A Thesis Submitted for the Degree of PhD at the University of Warwick

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Novel chromium compounds and

their use in the polymerisation of

methyl methacrylate

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A Thesis submitted for the Degree of Doctor of Philosophy

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18th January 1998

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All experimental work contained in this thesis is original research that was carried out by the author in the Department of Chemistry, University of Warwick, between October 1994 and October 1997. No material contained herein has been submitted for any other degree to this, or any other institution. Results from other authors are referenced in the usual manner throughout the text.

Signed   Date 18th January 1998

F: Summary

The controlled polymerisation of methacrylates has been extensively studied in recent years. The discovery of group transfer polymerisation (GTP) by DuPont initiated many investigations into this area, one of the main objectives was a commercially viable process giving access to the wealth of novel polymer architecture and properties afforded by controlled synthesis.

This work has investigated a number of chromium compounds and their use in the polymerisation of methyl methacrylate using a variety of agents, under various reaction conditions. In this work new chromium compounds have been prepared and existing compounds investigated further in an attempt to gain control over the polymer reaction, in particular the molecular weight, Mn, of the polymer formed. An unusual chromium - zinc metal compound has been prepared, and used in the polymerisation of MMA, however, this resulted in only low % conversion of monomer. Further work resulted in the preparation of chromium - Schiff base organometallic compounds. These compounds were extensively studied and resulted in the quantitative conversion of MMA over a 3 hour period, under certain conditions. Other compounds examined included aqueous organochromium complexes, which were stable in aqueous media for several days at low temperatures, these compounds were also used to polymerise MMA, low % conversion was again achieved. It was found that although all these compounds resulted in the polymerisation of MMA, by various mechanisms, control over Mn had not been achieved.

G: Abbreviations

AIBN	2,2'-Azobisisobutyronitrile
t-Bu	t-Butyl group
Bu	n-Butyl group
CCT	Catalytic chain transfer
CCTA	Catalytic chain transfer agent
DP	Number average degree of polymerisation
HPLC	High performance liquid chromatography
HEMA	Hydroxyethyl methacrylate
IR	Infrared spectroscopy
$\mathbf{k_d}$	Rate constant for dissociation of initiator
$\mathbf{k_i}$	Rate constant for initiation of monomer
$\mathbf{k_p}$	Rate constant for propagation
$\mathbf{k_r}$	Rate constant for reinitiation
$\mathbf{k_{tc}}$	Rate constant for termination by combination
$\mathbf{k_{td}}$	Rate constant for termination by disproportionation
MALDI-MS	Matrix-assisted laser desorption ionisation mass spectrometry
Me	Methyl group
MeOH	Methanol
mg	milligrams
mL	millilitres
MMA	Methyl methacrylate
Mn	Number average molecular weight
Mp	Peak average molecular weight
Mw	Weight average molecular weight
NMR	Nuclear magnetic resonance spectroscopy

PDi	Polydispersity index
PMMA	Poly(methyl methacrylate)
PPh$_3$	Triphenyl phosphine
ppm	Parts per million
PS	Poly styrene
PVC	Poly(vinyl chloride)
R$_i$	Rate of initiation
R$_p$	Rate of propagation/polymerisation
R$_t$	Rate of termination
SEC	Size exclusion chromatography
Sty	Styrene
TGA	Thermal gravimetric analysis
THF	Tetrahydrofuran
UV/Vis	Ultraviolet-visible spectroscopy
[X]	Molar Concentration of X

Chapter 1

Introduction

1. Introduction

Polymer chemistry is one of the largest branches of industrial chemistry in the world. Industry has been able to prepare an enormous variety of polymeric materials, with uses having ranged from surface coatings, packaging and adhesive coatings to medical prosthetics and contact lenses to electrical insulators. These polymeric materials have been made using a wide variety of polymer synthetic methods, which have included, anionic polymerisation, cationic, coordination and free radical polymerisation. Polymers have been made in solution, emulsion, suspension as well as under bulk conditions[1-10].

Commercially, polymers have been made using all these techniques, but only very few result in control over the product geometry and topology. Anionic polymerisation of vinyl monomers is one of the more successful. This process however, requires very pure reagents and/or solvents and often very low temperatures,[11]. These two factors have limited the commercial impact of anionic polymerisation. Radical polymerisation is perhaps the most versatile polymerisation technique, however, it suffers from a lack of control due to the very reactive nature of radical reactions.

The aim of this thesis is to examine new methods of polymerisation to attempt to obtain some control of these reactions. This thesis reports the investigation of many polymerisation reactions carried out using new chromium compounds and the reinvestigation of some older chromium chemistry.

1.1. An Introduction to Polymers[12]

An important feature of polymers is the size and distribution of chain-lengths of the molecules. Each polymer formed consists of molecules of different sizes and in that respect the polymers are described as polydisperse. The polymer samples formed are not pure compounds but are mixtures of molecules of varying lengths, as such statistics play a useful part in describing polymer mixtures and the size of molecules. (See section 1.6.1).

Polymers fall into several categories; if described by their method of origin these are as follows:-

- Synthetic organic polymers
- Biopolymers
- Semi-synthetic polymers
- Inorganic polymers

Synthetic organic polymers are by far the most technologically important and are often described merely as polymers. Polymer chains usually consist of a restricted number of chemically different organic monomers. A polymer comprised of one monomer is described as a homopolymer, two types of monomer is a copolymer or three is a terpolymer.

Biopolymers cover proteins, polynucleotides and natural rubber. Protein molecules are made up of up to 20 amino acid monomers, linked in a specific order and up to a specific chain length.

Semi-synthetic polymers are products of chemical reactions applied to biopolymers. An example is cellulose being reacted to form viscose. The final product is chemically the same, but the process allows the product to be physically altered.

Inorganic polymers include silicon based materials such as poly(dimethyl siloxane), natural silicates and ion exchange resins etc.

Further classification can be distinguished by chain structure, some examples are shown in figure 1-1.

Figure 1-1 Examples of chain structures
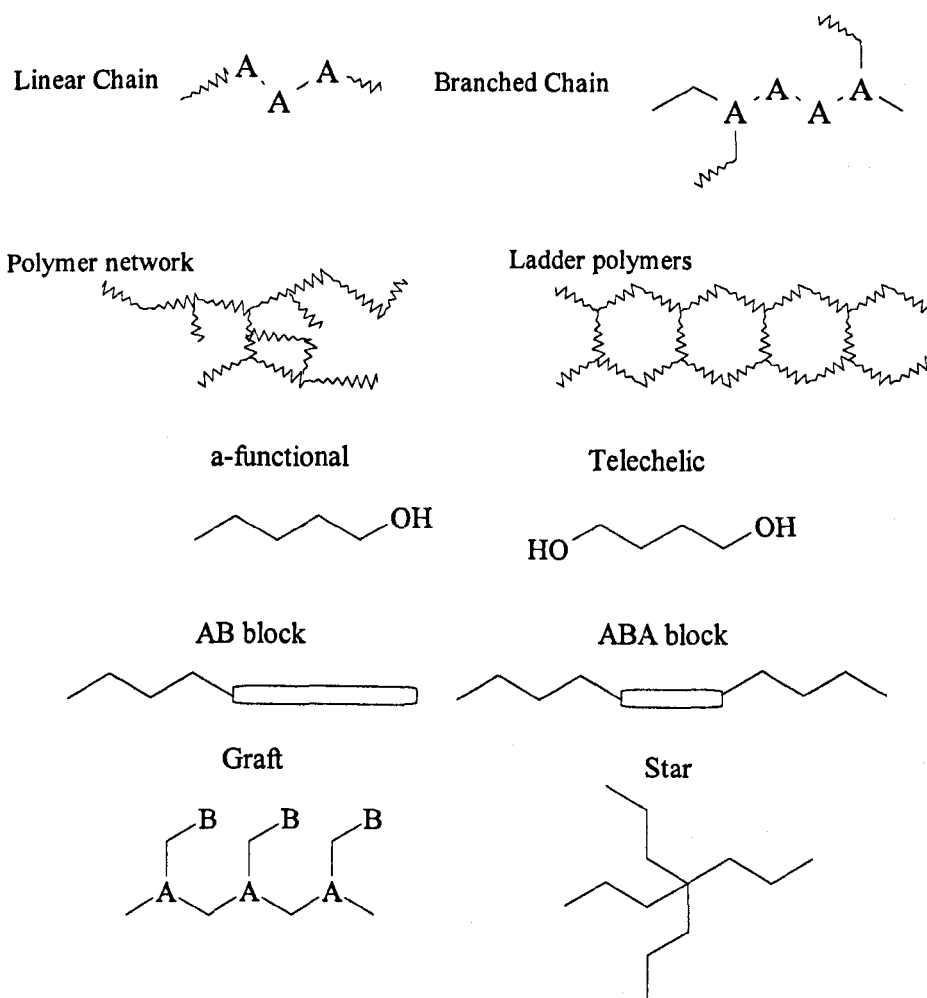
From these examples of polymer systems thousands of various products can be formed.

