mathring{A}$, $7 \times 10^5 - 5 \times 10^6\ \mathring{A}$, $5 \times 10^6 - 10^7\ \mathring{A}$. The sample was dissolved in tetrahydrofuran plus 0.1% 2.6, di-tert-butyl-p-cresol as inhibitor and eluted at a flow rate of 1 ml/min at ambient temperature. The apparatus was calibrated with polystyrene standards using the Mark-Houwink relationship $[\eta] = KM^{\alpha}$ where $K = 1.2 \times 10^{-4}$, $\alpha = 0.7$. The results were not corrected for peak broadening effects but were corrected for variation of refractive index with molecular weight at low molecular weights.

2.4. - CRYSTALLISATION EXPERIMENTS

In order to characterise more explicity the structure of the polystyrene samples an investigation of the crystallinity of several samples was undertaken. Hot stage microscope observations of the crystallisation of samples were attempted using the method adopted by Hay (90.).

A reference material similar to that used by Hay was used for control experiments. This was the xylene soluble fraction of an isotactic material prepared at 30°C by the method described by Burnett and Tait using an α- $TiCl_3/AlEt_3$ Ziegler catalyst system in toluene. Samples of the standard material and of several of the polymers prepared in the present work were placed between a microscope slide and coverslip and melted to form a thin film $\sim$0.05 - 1.0 mm thick. The

$(1\ \mathring{A} = 10^{-10} m.)$

development of any crystallizing entities in the polymer melt could then be followed using the polarizing microscope. The size, distribution and number of entities were monitored using a micrometer eyepiece. The melting behaviour was also studied using a differential scanning calorimeter for the standard sample and one of the magnesium reduced catalyst samples.

2.5. - SPECTROSCOPY

Infra-red spectra were measured for several polymer samples and compared with results obtained for a control sample of an isotactic polymer previously used in the crystallization experiments. These spectra were obtained for thin films of the material between sodium chloride plates. The films were either cast directly on to the plates using a toluene or o-dichloro-benzene solution of the polymer, or were pressed by melting the material at 140°C between microscope coverslips.

Proton n.m.r. spectra were measured using a solution of the polymer in tetrachloroethane at 100°C or in o-dichlorobenzene at 130°C on a Varian or P.E. R12B spectrometer using a frequency of 60 MHz or 100 MHz respectively.

^{13}C Nuclear magnetic resonance spectroscopy was also applied to some of the samples prepared in this work. The initial observations were made by Dr N C Billingham at the University of Sussex, Brighton, using a JEOL Spectrometer. The spectra were run at 25°C in $CDCl_3$ solution with a 1.0 sec. pulse repetition rate using a frequency of 25 Hz.

Later measurements were made on similar equipment recently installed here at Birmingham and operated by Mr M Tolley. The technique adopted for these measurements was similar to that used by Bovey [96] using a chloroform/o-dichlorobenzene solution of the polymer sample. The spectra were referenced internally using the chloroform which was assumed to be 77.2 ppm from T.M.S. . Cross reference to the results obtained by Bovey was made by considering $^{13}CS_2$ to be at 118.2 ppm from chloroform .

2.6. - CALCULATION OF KINETIC RESULTS

The kinetic results and the graphical interpretation of the rate data were prepared using programs written for an ICL 1906A computer, in the same way as for the earlier ethylene experiments, using the extended FORTRAN compiler and graph plotting was achieved by use of the CUGHOST routines available on the system (GEORGE 4) implemented at Birmingham.

The program listed in the Appendix, consists of two parts. The first program takes the experimental dilatometer readings which are stored on file in the computer filestore and from successive pairs of time and meniscus height observations calculates values for the cumulative contraction, the percentage conversion and the function; Log 10 (100% - % conversion). This program then calculates from the data the rate of contraction, the rate of polymerisation and time and contraction increments. Finally the program prints the input and the calculated data in tabular form and also stores the information on file.

The second program plots graphs for the functions reaction rate, conversion and Log_{10} (100% -%conversion) versus time from the stored results of the first program. This program uses routines from the CUGHOST library written at U.K.A.E.A. Culham laboratory and transferred to the 1906A by Oxford University.

The rate constant values for individual experiments were estimated using the proportional values found in the Log_{10} (100% - %conversion) versus times curve (see Figures 23 later in text). Those values where 200 min $<$ t $<$ 700 min were submitted to a least squares analysis to provide a value of the rate constant k^1 (determined from the slope of the best straight line). The least squares computation was also carried out using a program written for the ICL 1906A computer.

2.7. Results and Discussion

The preliminary large scale styrene polymerisation catalysed by a magnesium alkyl reduced catalyst yielded 25.5 gm of polymer (3.7% conversion) after three hours at 50°C. A catalyst concentration of 0.018 M titanium III chloride and 0.16M aluminium triethyl (Styrene = 7.27 M) were used in this experiment. On solvent extraction, this product proved to contain a high proportion (80.1%) of material soluble in methyl ethyl ketone (complete solvent extraction results appear in Table 3).

The infra-red spectras of films cast from this material, when compared with results from an atactic standard prepared by free radical reaction, showed that this fraction consisted mainly of atactic material. The bulk of the remaining material was found to form a fraction soluble in toluene whilst the small remaining fraction was soluble in orthodichlorobenzene. Proton magnetic resonance spectroscopy indicated that the toluene soluble fraction was largely isotactic. ^{13}C nuclear magnetic resonance spectroscopy confirmed the isotactic nature of samples from the toluene soluble and orthodichlorobenzene soluble fractions. These spectra were obtained from a solution of the sample dissolved in a mixture of chloroform and orthodichlorobenzene and showed features similar to those found previously by Bovey (91) for isotactic polystyrene. The presence of isotactic sequences indicates that a stereoregulating mechanism is operative in these polymerisations. A Ziegler type mechanism is probably responsible for the generation of this minor fraction of isotactic material in this system. The remaining atactic material can be generated by various mechanisms including the thermal polymerisation reaction.

SECTION 3 - THE KINETICS OF THE POLYMERISATION

3.1. - The General Behaviour of the Reaction Rate

The time dependency of the reaction rate and of the conversion to polymer are depicted in Figure 19 and Figure 20 for two typical experiments. The conditions used were 50°C, 0.014 M titanium III chloride, 0.0077 M aluminium tri-n-octyl and 6.2 M styrene concentrations. In general, the pattern of behaviour exhibited by this system is in line with the decay type kinetics illustrated in Figure 21 which have been previously observed in several Ziegler systems, especially those using aluminium alkyl co-catalysts 48,49.61.

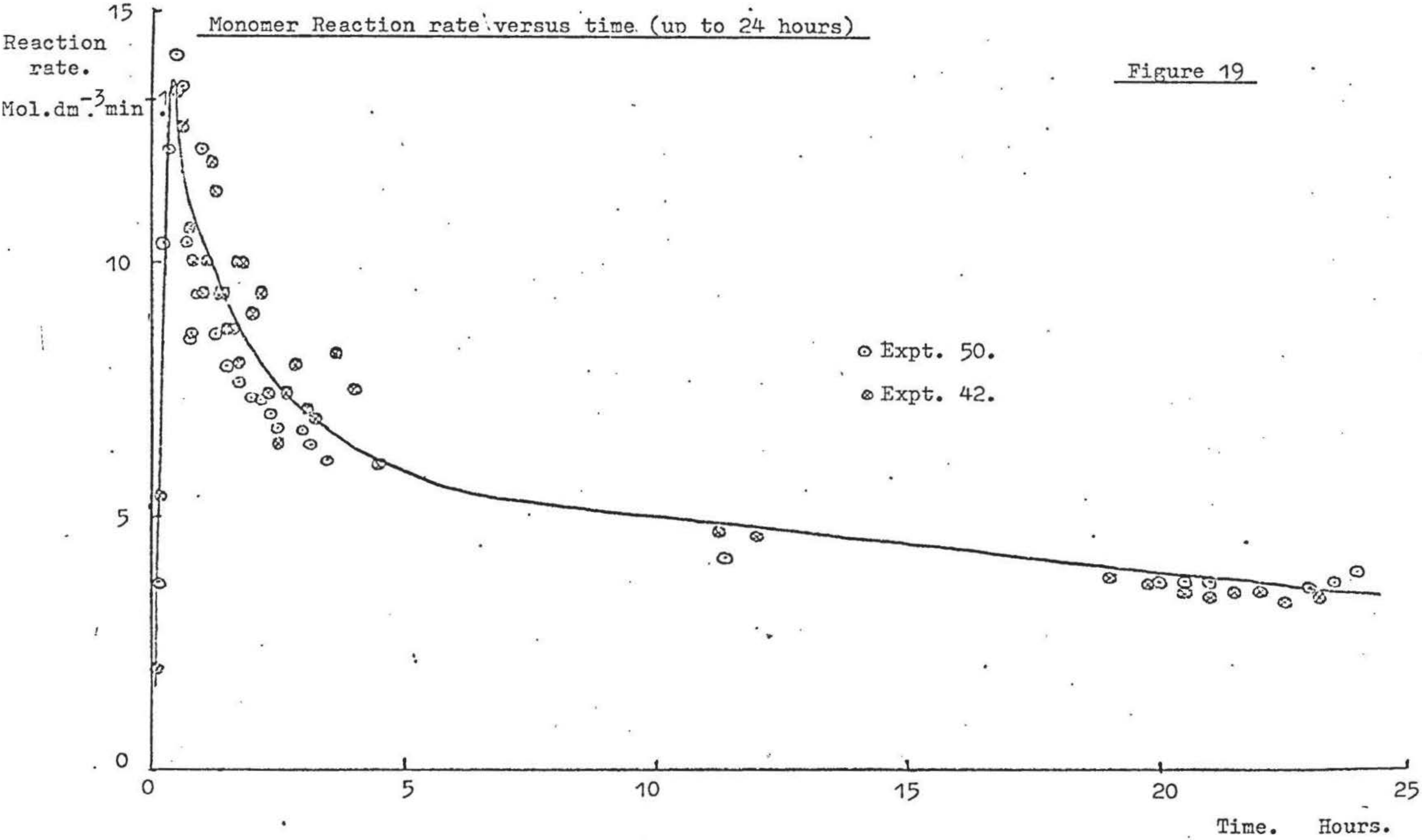
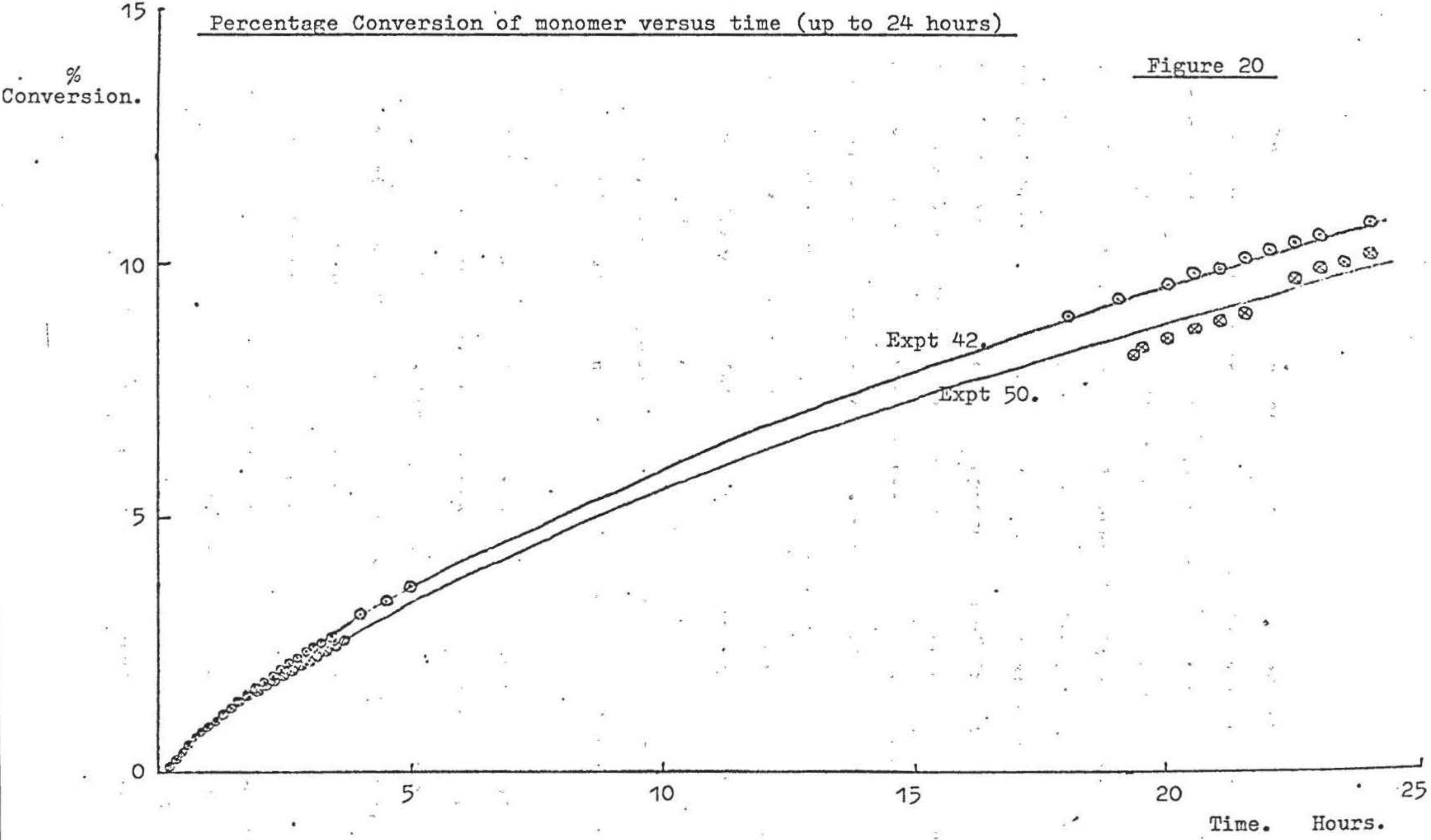

Monomer Reaction rate versus time (up to 24 hours)
Reaction rate. Mol.dm^{-3}.min^{-1}.
15
10
5
0
0
5
10
15
20
25
Time. Hours.
⊙ Expt. 50.
⊗ Expt. 42.

Figure 19


Percentage Conversion of monomer versus time (up to 24 hours)
Figure 20
% Conversion.
15
10
5
0
5
10
15
20
25
Time. Hours.
Expt 42.
Expt 50.

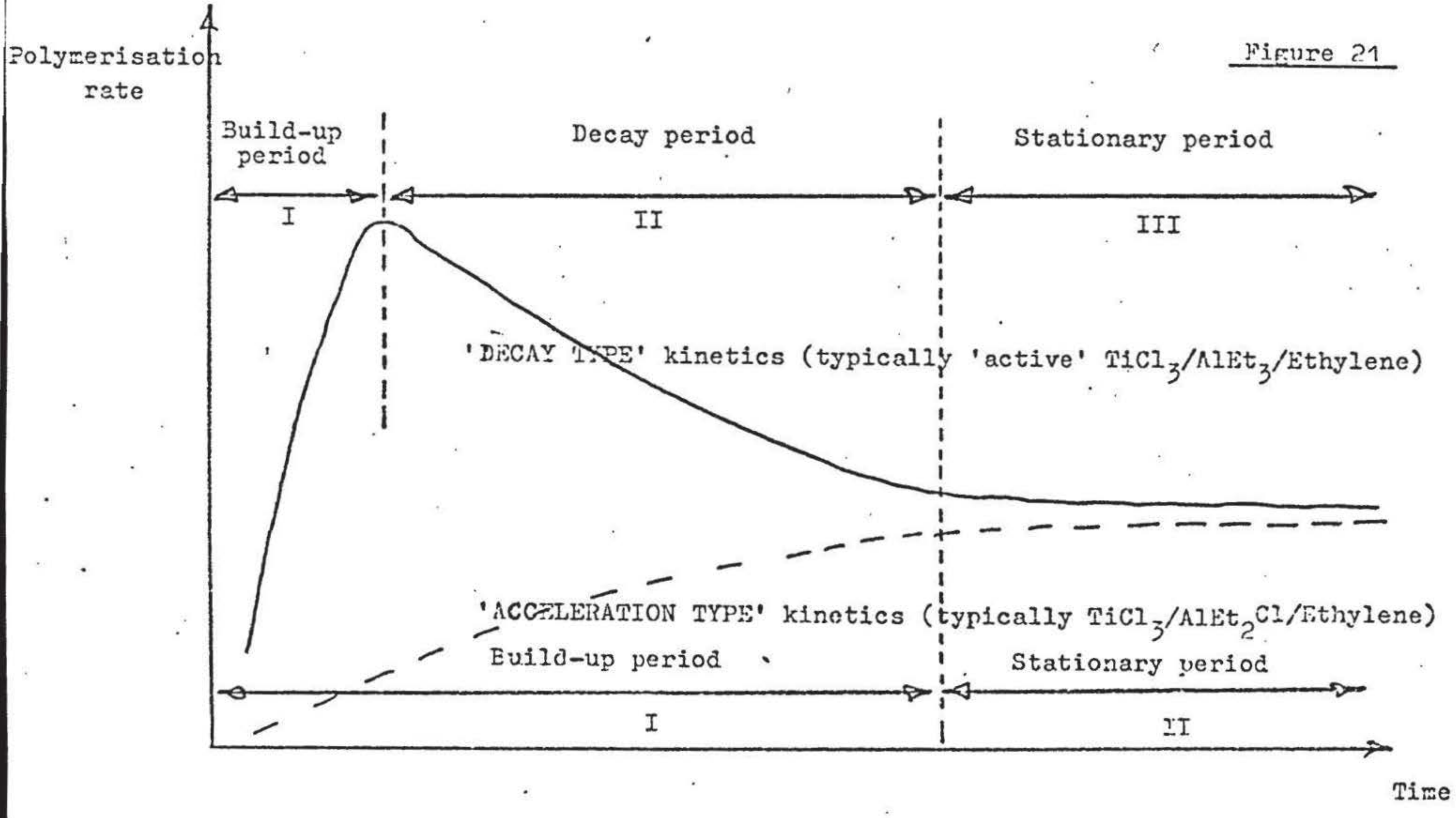
In the magnesium reduced titanium III chloride system, it was found that within a few minutes a high apparent rate was generated. However, this was almost momentary and very quickly a rapid decay in the rate set in. This high initial rate of decay itself falls away sharply with time for $t < \sim 200$ mins as shown in Figure 19. For times $> \sim 200$ mins the rate becomes almost constant; however, it still maintains a slight tendency to decay (an apparent levelling off towards an assymetric value) and this decrease may be observed over a long period as shown in Figure 22, when the experiment is taken to a high value of t ($>$ 5,500 mins).

Observations of this type of time dependency have previously been made in similar Ziegler systems where liquid monomers were employed. Burnett and Tait report a similar type of curve occurring with a styrene / $AlEt_2Cl$ / α-$TiCl_3$ system (87) and with a 4-methylpent-1-ene / $AlEt_2Cl$/VCl_3 system (92) and to a more limited extent in the 4 methylpent-1-ene / Al(iso-butyl)$_3$/ VCl_3 system (92).

This initial period of the reaction in which the marked increases and decreases in rate are found, is known as the 'settling period' and is typically characteristic of many Ziegler systems. No relationships have been established for correlating either the reaction rate or the time duration of this period to any of the component reagents of the system. However, a steady rate condition can normally be attained more rapidly at higher temperatures and physical treatments of the solid $TiCl_3$ catalyst component (e.g. ball milling) have also been found to affect the parameters of this period. Thus the

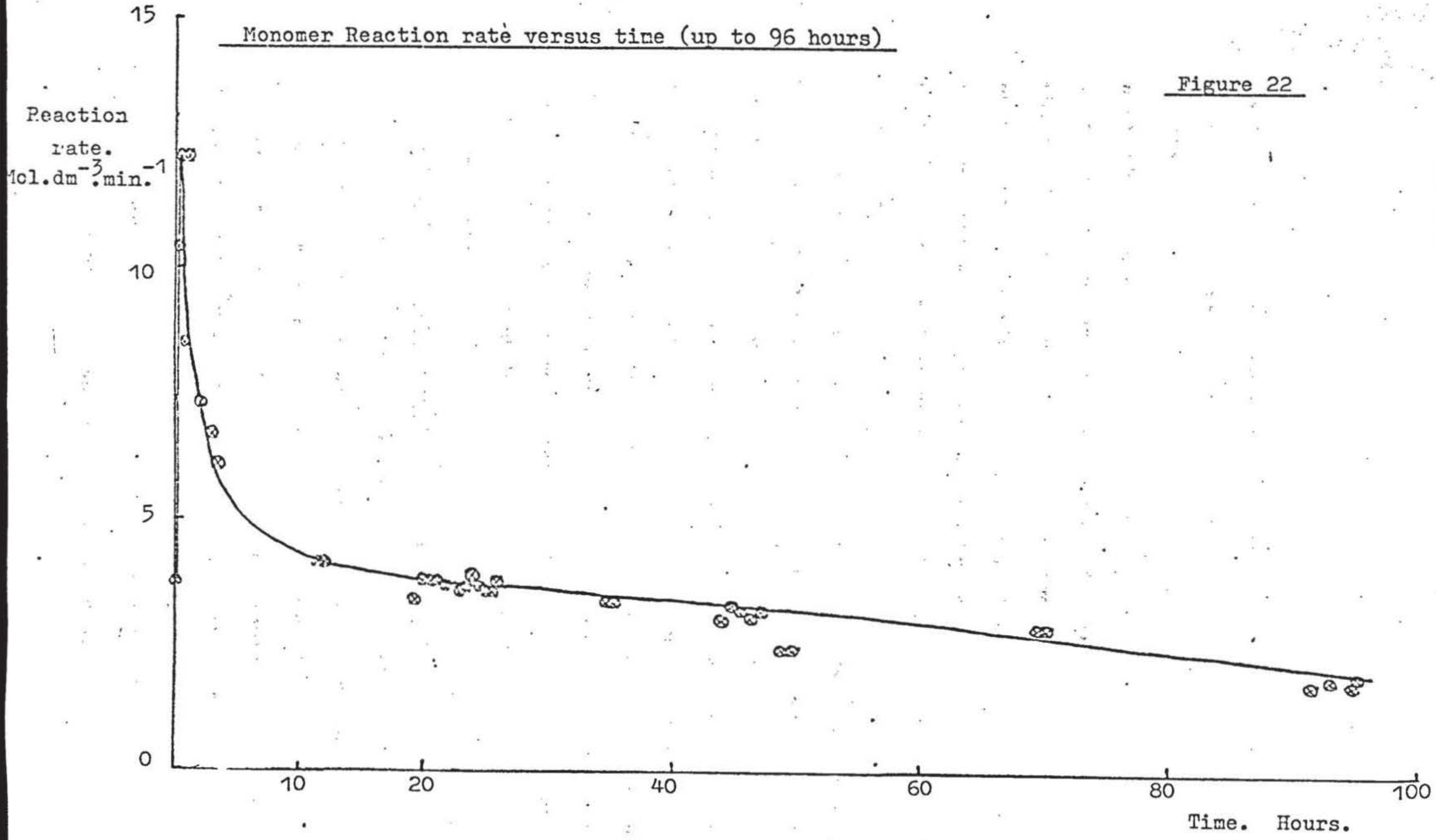
The basic characteristics of the Zeigler polymerisation rate-time curve

Figure 21



Monomer Reaction rate versus time (up to 96 hours)

Figure 22



settling period is generally considered to arise from two main sources, firstly the system building up to a balanced condition, i.e. the induction time necessary to produce a steady state of active centres and secondly from the physical breaking up and aggregation effects, i.e. physical changes in catalyst particle size and the formation of polymer on the catalyst surfaces. In general, it is found that steady rate conditions can apparently only be achieved when the mixture contains a uniform dispersion of catalyst particles coated with polymer.

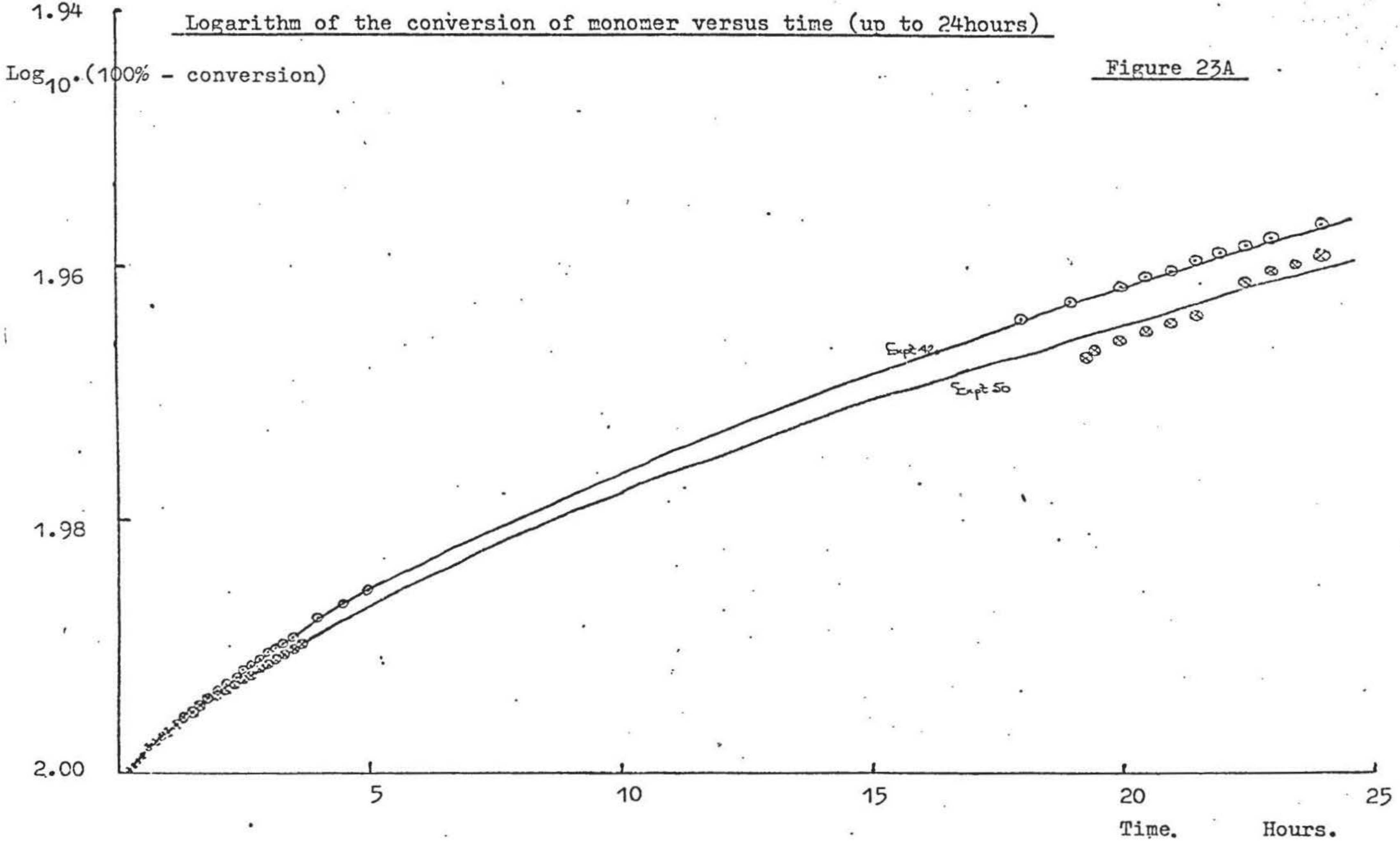
The reaction rate was determined for individual experiments from the nearly linear portion of the conversion time curve as indicated by the broken line in Figure 20. When the experimental data for the conversion to polymer is presented on a logarithmic plot as in Figure 23, a linear dependence is found in the region > 200 min < 750 min and a proportionality between the rate and monomer concentration is indicated. The reaction rate k^1 used in certain of the following graphs, is the constant found during this linear portion of the reaction curve.

3.2. - The Effect of Aluminium Alkyls upon the Rate of Reaction

The effect of various concentrations of aluminium alkyl upon the reaction rate was the first parameter of the polymerisation system to be investigated. Several experiments were carried out using two aluminium alkyls, aluminium triethyl (T.E.A; 1.2×10^{-5}M - 1.6 M) and aluminium tri-n-octyl (T.N.O.A; 3.1×10^{-4}M - 7.0×10^{-1}M). These results were obtained for a titanium III chloride concentration of 0.014 M and styrene concentration of 6.2 M at 50°C over 24 hours.

