NEW INITIATING SYSTEMS FOR THE POLYMERISATION OF ISOBUTENE

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Declaration

I declare that this thesis is my own composition and that the work that it descibes was carried out by myself unless specifically stated in the text. In addition, I declare that this work has not been submitted in any previous application for a higher degree.

The thesis describes the results of research carried out in the Department of Chemistry, The University of Edinburgh, under the supervision of Dr I. Gosney since 1st October 1993, the date of my admission as a research student.

à mes parents,

pour leurs soutien et continuels

encouragements tout au long de mes études

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Postgraduate courses attended

1. Medicinal Chemistry Lectures - Merck, Sharp and Dohme, Prof. R. Baker and Dr. P. Leeson, Department of Chemistry, The University of Edinburgh, 1994, 1995 and 1996.
2. NMR of biological molecules - Dr. P. Barlow and Dr. I. Sadler, Department of Chemistry, The University of Edinburgh, 1995.
3. Chemical Development in the Pharmaceutical Industry - SmithKline Beecham, various speakers, Department of Chemistry, The University of Edinburgh, 1996.
4. Industrial Fine Organic Chemistry - Prof. A. McKillop (University of East Anglia), Department of Chemistry, The University of Edinburgh, 1996.
5. Hydrogen Peroxide and its Derivatives in Industry - Solvay Interox, various speakers, Department of Chemistry, The University of Edinburgh, 1994.
6. Industrial Biocatalysts - SmithKline Beecham, various speakers, Department of Chemistry, The University of Edinburgh, 1994.
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Abstract

The work described in this thesis has been concerned with the preparation of high vinylidene end-group polyisobutene using new initiating systems such as alkoxydifluoroboranes ($ROBF_2$) and alkyldifluoroboranes (RBF_2), and their adducts with ethanol and Bronsted acids (water, sulfuric acid, trifluoromethanesulfonic acid, acetic acid and trifluoroacetic acid). In all cases, comparison is made with the currently used initiating system of a 1:1 complex of boron trifluoride with ethanol (BF_3.EtOH).

From nuclear magnetic resonance (NMR) spectroscopic studies, *n*-pentoxydifluoroborane ($C_5H_{11}OBF_2$) and methoxydifluoroborane (CH_3OBF_2) were found to have a trimeric structure in deuteriochloroform, whilst both pentafluorophenoxydifluoroborane ($C_6F_5OBF_2$) and phenoxydifluoroborane ($C_6H_5OBF_2$) existed as mixtures of trialkoxyborane [$(RO)_3B$] and boron trifluoride. In most cases, the addition of ethanol or Bronsted acids to alkoxydifluoroboranes led to decomposition of the latter and to the formation of complex mixtures of boron compounds, *viz.* monofluoroboranes [$(RO)_2BF$], trialkoxyboranes and boron trifluoride. By comparison, acetic acid and trifluoroacetic acid did not decompose methoxydifluoroborane. Both *n*-butyldifluoroborane ($C_4H_9BF_2$) and *n*-pentyldifluoroborane ($C_5H_{11}BF_2$) showed the same stability when their adducts with ethanol and trifluoroacetic acid were formed.

These boron trifluoride derivatives and their adducts were evaluated as initiating systems for the carbocationic polymerisation of isobutene at low temperature with particular reference to their influence on the extent of conversion, molecular weight (M_n) and more importantly, vinylidene content of the resulting polyisobutene. From experimental results, it is evident that BF_3.EtOH is a much more reactive initiating system than the adducts of ethanol with alkoxydifluoroboranes, which initiated the polymerisation of isobutene, but only when used in high concentrations, to produce polymers with a high vinylidene content (*ca.* 88%). Alkyldifluoroboranes, whether used with ethanol or trifluoroacetic acid as an initiator, proved to be inactive co-initiators for the polymerisation of isobutene. Of all the Bronsted acids used as initiators, trifluoroacetic acid produced polyisobutene in high yield when methoxydifluoroborane was used as the co-initiator.The molecular weight of the resulting polymer was found to be within the desired range (M_n 1000-1500) with a concomitant vinylidene end-group content of up to 75% being achieved.

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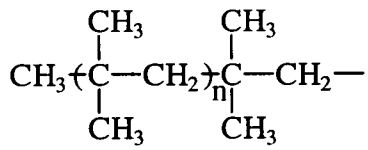
INTRODUCTION

A. Polybutene polymers with particular reference to polyisobutene

1. Preamble

Isobutene is one of the principal raw materials used by the petrochemicals industry in the manufacture of chemicals and polymers[1]. The major use of isobutene is in the manufacture of butyl rubber and derivatives, polyisobutenes, polybutenes, di- and triisobutene. The first major petrochemical operation was the manufacture of polyisobutene **1**[2].



1

Low, medium, or high molecular weight polymers, copolymers, and derivatives of polyisobutene are important and versatile materials made by carbocationic polymerisation. About 80% of the isobutene consumed in the United States goes into polymers. Of this, ca. 50% of the isobutene goes into butyl rubber, 25% into various low molecular weight polyisobutenes and polybutenes made from C_4 refinery streams, and about 5% into high molecular weight polyisobutenes.

Depending on their molecular weights, polyisobutenes range from liquids, viscous oily products, slow flowing semi-solids, to tough, non-flowing elastomers.

Isobutene is in a sense an "ideal" monomer. It is an extraordinarily reactive 'cationic' monomer under all manner of acidic conditions, and it is one of the few monomers

whose polymerisation can be readily controlled to give from the lowest oligomers, through medium molecular weights, up to the highest polymers.

1.1. Polybutenes

1.1.1. Manufacture

Polybutenes are manufactured from C_4 olefin refinery streams *via* catalytic cracking of petroleum. Butadiene-free C_4 fractions (butane-butylene fractions) typically contain propane-propylene (1-3%), 1-butene (10%), *cis*- and *trans*-2-butene (10-15%), isobutene (15-30%; sometimes as high as 60%), *n*-butane (30%), isobutane (30%), with the balance being molecules higher than C_5.

The basic polymerisation process in use today is a rather crude $AlCl_3$ slurry-initiated continuous polymerisation of refinery butane-butene feeds in the temperature range from ~ -60°C to ambient. Usually the C_4 feed is dried, desulfurized, cooled, and together with a stream of initiator injected into the reactor. The polymerisation is exothermic and the reactor has to be cooled. The effluent is neutralized, purified, packaged and stored.

1.1.2. Molecular weight control of Polybutenes

Polymer viscosity and molecular weight are regulated by controlling the polymerisation temperature and catalyst concentration. Molecular weights are also

influenced by feed composition, but this variable cannot be changed. Since isobutene is the most reactive feed component, practically all of it is converted into polymer. The conversion of butenes in the feed is usually low. Decreasing the polymerisation temperature results in higher selectivity of isobutene polymerisation, *i.e.* less butene copolymerisation. The butenes tend to terminate the polybutene propagating chain, and hence reduce molecular weights.

1.1.3. Structure, properties and uses

Since the C_4 streams used to prepare polybutenes contain isobutene as well as appreciable amounts of 1- and 2-butenes, the polymers produced are in fact copolymers of isobutene and small amounts of butenes.

Polybutenes are colourless, odourless viscous liquids that are soluble in hydrocarbons and ethers. The low molecular weight grades flow freely at room temperature, whereas the higher molecular weight grades (>1000) require heating for pumping. The latter are excellent lubricants and electrical insulators. Polybutenes are "non-drying", *i.e.* they do not crosslink when exposed to air, and they are thermally stable up to 280-300°C. The lowest molecular weight polybutenes (M_n~300) may become oxidised to a small extent when exposed to air at room temperature, but the more viscous grades are impermeable to gases, and consequently are more resistant to oxidation.

The most important use of polybutenes is in the manufacture of motor oil additives. Although some polybutenes may be blended directly into lubricating oils they

usually serve as chemical intermediates for additive synthesis. The unsaturation provides the functionality for post-polymerisation syntheses, *e.g.* the ene reaction with maleic anhydride. Other major uses are in formulation of sealants, coatings, adhesives, and laminating agents; in high-voltage electrical cables as impregnating oils and pipe oils; as lubricants for sheets metal cutting; and as compressor oil.

A major advantage of polybutenes is that they are non-toxic and non-irritating and thus find applications in paper treatment and lubricants that may come in contact with food products.

1.2. Polyisobutenes

In contrast to polybutenes, which are ill-defined copolymers produced by the use of C_4 refinery streams, polyisobutenes are pure homo-polymers of isobutene. Patent literature in particular, is extremely rich in disclosures of isobutene polymerisation processes, extensions and improvements of basic patents.

A variety of polyisobutene grades are commercially available. The main difference between these products is their molecular weight, which determines their ultimate use. Isobutene is one of the very few monomers that can be readily polymerised to practically any molecular weight level from liquid oligomers to tough elastomers, and all these materials exhibit characteristic useful properties rendering them valuable for a variety of end-uses. There are two fundamentally different ways to produce low molecular weight polyisobutenes : by direct polymerisation at relatively high temperatures and by degradation of higher molecular weight products.

The overall in-chain structure of low molecular weight polyisobutenes has been firmly established : linear, head-to-tail enchainment **1**.

However, there is room for better definition of the termini. It has been established that polyisobutenes contain various types of terminal unsaturations (see section 3) and that these functions determine some very important chemical properties, such as oxidative stability and the nature and scope of derivatives. Thus the exact knowledge of end-group structures is of great importance to the application chemist.

The properties and applications of polyisobutenes and polybutenes are quite similar, although, polyisobutene is more expensive than polybutene because it is manufactured by the use of pure isobutene feeds.

2. Isobutene-based carbocationic polymerisation

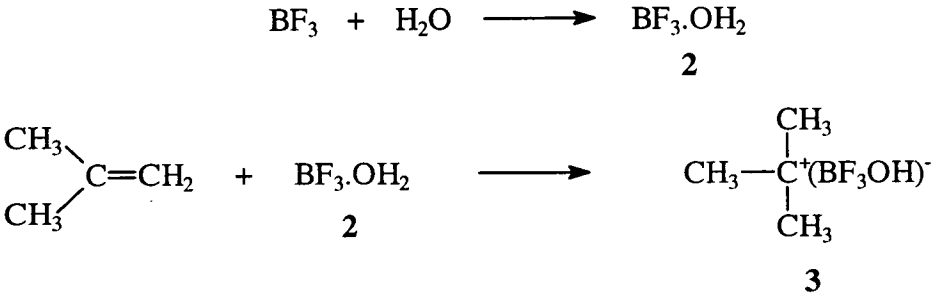
2.1. Initiation

The most important initiating systems both from the scientific and technological point of view are those involving Lewis acids[3-11].

A variety of Lewis acids are used to initiate cationic polymerisations, generally at low temperatures, to yield high polymer molecular weights. These include metal halides, *e.g.* $AlCl_3$, BF_3, $SnCl_4$, $SbCl_5$, $ZnCl_2$, $TiCl_4$, PCl_5, organometallic derivatives, *e.g.* $RAlCl_2$, R_2AlCl, R_3Al and oxyhalides, *e.g.* $POCl_3$, CrO_2Cl, $VOCl_3$. Initiation by Lewis acids either requires or proceeds faster in the presence of a proton donor such as water, alcohol or organic acids, or else, a cation donor such as *tert*-

butyl chloride or triphenylmethylfluoride. Thus, dry isobutene is unaffected by dry boron trifluoride, but polymerisation occurs immediately when trace amounts of water are added[12].

The proton donor or cation donor is referred to as the *initiator* while the Lewis acid is the *co-initiator* according to Kennedy's terminology[11]. The co-initiator, BF_3, and initiator, in this example, water, comprise an initiating system and form a complex **2** which proceeds to donate a proton or other cation (usually carbenium ion) to the monomer[13] initiating propagation (Scheme 1).



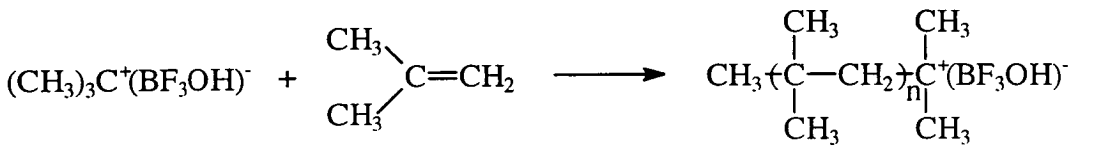
Scheme 1

It should be noted that the initiator-co-initiator complex $BF_3{\cdot}OH_2$ **2** is often shown as H^+ $(BF_3OH)^-$ but there is no evidence to support the latter type of species for many Lewis acids.

A variety of other cationic initiators have been studied[7] including protonic acids (Bronsted acids), acetyl perchlorate, iodine, electrolytic initiation and ionising radiation. The activity of these initiating systems will be discussed in more details in Part B.

2.2. Propagation

The initiator ion-pair **3** (consisting of the carbenium ion and its negative gegenion) produced in the initiation step proceeds to grow by the successive addition of monomer molecules[3-11] (Scheme 2).



3 **4**

Scheme 2 : Propagation reaction

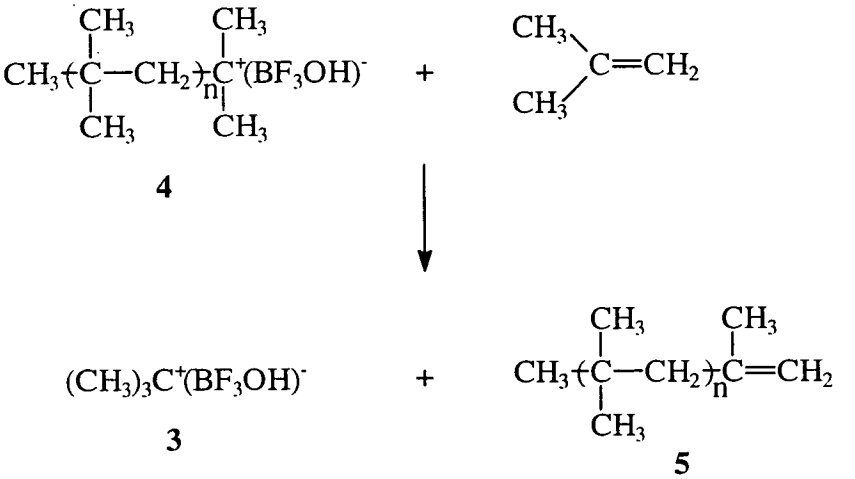
This addition can be thought of as occurring by insertion of monomer between the carbenium ion and its negative gegenion.

The propagation reaction can be complicated in some cases by the occurrence of intramolecular rearrangements due to hydride ion or carbanion shifts (see section 3). The extent of rearrangement during cationic propagation will depend on the relative stabilities of the propagating and rearranged carbenium ions and on the relative rates of propagation and rearrangement. Both factors favour propagation without rearrangement for most of the common monomers polymerised by cationic means. However, isomerisation occurs to a small extent in the polymerisation of isobutene.

2.3. Termination

Various reactions may lead to termination of chain growth in cationic polymerisation[3-11]. Most reactions which terminate the growth of a propagating chain do not, however, terminate the kinetic chain because a new propagating species is formed in the process.

Chain transfer to monomer (Scheme 3) is one of the most common chain-breaking reactions for many monomers. Transfer to monomer usually involves transfer of a proton to a monomer molecule with the formation of terminal unsaturation or vinylidene end-group **5** in the polymer molecule.



Scheme 3

Termination can also take place by rearrangement of the propagating ion-pair **4**. *Spontaneous termination* involves regeneration of the initiator-co-initiator complex **3**

by expulsion from the propagating ion-pair **4** with the polymer molecule left with terminal unsaturation.

Other termination reactions include termination by combination with counter-ion, back-biting, and chain transfer to solvent, impurity or to polymer.

3. End-group structure

The main end-group structures of polyisobutene[5] are shown in Figure 1.

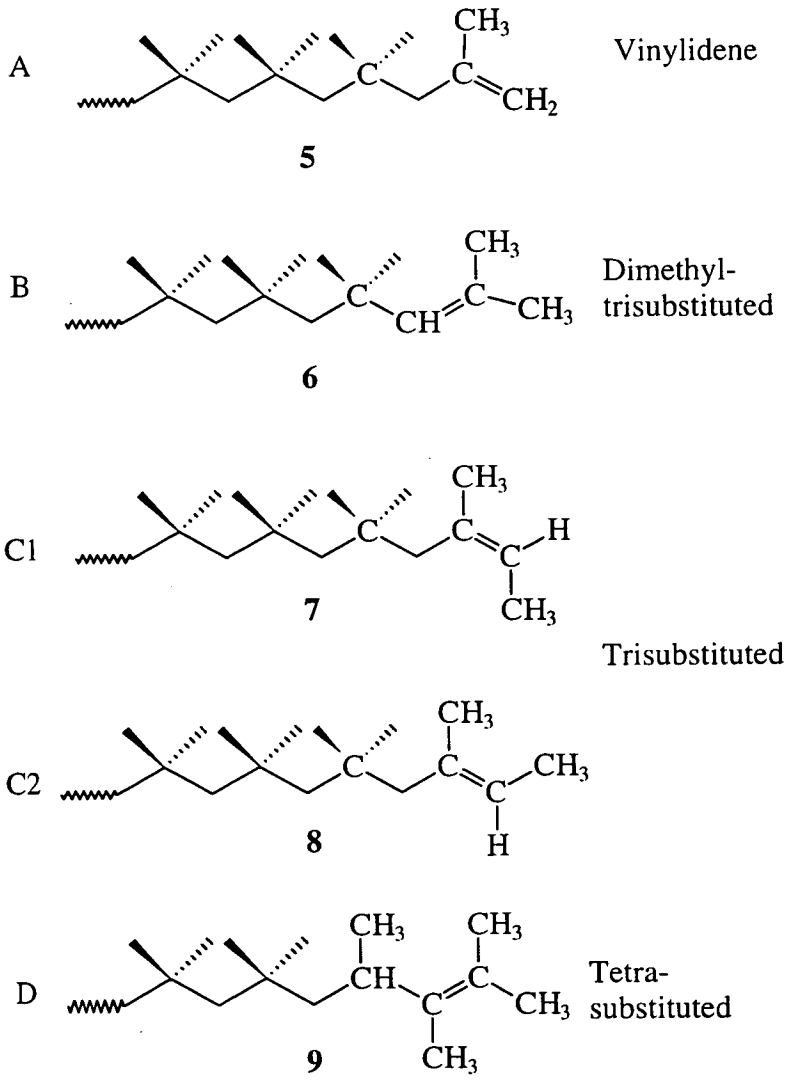


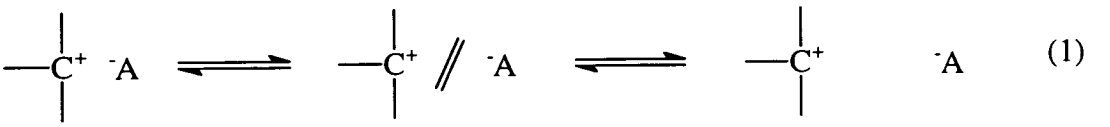
Figure 1. Main end-groups of polyisobutene

The exact mechanism of the formation of the different types of end-group that occur in polyisobutene is not certain, but resultant structure and composition can be controlled to a certain extent in batch reaction scale experiments. The type of termination is dependent upon solvent polarity, level of acidity and Lewis acid strength. Specifically with reference to vinylidene structure **5,** of the above parameters the conditions suggested by previous work to give the highest content were the following :

- decreasing the solvent polarity.
- performing the polymerisation in a non-acidic environment.
- use of relatively weak Lewis acid as the co-initiator

The effects of these are as follows :

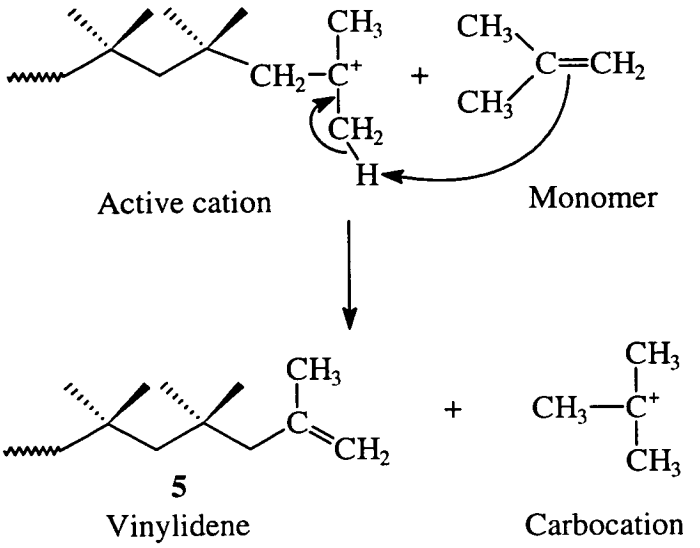
a) Solvent polarity : in a solvent, there are different ways in which the ions can be associated (equation 1).



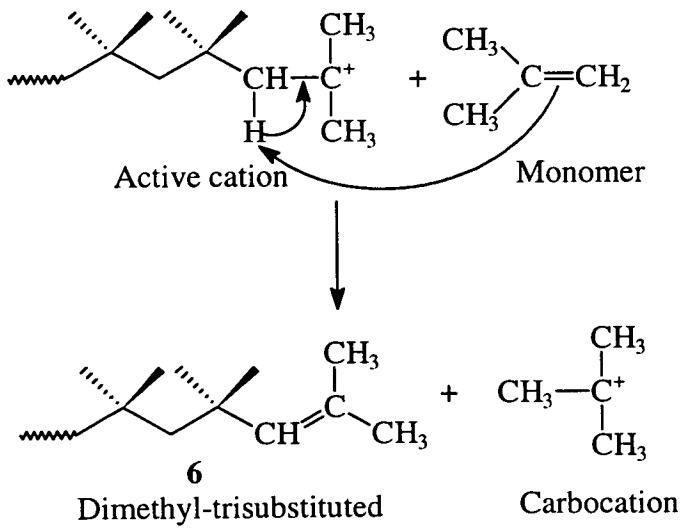
Scheme 4

The position of the equilibrium is determined by such factors as the polarity of the solvent and specific solvent effects. The extent to which the ions are associated affects the mechanism of chain transfer that occurs, the likelihood of intramolecular shifts and thus the type of end-group formed. Chain transfer to monomer to form

vinyledene end-groups **5** and dimethyl-trisubstituted end-groups **6** is illustrated in schemes 4 and 5.

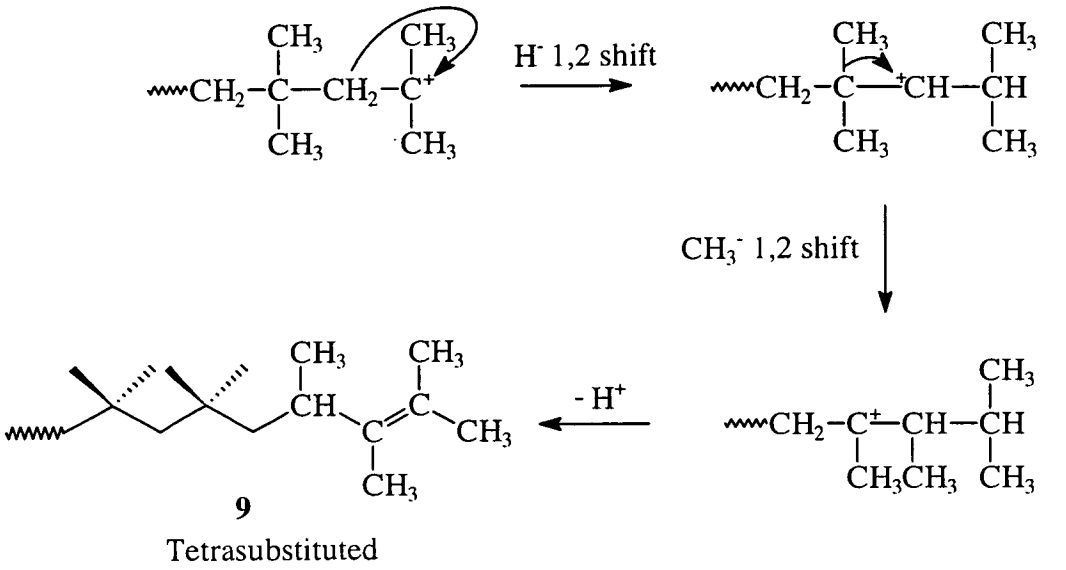


Scheme 4. Termination by chain transfer to monomer leading to vinylidene end-groups



Scheme 5. Termination by chain transfer to monomer leading to dimethyl-trisubstituted end-groups

Vinyledene end-groups are formed by chain transfer of a proton to a monomer. Also, hydride or methyl shifts (Scheme 6) can occur prior to loss of the proton to give other less reactive unsaturated end-groups, *e.g.* tetrasubstituted (type D) **9**.



Scheme 6

These shifts are more likely to occur in a polar solvent since the energy required is less than that needed in a non-polar solvent. With a polar solvent, the surrounding molecules have small positive and negative charges which are conductive to the lower energy shifting groups such as methyl or hydride. In a non-polar solvent, no such charges exist to stabilise the anion, and as a result it will be of a higher energy and less likely to exist.

b) Acidity of the reaction environment : the stabilising effect of the counter-anion toward the active cation will be decreased if there are other positively charged

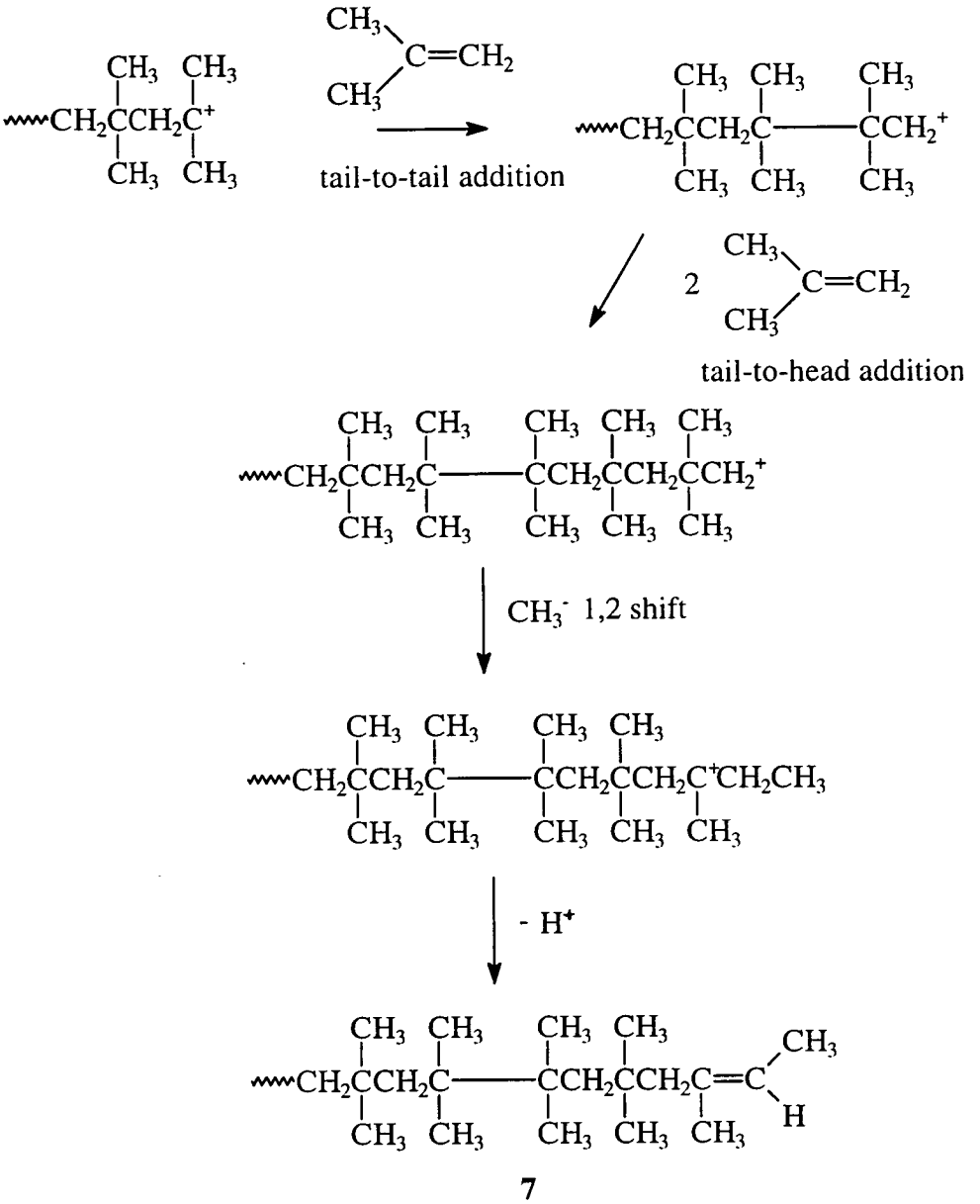
species in the reactor such as protons in an acidic environment. As well as this, if the vinylidene group is formed in acidic solution , *i.e.* an excess of H^+, there is more likely to be a rearrangement because of the stabilising effect of the acidic protons towards the methyl or hydride group shifting along the molecule backbone.

c)Lewis acid strength : the strength of the Lewis acid used in the activation of the initiator will affect the level of rearrangement. Lewis acids have the ability to accept electrons and consequently the stronger the acid, the greater affinity and electron-accepting ability it will have. The shift of a methyl or hydride is initiated by the formation of a slight positive charge at the site to which it intends to move.

Strong Lewis acids will increase the probability of such sites on the backbone and increase the likelihood of a shift occurring. If the Lewis acid is weak, then it has less electron-withdrawing ability, and therefore positively charged sites are less likely to occur.