1.2. Types of Polymerisation

In chain-growth polymerisation reactions each polymer molecule is formed by undergoing 3 reaction steps, *initiation, propagation* and *termination*. In special cases termination reactions may play only a small part or no part whatsoever in the reaction.

- Initiation:- Start of chain growth
- Propagation:- Continuation of chain growth
- Termination:- Termination of chain growth

The rates of each step in the reaction occur at different rates depending on many factors including solvent and monomer. The substituents on a monomer can be varied in different polymerisation processes in order to maximise the efficiency of the polymerisation.

1.2.1. Anionic Polymerisation

In the case of anionic polymerisation vinyl monomers need to carry electron withdrawing groups. The electron withdrawing group removes electron density from the double bond, stabilising the propagating ion. The effect of this is that the vinyl monomer prefers addition of nucleophilic initiator fragments and chain ends. Scheme 1-1 shows a general mechanism for an anionic polymerisation reaction.

Scheme 1-1 Reaction scheme for an anionic polymerisation reaction.

$$R^-M^+ \ + \ \overset{H}{\underset{H}{>}}{=}\overset{H}{\underset{X}{<}} \ \longrightarrow \ R{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}{-}\overset{\overset{H}{|}}{\underset{\underset{X}{|}}{C}}{^-}M^+ \qquad \textit{Initiation}$$

$$R\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}}^{-}M^{+} \;+\; CH_2=CHX \longrightarrow R\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}}^{-}\text{---------}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}^{\delta+}=\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}}^{\delta-}\text{-----}M^{+}$$

$$\longrightarrow R\overset{\overset{\displaystyle H\;\; H\;\; H\;\; H}{|\;\;|\;\;|\;\;|}}{\underset{\underset{\displaystyle H\;\; X\;\; H\;\; X}{|\;\;|\;\;|\;\;|}}{C\;C\;C\;C}}^{-}M^{+} \qquad\qquad \textit{Propagation}$$
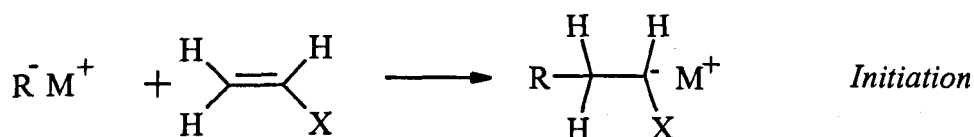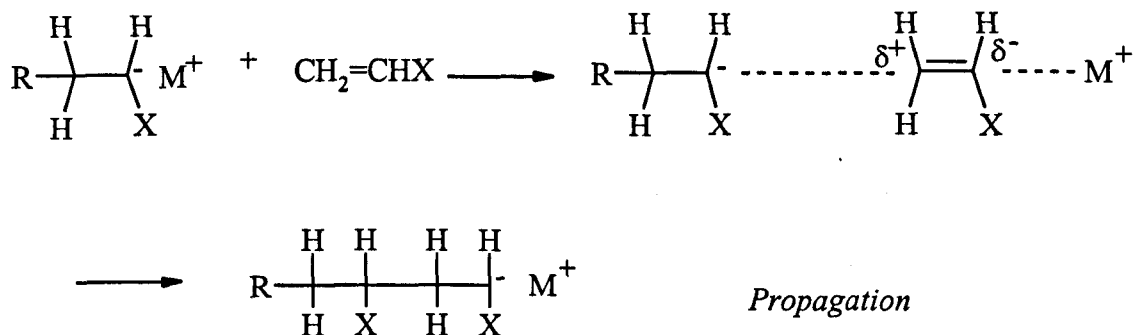
Each new vinyl monomer has the electron-withdrawing group X directly bound to the

negative carbanion resulting in head-to-tail polymerisation. The nature of the solvent

used in the system influences the dissociation of the ion pair, this in turn affects the

reaction rate and the stereochemistry of monomer insertion.

Anionic polymerisation is very sensitive to reaction conditions, requiring very pure

solvents and monomers and no trace of oxygen or water. In addition the reactions are

usually carried out at low temperatures (-78 °C) so as to lower side reactions under

ideal conditions. There is no termination step so this results in a polymer that has been

described as a *living polymer*[13].

In living polymers[11] all polymer chains remain active and will participate in a

polymerisation/depolymerisation equilibrium. This equilibrium can be altered

depending on the nature of the "capping agent" and the solvent used. Importantly the

living end groups can resume growing when a new monomer is added following

monomer depletion. This can result in the formation of block copolymers if a different

monomer has been used in the second addition. So called *living polymerisation*

reactions can give great control over molecular weight of the polymer formed. These

reactions will be discussed further in section 1.4.

1.2.2. Co-ordination Polymerisation

In coordination polymerisation both chain end and monomer are simultaneously

coordinated to one metal centre in a catalytic complex. The main advantage of this

method of polymerisation is that a very high degree of stereospecificity can be

achieved precisely because the monomer and the ligands on the metal influences

stereochemistry.

Ziegler-Natta is a widely used co-ordination polymerisation consisting of

combinations of transition metal halides, or esters of main group organometallics. The

original Ziegler-Natta system is the isospecific polymerisation of propylene with a

catalytic amount of titanium tetrachloride and excess triethyl aluminium in n-heptane

at 70 °C. The actual catalyst is heterogeneous and based upon $TiCl_3$, which is

insoluble and formed by the reduction of $TiCl_4$. Scheme 1-2 shows a simplified (not

balanced) representation of the formation of the catalytic system. Schemes 1-3 & 1-4

show a simplified representation of the polymerisation process.