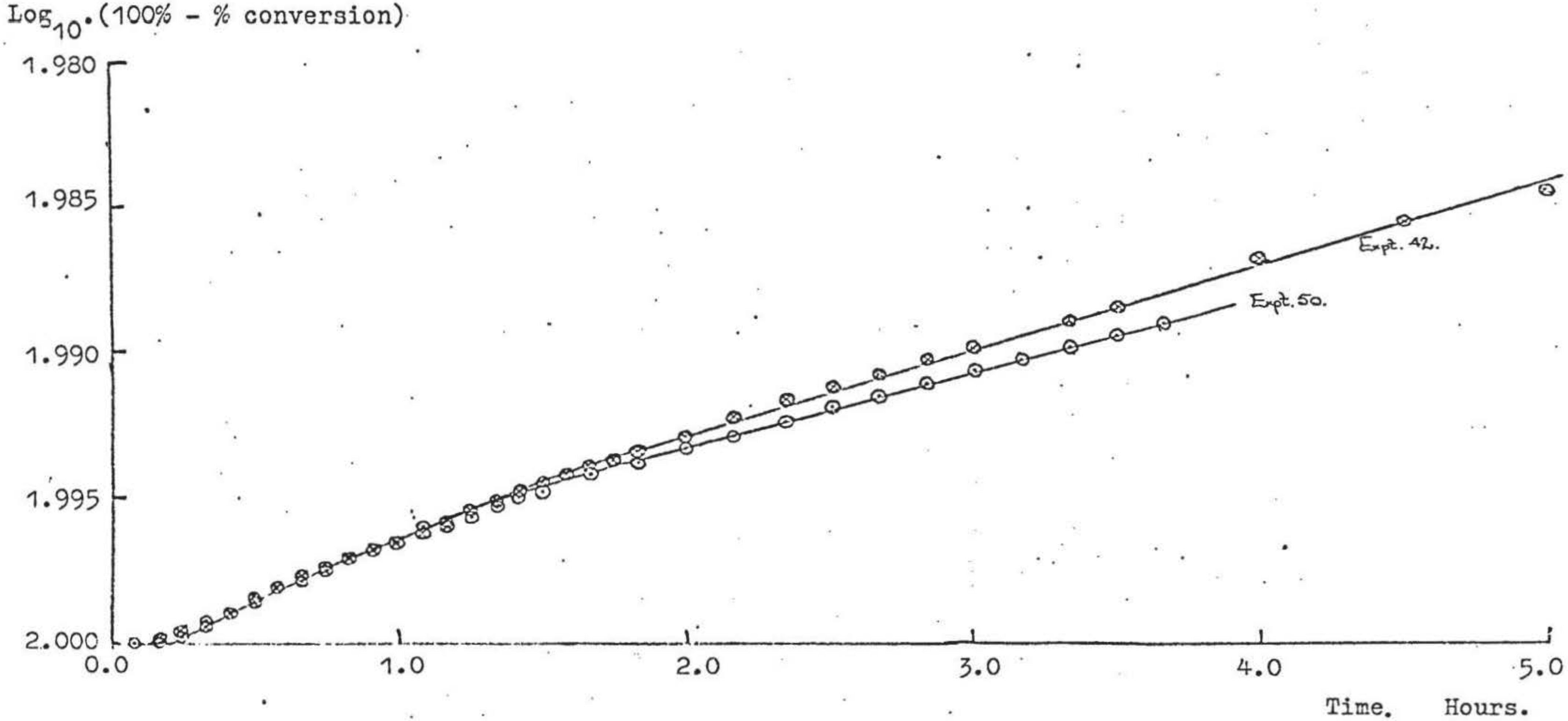
Logarithm of the conversion of monomer versus time (up to 24hours)

Figure 23A



Logarithm of the conversion of monomer versus time (up to 5hours)

Figure 23B



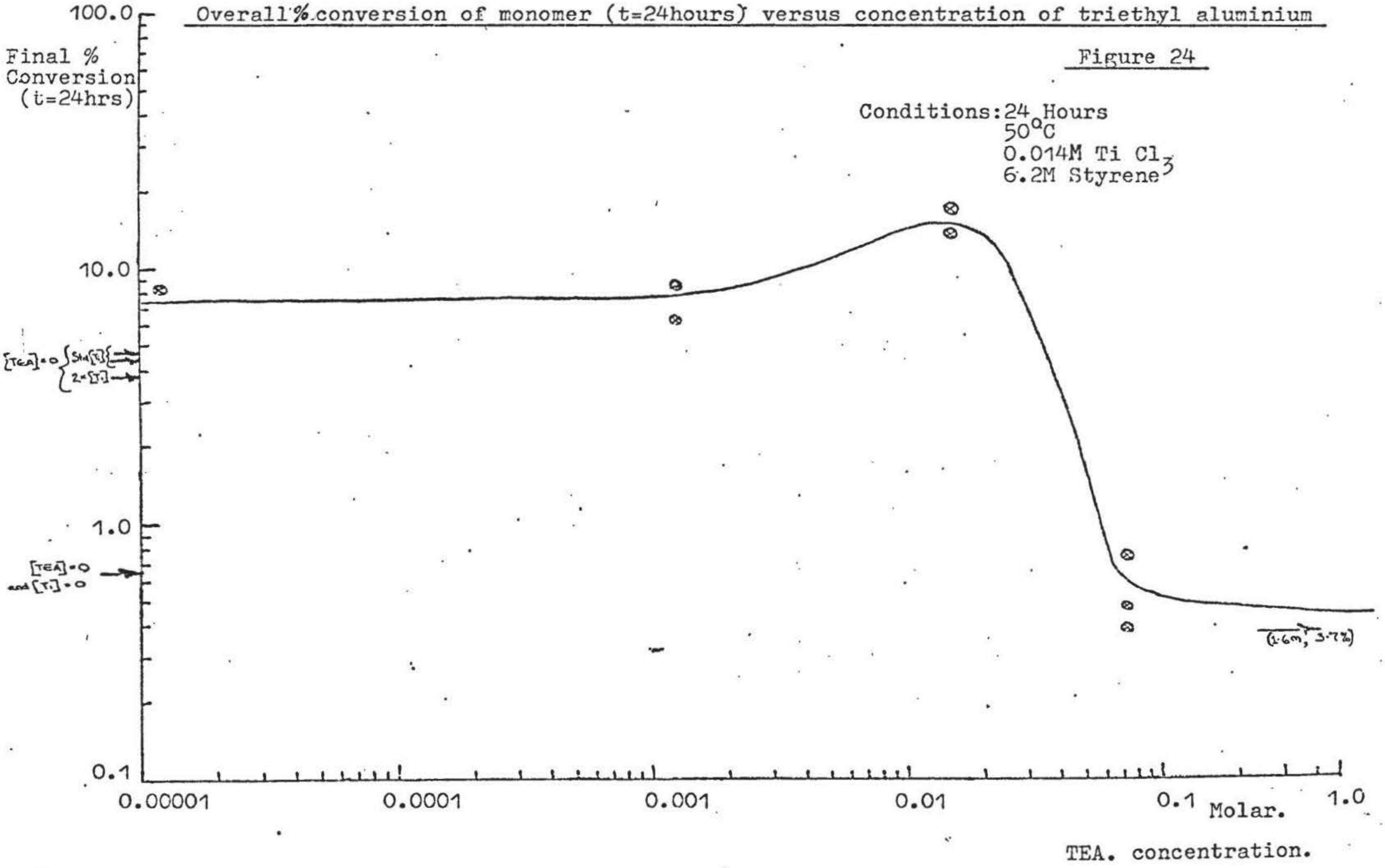
The initial experiments used aluminium triethyl as cocatalyst and it was found that at 50°C for ratios of Al/Ti $>$ 1.5 a marked depression in the overall average rate (expressed as Total Conversion to Polymer after 24 Hours) was observed as shown in Figure 24. In order to establish that the depression of the reaction rate was not the result of further reduction of the titanium III chloride by the excess T.E.A. present, a duplicate series of experiments were conducted using the less powerful reducing agent aluminium tri-n-octyl as cocatalyst. The earlier work of Howard etal (48) applying this catalyst system to ethylene polymerisation, showed the use of longer chain alkyls was preferred to T.E.A. in that case as a more stable system was established giving less rapid decay which resulted in higher overall average rates being produced.

The results obtained for styrene polymerisations using T.N.O.A. followed a pattern similar to those obtained for the T.E.A., as shown in Figure 25 and Figure 26. However, the graph obtained for the T.N.O.A. experiments shows a more consistent behaviour in the plateau region which appears to be more level than for the T.E.A. case. Thus, subsequent experiments involving variations in the other reactants used a 0.0077 M T.N.O.A. concentration as the standard co-catalyst component.

The similarity between the results obtained using the two alkyls, T.E.A. and T.N.O.A. (compare Figures 24 and 25) suggested that an alternative mechanism to that originally considered i.e. over reduction of the titanium, was operative as the reduction

Overall % conversion of monomer (t=24hours) versus concentration of triethyl aluminium

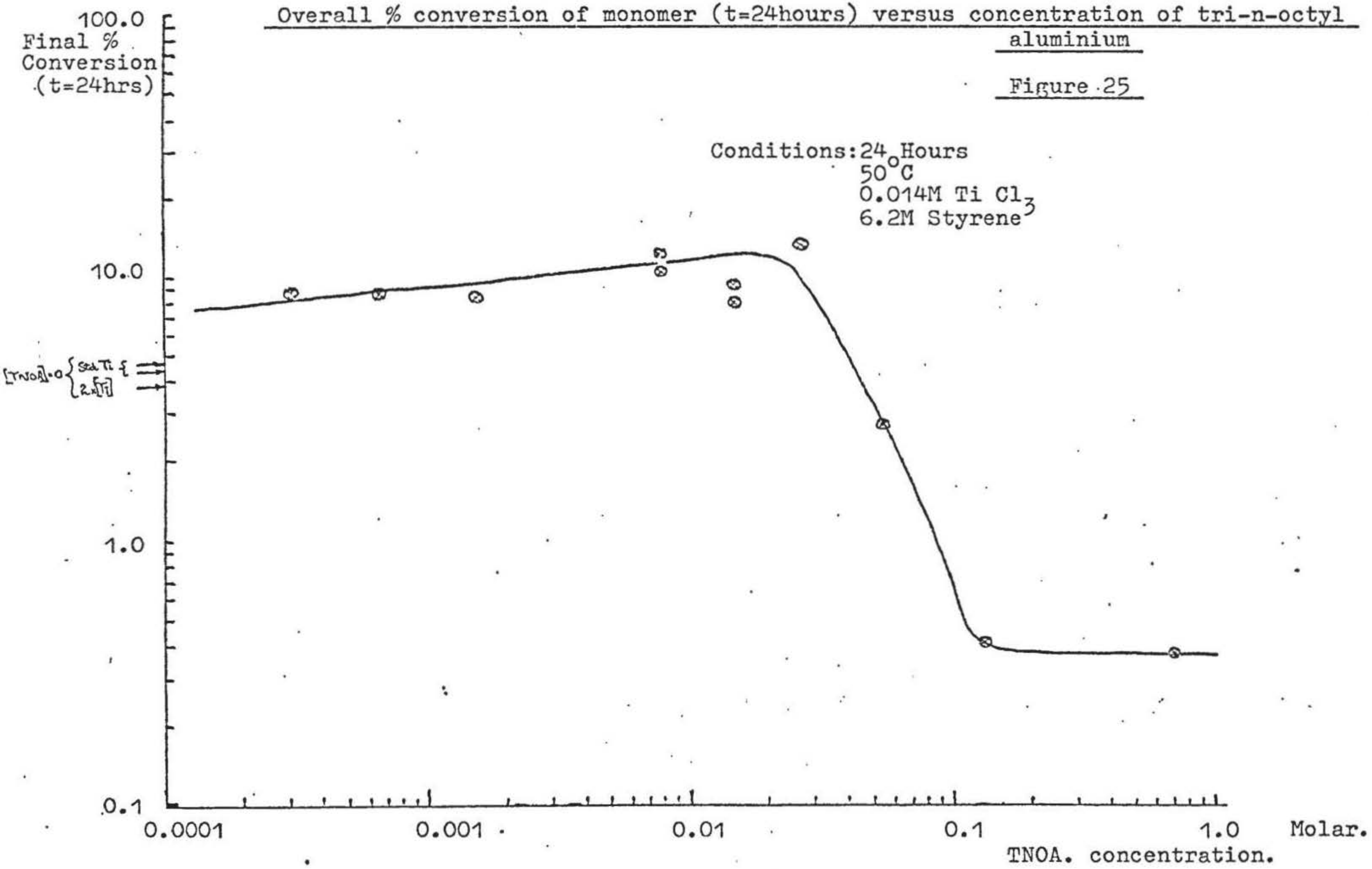
Figure 24



Conditions: 24 Hours
50°C
0.014M Ti Cl_3
6.2M Styrene

Overall % conversion of monomer (t=24hours) versus concentration of tri-n-octyl aluminium

Figure 25



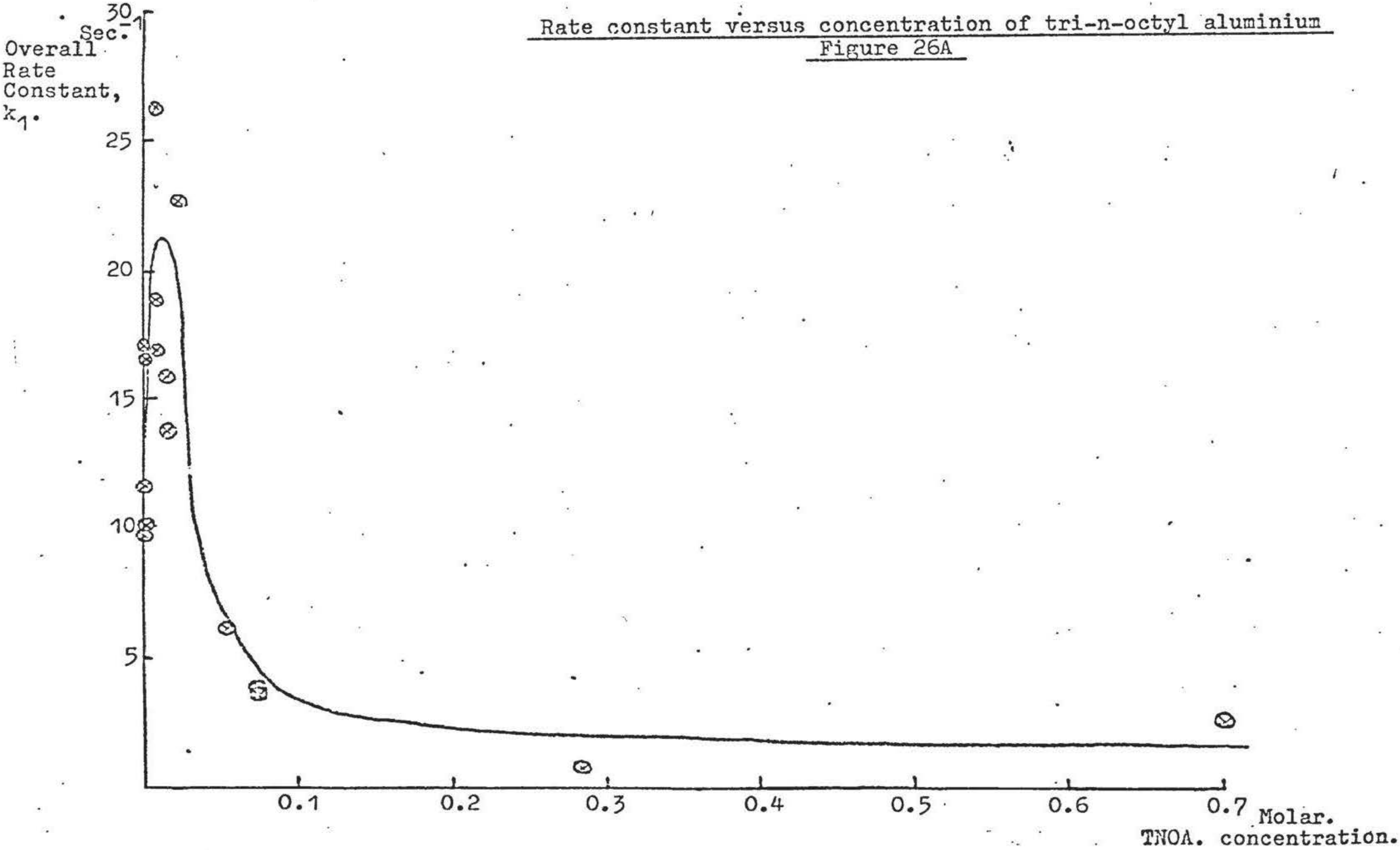
capability of two alkyls would be expected to be different. An alternative proposal for the loss of activity at high alkyl concentrations was that either a termination/transfer mechanism involving the alkyl or competitive absorption between monomer and alkyl was accounting for the depressed rate.

In the case of both alkyls the marked depression in rate occurs in the region Al / Ti = 1 to 2 which suggests that the same mechanism is operating with both alkyls. However, it is difficult to attach any significance to the observation that depressed rates occur for Al/Ti 1 since the alkyl is considered to perform several roles in the catalyst system. The catalytic activity of this system indicates that only a small percentage of the titanium present must function in the role of active sites.

As outlined in Chapter 1, at a 1 : 1 ratio, there should be a more than adequate sufficiency of alkyl to alkylate those titanium atoms which will form the active species. Hence at Al/Ti ratios of 1 : 1 and greater there is a sufficient excess alkyl present in the system for side reactions to occur. There are two mechanisms which may operate, firstly it may be a reaction of the transfer or termination type involving the alkyl species outlined in Chapter 1. Secondly, if both the alkyl and monomer can be adsorbed on to the catalyst surface, a competitive adsorption equilibrium will be set up partitioning the surface available between the monomer and lkyl species present. This will

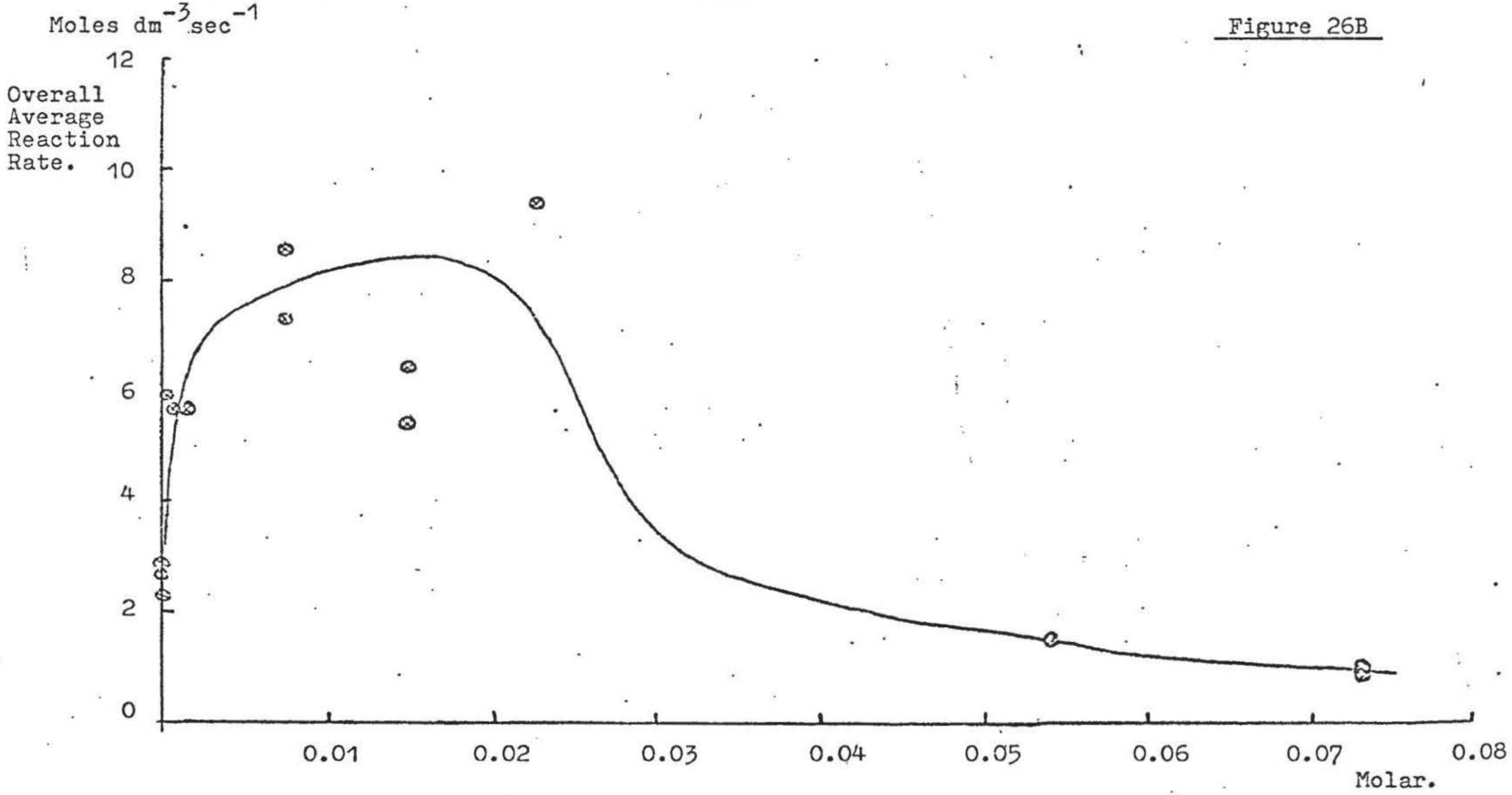
Rate constant versus concentration of tri-n-octyl aluminium

Figure 26A

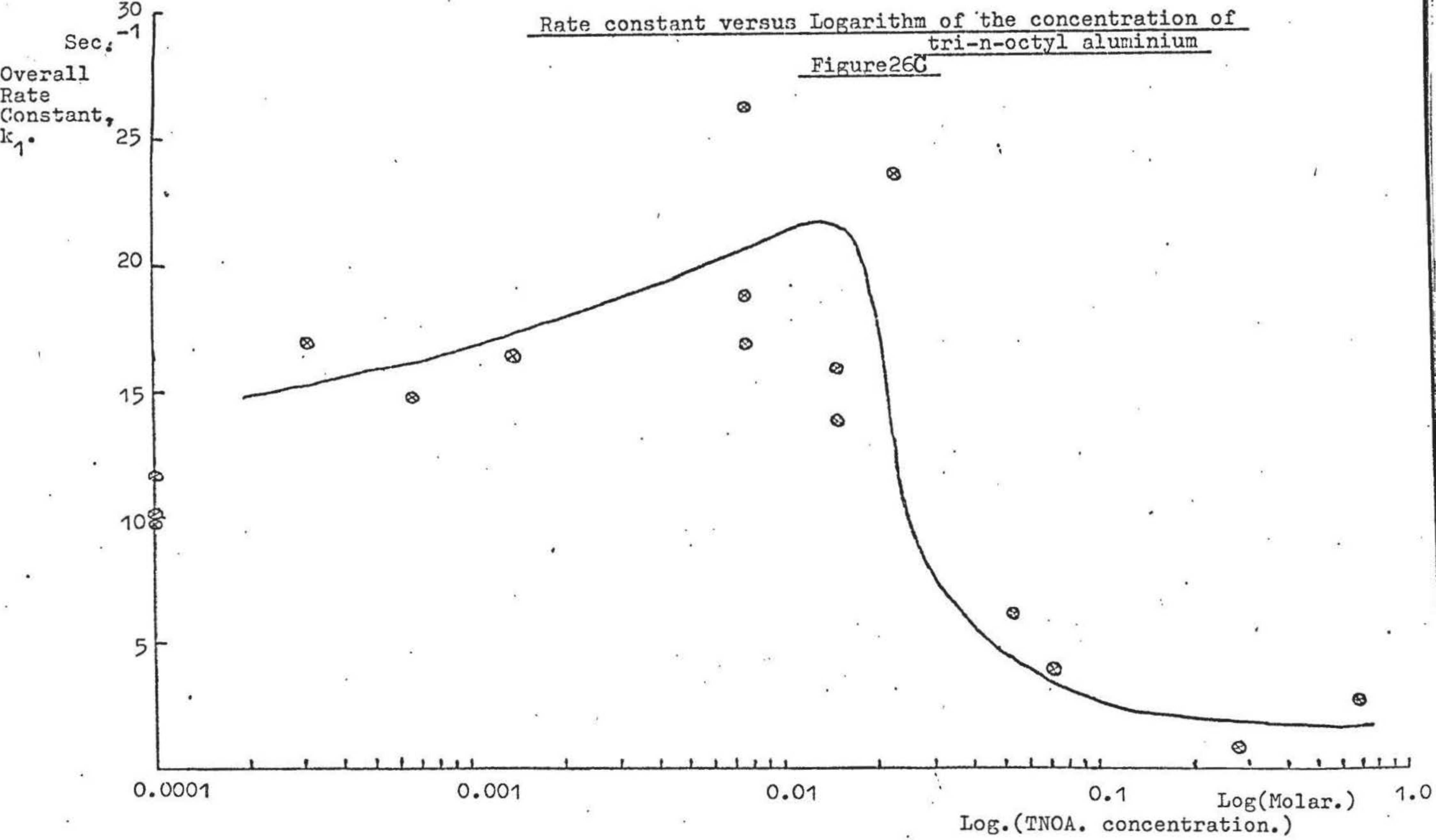


Reaction rate versus concentration of tri-n-octyl aluminium

Figure 26B

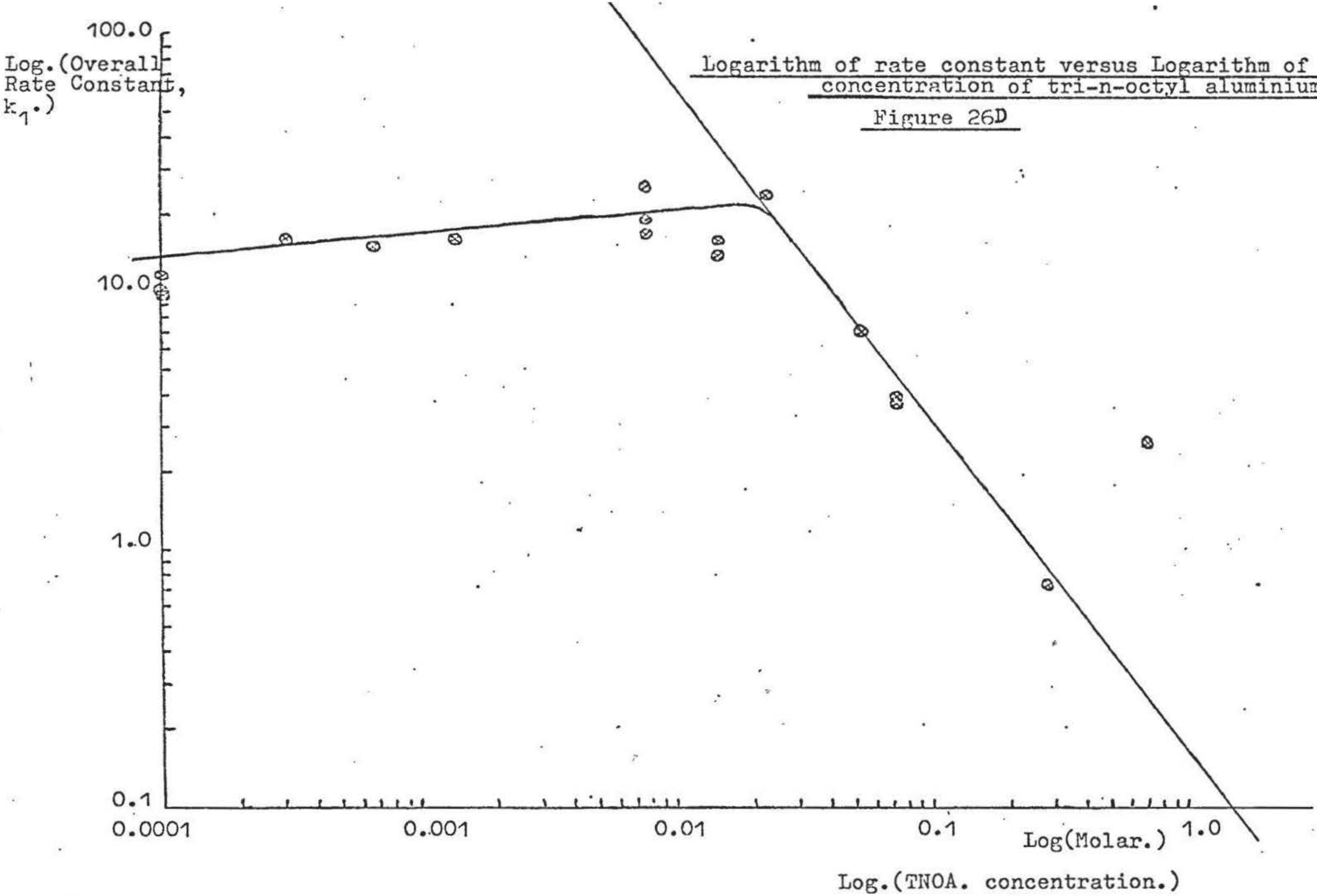


TNOA. concentration.



Rate constant versus Logarithm of the concentration of tri-n-octyl aluminium

Figure26C



Logarithm of rate constant versus Logarithm of the concentration of tri-n-octyl aluminium

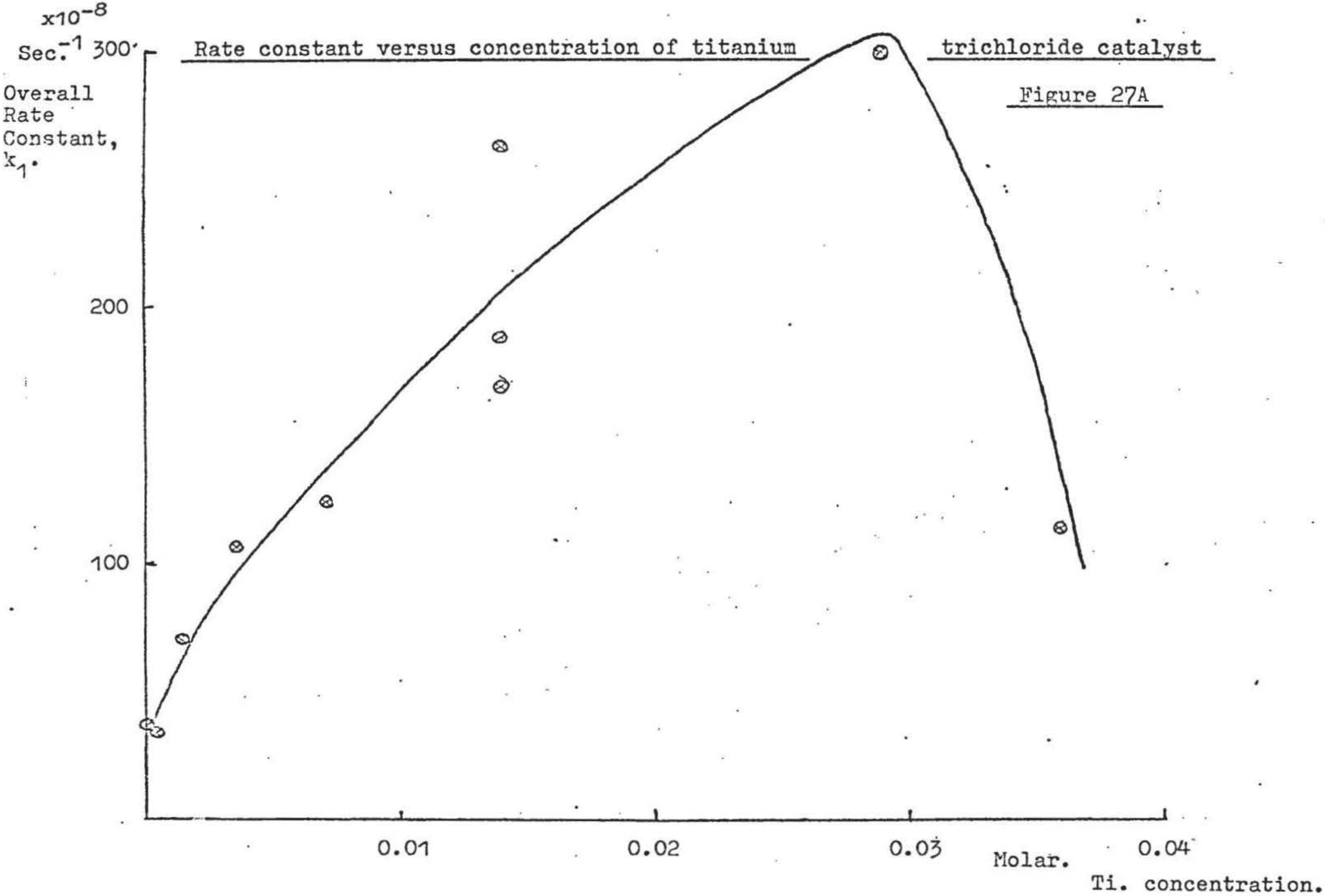
Figure 26D

result in depressed rates if the reaction proceeds through a mechanism involving absorbed monomer as has been cited previously by various authors (92, 93).