The nature of co-initiator used (BF_3 or $AlCl_3$) affects the end-group structure. For example, the major end-group obtained in the presence of $AlCl_3$ is proposed to be trisubstituted of type C **7**, the formation of which has recently[14] been explained by a tail-to-tail addition of a monomer molecule to the propagating chain (Scheme 7)

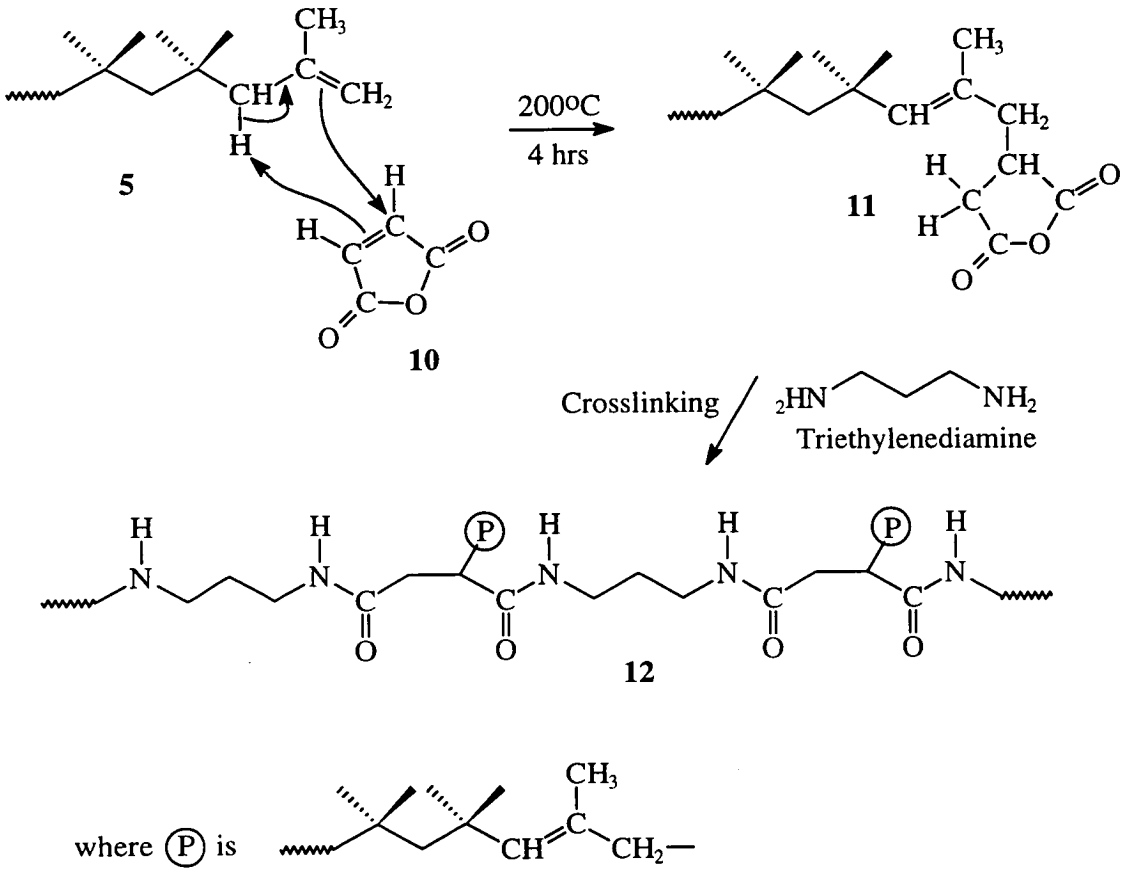
Use of BF_3 leads to higher proportions of reactive double bonds, particularly vinylidene of type A **5**, than aluminium-based Lewis acids. For example, the initiator system (1:1 molar BF_3.EtOH complex) has been demonstrated to result in minimal polymer olefinic end-group isomerisation and yields predominantly the more reactive terminal vinylidene end-group at up to 80% of total unsaturation.



Scheme 7

Internal unsaturation in olefin polymers is believed to be less desirable than terminal unsaturation due to the lower chemical reactivity of internally unsaturated polymers when compared to those terminally unsaturated. This is especially true of the reactivity toward compounds such as maleic anhydride **10** which forms an adduct with polyisobutene called polyisobutenyl succinic anhydride **11** (Scheme 8). These adducts

are most valuable products since they are converted into imides **12** by reaction with appropriate amines *e.g.*, triethylenediamine, for use as an additive for lubricating oil.



Scheme 8

B. Carbocationic polymerisation initiating systems

Carbocationic polymerisation may be initiated by chemical or physical methods[15]. Chemical methods of initiation make use of protic or Bronsted acids, stable cation salts, Friedel-Crafts acid-based initiating systems , some miscelleaneous cationogens, and charge-transfer complexes. Physical methods of initiation employ external sources of energy, *e.g.*, radiation and electrical, to generate initiating cations or cation radicals in the charge. Only chemical methods will be reviewed in more detail.

1. Bronsted acid-based initiating systems

1.1. Bronsted acids used to initiate polymerisations

Bronsted acids are potential sources of protons and are by definition initiators of carbocationic polymerisations. According to Bronsted, acids are proton donors but according to Lewis they are electron-pair acceptors[16]. It is often claimed that Lewis acids are a wider and more general class of substances that include Bronsted acids as a special case. Thus, BF_3 may be regarded to increase the acidity of liquid HF either because of the formation and ionisation of a hypothetical Bronsted acid HBF_4 **13** (equation 2),

$$BF_3 + 2HF \rightleftharpoons \underset{\mathbf{13}}{HBF_4} + HF \rightleftharpoons H_2F^+BF_4^- \qquad (2)$$

or because the BF_3 complexes with F^- and leaves behind H^+ (equation 3).

$$BF_3 + 2HF \rightleftharpoons H_2F^+ + BF_4^- \qquad (3)$$

An important distinction between Bronsted and Lewis acids is the behavior of these acids toward the same base B. Although all Bronsted acids lead to the same species BH^+, Lewis acids give rise to different complexes exhibiting different physicochemical properties.

Even strong Bronsted acids that rapidly protonate olefins usually produce only low molecular weight products. In practice, very few Bronsted acids produce high molecular weight polymer and then only with highly reactive monomers, *e.g.*, *N*-vinylcarbazole and α-methylstyrene. In contrast, Friedel-Crafts acid-based initiating system often lead to rapid polymerisation and high molecular weight material.

With regards to initiating ability, the most important property of Bronsted acids is acid strength[15], characterised by the equilibrium shown in equation 4,

$$HA \rightleftharpoons H^+ + A^- \qquad (4)$$

or preferably by (equation 5),

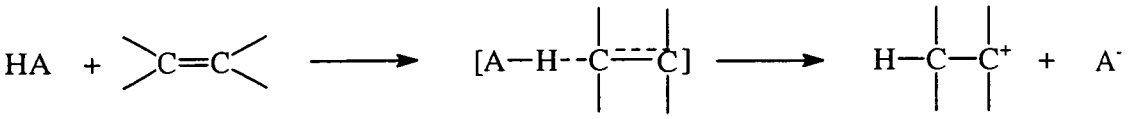
$$HA + S \rightleftharpoons HS^+ + A^- \qquad (5)$$

where S = solvent, since free protons do not exist in the condensed phase.

Because concentration of the solvent is constant, acidity is defined by the equilibrium constant (i):

$$K = [HS^+][A^-]/[HA] \qquad (i)$$

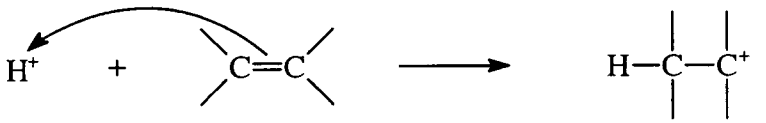
Since only undissociated acid HA and solvated proton HS^+ exist in solution, protonation of olefin is visualised to occur by a process akin to nucleophilic displacement involving proton transfer within acid-olefin coordination complexes[16] **14** (Scheme 9)



14

Scheme 9

and not by direct attack of the π double bond system on the proton (Scheme 10).



Scheme 10

Table 1 below shows the Bronsted acids frequently used for initiation processes together with some secondary reactions these acids are known to induce under polymerisation conditions.

Hydrogen halides HA (A=F, Cl, Br, I) as a group are rather undesirable initiators for the synthesis of high molecular weight polyolefins. In a few instances, HCl and HBr have been used to initiate polymerisation of styrene using polar solvents[17]; but in general, the molecular weight obtained is rather low.

Bronsted acids with less nucleophilic conjugate bases, such as H_2SO_4 and H_3PO_4, have been used in olefin oligomerisation[18]. The polymerisation of styrene with

H_2SO_4 and $HClO_4$ proceeds by a pseudo-cationic mechanism, which also yields a low molecular weight product[19].

Table 1. Bronsted acids used for polymerisation

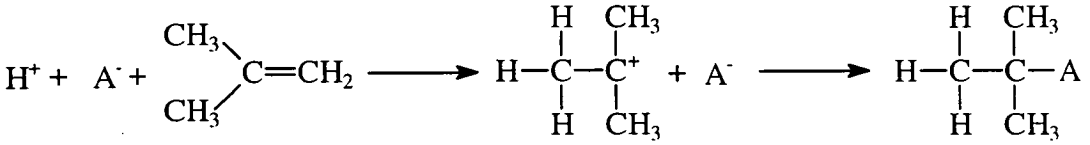
Bronsted acid	Side reactions
HBr	addition
HCl	addition, alkylation
HF	addition, alkylation, acylation, isomerisation
$HClO_4$	alkylation, acylation
$HClSO_3$	
$HFSO_3$	
H_2SO_4	alkylation, acylation, isomerisation
H_3PO_3	acylation, alkylation
$CH_2ClCOOH$	acylation
$CHCl_2COOH$	
CCl_3COOH	
CF_3COOH	acylation, isomerisation
Alkanesulfonic acids	alkylation
CF_3SO_3H	

Chlorosulfonic acid has been used to polymerise styrene[17,20] and butadiene[21], whilst fluorosulfonic acid has been used for styrene[17,20]. Trichloroacetic acid has been studied for the polymerisation of styrene[22], α-methylstyrene[22], for various dimethyl-substituted ethylenes[23], and for cyclopentadiene[24]. Dichloroacetic acid[25,26] and

trifluoroacetic acid[27] have been used also as an initiator for styrene and α-methylstyrene. Alkanesulfonic[28] acids are initiators for the polymerisation of isobutene. CF_3SO_3H has more recently[29,30] been used to polymerise styrene.

1.2. The chemistry of initiation by Bronsted acids

Bronsted acids HA are proton sources and as such may function as cationic polymerisation initiators[3]. The overall reactivity of a Bronsted acid in regard to a particular olefin is mainly governed by the proton affinity of the olefin. The utility of a Bronsted acid for initiation of carbocationic polymerisation is determined by the nucleophilicity of its conjugate base A^-. If the nucleophilicity of the conjugate base is high, protonation of the olefin may be followed rapidly by ion-pair collapse, which is a process equivalent to termination of a propagating chain (Scheme 11)



Scheme 11

In this sense, the addition of a Bronsted acid across a double bond may be viewed as initiation followed by immediate termination or "polymerisation without propagation". If the nucleophilicity of the conjugate base A^- is low, the life-span of the cation may increase, and in the presence of a suitable olefin, propagation may occur. For example, mixing HCl and isobutene rapidly produces *tert*-butyl chloride. Evidently the nucleophilicity of Cl^- is high and the rapid collapse of the ion-pair

prevents polymerisation. In contrast, with H_2SO_4 or H_3PO_4, *i.e.*, with Bronsted acids having less nucleophilic conjugate bases HSO_3^- or $H_2PO_4^-$, isobutene dimers or trimers are obtained.[18,31,32]

1.3. Bronsted acid/Lewis acid combinations

Bronsted acids alone can lead to rapid polymerisation and high molecular weight products only with the most reactive cationic monomers[3]. *N*-vinylcarbazole, for example, rapidly polymerises with HCl in toluene solution[33].

Although high molecular weight polyisobutene cannot be obtained by use of a simple Bronsted acid alone, Bronsted acid/Friedel-Crafts acid combinations such as $BF_3.H_2O$ **2** produce such polymers because the Friedel-Crafts acid is able to stabilise the highly nucleophilic conjugate bases of protic acids by complexation (Scheme 1). Solvation by polar solvents may help to stabilise the charged intermediates and delay the collapse of the ion-pair. Thus HCl or HBr in polar solvents such as ethylene dichloride have been shown to polymerise styrene, but the yields and molecular weights are very low[17]. In contrast, H_2SO_4[34], CCl_3COOH[26], CF_3COOH[17], and $HClO_4$[35], *i.e.*, Bronsted acids with relatively low nucleophilic conjugate bases, rapidly produce relatively high molecular weight polystyrenes.

The effect of solvent polarity on cationic initiation is very important[27]. For example, the order of reagent addition in the CF_3COOH/styrene system is of critical importance for the success of polymerisation. Thus, when CF_3COOH is added to styrene directly, practically no polymerisation occurs; but when styrene is added to

CF_3COOH, instantaneous polymerisation to high molecular weight is ensured. Evidently in the former case, ion generation could not occur because of the low polarity of the styrene medium, whereas in the latter instance, owing to the high polarity of CF_3COOH and stabilisation by complexation, polymerisation could proceed readily.

Efficient cationic polymerisation to high molecular weight products can occur only in the presence of relatively stable, weakly nucleophilic conjugate bases in order that the collapse of the propagating ion-pair is prevented, or at least delayed, thus allowing propagation to high polymers to proceed.

Although Bronsted acids carry their own conjugate base, a large amount of work is being devoted to find ways to control externally the rate of ion-pair collapse.

The rate of reaction between a particular cation and conjugate base to neutral species can be controlled to a modest degree by reaction conditions such as medium polarity, temperature and concentrations. Under the least favorable conditions for polymerisation (carbenium ion of relatively low stability, highly nucleophilic conjugate base, non-polar medium and high temperature), protonation may be followed rapidly by the collapse of the ion-pair. Under more favorable conditions (relatively stable carbenium ion, weakly nucleophilic conjugate base, polar medium and low temperature), rapid cationic polymerisation to high molecular weight product may occur.

2. Friedel-Crafts acid-based initiating systems

2.1. Definitons

Although Friedel-Crafts acids are constituents of the most important cationic initiating systems[3,7,15] and are used in innumerable other industrially useful processes, *e.g.*, Ziegler-Natta coordination polymerisation, butyl rubber manufacture, alkylations, acylations, and isomerisations, and are the subject of countless scientific investigations, a succinct scientifically valid definition or classification based on some fundamental property of these materials has not yet been developed.

Friedel-Crafts acids are by definition Lewis acids, *i.e.*, acceptors that possess at least one vacant orbital capable of accepting a pair of electrons of a donor Lewis base, or are able to produce such an orbital under the influence of a Lewis base.

Friedel-Crafts acid represent a sub-class of Lewis acids which also embrace charge-carrying electrophiles such as protons, inorganic cations, carbocations, oxonium ions, and sulfonium ions.

Friedel-Crafts acids are metal halides (*e.g.*, $AlCl_3$, BF_3, $SnCl_4$, $SbCl_5$, $ZnCl_2$, $TiCl_4$, PCl_5)[36], organometallic halides (*e.g.*, $RAlCl_2$, R_2AlCl, R_3Al)[37,38], or organometallics of Lewis acidic nature (*e.g.*, $POCl_3$, CrO_2Cl, $VOCl_3$)[39,40] that in conjonction with cationogens (proton or cation donors) co-initiate carbocationic polymerisation.

Much effort has been devoted to the development of a scale of Friedel-Crafts acidities in order to predict the behaviour of Friedel-Crafts acids or cationogen/Friedel-Crafts acids combinations as cationic initiating systems.

Unfortunately, Friedel-Crafts acidities are influenced by a variety of different factors, such as the electronic nature of the central metal, the nature and electronegativity of ligands on the metal, size and geometry of the assembly, reorganisation and back-donation (*e.g.*, boron halides), the nucleophilicity, size, and geometry of the donor base, as well as the strength of donor-acceptor complexes and their solvation energies, and such a scale has not been developed.

The electronic nature of the central metal strongly influences electron deficiency, *i.e.*, acid strength of Friedel-Crafts acids[41]. For example, extensive π-bonding betwen the vacant p orbital on the boron atom and a lone pair of electrons on the halogen gives an explanation for the unexpected experimental observation that the Lewis acidity sequence in the boron series is $BF_3 < BCl_3 < BBr_3 < BI_3$.

The electronegativity of ligands covalently bound to the metal significantly affects the overall Friedel-Crafts acidity. Thus increasing the number of electronegative groups around the central metal increases the Friedel-Crafts acidity. For example, Friedel-Crafts' acidity increases by replacment of the less electronegative methyl groups around boron with highly electronegative fluorines[42] : $Me_3B < Me_2BF < MeBF_2 < BF_3$.

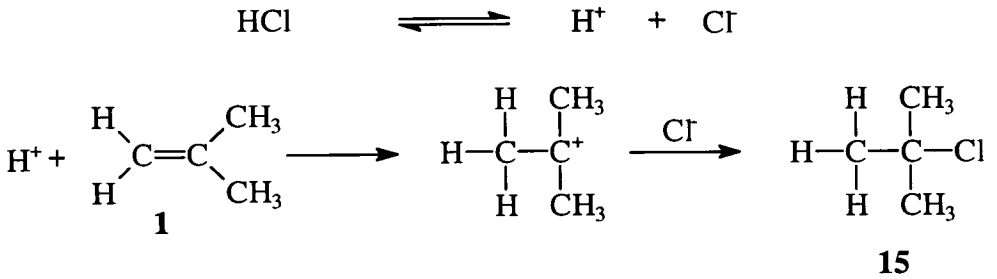
Several acidity scales have been constructed on the basis of polyisobutene yield or molecular weight, but they are of little predictive significance. For example, Chalmers' scale[43] ($BF_3 > AlBr_3 > TiCl_4 > TiBr_4 > BCl_3 > SnCl_4 > BBr_4$) lists BF_3 to be the most efficient Lewis acid. More recent results by Kennedy[44] showed that BCl_3 is by far a more efficient co-initiator than BF_3 in terms of both polyisobutene yield and molecular weight.

2.2. The chemistry of initiation by Lewis acids

Carbocationic polymerisations induced by Friedel-Crafts acids[3] are in no doubt the most important such processes from an industrial point of view.

The advantage of Friedel-Crafts systems over Bronsted acids is their ability to prolong the life-time of the kinetic chain and thus render propagation to high molecular weights possible. Owing to the highly nucleophilic conjugate bases of Bronsted acids, carbocationic polymerisation chain initiated by these acids are usually short, and consequently lead to low molecular weight products. Friedel-Crafts acids are capable of coordinatevely complexing conjugate bases of Bronsted acids which leads to very stable counter-anions. Thus, mixtures of Bronsted acids with Friedel-Crafts acids, are among the strongest acids known.

For example, hydrogen chloride will initiate a reaction with isobutene, but it will not lead to polymer because the highly nucleophilic chloride ion immediately terminates the carbocation to form *tert*-butyl chloride **15** (Scheme 12).

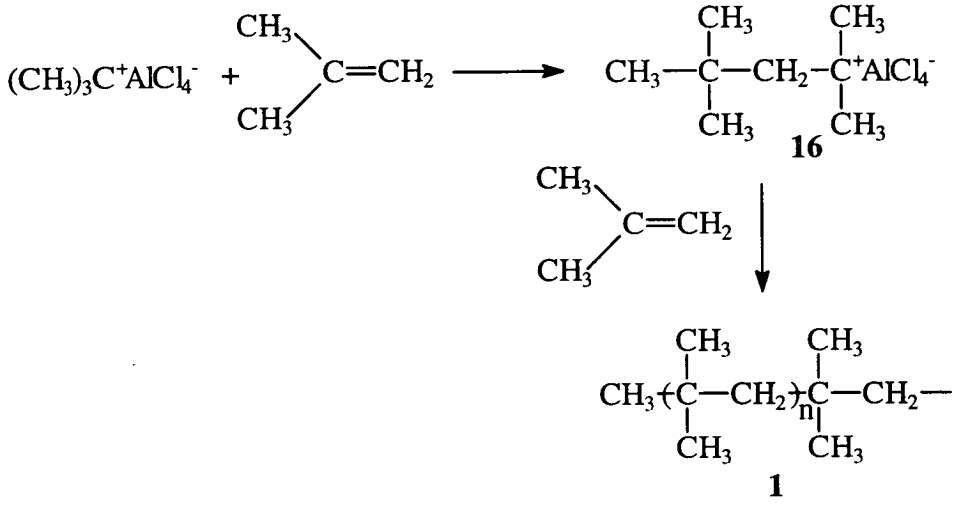


Scheme 12

The introduction of a Lewis acid such as $AlCl_3$ to the reaction has two effects :

- the acidity of HCl is increased, and

- the chloride ion reacts with the Lewis acid to form a less nucleophilic species ($AlCl_4^-$), which is much less likely to terminate the carbenium ion. This prolongs the life of the propagating carbenium ion **16** and allows propagation to proceed (Scheme 13).



Scheme 13

It was generally thought until recently that all Lewis acids required a proton or cation donor to initiate polymerisation. Many workers[45,46] have also found that the order of addition of the co-initiator, initiator, and monomer is critical in terms of reproducibility. The actual mechanism for most systems remains unclear. Indeed, it has been claimed[46] that isobutene polymerisation can be initiated using $TiCl_4$ without a protogen. This controversial "direct initiation" has also been described for isobutene using $AlCl_3$ and $AlBr_3$[47], or $EtAlCl_2$[48] initiating-systems. More recently, direct initiation of an isobutene polymerisation by BCl_3 has been proposed[49].

This direct initiation process can be represented as follows (equation 6) in the case of $AlBr_3$:

$$2AlBr_3 \rightleftharpoons AlBr_2^+(AlBr_4)^- \quad (6)$$

followed by reaction with monomer M (equation 7), thus :

$$AlBr_2^+(AlBr_4)^- + M \longrightarrow AlBr_2M^+(AlBr_4)^- \quad (7)$$

Much of the evidence to support the direct initiation process is indirect, consisting of kinetic, conductance, and spectrophotometric data for reaction systems at different levels of dryness and purity. The major difficulty in ascertaining whether direct initiation occurs in a particular reaction system and, if it does, its extent relative to the co-initiation process, is the large effect exerted by small amounts of proton or cation donors. Thus, water concentration of 10^{-3} appear sufficient to increase the initiation rate by a factor 10^3 for $TiCl_4$ and $AlCl_3$ in CH_2Cl_2.[50,51] These and other results do, however, indicate that if direct initiation ocurs, its contribution to the overall initiation process is small when a proton or cation donor is present. For most ordinary reaction systems, the moisture content (and/or level of other cation or proton donors) is often sufficient to result in an overwhelming proportion of initiation by the co-initiated route.

The activity of the initiator-co-initiator complex is dependent on its ability to donate a proton or cation to the monomer which, in turn, depends on the initiator, co-initiator, and monomer. The extent of formation of the initiator-co-initiator complex and its rate of addition to monomer generally increase with increasing acidity of the Lewis acid co-initiator. Thus the general order of activity of aluminium co-initiators

corresponds to their order of acidity : $AlCl_3 > AlRCl_2 > AlR_2Cl > AlR_3$. The activity of the initiator-co-initiator complex also increases with increasing acidity of the initiator, *e.g.*, hydrogen chloride > acetic acid > nitroethane > phenol > water >> methanol > acetone in the polymerisation of isobutene with $SnCl_4$.[52,53] For initiators such as organic halides, the initiation rate is dependent on carbenium ion stability[10]. Primary and secondary alkyl halides are generally ineffective in initiation, since primary and secondary carbenium ions are not formed in significant concentrations. Tertiary carbenium ions are sufficiently stable to be formed but are not more stable than the carbenium ions derived from their addition to monomers such as isobutene, styrene, or *N*-vinylcarbazole, and consequently the polymerisation of those monomers occurs. A word of caution is needed regarding these generalisations. The order of activity of a series of initiators or co-initiators may differ depending on the identity of the other component or the presence of competing reactions. For example the activity of boron halides in isobutene polymerisation ($BF_3 > BCl_3 > BBr_3$) with water as the initiator is the opposite of their acidities. Hydrolysis of the boron halides to inactive products, increasing in the order $BBr_3 > BCl_3 > BF_3$, is responsible for the observed polymerisation results[36].

2.3. Supported Lewis acids

Lewis acids are widely used as catalysts in carbocationic polymerisation processes to catalyse the polymerisation of monoolefins. Such carbocationic polymerisation catalysts have many advantages, including high yield, fast reaction rate, good

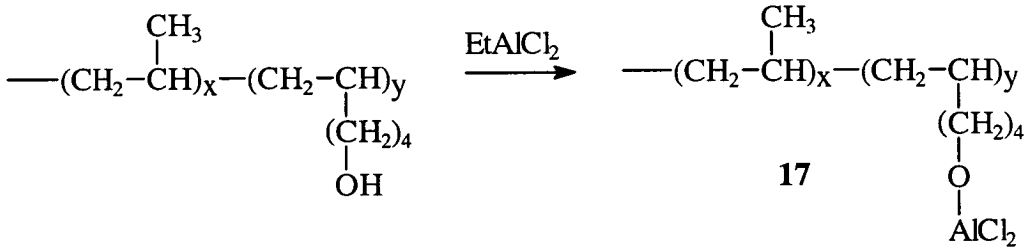
molecular weight control, and utility with a wide variety of monomers. However, conventional carbocationic polymerisation processes typically employ Lewis acid catalysts in an unsupported form. Hence, these catalysts cannot be re-cycled or re-used in a cost effective manner.

Catalyst recycling offer several important advantages in chemical production processes. These include waste reduction, lower cost and simpler product purification. All of them also save energy and benefit the environment. These considerations become even more important when the reaction requires a large quantity of catalyst, such as the oligomerisation of olefins. A variety of supported catalysts for the oligomerisation of olefins have been reported. Most of them are prepared by dispersing metal salts on inorganic substrates[54], such as magnesium oxide, alumina, silica or zeolite, followed by calcination/reduction. These highly dispersed particles allow effective metal utilisation, but the supported catalysts are usually hydrolysed and become part of the waste stream after a reaction cycle. Also there are several disadvantages associated with their use. One particularly strong disadvantage is that these approaches to supported catalyst generally produce only low molecular weight oligomers. Another disadvantage is that the catalysts (supported on inorganic substrates) typically leach out during the reaction since the catalysts tend to be not firmly fixed to the supporting substrate.

There are some examples of using polymers[55, 56] as the solid substrates, the most common one being a cross-linked polystyrene. Unfortunately, the activity of the polymer-bonded Lewis acid catalyst is always relatively low and the activity of the catalyst decreases after a few reaction cycles. The reasons for the deactivation may

be related to the poor stability of the polymer substrate and the slow diffusion of the catalyst into the polymer matrix. The use of crystalline polyolefin as the substrate has been recently introduced[57, 58].

Tchung[57] recently described a new class of supported Lewis acid catalysts which are based on partially crystalline polypropylene. The Lewis acid, such as $EtAlCl_2$, is chemically bonded to the side chain of polypropylene and serves as catalyst for the polymerisation of isobutene. The hydroxylated polypropylene[59] was prepared by Ziegler-Natta polymerisation with borane containing monomer and propylene. Borane groups in copolymers were subsequently oxidised to hydroxy groups by $NaOH/H_2O_2$. The hydroxyl groups are then reacted with $EtAlCl_2$, in order to attach the latter to the polymer (Scheme 14). This type of supported catalyst **17** can be easily recovered and reused for many reaction cycles without significant loss of its reactivity.



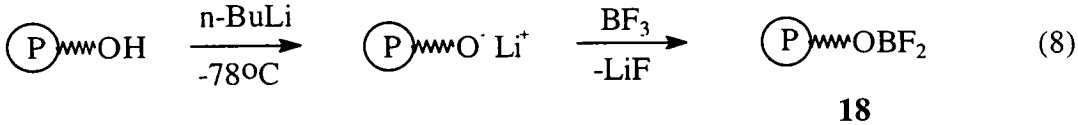
Scheme 14

The unique features of the structure of polypropylene offer a catalyst with high surface area and good mobility, which accounts for the high catalytic activity. In addition, polypropylene is chemically and physically stable during the process. The

active species PP-O-$AlCl_2$ **17** was used as the catalyst for the carbocationic polymerisation of isobutene. The resulting polyisobutenes are similar to those prepared by conventional aluminium catalysts, such as $AlCl_3$, $EtAlCl_2$ and Et_2AlCl, under similar reaction conditions.

One important feature of polyisobutene prepared by aluminium catalysts is the high rate of internal double bonds in the polymers (Type C end-groups **7** and **8**). However, it is very desirable to have terminal unsaturation (Type A vinylidene end-group **5**) to raise the possibility of functionalisation reactions. It is now known that BF_3 initiating systems give a higher concentration of vinylidene end-groups **5** in polyisobutene. However, BF_3 is causing great environmental concern.

Tchung[58] also proposed a new supported Lewis acid catalyst which involved a BF_3-derived species chemically bonded to the crystalline polyolefins, such as polypropylene and poly(1-butene). The hydroxylated polymers, P, polypropylene and poly(1-butene) were prepared by Ziegler-Natta polymerisation with the use of borane co-monomers as described before. The direct reaction of BF_3 with hydroxyl group was reported to be very slow and to possibly form BF_3/OH complexes. More effective condensation was carried out using alkoxides. The metalation of hydroxyl groups was carried out by simply reacting polymer particle with *n*-butyllithium solution. A BF_3/CH_2Cl_2 solution was then added for attachment of BF_3 (equation 8)



(8)

18

The supported catalysts **18** are active in the polymerisation of isobutene and are recovered and re-used for many reaction cycles without significantly losing their activity. Several advantages, such as chemical and physical stabilities of the substrate, convenient implantation to load high concentration of catalyst to the substrate, and high catalyst reactivity, have been observed. In addition, polyisobutene obtained in this process has high terminal unsaturation.