Scheme 1-2 Formation of the catalytic system

$$TiCl_4 \ + \ AlEt_3 \ \longrightarrow \ TiCl_3Et \ + \ AlEt_2Cl$$

$$TiCl_3Et \ + \ TiCl_3 \ \longrightarrow \ TiCl_3\downarrow \ + \ C_2H_6$$

$$TiCl_3Et \ + \ TiCl_4 \ \longrightarrow \ TiCl_3\downarrow \ + \ EtCl$$

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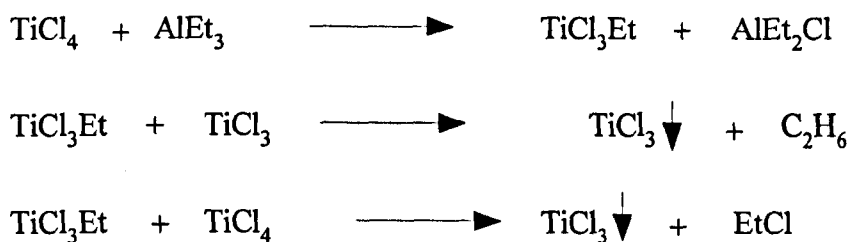
Scheme 1-3 Simplified representation of the Ziegler-Natta polymerisation system
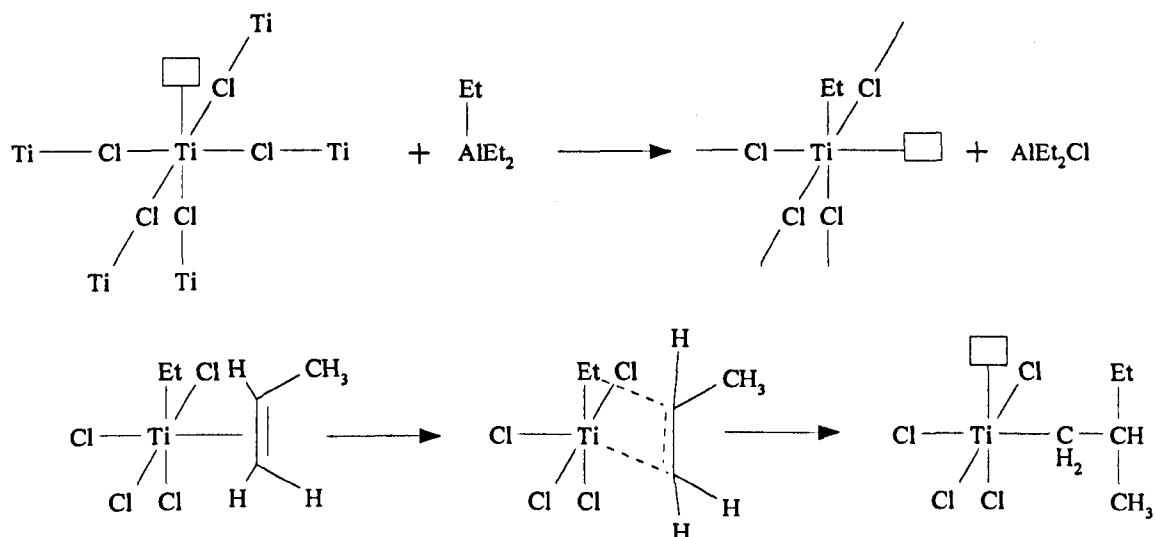
This represents the initiation step, following this is the first propagation step, scheme 1-4.

Scheme 1-4 Propagation step for Ziegler-Natta polymerisation
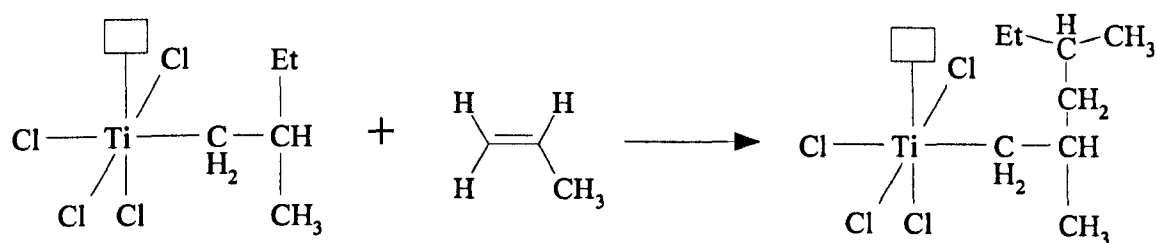
The reaction is very fast, which is caused by the accelerating effect of the catalyst due to the π-complex. This weakens the titanium-ethyl bond during the initiation step and this complex also weakens the Ti-CH$_2$ chain end during propagation. Coordination polymerisation is a reaction system which is successfully used for the polymerisation of many vinyl monomers, it results in a very stereochemically controlled reaction. The importance of this system is that it was the first extensively studied polymerisation system whereby a metal played an important part in the reaction mechanism.

1.2.3. Radical Polymerisation

Radical polymerisation is probably the most applied polymerisation system type in industrial use. It is the most versatile of polymerisations. A great variety of substituents on the monomer can be used. In radical addition polymerisation the presence of trace impurities such as water or oxygen does not hinder the reaction, to the extent of anionic polymerisation.

A general reaction scheme for radical polymerisation is shown in scheme 1-5.

Scheme 1-5 Radical addition polymerisation scheme

$I \xrightarrow{k_d} 2R\cdot$ *decomposition of initiator*

initiation of monomer

propagation

terminations

by combination

by disproportionation

combination with primary radical

9
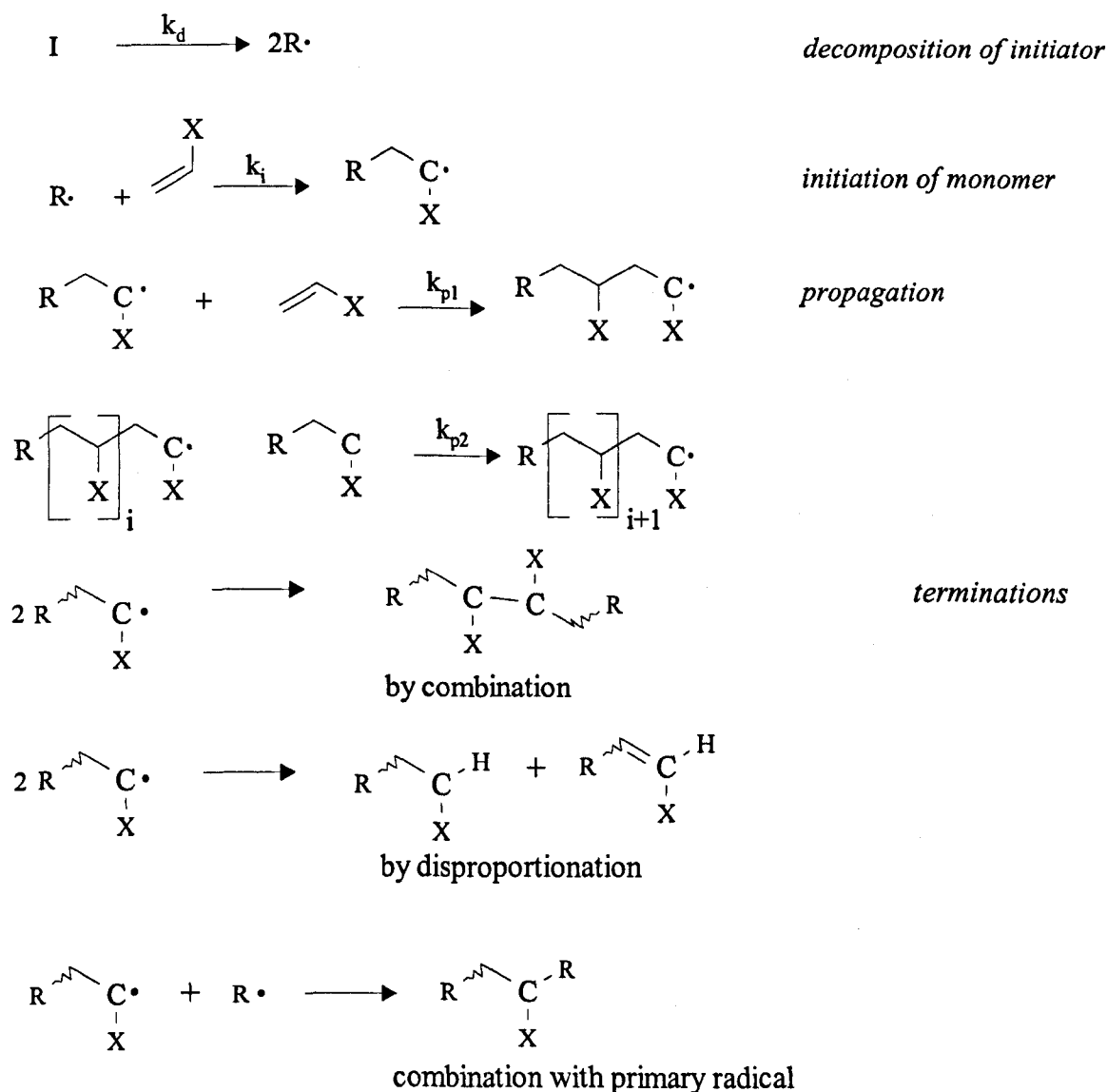
1.3. Controlled Polymerisation

Certain aspects of polymerisation architecture can be controlled and these are shown in figure 1-2.