The logarithmic plot of the T.N.O.A. results (Figure 26D) reveals there is no dependence between Log Rate constant and Log (Alkyl) for alkyl concentrations less than 0.05 M. The results obtained for (Alkyl) $>$ 0.05 M appear to lie on a straight line (gradient = (-1.3)). The graph confirms that the rate constant decreases for increasing alkyl concentrations above 0.05 M with an empirical proportionality of rate constant $\propto 1/(Al)^{-1.3}$. This relationship does not, however, give any further indication as to the mechanism involved in the deactivation processes.

3.3. - The Effect of Titanium III Chloride Concentration Upon the Rate of Reaction

The second parameter to be investigated was the effect of a variation in the concentration of the titanium III chloride catalyst component upon the reaction rate. Figure 27A shows the results obtained for these experiments. The curve resulting from this linear scale plot, may be represented as a straight line when the data is replotted logarithmically as in Figure 27B. This latter plot showed a linear dependency over the concentration range 3.6×10^{-4} M to 2.9×10^{-2} M and the gradient for this line was indicating an approximate proportionality between the rate of reaction and $\sqrt{(Ti)}$. When the experimental data was used to produce a plot of the average rate of monomer consumption per hour versus (Titanium) (Figure 28A), a similar curve was obtained. The logarithmic plot of these results

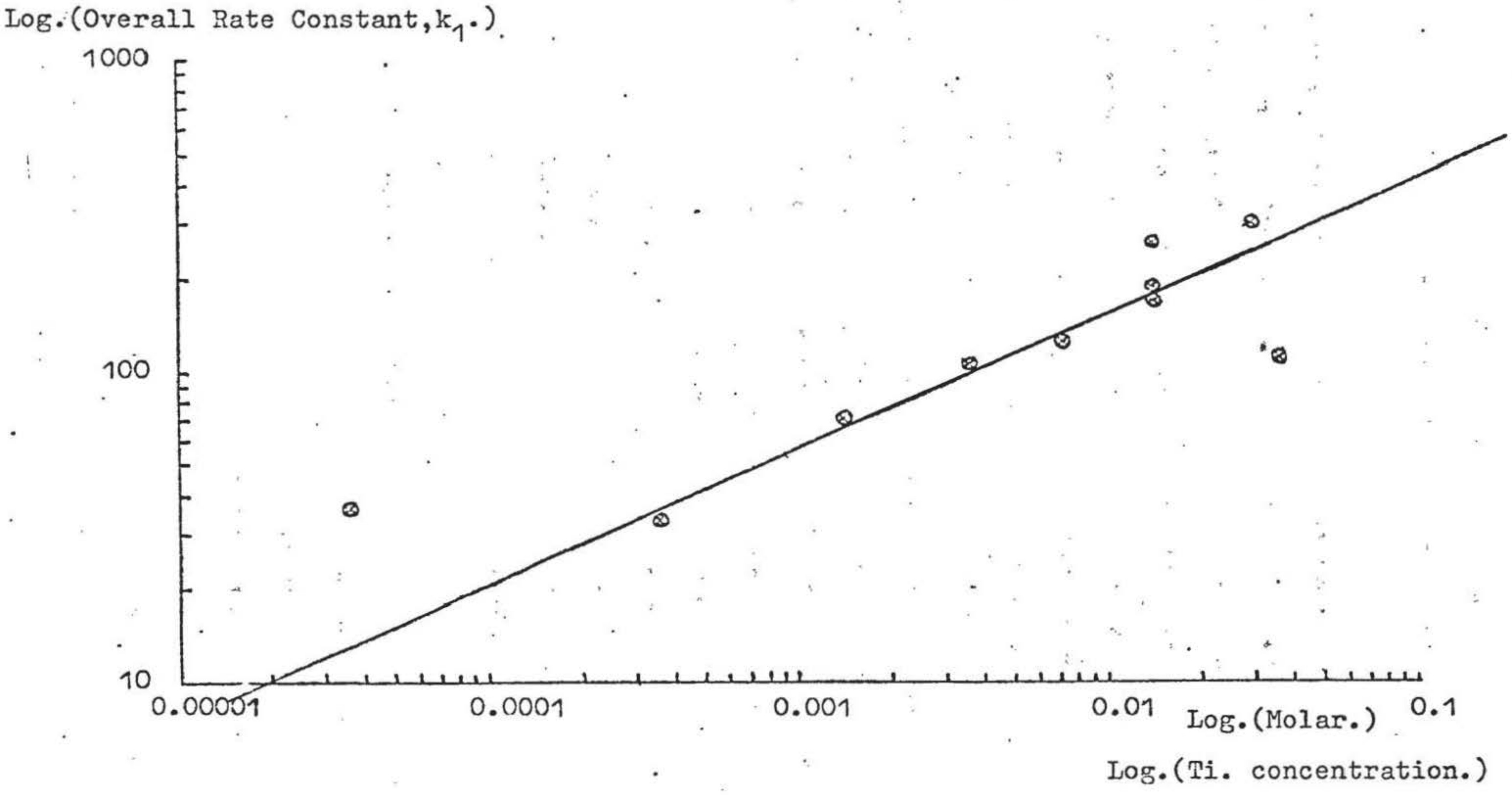


Rate constant versus concentration of titanium trichloride catalyst

Figure 27A

Logarithm of rate constant versus Logarithm of the concentration of titanium trichloride catalyst

Figure 27B

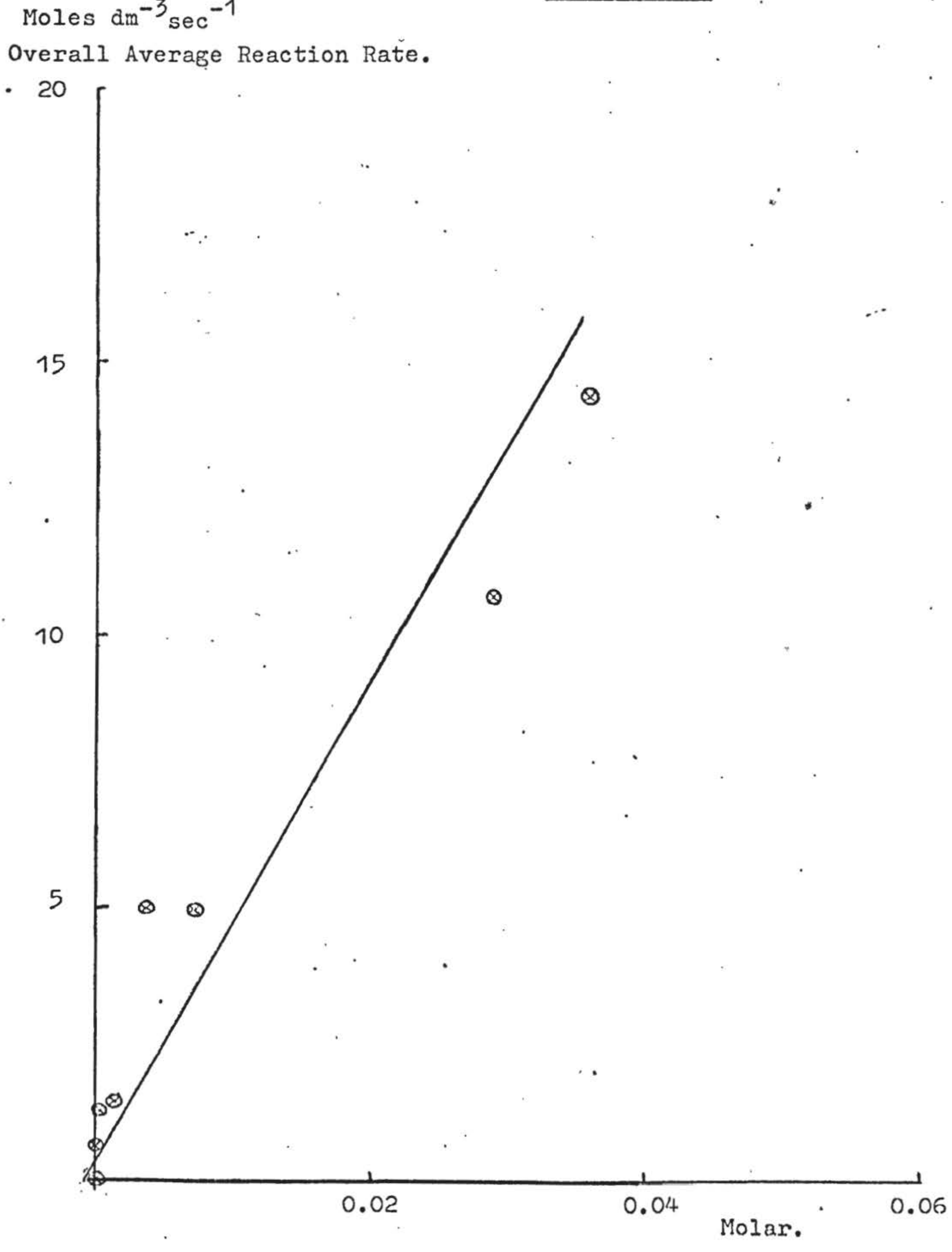


(Figure 28B) also showed the linear dependency with an approximate proportionality between reaction rate and $\sqrt{(Ti)^2}$, the least square straight line gradient = 0.47 ± 0.03 .

These observations are contrary to those normally found in heterogeneous Ziegler catalyst systems. The normal proportionality found is to $(Ti)^1$ which can be explained using the concept that the active catalyst sites are generated around certain titanium atoms and that a steady state concentration of these species is generated. However, this situation does not hold for all Ziegler systems without exception and modified behaviour has been found in certain homogeneous systems. In the Ziegler systems described by Henrici-Olive and Henrici-Olive (94) in which ethylene has been polymerised using a variety of homogeneous catalyst complexes generated from bis (cyclopentodienyl) titanium dichloride and an alkylaluminium chloride in toluene, a rapidly decaying type of rate curve has also been observed. This behaviour had been previously reported with a similar bis(cyclopentadienyl) titanium dichloride/ dimethyl aluminium chloride system for ethylene polymerisation in toluene some eight years earlier by Chien (95). The kinetic measurements reported in both instances suggest that the decay can be ascribed to a chain termination reaction which at a fixed temperature and monomer concentration, is dependent mainly upon the catalyst concentration. In the systems cited above, second order kinetics are found and the results indicate that a bimolecular mutual deactivation of the growing chains occurs for these particular cases.

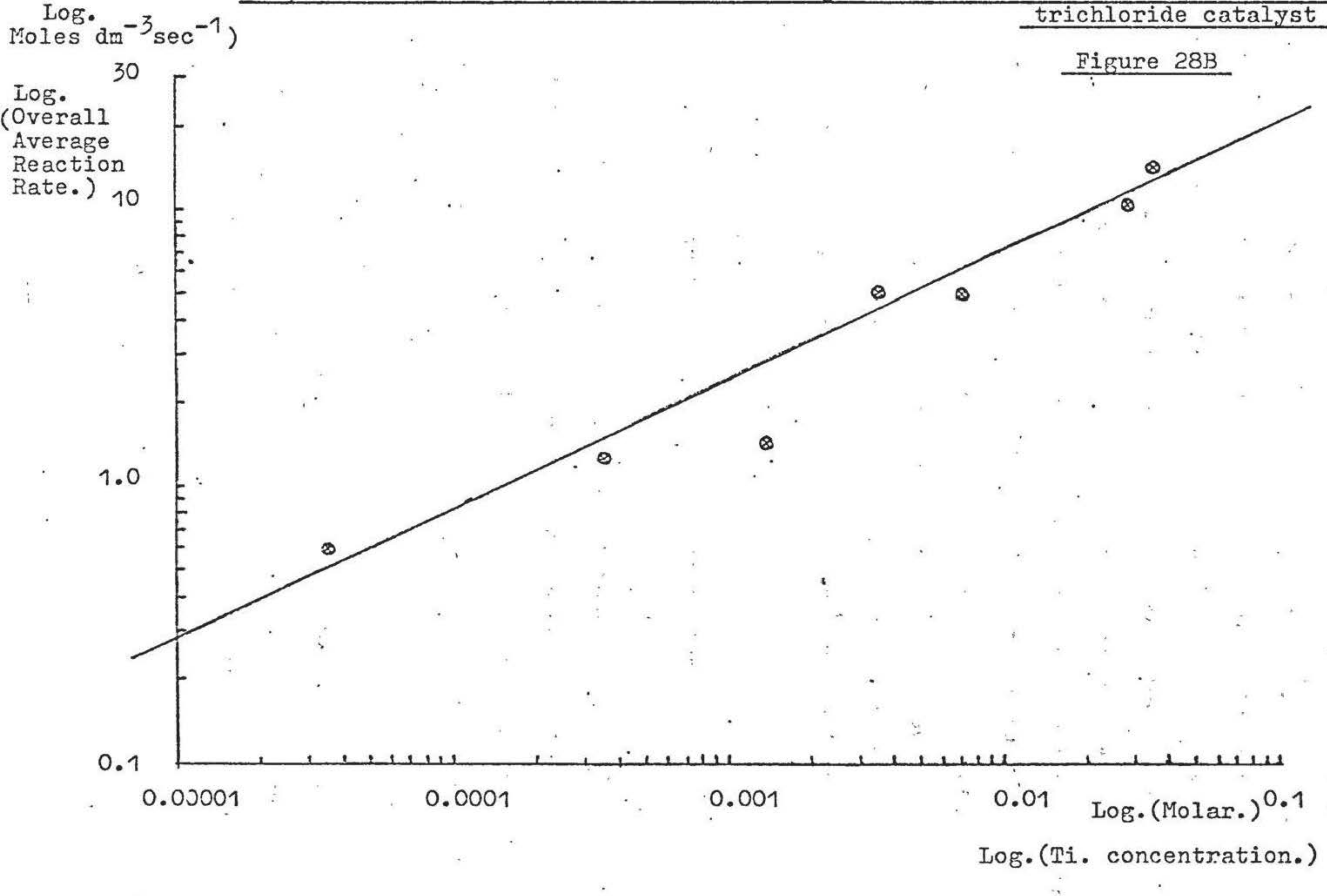
Rate of reaction versus the concentration of titanium trichloride catalyst

Figure 28A



Logarithm of the reaction rate versus Logarithm of the concentration of titanium trichloride catalyst

Figure 28B



The square root dependence of the reaction rate upon the titanium III chloride catalyst component, empirically determined for the magnesium reduced system in the present work, is difficult to explain by a simple chemical mechanism. This result suggests that a complex mechanism or combination of mechanisms which involve the titanium component must be operative. The magnesium reduced catalyst is thought to have a structure involving considerably more diorder than conventional heterogeneous catalysts and in this sense approaches more closely the homogeneous catalysts which do not possess a surface structure. The greater disorder found in the magnesium reduced system may allow a modification of the catalyst mechanism not usually found in the heterogeneous systems, to operate and cause this unusual knetic behaviour.

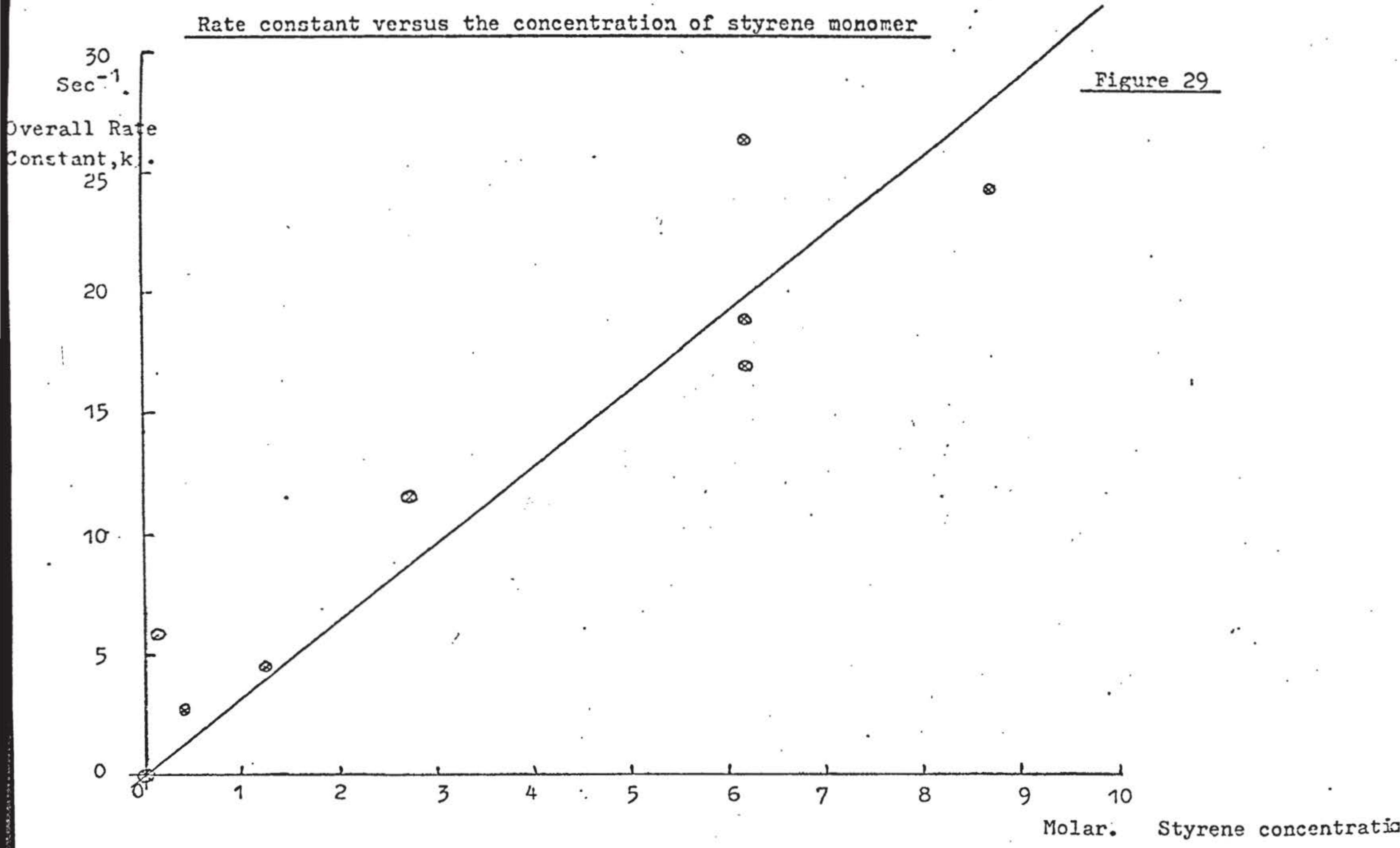
Ballard has found an interesting situation of a similar type in his work concerning the use of tribromozirconium hydride, derived from tribromozirconium alkyl, as a soluble transition catalyst for ethylene polymerisation in a toluene medium(102) He, proposes that the rapid decline in rate in his case is due to a dimerisation of the parent catalyst material Br_2ZrH or of the propagating centres giving species of significantly lower activity. By modificafion of the zirconium system with SiO_2 to produce heterogeneous catalysts analogous to their Ziegler counter parts, a much higher activity and longer life time has been imparted to these catalysts which suggests that these characteristics are at least in part due to the fact that in a heterogeneous system where active centres are bonded to a surface deactivation by reaction with each other, is relatively improbable. As the magnesium reduced catalyst has been shown by X ray diffsaction (48) to have a considerably greater degree of disorder than conventional crystalline titanium III chloride catalysts, it seems more likely that deactivation processes of the type outlined may also occur in this system i.e. due to Ti atoms being relatively mobile. The presence of aluminium alkyl also has a stabilising effect upon transition metal centres preventing deactivation by metal-metal interaction in the case of homogeneous Ziegler catalysts(94). In this system, the limiting effect upon the rate of an excessive concentration of aluminium alkyl as postulated earlier (probably due to competitive adsorption instead of monomer) does not preclude its acting in a preventative role.

3.4. - The Effect of Styrene Monomer Concentration upon the Rate of Reaction

A series of experiments was carried out to investigate the relationship between the reaction rate and monomer concentration (1.2×10^{-2} M - 8.7 M). The results obtained in these experiments are depicted by the linear plot shown in Figure 29. This indicates an approximate proportionality between the monomer concentration and reaction rate. The logarithmic plot of the results, Figure 30, confirms this approximation producing a straight line whose gradient is 0.75 ± 0.15.
A linear dependence of the rate on monomer concentration is generally found in Ziegler systems and this system appears to conform in this respect. A direct proportionality between reaction rate and styrene concentration was also found by Burnett and Tait for their α-$TiCl_3$ - $AlEt_3$ - styrene system (87).

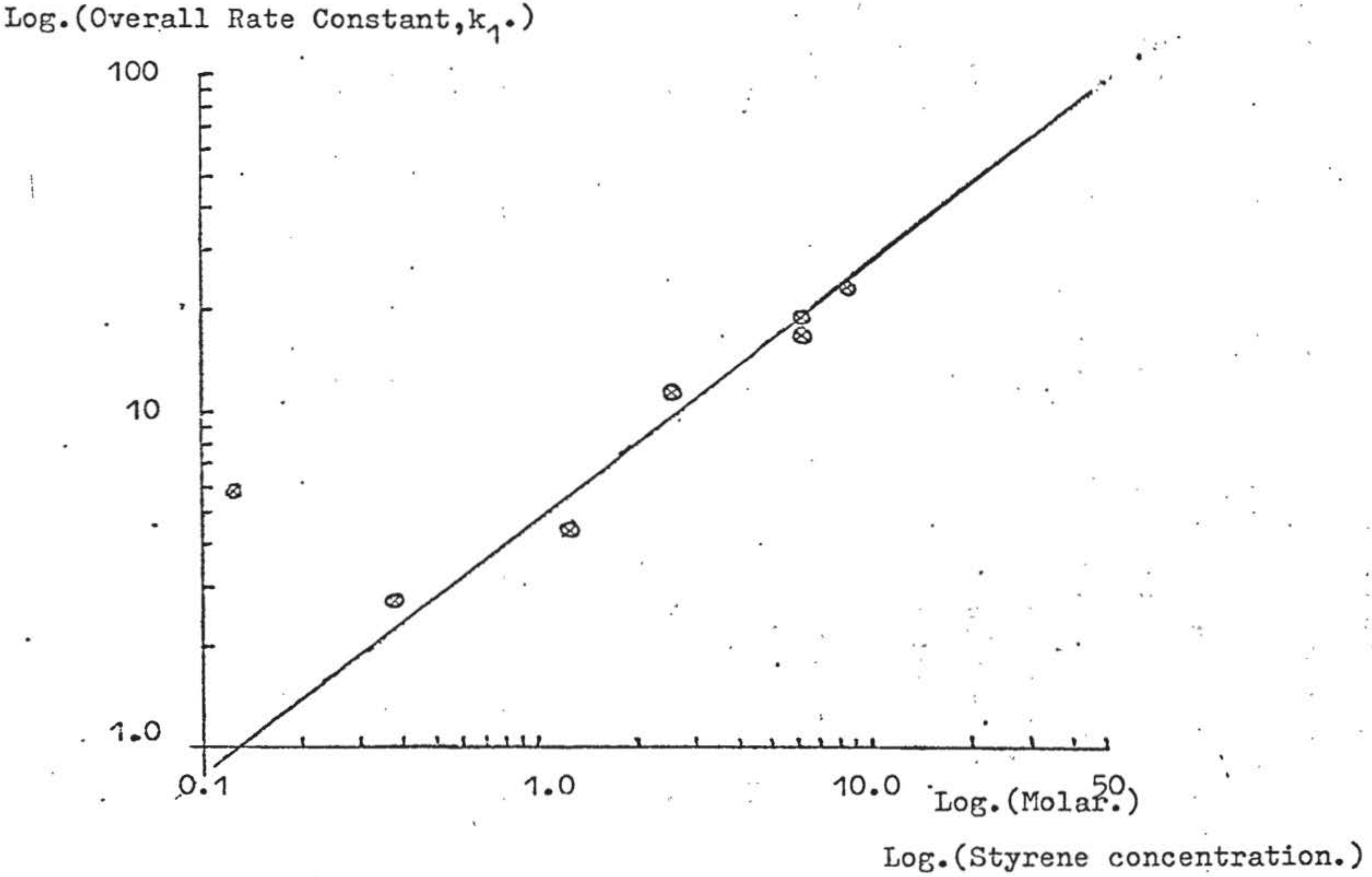
Rate constant versus the concentration of styrene monomer

Figure 29



Logarithm of rate constant versus Logarithm of the concentration of styrene monomer

Figure 30



3.5. - The Effect of Temperature Upon the Rate of Reaction

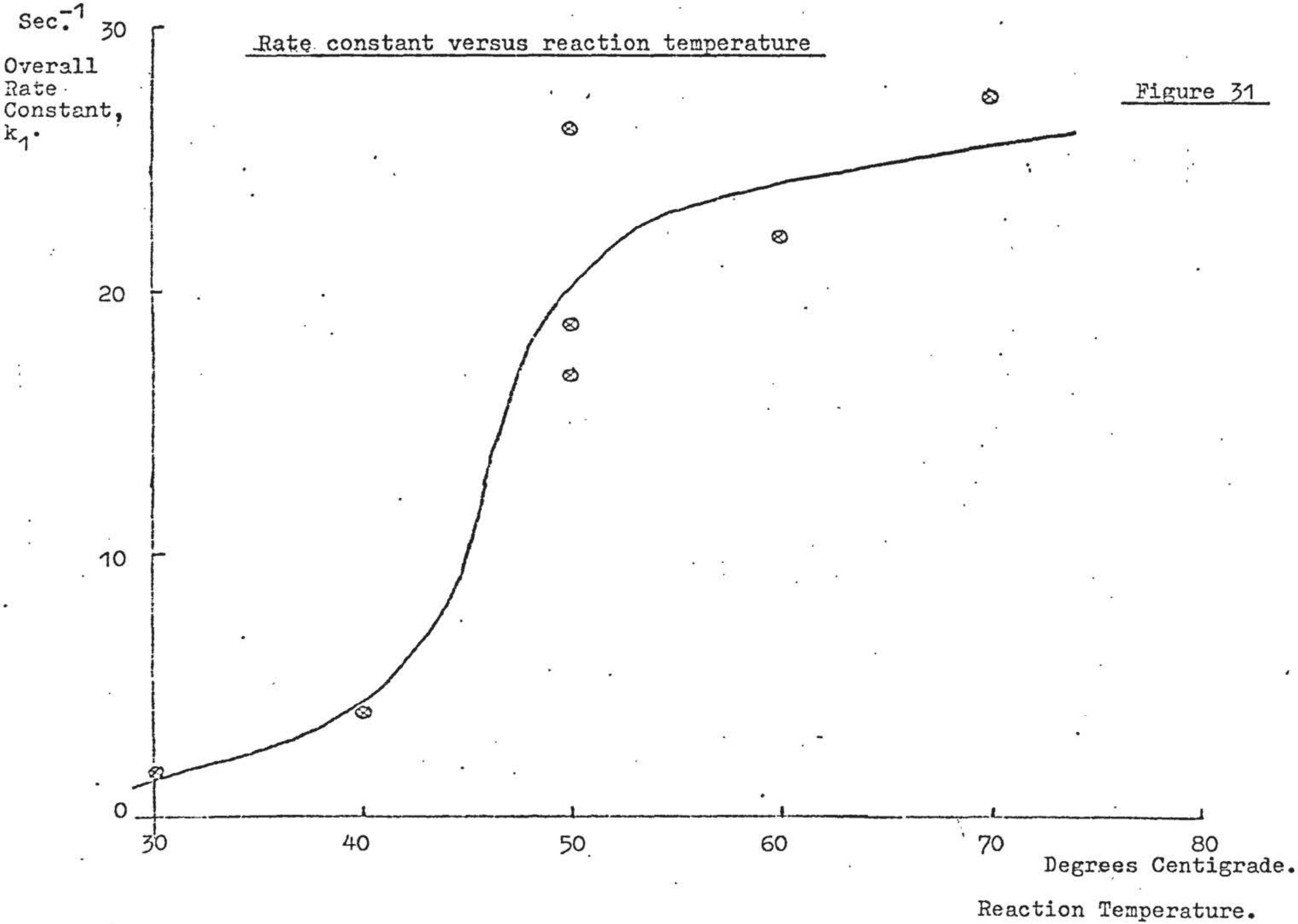
The variation observed in the reaction rate with temperature is shown in Figure 31 in which the reaction rate constant, k_1, is plotted versus temperature, T, directly on linear scales. Figure 32 shows an Arrherius plot of the data, Log $_{10}$ (Rate constant) versus 1/T for the experiments over a temperature range 30°C - 70°C. A least square analysis of the complete experimental data from this plot yields a value of 64 ± 30 kJ (15 ± 7 Kcals) for the overall activation energy, E, and the pre-exponential factor, A, $= 2.95 \times 10^4$ sec $^{-1}$ (Log A_{10} = 4.5). However, the results appear to consist of two distinct linear parts, as has been previously found for many Ziegler systems. The two parts depicted by the broken lines in Figure 32 give the following values:-

30°C - 50°C, Act. Energy, E = 100 ± 30 kJ (25 ± 7 Kcals)
(Log A = 11.3)
50°C - 70°C, Act. Energy, E = 20 ± 9 kJ (5 ± 2 Kcals)
(Log A = -2.6)

The decline in the rate of increase in the rate constant with respect to temperature above 50°C suggests that a reduction of the catalyst system may be taking place at the higher temperatures causing the catalyst system to become less active. A similar observation has previously been made at temperatures $>$50°C for the magnesium reduced catalyst activated by triethyl aluminium when used for ethylene polymerisation 49, 49A, and is typical of several Ziegler systems (97, 98).