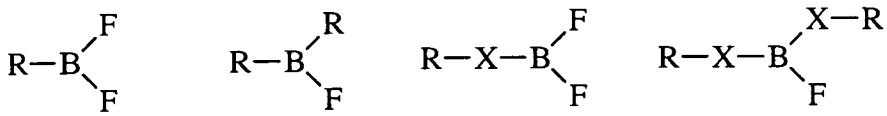
3. Initiating systems based on derivatives of boron trifluoride

3.1. Programme of research

At Grangemouth, BP Chemicals use boron trifluoride/alcohol complexes as initiating systems for the polymerisation of isobutene in order to obtain a highly reactive polymer with terminal unsaturation(see **5**) in the molecular weight range 750 to 2500. The trade name of this recently developed second generation polyisobutene with enhanced reactivity is Ultravis. Although the vinylidene content of Ultravis may reach 70%, efforts are being made to find alternative initiating systems, and at the same time improve polymer quality.

The aim of the present project was to prepare a range of liquid, albeit non-volatile boron trifluoride derivatives and to investigate their utility as Lewis-acid co-initiators for the polymerisation of isobutene. It was intended to form highly reactive polyisobutene oligomers in the molecular weight range 750 to 2500 with a minimum terminal olefinic vinylidene content of *ca.* 60%.

The first stage of the project was to prepare and evaluate as co-initiators a series of boron trifluoride derivatives initially selected from the following structures (Figure 2) and whose Lewis-acid activity had hitherto not been investigated for much purposes.



where R = alkyl or aryl, and X = O or S

Figure 2. Proposed boron trifluoride-derivatives

Based on the results from this first stage of the work, the second part of the research was to design, prepare and evaluate appropriate supported derivatives of boron trifluoride as co-initiators for the polymerisation of isobutene.

3.2. Alkoxy (and aryloxy) difluoroboranes, $ROBF_2$, and their adducts with alcohols and Bronsted acids

3.2.1. Preparation

Alkoxydifluoroboranes, $ROBF_2$ **19** have received scant attention[60]. Gasselin[61] has reported the preparation of methoxydifluoroborane **20** from sodium methoxide and boron trifluoride (equation 9),

$$BF_3 + NaOCH_3 \longrightarrow \underset{\mathbf{20}}{CH_3OBF_2} + NaF \qquad (9)$$

and also from boron trifluoride and trimethoxyborane **21** (equation 10).

$$\underset{\textbf{21}}{2BF_3 + (CH_3O)_3B} \longrightarrow \underset{\textbf{20}}{3CH_3OBF_2} \qquad (10)$$

This result is contrary to the findings of Meerwein and Pannwitz[62] who by the former reaction obtained the coordination compound **22** (equation 11).

$$BF_3 + NaOCH_3 \longrightarrow \underset{\textbf{22}}{BF_3.NaOCH_3} \qquad (11)$$

Goubeau and Lucke[63] prepared the same methoxydifluoroborane **20** by using Gasselin's second method[61], and deduced from Raman spectroscopy that the difluoroborane possessed a dimeric structure **20a** (Figure3).

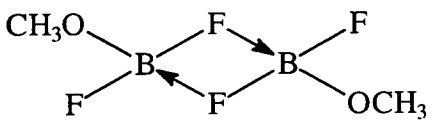


Figure 3. Proposed dimeric structure **20a** for methoxydifluoroborane

Similar conclusions have been drawn by Allen and Sudgen[64], but their method of preparation was not stated. Goubeau and Lucke[63] have observed that dimethoxyfluoroborane **23**, although having a constant boiling-point (52.7°C), could not be crystallised upon cooling, and instead afforded the difluoroborane **20**, presumably by disproportionation (equation 12).

$$\underset{\textbf{23}}{2(CH_3O)_2BF} \longrightarrow \underset{\textbf{20}}{CH_3OBF_2} + (CH_3O)_3B \qquad (12)$$

Meerwein and co-workers[65] suggested that boron trifluoride forms both a 1:2 and 2:1 coordination complex **24** and **25**, respectively, with trialkoxyborane, but that these complexes are very unstable, tending to disproportionate into monofluoroboranes **26** (equation 13) and alkoxydifluoroboranes **19** (equation 14).

$$\underset{\mathbf{24}}{2(RO)_3B.BF_3} \rightleftharpoons \underset{\mathbf{26}}{3(RO)_2BF} \qquad (13)$$

$$\underset{\mathbf{25}}{(RO)_3B.2BF_3} \rightleftharpoons \underset{\mathbf{19}}{3ROBF_2} \qquad (14)$$

Stacey and co-workers[66] attempted to prepare *di-n*-butoxyfluoroborane **27** by reaction of the boron trifluoride-ether complex and *tri-n*-butoxyborane **28** (equation 15) but a very unstable compound **27** was obtained and pointed to the occurrence of a disproportionation similar to that observed by Goubeau and Lucke[63].

$$\underset{\mathbf{28}}{(C_4H_9O)_3B} + BF_3.OEt_2 \xrightarrow[\text{reflux 6h.}]{Et_2O} \underset{\mathbf{27}}{(C_4H_9O)_2BF} \qquad (15)$$

Lappert[67] has prepared *n*-butoxydifluoroborane, $C_4H_9OBF_2$ **29**, in 90% yield by action of boron trifluoride on *tri-n*-butoxyborane **28** (equation 16), the reaction being reversible at high temperature .

$$\underset{\mathbf{28}}{(C_4H_9O)_3B} + 2BF_3 \xrightarrow[1h.]{0°C} \underset{\mathbf{29}\ (90\%)}{3C_4H_9OBF_2} \qquad (16)$$

The reaction of boron trifluoride and the 1:1:1 boron trifluoride-*n*-butanol-*tri*-*n*-butoxyborane complex **30** afforded *n*-butoxydifluoroborane **29** (equation 17) in high yield.

$$2[BF_3.(Bu^nO)_3B.Bu^nOH] + 3BF_3 \xrightarrow{20^\circ C} BF_3.2Bu^nOH + 6Bu^nOBF_2 \quad (17)$$

30 **29** (96%)

In a further development, Lappert and co-workers[68] prepared *n*-butoxydifluoroborane **29** in two different ways (equations 18 and 19).

$$BBu^n(OBu^n)_2 + 2BF_3 \xrightarrow{0^\circ C} Bu^nBF_2 + 2Bu^nOBF_2 \quad (18)$$

(81%) **29** (85%)

and

$$BPh(OBu^n)_2 + BF_3 \xrightarrow{0^\circ C} Ph(OBu^n)BF + Bu^nOBF_2 \quad (19)$$

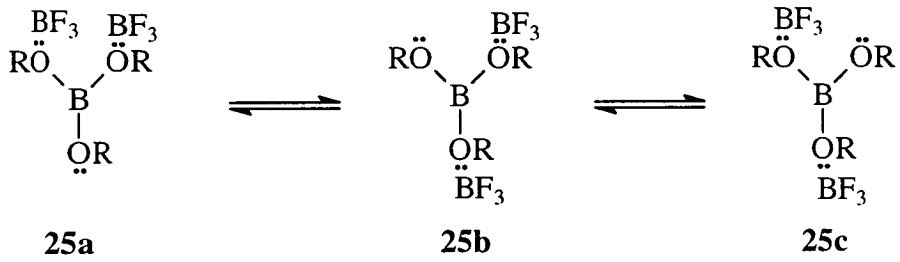
(72%) **29** (91%)

In 1960, McCusker and Kilzer[69] demonstrated that the compounds reported in the literature as alkoxydifluoroboranes $ROBF_2$ **19** had properties which were more characteristic of coordination compounds than of substituted boranes. Overall consideration of vapour densities, cryoscopic molecular weights, distillation behaviour and reaction with nitrogen bases led to the identification of the presumed alkoxydifluoroboranes as the previously identified coordination compound **25** of trialkoxyborane **31** and two moles of boron fluoride (equation 20). Comparison of

these substances with the well-established boron trifluoride-ether complex supported their identification as coordination compounds.

$$\underset{\textbf{31}}{2BF_3 + (RO)_3B} \longrightarrow \underset{\textbf{25}}{(RO)_3B.2BF_3} \qquad (20)$$

In 1961, Landesman and Williams[70] gave some evidence that the compounds produced by the reaction of one mole of various trialkoxyboranes $(RO)_3B$ **31** with two moles of boron trifluoride are in fact alkoxydifluoroboranes **19** with the cyclic trimeric structure **19a** (Figure 4) rather than the previously suggested coordination complex **25**. Presumably the latter would be a static adduct **25a** although the dynamic system with BF_3 migrating from oxygen to oxygen could also be considered as a complex (Figure 5).



25a **25b** **25c**

Figure 5. Complex of one mole trialkoxylborane with two moles boron trifluoride

In such a complex, boron trifluoride is exchanging between the different ester oxygen atoms. Since in either structure (**25a, b** or **c**), both the ester- and fluoride- substituted boron atoms are non-equivalent, the expected ^{11}B NMR spectrum should consist of two peaks; one at 0 ppm corresponding to where boron trifluoride complexes absorbed, and with twice the area of the other at 18 ppm where trialkoxyboranes are

usually located. However, the spectrum observed proved to be a sharp singlet at 0 ppm showing unequivocally that only one type of boron atom is present, and apparently in a tetrahedral configuration. The structure in agreement with these data is the cyclic trimer **19a** (Figure 4).

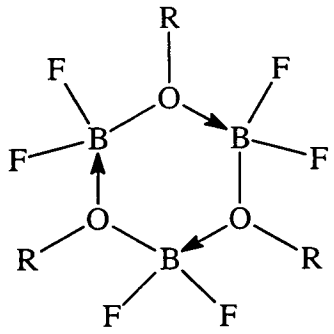


Figure 4. Alkoxydifluoroboranes trimeric structure **19a**

In a variant to Gasselin's[61] procedure, Chung and co-workers[58] have recently reported the preparation of *n*-pentoxydifluoroborane $C_5H_{11}OBF_2$ **32** by adding a saturated dichloromethane solution of BF_3 to lithium pentoxide **33** suspended in dichloromethane (equation 21) at room temperature.

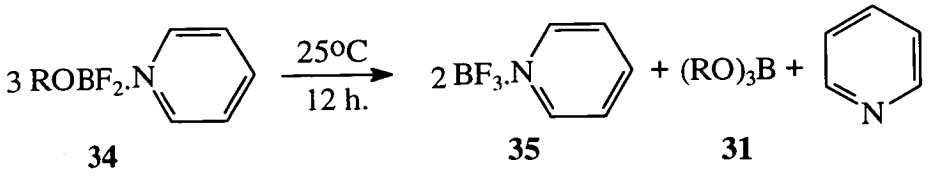
$$C_5H_{11}OH \xrightarrow[-78°C]{n\text{-BuLi/Et}_2O} C_5H_{11}O^-Li^+ \ (\mathbf{33}) \xrightarrow[\text{room temp.}]{BF_3/CH_2Cl_2} C_5H_{11}OBF_2 \ (\mathbf{32}) \qquad (21)$$

^{11}B NMR spectrum of the product isolated from the reaction after stirring for 15 minutes showed a single peak at 0 ppm, corresponding to the grouping OBF_2, a result that was also confirmed by elemental analysis with a mole ratio of 1:2 between boron and fluorine respectively.

Based on this evidence it is clear that only two methods are currently available for the preparation of alkoxydifluoroboranes $ROBF_2$ **19**, since the reaction of BF_3 with an alkoxide such as sodium methoxide is found to give only the coordination complex $BF_3.NaOCH_3$ **22**[62]. The first method involves condensation of BF_3 with trialkoxyborane [69] $(RO)_3B$ **31**, and is successful for various alkyl groups R, whilst the second method uses the reaction of BF_3 with a lithium alkoxide RO^-Li^+ in dichloromethane [58].

3.2.2. Alkoxydifluoroboranes adducts with alcohols and Bronsted acids

Apart from various studies into the structure of alkoxydifluoroboranes **19**, efforts have also been made to assess their reactivity towards nucleophiles. Nitrogen donors such as pyridine form a coordination complex **34** at low temperature but such complexes decomposes into **35** and $(RO)_3B$ **31** when the temperature is raised above -30°C [67, 71] (equation 22).



34 **35** **31** (22)

On the other hand, when methoxydifluoroborane CH_3OBF_2 **20** is treated with methanol[72], both a 1:1 and 1:2 complex are formed. By comparison, the ^1H NMR spectrum of a 1:2 molar ratio of methoxydifluoroborane **20** in neat methanol gave two signals, *viz.* one at 3.33 ppm which was assigned to the methyl groups, and the

other at 10.66 ppm which clearly indicated the formation of highly mobile protons. Lysenko *et al.*[72] proposed a system involving autoionisation of the solvent (methanol) as depicted in equation 23.

$$\underset{\mathbf{20}}{CH_3OBF_2} + 2CH_3OH \underset{\text{room temp.}}{\rightleftharpoons} [BF_2(OCH_3)_2]^-[CH_3OH_2]^+ \qquad (23)$$

In contrast to methoxydifluoroborane **20**, Lappert[67] has found that reaction of an equimolar amount of *n*-butoxydifluoroborane **29** with *n*-butanol gave a mixture of products **36**, together with a complex between boron trifluoride and the alcohol (equation 24). Hydrolysis of the same difluoroborane **29** also led to disproportionation as shown in equation 25.

$$3\ \underset{\mathbf{29}}{Bu^nOBF_2} + Bu^nOH \xrightarrow{20°C} \underset{\mathbf{36}}{[BF_3,\ (Bu^nO)_3B,\ Bu^nOH]} + BF_3.2Bu^nOH \qquad (24)$$

$$2Bu^nOBF_2 + 3H_2O \xrightarrow[4\ h.]{100\text{-}110°C} BF_3.2Bu^nOH + H_3BO_3 + HF \qquad (25)$$

3.3. Alkyl (and aryl) difluoroboranes, RBF_2, and their adducts with alcohols and Bronsted acids

3.3.1. Preparation

The most important methods for the preparation of alkyl (or aryl) difluoroboranes[60] have depended essentially on one of the following four procedures :

(i) interaction of organometallic compounds with boron halides

(ii) reaction of aminoboron compounds with halogenating agents

(iii) reaction of trialkylboranes with boron trifluoride, and

(iv) reaction of boronic or boronous acids or derivatives of (anhydrides, esters) with boron trifluoride

3.3.1.1. Use of organometallic compounds

Phenyldifluoroborane **38**, together with some diphenylfluoroborane **39**, has been obtained by the addition of boron trifluoride in anhydrous diethyl ether to phenylmagnesium bromide and subsequent direct distillation from the reaction mixture[73, 74] (equation 26); the *p*-tolyldifluoroborane **40** was similarly obtained.

$$BF_3.OEt_2 + PhMgBr \xrightarrow{Et_2O} \underset{\mathbf{38}}{PhBF_2} + \underset{\mathbf{39}}{Ph_2BF} \qquad (26)$$

This experiment was difficult to reproduce , but a 20% yield of phenyldifluoroborane **38** has been reported.

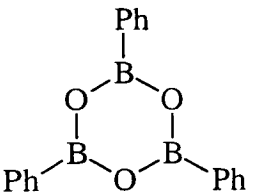
By equimolar interaction of boron trifluoride and diphenylzinc, phenyldifluoroborane **38** was obtained in 68% yield[75] (equation 27). A similar method had earlier been used for the preparation of methyldifluoroborane[76] **41**, but in that case, complete exchange took place (equation 28), whereas in the phenyl example only half exchange was possible.

$$Zn(C_6H_5)_2 + BF_3 \longrightarrow \underset{\textbf{38}}{C_6H_5ZnF} + C_6H_5BF_2 \qquad (27)$$

$$Zn(CH_3)_2 + 2BF_3 \longrightarrow ZnF_2 + \underset{\textbf{41}}{2(CH_3)BF_2} \qquad (28)$$

Although the use of Grignard reagents and zinc aryls has been claimed to be successful for the preparation of phenyldifluoroborane **38** and *p*-tolyldifluoroborane **40**, the product of each reaction was not fully characterised[73, 74].

McCusker *et al*[77] reported the first authentic aryldifluoroborane in 1957. Phenyldifluoroborane **38** was prepared by the reaction of boron trifluoride and triphenylboroxine **42** (equation 29).



42

$$+ \quad BF_3 \xrightarrow[7\ h.]{215^oC} PhBF_2 \qquad (29)$$

38 (18%)

This reaction was found to be extremely tedious and capable of giving yields of only about 16%.

In the same report, McCusker showed that the reaction of aryldichloroborane with antimony trifluoride and presumably other similar fluorinating agents provided the best method for the preparation of aryldifluoroboranes (equations 30 and 31). The reaction is rapid and yields are high.

$$3PhBCl_2 + 2SbF_3 \xrightarrow{45°C} \underset{\textbf{38}\ (66\%)}{3PhBF_2} + 2SbCl_3 \qquad (30)$$

$$p\text{-}TolBCl_2 + SbF_3 \xrightarrow{20°C} \underset{\textbf{40}\ (73\%)}{p\text{-}TolBF_2} + SbCl_3 \qquad (31)$$

McCusker *et al.*[77] also showed that the addition of organolithium or Grignard reagents to BF_3 results in multiple additions of the organometallic reagent, and therefore to full alkylation of boron trifluoride.

A number of methods for preparing alkyl or aryl difluoroboranes have been described[60], but by no means are the methods particularly convenient. These compounds can be obtained by treating the easily prepared or often commercially available, tetraorgano-tin compounds with boron trihalides. The reaction proceeds smoothly at ambient temperatures or on mild warming, and yields are good.

In 1960, Brinckman *et al.*[78] found that vinyldifluoroborane **43** could be prepared by treating boron trifluoride with divinylmercury **44** (equation 32) or divinylzinc **45** (equation 33).

$$\underset{\mathbf{44}}{Hg(CH{=}CH_2)_2} + BF_3 \xrightarrow[0.5\ h.]{\text{room temp.}} \underset{\mathbf{43}\ (19\%)}{(CH_2{=}CH)BF_2} \qquad (32)$$

$$\underset{\mathbf{45}}{Zn(CH{=}CH_2)_2} + BF_3 \xrightarrow[2\ h.]{\text{room temp.}} \underset{\mathbf{43}\ (27\%)}{(CH_2{=}CH)BF_2} \qquad (33)$$

Since divinylmercury **44** is toxic, and divinylzinc **45** is inflammable in air and also thermally unstable, use of these reagents was largely abandoned in favour of tetravinyltin **46** (equation 34).

$$\underset{\mathbf{46}}{Sn(CH{=}CH_2)_4} + BF_3 \xrightarrow[24\ h.]{60°C} \underset{\mathbf{43}\ (52\%)}{(CH_2{=}CH)BF_2} \qquad (34)$$

Similarly, propyldifluoroborane **47** was prepared by treating boron trifluoride with tetrapropyltin **48** (equation 35).

$$\underset{\mathbf{48}}{Sn(C_3H_7)_4} + BF_3 \xrightarrow[20\ h.]{110°C} \underset{\mathbf{47}\ (44\%)}{C_3H_7BF_2} \qquad (35)$$

Vinyldifluoroborane **43** is not further vinylated when heated with a variety of vinylmetallic reagents.

In 1961, Burg *et al*[79]isolated the very volatile methyldifluoroborane **41** from the reaction of BF_3 with tetramethyltin **49** (equation 36).

$$\underset{\mathbf{49}}{(CH_3)_4Sn} + 2BF_3 \xrightarrow[2\ h\ .]{100°C} \underset{\mathbf{41}}{CH_3BF_2} + (CH_3)_3SnBF_4 \qquad (36)$$

3.3.1.2. Use of aminoboron compounds

In 1959, Brinckman *et al.*[80] reported the formation of boron trichloride and alkyldifluoroboranes **37** from the mixing of boron trifluoride and alkydichloroboranes **50**. In other reactions, boron trifluoride and alkydichloroboranes **50** were formed by mixing boron trichloride and alkyldifluoroboranes **37** . Equilibria of the type shown in equation 37 are driven in the expected direction, removal of the strongest Lewis acid, by addition of base. Trimethylamine-ethyldichloroborane heated with boron trifluoride for 19 hours at 90°C gave as the only volatile product ethyldifluoroborane.

$$\underset{\mathbf{37}}{3RBF_2} + 2BCl_3 \rightleftharpoons \underset{\mathbf{50}}{3RBCl_2} + 2BF_3 \qquad (37)$$

Exchange phenomena were observed in the following sequence of reactions (Figure 6).

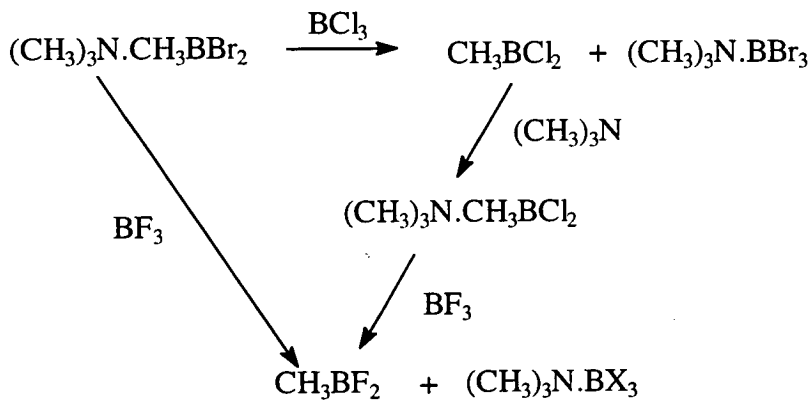


Figure 6.

In 1968, Noth and Vahrenkamp[81] prepared methyldifluoroborane **41** and phenyldifluoroborane **38** in good yield by the following reactions (equation 38 and 39 respectively).

$$CH_3B[N(CH_3)_2]_2 + BF_3 \longrightarrow \underset{\textbf{41}\ (90\%)}{CH_3BF_2} + [(CH_3)_2NBF_2]_2 \qquad (38)$$

$$C_6H_5B[N(CH_3)_2]_2 + BF_3 \xrightarrow{0°C} \underset{\textbf{38}\ (52\%)}{C_6H_5BF_2} + [(CH_3)_2NBF_2]_2 \qquad (39)$$

3.3.1.3. Use of trialkylboranes

In 1956, Bulls *et al.*[82] developed a synthesis of alkylhaloboranes that consisted of heating of a trialkyborane R_3B **51** with a trihaloborane under pressure, thus effecting a redistribution of alkyl and halogen groups (equation 40).

$$\underset{\textbf{51}}{R_3B} + BF_3 \rightleftharpoons R_2BF + \underset{\textbf{37}}{RBF_2} \qquad (40)$$

A temperature of 200°C and a reaction time of 20 hours was found to be satisfactory for the preparation of the butylfluoroboranes $C_4H_9BF_2$ **52** and $(C_4H_9)_2BF$ **53**. The products were obtained in 29.6% and 30.9% yield respectively.

Tuhagues and Laurent[83] in 1967, studied the products from the reaction of boron trifluoride with trialkylboranes **51** by ^{19}F and ^{11}B NMR spectroscopy and concluded that the reaction could be represented as in equation 41.

$$4\ R_3B + 2BF_3 \overset{20^oC}{\rightleftharpoons} 6R_2BF \overset{200^oC}{\rightleftharpoons} 3\ R_3B + 3RBF_2 \qquad (41)$$

51 **51** **37**

In esssence, this procedure represents a convenient way of preparing alkyldifluoroboranes RBF_2 **37** in good yields, providing that the compounds are distilled out of the reaction mixture as soon as they are formed.

3.3.1.4. Use of boronic acids and derivatives

By the reaction of boron trifluoride with the anhydride of methylboronic acid **54**, Burg[84] obtained methyldifluoroborane **41** in 60-80% yield accompanied by some boric oxide **57** (equation 42).

$$(CH_3BO)_3 + 2BF_3 \longrightarrow 3CH_3BF_2 + B_2O_3 \qquad (42)$$

54 room temp. **41** **55**

In 1955, McCusker *et al.*[85] reported the preparation of alkyldifluoroborane **37** in yields of 50% or higher from the reaction of boron fluoride with alkylboronic acids **56**. In this particular case, it is presumed that the initial function of the boron trifluoride was to dehydrate the acid according to the reaction shown in equation 43.

$$3RB(OH)_2 \longrightarrow (RBO)_3 + 2H_2O \qquad (43)$$

56 **57**

The use of a boronic acid **56**, rather than a boronic acid anhydride as starting material for the preparation of alkyldifluoroboranes **37**, has the advantage of eliminating the dehydration step in the synthesis. It is worth noting that crude moist alkylboronic acids may be used directly and even under these conditions, reaction of the acid with boron trifluoride proceeds smoothly. Moreover, the boric oxide **55** formed in the reaction dissolves in the lower layer of boron trifluoride hydrate whilst the alkyl boron oxide **57** remains as the upper layer. This has the effect of removing the boric oxide **55** from the liquid in which reaction is occurring, and consequently permits a more complete reaction between boron trifluoride and the alkyl boron oxide **57**. The use of this technique has permitted the convenient synthesis of the following alkyldifluoroboranes : *n*-$C_4H_{11}BF_2$ **53**, *n*-$C_5H_{11}BF_2$ **58**, *n*-$C_6H_{13}BF_2$, cyclo-$C_6H_{11}BF_2$, 2-sec-$C_5H_{11}BF_2$, t-$C_5H_{11}BF_2$.

One year later, Brindley *et al*[68] reported the reaction of boronic esters with boron trifluoride. For example, boron trifluoride reacted readily with di-*n*-butoxy-*n*-butylborane **59** at 0°C, to afford *n*-butyldifluoroborane **53** in 81% yield (equation 44)

$$\underset{\mathbf{59}}{BBu^n(OBu^n)_2} + 2\,BF_3 \xrightarrow{O^\circ C} \underset{\mathbf{53}}{Bu^nBF_2} + 2\,\underset{\mathbf{29}}{Bu^nOBF_2} \qquad (44)$$

3.3.1.5. Other methods

In 1955, Stone and Graham[86] found that diborane **60** and tetrafluoroethylene underwent an unusual reaction to give boron trifluoride, ethyldifluoroborane **61**,

diethylfluoroborane **62**, polymeric tetrafluoroethylene and a mixture of fluorinated olefins (equation 45).

$$\underset{\mathbf{60}}{B_2H_6} + C_2F_4 \xrightarrow[\text{room temp.}]{} BF_3 + \underset{\mathbf{61}}{EtBF_2} + \underset{\mathbf{62}}{Et_2BF} \qquad (45)$$

Ethyldifluoroborane **61** was purified by forming its trimethylamine complex **63**, distilling off any impurities, and displacing the ethyldifluoroborane **61** with the stronger Lewis acid boron trifluoride (equation 46).

$$\underset{\mathbf{63}}{Me_3N^+.\bar{B}F_2Et} + BF_3 \xrightarrow[\text{room temp.}]{} Me_3N^+.\bar{B}F_3 + \underset{\mathbf{61}}{EtBF_2} \qquad (46)$$

Unfortunately, a stable difluoroborane could not be isolated when using this method. In 1964, Coyle *et al.*[87] reported the first preparation of difluoroborane HBF_2 **64** in 20-25% yield by the pyrolysis of diborane **60** at 100°C or above in the presence of boron trifluoride or organoboron fluorides. A second synthetically useful route to difluoroborane **64** was found to be the reaction of dialkoxyborane $HB(OR)_2$ with an excess of boron trifluoride. HBF_2 **64** was shown to add smoothly to ethylene at room temperature to form ethyldifluoroborane **61** (equation 47).

$$\underset{\mathbf{64}}{HBF_2} + CH_2{=}CH_2 \xrightarrow[\text{room temp.}]{} \underset{\mathbf{61}}{(C_2H_5)BF_2} \qquad (47)$$

In 1968 the same group[88] reacted difluoroborane **64** with both propene and isobutene to obtain *n*-propyldifluoroborane **47** (equation 48) and *iso*-butyldifluoroborane **65**, respectively (equation 49).

$$HBF_2 + (CH_3)CH{=}CH_2 \xrightarrow[23\ h.]{room\ temp.} (C_3H_7)BF_2 \quad (48)$$
64 **47** (80%)

$$HBF_2 + (CH_3)_2C{=}CH_2 \longrightarrow \textit{iso}\text{-}(C_4H_9)BF_2 \quad (49)$$
64 **65** (10.5%)

It should to be noted, however, that the reaction of difluoroborane **64** with isobutene led to extensive polymerisation of the olefin whilst butyldifluoroborane **65** was obtained in 10% yield only.

In 1987 Jutzi *et al.*[89] reported the preparation of pentamethylcyclopentadienyl difluoroborane **66** in good yield from the reaction of pentamethylcyclopentadienyl lithium **67** with boron trifluoride-etherate (equation 50).

$$Me_5C_5Li + BF_3.OEt_2 \xrightarrow[35°C/2\ h.]{Et_2O} Me_5C_5BF_2 \quad (50)$$
67 **66** 76%

In 1988 Bir *et al.*[90] reported a simple method for the preparation of alkyl or aryl difluoroboranes **37**. The fluorination of a number of alkyl and arylchloro- or bromo-boranes succeeds in good yields upon transhalogenation with lithium or potassium fluoride under mild reaction conditions (equation 51).

$$RBCl_2 + LiF \xrightarrow[0°C]{Et_2O} RBF_2 + LiCl \quad (51)$$
50 **37** (65-76%)

Phenyl- , 2-methylphenyl-, 2,4,6-trimethylphenyl, 2-(trimethylsilyl)phenyl-, 3-(trimethylsilyl)phenyl-, 4-(trimethylsilyl)phenyl-, 1,4-phenylen-, and *n*-octyl difluoroboranes were prepared this way.