Figure 1-2 Controlled architecture in polymers
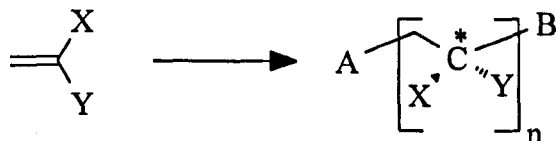
X and Y represent functionality, A and B represent different end groups, n is the degree of polymerisation and * indicates a chiral centre.

Anionic polymerisation can be used to control the molecular weight of a polymer. Coordination polymerisation, for example Zieglar-Natta polymerisation, is able to control to a large degree the stereochemistry of a polymer because it is able to fix the reactants in a certain way. However, radical polymerisation is a very uncontrolled reaction. Its versatility is based on the advantages where it is tolerant to trace impurities. Dry solvents are not required, there is a tolerance to functional monomers and reactions can be conducted in aqueous media. Radical polymerisation is a reaction system where controlling the polymer's architecture has proved very difficult.

1.3.1. Stereochemistry of vinyl polymerisation

In an organic molecule the terms S and R are used to describe the chirality of the molecule. Backbone carbon atoms have four different substituents, this is the same as in a simple organic molecule. As the two chains shown in figure 1-3 are of different lengths they cannot be superimposed, hence the carbon atom is chiral.

Figure 1-3 An example of polymer isomerism
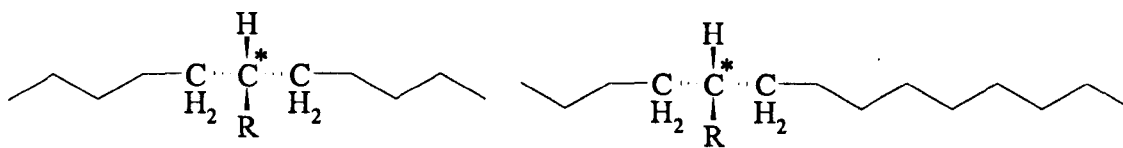
If one looks along the carbon chain then each carbon centre can be assigned an

R(Rectus) or S(Sinister) configuration, as a consequence then a whole chain can be

represented by the following, for example:-

RRRRR, or RSRSRS or RSSRSRRRSS. These configurations have been named. If

the centres have the same configuration i.e. RRRR or SSSS then it is termed *isotactic*,

if the successive units have opposite configurations, RSRSRS, then the term is

syndiotactic, finally, if the centres are randomly distributed, RRSRSSRRRSSRSS,

then the chain is *atactic*.

Due to a polymers large variety of molecular weights in any given sample, a polymer

does not have a melting point, it is better described as a melting point range. In

addition due to the large chain lengths and side chains an extra feature is incorporated

into polymers, Tg, the glass transition temperature. Below this point a polymer

behaves like glass, in that it is brittle and can easily break. Above this point they act

like rubber and are more flexible. Polymers have a huge degree of variety in degrees

of crystalinity as result of the different configurations that a polymer can adapt to

depending on the temperature of the system. A polymers stereochemistry will affect

the Tg of a sample, this in turn affects the physical properties of the system.

The importance of controlling the stereochemistry of a polymer can be seen in the

example of polypropylene. Isotactic polypropylene possess stereoregularity, this

allows the polymer to crystallise with a melting point (Tm) of >170 °C, however,

atactic polypropylene is amorphous, with no Tm (it possess a large melting point

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range) which results in a softening point (Tg) of -20 °C, hence a large difference in the polymers thermal and mechanical properties.

1.3.2. Other Aspects of Controlled Polymerisation

Molecular weight and molecular weight distributions are important features of a polymer. A polymer with a high Mn will have different properties to a low molecular weight polymer, and a polymer with a broad distribution will behave differently from a narrow distribution polymer. Hence the need to control molecular weight. The end groups present on a polymer chain can have important implications for the reactivity and functionality of a polymer chain. If functional initiators are used then it is possible to have a chain where further polymer chains can be grafted onto the original chain. It is all these aspects that a polymer chemist may wish to control. Established anionic polymerisation reactions require difficult conditions and are expensive so their commercial use is limited. Some research in this thesis has been carried out to investigate controlled radical polymerisation.

1.4. Living Polymerisation

Figure 1-4 shows a typical living and free radical polymerisation molecular weight plot against percentage conversion of monomer.

Figure 1-4 A molecular weight verses conversion plot for a typical free radical polymerisation and a living polymerisation reaction
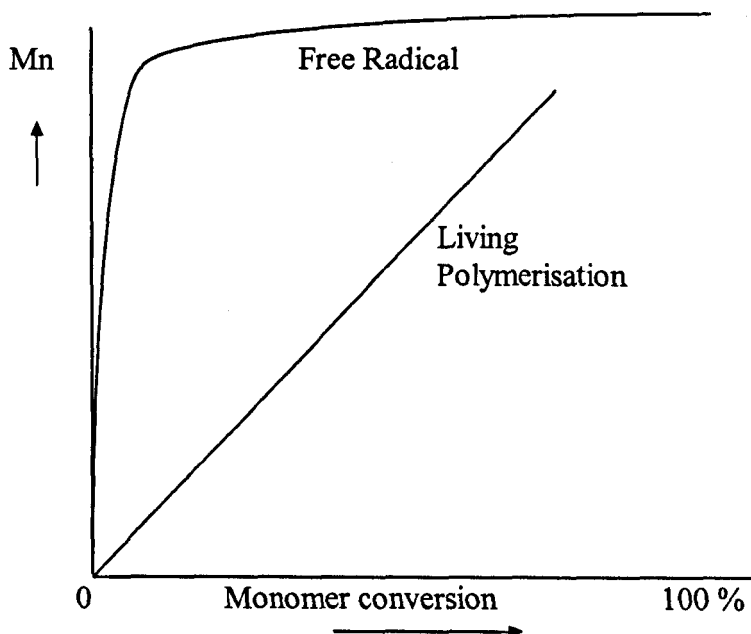
Free radical polymerisation shows that the reaction produces polymers with a high molecular weight from the beginning of the reaction, conversion increases over time but with little effect on the molecular weight of the polymer. In the case of a living polymerisation reaction the molecular weight increases in line with the conversion of the reaction.

Living polymerisation reactions are characterised by the fact that the polymer chains remain active after consumption of the monomer. The chain ends are not terminated in the way described earlier and with the addition of extra monomer, or a different monomer chain growth can continue.

It was in 1936 that Ziegler[14] reported the polymerisation of styrene and butadiene

using an anionic initiator without the usual termination reactions. Only in recent years

has progress been made in investigating living radical polymerisation reactions[15].

1.4.1.1.Free Radical Carbon-Carbon Bond Formation

Transition metal compounds have been used to form carbon to carbon bonds by

organic chemists for many years. A review by Iqbal et al[16] discusses the transition

metal free-radical reactions in organic synthesis and the progress made by these

methods. The review discusses both oxidative and reductive processes using the

following metals: titanium, vanadium, manganese, iron, cobalt, copper, niobium,

ruthenium and chromium. This development has taken place over the last ten years, it

has shown that free radical reactions are, under certain conditions, controllable. In

recent years there has been the emergence of transition metal-based radical reactions,

this has been largely due to the work of Kharasch[17], Minisci [18], Kochi [19]. They have

shown that carbon-centred radicals can be generated using organometallic reagents.

Transition metal-promoted reactions of carbon-centred radicals may be divided into

oxidative reactions and reductive reactions. In an oxidative reaction the metal acts as

an oxidant. It involves the generation of radicals by an electron transfer from a radical

precursor to the metal complex.

The reaction proceeds via an organometallic reagent which may lead to the carbon

centred radical on homolytic cleavage of carbon-metal bond.(Scheme 1-6).