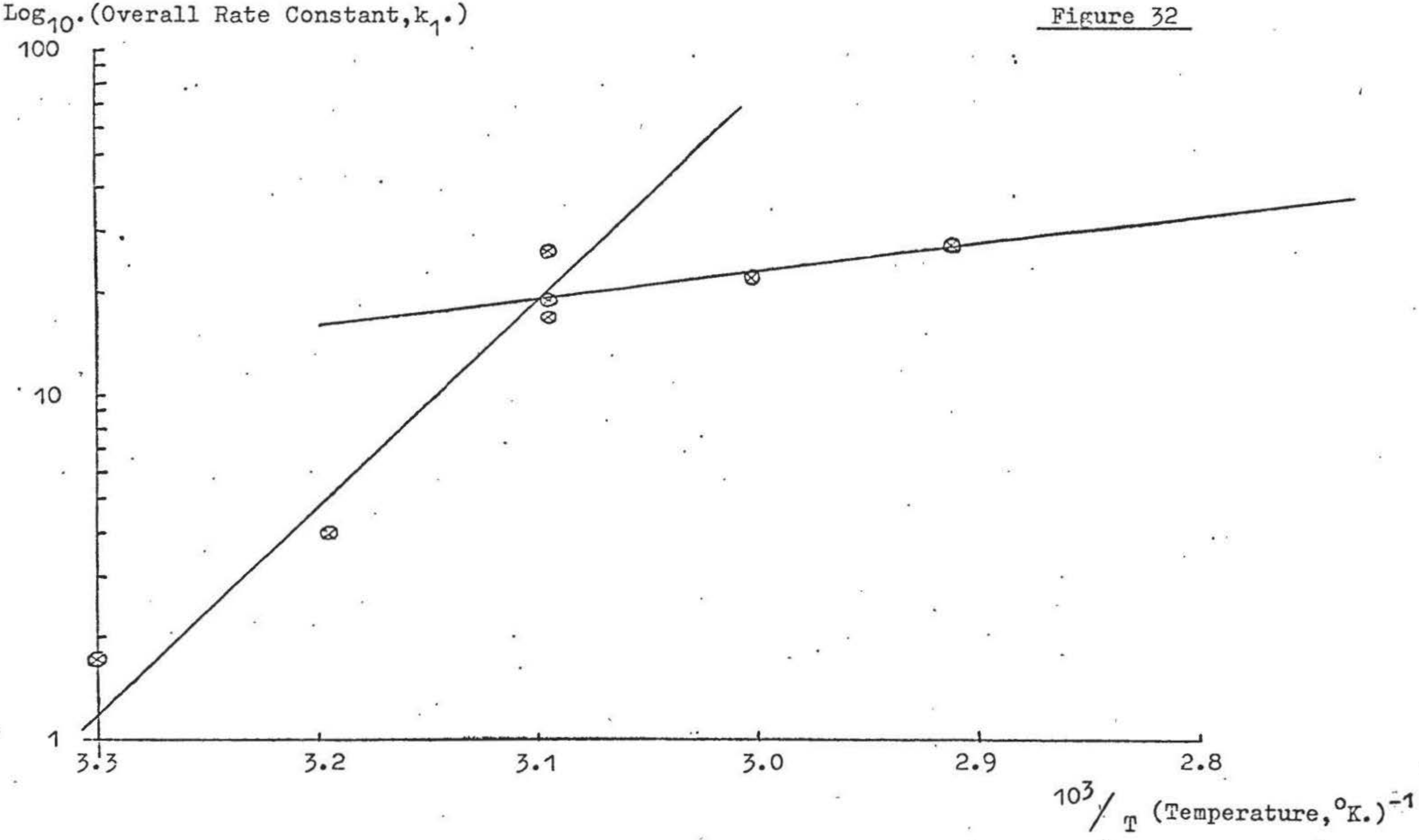
Rate constant versus reaction temperature

Figure 31



Arrhenius plot—Logarithm of rate constant versus reciprocal of temperature

Figure 32



SECTION 4 - THE MOLECULAR WEIGHT BEHAVIOUR OF THE POLYMERISATION

The previous section outlined the main kinetic features investigated for the polymerisation of styrene with this Ziegler system. This section discusses the influence of the reaction parameters, i.e. temperature, reagent concentrations, upon the molecular weight of the polymer product. The data from these results and those from the kinetic investigation, are used together to provide an estimate of the concentration of active catalytic sites and the lifetime of the growing polymer chain using a simple technique previously applied to the investigation of the activity of this catalyst towards ethylene(49, 49A).

4.1. - Molecular Weight Determinations

Early determinations of the molecular weight were made by estimation of the intrinsic viscosity. The limiting viscosity number was evaluated by using the standard dilution techniques with plots of $\frac{t - to}{C\,to}$ and $\log_e \frac{t/to}{C}$. No kinetic energy corrections were made in the calculation of the viscosity data as the efflux time of the solvent was long enough, (~ 100 sec) to make such corrections unnecessary for the viscosity numbers involved in this work. Likewise, it was considered unnecessary to correct for the effect of shear rate upon the limiting viscosity numbers as its determination involves extrapolation to zero concentration.

Calculation of Mv

The estimate of the number average molecular weight was obtained from the limiting viscosity number results by using this relationship.

This is a form of the general empiral relationship known as the Mark-Houwink equation,

$(\eta) = kM^{\alpha}$

where (η) = limiting viscosity number

k, α are constants for a given polymer, solvent and temperature.

M = Viscosity average molecular weight.

which superseded the earlier Staudinger relationship

$(\eta) = kM$

where k = constant of the polymer-solvent system.

The constants of the Mark-Houwink relationship quoted above were evaluated for the styrene/o-dichlorobenzene system by Krigbaum (89) and are shown below.

4.2. - Molecular Weight Determinations by Gel Permeation Chromatography

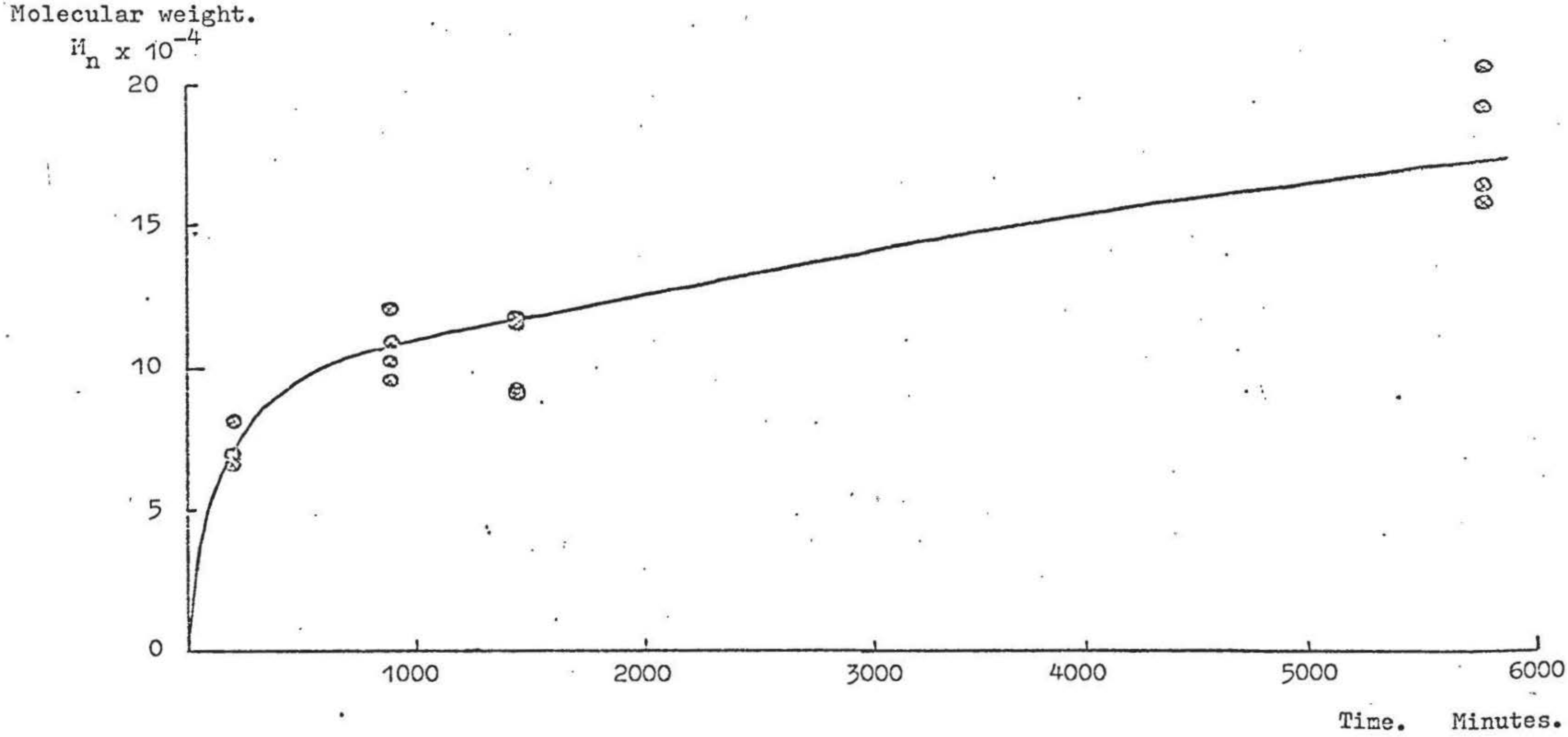
The determinations of molecular weight by gel permeation chromatography were carried out by Mr S W Hawley at RAPRA Shrewsbury, using apparatus which had been calibrated with polystyrene standards. Molecular weight calibration was made using the Mark-Houwink relationship $(\eta) = kM^{\alpha}$ where $k = 1.2 \times 10^{-4}$, $\alpha = 0.71$.

4.3. - The Effect of Polymerisation Time Upon the Number Average Molecular Weight, Mn and Weight Average Molecular Weight, Mw

The number average molecular weight, M_n and weight average molecular weight, M_w were determined for polymer samples prepared under similar experimental conditions after polymerisation times from three to ninety-six hours, and these

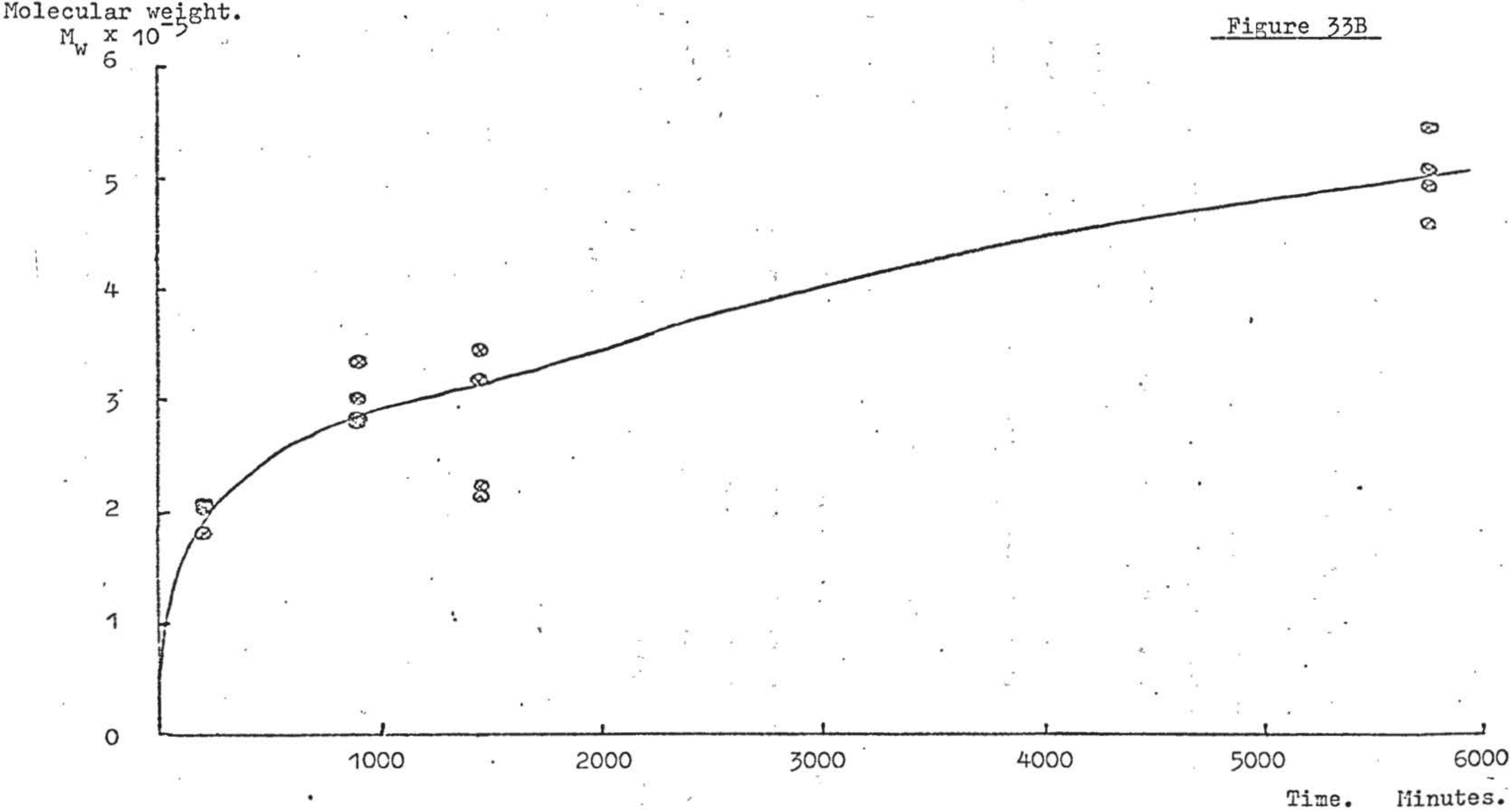
Number Average Molecular weight versus time.

Figure 33A



Weight Average Molecular weight versus time.

Figure 33B

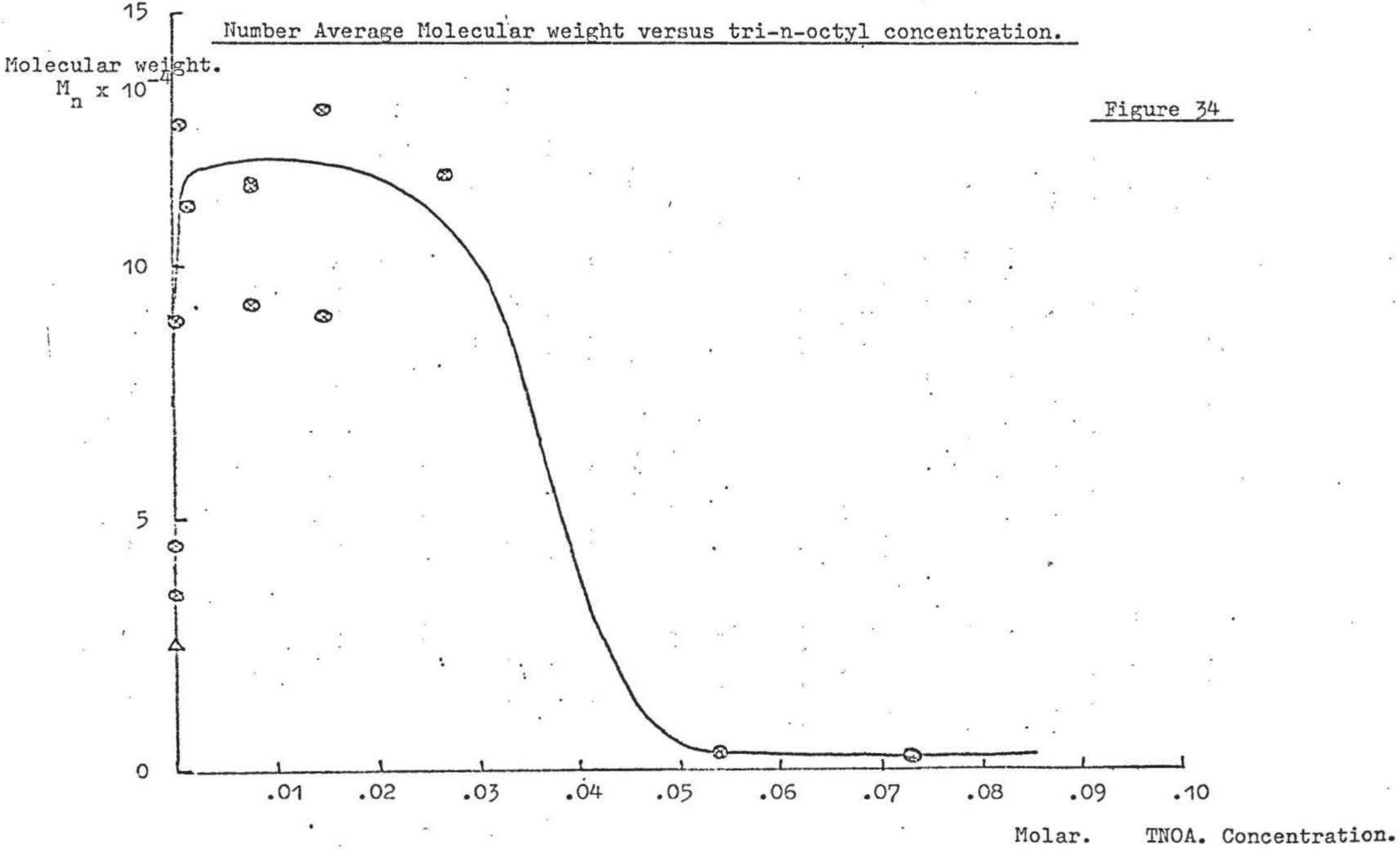


results are shown in Figure 33A and Figure 33B respectively. The plots indicate that the molecular weight increases with time throughout this period although the initial sharp increase slows down to a gradual increase after ~ 300 mins. Under the conditions studied the molecular weight does not appear to reach a limiting value as has been found with other similar Ziegler systems using ethylene (49, 49A, 98).

4.4. - The Effect of Aluminium Alkyls upon the Molecular Weight of the Polymer

The results obtained for experiments carried out at various TNOA concentrations between 3.1×10^{-4} M and 7×10^{-2} M are shown in Figure 34. In this system the number average molecular weight after 24 hours was found to rise for low concentrations of the alkyl up to approximately 1×10^{-3} M, then a plateau region occurs between 1×10^{-3} M and 5×10^{-2} M where values for M_n are approximately 1×10^{-5}. At a concentration of approximately 0.035 M (Al/Ti = 2.5) there is a significant fall in the molecular weight produced. Values of $M_n < 5 \times 10^3$ are found for the experiments at $>$0.05 M concentration (Al/Ti $>$ 4.0).

The decrease in molecular weight for high concentrations of alkyl is attributed to the effect of chain transfer with alkyl and occurs in the region where the depressed reaction rates were observed. If a chain transfer process involving adsorbed alkyl occurs in the system behaviour of this type might be expected as competitive adsorption between monomer and alkyl would be involved together with a lowering of molecular weight caused by chain transfer.



Number Average Molecular weight versus tri-n-octyl concentration.

Figure 34

4.5. - The Effect of the Titanium III Chloride Concentration Upon the Molecular Weights of the Polymer

Figure 35 shows the variation in molecular weight found in experiments using concentrations of titanium III chloride from 3.6×10^{-5} M to 3.6×10^{-2} M. At the lower concentrations the normal behaviour expected from a Ziegler system is found in that the molecular weight increases with increase in the titanium concentration. However, in this system it was found that at the higher concentrations used the graph forms a plateau region with fairly constant M_n values as the increase in molecular weight apparently tails off.

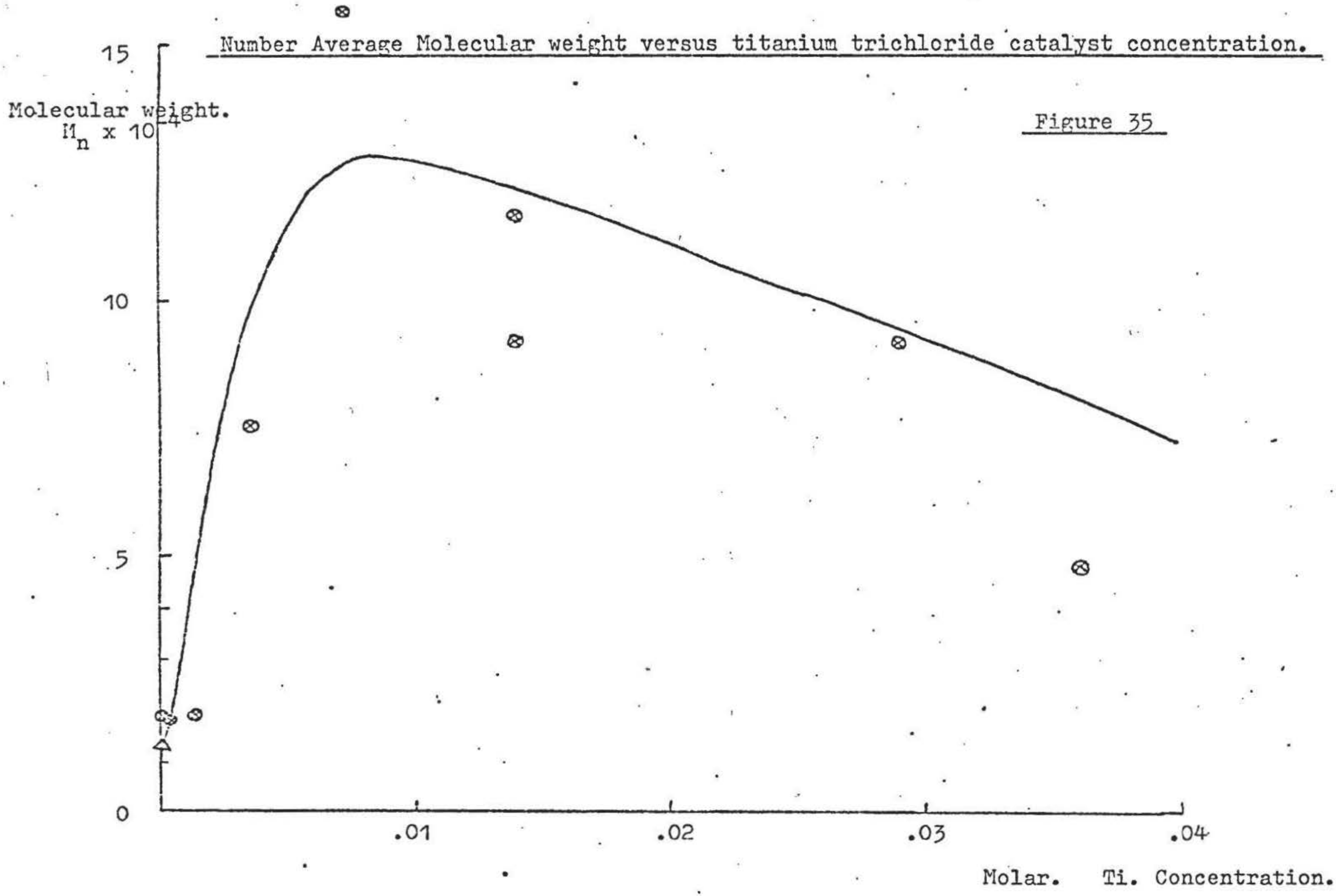
The unique behaviour observed earlier for the kinetic behaviour with relation to the titanium concentration may give some explanation of the latter observation. If a modification or deactivation reaction is occurring which involves the growing chain and the titanium active catalyst centres, it is likely that such a mechanism results in a transfer/termination of the polymer chains. Higher concentration of titanium species would make the possibility of this mechanism more likely and therefore as the rate of termination/transfer processes increases, the overall molecular weight will fall.

4.6. The Effect of the Styrene Monomer Concentration Upon the Molecular Weight of the Polymer

The variation of the molecular weight found in the experiments carried out using styrene monomer concentrations from 1.2×10^{-2} M to 8.7 M is shown in Figure 36. A plot of

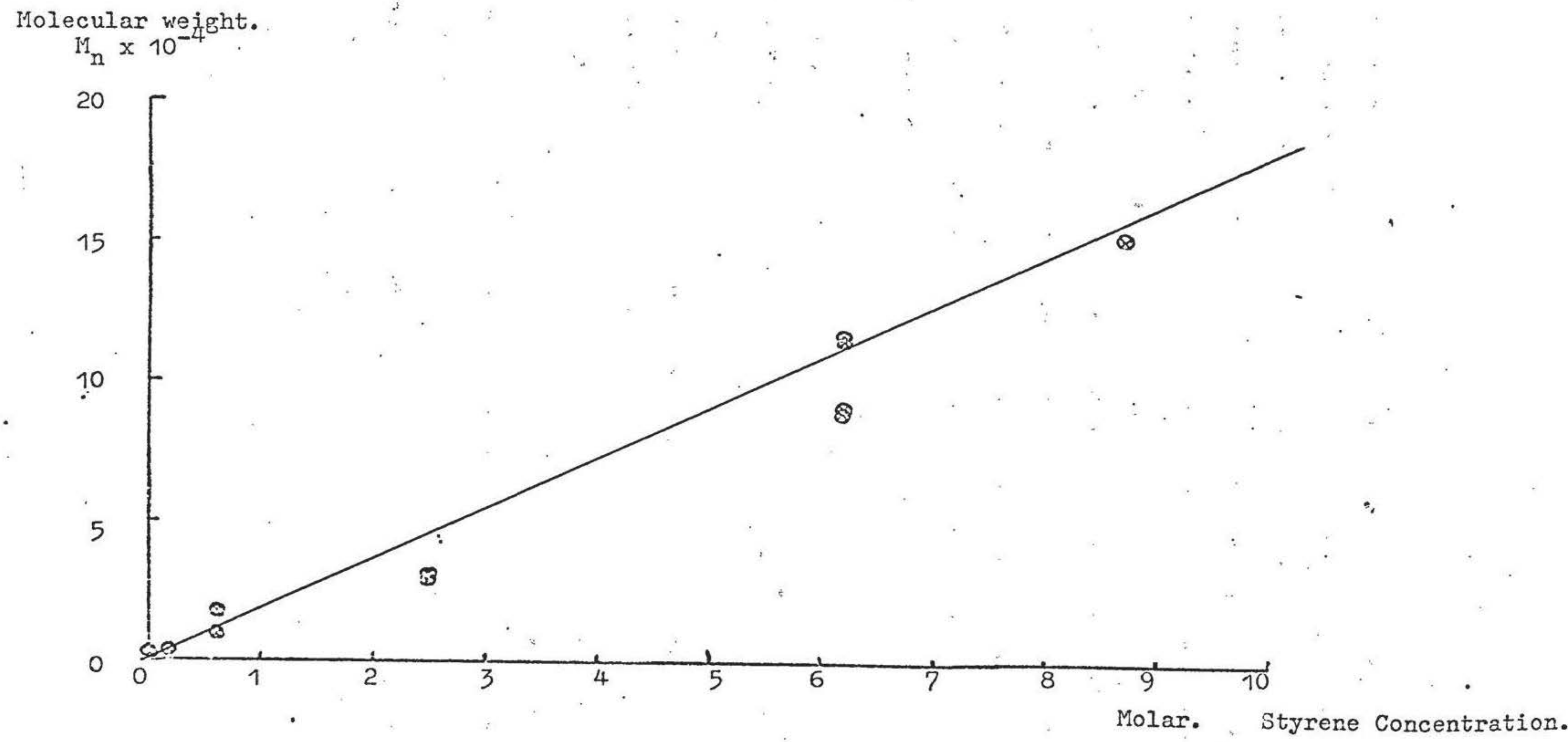
Number Average Molecular weight versus titanium trichloride catalyst concentration.

Figure 35



Number Average Molecular weight versus styrene monomer concentration.

Figure 36



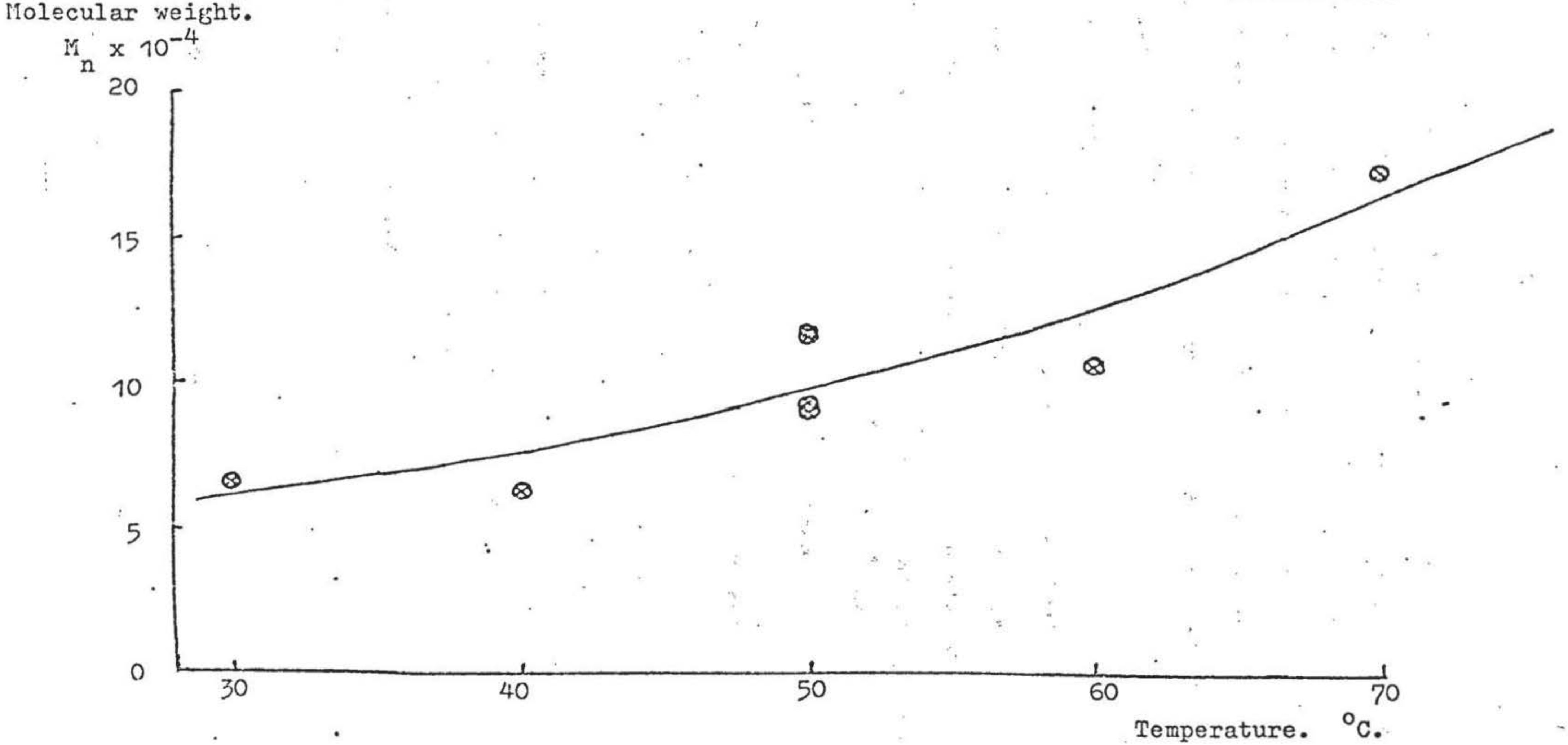
the molecular weight after 24 hours versus the styrene concentration shows that M_n increases as [styrene] increases. For the experiments carried out it seems that this relationship is approximately a linear proportionality in this case. From this observation it can been inferred that the monomer is not involved in chain transfer processes with growing polymers which would cause a lower M_n at high values of [styrene]. This is in line with the previous observations which indicate that the transfer processes in this system appear to involve the titanium and alkyl components. This observation is not as has been generally found in Ziegler systems of a similar nature where a chain transfer process, as mentioned above, involving the monomer is operative (97, 98).