Very recently, Vedejs *et al.*[91] reported the synthetic utility of alkyl- or aryltrifluoroborate species as *in situ* sources of trivalent boron halide Lewis acids. For example, reaction of phenylboronic acid $ArB(OH)_2$ with KHF_2 afforded the crystalline salt potassium phenyltrifluoroborate $KArBF_3$, which in the presence of chlorotrimethylsilane reacted to give ^{11}B NMR signals typical of $PhBF_2$ **38** in acetonitrile. The mechanistic details of the process by which fluoride ion is removed from boron have not been studied, and hitherto no effort has been made to isolate the phenyldifluoroborane **38**.

3.3.2. Alkyldifluoroboranes adducts with alcohols and Bronsted acids

The earliest systematic investigation of the effect of varying substituents on the boron atom was performed by Burg and Green[42], who showed that successive substitution of methyl groups for the more highly electronegative fluorine led to decreasing acidity towards trimethylamine in the sequence BF_3 > CH_3BF_2 > $(CH_3)_2BF$ > $(CH_3)_3B$. The acceptor tendency of boron in alkyldifluoroborane **37** has been shown to be less than in boron trifluoride. While only a slight dissociation of boron trifluoride.etherate occurs upon vaporisaton, complete dissociation of amyldifluoroborane.etherate occurs under the same conditions. The decreased strength of the donor acceptor bond in this complex probably results from a reduced

residual positive charge on the boron. Several complexes of difluoroborane with amines[92] and phosphines[93] have been reported in the literature.

Alkyldifluoroboranes RBF_2 **37** are expected to behave in a similar way as BF_3 towards Bronsted acids and alcohols. In particular, aliphatic alcohols form 1:1 and 2:1 adducts with boron trifluoride under appropriate conditions[94-96]. Since Landolph[97] first reported the reaction of boron trifluoride in 1:1 equivalent proportions with aldehydes, ketones, and other carbonyl compounds, many coordination compounds between boron trifluoride and organic molecules, containing donor atoms, have been mentioned in the literature[94, 98]. These compounds have been used extensively as catalysts in condensations, alkylations, and polymerisation reactions, and the interpretation of this catalytic activity has been based largely on the concept of an increased acidity conferred upon the organic molecule when coordinated to boron trifluoride.

Two series of addition compounds are formed by the reaction of boron trifluoride with the aliphatic acids, *viz.* $RCOOH.BF_3$ **68** and $(RCOOH)_2.BF_3$ **69** , the structure of which is shown in figure 7.

68 **69**

Figure 7. 1:1 and 2:1 adducts between aliphatic acids and boron trifluoride

A variety of thermodynamic and spectroscopic studies of boron trifluoride complexes with organic molecules[99] have been made to evaluate the energetics and stoichiometry of complex formation, together with steric hindrance to complexation,

and the relative basicities of the ligands. An efficient approach involves NMR spectroscopic measurements at temperatures low enough to slow exchange, thereby permitting the observation of separate resonance signals for bulk and co-ordinated ligand.

RESULTS AND DISCUSSION

A. Alkoxydifluoroboranes and alkyldifluoroboranes and their adducts with ethanol and Bronsted acids

1. Alkoxydifluoroboranes ($ROBF_2$) and adducts with ethanol and Bronsted acids

1.1. Alkoxydifluoroboranes

1.1.1. *N*-pentoxydifluoroborane

A modified version of the method used by Chung[58] was employed to prepare *n*-pentoxydifluoroborane **32**. In Chung's procedure, a saturated solution of BF_3 in dry methylene chloride was added to the previously prepared lithium alkoxide at room temperature (equation 21).

In our hands, this method was not successful because the boron trifluoride-saturated dichloromethane solution proved extremely difficult to keep due to the high volatility of boron trifluoride (bp = -101°C). Instead it was decided to prepare lithium pentoxide by adding *n*-butyllithium to a solution containing pentanol in diethyl diethyl ether at -78°C. After removing the diethyl ether, the resulting lithium pentoxide was then dissolved in dichloromethane and BF_3 was simply bubbled through the solution at 0°C until no more gas was absorbed (equation 52).

$$C_5H_{11}OH \xrightarrow[Et_2O/-78°C]{n\text{-BuLi}/Et_2O} C_5H_{11}O^-Li^+ \quad \mathbf{33} \xrightarrow[CH_2Cl_2/0°C]{BF_3} C_5H_{11}OBF_2 \quad \mathbf{32} \qquad (52)$$

This procedure proved successful and after filtering off the lithium fluoride and evaporation of the solvent, $C_5H_{11}OBF_2$ **32** was obtained in 96% yield as a colourless liquid which gradually turned yellow on exposure to light.

The product was analysed by NMR spectroscopy. Both the ^{13}C- and ^{1}H-NMR spectra displayed sharp peaks due to the pentoxy group, whilst the ^{11}B NMR spectrum showed a sharp signal at 0.5 ppm ; the ^{19}F NMR spectrum showed two sharp and closely spaced peaks at -149.25 and -149.22 ppm corresponding to ^{10}B and ^{11}B isotopes.

As noted earlier, both a coordination complex of the type $(RO)_3B.2BF_3$[69] **25** and alkoxydifluoroborane $ROBF_2$ monomer[61] **19**, dimer[63] **20a** and trimer[70] **19a** have been proposed for the structure of alkoxydifluoroboranes. Some clarification of the nature of the structure was obtained from the analysis of the above NMR spectra. Thus, the observation by Landesman *et al.*[70] and later confirmed by Tuhagues *et al.*[71] that chemical shifts in the region of 0 ppm for boron compounds are indicative of the trimeric structure **19a** is valid for the product obtained.

For example $BF_3.H_2O$ and BF_3.MeOH absorb at 0.2 and -0.7 ppm[100] respectively. However, in the event of an adduct such as $(C_5H_{11}O)_3B.2BF_3$ **70** being formed, two boron peaks would be expected and this is not the case. It is more feasible that the species present has the trimeric structure **32a** (Figure 9) with co-ordination through the oxygen atoms.

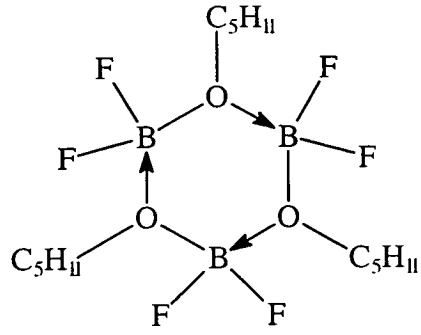


Figure 8. Trimeric structure **32a**

1.1.2. Pentafluorophenoxydifluoroborane

The same modified version of the method used by Chung[58] described in the section 1.1.1 was employed to attempt the prepararation of pentafluorophenoxydifluoroborane **71**. This involved preparing lithium pentafluorophenoxide **72** by adding *n*-butyllithium to a solution containing pentafluorophenol in diethyl ether at -78°C. After removing the ether, the resulting lithium pentafluorophenoxide **72** was then dissolved in dry dichloromethane and BF_3 was simply bubbled through the solution at 0°C until no more gas was absorbed (equation 53).

$$C_6F_5OH \xrightarrow[Et_2O/-78°C]{n\text{-}BuLi/Et_2O} C_6F_5O^-Li^+ \;\mathbf{72} \xrightarrow[CH_2Cl_2/0°C]{BF_3} C_6F_5OBF_2\;\mathbf{71} \qquad (53)$$

The method was apparently successful, but the NMR spectra showed the presence of a mixture of products. The ^{11}B NMR spectrum showed two groups of signals, viz.,

one broad peak at 17.4 ppm which was assigned to a mixture of trialkoxyborane $(C_6F_5O)_3B$**73** and fluoroborane $(C_6F_5O)_2BF$ **74** and a much sharper peak at 0.8 ppm assigned to BF_3 (Figure 9). Both trialkoxyboranes and dialkoxyfluoroboranes are characterised by ^{11}B NMR peaks in the range of 15-18 ppm according to the literature[100]. The integrated ratio of these two peaks was about 1:2. The ^{19}F NMR spectrum confirmed this result by showing a peak at -130.4 ppm, which was assigned to the fluoroborane $(C_6F_5O)_2BF$ **74** together with a sharp peak at -153.2 ppm corresponding to BF_3. Although alkoxydifluoroboranes and oxy-addition compounds of BF_3 both absorb in the 150 ppm area, it seems likely that pentafluorophenoxydifluoroborane **71** exists as a coordination compound of the type $(C_6F_5O)_3B.2BF_3$ **75** in keeping with the proposal of McCusker[69] (see section 3.1.1) rather than a trimer. This proposal fits both the chemical shift data and stoichiometry of boron with fluorine.

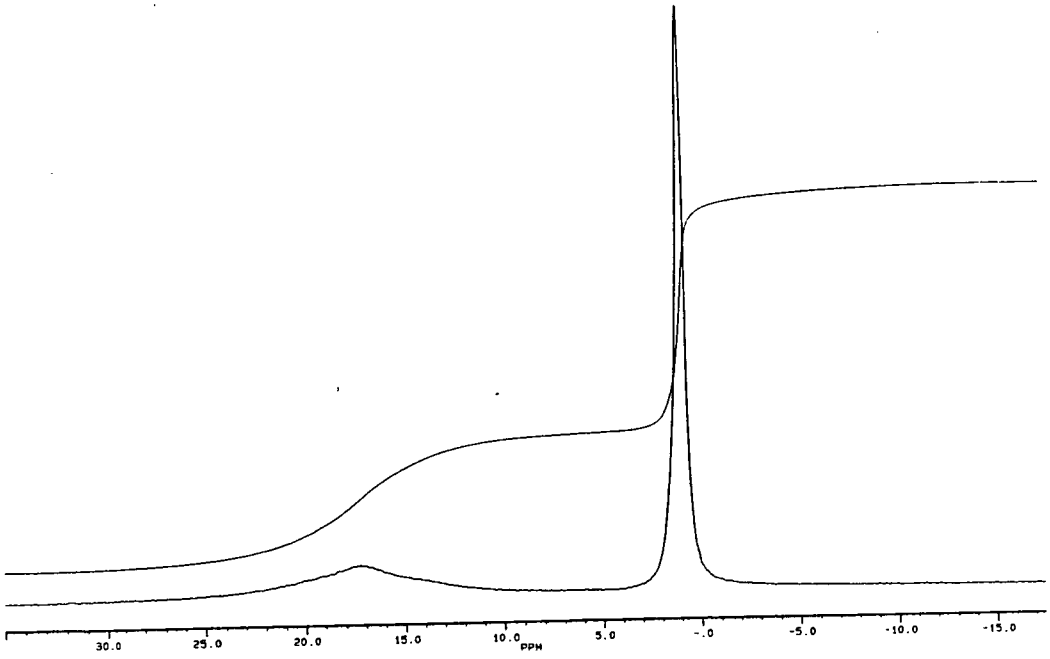


Figure 9. ^{11}B NMR spectrum of the product of the reaction of lithium pentafluorophenoxide with boron trifluoride

The involvement of di-pentafluorophenylfluoroborane **74** can be explained by a slow conversion of pentafluorophenoxydifluoroborane **71** to *tri*-pentafluorophenoxyborane **73** as shown in equations 54 and 55.

$$\underset{\mathbf{71}}{2C_6F_5OBF_2} \longrightarrow \underset{\mathbf{74}}{(C_6F_5O)_2BF} + BF_3 \qquad (54)$$

$$\underset{\mathbf{71}}{C_6F_5OBF_2} + \underset{\mathbf{74}}{(C_6F_5O)_2BF} \longrightarrow BF_3 + \underset{\mathbf{73}}{(C_6F_5O)_3B} \qquad (55)$$

A combination of stereoelectronic effects provided by the pentafluorophenyl group could be an explanation for not obtaining any of the expected trimeric structure but instead the coordination compound $(C_6F_5O)_3B.2BF_3$**75**.

1.1.3. Phenoxydifluoroborane

The same modified version of the method used by Chung[58] as described in section 1.1.1 was employed to prepare phenoxydifluoroborane **76**. As before, the technique involved preparing lithium phenoxide **77** by adding *n*-butyllithium to a solution containing phenol in diethyl ether at -78°C. After removing the ether, the resulting lithium phenoxide **77** was then dissolved in dry dichloromethane and BF_3 was simply bubbled through the solution at 0°C until no more gas was absorbed (equation 56). The method was apparently successful, but as in the case of pentafluorophenoxydifluoroborane **71**, the product failed to show the characteristics of a trimeric structure. Indeed, the ^{11}B NMR spectrum displayed two groups of signals with one broad peak at 15.9 ppm which was assigned to a mixture of

trialkoxyborane $(C_6H_5O)_3B$ **78** and fluoroborane $(C_6H_5O)_2BF$ **79** and a sharp peak at 1 ppm assigned to BF_3. The ratio of these two peaks was *ca.* 1:2. The ^{19}F NMR spectrum confirmed this result by showing a peak at -129.7 ppm which was assigned to the fluoroborane $(C_6H_5O)_2BF$ **79** and a sharp peak at -152.3 ppm which was assigned to BF_3.

$$C_6H_5OH \xrightarrow[Et_2O/-78°C]{n\text{-BuLi}/Et_2O} \underset{\mathbf{77}}{C_6H_5O^-Li^+} \xrightarrow[CH_2Cl_2/0°C]{BF_3} \underset{\mathbf{76}}{C_6H_5OBF_2} \qquad (56)$$

As explained earlier, both alkoxydifluoroboranes and oxy addition compounds of BF_3 give rise to peaks in the 150 ppm area, and on this evidence, it seems likely that phenoxydifluoroborane is a coordination compound of the type $(C_6H_5O)_3B.2BF_3$ **80** rather than a trimer. This fits both the chemical shifts and stoichoimetrically with the boron and the fluorine NMR data.

The involvement of diphenylfluoroborane **79** can be explained by a slow conversion of phenoxydifluoroborane **76** to triphenoxyborane **78** as shown in equations 57 and 58.

$$\underset{\mathbf{76}}{2C_6H_5OBF_2} \longrightarrow \underset{\mathbf{79}}{(C_6H_5O)_2BF} + BF_3 \qquad (57)$$

$$\underset{\mathbf{76}}{C_6H_5OBF_2} + \underset{\mathbf{79}}{(C_6H_5O)_2BF} \longrightarrow BF_3 + \underset{\mathbf{78}}{(C_6H_5O)_3B} \qquad (58)$$

As for pentafluorophenyl, steric hinderance of the phenyl group could also be an explanation for not observing a trimeric structure, but rather the coordination compound $(C_6H_5O)_3B.2BF_3$ **80**.

1.1.4. Methoxydifluoroborane

Methoxydifluoroborane **20** was prepared by the method of McCusker[69] which involved bubbling BF_3 gas through trimethoxyborane $(CH_3O)_3B$ **21** at 0°C (equation 59).

$$\underset{\mathbf{21}}{(CH_3O)_3B} + 2BF_3 \xrightarrow{0°C} \underset{\mathbf{20}}{3CH_3OBF_2} \qquad (59)$$

The product was characterised by NMR spectroscopy. Both ^{13}C NMR and ^{1}H NMR spectra showed sharp methoxy peaks, whilst the ^{11}B NMR spectrum displayed only a sharp single peak at 0.4 ppm. This particular aspect showed unequivocally that the starting material trimethoxyborane **21** which gives a single peak at 18 ppm[100], was not present in the product whose ^{19}F NMR spectrum contained two sharp peaks at -153.3 and -153.4 ppm corresponding to ^{10}B and ^{11}B isotopes. These shifts are in agreement with the literature values[100].

The ^{11}B NMR spectroscopy results confirmed the results obtained by Landesman and Williams[70] who proposed a trimer **19a** for the structure of alkoxydifluoroboranes. Indeed, the structure in agreement with one type of boron (a single peak in the 0 ppm area) is the cyclic alkoxydifluoroborane trimer **20b** (Figure 10).

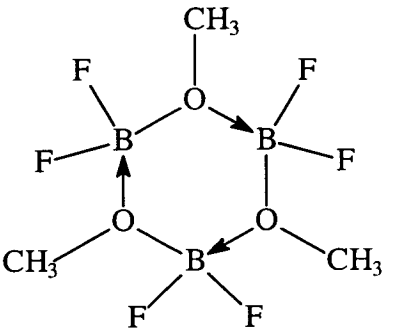


Figure 10. Methoxydifluoroborane (trimeric structure **20b**)

1.2. Alkoxydifluoroboranes adducts with ethanol

1.2.1. Addition of ethanol to *n*-pentoxydifluoroborane

Ethanol was added to *n*-pentoxydifluoroborane **32** in the glove box in order to form the 1:1 adduct $C_5H_{11}OBF_2$.EtOH **81**. The product was analysed by NMR spectroscopy in the hope that some clarification into its structure might be gained, but unfortunately, the spectra were difficult to interpret. In particular, the ^{11}B NMR spectrum showed two peaks in a ratio of 1:2 ; a broad peak absorbed at 18.8 ppm and corresponded to a mixture of tripentoxyborane $(C_5H_{11}O)_3B$ **82** and dipentoxyfluoroborane $(C_5H_{11}O)_2BF$ **83** whilst a major peak occurred at 0 ppm , which was assigned to BF_3 (Figure 11). If the complex was simply the adduct $C_5H_{11}OBF_2$.EtOH **81**, one boron peak would be expected.

The ^{19}F NMR spectrum also showed two peaks, *viz.* a small signal at -133.7 ppm which was assigned to dipentoxyfluoroborane $(C_5H_{11}O)_2BF$ **83** and a much larger one at -153.8 ppm.

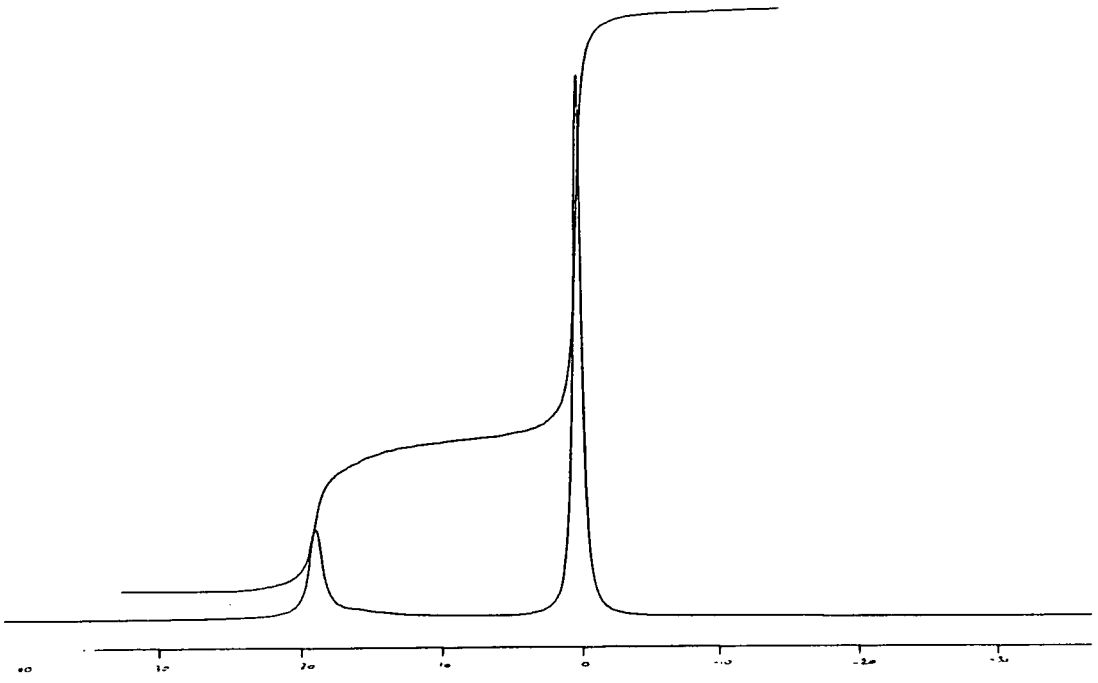


Figure 11. ^{11}B NMR spectrum of the adduct of *n*-pentoxydifluoroborane with ethanol

Although both alkoxydifluoroboranes **19** and BF_3.ROH complexes absorb in the latter region, *e.g.* BF_3.EtOH occurs at -151.6 ppm, it seems most likely that the complex formed is actually a [$(C_5H_{11}O)_3B$, $2BF_3$, EtOH] **84** mixture.The identification of dipentoxyfluoroborane $(C_5H_{11}O)_2BF$ **83** can be explained by a slow decomposition of *n*-pentoxydifluoroborane **32** to tripentoxyborane **82** as shown in equations 60 and 61.

$$\underset{\mathbf{32}}{2C_5H_{11}OBF_2} \longrightarrow \underset{\mathbf{83}}{(C_5H_{11}O)_2BF} + BF_3 \qquad (60)$$

$$\underset{\mathbf{32}}{C_5H_{11}OBF_2} + \underset{\mathbf{83}}{(C_5H_{11}O)_2BF} \longrightarrow BF_3 + \underset{\mathbf{82}}{(C_5H_{11}O)_3B} \qquad (61)$$

Both the ^{13}C and the ^{1}H NMR spectra of the complex comply with this interpretation. Peaks α and β to the oxygen were broad on both spectra but there was only one ethoxy and one pentoxy environment. The ^{1}H NMR spectrum also showed an acidic proton at 7.28 ppm.

From a consideration of the above evidence, it appears that addition of ethanol to *n*-pentoxydifluoroborane **32** leads to a similar compound to that originally proposed by Lappert[67], *viz.* the complex mixture [$(C_5H_{11}O)_3B$, $2BF_3$, EtOH] **84** rather than $C_5H_{11}OBF_2$.EtOH **81**.

1.2.2. Addition of ethanol to $(C_6F_5O)_3B.2BF_3$

Although pentafluorophenoxydifluoroborane **71** was shown to have the structure of a coordination compound of the type $(C_6F_5O)_3B.2BF_3$ **75**, the 1:1 adduct with ethanol was prepared by addition of ethanol to the adduct **75** in the glove box and analysed by NMR spectroscopy. It was found to give a similar complex mixture as **84**.

The ^{11}B NMR spectrum showed three peaks with one at 18.0 ppm which was assigned to the trialkoxyborane $(C_6F_5O)_3B$ **73**, one at 16.8 ppm which was assigned to the fluoroborane $(C_6F_5O)_2BF$ **74** and a large peak at 0.2 ppm which was assigned to BF_3. The integrated ratio of peaks was roughly 1:2 (the sum of the peaks at 18.0 and 16.8 ppm : peak at 0.2 ppm). The ^{19}F NMR spectrum showed two peaks, *viz.* a small peak at -133.5 ppm that was assigned to $(C_6F_5O)_2BF$ **74** and a larger peak at -153.6 ppm.

Although compounds of the type $ROBF_2$ **19** and BF_3.ROH both absorb in the 150 ppm area, it seems likely that the complex formed is actually of the type [$(C_6F_5O)_3B$, $2BF_3$, EtOH] **85** as described by Lappert[67]. This interpretation fits with both the chemical shifts and the stoichiometry of the observed ^{19}F and the ^{11}B NMR spectra.

1.2.3. Addition of ethanol to methoxydifluoroborane

Analysis of the NMR spectra of the 1:1 methoxydifluoroborane.ethanol adduct showed clearly the characteristics of a complex mixture of the type [$(CH_3O)_3B$, $2BF_3$, EtOH] **86** as described by Lappert[67] rather than the simple adduct CH_3OBF_2.EtOH **87** reported by Lysenko[72]. In particular, the ^{11}B NMR spectrum displayed two peaks in a ratio 1:2 with a broad peak at 18.9 pm, which was assigned to a mixture of trimethoxyborane $(CH_3O)_3B$ **21** and fluoroborane $(CH_3O)_2BF$ **23**, and a larger peak at 0.2 ppm which was assigned to BF_3. The presence of a small amount of monofluoroborane due to the decomposition of methoxydifluoroborane **20** into trimethoxyborane **21** (equations 62 and 63) was confirmed by the appearance of a minor peak at -135.2 ppm in the ^{19}F NMR spectrum whilst a major peak was found at -154.7 pm.

$$\underset{\mathbf{20}}{2CH_3OBF_2} \longrightarrow \underset{\mathbf{23}}{(CH_3O)_2BF} + BF_3 \qquad (62)$$

$$\underset{\mathbf{20}}{CH_3OBF_2} + \underset{\mathbf{23}}{(CH_3O)_2BF} \longrightarrow BF_3 + \underset{\mathbf{21}}{(CH_3O)_3B} \qquad (63)$$

Once again, although both alkoxydifluoroboranes $ROBF_2$ **19** and BF_3.ROH absorb in the 150 ppm area, from a consideration of the above results, it appears that addition of ethanol to methoxydifluoroborane **20** leads to a similar compound to that originally proposed by Lappert[67], $[(CH_3O)_3B, 2BF_3, EtOH]$ **86**.

Both the ^{13}C and the ^{1}H NMR spectra agreed with this interpretation . Peaks α and β to the oxygen were broad but there was only one type of methoxy and one type of ethoxy in a 1:1 ratio. The ^{1}H NMR spectrum also showed a large peak at 9.7 ppm corresponding to the acidic proton of ethanol (Figure 12).

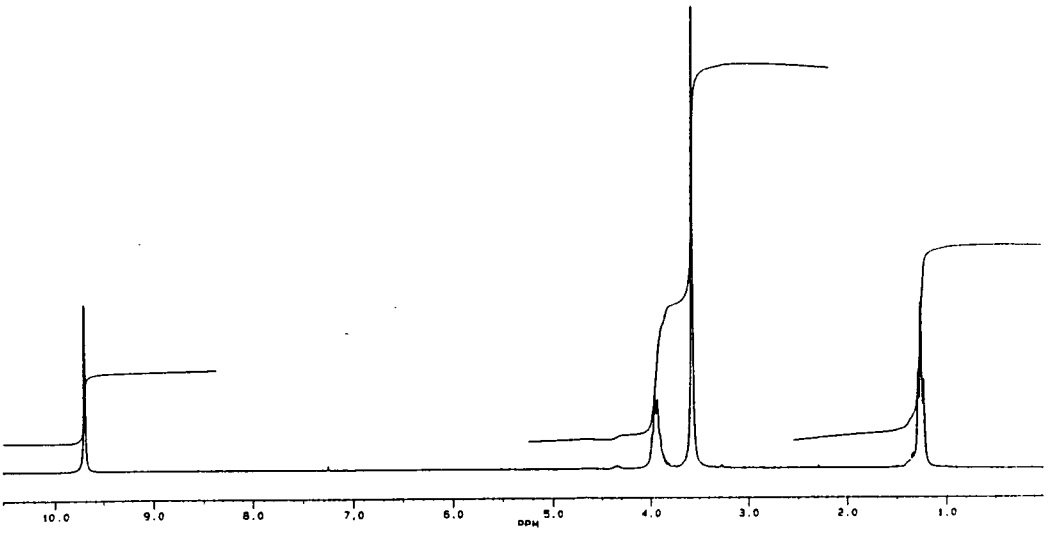


Figure 12. ^{1}H NMR spectrum of the adduct of methoxydifluoroborane with ethanol

1.2.4. Conclusion

In all cases of addition of ethanol to alkoxydifluoroboranes $ROBF_2$ **19**, the presence of $(RO)_2BF$ **26**, $(RO)_3B$ **31** and BF_3 species was confirmed by ^{11}B and ^{19}F NMR

spectroscopy. Moreover, an acidic proton was identified in the ^{1}H NMR spectrum, with broadening of the peaks α and β to the oxygen being observed in both the ^{1}H and the ^{13}C NMR spectra ; integration was also consistent with a 1:1 ratio of alcohol to boron species. The alkoxydifluoroborane.ethanol adducts despite having a BF_3 component did not however show any characteristics of free BF_3.EtOH. The NMR spectra of both materials are quite different, and it is therefore likely that in solution the Lewis acid is not simply BF_3.EtOH, but a more complicated conglomeration of boron compounds.

1.3. Alkoxydifluoroboranes adducts with Bronsted acids

1.3.1. Methoxydifluoroborane.acetic acid adduct

Dry acetic acid was added to methoxydifluoroborane **20** in the glove box at room temperature in order to form the 1:1 adduct $CH_3OBF_2.CH_3COOH$ **88**. The product was analysed by NMR spectroscopy. In particular, the ^{11}B NMR spectrum showed a single peak at -0.1 ppm, which meant that only one type of boron species, presumably the methoxydifluoroborane **20**, was present in solution. This was confirmed by ^{19}F NMR spectroscopy with only one peak at -147.8 ppm. Both ^{13}C NMR and ^{1}H NMR spectroscopy confirmed that the difluoroborane **20** was not decomposed by the addition of acetic acid, which was identified from its acidic proton in the ^{1}H NMR spectrum at 10.7 ppm.

Although addition of acetic acid to the difluoroborane **20** did not lead to the formation of a BF_3 adduct, it is interesting to note that 'free' methoxydifluoroborane **20** absorbs at -153.3 ppm for ^{19}F and 0.4 ppm for ^{11}B NMR spectroscopy. The change in chemical shift suggests that in this particular case, the adduct $CH_3OBF_2.CH_3COOH$ **88** is formed rather than a complex mixture of trimethoxyborane **21** , boron trifluoride and acetic acid.

1.3.2. Methoxydifluoroborane.trifluoroacetic acid adduct

Dry trifluoroacetic acid was added to methoxydifluoroborane **20** in the glove box at room temperature in order to form the 1:1 adduct $CH_3OBF_2.CF_3COOH$ **88**. The ^{11}B NMR spectrum of the 1:1 mixture of methoxydifluoroborane **20** and trifluoroacetic acid displayed only one peak at 0.0 ppm from which it is evident that there is only one type of boron compound, presumably the difluoroborane CH_3OBF_2 **20**. This conclusion was further confirmed by ^{19}F NMR spectroscopy which showed only one peak at -147.8 ppm. Both the ^{13}C NMR and the ^{1}H NMR spectra confirmed that the difluoroborane **20** was not decomposed into trimethoxyborane **21** and boron trifluoride by the addition of trifluoroacetic acid, which was identified from its acidic proton at 8.94 ppm in the ^{1}H NMR spectrum.