Scheme 1-6 Oxidative process

$$L_mM^n \;+\; \text{(alkene with } \overset{H}{X:}\text{)} \longrightarrow \text{(alkene with } \overset{H\,+}{X\!\cdot}\text{)} \longrightarrow \;\cdot C\!-\!C(X) \;+\; H^+$$

$$\Big\downarrow L_mM^{n-1}$$

$$Z\!:\!\overset{|}{\underset{|}{C}}\!- \;\;+\;\; L_mM^n \longrightarrow Z^+ \;+\; \cdot\overset{|}{\underset{|}{C}}\!-$$

$$\Big\downarrow L_mM^{n-1}$$
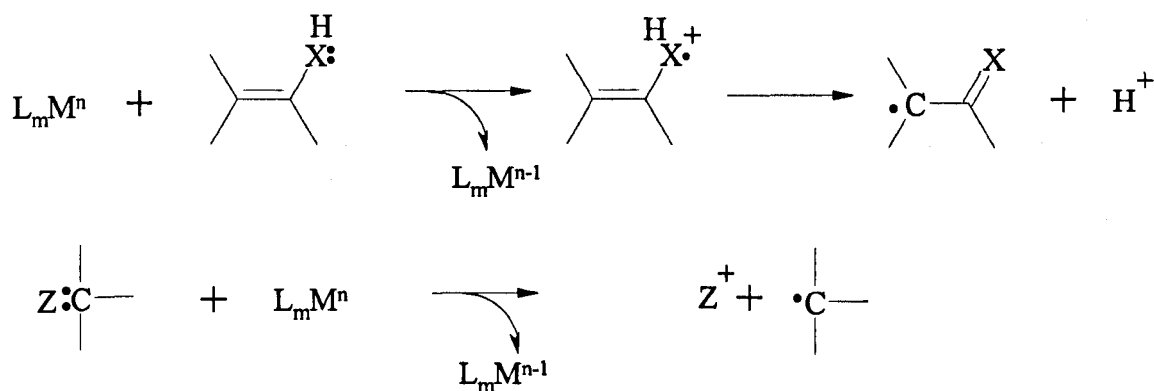
[where L = ligand, M = metal and n is the charge of the metal, X = hetero atom]

In a reductive reaction the metal acts as reductant in this process and the carbon-centred radical can be generated by an atom transfer or electron transfer from metal to complex to the radical precursor. The reaction may then proceed via an organometallic reagent which may then lead to a free radical via homolytic cleavage of the metal-carbon bond (scheme 1-7).

Scheme 1-7 Reductive process

$$L_mM^n \;+\; -\overset{|}{\underset{|}{C}}\!-X \longrightarrow -\overset{|}{\underset{|}{C}}\!\cdot \;+\; L_mM^{n+1}X$$

$$L_mM^n \;+\; -\overset{|}{\underset{|}{C}}\!-X \longrightarrow \left[-\overset{|}{\underset{|}{C}}\!-X\right]^- \longrightarrow -\overset{|}{\underset{|}{C}}\!\cdot \;+\; X^-$$

$$\Big\downarrow L_mM^{n+1}$$
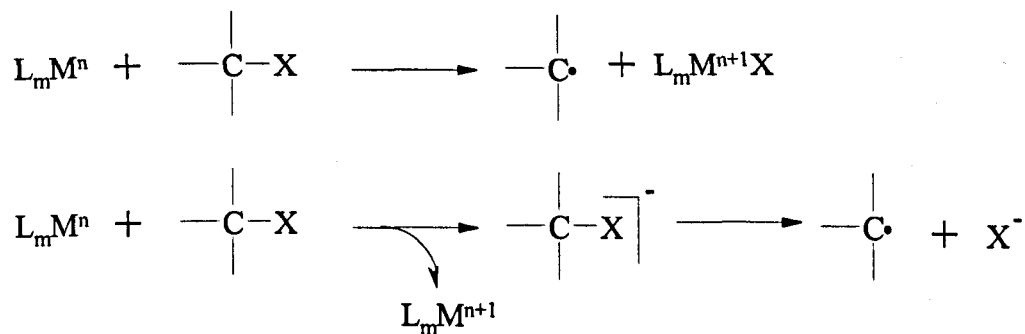
[X = leaving atom, M = transition metal, L = ligand]

Two reactions are shown in figures 1-5 and 1-6. The first is a oxidative reaction involving cobalt and the second is an example involving a chromium organometallic compound and a reductive process.

Figure 1-5 An example of a Cobalt Oxidative reaction
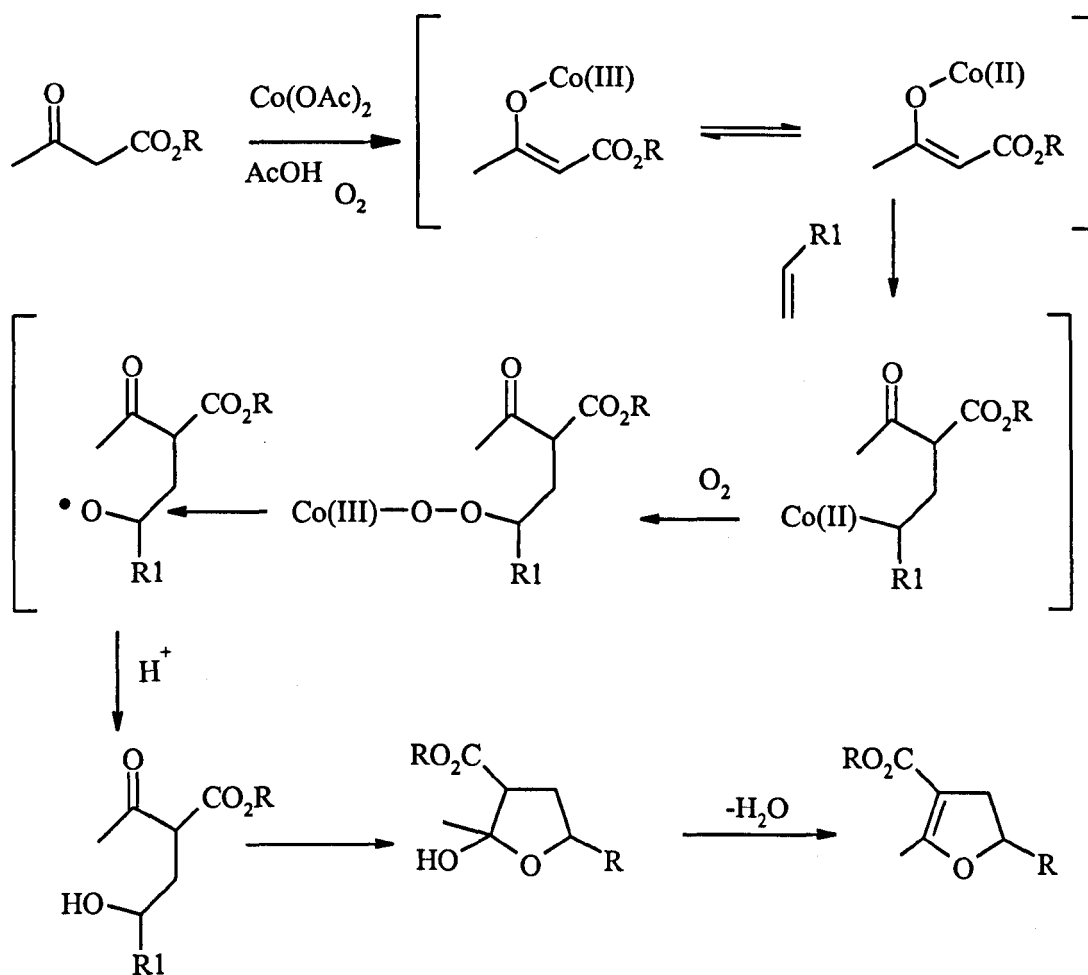
Figure 1-6 Chromium(II) promoted synthesis of substituted tetrahydrofurans
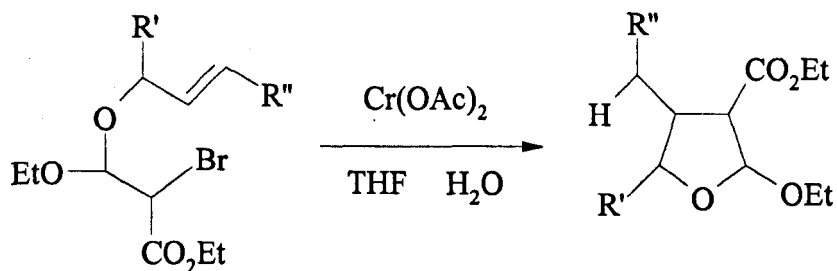
These reactions show the possibility that radical reactions might be controlled and

lead to carbon-carbon bond formation, as in a polymerisation reaction.