4.7. - The Effect of Temperature Upon the Molecular Weight of the Polymer

The effect of temperature upon the molecular weight of the polymer is shown in Figure 37. The molecular weight is found to increase with increase in temperature throughout the range investigated 30°C - 70°C. This result is contrary to that found in several Ziegler systems including this one when used for ethylene polymerisation. The ethylene results showed a decrease in molecular weight for temperatures $>30^\circ$C. A decrease of this nature arises if the termination reaction has a greater activation energy than the propagation reaction, which, from the results obtained between 30°C - 70°C, is apparently not the case in this system.

Number Average Molecular weight versus Reaction temperature.

Figure 37



4.8. - Determination of the Active Site Concentration

An estimate of the number of catalytic sites actively participating in the polymerisation was made using the simple procedure adopted for previous work using this system with ethylene (49, 49A). This technique employs the following assumptions concerning the kinetics of the polymerisation.

It is assumed that:-

i) There is a steady state concentration (C*) of active sites set up before the first measurement on the system is made, i.e. the active sites are generated during the early stages of the reaction, during the settling period, and a steady state concentration is thereafter maintained.

i.e. $\frac{d(C^*)}{dt} = 0$ for all measured reaction times ($t \geqslant 180$ mins)

ii) Chain transfer and chain termination reactions occur without the destruction of activity, i.e. there is no nett catalyst deactivation during the reaction under the conditions employed superfluous.

As the mechanism of transfer is uncertain, a first order constant is assumed for the purposes of the reaction scheme.

a) $C^* - P_{n-1} + M \xrightarrow{R_p} C^* - P_n$

Where C* is an active site.

P_n is a growing polymer chain consisting of n monomer units.

M is a monomer molecule.

Now if R_p = Rate of chain propagation

$$R_p = k_p\ (C^*)(M)$$

Where k_p = rate constant of propagation

$$k_p = \frac{R_p}{(C^*)(M)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

b) $C^* - P_n \xrightarrow{R_t} C^* + P_n$

Where the site C* still retains catalytic activity

Now if R_t = Rate of chain transfer

$$R_t = k_t \; (C^*)$$

Where k_t = Rate Constant for chain transfer

$$k_t = \frac{R_t}{(C^*)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

If also Y_t= Yield of polymer (g) at time, t.

$(\bar{M}_n)_t$ = Number average molecular weight of polymer at time, t.

and N_t = Total number of polymer molecular plus total number of growing chains at time, t, (in moles).

Then clearly,

$$N_t = \frac{Y_t}{(\bar{M}_n)_t}$$

Therefore where Y_t is plotted versus N_t, i.e.

$$\frac{Y_t}{(\bar{M}_n)_t}$$

When $Y_t \rightarrow 0$, $t \rightarrow 0$, $N_t \rightarrow (C^*)$

(See assumption i).).

Hence the intercept of such a plot = $\sim (C^*)$

In addition:-

At anytime since

$$R_{tot} = \frac{d_Y}{d_t} = \text{Measured rate of monomer consumption.}$$

$$\frac{dN}{dY} . R_{tot} = \frac{dN}{dY} . \frac{dY}{dt}$$

$$= \frac{dN}{dt}$$

$$= R_t$$

Using (2) $k_t = \frac{R_t}{(C^*)}$

Therefore $k_t = \frac{\frac{dN}{dY} . R_p}{(C^*)}$

Also from (1)

$$k_p = \frac{R_p}{(C^*)(M)}$$

Thus estimates can be made of values of (C^*), k_p and k_t from results of Yield, $\bar{M}_n$ and R_p. Figure 38 shows the Y_t versus $Y_t/(\bar{M}_n)_t$ plot for a styrene polymerisation using the magnesium reduced Ziegler catalyst system at 50°C. Within the experimental limitations of this Ziegler type polymerisation the results appear to conform reasonably well with the linear relationship found in the ethylene case, although as in that case some deviation seems to occur for the higher values of $t(Y_t)$. The straight line found earlier for ethylene and assumed to be operative for this case, enables k_t to be found from the gradient of dN_t/dY_t. The linear nature of the relationship supports the assumption that (C^*) is constant (i.e. $d(C^*)/dt = 0$).

From the graph shown in Figure 38, a value of $5.0 \pm 0.7 \times 10^{-6}$ was found for the gradient and $1.1 \pm 0.5 \times 10^{-5}$ moles for the intercept with the y axis. The slope is equal to the differential $\frac{dN}{dY}$. The intercept is equivalent to the concentration of active sites C* and equals 1.13×10^{-5} moles which suggests that only about 0.08% of the titanium atoms present act as active catalytic centres. This value is almost 10^{-3} times smaller than the % of active sites determined using this type of technique with this catalyst system

Plot of ${}^{Y_t}/_{(M_n)_t}$ versus Y_t for the styrene/magnesium reduced catalyst system at 50 °C.

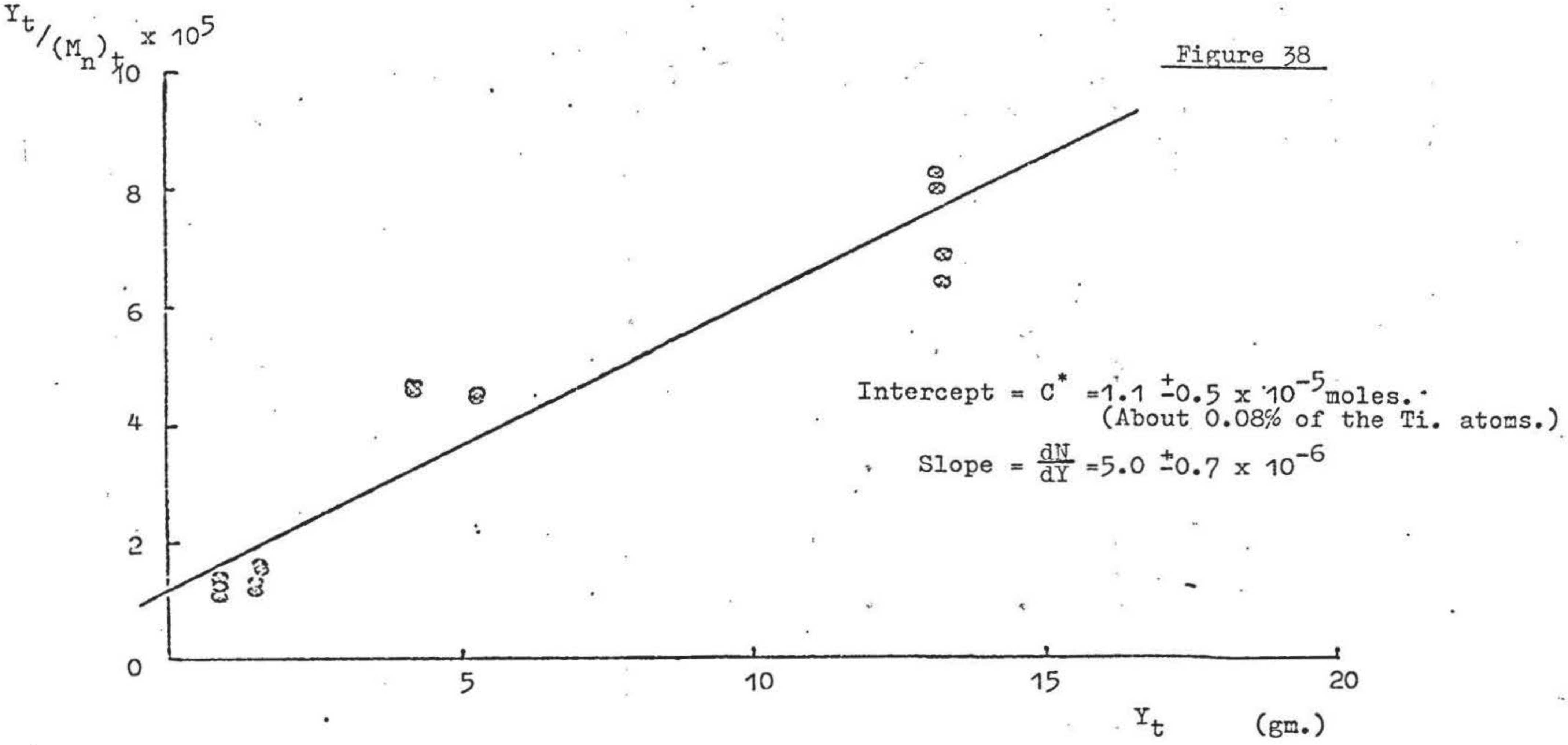


Figure 38

Intercept = $C^* = 1.1 \pm 0.5 \times 10^{-5}$ moles.
(About 0.08% of the Ti. atoms.)

Slope = $\frac{dN}{dY} = 5.0 \pm 0.7 \times 10^{-6}$

when used for ethylene polymerisation (49, 49A). However, the % active sites obtained with ethylene is much larger than found in most Ziegler catalysed systems, where in general the % active sites for conventional catalysts determined by various methods, appears to lie between 0.1% and 1.0%.

Assuming $k_p = \frac{R_p}{(C^*)(M)}$ as stated earlier

Where $R_p = 8.4 \times 10^{-6}$ mol dm^{-3}sec^{-1} (overall average polymerisation rate)

$(C^*) = 1.1 \times 10^{-5}$ moles

$(M) = 6.2$ moles

$\therefore k_p = 1.2 \times 10^{-1} \text{mol}^{-1}\text{dm}^{-3}\text{sec}^{-1}$

$k_t = \frac{dN}{dY} \cdot \frac{R_p}{(C^*)}$

Where $\frac{dN}{dY} = 4.97 \times 10^{-6}$

$\therefore k_t = 3.8 \times 10^{-6}$

4.9. The Lifetime of the Growing Polymer Chain

The average value for the lifetime of a growing polymer chain was estimated using the expression:-

$$L = \frac{\bar{P}n\ (C^*)}{R_p}$$

Where L = Average lifetime of growing polymer chain

P_n = Number average degree of polymerisation

R_p = Rate of polymerisation

As $\bar{P}_n = \frac{\bar{M}_n}{104}$ for any time t, $\bar{M}_n$ was taken to be the number average molecular weight at the end of the polymerisation experiment (i.e. when t = 24 hours).

The value for L was 1150 secs . (19.2 mins, 0.32 hrs)

$$\text{Where } \bar{P}_n = 880 \text{ , } M_n(t = 24 \text{ hrs}) = 9.15 \times 10^4$$
$$(C^*) = 1.1 \times 10^{-5}$$
$$R_p = 8.4 \times 10^{-6}$$

Thus the average lifetime of the growing polymer chain has a value of 1150 secs ~ 20 mins. This agrees favourably with the values found in the previous work with ethylene in which lifetimes ranged from 10 mins at 50°C up to 24 mins at 0°C. However, the results found with this catalyst using ethylene monomer were shorter than those generally reported for the Ziegler catalyst systems. Greiveson (97) found a value of 30 mins for an ethylene system and Chien (95) quotes a value of 24 mins but various other authors (99, 100, 101) have found lifetimes considerably longer of the order of several hours using Ziegler systems with both ethylene and propylene monomers.

4.10. - Crystallization Kinetics Experiments on the Magnesium Reduced Catalyst Prepared Polystyrene

The crystallization kinetics of a standard sample of isotactic polystyrene were observed using the techniques of J N Hay (90). Determination of the nucleation rate and spherulitic growth rate were made on this sample using a thermostatted hot stage fitted for a Leitz Dialux-Pol polarizing microscope. The size,distribution and number of crystallizing entities was measured visually with a micrometer eyepiece for thin film polymer samples placed on thin glass microscope cover slips. Similar experiments were conducted with various samples of the polystyrene recovered from experiments using the magnesium reduced Ziegler catalyst. No visible crystallization of the polymer samples was detected for six samples produced under various reaction conditions. Differential scanning calorimetry experiments were also carried out on the samples and the standard material. Crystallization was observed in the traces for the standard material but not in traces using the material produced in this work.

SECTION 5 - THE PREPARATION OF STYRENE-4-METHYL-PENT-L-ENE COPOLYMERS

In addition to the styrene experiments, four experiments were carried out to prepare polymers using 4-methylpent-1-ene (4-MP-1). These experiments consisted of a homopolymerisation of 4-MP-1 monomer and three copolymerisations of 4-MP-1 with styrene using monomer ratios of 7 : 3, 1 : 1 and 1 : 4 respectively. The results produced are shown in Table 4. The homopolymerisation of 4-MP-1 produced a very poor yield of a waxy residue upon filtration, and further examination of this negligible quantity of material proved impossible.

A sample of the product from each of the styrene/4-MP-1 experiments was dissolved in dichloromethane and the ultraviolet spectrum of the solution obtained at various concentrations. The spectrum obtained from a sample of styrene homopolymer prepared in the earlier experiments was treated in a similar manner. From the results the proportion of styrene present in the product from these styrene/4-MP-1 experiments was estimated and is shown in Table 5.

Solubility tests were carried out on samples of the polymer produced in the mixed monomer experiments to ascertain whether the material produced was polystyrene-Co-4-Methylpent-1-ene. The technique employed was the solvent extraction

TABLE 4

Results from 4-Methylpent-1-ene experiments.

Expt.	Concentration of Styrene Monomer	Concentration of 4-MP-1 Monomer	Ratio 4-MP-1/Styrene Mole fraction percentage	Yield (gms)
S/42	6.23 M	0.00	-	4.2248
M/1	0.00	6.21 M	-	0.0175
M/2	0.00	6.22 M	-	0.0388
SM/1	4.97 M	1.24 M	20%/80%	2.0454
SM/2	3.11 M	3.11 M	50%/50%	1.2653
SM/3	1.86 M	4.36 M	70%/30%	0.6726

---o0o---

TABLE 5

Ultra-voilet spectroscopy investigation of composition of styrene/4-methylpent-1-ene polymers.

Expt.	Ratio of 4-MP-1/styrene (Mole fraction percentage)		Percentage of Styrene incorporated in Polymer
S/42	0%	100%	100%
SM/1	20%	80%	84.6%
SM/2	50%	50%	94.9%
SM/3	30%	70%	82.4%

---o0o---

method used previously by Anderson Burnett and Tait A polystyrene sample made in these experiments was used as a control sample for comparison. The material from the copolymer experiments was found to be as insoluble as the polystyrene sample in cold heptane extraction. Thus no positive evidence was obtained to show that the material was a copolymer rather than a mixture of homopolymers. However, Anderson <u>et al</u> report that the rate of polymerisation for their (Styrene/4-Methylpent-1-ene)/ α-$TiCl_3$/$AlEt_3$ system(103) was markedly affected by the solvent used. A pronounced effect was observed when the reaction was carried out in toluene rather than n-heptane. In the former case a five fold increase in rate is found in comparison to the n-heptane rate. The solvent used in these experiments was iso-octane a branched aliphatic solvent which resembles more closely the n-heptane. This may be in part responsible for the poor activity found in these experiments.

SUMMARY

The results presented in this Chapter of the work have shown that the magnesium reduced catalyst system is capable of catalysing the polymerisation of styrene through a Ziegler mechanism. The catalyst exhibits markedly reduced activity in comparison with its use in propylene and ethylene systems. The typical specific activity obtained in styrene experiments was 1.0 gm/gm $TiCl_3$/hr whereas the figures obtained with propylene and ethylene were 100 gm/gm $TiCl_3$/hr and 10000 gm/gm $TiCl_3$/hr respectively. The activity towards styrene of the magnesium reduced system is lower than has been achieved using a conventional aluminium reduced system employing α-$TiCl_3$. The material prepared by the magnesium reduced system typically has a number average molecular weight of 1.1×10^5 and a weight average molecular weight of 2.2×10^5. Investigations into the tacticity of the material have shown that it contains an isotactic fraction which may be detected by proton magnetic resonance spectroscopy, and by 13 C magnetic resonance spectroscopy. This fraction is considered to be produced entirely by the operation of a stereoregulating Ziegler catalyst mechanism. However, the major part of the material consists of randomly arranged sequences as shown by the inability of the unfractionated material to crystallise during the crystallinity studies, although crystallisation was readily achieved using a sample of a standard isotactic material.

The atactic polystyrene may be generated in two ways, firstly due to thermal polymerisation and secondly, through non-stereo regulated catalysis. Determination of the rate of nucleation and of the crystallisation kinetics was carried out on the sample of the standard isotactic material but no such work could be carried out with our material as it failed to crystalise.

An attempt to quantitatively estimate the percentage isotacticity present from infra-red and magnetic resonance spectroscopic data also proved impossible.
However, determinations of the percentage isotacticity occurring in unfractionated poly-propylene samples prepared by this catalyst has indicated that not more than 33% isotacticity is present. The estimation was made using a solvent extraction technique and also a comparison of infra-

red absorption frequencies method. Due to the presence in the styrene monomer of the phenyl group, considerably more bulky than the methyl group of the propylene monomer, it might be expected that in a Ziegler mechanism it will be much more difficult to attain the correct spatial position of the reacting species in the stereoregulating catalytic centre. Reaction at the Ziegler centre where the tactic material is produced will therefore be reduced. Thus the alternative non-stereoregulating and thermal mechanisms are likely to be of greater importance in the polystyrene system than the polypropylene one as confirmed by the experimental observations which indicate that an even larger percentage of atactic material is produced in the polystyrene case.

The observations made concerning the magnesium reduced catalyst in comparison with conventional catalyst confirm the data which has already been obtained regarding the system. Previous work on Ziegler systems has shown styrene to be a less active monomer compared to propylene and very much less active compared to ethylene which is also true in this case. Earlier work has shown that the different properties of the magnesium reduced system are due to the very disordered structure of the material which is similar to that of a glass. Confirmation that such disorder was present in $TiCl_3$ prepared using the alkyl magnesium halide method has been made by Roper(48) using X-ray diffraction observations. He also proposes that the disorder found in these catalysts prepared from Grignard reagents as used in the present work is due to a "Co-crystallisation" of magnesium halide and titanium III chloride in a similar manner to that which has been proposed for the aluminium halides in conventional systems. The disorder arises due to both the increased diameter of the magnesium atom disrupting the titanium III chloride lattice which accommodates the smaller size aluminium atoms and the difference in charge (Mg^{2+} versus Ti^{3+}).

In general, in Ziegler systems it has been found that material of greater isotacticity is prepared from the ordered α, γ crystalline lattice forms rather than the β or soluble catalyst forms. Thus the greater disorder of the glass like structure found with the magnesium system would be expected to produce a more atactic material than the conventional crystalline system, as has been found in the present work. The reduced catalytic activity compared with conventional catalysts was not expected from the behaviour of the magnesium reduced catalyst with ethylene. However, this might be explained if the disordered structure proposed for the catalyst is considered to be of a somewhat porous nature. In the ethylene case the enhanced activity might arise from diffusion of the small monomer units to potential sites in the interior of the catalyst structure via the porous nature of the material caused by the magnesium disrupted structure. Propagation of polymer chains at such a site might cause physical breakdown of the particle structure and have a cumulative effect. However, if in the styrene case the monomer units are generally too bulky to diffuse into any porous regions of the catalyst, no enhancement of activity would occur.

The investigation of kinetics of the polymerisation reveals that in general the system exhibits the characteristics expected from a Ziegler system. The notable exception in this case is the square root dependancy found for the Ti relationship of the concentration to the reaction rate. This indicates a more complex mechanism is operative than generally found in Ziegler systems, which normally exhibit a linear dependence. Firstly, if the magnesium reduced system is considered to be mid-way between the soluble catalyst systems and the crystalline heterogeneous systems, then a complex system may be expected as second order kinetics have been found for soluble systems instead of the first order kinetics found in the crystalline heterogeneous systems. Secondly, an explanation of this observation which may be proposed is that a termination mechanism involving the titanium species is operative in this particular system.

The kinetic investigation revealed that the system exhibits an interesting behaviour towards the aluminium trialkyl component in that at an Al : Ti ratio greater than $\sim$ 1.5 (conc. Al Alkyl > 0.02M) there is a marked depression of the rate and from ratios > 2.5, there is also a fall in the polymer molecular weight. This depressed rate is ascribed to either the result of transfer/termination reactions involving the metal alkyls or to competitive alkyl/monomer absorption being rate limiting. Overall, the reaction rate exhibits the decay type pattern of kinetics. A sharp maximum in the rate is generated initially in the first few minutes of the polymerisation. This rate rapidly decays over the first two hours of the reaction until it levels off to an approximately steady state condition which decays minimally during the remainder of the reaction when observed for up to 96 hours.

The relationship between the rate and the titanium concentration is approximately Rate = k $\sqrt{(Ti)^2}$ which it is unusual to find in Ziegler systems. The effect of monomer upon reaction rate appears to be as normal in Ziegler systems and approximates to a first order dependancy. An Arrhenius plot of the temperature curves yields an overall activation energy E of 60 ± 30 KJ. However, this plot appears to consist of two distinct portions indicating a change in mechanism taking place at about 50°C.

The observations of the molecular weight relationship towards the reaction parameters, time, and reagent concentrations are conventional for a Ziegler system. However, a limiting value of molecular weight is not reached as readily as is found in other Ziegler systems. The molecular weight results also suggest that at high titanium catalyst concentration, the titanium component may be involved in a chain transfer process indicated by the fall in $\bar{M}_n$ at the higher (Ti) values.

The value found for the % active centres present is small 0.08% almost 10^{-3} times smaller than the equivalent value using ethylene monomer. Consequently, a larger value of average chain lifetime is found 53 mins.

Copolymerisation of 4-methylpent-1-ene monomer with styrene in this system proved unsuccessful. However, low reaction rates have previously been reported by Anderson etal(103) for a similar mixed, monomer system with n-heptane. As isooctane has been used in this work, it is likely that a similar solvent effect may be operative and any future development of such a mixed monomer copolymerisation would be well advised to use an aromatic solvent such as toluene, with which Anderson found markedly increased rates.(103)

Future development of the catalyst should involve the use of mixed monomer copolymerisation system such as the styrene/4-methylpent-1-ene system as results on copolymerisation reactivity ratio will be a valuable insight into the properties of the catalyst system. The present work has not tried to investigate any of the properties of the copolymerisation on a quantitative basis but merely a qualitative one.

A further field of development at present unexplored is whether the material produced by this catalyst consists basically of a large atactic fraction and a small isotactic fraction each of high purity or whether the material consists of individual chains containing sequences of differing lengths of tactic arrangements conferring the different properties on the various chains. It might be possible to obtain such information from the reaction product by a more detailed magnetic resonance spectroscopy study coupled with more sophisticated solvent fractionation techniques. The results obtained would be valuable in that they may be able to throw light on the question of whether the active Ziegler centre is of one type (or two types) with consistent properties or whether centre are generated with a range of characters which therefore produce chains of varying degrees of order.

---o0o---

CHAPTER 4

ACETYLENE-ETHYLENE COPOLYMERISATIONS

The magnesium reduced catalyst system was used for an investigation into its activity towards acetylene. In particular a study was made of its use together with ethylene as a mixed monomer system in the hope of preparing poly-ethylene-co-acetylene (i.e. polyethylene material with a controlled amount of linear unsaturation).

Experimental Procedure

The technique adopted for these experiments was as that used in the earlier ethylene work. The acetylene monomer was supplied from a compressed gas cylinder and after purification was fed separately into the reactor. The purification consisted of passing the acetylene through a Drechsel bottle containing concentrated sulphuric acid followed by a splash trap whence it passed through a column of molecular sieve type 4A 1/16" pellets. After purification the gas was admitted into the reactor through an additional nylon tubing inlet and dip tube. The dip tube was arranged so that its depth of immersion could be altered in order that the acetylene could be either bubbled into the reaction mixture or introduced into the cap gas above the liquid surface. The polymerisations were carried out using a titanium III chloride concentration of M and an aluminium triethyl concentration of M, for 3 hours at 50°C. The initial experiment followed the normal procedure adopted for ethylene polymerisations (See Chapter 2) excepting that after the reaction had proceeded for about 10 mins the ethylene was replaced by acetylene being bubbled into the reaction mixture.

However, the reaction rate quickly dropped to an absorption rate of 1 dm^3 Acetylene hr^{-1}. This technique produced a very small yield of a jet black material, characteristic of a polyacetylene. A further four experiments were then conducted to introduce less acetylene into the system with the intention of producing materials containing more saturated units. The remaining experiments used the technique of bleeding the acetylene monomer into the cap gas just above the surface of the liquid whilst continuing to bubble ethylene into the reaction mixture. The reaction product in each case was worked up in the way previously described for the ethylene experiments.

The dried polymers were examined and their characterisation attempted. The samples proved to be insoluble in a range of common organic solvents including hexane, tolune, acetone, dekalin and carbon tetrachloride. The insoluble nature of the polymer also made these materials unsuited to many forms of spectroscopic analysis and also for viscometry measurements. However, an elemental analysis of the initial polymer sample can be found in Table 6 . The material produced in the mixed monomer experiments was a purple-black granular powder. These polymers were also insoluble at ambient temperature and if heated in order to assist dissolution, formed gelatinous rubbers swollen by the solvent.

Results and Discussion

The study of this polymerisation was rather limited since the initial few experiments showed the material produced to be intractable and unsuited to further investigation by conventional methods. However, the experiments undertaken

TABLE 6

Elemental Analysis Results from the materials prepared in the Ethylene/Acetylene Experiments.

Expt. No.	% C	% H
1	81.6	6.5
2	85.8	14.7
3	72.2	12.7
4	85.5	14.7
5	86.1	10.8
Theoretical %		
$(CH_2)_n$	85.7	14.3
$(CH)_n$	92.3	7.7

A further analysis of material from experiment 1 after several weeks gave the following results, using an alternative procedure.

% C	% H	% Cl	% Ash
28.7	5.5	1.2	31.8
29.0	5.9	1.9	30.4

Assuming the ash to be TiO_2 then % Ti 19.1 , 18.3 . The ratio of the Carbon and Hydrogen in these results is

% C	% H
83.9	16.1
83.1	16.9

showed that the magnesium reduced catalyst system was capable of polymerising acetylene monomer and mixtures of it with ethylene although the rate of polymerisation was rather low. Several authors have previously prepared polyacetylene materials which are generally a jet black fibrous solid of a highly crystalline nature. Many of the reports cite the use of various Ziegler catalyst systems. Natta employed several systems for acetylene polymerisation(104) based on titanium alkoxides and aluminium or lithium alkyls in an n-heptane solvent at 45°C - 75°C, typical examples being, (i) $Al(Et)_3$ - $Ti(OC_3H_7)_4$, (ii) $Al(C_6H_{13})_3$ - $Ti(OC_4H_9)_4$, (iii) $Li(C_5H_{11})$ - $Ti(OC_3H_7)_4$. His best results were obtained for systems (i) and (iii) at Al/Ti = 1.4 to 2.5 when material of high crystallinity with a trans configuration was obtained. Alkoxides of various transition metals e.g. $Ti(OC_4H_9)_4$, $VO(C_5H_7O_2)_2$, $Cr(C_5H_7O_2)_3$, $Co(C_5H_7O_2)_3$ have been used in Ziegler systems with aluminium triethyl by Nicolescu and Angelescu for polymerising acetylene(105). These authors carried out atmospheric pressure experiments at 0°C in redistilled toluene yielding a bright black solid which could be extracted with warm acetone over 8 hours. Kambara and Hatano(106) have also carried out preparations using the catalysts described by Natta. Watson etal(107) used Ziegler catalysts prepared from titanium tetrachloride and aluminium trisobutyl or n-butyl lithium or zinc diethyl to produce polymers of acetylene, propyne, and butyne-1. Infra-red spectra of these polymers were obtained showing absorption bands at 3.4, 6.1 and 9.9 μ. The band at 6.1 μ is attributed to out of plane deformation of trans ethylenic hydrogens along a highly conjugated polymer chain. Further infrared studies, differential scanning calorimetry and thermogravimetric analysis determinations have been made by Kleist and Byrd but the samples obtained in this work were not produced with Ziegler catalysts instead catalyst systems based on dimethylglyoximate and on sodium borohydride are used.(108)

The sodium borohydride method was developed by Luttinger(109) and produces a polymer containing predominantly sequences of conjugated double bonds in the trans configuration. Noguchi and Kambara developed the dimethylglyoximate based catalyst(110) which produces a predominantly cis-polymer. Nickel compounds have been reported by the Russian authors Chukhadzhyan etal(111) to be active catalysts yielding benzene polymers and oligomers from acetylene.