1.3.3. Addition of trifluoroacetic acid to $(C_6F_5O)_3B.2BF_3$ and $(C_6H_5O)_3B.2BF_3$

Although pentafluorophenoxydifluoroborane was found to have the structure of a coordination compound of the type $(C_6F_5O)_3B.2BF_3$ **75** rather than a trimeric structure, presumably because of steric hinderance, trifluoroacetic acid was added to adduct **75** in the glove box at room temperature in a 1:1 ratio. NMR spectroscopy analysis showed that the structure of the product is of the type $[(C_6F_5O)_3B, 2BF_3, CF_3COOH]$ **90**. Both the ^{11}B and ^{19}F NMR spectra were similar to that of **75**, with an additional peak at -76.2 ppm, which corresponds to the CF_3 group of trifluoroacetic acid, in the ^{19}F NMR spectrum. The same result was observed for the addition of trifluoroacetic acid to $(C_6H_5O)_3B.2BF_3$ **80** which lead to the formation of the complex adduct $[(C_6H_5O)_3B, 2BF_3, CF_3COOH]$ **91**.

1.3.4. Other adducts

Several other adducts of methoxydifluoroborane **20** were prepared. Adducts with sulfuric acid H_2SO_4, triflic acid CF_3SO_3H and water were prepared by simply adding in a 1:1 ratio, sulfuric acid, triflic acid and water respectively to methoxydifluoroborane **20** under inert atmosphere at room temperature. Following disappointing polymerisation results with these adducts used as initiating systems, no further analysis was carried out.

2. Alkyldifluoroboranes (RBF_2) and adducts with ethanol and Bronsted acids

2.1.Preparation of alkyldifluoroboranes

The method of Tuhagues and Laurent[83] was adopted for the preparation of alkyldifluoroboranes **37**. After studying the product of the reaction of boron trifluoride and trialkylborane R_3B **51** by ^{19}F NMR and ^{11}B NMR spectroscopy, these workers concluded that the reaction could be represented as in equation 41. At room temperature, the reaction of boron trifluoride with trialkylborane **51** only produced monofluoroboranes R_2BF, whereas when the reaction is carried out at the trialkylborane's **51** boiling point temperature ca. 200°C, alkyldifluoroboranes are obtained in very good yield, providing that they are distilled out of the reaction mixture as soon as they are formed (equation 64).

$$\underset{\mathbf{51}}{4\,R_3B} + 2BF_3 \overset{200^oC}{\rightleftharpoons} \underset{\mathbf{51}}{3\,R_3B} + \underset{\mathbf{37}}{3RBF_2} \qquad (64)$$

This a convenient way of preparing alkyldifluoroboranes RBF_2 in good yield.

Trialkylboranes R_3B **51** were prepared in a rapid and highly efficient manner *via* a modified organometallic route involving the direct reaction of magnesium, organic halide and boron trifluoride.etherate in ethyl ether as described by Brown *et al.*[101,102] (equation 65).

$$3RX + 3Mg + BF_3.OEt_2 \xrightarrow{Et_2O} \underset{\mathbf{51}}{R_3B} + 3FMgX \qquad (65)$$

The slow reactions were dramatically accelerated when refluxing the reaction mixture in an ultrasound bath.

Both tri-*n*-butylborane $(C_4H_9)_3B$ **92** and tri-*n*-pentylborane $(C_5H_{11})_3B$ **93** were prepared this way. The products were identified by a single peak at 86-87 ppm in the ^{11}B NMR spectrum in ether.

N-butyldifluoroborane $C_4H_9BF_2$ **53** and *n*-pentyldifluoroborane $C_5H_{11}BF_2$ **58** were then prepared by bubbling BF_3 through tri-*n*-butylborane $(C_4H_9)_3B$ **92** and tri-*n*-pentylborane $(C_5H_{11})_3B$ **93** respectively at high temperature, according to Tuhagues and Laurents' procedure[83]. The ^{11}B NMR spectrum of both product displayed a triplet in the 30 ppm area and the ^{19}F NMR spectrum a quartet in the -74 pm region. These shifts are in agreement with the literature[83].

2.2. Alkyldifluoroboranes adducts with ethanol and trifluoroacaetic acid

2.2.1. Addition of ethanol to *n*-butyldifluoroborane and *n*-pentyldifluoroborane

Ethanol was added to *n*-butyldifluoroborane **53** in a 1:1 ratio at room temperature in the glove box in order to form the 1:1 $C_4H_9BF_2$.EtOH **94** adduct. The product was analysed by NMR spectroscopy. Both ^1H NMR and ^{13}C NMR spectra showed the presence of *n*-butyldifluoroborane **53** and ethanol in a ratio 1:1. A sharp peak was

seen at 7.8 ppm in the ^{1}H spectrum corresponding to the acidic proton of ethanol (Figure 13).

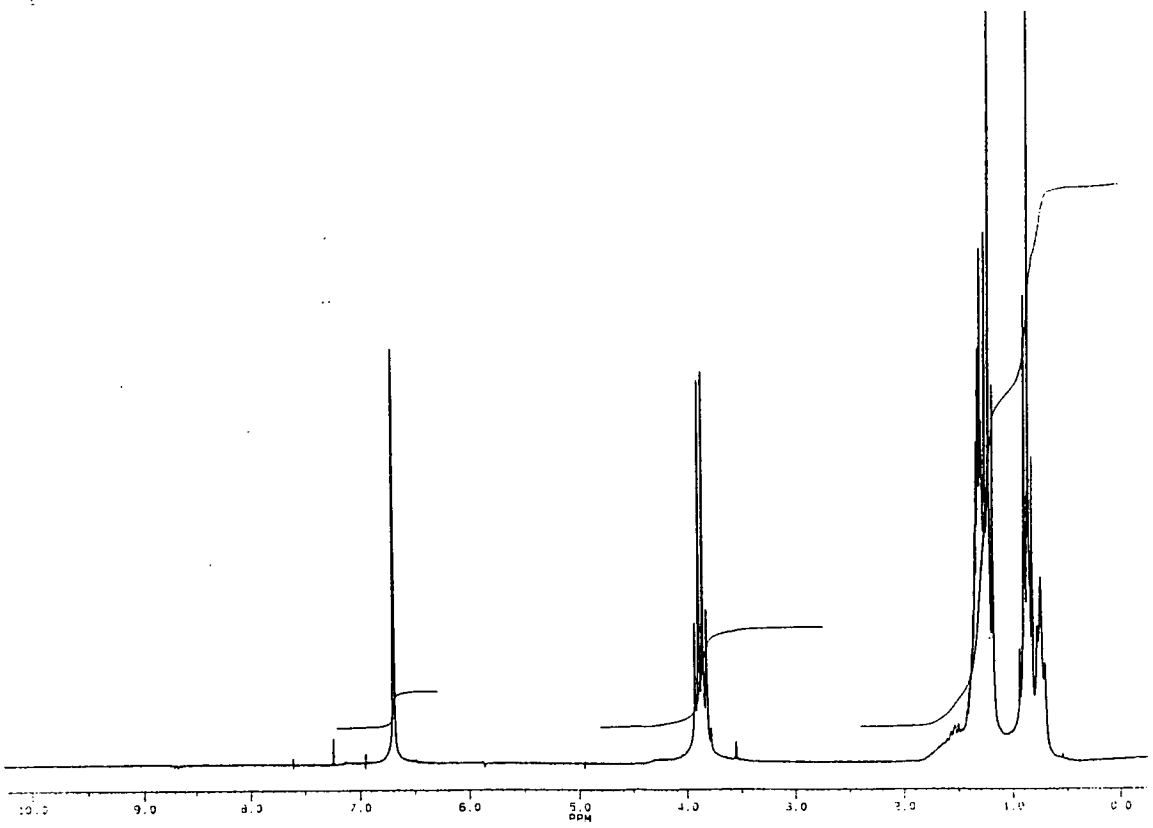


Figure 13. ^{1} H NMR spectrum of the adduct of *n*-butyldifluoroborane with ethanol

Instead of a triplet at 29.8 ppm as for *n*-butyldifluoroborane, the ^{11}B NMR spectrum of the adduct displayed a broad peak at 28.5 ppm. A bigger change in chemical shift was observed on the ^{19}F NMR spectrum with a very broad peak at -90 pm compared to a quartet at -73.6 ppm for *n*-butyldifluoroborane **53**.

These observations suggest that addition of ethanol to *n*-butyldifluoroborane **53** lead to the formation of the complex $C_4H_9BF_2$.EtOH **94** since the NMR spectra of the adduct did not show the presence of other boron or BF_3 species.

Similar results were obtained for the addition of ethanol to *n*-pentyldifluoroborane **58** which lead to the formation of the complex *n*-pentyldifluoroborane.ethanol, $C_5H_{11}BF_2$.EtOH **95**.

2.2.2. Addition of trifluoroacetic acid to *n*-butyldifluoroborane and *n*-pentyldifluoroborane

Dry trifluoroacetic acid was added to *n*-butyldifluoroborane **53** in a 1:1 ratio at room temperature in the glove box in order to form the 1:1 $C_4H_9BF_2.CF_3COOH$ **96** adduct. The product was analysed by NMR spectroscopy. The ^1H NMR of the adduct was consistent with the presence of *n*-butyldifluoroborane **53** and trifluoroacetic acid in a 1:1 ratio. The ^{19}F NMR and ^{11}B NMR spectra did not show any change in the chemical shifts compared to *n*-butyldifluoroborane **53**. The ^{19}F NMR spectrum displayed a quartet at -73.1 ppm and the ^{11}B NMR spectrum showed a triplet at 29.8 ppm. An additional peak was seen on the ^{19}F NMR spectrum corresponding to the CF_3 group of trifluoroacetic acid.

Similar results were obtained when trifluoroacetic was added to *n*-pentyldifluoroborane in a 1:1 ratio in order to form the 1:1 adduct $C_4H_9BF_2.CF_3COOH$ **97**. In both cases, the NMR spectra did not show the presence of BF_3 species.

3. Conclusion

N-pentoxydifluoroborane $C_5H_{11}OBF_2$ **32** and methoxydifluoroborane CH_3OBF_2 **20** were found to have the trimeric structure reported in the literature for ethoxydifluoroborane[70]. However NMR spectroscopy cleary showed that pentafluorophenoxydifluoroborane $C_6F_5OBF_2$ **71** and phenoxydifluoroborane $C_6H_5OBF_2$ **76** both exist as mixtures of trialkoxyborane $(RO)_3B$ **31** and boron trifluoride. In most cases, the addition of ethanol or Bronsted acids to alkoxydifluoroboranes led to decomposition of the latter and to complex mixtures of boron compounds, *viz.* monofluoroborane $(RO)_2BF$, trialkoxyborane $(RO)_3B$ and boron trifluoride. Only the NMR spectra of the adducts of methoxydifluoroborane CH_3OBF_2 **20** with acetic acid and trifluoroacetic acid showed the presence of the two compounds in a 1:1 ratio with no apparent sign of decomposition products such as boron trifluoride.Both *n*-butyldifluoroborane $C_4H_9BF_2$ **55** and *n*-pentyldifluoroborane $C_5H_{11}BF_2$ **96** showed the same characteristics when their adducts with ethanol and trifluoroacetic acid were formed, i.e. no decomposition products were identified.

It is to be noted that no attempt was made in this work to evaluate the energetics or heat of complex formation of the different adducts prepared. This would require further thermodynamic or spectroscopic studies. The aim of the NMR analysis carried out on these adducts was simply to get a better idea of the species likely to initiate the polymerisation of isobutene.

B. Determination of molecular weight and end-group structure of polyisobutene

1. Determination of the number average molecular weight (*Mn*) of polyisobutene (PIB)

1.1. Definitions

Molecular weight[103,104] is the dimensionless quantity equivalent to molar mass (g/mol), usually used in polymer chemistry. Indeed, polymers are generally polydisperse, meaning that in a sample the individual molecules are not all of the same size and there is a range of molecular weights accordingly. Inevitably, because of the random nature of the growth process, the product is a mixture of chains of different length - a distribution of chain lengths - which can be calculated statistically. Hence, the polymer is characterised best by a molecular weight distribution and the associated molecular weight averages, rather than by a single molecular weight.

The simplest average is the number average molecular weight denoted as M_n. The total weight of a polymer sample, w, is the sum of the weight of each molecular species present (i) :

$$w = \sum w_i = \sum N_i M_i \qquad \text{(i)}$$

where N and M are the number of moles and molecular weight, respectively, of each species i. The number average molecular weight, M_n, is the weight w of sample per mole (ii) :

$$M_n = w / \sum N_i = \sum M_i N_i / \sum N_i \qquad \text{(ii)}$$

Other molecular weight averages include the weight average molecular weight, denoted by M_w, which is defined by analogy with (ii) with w_i replacing N_i. Since the weight of the fraction with relative molecular weight M_i is specified as $w_i = N_iM_i$, the weight average molecular weight is expressed as in (iii) :

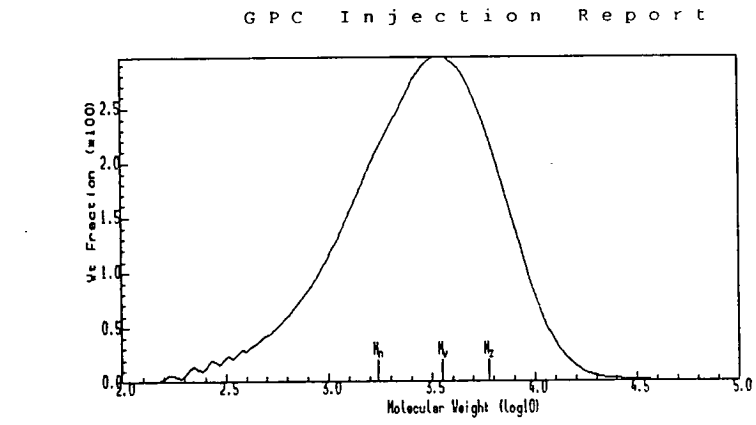
$$M_w = \sum w_iM_i / \sum w_i = \sum N_iM_i^2 / \sum N_iM_i \qquad \text{(iii)}$$

Molecular weight distribution is an important characteristic of polymers because, like molecular weight, it can significantly affect polymer properties. Just as low-molecular weight polyisobutene (PIB) behaves differently from the high-molecular weight material, a sample of PIB having a narrow molecular weight range will exhibit different properties from one having a broad range, even if the average molecular weights of the two samples are the same. Techniques for determining molecular weight distribution involve fractionation of the polymer sample and comparison of the fractions thus obtained with samples of known absolute molecular weight by means of some calibration procedure.

1.2. Gel Permeation Chromatography (GPC)

Gel Permeation Chromatography[103,104] is the most widely used method for determining molecular weight distribution. Separation is accomplished on a column packed with a highly porous material that separates the molecules according to size, a technique sometimes called size exclusion chromatography, often referred to as molecular sieving. Small molecules are able to diffuse into the pores of the column

packing more efficiently, and hence they travel through the column more slowly. Higher molecular weight fractions are thus eluted first. Column packing materials come in a variety of forms, but most commonly they consist of fine, semirigid beads of polystyrene crosslinked with divinylbenzene and swollen with solvent, or rigid porous beads of glass or silica. Detection of polymer fractions in the eluent is most commonly accomplished with refractive index or spectroscopic detectors. Commercially available instruments provide automated sample injection and fraction collection, rapid flow-through by high-pressure pumping, and computer-assissted treatment of data.



Sample Name : PIB 69
Sample Type : Sample Amount=1.0000
Sample Id :T=21C
Bottle No :3

Channel : 42 - Channel #42
Acquired on 14-FEB-1996 at 13:43

Run sequence : PIBS Method : PIBB Calibration : FEB93
New Machine

MOLECULAR WEIGHT AVERAGES

Number average molecular weight...(Mn)	1727
Weight average molecular weight...(Mw)	3551
Molecular weight at peak maximum..(Mp)	3493 (3.543)

Figure 14. Molecular weight distribution of polyisobutene

A typical gel permeation chromatogram plots detector response against the volume of dilute polymer solution that passes through the column. To obtain molecular weights

at a given retention volume, the chromatogram may be compared with reference chromatogram obtained with fractions of known average molecular weight in the same solvent at the same temperature. GPC thus provides a rapid and convenient method of obtaining molecular weight distribution as shown in figure 14 once the appropriate calibrations have been worked out.

2. Determination of end-group structure of polyisobutene

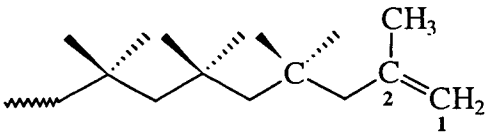
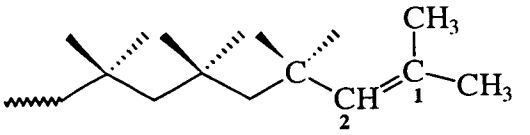
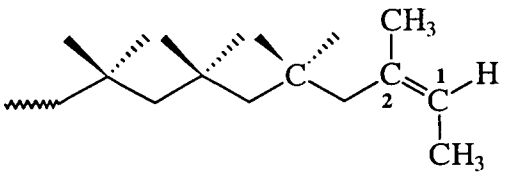
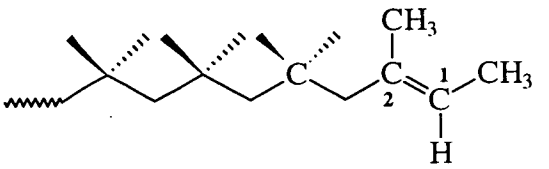
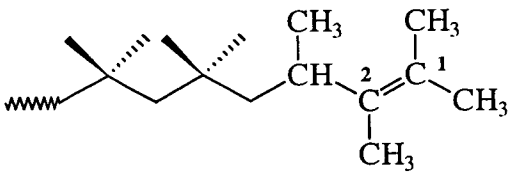
Commercial Ultravis has a high level of the reactive vinylidene end-groups. The product specification for Ultravis is the level of these vinylidene end-groups and therefore a reliable and accurate value of this parameter is essential for both quality control and sales specification of the material.

Several methods are used for determination of the end-group structure of polyisobutene, including NMR spectroscopy and IR spectroscopy.

2.1. Quantification of vinylidene end-group in polyisobutene using ^{13}C NMR spectroscopy

NMR data for the main end-groups of polyisobutene are well-known and have been reported in the literature[14,105]. The ^{13}C NMR spectrum of an Ultravis sample is shown in figure 15. ^{13}C NMR chemical shifts of these main end-groups are reported in Table 2 below .

Table 2. ^{13}C NMR shifts of polyisobutene main end-groups

	Structure	δ (ppm) C_1	δ (ppm)C_2
A	 **5**	114.6	143.6
B	 **6**	127.8	135.5
C1	 **7**	122.3	134.2
C2	 **8**	122.7	133.8
D	 **9**	121.5	133.1

The vinylidene content in polyisobutenes can be calculated as a percentage of all the different types of unsaturated end-groups (A-D) detected in the ^{13}C NMR spectrum of the polymer sample . The major drawback to this method is that minor end-groups may not be detected if the signal to noise ratio of the spectrum is poor. Thus, in a spectrum with very good signal to noise ratio, more minor end-groups are detected

and consequently the measured level of vinylidene drops. Spectrometer and time constraints often mean it is impossible to detect all the minor end-groups and hence measure the vinylidene content accurately.

A more reliable and accurate method for determining vinylidene content in PIB was developed by BP[105]. This method makes use of an internal standard, *viz.* 1,3,5-*tri-t*-butylbenzene. The olefinic resonances of this material do not overlap significantly with any of the unsaturated end-groups of PIB. Each end-group is measured directly against the internal standard. This method has been successfully repeated at the University on the 200 MHz spectrometer. The expanded area (110-150ppm) of the ^{13}C NMR spectrum of a high vinylidene end-group PIB sample is shown in figure 16. The equation used to calculate the weight percentage of vinylidene end-group is as follows :

$$\text{Weight \% vinylidene} = \frac{\text{Peak area vinylidene} \times M_n\text{PIB} \times w_s \times 3 \times 100}{M_s \times \text{wPIB} \times \text{Peak area standard}}$$

where Peak area vinylidene = integral over the peaks at 114.6 and 143.6 ppm

M_nPIB = M_n value (determined by GPC) for the polyisobutene

w_s = weight of standard used

M_s = molecular weight of standard (1,3,5 *tri-t*-butylbenzene = 246)

Peak area standard = integral over the two standard peaks (149 and 119 ppm for 1,3,5 tri-t-butylbenzene)

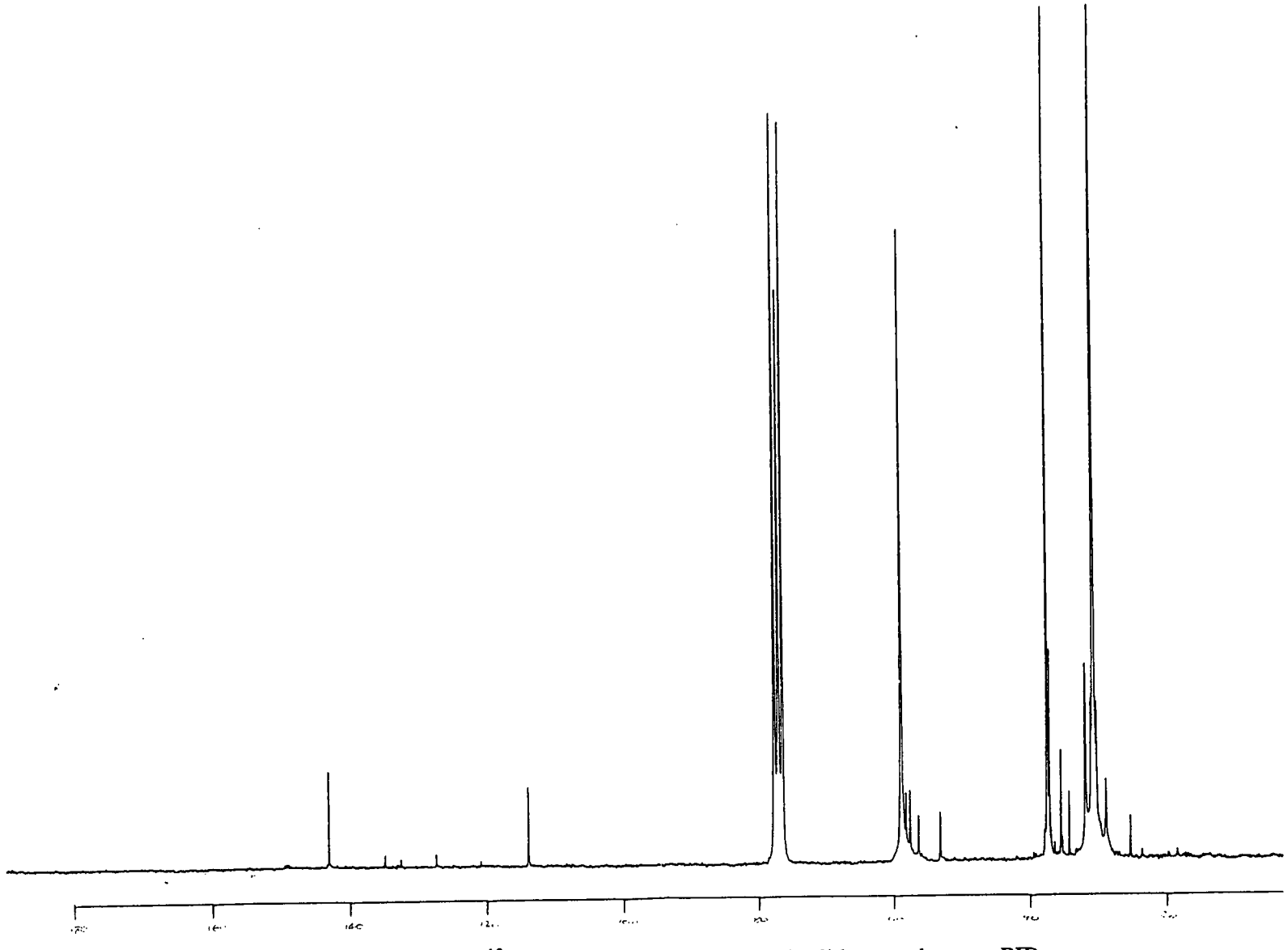


Figure 15. ^{13}C NMR spectrum of high vinylidene end-group PIB

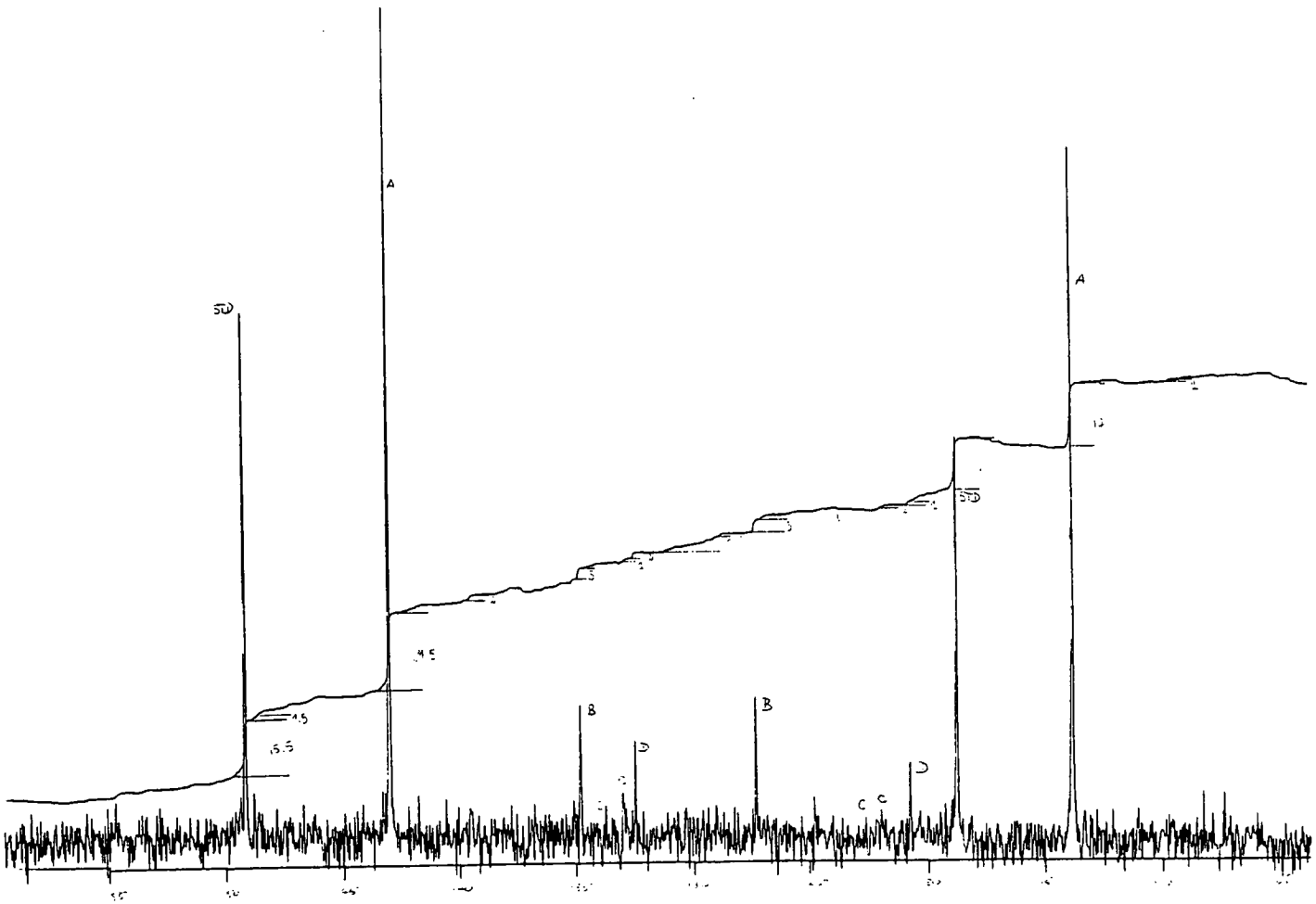


Figure 16. ^{13}C NMR spectrum of high vinylidene end-group PIB (expanded area 110-150 ppm)

Each olefinic type can be calculated as a percentage using this equation. The combined total is then substracted from 100 to give the percentage non-assigned "other" olefins.

2.2. Quantification of vinylidene end-group in polyisobutene using IR spectroscopy

IR spectroscopy is faster than NMR spectroscopy and offers better reproducibility in the determinition of vinylidene content of PIB[106]. However, it requires a calibration curve which is obtained from NMR results.

Vinylidene **5** absorb at 890 cm^{-1} for C-H and 1640 cm^{-1} for C=C (Figure 17). The calibration curve is generated by relating one of these aborbance with the vinylidene content obtained by ^{13}C NMR spectroscopy using some polymer calibration standards. Once generated, the calibration curve is then used to determine the vinylidene content of other samples.