1.4.1.2. Atom Transfer Radical Polymerisation Reactions Using Different Transition Metals

i) ATRP reactions using ruthenium complexes

Sawamoto[20] investigated the possibility of living radical polymerisation of vinyl monomers by the activation of a carbon-halogen terminal bond from an organic halide. This involved the reaction of tris-triphenylphosphineruthenium chloride, [Ru(PPh$_3$)$_3$Cl$_2$], in the presence of carbon tetrachloride, shown in figure 1-7.

Figure 1-7 Ruthenium(II) mediated ATRP

Ru(II) = RuCl$_2$(PPh$_3$)$_3$

Living Polymer
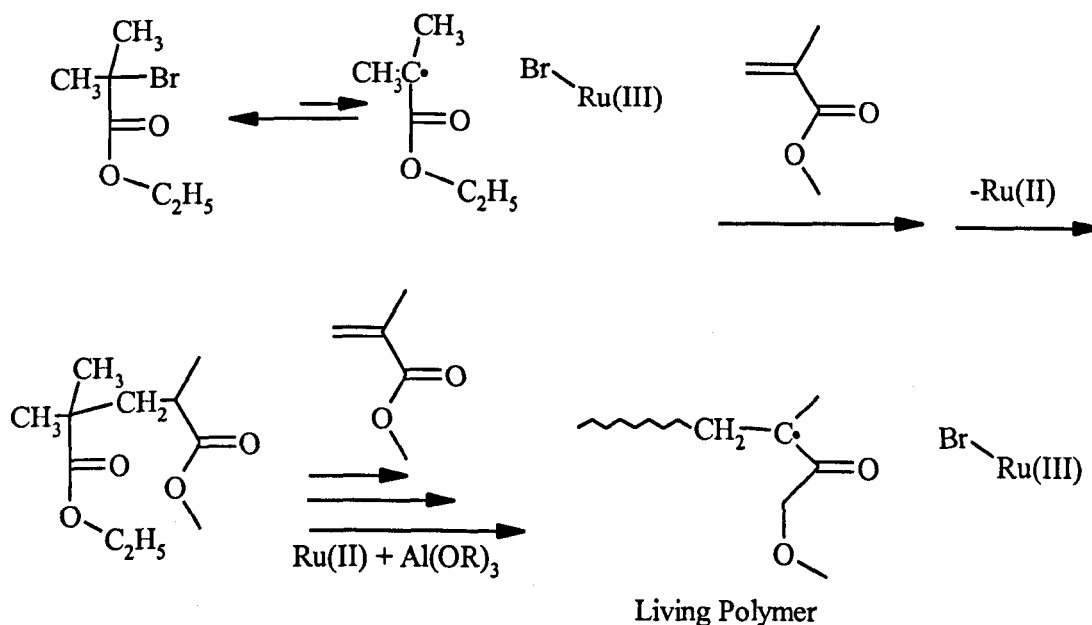
This ruthenium based polymerisation is heterogeneous and carried out in toluene at 60 °C. The results showed a linear increase in molecular weight with percentage conversion of monomer and a narrow molecular weight distribution, indicative of living polymerisation reaction. Other work was carried out using styrene and acrylates, and block copolymers have also been made[21,22].

ii) ATRP reactions using copper complexes

Work was also carried out by Matyjaszewski and Wang using copper complexes to demonstrate ATRP reactions involving styrene[23,24].

The reaction involves copper halide (CuCl or CuBr) with 2,2'-bipyridine and styrene with 1-phenylethyl bromide as the initiator. The catalyst is formed *in situ* and the polymerisation is heterogeneous, carried out under bulk conditions at 100 °C. More recently 4,4'-dialkyl substituted bipyridines have been used, to enhance the solubility of the copper catalyst. This in turn improves the results of the polymerisation reaction. The polydispersity obtained from this reaction has been lowered to just 1.05.

A mechanism has been proposed for the polymerisation of vinyl monomers using copper complexes and this is shown in figure 1-8.

Figure 1-8 Proposed mechanism of Cu(bpy)$_2$ ATRP reaction

$$R-X \ + \ CuX/2\,bipy \ \underset{k_{eq}}{\rightleftharpoons} \ R\bullet \ + \ CuX_2/2\,bipy \qquad \textit{Initiation}$$

$$R\bullet \ + \ monomer \ \xrightarrow{k_i} \ M\overset{\bullet}{_1}$$

$$M_n-X \ + \ CuX/2\,bipy \ \underset{k_{eq}}{\rightleftharpoons} \ M\overset{\bullet}{_n} \ + \ CuX_2/2bipy$$

$$\textit{Propagation}$$

$$M\overset{\bullet}{_n} \ + \ monomer \ \xrightarrow{k_p} \ M\overset{\bullet}{_{n+1}}$$

$$M\overset{\bullet}{_n} \ + \ M\overset{\bullet}{_m} \ \xrightarrow{k_t} \ M_{n+m} \qquad \textit{Termination}$$
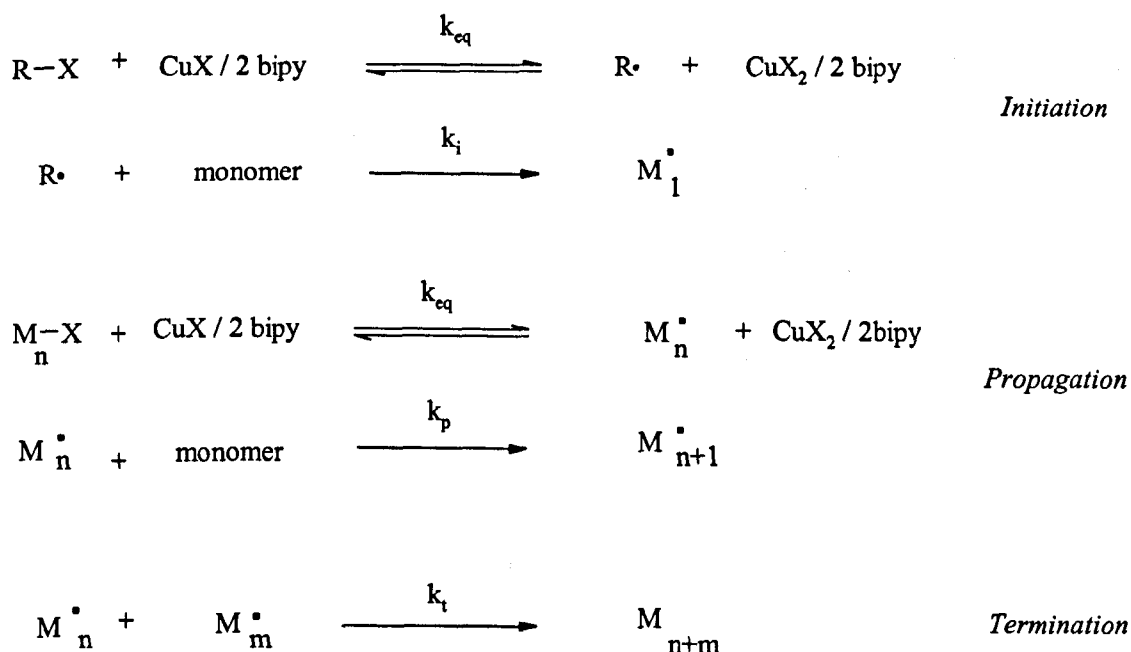
This mechanism shows a free radical reaction with transfer and termination reactions suppressed by the rapid equilibrium between active and dormant species.