The product of the initial experiment using acetylene with the magnesium reduced catalyst was a jet black insoluble solid formed in fibrous flakes which closely resembled the poly acetylene material reported by the earlier authors. An elemental analysis was carried out on this polymer, the results of which are given in Table 6 , and show that the product is severely contaminated by inorganic salts. The ash content is due to the decomposition products of the catalyst which become trapped in the polymer. The inorganic material proved impossible to remove by vigorous washing of the polymer which suggests it could be retained due to the formation of a stable complex. The polymer was insoluble in any of the common organic solvents and thus the molecular weight could not be estimated. Due to the insolubility of the material, it was impossible to produce cast films from which to obtain an infra-red spectrum. The spectrum produced by a KBr pressed pellet, could not be successfully resolved and insufficient material was available for further study.

The experiments using mixed ethylene/acetylene feeds produced blue/purple coloured materials. When the acetylene was bubbled into the ethylene system, the rate of absorption of the ethylene decayed rapidly to zero. The magnesium reduced catalyst appears to absorb acetylene preferentially. However, the rate of polymerisation of the acetylene is much lower as shown by the significantly lower rate of absorption of acetylene compared to ethylene. In the later experiments, in which smaller quantities of acetylene were introduced, the ethylene polymerisation was only moderately suppressed and it was found that some recovery of ethylene polymerisation rate was achieved when the rate of acetylene feed was reduced or terminated. This observation suggests that although the magnesium reduced catalyst system is very much more reactive with ethylene than acetylene in terms of polymerisation rate, when there is competitive feed of the two monomers, acetylene is absorbed and hence polymerised in preference to ethylene.

The materials prepared from the mixed monomers appeared to be polyolefins containing some unsaturation. They were insoluble in common organic solvents at ambient temperatures. When a sample was heated in a high boiling point aromatic hydrocarbon solvent (dekalin), in order to dissolve it, a solvent swollen cross-linked rubber gel was formed instead of the solution normally prepared in the case of a homopolyethylene. Although these materials were cross-linked, it proved impossible to determine whether they were homogeneous polyethylene containing unsaturation (polyethylene-co-acetylene) or a heterogeneous mixture of polyethylene and polyacetylene. Elemental analysis of these samples is also given in Table and as in the case of the earlier material, little spectroscopic data was obtained on these samples.

Summary

The magnesium reduced catalyst system was active in polymerising acetylene to an insoluble black material, presumably polyacetylene. The catalyst was also capable of generating unsaturated polymeric materials from mixed ethylene/acetylene monomer feeds. Practical difficulties were encountered in controlling the amount of acetylene introduced into the polymerisation system. Acetylene polymerised on the catalyst very much more slowly than ethylene but was preferentially absorbed. Thus, the introduction of acetylene effectively inhibits an ethylene polymerisation, making control over the relative proportions of the two monomers in the polymer very difficult. Secondly, there are practical difficulties in the characterisation of these polymers although samples appear to contain some unsaturation. However, these were insoluble materials at ambient temperature and sensitive to cross-linking at elevated temperatures and so it proved impossible to produceasolution for further investigations and characterisation.

These experiments have shown that if practical methods can be devised to overcome the temperature/solubility problem in the analysis of these materials, the magnesium reduced catalyst is capable of producing unsaturated polymers and is worthy of further investigation. There is plenty of opportunity for the development of more sophisticated techniques for feeding the monomer mixtures into the system. By using a more precisely controlled method of metering the acetylene into the polymer, it should be possible to produce a range of materials of varying degrees of unsaturation. Samples of such materials could be studied to investigate whether any changes in the physical characteristics of the material take place as the degree of unsaturation increases. Such materials would also prove valuable precursors for further experiments as the inclusion of the relatively vinyl linkages makes them into suitable starting materials for other reactions. For example, the material would be a suitable alternative to the styrene-butadiene copolymers with an unsaturated content cited in the experiments outlined in Chapter 2. Thus, scope for considerable future development remains once the practical problems associated with this work can be resolved.

---oOo---

APPENDIX I

Listing of Computer Programs

The following pages contain listings of the FORTRAN statements used in the computer programs written for calculation of the kinetic data. The programs were normally retained on-line in a filestore although they could be run directly from punched cards.

Filestore DBGPFILE contains the program for calculation of the data from the ethylene polymerisations.

Filestore JC1 consists of job control statements for running the styrene data program.

Filestore DBPF2 is the calculation program for the styrene polymerisations. Once the Fortran compilation had been carried out satisfactorily this program was retained in machine code form for running subsequent programs.

Filestore DBGPP4 is the graphical output program for the plotting of results obtained from DBPF2.

Filestore DBSHP42 is a typical input data filestore for the styrene polymerisation data.

Filestore DBE1 stores the indicator which signifies all the data for the program has been loaded during a particular job.

The programs were generally run by feeding the data directly into a computer filestore using an on-line teletype terminal. The program was initiated using a command from the teletype, eg RJ ␣ SHP42, JC1 (PARAM42).

The program and the data could also be directly run from a punched card deck.

OUTPUT FROM THESISLIST OF DBGPFILE

```
      MASTERMAIN
C     POLYMERISATION DATA PROGRAM
C     TIME=DATA(N,1)
C     READ M=DATA(N,2)
C     FLOW IN=DATA(N,3)
C     FLOW OUT=DATA(N,4)
C     INPUT PRESS.=DATA(N,5)
C     TEMP.=DATA(N,6)
C     RESULT(N,1)=METER DIFF.
C     RESULT(N,2)=AV.INPUT FLOW RATE
C     RESULT(N,3)=VOLUME GAS IN.
C     RESULT(N,4)=VOLUME GAS ABSORBED
C     RESULT(N,5)=TOTAL GAS ABSORBED
C     RESULT(N,6)=RATE GAS ABSORBED
C     RESULT(N,7)=METER OUTPUT RATE
      DIMENSION DATA(100,6),RESULT(100,12),TITLE(3,15),X(100),Y(100)
      READ(5,60)HEIGHT
   60 FORMAT(F10.0)
      NEXPT=0
    7 WRITE(6,104)
  104 FORMAT(1H1,29H POLYMERISATION DATA PROGRAM.//)
      READ(5,103)((TITLE(I,J),J=1,15),I=1,3)
  103 FORMAT(10A8)
      WRITE(6,102)((TITLE(I,J),J=1,15),I=1,3)
  102 FORMAT(1H0,15A8)
      READ(5,101)YIELD
  101 FORMAT(F10.0)
      N=0
  100 N=N+1
      READ(5,99)(DATA(N,J),J=1,6)
   99 FORMAT(6F10.0)
      IF(DATA(N,1).NE.-100.0)GO TO 100
      N=N-1
      WRITE(6,98)N
   98 FORMAT(1H0,5X,I3,24H DATA READINGS RECORDED.)
      WRITE(6,97)
   97 FORMAT(1H0,5X,23HTABLE OF DATA READINGS.//8X,4HTIME,3X,5HMETER,5X,
     13HGAS,6X,3HGAS,4X,5HINPUT,3X,5HTEMP./7X,6H(MINS),1X,7HREADING,3X,5
     2HINPUT,4X,6HOUTPUT,2X,6HPRESS.,3X,1H0/14X,8H(LIT/HR),1X,8H(LIT/HR)
     3,1X,8H(LIT/HR),1X,6HCM.HG.,2X,4H( C)/)
      WRITE (6,96)((DATA(M,J),J=1,6),M=1,N)
   96 FORMAT(7X,F6.2,1X,F8.3,1X,F8.4,1X,F8.4,1X,F6.2,1X,F6.2)
      GSUMIN=0.0
      DO 10 M=1,(N-1)
      TIMINT=(DATA((M+1),1)-DATA(M,1))/60.0
      RESULT((M+1),2)=(DATA((M+1),3)+DATA(M,3))/2.0
      RESULT((M+1),3)=TIMINT*RESULT((M+1),2)
      RESULT((M+1),1)=DATA((M+1),2)-DATA(M,2)
      RESULT((M+1),4)=RESULT((M+1),3)-RESULT((M+1),1)
      RESULT((M+1),5)=RESULT(M,5)+RESULT((M+1),4)
```

```
      RESULT((M+1),6)=RESULT((M+1),4)/TIMINT
      RESULT((M+1),7)=RESULT((M+1),1)/TIMINT
      GSUMIN=GSUMIN+RESULT((M+1),3)
   10 CONTINUE
      WRITE(6,104)
      WRITE(6,102)((TITLE(I,J),J=1,15),I=1,3)
      WRITE(6,95)
   95 FORMAT(1H0,5X,22HTABLE OF DATA RESULTS.)
      WRITE(6,50)
   50 FORMAT(1H0,7X,4HTIME,3X,5HMETER,5X,3HGAS,6X,3HGAS,4X,5HINPUT,3X,5H
     1TEMP.,2X,5HMETER,3X,8HAV.INPUT,2X,5HINPUT,5X,3HGAS,4X,7HTOT.GAS,2X
     2,8HRATE GAS,2X,5HMETER)
      WRITE(6,51)
   51 FORMAT(1H ,6X,6H(MINS),1X,7HREADING,3X,5HINPUT,4X,6HOUTPUT,2X,6HPR
     1ESS.,3X,1H0,5X,5HDIFF.,5X,4HRATE,4X,6HVOLUME,2X,8HABSORBED,1X,8HAB
     2SORBED,1X,8HABSORPTN,3X,4HRATE)
      WRITE(6,52)
   52 FORMAT(1H ,13X,8H(LIT/HR),1X,8H(LIT/HR),1X,8H(LIT/HR),1X,6HCM.HG.,
     12X,4H( C),3X,6H(LITS),2X,8H(LIT/HR),2X,6H(LITS),3X,6H(LITS),3X,6H(
     2LITS),2X,8H(LIT/HR),1X,8H(LIT/HR)//)
      WRITE(6,94)((DATA(M,J),J=1,6),(RESULT(M,K),K=1,7),M=1,N)
   94 FORMAT(7X,F6.2,1X,F8.3,1X,F8.4,1X,F8.4,1X,F6.2,1X,F6.2,1X,F8.3,1X,
     1F8.4,1X,F8.4,1X,F8.4,1X,F8.4,1X,F8.4,1X,F8.4)
      READ(5,101)EXTRA
      IF(YIELD.LE.0.0)GO TO 8
      GASABS=(YIELD/28.05)*22.4
      GSUMOT=DATA(N,2)-DATA(1,2)
      APGASA=GSUMIN-GSUMOT
      ERROR=APGASA/GASABS
      CALCGI=GASABS+GSUMOT
      CFACT=CALCGI/GSUMIN
      WRITE(6,104)
      WRITE(6,102)((TITLE(I,J),J=1,15),I=1,3)
      WRITE(6,93)YIELD,GASABS,GSUMOT,APGASA,ERROR,GSUMIN,CALCGI,CFACT
   93 FORMAT(1H0,5X,6HYIELD=,F6.2/6X,8HGAS ABS=,F8.3/6X,12HTOT.GAS OUT=,
     1F8.3/6X,12HAPP.GAS ABS=,F8.3/6X,6H% ABS=,F9.6/6X,12HAPP.GAS IN.=,F
     28.3/6X,13HCALC.GAS IN.=,F8.3/6X,6HCFACT=,F9.6)
      GSITWO=0.0
      DO 11 M=1,(N-1)
      TIMINT=(DATA((M+1),1)-DATA(M,1))/60.0
      RESULT((M+1),3)=RESULT((M+1),3)*CFACT
      RESULT((M+1),4)=RESULT((M+1),3)-RESULT((M+1),1)
      RESULT((M+1),5)=RESULT(M,5)+RESULT((M+1),4)
      RESULT((M+1),6)=RESULT((M+1),4)/TIMINT
      GSITWO=GSITWO+RESULT((M+1),3)
   11 CONTINUE
      WRITE(6,104)
      WRITE(6,102)((TITLE(I,J),J=1,15),I=1,3)
      WRITE(6,92)
   92 FORMAT(1H0,5X,32HTABLE OF CORRECTED DATA RESULTS.)
```

```
      WRITE(6,50)
      WRITE(6,51)
      WRITE(6,52)

      WRITE(6,94)((DATA(M,J),J=1,6),(RESULT(M,K),K=1,7),M=1,N)
      WRITE(6,104)
      WRITE(6,102)((TITLE(I,J),J=1,15),I=1,3)
      WRITE(6,91)GSITWO
   91 FORMAT(1H0,5X,12HTOT.GAS ABS=,F6.2)
    8 NEXPT=NEXPT+1
      K=0
   40 K=K+1
      J=K+1
      X(K)=DATA((K+1),1)
      Y(K)=RESULT((K+1),6)
      IF(J.LT.N)GO TO 40
      WRITE(6,104)
      WRITE(6,102)((TITLE(I,J),J=1,15),I=1,3)
      WRITE(6,41)K
   41 FORMAT(1H0,5X,I3,25H GRAPH READINGS RECORDED.)
      FLOMAX=0.0
      DO 30 M=1,K
      IF(Y(M).GT.FLOMAX)FLOMAX=Y(M)
   30 CONTINUE
      WRITE(6,42)FLOMAX
   42 FORMAT(1H0,5X,14HMAX.ABS.RATE =,F8.3)
      IF(FLOMAX.LE.5.0)GO TO 28
      IF(FLOMAX.LE.10.0)GO TO 31
      IF(FLOMAX.LE.20.0)GO TO 32
      IF(FLOMAX.LE.30.0)GO TO 33
      IF(FLOMAX.LE.40.0)GO TO 34
      IF(FLOMAX.LE.50.0)GO TO 35
      IF(FLOMAX.LE.60.0)GO TO 36
      IF(FLOMAX.LE.70.0)GO TO 37
      IF(FLOMAX.LE.80.0)GO TO 38
      IF(FLOMAX.LF.90.0)GO TO 39
   28 CALL REGION(0.,200.,0.,5.)
      GO TO 29
   31 CALL REGION(0.,200.,0.,10.)
      GO TO 29
   32 CALL REGION(0.,200.,0.,20.)
      GO TO 29
   33 CALL REGION(0.,200.,0.,30.)
      GO TO 29
   34 CALL REGION(0.,200.,0.,40.)
      GO TO 29
   35 CALL REGION(0.,200.,0.,50.)
      GO TO 29
   36 CALL REGION(0.,200.,0.,60.)
      GO TO 29
   37 CALL REGION(0.,200.,0.,70.)
```

```
      GO TO 29
   38 CALL REGION(0.,200.,0.,80.)
      GO TO 29
   39 CALL REGION(0.,200.,0.,90.)
   29 CALL LIMITS(2.5,22.5,5.,20.)
C     THESE CALLS DEFINE THE RANGE OF UNITS AND SPACE LIMITATION OF
C     THE GRAPH
      CALL BORDER
      CALL AXESSI(10.0,2.0)
      CALL CRSET(0)
      CALL CRSIZE(HEIGHT)
      CALL PLOTCL(5.0,39.0,31HRATE OF ABSORPTION VERSUS TIME.,31)
      CALL GRPHPT(X,Y,1,K,62)
      CALL FRAME
      IF(EXTRA.NE.-100.0)GO TO 7
      WRITE(6,104)
      WRITE(6,90)NEXPT
   90 FORMAT(1H0,5X,I3,16HEXPTS PROCESSED.)
      CALL GREND
      STOP
      END



      FINISH
```

```
  OUTPUT FROM THESISLIST OF  JC1
------------------------------------------



PROG LOAD BINDBPF1,TIME1MINS,*CR5 DBSHP%A,*CR3 DBE1,*CP1 DBSHP%AR1(WRIT
1A PROG LOAD BINDBPF2,TIME1MINS,*CR5 DBSHP%A,*CR3 DBE1,*CP1 DBSHP%AR1(WR
2A PROG LOAD BINDBPF3,TIME1MINS,*CR5 DBSHP%A,*CR3 DBE1,*CP1 DBSHP%AR1(WR
3A S DBSHP%AR1
S DBSHP%AA2
S DBSHP%AB2
S DBSHP%AC2
ENDJOB
```

```
OUTPUT FROM THESISLIST OF  DEPF2
-----------------------------------------
```

```
      PROGRAM(DILPLTS2)
      INPUT3=CR3
      INPUT4=CR4
      INPUT5=CR5
      OUTPUT6=LPO
      OUTPUT7=CP1
      OUTPUT8=CP2
      END
```

```
      MASTERMAIN
C     DILATOMETRY DATA PROGRAM
C     TIME=DATA(N,1)
C     CATHETOMETER READINGS=DATA(N,2)
C     RESULT(N,1)=PER CENT CONTRACTION
C     RESULT(N,2)=PER CENT CONVERSION
C     RESULT(N,3)=LOG.10(100-P.C.CONV.)
C     RESULT(N,4)=AVERAGE TIME
C     RESULT(N,5)=TIME INCREMENT
C     RESULT(N,6)=CONTRACTION INCREMENT
C     RESULT(N,7)=RATE OF CONTRACTION
C     RESULT(N,8)=RATE OF POLYMERISATION
C     YIELD=WT.OF P.S.IN GMS.
C     VMONMR=INITIAL VOLUME OF STYRENE.
C     ALKYL=VOLUME OF ALUMINIUM ALKYL ADDED.
C     CATLST=MLS. OF TI. TRICHLORIDE CATALYST ADDED.
C     TOTVOL=TOTAL VOLUME OF REACTANTS.
      DIMENSION DATA(100,6),RESULT(100,12),TITLE(3,15),X(100),Y(100)
      NEXPT=0
    7 WRITE(6,104)
  104 FORMAT(1H1,29H POLYMERISATION DATA PROGRAM.//)
      READ(5,103)((TITLE(I,J),J=1,15),I=1,3)
  103 FORMAT(10A8)
      WRITE(6,102)((TITLE(I,J),J=1,15),I=1,3)
  102 FORMAT(1H0,15A8)
      READ(5,101)YIELD
  101 FORMAT(F10.0)
      READ(5,101)VMONMR
      READ(5,101)ALKYL
      READ(5,101)CATLST
      READ(5,101)TOTVOL
      N=0
  100 N=N+1
      READ(5,99)(DATA(N,J),J=1,6)
   99 FORMAT(6F10.0)
      IF(DATA(N,1).NE.-100.0)GO TO 100
      N=N-1
      WRITE(6,98)N
   98 FORMAT(1H0,5X,I3,24H DATA READINGS RECORDED.)
      WRITE(6,97)
   97 FORMAT(1H0,5X,23HTABLE OF DATA READINGS.//9X,4HTIME,4X,5HMETER/8X,
     16H(MINS),2X,7HREADING/16X,6H(CMS.)/)
      WRITE(6,96)((DATA(M,J),J=1,2),M=1,N)
   96 FORMAT(7X,F8.3,1X,F8.4)
      DMAX=0.0
      DO 10  M=1,N
      IF(DATA(M,2).LT.DMAX)GO TO 1
      DMAX=DATA(M,2)
      NDATA=M
    1 CONTINUE
```

```
10 CONTINUE
   TCTRCT=DMAX-DATA(N,2)
   WRITE(6,79)DMAX,DATA(N,2),TCTRCT
79 FORMAT(1H0,5X,14HMAX. READING =,F8.4//6X,14HMIN. READING =,F8.4//
  1X,19HTOTAL CONTRACTION =,F8.4)
   WRITE(6,50)YIELD,VMONMR,ALKYL,CATLST,TOTVOL
50 FORMAT(1H0,5X,5HYIELD,10X,F6.3,17H GMS. OF POLYMER.//7X,10HREACTA
  1TS./5X,7HMONOMER,8X,F6.3,17H CCS. OF STYRENE./5X,5HALKYL,10X,F6.
  213H CCS. OF TAA./5X,8HCATALYST,7X,F6.2,31H MLS. OF MG.RED.TI.TRIC
  3LORIDE./5X,12HTOTAL VOLUME,3X,F6.3,5H CCS.//)
   WMONMR=VMONMR*0.906
   TCONV=100.0*YIELD/WMONMR
   FACT=TCONV/TCTRCT
   WRITE(6,78)WMONMR
78 FORMAT(1H0,5X,9HMONOMER =,F8.4,5H GMS.)
   WRITE(6,51)TCONV
51 FORMAT(1H0,5X,26HTOTAL PER CENT CONVERSION ,F6.2)
   WRITE(6,74)FACT
74 FORMAT(1H0,5X,18HCONVERSION FACTOR=,F10.6)
   DO 9 M=1,N
   RESULT(M,1)=DMAX-DATA(M,2)
   IF(M.LT.NDATA)RESULT(M,1)=0.0
   RESULT(M,2)=FACT*RESULT(M,1)
   RESULT(M,3)=ALOG10(100.0-RESULT(M,2))
 9 CONTINUE
   WRITE(6,104)
   WRITE(6,102)((TITLE(I,J),J=1,15),I=1,3)
   WRITE(6,95)
95 FORMAT(1H0,5X,22HTABLE OF DATA RESULTS.)
   WRITE(6,77)
77 FORMAT(1H0,8X,4HTIME,4X,5HMETER,3X,8HCONTRCTN,1X,8HCONVERSN,3X,3HL
  1OG)
   WRITE(6,76)
76 FORMAT(1H0,7X,6H(MINS),2X,7HREADING,3X,6H(CMS.),4X,4H(%.),3X,8H(1
  10-%C))
   WRITE(6,75)
75 FORMAT(1H0,15X,6H(CMS.)/)
   WRITE(6,94)((DATA(M,J),J=1,2),(RESULT(M,K),K=1,3),M=1,N)
94 FORMAT(7X,F8.3,1X,F8.4,1X,F8.4,1X,F8.4,1X,F8.4)
   RFACT=10.0*WMONMR*FACT/TOTVOL*104.16
   WRITE(6,73)RFACT
73 FORMAT(1H0,5X///6X,23HRATE CONVERSION FACTOR=,F15.6)
   DO 11 M=1,(N-2)
   RESULT((M+1),4)=(DATA((M+2),1)+DATA(M,1))/2.0
   RESULT((M+1),5)=DATA((M+2),1)-DATA(M,1)
   RESULT((M+1),6)=RESULT((M+2),1)-RESULT(M,1)
   RESULT((M+1),7)=RESULT((M+1),6)/RESULT((M+1),5)
   RESULT((M+1),8)=RESULT((M+1),7)*RFACT
11 CONTINUE
   WRITE(6,104)
```

```
      WRITE(6,102)((TITLE(I,J),J=1,15),I=1,3)
      WRITE(6,95)
      WRITE(6,71)
   71 FORMAT(1H0,6X,8HAVERAGED,3X,4HTIME,3X,8HCONTRCTN,3X,4HRATE,6X,4HR
     1TE)
      WRITE(6,70)
   70 FORMAT(1H0,8X,4HTIME,3X,8HINCREMNT,1X,8HINCREMNT,1X,8HCONTRCTN,2X,
     18HPOLYMSTN)
      WRITE(6,69)
   69 FORMAT(1H0,7X,6H(MINS),3X,6H(MINS),3X,6H(CMS.),2X,8H(CM/MIN),1X,1
     1H(MOL/L/MN))
      WRITE(6,72)((RESULT(M,K),K=4,8),M=1,N)
   72 FORMAT(7X,F8.3,1X,F8.3,1X,F8.4,1X,F8.4,1X,F10.4)
      WRITE(7,103)((TITLE(I,J),J=1,15),I=1,3)
      WRITE(7,68)((DATA(M,J),J=1,2),(RESULT(M,K),K=1,3),M=1,N)
   68 FORMAT(F10.3,F10.4,F10.4,F10.4,F10.4)
      FLAG=0.0-100.0
      WRITE(7,66)FLAG
   66 FORMAT(F10.1/)
      WRITE(8,103)((TITLE(I,J),J=1,15),I=1,3)
      WRITE(8,67)((RESULT(M,K),K=4,8),M=1,N)
   67 FORMAT(F10.3,F10.3,F10.4,F10.4,F10.4)
      WRITE(8,66)FLAG
      NEXPT=NEXPT+1
      READ(3,101)EXTRA
      IF(EXTRA.NE.-100.0)GO TO 7
      WRITE(6,104)
      WRITE(6,90)NEXPT
   90 FORMAT(1H0,5X,I3,16HEXPTS PROCESSED.)
      STOP
      END




      FINISH
```

```
 OUTPUT FROM THESISLIST OF  DBGPP4
-----------------------------------


      PROGRAM(PLOTTER)
      INPUT2=CR2
      INPUT3=CR3
      INPUT4=CR4
      INPUT5=CR5
      OUTPUT6=LP0
      TRACE2
      END


      MASTERMAIN
C     POLYMERISATION RESULTS PLOTTING PROGRAM
C     TIME=DATA(N,1)
C     CATHETOMETER READINGS=DATA(N,2)
C     RESULT(N,1)=PER CENT CONTRACTION
C     RESULT(N,2)=PER CENT CONVERSION
C     RESULT(N,3)=LOG.10(100-P.C.CONV.)
C     RESULT(N,4)=AVERAGE TIME
C     RESULT(N,5)=TIME INCREMENT
C     RESULT(N,6)=CONTRACTION INCREMENT
C     RESULT(N,7)=RATE OF CONTRACTION
C     RESULT(N,8)=RATE OF POLYMERISATION
      DIMENSION DATA(100,6),RESULT(100,12),TITLE(3,15),X(100),Y(100),PHR
     1ASE1(10),PHRASE2(10),PHRASE3(10),PHRASE4(10),PHRASE5(10),PHRASE6(1
     20),PHRASE7(10),PHRASE8(10),PHRASE9(10)
      EXTERNAL CUPY
      READ(2,97)HEIGHT
      WRITE(6,20)HEIGHT
   20 FORMAT(1H0,5X,7HHEIGHT=,F6.2)
      NEXPT=0
    7 WRITE(6,104)
  104 FORMAT(1H1,29H POLYMERISATION DATA PROGRAM.//)
      READ(4,103)((TITLE(I,J),I=1,3),J=1,15)
  103 FORMAT(10A8)
      WRITE(6,102)((TITLE(I,J),I=1,3),J=1,15)
  102 FORMAT(1H0,15A8)
      N=0
  100 N=N+1
      READ(4,68)(DATA(N,J),J=1,2),(RESULT(N,K),K=1,3)
   68 FORMAT(5F10.0)
      IF(DATA(N,1).NE.-100.0)GO TO 100
      N=N-1
      WRITE(6,98)N
   98 FORMAT(1H0,5X,I3,24H DATA READINGS RECORDED.)
      WRITE(6,95)
   95 FORMAT(1H0,5X,22HTABLE OF DATA RESULTS.)
      WRITE(6,77)
   77 FORMAT(1H0,3X,4HTIME,4X,5HMETER,3X,8HCONTRCTN,1X,8HCONVERSN,3X,3HL
     1OG)
      WRITE(6,76)
   76 FORMAT(1H0,7X,6H(MINS),2X,7HREADING,3X,6H(CMS.),4X,4H(%.),3X,8H(10
     10-%C))
      WRITE(6,75)
   75 FORMAT(1H0,15X,6H(CMS.)/)
      WRITE(6,94)((DATA(M,J),J=1,2),(RESULT(M,K),K=1,3),M=1,N)
   94 FORMAT(7X,F8.3,1X,F8.4,1X,F8.4,1X,F8.4,1X,F8.4)
      READ(5,103)((TITLE(I,J),I=1,3),J=1,15)
      WRITE(6,104)
      WRITE(6,102)((TITLE(I,J),I=1,3),J=1,15)
      M=0
```

```
101  M=M+1
      READ(5,68)(RESULT(M,K),K=4,8)
      IF(RESULT(M,4).NE.-100.0)GO TO 101
      M=M-1
      WRITE(6,99)M
 99   FORMAT(1H0,5X,I3,23H DATA RESULTS RECORDED.)
      WRITE(6,95)
      WRITE(6,71)
 71   FORMAT(1H0,6X,8HAVERAGED,3X,4HTIME,3X,8HCONTRCTN,3X,4HRATE,6X,4HRA
     1TE)
      WRITE(6,70)
 70   FORMAT(1H0,3X,4HTIME,3X,8HINCREMNT,1X,8HINCREMNT,1X,8HCONTRCTN,2X,
     18HPOLYMSTN)
      WRITE(6,69)
 69   FORMAT(1H0,7X,6H(MINS),3X,6H(MINS),3X,6H(CMS.),2X,8H(CM/MIN),1X,10
     1H(MOL/L/MN))
      WRITE(6,72)((RESULT(J,K),K=4,8),J=1,M)
 72   FORMAT(7X,F8.3,1X,F8.3,1X,F8.4,1X,F8.4,1X,F10.4)
  8   NEXPT=NEXPT+1
      CALL COPY(24,PHRASE1(1),1,TITLE(1,1),1)
      CALL COPY(16,PHRASE1(4),1,TITLE(1,5),1)
      DATA PHRASE1(6)/'                                         '/
      DATA PHRASE2(1)/'RATE OF POLYMERISATION VERSUS TIME.
     1                                 '/
      DATA PHRASE3(1)/'RATE.
     1                                 '/
      DATA PHRASE4(1)/'TIME.
     1                                 '/
      DATA PHRASE5(1)/'CONVERSION VERSUS TIME.
     1                                 '/
      DATA PHRASE6(1)/'CONVSN.
     1                                 '/
      DATA PHRASE7(1)/'LOG 10(100 P.C. - P.C.CONV.) VERSUS TIME.
     1                                 '/
      DATA PHRASE8(1)/'LOG 10
     1                                 '/
      DATA PHRASE9(1)/'(100-CONV.)
     1                                 '/
      K=0
      L=0
 40   K=K+1
      L=L+1
      J=L+1
      X(K)=RESULT((K+1),4)
      Y(K)=RESULT((K+1),8)
      IF(Y(K).LT.0.0)Y(K)=0.0
      IF(J.GT.1.AND.X(K).LE.0.0)K=K-1
      IF(J.LT.M)GO TO 40
      WRITE(6,104)
      WRITE(6,102)((TITLE(I,J),I=1,3),J=1,15)
```

```
      WRITE(6,41)K
   41 FORMAT(1H0,5X,I3,25H GRAPH READINGS RECORDED.)
      FLOMAX=0.0
      DO 30 L=1,K
      IF(Y(L).GT.FLOMAX)FLOMAX=Y(L)
   30 CONTINUE
      WRITE(6,42)FLOMAX
   42 FORMAT(1H0,5X,14HMAX.PSN.RATE =,F8.3)
      LINE=0
   43 CALL PSPACE(0.160,0.960,0.120,0.720)
C     THESE CALLS DEFINE THE RANGE OF UNITS AND SPACE LIMITATION OF
C     THE GRAPH
      IF(FLOMAX.LE.5.0)GO TO 28
      IF(FLOMAX.LE.10.0)GO TO 31
      IF(FLOMAX.LE.20.0)GO TO 32
      IF(FLOMAX.LE.30.0)GO TO 33
      IF(FLOMAX.LE.40.0)GO TO 34
      IF(FLOMAX.LE.50.0)GO TO 35
      IF(FLOMAX.LE.60.0)GO TO 36
      IF(FLOMAX.LE.70.0)GO TO 37
      IF(FLOMAX.LE.80.0)GO TO 38
      IF(FLOMAX.LE.90.0)GO TO 39
   28 CALL MAP(0.,1500.,0.,5.)
      GO TO 29
   31 CALL MAP(0.,1500.,0.,10.)
      GO TO 29
   32 CALL MAP(0.,1500.,0.,20.)
      GO TO 29
   33 CALL MAP(0.,1500.,0.,30.)
      GO TO 29
   34 CALL MAP(0.,1500.,0.,40.)
      GO TO 29
   35 CALL MAP(0.,1500.,0.,50.)
      GO TO 29
   36 CALL MAP(0.,1500.,0.,60.)
      GO TO 29
   37 CALL MAP(0.,1500.,0.,70.)
      GO TO 29
   38 CALL MAP(0.,1500.,0.,80.)
      GO TO 29
   39 CALL MAP(0.,1500.,0.,90.)
   29 CALL SCALES
      CALL GRATIC
      CALL BORDER
      CALL CTRSET(4)
      CALL PTPLOT(X,Y,1,K,50)
      IF(LINE.EQ.1)CALL CURVEO(X,Y,1,K)
      CALL PSPACE(0.,1.188,0.,0.84)
      CALL MAP(0.,29.7,0.,21.)
      CALL BORDER
```

```
      GO TO 129
  132 CALL MAP(0.,1500.,0.,20.)
      GO TO 129
  133 CALL MAP(0.,1500.,0.,30.)
      GO TO 129
  134 CALL MAP(0.,1500.,0.,40.)
      GO TO 129
  135 CALL MAP(0.,1500.,0.,50.)
      GO TO 129
  136 CALL MAP(0.,1500.,0.,60.)
      GO TO 129
  137 CALL MAP(0.,1500.,0.,70.)
      GO TO 129
  138 CALL MAP(0.,1500.,0.,80.)
      GO TO 129
  139 CALL MAP(0.,1500.,0.,90.)
  129 CALL SCALES
      CALL GRATIC
      CALL BORDER
      CALL CTRSET(4)
      CALL PTPLOT(X,Y,1,K,51)
      IF(LINE.EQ.1)CALL CURVEO(X,Y,1,K)
      CALL PSPACE(0.,1.188,0.,0.84)
      CALL MAP(0.,29.7,0.,21.)
      CALL BORDER
      CALL CTRSET(1)
      CALL CTRSIZ(HEIGHT)
      CALL UNDLIN (2)
      CALL PLOTCS(6.0,18.6,PHRASE5,80)
      CALL UNDLIN(1)
      CALL PLOTCS(6.,18.1,PHRASE1,30)
      CALL UNDLIN(0)
      CALL PLOTCS(1.5,15.5,PHRASE6,80)
      CALL PLOTCS(22.0,2.0,PHRASE4,80)
      CALL FRAME
      CALL FRAME
      LINE=LINE+1
      IF(LINE.EQ.1)GO TO 143
      K=0
      J=0
   48 K=K+1
      J=J+1
      X(K)=DATA(K,1)
      Y(K)=RESULT(K,3)
      IF(Y(K).LT.0.0)Y(K)=0.0
      IF(J.LT.M)GO TO 48
      WRITE(6,104)
      WRITE(6,102)((TITLE(I,J),I=1,3),J=1,15)
      WRITE(6,52)K
   52 FORMAT(1H0,5X,I3,25H GRAPH READINGS RECORDED.)
```

```
      XMIN=2.0
      DO 51 L=1,K
      IF(Y(L).LT.XMIN)XMIN=Y(L)
   51 CONTINUE
      WRITE(6,53)XMIN
   53 FORMAT(1H0,5X,14HMIN. READING =,F8.3)
      LINE=0
  243 CALL PSPACE(0.160,0.960,0.120,0.720)
C     THESE CALLS DEFINE THE RANGE OF UNITS AND SPACE LIMITATION OF
C     THE GRAPH
      IF(XMIN.GE.1.7)GO TO 228
      IF(XMIN.GE.1.5)GO TO 231
      IF(XMIN.GE.1.3)GO TO 232
      IF(XMIN.GE.1.0)GO TO 233
      IF(XMIN.GE.0.7)GO TO 234
      IF(XMIN.GE.0.5)GO TO 235
      IF(XMIN.GE.0.3)GO TO 236
      IF(XMIN.GE.0.2)GO TO 237
      IF(XMIN.GE.0.1)GO TO 238
      IF(XMIN.GE.0.0)GO TO 239
  228 CALL MAP(0.,1500.,1.7,2.)
      GO TO 229
  231 CALL MAP(0.,1500.,1.5,2.)
      GO TO 229
  232 CALL MAP(0.,1500.,1.3,2.)
      GO TO 229
  233 CALL MAP(0.,1500.,1.0,2.)
      GO TO 229
  234 CALL MAP(0.,1500.,0.7,2.)
      GO TO 229
  235 CALL MAP(0.,1500.,0.5,2.)
      GO TO 229
  236 CALL MAP(0.,1500.,0.3,2.)
      GO TO 229
  237 CALL MAP(0.,1500.,0.2,2.)
      GO TO 229
  238 CALL MAP(0.,1500.,0.1,2.)
      GO TO 229
  239 CALL MAP(0.,1500.,0.,2.)
  229 CALL SCALES
      CALL GRATIC
      CALL BORDER
      CALL CTRSET(4)
      CALL PTPLOT(X,Y,1,K,45)
      IF(LINE.EQ.1)CALL CURVEO(X,Y,1,K)
      CALL PSPACE(0.,1.183,0.,0.84)
      CALL MAP(0.,29.7,0.,21.)
      CALL BORDER
      CALL CTRSET(1)
      CALL CTRSIZ(HEIGHT)
```

```
      CALL UNDLIN(2)
      CALL PLOTCS(6.0,16.6,PHRASE7,80)
      CALL UNDLIN(1)
      CALL PLOTCS(6.,18.1,PHRASE1,80)
      CALL UNDLIN(0)
      CALL PLOTCS(1.0,15.5,PHRASE8,80)
      CALL PLOTCS(0.5,15.0,PHRASE9,80)
      CALL PLOTCS(22.0,2.0,PHRASE4,80)
      CALL FRAME
      CALL FRAME
      LINE=LINE+1
      IF(LINE.EQ.1)GO TO 243
      READ(3,97)EXTRA
   97 FORMAT(F10.0)
      IF(EXTRA.NE.-100.0)GO TO 7
      WRITE(6,104)
      WRITE(6,90)NEXPT
   90 FORMAT(1H0,5X,I3,16HEXPTS PROCESSED.)
   45 CALL GREND
      STOP
      END
```

```
      FINISH
```

```
 OUTPUT FROM THESISLIST OF  DRSHP42
--------------------------------------




RUN NUMBER:SHP/42                                 DATE:14/5/75
DILATOMETER NO.:6                                                              TEMPE
          TOTAL VOLUME:60MLS.                               43MLS. STYRENE.
          POLYMERISATION TIME:24HRS.                                  0.21MLS. TNO
          34.5MLS. DDGC/11 CATALYST.
4.2248
43.0
0.21
34.5
60.0
0.0        12.765
5.0        13.240
10.0       13.237
15.0       13.232
20.0       13.226
25.0       13.217
30.0       13.207
35.0       13.197
40.0       13.188
45.0       13.181
50.0       13.173
55.0       13.166
60.0       13.159
65.0       13.152
70.0       13.144
75.0       13.134
80.0       13.127
85.0       13.120
90.0       13.113
95.0       13.107
100.0      13.100
105.0      13.092
110.0      13.085
120.0      13.074
130.0      13.058
140.0      13.046
150.0      13.036
160.0      13.027
170.0      13.014
180.0      13.003
200.0      12.982
210.0      12.972
240.0      12.933
270.0      12.905
300.0      12.879
1080.0     12.336
1140.0     12.301
1200.0     12.268
1230.0     12.252
1260.0     12.237
```

```
1290.0     12.222
1320.0     12.206
1350.0     12.191
1380.0     12.176
1440.0     12.145
-100.0
```