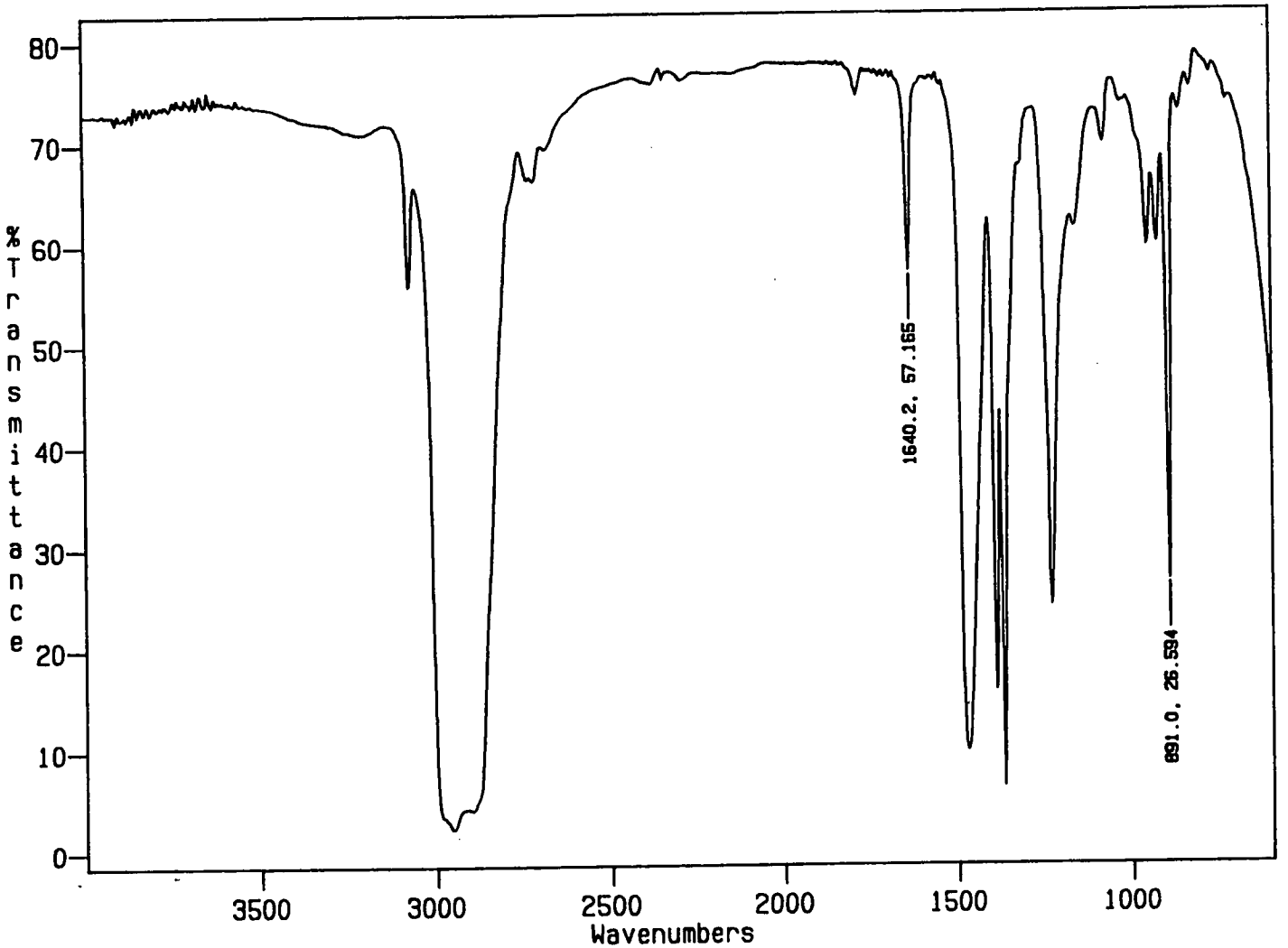


Figure 17. Infrared spectrum of high vinylidene end-group PIB

2.3. Identification of olefinic end-groups in PIB using ^{1}H NMR spectroscopy

^{1}H NMR spectroscopy is a much more rapid technique than ^{13}C NMR spectroscopy but unfortunately does not have the same chemical shift dispersion, and therefore it is not possible to discriminate between all of the different types of end-groups. However, the literature shows that vinylidene **5** and trisubstituted **6**, **7** and **8** double bonds can be differentiated[107,108], and it has also proved possible to estimate the level of tetra-substituted double bonds **9**.

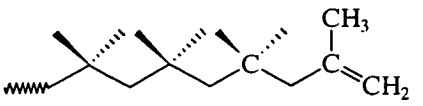
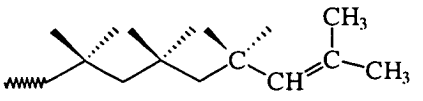
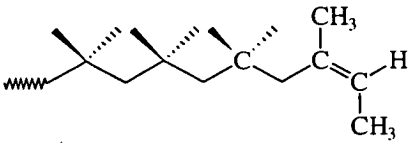
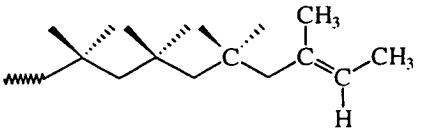
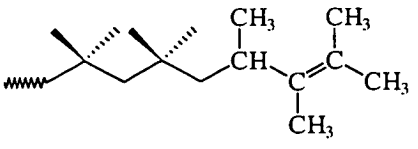
The use of ^{1}H NMR spectroscopy to quantify the olefinic end-groups in PIB has largely been abandoned in favour of ^{13}C NMR spectroscopy, but it is worth noting that it can provide a rapid method for identifying end-groups in PIB. Table 3 shows some of the end-groups which have been identified in PIB and their ^{1}H NMR chemical shifts.

The ^{1}H NMR spectra of two different types of PIB are shown in figures 18 and 19. Figure 18 shows the ^{1}H NMR spectrum of a PIB prepared with a BF_3-type initiating system, a polymer commercially called Ultravis. The spectrum clearly shows the high vinylidene **5** content of this polymer with the two peaks at 4.66 and 4.88 ppm. There is also a small amount of dimethyl-trisubstituted end-group (Type B **6**) with a peak at 5.18 pm as well as some trisubstituted (Types C1 **7** and C2 **8**).

By contrast, PIB prepared with aluminium chloride-type initiating systems display a completely diferent end-group structure. The ^{1}H NMR spectrum of such a polymer shows that it contains hardly any vinylidene end-group **5** but peaks corresponding to trisubstituted end-group can be seen at 5.18 ppm (C1 **7**) and 5.37 ppm(C2 **8**).

^{1}H NMR is a rapid and efficient technique for identifying the different types of end-groups in PIB.

Table 3. ^{1}H NMR chemical shift of PIB main end-groups

	End-group type	^{1}H NMR chemical shift
A	 **5**	4.66, 4.88
B	 **6**	5.18
C1	 **7**	5.18
C2	 **8**	5.37
D	 **9**	2.88

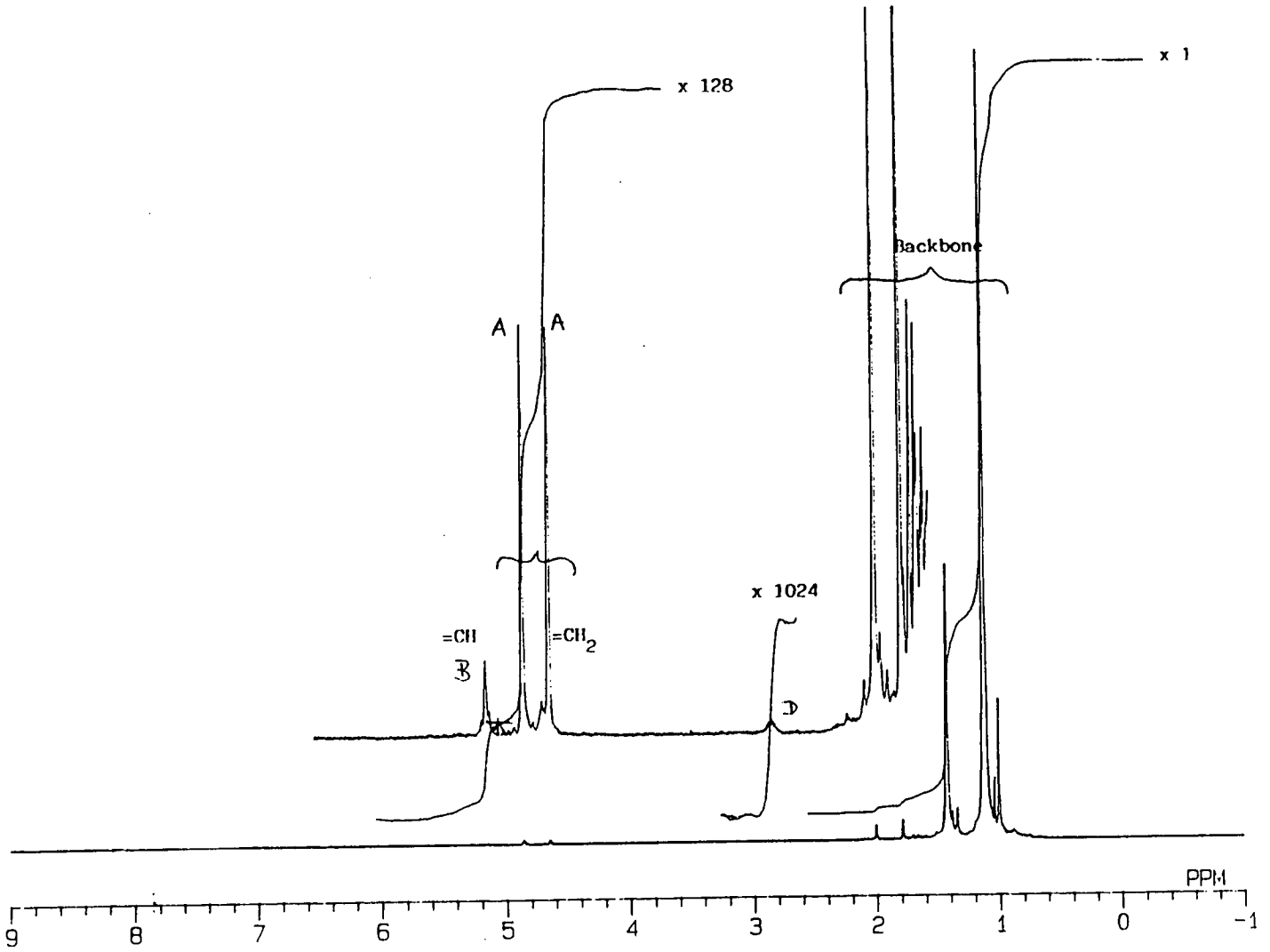


Figure 18. ^{1}H NMR spectrum of PIB prepared using a BF_3-type initiating system

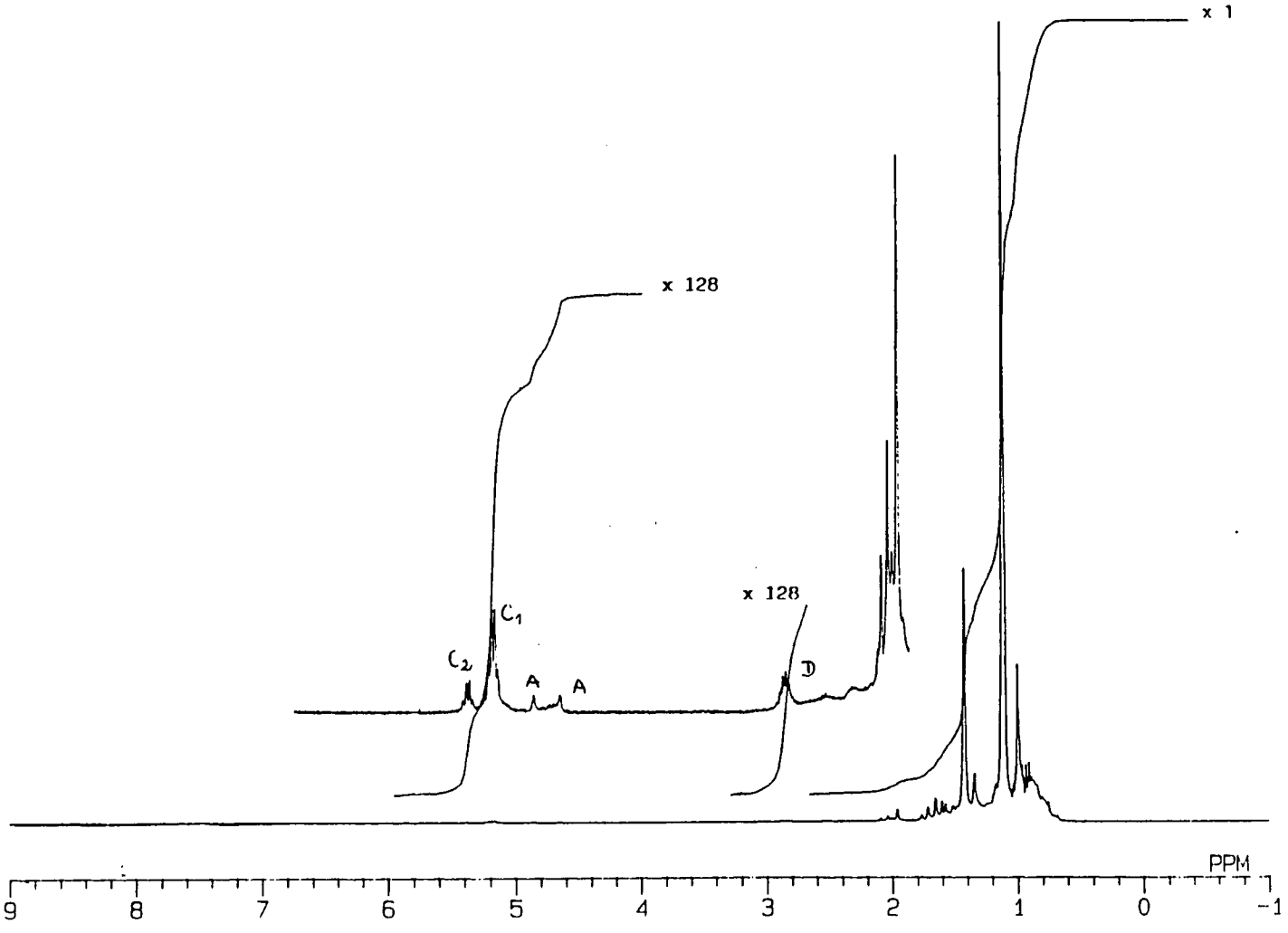


Figure 19. ^{1}H NMR spectrum of PIB prepared using an $AlCl_3$-type initiating system

C. Polymerisation of isobutene

The aim of the project is to evaluate as co-initiators for the polymerisation of isobutene, various boron trifluoride derivatives such as alkoxydifluoroboranes $ROBF_2$ **19** and alkyldifluoroboranes RBF_2 **37** and their adducts with ethanol or other Bronsted acids.

BP Chemicals manufacture a grade of polyisobutene (PIB) with high level of reactive vinylidene end-group **5** by using BF_3.EtOH as the initiating system. The advantage of using boron trifluoride complexes over aluminium chloride complexes is that resulting polymers have high vinylidene **5** content, typically about 70% for 1000 to 3000 molecular weight. Nonetheless much effort is still placed in the development of methods for improving the quality of the Ultravis product by raising the vinylidene end-group content.

Alternative Lewis acids have been looked at by Chung *et al.*[58] who have reported on the use of supported boron fluorides complexes as initiating systems for the polymerisation of isobutene and recently claimed to produce polyisobutene with greater than 85% vinylidene end-group.

The present work looks at alkoxydifluoroboranes $ROBF_2$ **19** and alkyldifluoroboranes RBF_2 **37** and their adducts with ethanol or other Bronsted acid as alternative initiating systems for the polymerisation of isobutene to discover their influence on conversion, molecular weight and more importantly vinylidene content of the resulting polyisobutene.

1. Polymerisation of isobutene using ethanol as an initiator

1.1. BF_3 as co-initiator

BF_3.EtOH is the initiating system currently used at BP Chemicals, Grangemouth to produce high vinylidene content PIB of the Type A **5**. Several batch polymerisation experiments under such conditions were carried out in order to gain familiarity with the technique. A diagram of the apparatus can be seen in Appendix 1. The batch experiment involves adding the required molar ratio of initiating system (BF_3.EtOH) *via* syringe to the cooled feedstock (isobutene in isobutane 40% at -30°C), followed by stirring the exothermic reaction for 20 minutes at *ca.* -30°C before quenching it by addition of ammonia. Following isolation of the PIB, isobutene conversion, molecular weight M_n and vinylidene content were determined and the results are reported in Table 4.

Table 4. Batch polymerisation of isobutene using BF_3.EtOH as an initiating system

Ratio (I : IB)	Yield (%)	M_n	Vinylidene end-group (%)
1:470	81.6	1220	82.3
1:420	72.4	1210	82.3
1:456	83.2	1141	82

Ratio I : IB = molar ratio initiating system : isobutene

Mn = Molecular weight

BF_3.EtOH is a very active initiating system and only a small molar ratio of initiating system to isobutene is needed to initiate the polymerisation (*ca.* 1: 450) and produce PIB in good yield. The conversion of isobutene was about 80% for polymers of molecular weight 1200. Vinylidene contents measured by IR spectroscopy reached 80% which is very favorable to further functionalisation of PIB.

1.2. *N*-pentoxydifluoroborane as co-initiator

From Chung's[58] recent paper, it is possible to gain the impression that these alkoxydifluoroboranes $ROBF_2$ **19** are very reactive and produce polymers with a high vinylidene content (>85%). For example, 100% conversion was obtained within 5 minutes at 0°C using *n*-pentoxydifluoroborane $C_5H_{11}OBF_2$ **32** as the initiating system. It is to be noted that Chung did not report using any initiator and it is assumed that water was relied on to act in this capacity. Based on the results at hand, it was important to establish whether such experimental conditions are responsible for the polymerisation reported. Indeed, Chung used a high vacuum apparatus[109] which allowed work at higher temperatures. A diagram of the apparatus is shown in appendix 2. The system consists of two 100 ml flasks (10 and 20) and one stopcock (30) used to separate the flasks. The other stopcock (40) was used to control the vacuum condition and nitrogen flow. In the glove box, the Lewis acid catalyst was charged to the flask A, the valve (40) was then closed. The whole apparatus was then moved to a vacuum line and was pumped to high vacuum before closing the valve (40). Isobutene (4 ml)was condensed into the flask B and dissolved in about 20 ml

hexane which was vacuum-distilled into the flask B. The isobutene solution was then warmed up to the required temperature and transferred to the catalyst in flask A.

Hence, it was decided to determine how alkoxydifluoroboranes **19** and their adducts with ethanol behave relative to BF_3.EtOH under our experimental conditions. Unfortunately, it proved difficult to prepare batch polymers from the difluoroborane **32** on its own and from its adduct with ethanol **84** under identical conditions to those employed with BF_3.EtOH. It was found to be necessary to reduce the scale of the experiment ten times in order to have a better control of the level of moisture in the apparatus. Once established, this smaller scale polymerisation experimental procedure (30g feedstock, *i.e.* 12g isobutene) was retained for all further polymerisations. A diagram of the apparatus can be seen in appendix 3 and details of the procedure are described in the experimental section.

Interestingly, *n*-pentoxydifluoroborane $C_5H_{11}OBF_2$ **32** on its own with no initiator did not bring about polymerisation of isobutene even when the ratio of initiating system to isobutene was increased from 1:415 to 1:108 (see Table 5).

Similar low reactivity was observed for the ethanol adduct which was found to have the structure [$(C_5H_{11}O)_3B$, BF_3, EtOH] **84** and polymerisation occurred only when the difluoroborane **32** and ethanol were added individually to a heptane solution at room temperature in order to generate **84** immediately prior to addition of isobutene to the solution cooled at *ca.* -20°C. Notably, a very high concentration of initiating system was required for only a small conversion (3%), although the ^1H NMR spectrum of the polymer obtained showed that it is an Ultravis-type material. Two peaks at 4.64 and 4.85 ppm clearly indicated a high vinylidene content.

It is very difficult to know the nature of the species that actually initiated the polymerisation. As discussed in the previous chapter, it appears that the addition of ethanol to the difluoroborane $C_5H_{11}OBF_2$ **32** leads to a similar mixture to that originally proposed by Lappert[67], *i.e.* $[(C_5H_{11}O)_3B, BF_3, EtOH]$ **84** type material following the decomposition of the difluoroborane rather than the simple complex $C_5H_{11}OBF_2.EtOH$ **81**.

In view of this, and the fact that much higher concentrations of initiating system were necessary to bring about any polymerisation, it is clearly evident that the BF_3.EtOH system is a much more reactive initiating system.

Table 5. Polymerisation of isobutene using *n*-pentoxydifluoroborane $C_5H_{11}OBF_2$ **32** as a co-initiator

Initiating system	**T(°C)**	**Ratio (I : IB)**	**Yield (%)**
$C_5H_{11}OBF_2$	-20	1:108	0
$C_5H_{11}OBF_2$	-20	1:415	0
$C_5H_{11}OBF_2$ + EtOH (1:0.49)	-15	1:76	0
$C_5H_{11}OBF_2$ + EtOH (1:1)	-15	1:82	0
$C_5H_{11}OBF_2$ + EtOH (1:0.54) in 30ml heptane (*in situ*)	-10	1:26	3

1.3. $(C_6F_5O)_3B.2BF_3$ as co-initiator

Pentafluorophenoxydifluoroborane **71** was found to exist as a coordination compound of the type $(C_6F_5O)_3B.2BF_3$ **75** rather than a trimer. Ethanol was added to the adduct **75** in anhydrous heptane at room temperature. NMR spectroscopy analysis did not allow any conclusions to be drawn concerning the structure of the adduct. It seems that the adduct formed is actually a complex mixture of the type $[(C_6F_5O)_3B, 2BF_3, EtOH]$ **90**. Consequently, it is difficult to know what species is initiating the polymerisation, although the results were very poor and high concentrations of initiating system together with higher temperatures were required to obtain even very small amount of polymer. The results are summarised in the Table 6.

Table 6. Polymerisation of isobutene using **75** as a co-initiator

Initiating system	**T(°C)**	**Ratio (I : IB)**	**Yield (%)**
Adduct **75** + EtOH (1:0.92)in 30ml heptane (*in situ*)	-25	1:304	0
Adduct **75** + EtOH (1:0.88)in 30ml heptane (*in situ*)	-10	1:50	2
Adduct **75** +EtOH (1:0.89)in 30ml heptane (*in situ*)	-11	1:39	3
Adduct **75** + EtOH (1:0.72)in 30ml heptane (*in situ*)	-22	1:45	1

1.4. Methoxydifluoroborane as co-initiator

The adduct formed from methoxydifluoroborane **20** and ethanol led to a slightly higher conversion into polymer, but relatively low molecular weight. Nonetheless, the polymer was formed with a very high vinylidene end-group content (>85%). (see Table 7)

Detailed NMR examination showed that the methoxydifluoroborane adduct with ethanol was a complex mixture of the type [$(CH_3O)_3B$, $2BF_3$, EtOH] **86** rather than the expected adduct CH_3OBF_2.EtOH **87**, and from this evidence it is possible that the polymer formed was actually initiatiated by BF_3.EtOH.

Table 7. Polymerisation of isobutene using methoxydifluoroborane CH_3OBF_2 **20** as a co-initiator and ethanol as an initiator

Initiating system	**Ratio (I : IB)**	**Yield (%)**	M_n	**Vinylidene end-group (%)**
CH_3OBF_2 + EtOH (1:0.82) in 30ml heptane (*in situ*)	1:35	17	330	86.7
CH_3OBF_2 + EtOH (1:0.54) in 15ml heptane (*in situ*)	1:28	15	549	88.4

It is also interesting to note the influence of the polymerisation temperature on the molecular weight of the PIB obtained. Molecular weights of polymers invariably increase with lowering of temperature in carbocationic polymerisation. This outcome is confirmed in this case also for polymerisations that have been carried out at -10°C

and -25°C respectively (see Table 8). Lowering of the temperature increased the molecular weight from 330 to 549 respectively.

Table 8. Influence of the reaction temperature on the molecular weight of PIB.

Initiating system	**T (°C)**	**Conversion (%)**	**Molecular weight M_n**
CH_3OBF_2 + EtOH (1:0.82) in 30ml heptane (*in situ*)	-10	17	330
CH_3OBF_2 + EtOH (1:0.54) in 15ml heptane (*in situ*)	-25	15	549

The usefulness of CH_3OBF_2 **20** as a co-initiator was also explored with *tert*-Butyl chloride as an initiator or cation donor (*i.e.* $(CH_3)_3C^+$) instead of ethanol. *Tert*-Butylchloride did not decompose methoxydifluoroborane **20** and NMR spectroscopy analysis confirmed the presence of the two compounds in a 1:1 ratio. Once more, a high ratio of initiating system to isobutene was necessary to bring about polymerisation even to a small extent (see Table 9).

The molecular weight of the material obtained was in the 523-535 range for reaction temperatures of -20°C. Moreover, the vinylidene content was not as high as when using ethanol as the initiator.

Table 9. Polymerisation of isobutene using methoxydifluoroborane CH_3OBF_2 **20** as a co-initiator and *tert*-butylchloride $(CH_3)_3CCl$ as an initiator

Initiating system	**Ratio (I : IB)**	**Yield (%)**	M_n	**Vinylidene end-group (%)**
$CH_3OBF_2.Me_3CCl$(1:0.94) in 10ml CH_2Cl_2 (*in situ*)	1:13	8	535	71.2
$CH_3OBF_2.Me_3CCl$(1:0.86) in 10ml heptane (*in situ*)	1:10	12	523	76.7

The alternative use of heptane or dichloromethane for the preparation of the initiating system did not seem to have any influence on the type of polymer obtained ; in both cases, an Ultravis type material is formed.

In view of these results, it is evident that BF_3.EtOH is much more reactive than alkoxydifluoroborane complexes for polymerisation of isobutene. Alkoxydifluoroborane adducts initiated the polymerisation of isobutene, but only when used in high concentrations, although the polymer produced did have a high vinylidene content.

Further investigations carried out jointly at BP Chemicals[110] showed that the nature of the feedstock had a strong influence on the polymer yield and its vinylidene content. Yields were increased upon using *n*-butoxydifluoroborane as a co-initiator and ethanol as an initiator, with pure isobutene rather than the C_4-feedstock of isobutene in isobutane (40%) used at the University.

Nonetheless, it is important to note that the polymerisation might be initiated by a BF_3.alcohol species rather than the expected difluoroborane complex. This is

evidenced from NMR spectroscopy studies of these adducts which showed that addition of ethanol to alkoxydifluoroboranes $ROBF_2$ **19** led to complex mixtures of the type $[(RO)_3B, 2BF_3, EtOH]$ rather than the simple complexes $ROBF_2.EtOH$.

This evidence, coupled with the poor yields obtained even with heptane or dichloromethane as solvent systems gives no support to the validity of polymer supported difluoroboranes initiating systems for the polymerisation of isobutene

1.5. *N*-butyldifluoroborane as co-initiator

As the results in Table 10 show, *n*-butyldifluoroborane $C_4H_9BF_2$ **53** did not initiate the polymerisation of isobutene even under a variety of conditions whereby, the co-initiator was used on its own, or along with an initiator (ethanol). In addition, it was either injected directly into the C_4, or prepared *in situ* in several different solvents (heptane, hexane, dichloromethane). None of these initiating systems produced any polymer.

Another series of experiments was carried out whereby the co-initiator *n*-butyldifluoroborane $C_4H_9BF_2$ **53** was injected into the C_4 containing ethanol since this technique proved to be successful in other examples. Unfortunately, this method did not lead to any polymerisation. (see Table 11)

Table 10. Polymerisation of isobutene using *n*-butyldifluoroborane $C_4H_9BF_2$ **53** as a co-initiator

Initiating system	**T(°C)**	**Ratio (I : IB)**	**Yield (%)**
$C_4H_9BF_2$	-30	1:82	0
$C_4H_9BF_2$ + EtOH (1:0.84)	-30	1:75	0
$C_4H_9BF_2$ + EtOH (1:0.94)in 10ml CH_2Cl_2 (*in situ*)	-30	1:160	0
$C_4H_9BF_2$ + EtOH (1:0.94)in 10ml heptane (*in situ*)	-30	1:55	0
$C_4H_9BF_2$ + EtOH (1:0.94)	-7	1:166	0
$C_4H_9BF_2$ + EtOH (1:0.86)in 10ml hexane (*in situ*)	-30	1:195	0

Table 11. Initiating system = $C_4H_9BF_2$ injected into C_4 containing EtOH

Initiating system	**T(°C)**	**Ratio (I : IB)**	**Yield (%)**
$C_4H_9BF_2$ + EtOH (1:0.84)	-30	1:80	0
$C_4H_9BF_2$ + EtOH (1:0.84)	-30	1:63	0
$C_4H_9BF_2$ + EtOH (1:0.84)	-30	1:104	0
$C_4H_9BF_2$ + EtOH (1:0.94)	-7	1:52	0
$C_4H_9BF_2$ + EtOH (1:0.84)	-30	1:67	0

1.6. *N*-pentydifluoroborane as co-initiator

Disappointing results were also obtained with *n*-pentyldifluoroborane $C_5H_{11}BF_2$ **58** as shown in Table 12. Whether injected on its own into the C_4, or pre-complexed with ethanol, or even injected into the C_4 feedstock containing ethanol, no polymerisation of isobutene occurred.

Table 12. Polymerisation of isobutene using *n*-pentyldifluoroborane $C_5H_{11}BF_2$ **58** as a co-initiator.

Initiating system	**T(°C)**	**Ratio (I : IB)**	**Yield (%)**
$C_5H_{11}BF_2$injected into C_4 + EtOH ($C_5H_{11}BF_2$:EtOH 1:0.87)	-30	1:50	0
$C_5H_{11}BF_2$ + EtOH (1:0.88)	-30	1:80	0
$C_5H_{11}BF_2$ + EtOH(1:0.87)	-30	1:92	0
$C_5H_{11}BF_2$	-30	1:60	0

2. Polymerisation of isobutene using Bronsted acids as initiators

In view of the previous low isobutene conversions obtained when using ethanol, several Bronsted acids were considered as co-initiators for the polymerisation of isobutene. Indeed, although high molecular weight polyisobutene cannot be obtained by the use of Bronsted acids alone, Bronsted acids/Friedel-Crafts acid combinations

produce such polymers because the Friedel-Crafts acid is able to stabilise the highly nucleophilic conjugate bases of protic acids by complexation. Several adducts of different Bronsted acids with alkoxydifluoroboranes $ROBF_2$ **19** and alkyldifluoroboranes RBF_2 **37** were prepared and evaluated as initiating systems for the polymerisation of isobutene.