The initiation of the monomer gives M˙₁, this then becomes stabilised by a halide atom from the copper species, slowing down the propagation process but in addition helping control the same process. There is then a rapid equilibrium between the propagating species $M_n^\cdot$,M_n-X and the addition of another monomer unit. This slows down the propagation and in particular limits the amount of termination reactions that can occur. The lowering of termination reactions allows greater control over the polymerisation process and will help lower the polydispersity of the polymer. Matyjaszeski[25] has described the role of the ligand as to solubilise the copper and the active catalyst and has been described as 'Cu(I)/bipy'. Since then however, a number of possible copper species have been described as being in solution[26]. These are shown in figure 1-9 (not stoichiometrically balanced).

Figure 1-9 Copper bipyridine species in solution

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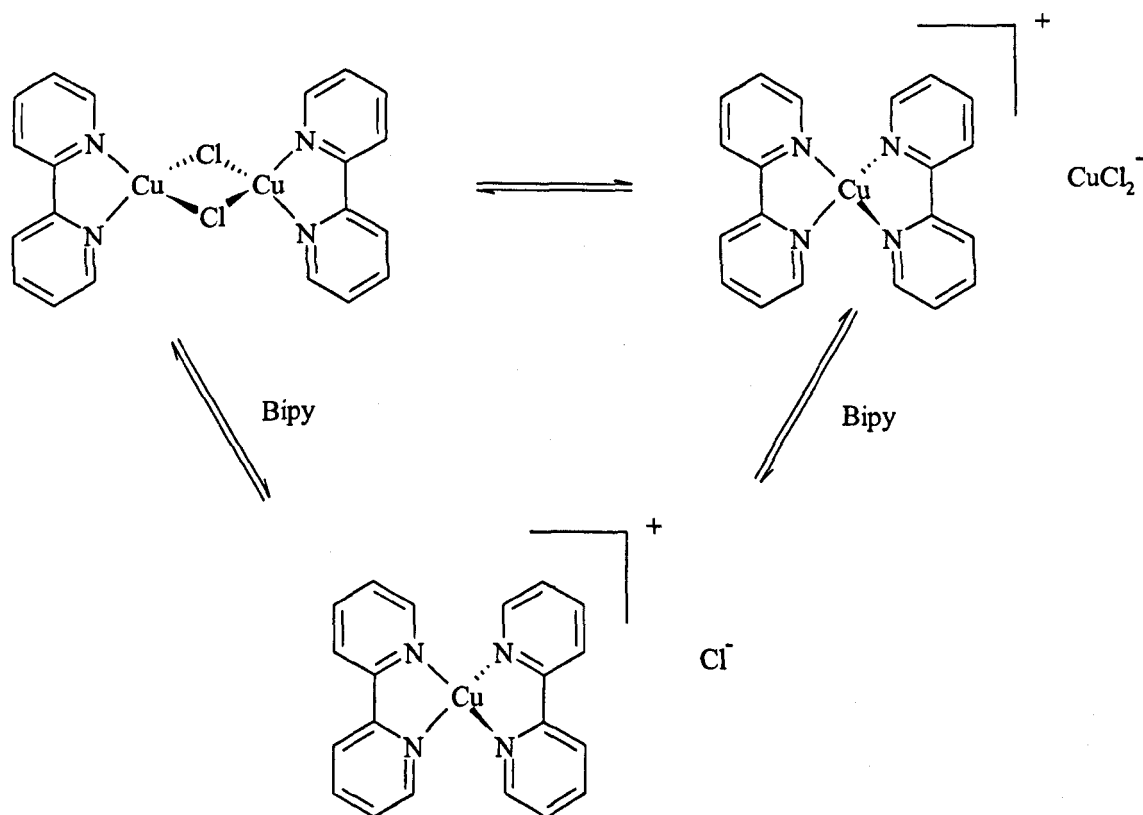
This has shown that more than one equivalent of ligand is required, and that more than one metal atom may be required in the reaction.

iii) ATRP reactions using nickel complexes

Work examining the use of nickel complexes has been carried out by Teyssie[27]. This work involved [Ni(C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-o,o'-)Br] in the presence of carbon tetrachloride to polymerise MMA.

As nickel(II) complexes are stable in water the polymerisation was carried out as a suspension polymerisation. Some control over Mn and PDi was achieved. In addition Sawamoto[28] investigated NiBr$_2$(PPh$_3$)$_2$ and MMA and found that this resulted in the living radical polymerisation of MMA.

iv) Living free radical reactions using cobalt complexes

A cobalt macrocycle, the structure of which is shown in figure 1-10, has been examined as an initiator of living radical polymerisation, by Wayland et al[29-32].

Figure 1-10 Structure of neopentyl cobalt(III) tetramesitylporphyrin
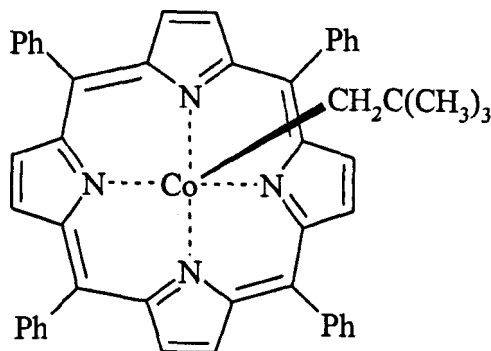
Their results have shown molecular weights as high as 150,000 with a polydispersity of 1.2. The mechanism is believed to go via a redox reaction involving a cobalt(II) and cobalt(III) system with the metal reversibly end-capping the polymer chain.

v) ATRP reactions using iron complexes

Finally Sawamoto[22,33] has also investigated the use of iron complexes for ATRP reactions. The complex [FeCl$_2$(PPh$_3$)$_3$] was used with MMA. This proved to give a faster rate than similar ruthenium and niobium complexes examined. Matyjaszewski has also examined iron complexes for the polymerisation of styrene[34] and found evidence of living polymerisation using FeBr$_2$ with 4,4'-d-(d-(5-nonyl)-2,2'-bipyridine. These polymerisation experiments resulted in molecular weight distributions as low as 1.17 and in addition conversion of 70 %.

Due to the wide variety of transition metals used for ATRP reactions this lead to the thought that chromium complexes could be investigated for ATRP properties. Chromium compounds have already been shown to undergo radical carbon-carbon bond formation reactions (figure 1-6), thus a chromium(II)/chromium(III) oxidation couple could be used to facilitate atom transfer reactions.

1.5. An Introduction To Chromium Chemistry

The transition metal chromium has played a large role in the development of inorganic chemistry [35,36]. Chromium was discovered in 1797 by Louis N. Vauqelin in the mineral crocoite (PbCrO$_4$). It was named for the varied colours of its compounds, χρωμα (chroma) meaning colour. Chromium has the atomic number 24. Owing to the distribution of its isotopes its atomic mass is 51.9961, and its electron distribution is [Ar]3d^{5}4s^1.

Chromium compounds exist in an unusually large number of oxidation states from -4 to +6. Only the +2 to +6 states are accessible in water. 6-Coordinate chromium(VI) is a very powerful oxidant and the use of chromium-based oxidants in organic chemistry has been documented [37-39]. Chromium(II) however, is a strong reducing agent. Chromium (III) on the other hand is very stable.

From the ore chromite (FeCr$_2$O$_4$) the product ferrochrome is produced by reduction with coal. This is used in the manufacture of alloy steals. Pure chromium is used in iron free alloys and metal-containing ceramics are produced by reducing Cr$_2$O$_3$ usually with aluminium, carbon or silicon.