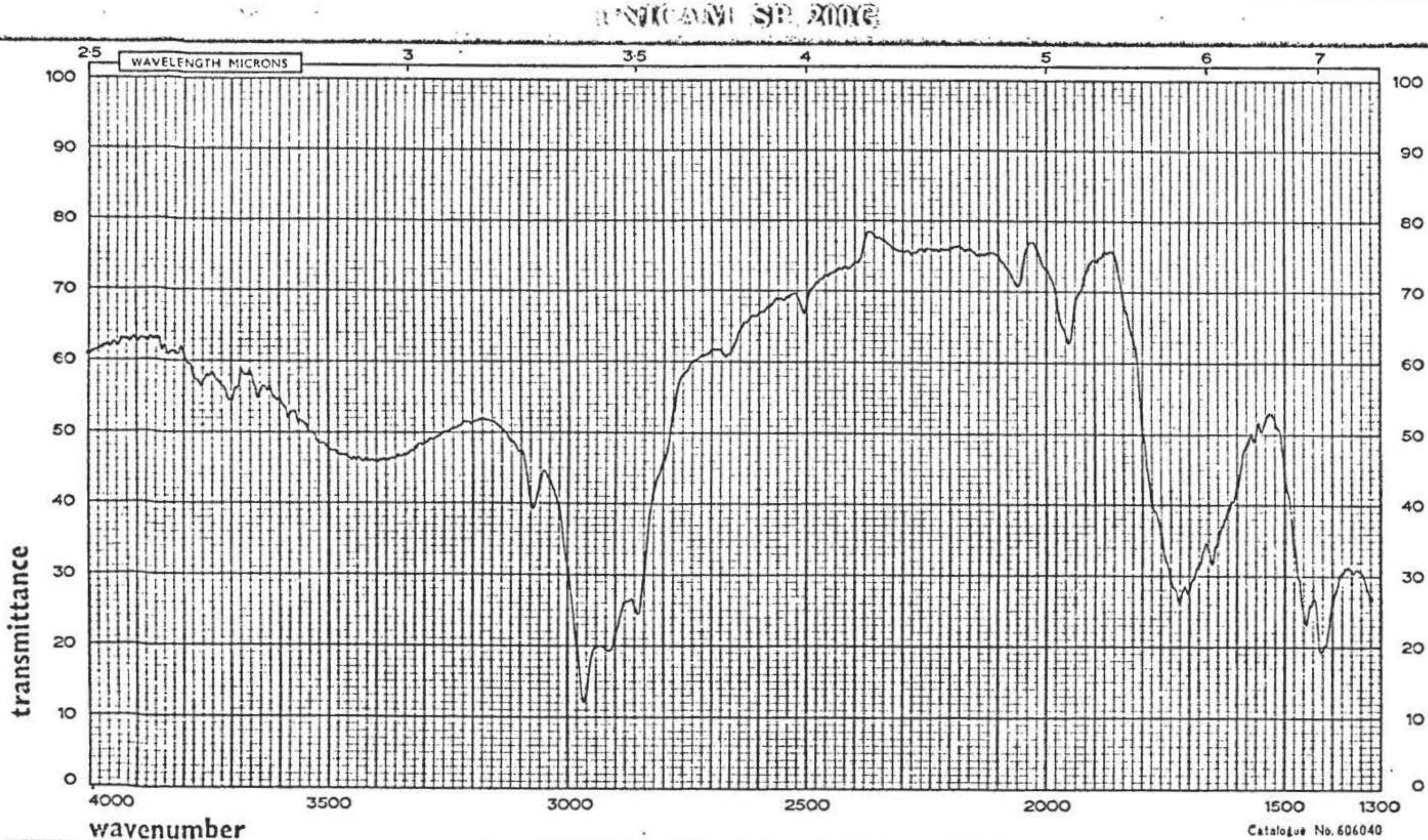
```
 OUTPUT FROM THESISLIST OF  DBE1
---------------------------------------



-100.0
```

APPENDIX II

Spectroscopy



Catalogue No. 606040

ALIGN WITH INDEX
ON THE RECORDER

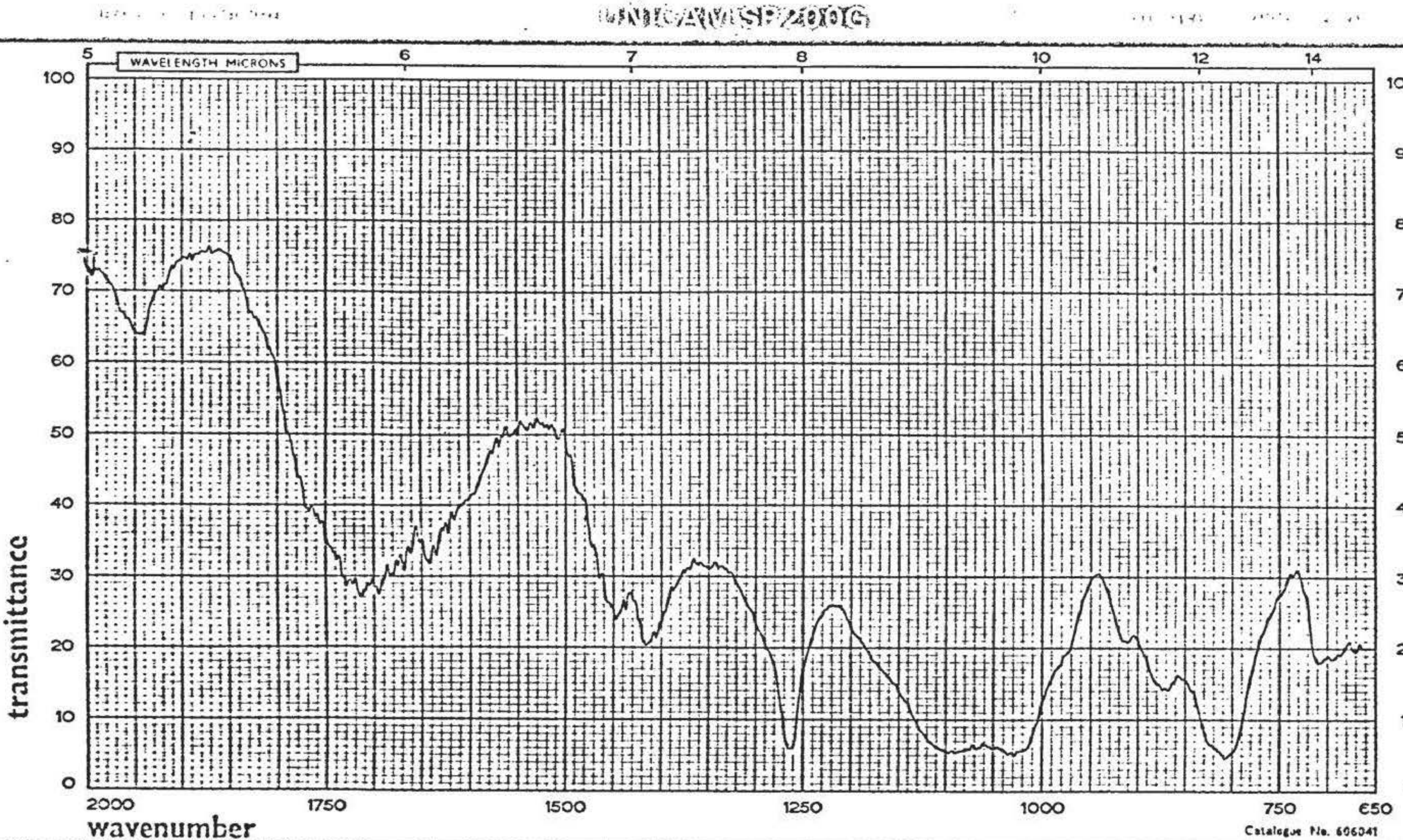
Film of BE 2
cast from the hot iso-amyl acetate fraction.

FORMULA

PHASE
THICKNESS
REMARKS

SCAN SPEED
DATE
OPERATOR

REFERENCE



ALIGN WITH INDEX
ON THE RECORDER

Film of BE2 cast from
the hot isoamyl acetate
fraction.

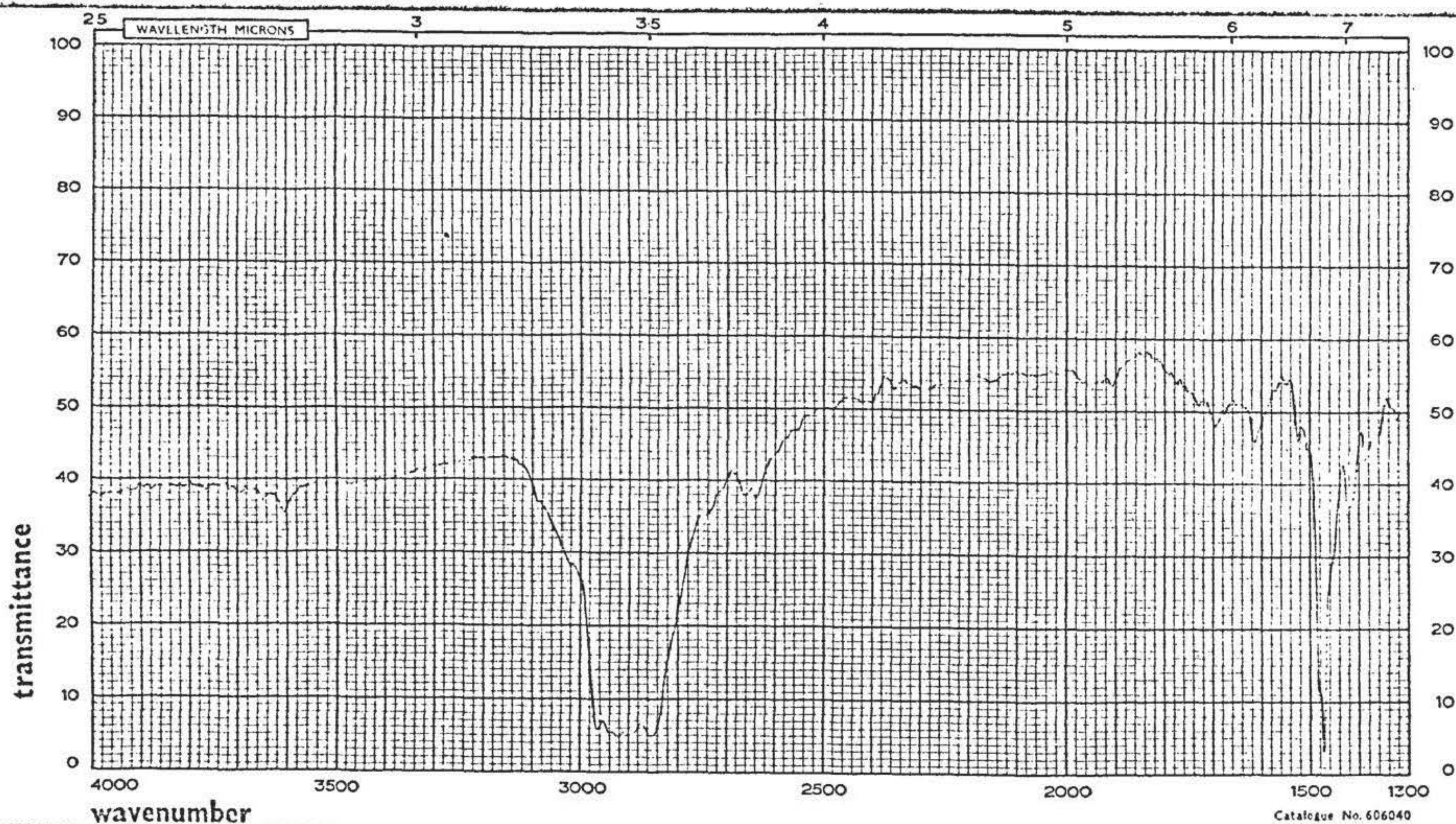
FORMULA

PHASE
THICKNESS
REMARKS

SCAN SPEED
DATE
OPERATOR

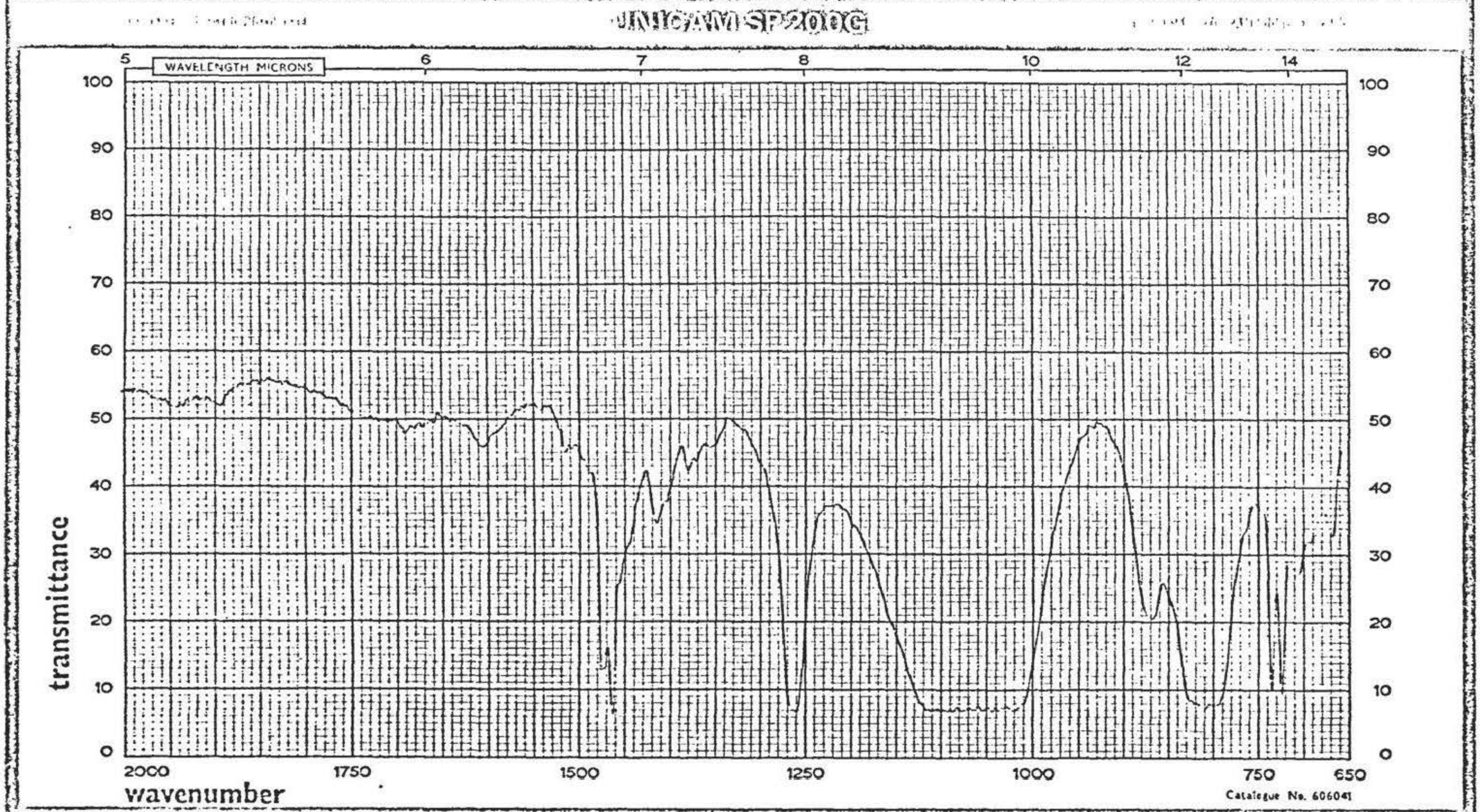
REFERENCE

UNICAM SP 200G



Catalogue No. 606040

ALIGN WITH INDEX ON THE RECORDER ∇	SAMPLE Film of SE1 cast from the REFERENCE Xylene fraction.	FORMULA	PHASE THICKNESS REMARKS	SCAN SPEED DATE OPERATOR	REFERENCE



ALIGN WITH INDEX ON THE RECORDER

SAMPLE Film of SE 1 cast from the xylene fraction.