2.1. Polymerisation of isobutene using acetic acid as an initiator

The adduct between methoxydifluoroborane CH_3OBF_2 **20** and acetic acid ($CH_3OBF_2.CH_3COOH$ **88**) was used as an initiating system for the polymerisation of isobutene but unfortunately no reaction was observed. Acetic acid was also used without a co-initiator but it failed to initiate any polymerisation (see Table 13). As a consequence, it was decided to raise the acidity and to use a stronger acid such as trifluoromethanesulfonic acid (triflic acid) to bring about polymerisation of isobutene.

Table 13. Polymerisation of isobutene using acetic acid as an initiator

Initiating system	**T(°C)**	**Ratio (I : IB)**	**Yield (%)**
CH_3OBF_2 + CH_3COOH (1:0.71)in CH_2Cl_2 (*in situ*)	-30	1:14	0
CH_3OBF_2 + CH_3COOH (1:0.71)in CH_2Cl_2 (*in situ*)	-30	1:10	0
CH_3COOH	-30	1:20	0

2.2. Polymerisation of isobutene using trifluoromethanesulfonic acid as an initiator

Triflic acid, either on its own, or complexed with methoxydifluoroborane CH_3OBF_2 **20** did produce some polymer in a very exothermic reaction. in all cases, about 60% of the feedstock was converted into polymer (see Table 14), albeit of very low molecular weight. Analysis of the material by IR spectroscopy showed the presence of internal vinylidene groupings which are known to absorb at 894 cm^{-1}. In fact, the IR spectrum of the material prepared with triflic acid on its own, and of the product obtained with the adduct between methoxydifluoroborane CH_3OBF_2 **20** and triflic acid CF_3SO_3H showed the same characteristics being not an Ultravis type polymer and containing internal vinylidenes which are not as interesting as vinylidene end-groups for further functionalisation of PIB. Furthermore, triflic acid is a very strong acid and would be environmentally difficult to handle on a larger scale.

Table 14. Polymerisation of isobutene using triflic acid as an initiator

Initiating system	**T(°C)**	**Ratio (I : IB)**	**Yield (%)**
CH_3OBF_2 + CF_3SO_3H (*in situ*)	-30	1:28	61
CH_3OBF_2 + CF_3SO_3H in CH_2Cl_2 (*in situ*)	-30	1:20	69
CF_3SO_3H (in situ)	-30	1:35	60

2.3. Polymerisation of isobutene using sulfuric acid as an initiator

As expected, sulfuric acid produced PIB in good yield (see Table 15). Presumably, the relatively poor nucleophilic conjugate base HSO_3^- of sulfuric acid stabilises the initiator ion-pair, and thus allows propagation to occur, although only a very broad low molecular weight (about 300) polymer was formed.

Table 15. Polymerisation of isobutene using sulfuric acid as an initiator

Initiating system	**Ratio (I : IB)**	**Yield (%)**	M_n	**Vinylidene end-group (%)**
CH_3OBF_2 + H_2SO_4 (1:0.64) in 10ml CH_2Cl_2 (*in situ*)	1:17	70	287	35.0
CH_3OBF_2 + H_2SO_4 (1:0.54) in 6ml CH_2Cl_2 (*in situ*)	1:14	69	357	29.7
CH_3OBF_2 + H_2SO_4 (1:0.76) in 5ml CH_2Cl_2	1:12	46	347	26.1
CH_3OBF_2 + H_2SO_4 (1:0.56) in 6ml CH_2Cl_2	1:16	79	297	30.8
H_2SO_4 (1:0.64) in 6ml CH_2Cl_2(*in situ*)	1:20	70	253	14.1

IR analysis of these materials gave vinylidene contents of about 30% when methoxydifluoroborane CH_3OBF_2 **20** was used as the co-initiator. Even so, examination of the ^{13}C NMR and ^1H NMR spectra revealed only a small amount of these vinylidene groupings to be actually at the end of the chain, the majority being

internal vinylidene. In particular, the ^{13}C NMR shifts for the internal vinylidene appear at 115.7 and 145.2 ppm, a result that was confirmed by the appearance of the absorbance at 894 cm^{-1} in the IR spectrum corresponding to internal vinylidene. Other end-groups were also detected on the ^{13}C NMR spectrum including some internal dimethyl-trisubstituted of type B **6**.

It is interesting to note that the total vinylidene content of the polymer obtained is considerably improved when using the adduct between methoxydifluoroborane CH_3OBF_2 **20** and H_2SO_4 rather than sulfuric acid on its own as an initiating system. For example, the vinylidene content of the polymer prepared using H_2SO_4 on its own is only 14%, whereas it is raised to 35% with using methoxydifluoroborane CH_3OBF_2 **20** as a co-initiator, even under the same conditions and for the same molecular weight. With sulfuric acid as an initiator, the polymerisation of isobutene did not produce an Ultravis-type polymer but rather a low molecular weight material containing internal double bonds.

2.4. Polymerisation of isobutene using water as an initiator

Disappointingly the adduct between methoxydifluoroborane CH_3OBF_2 **20** and water as an initiating system did not produce enough material for analysis. A very small amount of polymer (*ca.* 2%) was obtained when the adduct was prepared *in situ* in heptane at room temperature , then cooled to *ca.*-30°C and the C_4-feedstock (isobutene in isobutane 40%) added directly (see Table 16).

Table 16. Polymerisation of isobutene using water as an initiator and methoxydifluoroborane CH_3OBF_2 **20** as a co-initiator

Initiating system	**T(°C)**	**Ratio (I : IB)**	**Yield (%)**
CH_3OBF_2 + H_2O (1:1) (*in situ*)	-30	1:17	0
CH_3OBF_2 + H_2O (1:0.88) in CH_2Cl_2 (*in situ*)	-30	1:16	0
CH_3OBF_2 + H_2O (1:0.75) in heptane (*in situ*)	-30	1:15	2

In combination with these studies, and by a similar method to that of Chung's[58] work, a polymerisation was also carried out at BP Chemicals[110], Grangemouth, with pure isobutene, using butoxydifluoroborane $C_4H_9OBF_2$ **29** as a co-initiator and residual moisture in the polymerisation glassware and reagents as an initiator. A consequence of relying on residual moisture in reactor is that the molar ratio of the initiating adduct is unknown. It is highly unlikely that anything approaching a 1:1 complex would be formed (the moisture content should be much less than one equivalent of difluoroborane).

Under these conditions, a very broad low molecular weight polymer was formed in 30% yield. IR and NMR spectroscopy analysis of the polymer showed that more than half of the double bonds in the polymer are positioned internally (internal of type A and B).

The same experiment was also carried out at the University with both methoxydifluoroborane CH_3OBF_2 **20** and *n*-pentoxydifluoroborane $C_5H_{11}OBF_2$ **32**

and using the C_4-feedstock (isobutene in isobutane 40%), but no polymer was obtained.

The reason why so much internal double bonding is formed when using butoxydifluoroborane **29** and residual moisture as an initiating system is not known. The chemical shifts reported by Chung[58], who used *n*-pentoxydifluoroborane $C_5H_{11}OBF_2$ **32** and residual moisture as an initiating system are consistent with terminal vinylidenes **5**. It is even more complicated when comparing alkoxydifluoroboranes and water-initiated polymers to that prepared using $BF_3.H_2O$ complex. Whilst both initiating system produce low molecular weight material, the end-groups of the polymer prepared using $BF_3.H_2O$ as an initiating system are typical of normal Ultravis (Type A vinylidene **5**).

Similar polymerisation experiments were also attempted with the adduct between *n*-butyldifluoroborane $C_4H_9BF_2$ **53** and water (see Table 17), using the C_4-feedstock (isobutene in isobutane 40%), but this species did not initiate the polymerisation.

Table 17. Polymerisation of isobutene using water as an initiator and *n*-butyldifluoroborane $C_4H_9BF_2$ **53** as a co-initiator

Initiator system	**T(°C)**	**Ratio (I : IB)**	**Yield (%)**
$C_4H_9BF_2$ + H_2O (1:0.97)	-30	1:87	0
$C_4H_9BF_2$ + H_2O (1:0.97) in 10ml CH_2Cl_2 (*in situ*)	-30	1:109	0

2.5. Polymerisation of isobutene using trifluoroacetic acid as an initiator

2.5.1. Methoxydifluoroborane.trifluoroacetic acid adduct as initiating system by addition to isobutene at -30°C

The use of trifluoroacetic acid on its own as an initiator did not initiate the polymerisation of isobutene. However, when complexed with methoxydifluoroborane CH_3OBF_2 **20** in a 1:1 ratio, PIB was produced in good yield (see Table 18). The reaction carried out at -30°C was very exothermic and the temperature rose to about 0°C within a few minutes of addition of the initiating system.

An increase in the ratio of initiating system to isobutene resulted in a considerable drop in isobutene conversion. For example, when 1 equiv. of the complex $CH_3OBF_2.CF_3COOH$ **89** was added to 100 equiv. of isobutene, the yield of polymer reached 80% whereas for a 1:200 ratio of initiating system to isobutene, the conversion achieved was only 27%. From this result, it is evident that this initiating system is not as reactive as BF_3.EtOH, which allow conversions of 80% when used in only a ratio of 1:500.

The initiating system proved to be even less reactive when dissolved in dichloromethane prior to injection into the isobutene. Indeed, conversion of only 55% was obtained when 1 equiv. of $CH_3OBF_2.CF_3COOH$ **89** in CH_2Cl_2 was injected into 10 equiv. of isobutene.

Nonetheless the molecular weight of the polymers obtained with $CH_3OBF_2.CF_3COOH$ **89** as an initiating system were found to be within the desired range (1000-1500).

Table 18. Polymerisation of isobutene using $CH_3OBF_2.CF_3COOH$ injected into the C_4 as an initiating system (T=-30°C).

Initiating system	**Ratio (I : IB)**	**Yield (%)**	M_n	**Vinylidene end-group (%)**
CH_3OBF_2 + CF_3COOH (1:0.9)	1:80	78	1021	66.9
CH_3OBF_2 + CF_3COOH (1:1.05)	1:98	69	1501	58.7
CH_3OBF_2 + CF_3COOH (1:0.92)	1:150	80	1727	63.0
CH_3OBF_2 + CF_3COOH (1:1.03)	1:210	27	1829	62.5
CH_3OBF_2 + CF_3COOH (1:0.98) in CH_2Cl_2	1:80	15	1140	67.3
CH_3OBF_2 + CF_3COOH (1:0.49)	1:75	72	802	75.2
CH_3OBF_2 + CF_3COOH (1:0.43) in CH_2Cl_2	1:85	72	778	74.1

More importantly, these polymers also possessed the desired high vinylidene content of 60% or more, and even up to 75% when the complex $CH_3OBF_2.CF_3COOH$ **89** was used in a ratio of 1:0.5. Unfortunately, IR spectroscopy on these polymer showed the

appearance of a small absorbance at 1778 cm^{-1} which was assigned to the CF_3CO- group Although not seen in the ^{13}C NMR spectrum, the presence of CF_3 groups in the polymer was confirmed by a peak at -76 ppm on the ^{19}F NMR spectrum.

It should be noted that from NMR evidence that the species initiating the polymerisation of isobutene is a simple complex of CH_3OBF_2 with CF_3COOH. Indeed, NMR analysis of the adduct did not show the presence of other species such as BF_3 species (see section 1.3.2, Part A).

2.5.2. Methoxydifluoroborane.trifluoroacetic acid adduct as initiating system by reverse addition

Several polymerisations reactions were carried out by injection of isobutene feedstock into the initiating system, $CH_3OBF_2.CF_3COOH$ **89** either neat or in solution. The results are recorded in Table 19, and under these conditions, the initiating system is referred to as *in situ*.

In most cases, polymerisation proceeded readily, but the molecular weights were slightly lower, especially when the initiating system was used neat. For polymerisation in heptane, the same adduct produced PIB of molecular weight in the range 700-900.

Once again the ratio of initiating system to isobutene needed to be high to obtain a good conversion into polymer, this showing the relatively low reactivity of these systems when compared with BF_3.alcohol complexes. In fact, one equiv. of the complex **89** to 200 equiv. isobutene produced PIB in only 5% yield.

As before, the vinylidene content of the polymers obtained was determined by IR spectroscopy, and in all cases, proved to be very high with 60 to 70% being of Type A **5**. However, as previously the IR spectrum coupled with the ^{19}F NMR spectrum showed the incorporation of fluorine in the polymer structure.

Table 19. Polymerisation of isobutene using $CH_3OBF_2.CF_3COOH$ **89** as an initiating system by reverse addition

Initiating system	**Ratio (I : IB)**	**Yield (%)**	***Mn***	**Vinylidene end-group (%)**
CH_3OBF_2 + CF_3COOH (1:0.94) (*in situ*)	1:20	78	579	64.4
CH_3OBF_2 + CF_3COOH (1:0.98) (*in situ*)	1:80	92	586	70.1
CH_3OBF_2 + CF_3COOH (1:0.98) in 10ml heptane (*in situ*)	1:20	73	802	43.2
CH_3OBF_2 + CF_3COOH (1:0.71) in 6ml heptane (*in situ*)	1:55	69	715	65.0
CH_3OBF_2 + CF_3COOH (1:1.06) in 6ml heptane (*in situ*)	1:72	75	954	63.7
CH_3OBF_2 + CF_3COOH (1:0.98) in 6ml heptane (*in situ*)	1:203	5		

2.5.3. Adducts 90 and 91 as initiating systems

Both pentafluorophenoxydifluoroborane **71** and phenoxydifluoroborane **76** were found to exist as coordination compounds of the type $(C_6F_5O)_3B.2BF_3$ **75** and $(C_6H_5O)_3B.2BF_3$ **80** respectively, and to form mixtures of the type [$(RO)_3B$, BF_3, CF_3COOH] with trifluoroacetic acid.

Moreover, such mixtures brought about polymerisation of isobutene, but produced PIB in low yield. When compared to the mixtures from ethanol which were also shown to be of the type [$(RO)_3B$, BF_3, EtOH], trifluoroacetic acid produced polymer in higher yields with relatively high molecular weights (500-1500) and vinylidene contents that reached 87.5% (see Table 20).

Table 20. Polymerisation of isobutene using [$(C_6F_5O)_3B$, $2BF_3$, CF_3COOH] **90** and [$(C_6H_5O)_3B$, $2BF_3$, CF_3COOH] **91** as initiating systems

Initiating system	**Ratio (I : IB)**	**Yield (%)**	M_n	**Vinylidene end-group (%)**
Adduct **75** + CF_3COOH (1:0.78)	1:110	14	1465	44.5
Adduct **75** + CF_3COOH (1:0.93)	1:50	12	672	87.4
Adduct **75** + CF_3COOH (1:0.67) in CH_2Cl_2 (*in situ*)	1:56	6	665	78.9
Adduct **80** + CF_3COOH (1:0.7)	1:76	5	520	71.4
Adduct **80** + CF_3COOH (1:0.86) in CH_2Cl_2 (*in situ*)	1:35	37	652	66.4

It is difficult to know what species actually initiated the polymerisation, but one way of proving whether or not the polymerisation is initiated by $BF_3.CF_3COOH$ would be to prepare the latter complex and to compare analysis of the polymer formed. To date, the BF_3 adduct with trifluoroacetic acid has not been reported in the literature and efforts to try to prepare it were unsucessful. It should be possible to draw similarities with the corresponding chloroacetic acid coordination compounds with boron trifluoride which have been reported. Indeed, $(ClCH_2COOH)_2.BF_3$ was reported to be stable at room temperature, whereas the dichloroacetic acid adduct decomposes at room temperature, and trichloroacetic acid will absorb boron trifluoride only at very low temperature. This series of experiment did not allow one to draw any conclusion as to the true nature of the species that initiated the polymerisation of isobutene.

In order to shed some light on this, another set of control experiments was carried out with BF_3 and methanol to show that the presence of trifluoroacetic acid in the system did have an influence on the nature of the polymer obtained. The $BF_3.CH_3OH$ adduct was prepared and then used to initiate the polymerisation of isobutene ; only a small amount of the coordination compound was necessary to produce an Ultravis-type polymer in a very exothermic reaction (Mn = 967 ; vinylidene content = 84.2%).

By contrast, when BF_3 was then bubbled into a 1:1 $CF_3COOH.CH_3OH$ solution until no more gas was absorbed, the resulting mixture was found to be much less reactive than the $BF_3.CH_3OH$ complex, but PIB was produced in good yield, albeit with a significantly lower vinylidene content (see Table 21).

Table 21. Control experiments with methanol

Initiating system	Ratio (I : IB)	Yield (%)	M_n	Vinylidene end-group (%)
BF_3 + CF_3COOH + CH_3OH (0.53:1:0.97)	1:10	63	728	43.7
BF_3 + CF_3COOH + CH_3OH (0.53:1:0.97)	1:50	46	543	55.4
$BF_3.CH_3OH$ (1:0.93)	1:400	79	967	84.2

It is difficult to understand why the addition of trifluoroacetic acid decreases the activity of the $BF_3.CH_3OH$ initiating system whereas it considerably increases the activity of alkoxydifluoroboranes for the polymerisation of isobutene.

2.5.4. *N*-butyldifluoroborane and *n*-pentyldifluoroborane as co-initiators

Analysis of the NMR spectra of the 1:1 mixture of *n*-butyldifluoroborane **53** and trifluoroacetic acid did not show the presence of BF_3 species. The mixture failed to initiate the polymerisation of isobutene. *N*-pentyldifluoroborane **58** did not initiate the polymerisation of isobutene either when added to the C_4 containing trifluoroacetic acid (see Table 22).

Table 22. Polymerisation of isobutene using *n*-butyldifluoroborane $C_4H_9BF_2$ **53** and *n*-pentyldifluoroborane $C_5H_{11}BF_2$ **58** as co-initiators

Initiating system	T(°C)	Ratio (I : IB)	Yield (%)
$C_4H_9BF_2$ + CF_3COOH (1:0.97)	-30	1:136	0
$C_4H_9BF_2$ + CF_3COOH (1:0.97) in 10ml CH_2Cl_2 (*in situ*)	-30		0
$C_5H_{11}BF_2$injected into C_4 + CF_3COOH ($C_5H_{11}BF_2$: CF_3COOH 1:0.83)	-30	1:60	0

3. Conclusion and further work

In our experimental conditions, it is evident that BF_3.EtOH is a much more reactive initiating system than alkoxydifluoroboranes and their adducts with ethanol for the polymerisation of isobutene. Alkoxydifluoroboranes adducts with ethanol initiated the polymerisation of isobutene but only when used in high concentrations, although the polymer produced did have a high vinylidene content. This evidence, coupled with the difficulty of understanding what species did actually bring about polymerisation, gives no support to the validity of polymer supported alkoxydifluoroboranes initiating systems. Alkydifluoroboranes , whether used with ethanol or trifluoroacetic acid as an initiator proved to be inactive co-initiators for the polymerisation of isobutene.

However, of all the Bronsted acids used as initiators, trifluoroacetic acid produced PIB in high yield when used with methoxydifluoroborane CH_3OBF_2 **20** as the co-

initiator. The molecular weights of the polymers obtained were found to within the desired range (1000-1500), and vinylidene end-group contents of up to 75% were achieved.

In view of these results, it is clear that the proposed boron trifluoride derivatives are less desirable co-initiators than BF_3 in terms of activity, and hence further work include trying to find a way of recovering the currently used initiating system BF_3.EtOH at the end of the polymerisation reaction, together with investigating other systems showing similar Lewis acidity as BF_3.

EXPERIMENTAL

Symbols and abbreviations

b	broad
BP	boiling point
cm	complex multiplet
d	doublet
δ	chemical shift
J	spin-spin coupling constant
Lit	literature value
m	multiplet
NMR	Nuclear Magnetic Resonance spectroscopy
PIB	Polyisobutene
ppm	parts per million
s	singlet
t	triplet
q	quartet
ν_{max}	maximum wave number

1. Instrumentation and general techniques

1.1. NMR Spectroscopy

Routine ^{1}H NMR spectra were obtained using a Joel PMX-60 spectrometer or a VARIAN Gemini 2000 operating at 199.97 Mhz. Higher field spectra were obtained on a Bruker WP-200SW operating at 200.13 MHz for ^{1}H and 50.32 MHz for ^{13}C, operated by Mr W. Kerr or on a Bruker AC-250 spectrometer operating at 250.13 Mhz for ^{1}H and at 62.9 MHz for ^{13}C, operated by Mr J.R.A. Millar. Chemical shifts (δ) are reported in parts per million using tetramethylsilane (δ 0.0) as a reference.

^{11}B NMR spectra were obtained on a Bruker WP-200SW operating at 64.21 MHz, operated by Mr W. Kerr. Chemical shifts (δ) are reported in parts per million using boron trifluoride etherate (δ 0.0) as a reference.

^{19}F NMR spectra were obtained on a Bruker AC-250 spectrometer operating at 235.36 MHz, operated by Mr J.R.A Millar. Chemical shifts (δ) are reported in parts per million using $CFCl_3$ (δ 0.0) as a reference.

1.2. Infrared spectroscopy

Infrared spectra were recorded on a Bio-Rad FTS-7 spectrometer. Samples were recorded as thin films on sodium chloride plates.

Vinylidene content in polyisobutene was determined by infrared spectroscopy at BP Chemicals (Grangemouth). The samples were analysed using the Nicolet 740 operated by S. French.

1.3. Gel Permeation Chomatography

The molecular weight of polymers was determined by Gel Permeation Chromatography (GPC) at BP Chemicals (Grangemouth). The spectra were obtained by C.Cura with the following equipment and experimental method :

Injector	- Waters WISP 700 Autosampler
Pump	- Waters 610
Columns	- Waters Ultrastyragel 10^4, 10^3, 500, 100 Angstrom nominal pore size, 300 mm x 7.8 mm i.d., with pre-column filter
Column Oven	- Waters oven, set at 35°C
Detector	- Waters 410 Differential Refractometer, at 35°C
Controller	- Waters 600E
Software	- VG Multichrom, VG-GPC package (version 2.0)

Samples were prepared as solutions of 0.1g of PIB in 10 ml THF (HPLC grade, stabilised with 2,6-di-*t*-butyl-*p*-cresol). To each solution was added 10 µl of toluene as internal marker. The solution were filtered into 4 ml autosampler vials and 100 µl was injected onto the columns. The solvent flow-rate was 1.0 ml/min and the run-time was 50 minutes per sample.

1.4. Drying of glassware and inert gases

For the preparation of air and moisture sensitive BF_3 derivatives and complexes, all the manipulations were caried out in an inert atmosphere glove box or using standard vacuum line techniques[111].

For the polymerisation of isobutene, all flasks were dried thoroughly by heating with a strong Bunsen flame whilst flushing with a strong flow of argon.

Argon or nitrogen gas used for reactions, glove box and Schlenk line were dried by passsing the gas through a series of Dreschel vessels containing concentrated sulphuric acid, calcium chloride and self-indicating silica gel.

1.5. Drying and purification of solvents[112]

Methylene chloride and ethanol were dried by distilling from finely-divided calcium hydride (Fisons) under argon or nitrogen atmosphere. Diethyl ether was dried by distillation from sodium and benzophenone, under argon or nitrogen atmosphere. The

solvent was collected when the deep purple colour, due to sodium benzophenone ketyl, had formed. Heptane was distilled from sodium just before use.

2. Preparation of BF_3 derivatives and adducts

2.1. Alkoxydifluoroboranes ($ROBF_2$)

2.1.1. *N*-pentoxydifluoroborane ($C_5H_{11}OBF_2$)

A modified version of the method used by Chung[58] was employed.

Pentanol was dried by distillation from finely divided calcium hydride prior to use.

To dry diethyl ether (10ml) at -78°C under argon was added dry pentanol (1.02g, 11.6mmol) followed by drop-wise addition of *n*-butyllithium (9ml, 1.7M in pentane, 15.3 mmol) and the mixture stirred at -78°C for 10 minutes. The reaction mixture was then allowed to warm to room temperature and stirred for an additional 10 minutes. Diethyl ether was removed *in vacuo* and the resulting lithium pentoxide **33** was dissolved in 30ml dichloromethane. BF_3 gas was passed through the reaction mixture at 0°C until no more gas was absorbed. After stirring for 30 minutes, the resulting lithium fluoride was filtered-off and the solvent evaporated *in vacuo* to yield $C_5H_{11}OBF_2$ **32** (1.51g, 96%) as a colourless liquid. ^1H NMR (200.13 MHz, $CDCl_3$) δ 4.23 (2H, t, J = 7.5Hz), 1.79 (2H, m), 1.24-1.42 (4H, cm), 0.89 (3H,t, J = 7.5Hz) ppm ; ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 71.1 (CH_2), 28.6 (CH_2), 26.7 (CH_2),

22.0 (CH_2), 13.7 (CH_3) ppm ; ^{11}B NMR (64.21 MHz, $CDCl_3$) δ 0.5 (OBF_2) ppm ; ^{19}F NMR (235.36 MHz, $CDCl_3$) δ -149.2 (OBF_2) ppm.

2.1.2. $(C_6F_5O)_3B.2BF_3$

A modified version of the procedure used by Chung[58] was employed.

To dry diethyl ether (10ml) at -78°C under argon was added pentafluorophenol (1.06g, 5.8mmol) followed by drop-wise addition of *n*-butyllithium (4ml, 1.7M in pentane, 6.8mmol) and the mixture stirred at -78°C for 10 minutes. The reaction mixture was then allowed to warm to room temperature and stirred for a further 10 minutes. The diethyl ether was removed *in vacuo* and the resulting lithium pentafluorophenoxide **72** was dissolved in 30ml dichloromethane after which BF_3 gas was passed through the reaction mixture at 0°C until no more gas was absorbed. After stirring for 30 minutes, the resulting lithium fluoride was filtered-off and the solvent evaporated *in vacuo* to yield the complex $(C_6F_5O)_3B.2BF_3$.**75** ^{11}B NMR (64.21 MHz, $CDCl_3$) δ 17.4 (b, $(C_6F_5O)_3B$ and $(C_6F_5O)_2BF$), 0.8 (s, BF_3) ppm ; the integrated ratio of these 2 peaks is about 1:1 ; ^{19}F NMR (235.36 MHz, $CDCl_3$) δ -130.4 (s,OBF), -153.2 (s, BF_3), -157.5- -168.5 (cm, C_6F_5) ppm.

2.1.3. $(C_6H_5O)_3B.2BF_3$

A modified version of the method used by Chung[58] was employed.

To dry diethyl ether (10ml) at -78°C under argon was added phenol (0.49g, 5.3mmol) followed by drop-wise addition of *n*-butyllithium (4ml, 1.6M in hexanes, 6.4mmol) and the mixture stirred at -78°C for 10 minutes. The reaction mixture was then allowed to warm to room temperature and stirred for an additional 10 minutes. The diethyl ether was removed *in vacuo* and the resulting lithium phenoxide **77** was dissolved in 30ml dichloromethane following which BF_3 gas was then passed through the reaction mixture at 0°C until no more gas was absorbed. After stirring for 30 minutes, the resulting lithium fluoride was filtered-off and the solvent evaporated *in vacuo* to yield the complex $(C_6H_5O)_3B.2BF_3$ **80**. ^{11}B NMR (64.21 MHz, $CDCl_3$) δ 15.9 (b, $(C_6H_5O)_3B$ and $(C_6H_5O)_2BF$), 1 (s, BF_3) ppm ; the integrated ratio of these two peaks is about 1:2 ; ^{19}F NMR (235.36 MHz, $CDCl_3$) δ -129.7 (s,OBF), -152.3 (s, BF_3) ppm ; ^1H NMR (250.13 MHz, $CDCl_3$) δ 7.09-7.15 (2H, cm), 7.19-7.25 (1H, cm), 7.32-7.4 (2H, cm) ppm.

2.1.4. Methoxydifluoroborane (CH_3OBF_2)

Methoxydifluoroborane was prepared according to the method of McCusker[69].

BF_3 gas was passed through trimethoxyborane **21** (8.4g, 81mmol) at 0°C until no more gas was absorbed to yield a colourless solid (18.6g, 97%). ^1H NMR (200.13 MHz, $CDCl_3$) δ 3.9 (s, CH_3) ppm ; ^{13}C NMR (62.89 MHz, $CDCl_3$) δ 55.7 (CH_3) ppm ; ^{11}B NMR (64.21 MHz, $CDCl_3$) δ 0.36 (OBF_2) ppm ; ^{19}F NMR (235.36 MHz, $CDCl_3$) δ -153.4 (OBF_2) ppm.

2.2. Formation of adducts of alkoxydifluoroboranes with ethanol and Bronsted acids

2.2.1. Addition of ethanol to *n*-pentoxydifluoroborane ($C_5H_{11}OBF_2$)

Dry ethanol (0.2g, 4.35mmol) was added cautiously to *n*-pentoxydifluoroborane **32** (0.64g, 4.71mmol) at room temperature with a syringe in a glove box to form a 1:0.92 adduct during which a slight exotherm and fumes were observed. The adduct comprised of [$(C_5H_{11}O)_3B$, $2BF_3$, EtOH] **84** was used immediately without further purification. ^1H NMR (200.13 MHz, $CDCl_3$) δ 7.28 (1H, s, EtO<u>H</u>), 3.69-3.81 (4H, bcm, $2CH_2$), 1.42-1.63 (2H, bcm, CH_2), 1.28 (7H, bcm, $1CH_3$ and $2CH_2$), 0.87 (3H, cm, CH_3) ppm ; ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 63.6 (b, CH_2), 59.2 (b, CH_2), 31.0 (CH_2), 27.5 (b, CH_2), 22.2 (CH_2), 16.9 (b, CH_3), 13.8 (CH_3) ppm ; ^{11}B NMR (64.21 MHz, $CDCl_3$) δ 18.8 (b, $(C_5H_{11}O)_3B$ and $(C_5H_{11}O)_2BF$), 0.0 (s, BF_3) ppm ; the integrated ratio of these two peaks was *ca.* 1:2 ; ^{19}F NMR (235.36 MHz, $CDCl_3$) δ -133.7 (OBF), -153.8 (BF_3) ppm.

2.2.2. Addition of ethanol to $(C_6F_5O)_3B.2BF_3$

Dry ethanol (0.122g, 2.65mmol) was added to $(C_6F_5O)_3B.2BF_3$ **75** (0.624g, 2.69mmol) at room temperature in a glove box to form a 1:0.98 adduct during which a slight exotherm and fumes were observed. The adduct comprised of [$(C_6F_5O)_3B$,

$2BF_3$, EtOH] **85** was used immediately without further purification. ^1H NMR (250.13 MHz, $CDCl_3$) δ 7.25 (bs, EtO<u>H</u>), 3.96 (2H, bm, CH_2), 1.29 (3H, t, CH_3) ppm ; ^{11}B NMR (64.21 MHz, $CDCl_3$) δ 18.0 (b, $(C_6F_5O)_3B$), 16.8 (b, $(C_6F_5O)_2BF$), 0.2 (s, BF_3) ppm ; ^{19}F NMR (235.36 MHz, $CDCl_3$) δ -133.5 (bs, OBF), -153.6 (s, BF_3), -158.3-169.6 (cm, C_6F_5) ppm.

2.2.3. Addition of ethanol to methoxydifluoroborane (CH_3OBF_2)

Dry ethanol (0.134g, 2.91mmol) was added slowly to methoxydifluoroborane **20** (0.24g, 3.04mmol) at room temperature in a glove box to form a 1:0.96 adduct during which a slight exotherm and fumes were observed. The adduct comprised of $[(CH_3O)_3B, 2BF_3, EtOH]$ **86** was used immediately without further purification.^1H NMR (250.13 MHz, $CDCl_3$) δ 9.4 (1H, s, EtO<u>H</u>), 3.8 (2H, bm, CH_2), 3.44 (3H, s, C<u>H</u>$_3$OBF_2), 1.16 (3H, bm, C<u>H</u>$_3$CH_2OH) ppm ; ^{13}C NMR (62.89 MHz, $CDCl_3$) δ 60.2 (b, CH_2), 50.6 (CH_3), 15.4 (b, CH_3) ppm ; ^{11}B NMR (64.21 MHz, $CDCl_3$) δ 18.9 (b, $(CH_3O)_3B$ and $(CH_3O)_2BF$), 0.2 (s, BF_3) ppm ; the integrated ratio of these two peaks was *ca.* 1:2 ; ^{19}F NMR (235.36 MHz, $CDCl_3$) δ -135.2 (OBF) ; -154.7 (BF_3) ppm.

2.2.4. Addition of *tert*-butyl chloride to methoxydifluoroborane (CH_3OBF_2)

tert-Butylchloride (0.232g, 2.51mmol) was added to methoxydifluoroborane **20** (0.226g, 2.86mmol) at room temperature in a glove box to form a 1:0.88 adduct

which was used immediately without further purification. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 3.82 (3H, s, $C\underline{H}_3OBF_2$), 1.53 (9H, s, $(C\underline{H}_3)_3CCl$) ppm ; ^{13}C NMR (62.88 MHz, $CDCl_3$) δ 67.0 (C), 55.5 (CH_3), 34.1 ($3CH_3$) ppm ; ^{11}B NMR (64.21 MHz, $CDCl_3$) δ 0.3 (OBF_2) ppm ; ^{19}F NMR (235.36 MHz, $CDCl_3$) δ -157.3 (OBF_2) ppm.

2.2.5. Addition of acetic acid to methoxydifluoroborane (CH_3OBF_2)

Acetic acid was purified with CrO_3 and dried with acetic anhydride[112] and distilled prior to use.

Acetic acid (0.119g, 1.98 mmol) was added slowly to methoxydifluoroborane **21** (0.16g, 2.03mmol) at room temperature in a glove box to form a 1:0.97 adduct $CH_3OBF_2.CH_3COOH$ **88** which was used immediately without further purification. ^{1}H NMR (200.13 MHz, $CDCl_3$) δ 10.77 (1H, s, $CH_3COO\underline{H}$), 3.63 (3H, s, $C\underline{H}_3OBF_2$), 2.03 (3H, s, $C\underline{H}_3COOH$) ppm ; ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 175.9 (C=O), 52.6 (CH_3), 19.9 (CH_3) ppm ; ^{11}B NMR (64.21 MHz, $CDCl_3$) δ -0.1 (OBF_2) ppm ; ^{19}F NMR (235.36 MHz, $CDCl_3$) δ -147.8 (bs, OBF_2) ppm.

2.2.6. Addition of trifluoroacetic acid to methoxydifluoroborane (CH_3OBF_2)

Trifluoroacetic acid was dried with trifluoroacetic anhydride[112] and distilled prior to use.

Trifluoroacetic acid (0.623g, 5.46mmol) was added slowly to methoxydifluoroborane **20** (0.429g, 5.37mmol) at room temperature in a glove box to form a 1:1.01 adduct during which a slight exotherm and fumes were observed. The adduct $CH_3OBF_2.CF_3COOH$ **89** was used immediately without further purification. ^1H NMR (200.13 MHz, $CDCl_3$) δ 8.94 (1H, s, $CF_3COO\underline{H}$), 3.95 (3H, s, CH_3) ppm ; ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 159.3 (q, J = 39Hz, C=O), 114.5 (q, J = 278Hz, CF_3), 54.8 (CH_3) ppm ; ^{11}B NMR (64.21 MHz, $CDCl_3$) δ 0.0 (OBF_2) ppm ; ^{19}F NMR (235.36 MHz, $CDCl_3$) δ -76.7 (3F, s, CF_3), -148.3 (2F, s, OBF_2) ppm.

2.2.7. Addition of trifluoroacetic acid to $(C_6F_5O)_3B.2BF_3$

Dry trifluoroacetic acid (0.373g, 3.27mmol) was added slowly to $(C_6F_5O)_3B.2BF_3$ **75** (0.772g, 3.33mol) at room temperature in a glove box to form a 1:0.99 adduct during which a slight exotherm and fumes were observed. The complex comprised of [$(C_6F_5O)_3B$, $2BF_3$, CF_3COOH] **90** was used immediately without further purification. ^{11}B NMR (64.21 MHz, $CDCl_3$) δ 17.2 (b, $(C_6F_5O)_3B$ and $(C_6F_5O)_2BF$), 0.8 (bs, BF_3) ; the integrated ratio of these two peaks was *ca.* 1:1 ; ^{19}F NMR (235.36 MHz, $CDCl_3$) δ -76.2 (3F, CF_3), -152.7 (2F, BF_3), -160.6-164.0 (5F, C_6F_5) ppm.

2.2.8. Addition of trifluoroacetic acid to $(C_6H_5O)_3B.2BF_3$

Dry trifluoroacetic acid (0.517g, 4.53mmol) was added slowly to $(C_6H_5O)_3B.2BF_3$ **80** (0.643g, 4.53mol) at room temperature in a glove box to form a 1:1 adduct during

which a slight exotherm and fumes were observed. The complex comprised of [$(C_6H_5O)_3B$, $2BF_3$, CF_3COOH] **91** was used immediately without further purification. ^{11}B NMR (64.21 MHz, $CDCl_3$) δ 15.5 (b, $(C_6H_5O)_3B$ and $(C_6H_5O)_3BF$), 1.3 (bs, BF_3) ; the integrated ratio of these two peaks was *ca.* 1:1 ; ^{19}F NMR (235.36 MHz, $CDCl_3$) δ -76.11 (CF_3), -126.2 (OBF), -150.6 (BF_3) ppm.

2.3. Alkyldifluoroboranes (RBF_2)

2.3.1. Preparation of tri-*n*-butylborane ($(C_4H_9)_3B$)

The reaction was carried out according to the method of Brown *et al.*[101,102].

N-bromobutane was dried over $CaCl_2$ and distilled. After drying over P_2O_5, the solvent was distilled again and stored over freshly activated alumina[112].

Into a 500ml three-neck flask fitted with a condensor were added magnesium turnings (4.9g, 202mmol), which were dried by heating with a Bunsen flame and then cooled under argon. $BF_3.Et_2O$ (7.1g, 50mmol), together with a crystal of iodine in dry diethyl ether (50ml) were introduced into the flask under an argon atmosphere. The mixture was stirred and the reaction initiated by dropwise addition of a small portion of *n*-bromobutane (2.7ml, 3.42g, 25mmol).The remainder of the *n*-bromobutane (20.55g, 150mmol) was dissolved in dry diethyl ether (30ml) and added slowly over a period of 30-45 min., to maintain the diethyl ether boiling under reflux. After the addition of alkyl halide was completed, stirring was continued for a further 2h. following which water (0.9ml, saturated with ammonium chloride) was added to the

reaction mixture. The reaction mixture was allowed to settle and the clear supernatant ethereal layer separated, dried and removed *in vacuo* to give a yellow liquid. Kugelrohr distillation of the crude product (110°C/20mmHg) yielded tri-*n*-butylborane **92** (5.84g, 55%) as a colourless liquid. ^{11}B NMR (64.21 MHz, Et_2O) δ 86.7 ppm.

2.3.2. Preparation of *n*-butyldifluoroborane ($C_4H_9BF_2$)

The method of Tuhagues and Laurent[83] was adopted for this preparation.

Tri-*n*-butylborane **92** (9.72g, 55.3mmol) was added to the reaction flask with a syringe and the flow of BF_3 was controlled by use of a Dreschel bottle with paraffin oil. When BF_3 was bubbled slowly through the borane, the temperature of the reaction mixture rose from room temperature up to 35°C. Thereafter, it was heated to 210°C while maintaining the flow of BF_3. After 10 min., the temperature decreased to 175°C and a volatile, colourless liquid distilled from the mixture with a b. pt 35°C. The endothermic reaction continued until almost all of the tri-*n*-butylborane had disappeared to afford *n*-butyldifluoroborane **53** (14.3g, 82%) ; bp = 35°C (Lit[83] = 36°C) ; ^1H NMR (200.13 MHz, $CDCl_3$) δ 1.26-1.43 (4H, cm, $2CH_2$), 0.85-1 (5H, cm, CH_3CH_2) ppm ; ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 24.3 (CH_2), 24.9 (CH_2), 13.5 (CH_2), 13.5 (CH_3) ; ^{11}B NMR (64.21 MHz, $CDCl_3$) δ 29.8 (t, J = 80Hz) ppm ; ^{19}F NMR (235.36 MHz, $CDCl_3$) δ -73.6 (q, J = 80Hz) ppm.

2.3.3. Preparation of tri-*n*-pentylborane ($(C_5H_{11})_3B$)

This preparation was carried out according to the general procedure described by Brown *et al.*[101,102].

Thus, *N*-bromopentane was dried over anhydrous $CaCl_2$ and distilled prior to use.

Into a 500ml three-necked flask fitted with a condensor magnesium turnings (4.86g, 200mmol) were introduced and dried by heating with a Bunsen flame under argon. After cooling, $BF_3.Et_2O$ (7.1g, 50mmol), together with a crystal of iodine, and anhydrous diethyl ether (50ml) were introduced into the flask and the reaction initiated by a drop-wise addition of *n*-bromopentane (2.95ml, 3.77g, 25mmol). The remainding of *n*-bromopentane (22.65g, 150mmol) was dissolved in diethyl ether (30ml) and added slowly to the reaction mixture over a period of 1 hour, to maintain boiling of the solvent under reflux conditions. The reaction mixture was then placed in a heated ultra-sound bath for 30 minutes, and water (0.9ml, saturated with ammonium chloride) was added. The reaction mixture was allowed to settle and the clear supernatant ethereal layer separated, dried and removed *in vacuo* to afford the crude product as a yellow liquid. Kugelrohr distillation of this product (150°C/10mmHg) yielded tri-*n*-pentylborane **93** (9.35g, 72%) as a colourless liquid.

^{11}B NMR (64.21 MHz, Et_2O) δ 86.9 ppm.

2.3.4. Preparation of *n*-pentyldifluoroborane ($C_5H_{11}BF_2$)

The method of Tuhagues and Laurent[83] was adopted for this preparation.

Tri-*n*-pentylborane **93** (9g, 40.2mmol) was added to the reaction flask with a syringe and the flow of BF_3 was controlled by use of a Dreschel bottle with paraffin oil. When BF_3 was bubbled slowly through the borane, the temperature of the reaction mixture rose from room temperature up to 35°C. Thereafter, it was heated to 210°C while maintaining the flow of BF_3. After 10 min., the temperature decreased to 175°C and a volatile colourless liquid distilled off at 65°C. The endothermic reaction continued until almost all of the tri-*n*-pentylborane disappeared to yield *n*-pentyldifluoroborane **58** (11.1g, 77%) ; bp = 65°C (Lit[83] = 65°C) ; ^{1}H NMR (200.13 MHz, $CDCl_3$) δ 1.26-1.48 (6H, cm, $3CH_2$), 0.85-1 (5H, cm, CH_3CH_2) ppm ; ^{11}B NMR (64.21 MHz, $CDCl_3$) δ 29.8 (t, J = 80Hz) ppm ; ^{19}F NMR (235.36 MHz, $CDCl_3$) δ -73.6 (q, J = 77Hz) ppm.

2.4. Formation of adducts of alkyldifluoroborane and ethanol and Bronsted acids

2.4.1. Addition of ethanol to *n*-butyldifluoroborane ($C_4H_9BF_2$)

Dry ethanol (0.406g, 8.82mmol) was added slowly to *n*-butyldifluoroborane **53** (1.105g,10.4mmol) at room temperature in a glove box with formation of a slight exotherm and evolution of colourless fumes to give the adduct $C_4H_9BF_2$.EtOH **94**

which was used immediately without further purification. ^{1}H NMR (200.13 MHz, $CDCl_3$) δ 7.78 (1H, b, EtO<u>H</u>), 3.85 (2H, q, $CH_3C\underline{H}_2OH$), 1.18-1.54 (7H, cm, $1CH_3$ and $2CH_2$), 0.65 (2H, b, CH_2), 0.86 (3H, m, CH_3) ppm ; ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 59.1 ($CH_3\underline{C}H_2OH$), 25.5 (CH_2), 25.2 (CH_2), 16.8 ($\underline{C}H_3CH_2OH$), 13.7 (CH_2), 13.7 (CH_3) ppm ; ^{11}B NMR (64.21 MHz, $CDCl_3$) δ 28.5 (b) ppm ; ^{19}F NMR (235.36 MHz, $CDCl_3$) δ -90 (vb) ppm.

2.4.2. Addition of trifluoroacetic acid to *n*-butyldifluoroborane ($C_4H_9BF_2$)

Dry trifluoroacetic acid (1.074g, 9.42mmol) was added slowly to *n*-butyldifluoroborane **53** (1.02g, 9.64mmol) at room temperature in a glove box to form the adduct $C_4H_9BF_2.CF_3COOH$ **96** which was used immediately without further purification. ^{1}H NMR (200.13 MHz, $CDCl_3$) δ 11.23 (1H, s, $CF_3COO\underline{H}$), 1.23-1.47 (4H, cm, $2CH_2$), 0.82-1.0 (5H, cm, $1CH_3$ and $1CH_2$) ppm ; ^{11}B NMR (64.21 MHz, $CDCl_3$) δ 29.8 (t, J = 80Hz) ppm ; ^{19}F NMR (235,36 MHz, $CDCl_3$) δ -73.6 (2F, b, BF_2), -76.1 (3F, s, CF_3) ppm.

2.4.3. Addition of ethanol to *n*-pentyldifluoroborane ($C_5H_{11}BF_2$)

Dry ethanol (0.16g, 3.4mmol) was added slowly to *n*-pentyldifluoroborane **58** (0.46g, 3.87mmol) at room temperature in a glove box during which a slight exotherm together with the evolution of colourless fumes was observed to give the adduct $C_5H_{11}BF_2.EtOH$ **95** which was used immediately without further purification. ^{1}H

NMR (200.13 MHz, $CDCl_3$) δ 7.0 (1H, s, EtO<u>H</u>), 3.88 (2H, q, $CH_3C\underline{H}_2OH$), 1.14-1.42 (9H, cm, $1CH_3$ and 3 CH_2), 0.85 (3H, m, CH_3), 0.7 (2H, cm, CH_2) ppm ; ^{11}B NMR (64.21 MHz, $CDCl_3$) δ 26.1 (b) ppm. ; ^{19}F NMR (235.36 MHz, $CDCl_3$) δ -90 (vb) ppm.

2.4.4. Addition of trifluoroacetic acid to *n*-pentyldifluoroborane ($C_5H_{11}BF_2$)

Dry trifluoroacetic acid (0.41g, 3.59mmol) was added slowly to *n*-pentyldifluoroborane **58** (0.49g, 4.12mmol) at room temperature in a glove box to afford the adduct $C_5H_{11}BF_2.CF_3COOH$ **97** which was used immediately without further purification. ^1H NMR (200.13 MHz, $CDCl_3$) δ 11.32 (1H, s, $CF_3COO\underline{H}$), 1.14-1.59 (6H, cm, $3CH_2$), 0.82-1.16 (5H, cm, $1CH_3$ and $1CH_2$) ppm ; ^{11}B NMR (64.21 MHz, $CDCl_3$) δ 29.9 (t, J = 80Hz) ppm ; ^{19}F NMR (235,36 MHz, $CDCl_3$) δ -73.7 (2F, b, BF_2), -76.2 (3F, s, CF_3) ppm.

2.5. Other BF_3 derivatives

2.5.1. Attempted preparation of adduct between boron trifluoride and trifluoroacetic acid

BF_3 gas was passed with care through dry trifluoroacetic acid at various temperatures (+20°C - -20°C) for 30 min.. In each case, the reaction mixture was weighed before and after the passage of the gas but no weight gain was found to occur.

2.5.2. Preparation of adduct between boron trifluoride and 1:1 mixture of methanol and trifluoroacetic acid

Dry methanol (1.692g, 52.8mmol) was added to dry trifluoroacetic acid (6.218g, 54.5mmol) to form a 1:0.97 $CF_3COOH.CH_3OH$ adduct. BF_3 was then passed through the reaction mixture at 0°C until no more gas was absorbed (1.969g, 29 mmol). Weight gain of the reaction mixture indicated the formation of a 1:0.97:0.53 $CF_3COOH.CH_3OH.BF_3$ adduct.

3. Polymerisation of isobutene

3.1. Batch polymerisation of isobutene

The apparatus was arranged as shown in Appendix 1.

To the dried, weighed, argon-purged reactor vessel in a dry ice/isopropanol bath at *ca.* -20°C was added *ca.* 300g of C_4 feedstock (isobutene in *n*-butane 40%). The system was allowed to cool until minimal C_4 evaporation/condensation was observed. Vessel and stock were then re-weighed and the mass of feed-stock charged to the reactor calculated by difference in weight.

The required ratio of initiating system was then added to the stirred feedstock *via* a syringe. The temperature change, if any, was noted and stirring was continued at -20°C for 20 minutes. The reaction was then terminated by addition of dilute ammonia or saturated $NaHCO_3$ solution (depending on the initiator used : alcohol or

acid) following which the reaction mixture was allowed to stand for a few hours at room temperature in order to allow evaporation of excess C_4.

The resulting polymer was then dissolved in a minimum amount of heptane and the solution was washed with water (5x100ml) and dried over excess magnesium sulphate. It was then subject to rotary evaporation at 100°C/0.5mmHg for 30 minutes to remove solvent and light polymer, and recover the polymer under standard conditions.

The conversion of monomer into polymer was recorded and the sample analysed for molecular weight by Gel Permeation Chromatography, whereas the vinylidene content was determined by IR spectroscopy or NMR spectroscopy.

N.B. It should be noted that light polymer refers to a mixture of di-, tri-, tetra-, penta-, and hexa-meric oligomers of isobutene.

3.2. Small-scale polymerisation of isobutene

3.2.1. Injection of initiating system (co-initiator/initiator) into isobutene

The apparatus was arranged as depicted in Appendix 3. 30g C_4 feedstock was condensed into a 100ml three-necked marked flask under an argon atmosphere and then transferred to a 250ml three-necked reaction flask contained in a dry ice/isopropanol bath (*ca.*-30°C) *via* a cannula. The initiating system was added to the stirred feedstock *via* a syringe and the temperature change, if any, was noted and stirring continued at *ca.* -30°C for 20 minutes. The reaction was stopped by addition

of dilute ammonia or saturated $NaHCO_3$ solution (depending on the initiator used : alcohol or acid) and the mixture was allowed to stand for a few hours to allow evaporation of excess C_4. The resulting polymer was dissolved in a minimum quantity of heptane and the solution was washed with water (5x50ml) then dried over excess magnesium sulphate. It was then subject to rotary evaporation at 100°C/0.5mmHg for 30 minutes to remove solvent (and light polymer) and recover the polymer under standard conditions. The conversion of monomer into polymer was recorded and the sample analysed for molecular weight by Gel Permeation Chromatography and vinylidene content by IR spectroscopy or NMR spectroscopy.

3.2.2. Use of initiating system (co-initiator/initiator) *in situ*

The required molar ratio of initiating system was injected directly into a 250ml dried three-necked flask under argon with a syringe together with 5-10ml of dried solvent (dichloromethane or heptane) and the solution cooled to *ca.* -30°C in an isopropanol/dry ice bath.In a separate step, 30g C_4 feedstock was condensed into a dried 100ml three- necked flask and transferred to the stirred initiating system solution *via* a cannula. The temperature change, if any, was noted and stirring was continued at -30°C for 20 minutes. The reaction was then stopped by addition of dilute ammonia if the initiator was an alcohol or saturated $NaHCO_3$ solution if the initiator was a Bronsted acid and worked up as described in section 3.2.1. to give polyisobutene.

3.2.3. Use of Initiator *in situ*, with co-initiator injected

C_4 feedstock (30g) was condensed into a dried 100ml three-necked marked flask under an argon atmosphere and subsequently transferred to a 250ml dried three-necked reaction flask *via* a cannula. The mixture was allowed to cool to *ca.* -30°C in a dry ice/isopropanol bath following which the initiator was added to the reaction mixture by means of a syringe. The required molar ratio of co-initiator was then added *via* a syringe to the stirred C_4 and initiator mixture and the temperature change, if any, was noted and stirring continued at *ca.* -30°C for 20 minutes.The reaction was then stopped by addition of dilute ammonia if the initiator was an alcohol or saturated $NaHCO_3$ solution if the initiator was a Bronsted acid. The reaction was worked up as described in section 3.2.1. to give polyisobutene.

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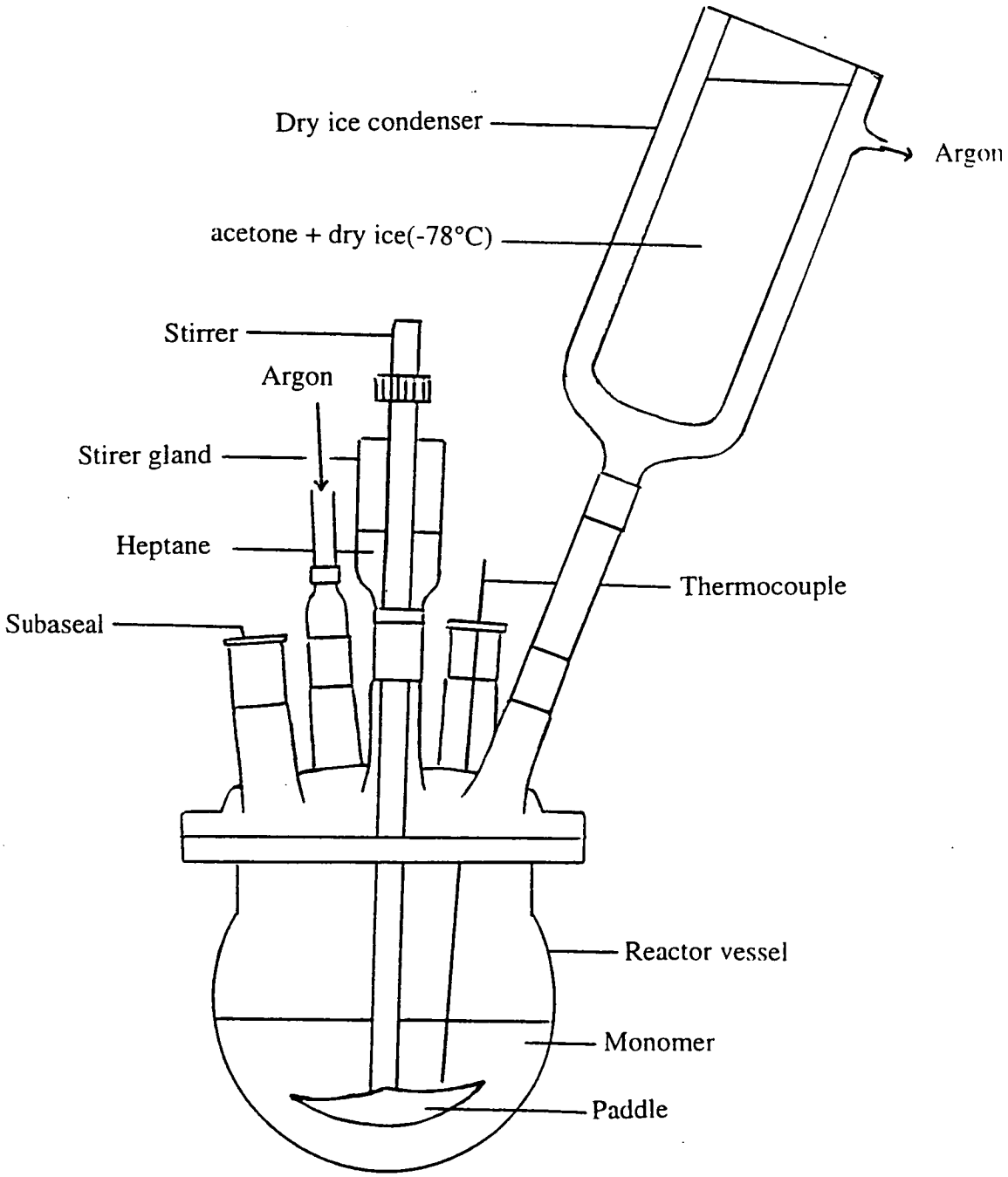
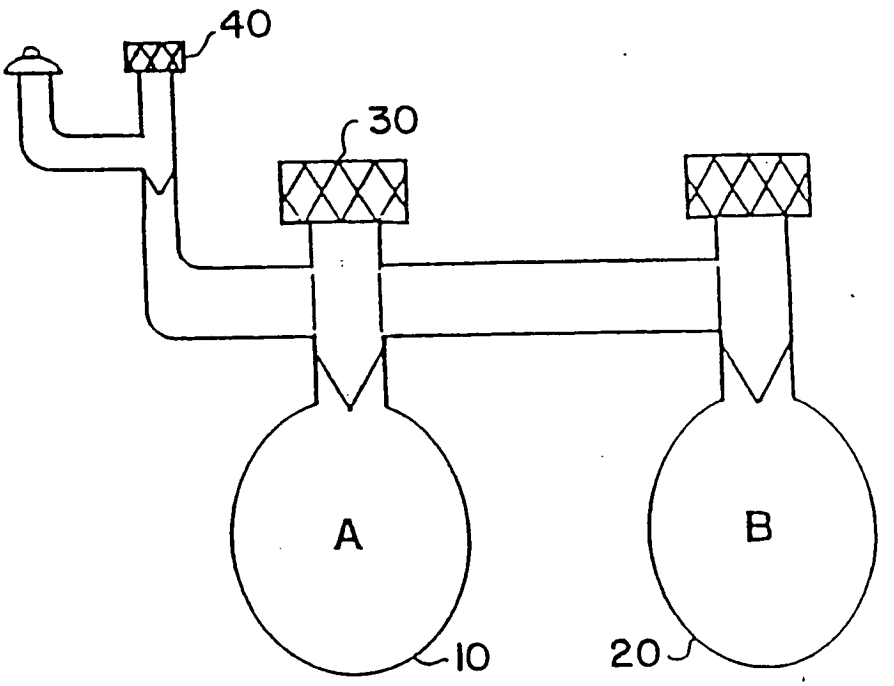
Appendices

APPENDIX 1 Batch polymerisation apparatus

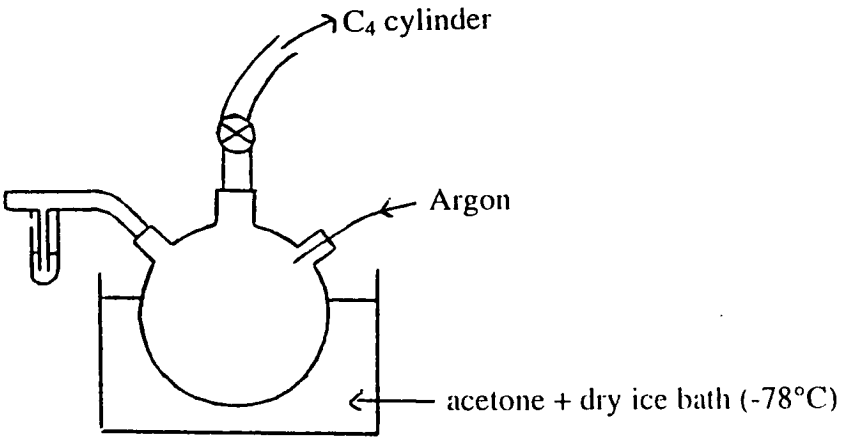


APPENDIX 2 High vacuum polymerisation apparatus



APPENDIX 3 Small scale polymerisation apparatus

Condensation of 30g isobutene in isobutane (40%)



Transfer to the reaction flask