REFERENCE

FORMULA

PHASE

THICKNESS

REMARKS

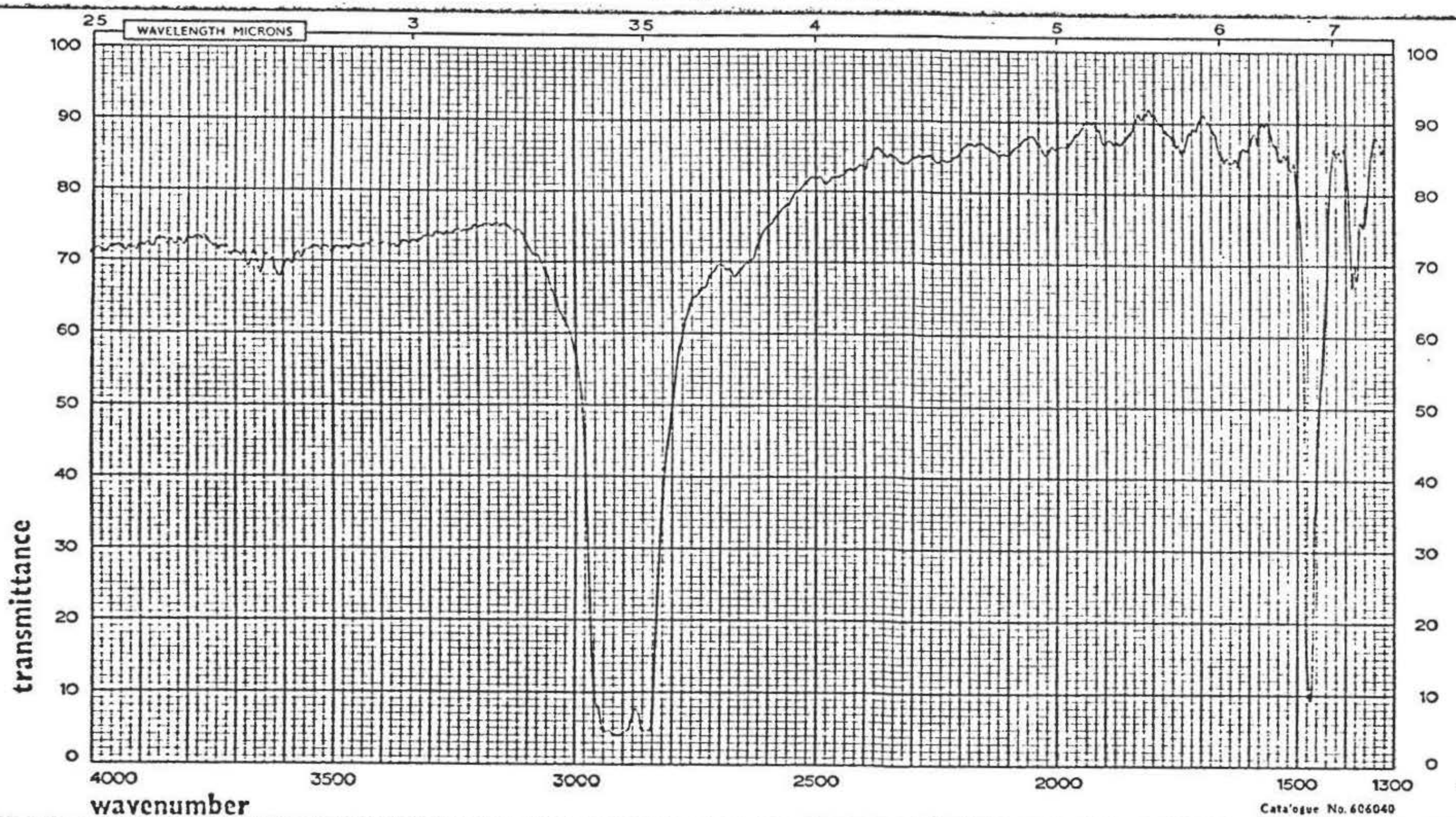
SCAN SPEED

DATE

OPERATOR

REFERENCE

UNICAM SP 200G



Catalogue No. 606040

ALIGN WITH INDEX
ON THE RECORDER

SAMPLE i E. film (taken from plastic bag)
REFERENCE

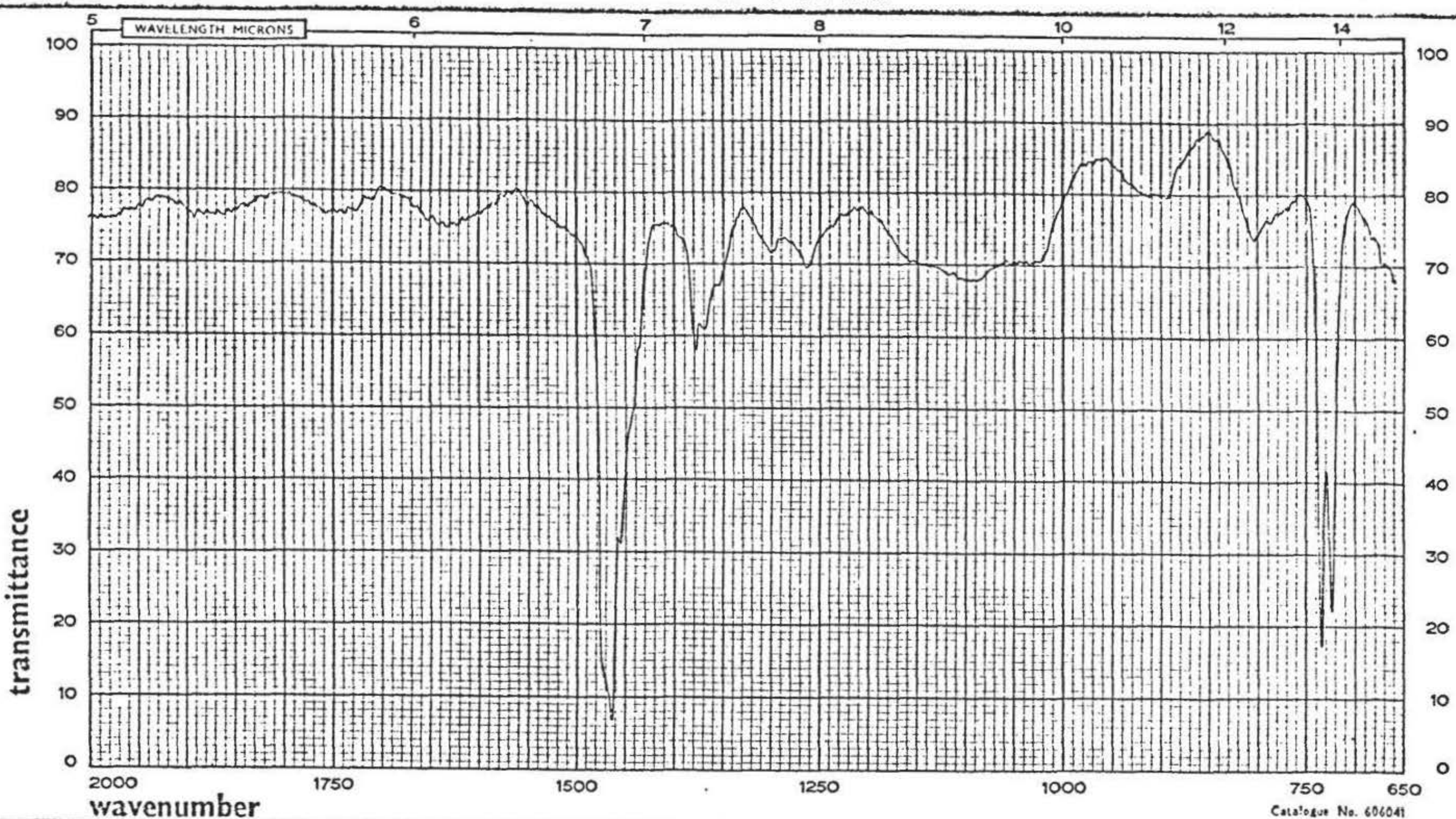
FORMULA

PHASE
THICKNESS
REMARKS

SCAN SPEED
DATE
OPERATOR

REFERENCE

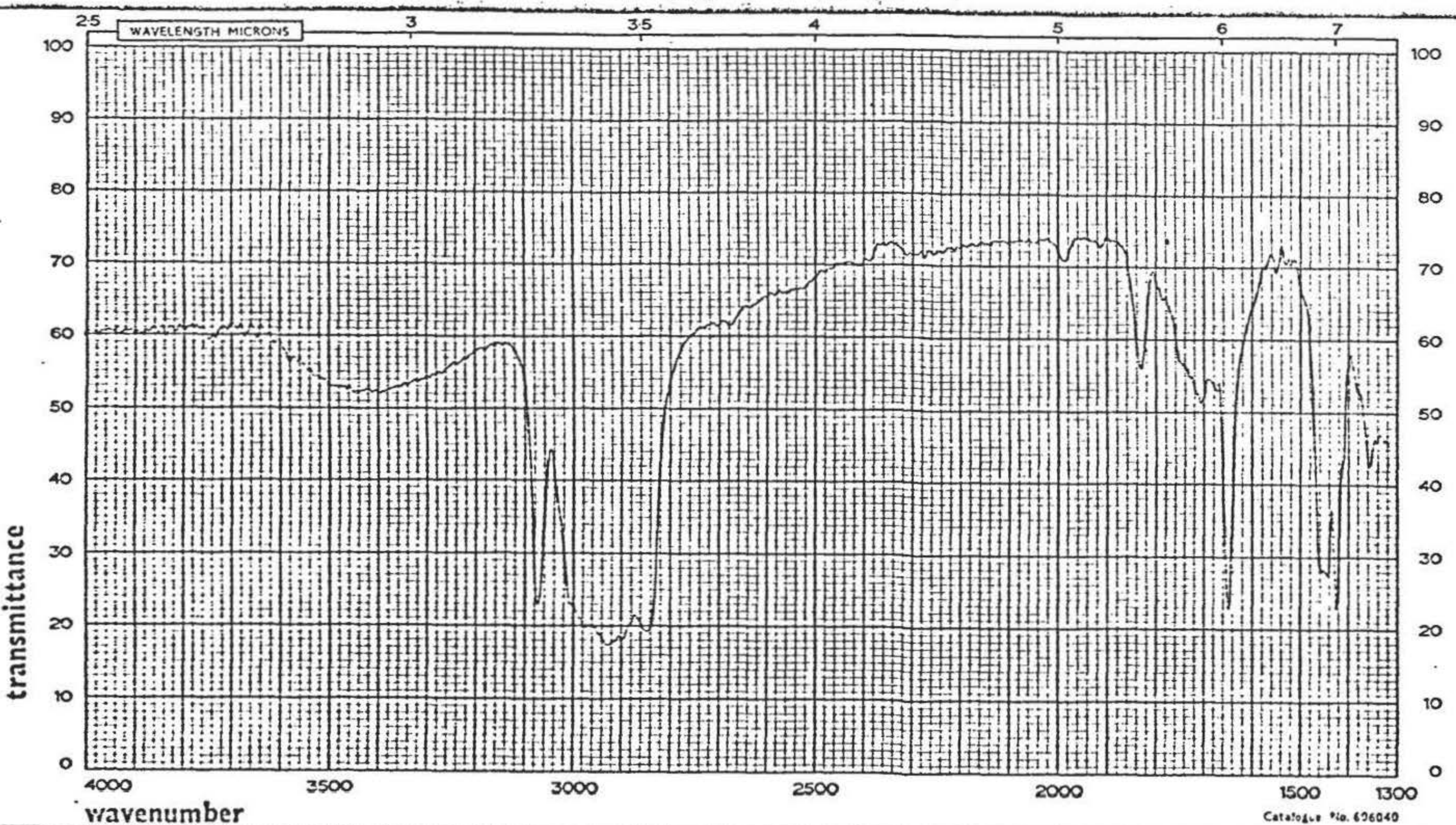
UNICAM SP200G



Catalogue No. 606041

ALIGN WITH INDEX ON THE RECORDER ∇	SAMPLE Polyethylene film REFERENCE (taken from plastic bag)	FORMULA	PHASE THICKNESS REMARKS	SCAN SPEED DATE OPERATOR	REFERENCE

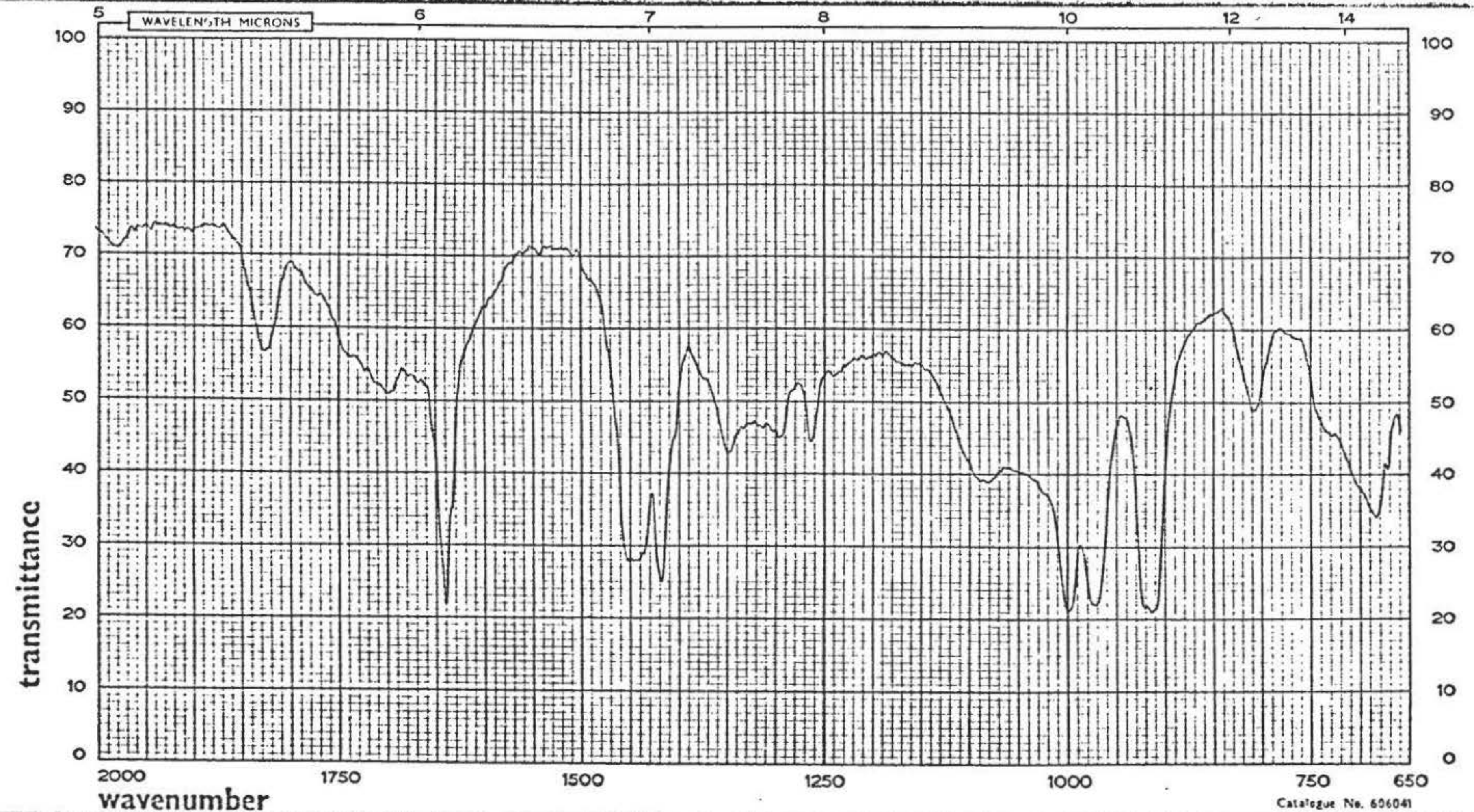
UNICAM SP. 200G



Catalogue No. 696040

ALIGN WITH INDEX ON THE RECORDER ∇	SAMPLE Pure polybutadiene film. REFERENCE (Cast from CE)	FORMULA	PHASE THICKNESS REMARKS	SCAN SPEED DATE OPERATOR	REFERENCE

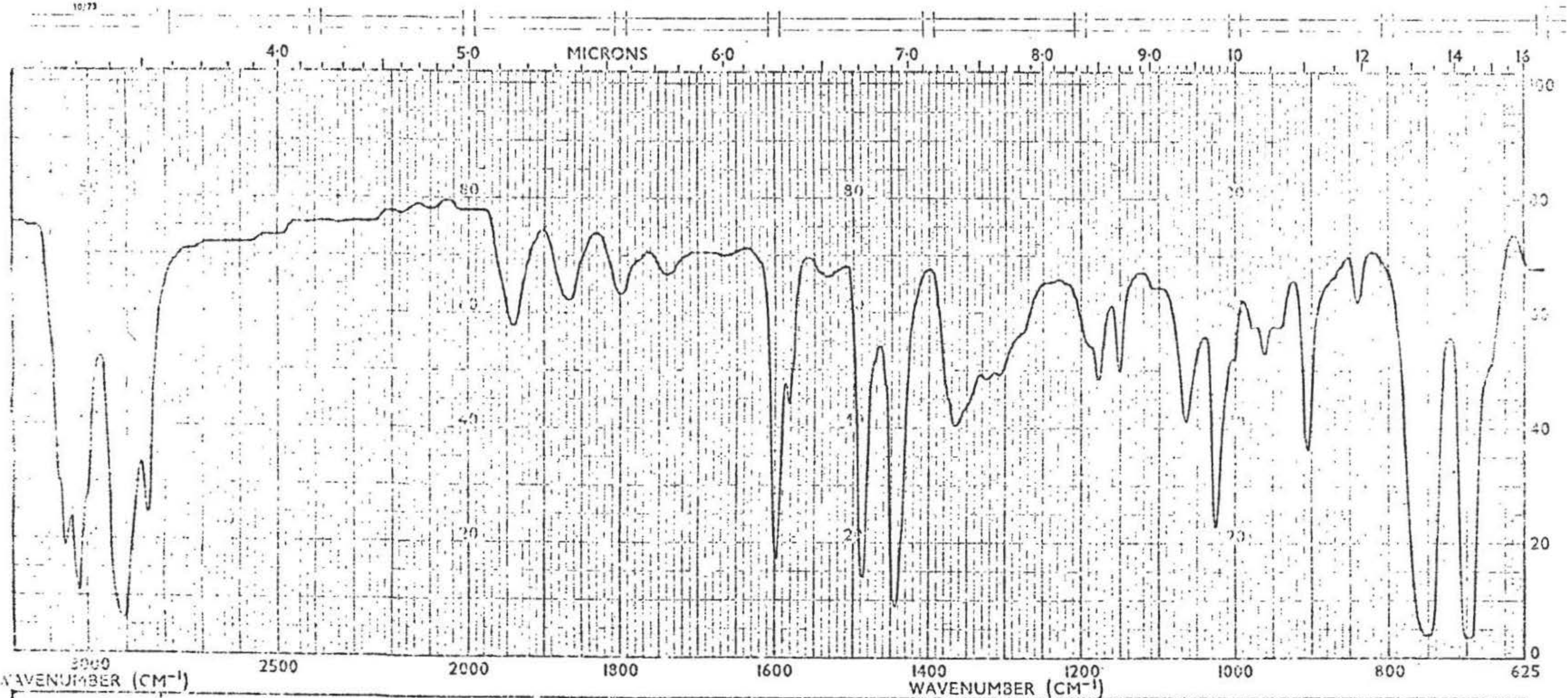
UNICAM SP200G



Catalogue No. 606041

ALIGN WITH INDEX ON THE RECORDER ▼	SAMPLE Pure polybutadiene film (Cast from TCE) REFERENCE	FORMULA 1	PHASE THICKNESS REMARKS	SCAN SPEED DATE OPERATOR

REFERENCE



Polystyrene film 0·02mm.	SOLVENT CONCENTRATION CELL PATH REFERENCE	REMARKS	SCAN SPEED SLIT	OPERATOR DATE
			Intek RPK/210/1001 472-5009	REF. NO.

REFERENCES

①R.J.Ceresa - Block and Graft Copolymers, Butterworths, London 1962, Chapter 1, p.1.

②D.C.Allport and W.H.Jones, Ed., Block Copolymers, Applied Science Publishers Limited, London 1973, Introduction, p.xvii.

③A) E.L.Eliel, Stereochemistry of Carbon Compounds, McGraw-Hill, New York 1962, Chapter 5, p.92.

B) R.S.Cahn and C.K.Ingold J.Chem.Soc., 612 (1951).

④E.Simon, Annalen, 31, 271 (1839).

⑤J.Blyth and A.W.Hoffman, Annalen, 53, 314 (1845).

⑥M.Berthelot, Bull.soc.chim.(2), 6, 294 (1886).

⑦A) I.Ostromislensky, J.Russ.Phys.Chem.Soc., 44, 204 (1911).

B) I.Ostromislensky, U.S. Patents 1, 683, 401-5 (1928), (to Naugatuck Chem.Co.).

⑧H.Staudinger and W.Frost, Ber., 68, 2351 (1935).

⑨H. von Pechmann, Ber., 31, 2643 (1898).

⑩W.H.Carothers, J.W.Hill, J.E.Kirby and R.A.Jacobson, J.Am.Chem.Soc., 52, 5279 (1930).

⑪A) E.W.Fawcett and R.O.Gibson, J.Chem.Soc., 386 (1934).

B) H.Staudinger, Trans, Faraday Soc., 32, 97 (1936). (p.119 - Remarks of E.W.Fawcett in general discussion following presentation of the above paper).

⑫A) E.W.Fawcett, R.O.Gibson, M.W.Perrin, J.G.Paton and E.G.Williams, Brit.Patent 471, 590 (1936), (to Imperial Chemical Industries Limited).

B) E.W.Fawcett, R.O.Gibson and M.W.Perrin, U.S. Patents 2, 153, 553 and 2, 188, 465 (1936), (to Imperial Chemical Industries Limited).

⑬A) K.Ziegler, E.Holzkamp, H.Breil and H.Martin, Angew.Chemie, 67, 426 and 541 (1955).

B) K.Ziegler and H.Martin, Makromol.Chemie, 19, 186 (1956).

C) K.Ziegler, Belg.Patent 533, 362 (1954).

⑭A) A.Clark, J.P.Hogan, R.L.Banks and W.C.Lanning, Ind.Eng.Chem., 48, 1152 (1956).

B) R.Hayes and W.Webster, Plastics Institute, Transactions, 32, 219 (1964).

C) J.P.Hogan and J.L.Banks, U.S. Patent 2, 825, 721 (1958), (to Phillips Petroleum Co.).

⑮ G.Natta and F.Danusso, Ed., Stereoregular Polymers and Stereospecific Polymerisations, Volumes I and II, Pergamon Press, London, 1967.

⑯ G.Natta, Makromol. Chemie, 16, 213 (1955).

⑰ C.H.Bamford, W.G.Barb, A.D.Jenkins, and P.F.Onyon, The Kinetics of Vinyl Polymerisation by Radical Mechanisms, Academic Press, New York, 1958.

⑱ P.A.Plesch, Ed., Chemistry of Cationic Polymerisation, Macmillan, New York, 1963.

⑲ A) M.Szwarc, Carbanions, Living Polymers and Electron-Transfer Processes, Interscience, New York, 1968.

B) F.W.Billmeyer, Jnr., Textbook of Polymer Science, Interscience, New York, 1962.

⑳ A) L.Reich and A.Schindler, Polymerisation by Organometallic compounds, Interscience, New York, 1966.

B) N.G.Gaylord and H.F.Mark, Linear and Stereospecific Addition Polymers, Interscience, New York, 1959.

C) R.A.V.Raff and K.W.Doak, Eds., Crystalline Olefin Polymers, Parts 1 and 2, Interscience, New York, 1964.

D) H.V.Boenig, Polyolefins: Structure and Properties, American Elsevier, New York, 1966.

㉑ M.Fischer, German Patent 874, 215 (1953), (to Badische Anilin und Soda Fabrik A.G.).

㉒ M.J.Roedel, U.S. Patent 2, 462, 678 and
2, 475, 520 (1949),
2, 497, 323 and 2, 511, 480 (1950), 2, 762, 791, (1956) and 2,983, 704 (1961) (to E.I. du Pont de Neumours 2nd Co., Inc.).

㉓ D.F.Herman and W.K.Nelson, J.Am.Chem.Soc., 75, 3877 (1953).

㉔ G.Natta, P.Pino, P.Corradini, F.Danusso, E.Mantica, G.Mazzanti and G.Moraglio, J.Am.Chem.Soc., 77, 1708 (1955).

㉕ A) G.Natta, J.Polymer Sci., 16, 143 (1955).

B) G.Natta and P.Corradini, Makromol.Chemie, 16, 77 (1955).

㉖ K.Ziegler, Angew. Chemie, 76, 545 (1964).

㉗ G.Natta, Science, 147, 261 (1965).

㉘ W.R.Sorenson and T.W.Campbell, Preparative Methods of Polymer Chemistry, Interscience, New York, Second Ed., 1968, Chapter 4, Section viii, p.287.

㉙ G.Natta, P.Corradini, I.W.Bassi and L.Porri, Atti.Acad. Naz.Lincei, 24, 121 (1958).

㉚ P.A.Gautier, S.Mostert and H.Verbrugge, British Patent 1, 139, 450 (1969), (to Shell Internationale Research Maatschappij N.V.).

㉛ G.Natta, P.Corradini, and G.Allegra, Atti.Acad.Naz. Lincei, 26, 155 (1959).

㉜ A) W.Klemm and E.Krose, Z.Anorg., 253, 209 and 217, (1947).

B) Brauer, Handbook of prep.inorganic chem. Academic Press, New York, 2nd Ed, 1965, Vol.2, p.1187.

㉝ A) W.C.Schumb and R.F.Sundström, J.Am.Chem.Soc., 55, 596 (1933).

B) T.Ishino, H.Tamura, and O.Nakagawa, Kogyo Kogaku Zasshi, 64, 1344 (1961).

㉞ G.Natta, P.Corradini and G.Allegra, J.Polymer Science, 51, 399 (1961).

㉟ V.M.Buls and T.L.Higgins, J.Polymer Sci., A1 (8), 1025 (1970).

㊱ I.Posquon, Pure Applied Chem., 15, 465 (1967).

㊲ G.Natta and G.Mazzanti, Tetrahedron, 8, 86 (1960).

㊳ J.Boor, Macromolecular Reviews, 2, 115 (1967).

㊴ C.D.Nenitzescu, C.Huch and A.Huch, Angew.Chemie, 68, 438 (1956).

㊵ F.J.Carol and W.L.Carrick, J.Am.Chem.Soc., 83, 2654 (1961).

㊶ P.Cossee, Trans. Faraday Soc., 58, 1226 (1962).

㊷ J.Boor and E.A.Youngman, J.Polymer Sci., B, 2, 265 (1964), J.Polymer Sci., B, 4, 913 (1965).

㊸ P.Cossee, J.Catalysis, 3, 80 (1964).

㊹ J.Boor, Ind.Eng.Chem.Prod.Res. and Dev., 9, 437 (1970).

㊺ V.W.Buls and T.L.Higgins, J.Polymer Sci., A-1 (8), 1025 (1970).

㊻ D.R.Armstrong, P.G.Perkins, and J.J.P.Stewart, J.C.S.Dalton, 1972 (1972).

㊼ R.N.Haward and A.N.Roper, German Patent 2, 003, 075 (1969), (Brit. Patent Appln 3956/69). German Patent 2, 061, 407 (1971), (Brit. Patent Appln. 15945/70).

㊽ R.N.Haward, A.N.Roper and K.L.Fletcher, Polymer, 14, 365 (1973).

㊾ D.G.Boucher, I.W.Parsons and R.N.Haward, Makromol.Chemie, 175, 3461 (1974).

(49A) D.G.Boucher, M.Sc.Thesis, submitted to Birmingham University, Chapter 2, p.25, 1973.

㊿ K.Gardner, Ph.D.Thesis, submitted to Birmingham University.

(51) E.W.Duck, D.Grant, A.V.Butcher and D.G.Timms European Poly.J., 10, 77 (1974).

(52) PH. Radenkov, T.Petrova, L.Petkov and D.Jelyazkova, European Polymer Journal, 11, 313 (1975).

(53) A) J.C.W.Chien, J.Am.Chem.Sco., 81, 86 (1959).

B) G.Natta, P.Pino, G.Mazzanti, U.Giannini, E.Mantica and M.Peraldo, J.Polymer Sci, 26, 120 (1957).

(54) A) L.Reich and A.Schindler, Polymerisation by Organometallic Components, Interscience, New York, 1966, Chapter 4, p.295.

B) G.Natta, L.Guiffre and I.Pasquan, Atti.Accad.Naz.Lincei Rend.Classe Sci.Fis.Mat.Nat., 25, (8), 417 (1958).

(55) G.E.Coates, M.L.H.Green and K.Wade, Organometallic Compounds, Volume 1, Methuen and Co. Ltd., London, Third Ed., 1967, Chapter 1, p.4.

(56) H.Gilman and J.W.Morton, Organic Reactions, 8, 258 (1954).

(57) R.G.Jones and H.Gilman, Organic Reactions, 6, 339 (1951).

(58) G.E.Coates, M.L.H.Green and K.Wade, Organometallic Compounds, Volume 1., Methuen and Co. Ltd., London, Third Ed., 1967, Chapter 3, p.295.

(59) G.Greber and G.Egle, Makromol. Chemie, 64, 68 (1963).

60 I.D.McKenzie, P.J.T.Tait and D.R.Burfield, Polymer, 13, 307 (1972).

(61) T.Keii, Kinetics of Ziegler Natta Polymerisation, Chapman and Hall, London, 1972, Chapter 2, p.15 and Chapter 5, p.129.

(62) D.Braun, Makromol. Chemie, 30, 85 (1959).

(63) G.B.Bachman, H.Hellman et al, J.Org.Chem., 12, 108 (1947).

(64) C.C.Price, Organic Reactions, 3, 1 (1946).

(65) A.I.Vogel, A Textbook of Practical Organic Chemistry, Longmans, London, Third Ed., 1956, Chapter 3, Preparation 8, p.237.

(66) R.D.Rieke and S.E.Bales, J.Chem.Soc., Chem. Comm., 879 (1973).

(67) W.Kern, R.C.Schulz and D.Brown, J.Polymer Sci., 48, 91 (1960).

(68) F.C.Leavitt and C.U.Matternas, J.Polymer Sci., 45, 249 (1960).

(69) M.B.Huglin, Polymer, 5, 135 (1964).

(70) R.L.Eppley and J.A.Dixon, J.Organometallic Chem., 8, 176 (1967).

(71) K.Ziegler, H.G.Gellert, H.Martin, K.Nagel and J.Schneider, Annalen, 589, 91 (1954).

(72) W.Hallwachs and A.Schafarik, Annalen, 109, 206 (1859).

(73) A.V.Grosse and J.M.Mavity, J.Organic Chem., 5, 106 (1940).

(74) H.Wislicenus and L.Kaufmann, Ber., 28, 1323 (1895).

(75) G.Kockelbergh and G.Smets, J.Polymer Sci., 33, 227 (1958).

(76) H.Gilman and A.H.Blatt, Ed., Organic Synthesis, Collective Volume 1, Wiley, New York, Second Ed., 1941, p.377.

(77) N.A.Plate, M.A.Jampolskaya, S.L.Davydova and V.A.Kargin, J.Polymer Sci., (C) 22, 547 (1969).

(78) E.I.Becker and M.Tsutsui (Ed), Organometallic Reactions, Volume 1, Wiley, New York, 1970, p.1.

(79) E.G.Hoffman, Trans.Faraday, Soc., 58, 642 (1962).

(80) D.G.H.Ballard, Chemistry in Britain, 10, 20 (1974).

(81) G.Natta, F.Danusso, and I.Pasquon, Collection Czech.Chem. Commun.Supplement to Volume 22, p.19 (1957).

(82) G.Natta and P.Corradini, Rend.Accad.Naz.Lincei, (8), 18, 19 (1955).

(83) G.Natta and P.Corradini, Makromol.Chemie, 16, 77 (1955).

(84) A) C.G.Overbeger, F.Ang and H.Mark, J.Polymer Sci., 35, 381 (1959).

B) C.G.Overberger and P.A.Jarovitzky, J.Polymer Sci., C4, 37 (1964).

(85) R.J.Kern, H.G.Hurst and W.R.Richard, J.Polymer Sci., 45, 195 (1960).

(86) S.Murahashi, S.Nozakura, M.Sumi and K.Hatada, Bull.Chem. Soc.Japan, 32, 534 and 1094 (1959).

(87) G.M.Burnett and P.J.T.Tait, Polymer, 1, 151, (1960).

(88) F.D.Otto and G.Parravano, J.Polymer Sci., A2, 5131 (1964).

(89) W.R.Krigbaum, D.K.Carpenter and S.Newman, J.Phys.Chem. 62, 1586 (1958).

(90) J.N.Hay, J.Polymer Sci., A-3, 433 (1965).

(91) A) F.A.Bovey, F.P.Hood, E.W.Anderson, and L.C.Snyder, J.Chem. Physics, 42, 3900 (1965).

B) F.Heatley and F.A.Bovey, Macromolecules, 1, 301 (1968).

C) F.A.Boveym Polymer Conformation and Configuration Academic Press, New York, London, 1969, Chapter 1, p.27.

(92) A) I.D.McKenzie, P.J.T.Tait and D.R.Burfield, Polymer 13, 307 (1972).

B) D.R.Burfield, I.D.McKenzie and P.J.T.Tait, Polymer, 13, 302 (1972).

(93) A) K.Vesely, J.Ambroz, R.Vilim, and O.Hamrik, J.Polymer Sci., 55, 25 (1961).

B) K.Vesely, Pure Appl.Chem., 4, 407 (1962).

(94) G.Henrici-Olive and S.Henrici-Olive, Ang.Chem.Int.Ed., 6, 790 (1967).

(95) J.C.W.Chien, J.Am.Chem.Soc., 81, 86 (1959).

(96) L.F.Johnson, F.Heatley and F.A.Bovey, Macromolecules 3, 175 (1970).

(97) B.M.Grieveson, Makromol. Chemie, 84, 93 (1965).

---

(98) I.D.McKenzie and P.J.T.Tait, Polymer, 13, 510 (1972).

(99) M.N.Berger, G.Boocock and R.N.Haward, Advances in Catalysis, 19, 211 (1968).

(100) C.F.Feldman and E.Perry, J.Polymer Sci., 46, 217 (1960).

(101) G.Bier, W.Hoffman, G.Lehmann, and G.Seydel, Makromol. Chemie, 58, 1 (1962).

(102) D.G.H.Ballard, Advances in Catalysis, 23, 263 (1973).

(103) I.H.Anderson, G.M.Burnett and P.J.T.Tait, Proc.Chem.Soc., 225 (1960).

(104) A) G.Natta, G.Mazzanti, and P.Corradini, Atti.Acad.Naz 1. Lincei Rend.Classe Sci.Fis.Mat.Nat., (8) 25, 3 (1958).

B) G.Natta, P.Pino and G.Mazzanti, Ital.Patent 530.753.

(105) IV. Nicolescu and E.M.Angelescu, J.Polymer Sci., A-3, 1227 (1965).

(106) A) S.Kambara and M.Hatano, Bull.Tokyo Inst.Technol. Spec.No.52, 541, 64, 10 (1963).

B) M.Hatano, Kogyo Kagaku Zosshi, 65, 723 (1962).

(107) W.H.Watson, W.S. McMordie and L.G.Lands, J.Polymer Sci., 55, 137 (1961).

(108) F.D.Kleist and N.R.Byrd, J.Polymer Sci., A-1, 7, 3419 (1969).

(109) L.B.Luttinger, Chemistry and Industry 1135 (1960).

(110) H.Noguchi and S.Kambara, J.Polymer Sci., B, 1, 553 (1963).

(111) G.A.Chukhadzhyan, Zh.I.Abramyan and G.A.Gevorkyan, Polymer Sci. USSR, 12, 2791 (1970).