1.5.1.1.Chromium Halides

The known halides of chromium are shown in table 1-1 from which the instability of a hexavalent halide is evident. The halides are prepared by a direct reaction of the metal with the appropriate halogen. The chromium(II) halides are prepared by reduction of the trihalides with H$_2$, or by heating chromium metal with HX.

Table 1-1 Chromium halides

Fluorides	Chlorides	Bromides	Iodides
CrF_5 red, mp 30 °C	-	-	-
CrF_4 colourless, mp 277 °C	$CrCl_4$ gas phase only	$CrBr_4$ gas phase only	-
CrF_3 green, mp 1404 °C	$CrCl_3$ violet, mp 1150 °C	$CrBr_3$ dark green, mp 1130 °C	CrI_3 black, mp >600 °C
CrF_2 green, mp 894 °C	$CrCl_2$ white, mp 824 °C	$CrBr_2$ white, mp 30 °C	CrI_2 red-brown, mp 868 °C

The chromium chloride in the highest oxidation state is $CrCl_4$. This is not a stable compound under ordinary circumstances but may be produced by evaporation of gaseous $CrCl_3$ at ~560 °C and then trapped in an argon matrix.

However, probably the most important chromium halide is $CrCl_3$, which is the starting material for much of synthetic chromium chemistry. Pure $CrCl_3$ does not dissolve in water, but addition of a trace amount of chromium(II) causes it to readily dissolve. The reason of this is believed to be catalytic electron transfer. This is the reduction of substantially inert chromium(III) on the crystal surface to a labile chromium(II), which in turn dissolves and reduces more chromium(III). This effect is used to prepare $[CrCl_3(THF)_3]$, which is a useful precursor in organometallic chromium chemistry.

1.5.1.2.Chromium(II) Organometallic Compounds

Due to the reactivity of chromium(II) compounds far fewer have been made compared to chromium(III). Solvated species of the general formula $R_nCrCl_{2-n}S_x$, can be prepared directly from CrX_2, or $CrX_2(THF)_2$ using a Grignard reagent. The only other $RCrClS_x$ complex, a mesityl chloride, was prepared by ligand exchange between solvated bis(mesityl)chromium and $CrCl_2$.

However, numerous examples of R_2CrS_x have been synthesised by the Grignard route, for example $(mesityl)_2CrS_x$ where S_x is $(THF)_3$ or $((THF)(BIPY))$. The substitution of a nitrogen or phosphor donor in place of the THF increases the stability of the molecule.

An example of an alternative to the Grignard route is shown in figure 1-11.

Figure 1-11 An example of preparing a chromium(II) organometallic complex

$$LiPh \quad + \quad CrCl_2(THF)_2 \quad \xrightarrow[\text{-70 °C}]{\text{THF}} \quad Ph_2Cr(THF)_n \quad \xrightarrow{\text{bipy}} \quad Ph_2Cr(bipy)_2$$
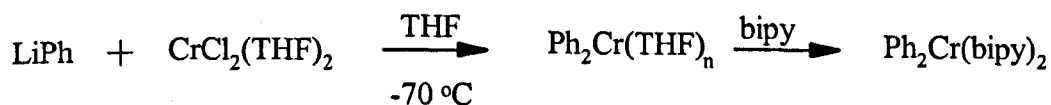
Chromium(III) organometallic compounds

Neutral, solvated mono(organo)chromium(III) compounds can be represented as $RCrCl_2S_n$, and many methods are used to prepare this class of compounds.

$CrR_3(THF)_n$ reacting with $CrCl_3(THF)_3$ gives the appropriate product, as does the reaction of a Grignard reagent with $CrCl_3(THF)_3$ at the correct temperature. However, a more important class of chromium(III) organometallics for the work in this thesis are the solvated mono(organo)chromium(III) cations. They are discussed more fully in section 1.5.1.6.

The general formula is $[RCr(OH_2)_5]^{2+}$, they are formed from the reaction of chromium(II) perchlorate in perchloric acid. Oxidation of chromium(II) salts by hydroperoxides and peroxides gives cationic products, also the interaction of chromium(II) with alkylbis(dimethylglyoximato)cobalt gives $[RCr(OH_2)_5]^{2+}$. These reactions generally yield a free radical which then attacks chromium(II) to give the product.

1.5.1.3. Aqueous Organochromium Complexes

Metal-mediated vinyl polymerisation is of major academic and industrial interest. Most polymerisation systems are sensitive to protic environments due to the instability of M-R bonds towards reaction to give M-OX species.

Extremely few M-R bonds are stable in the presence of water, an environmentally desirable reaction medium. There are in fact only three metals which have such bonds, *rhodium, cobalt* and *chromium* that are stable in the aqueous environment.

In nature the only metal-carbon bond of importance is found in a coenzyme, Vitamin B_{12}, which has a cobalt metal centre and a macrocycle-type ring around it. From this compound research was carried out to develop derivatives of the coenzyme. Many have, been made, including the one shown in figure 1-12.

Figure 1-12 Cobalt macrocycle, CoBF
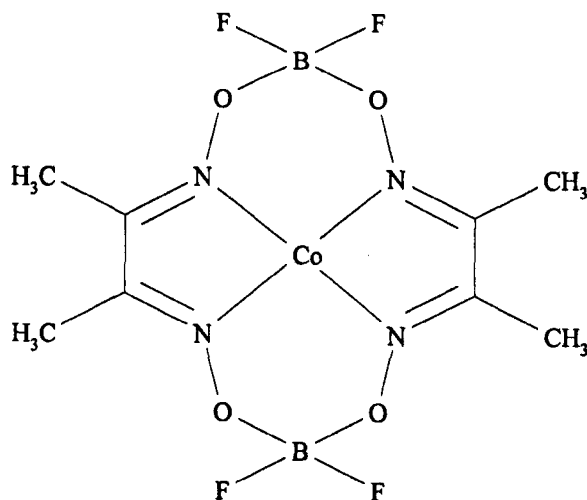
The methyl groups on the ring can be changed to a wide variety of different alkyl groups which will affect the reactivity of these compounds. These model complexes are used as catalytic chain transfer agents as first discovered by Enikolopyan[40]. An

important feature of this class of compounds, however, is their stability in water. The metal-carbon bond is not hydrolysed immediately in water.

In the case of rhodium complexes, $RhCl_3.3H_2O$ is reacted with boiling perchloric acid, $HClO_4$, which gives the complex $[Rh(H_2O)_6]^{3+}$. This can then, under certain conditions, react to form alkyl-metal compounds[41].

Of importance to this work however are the complexes using chromium as the central atom. Some examples include $[(H_2O)_5\text{-}Cr\text{-}CHCl_2]^{2+}$ and $[(H_2O)_5\text{-}Cr\text{-}CH_2Ph]^{2+}$, this particular range of water-based compounds were first made in 1957 by Anet and Leblanc[39]. They have the unusual, stable M-R bond, although it can be broken under certain conditions.

The general formula of this class of complexes is $[(H_2O)_5\text{-}Cr\text{-}R]^{2+}$ the chromium atom is in the +3 oxidation state. The alkyl group can be extremely varied, complexes have been made with the following organic groups present;

- alkyls [R= $-CH_3$, $-CH_2CH_3$, $CH(CH_3)_2$]

- haloalklys [R= $-CHCl_2$, $-CF_3$]

- arylalkyls [R= $-CH_2Ph$, $CH_2C_6H_4\text{-}m\text{-}CH_3$]

- alkoxyalkyls, [R= $-CH_2OCH_3$, $CH(CH_3)OC_2H_5$]

- hydroxalkyls [R= $-CH_2OH$, $-CH(CH_3)OH$]

It is now realised that this class of complexes, $[(H_2O)_5\text{-}Cr\text{-}R]^{2+}$ are capable of a considerable number of distinct reactions. A brief review of the chemistry of aqueous organochromium complexes follows.

Aqueous chromium(II) solutions, $[Cr(H_2O)_6]^{2+}$, are strongly reducing and they have long been used in electron transfer investigations, but are now used as reducing agents in organic chemistry [42].

Aqueous chromium(II) complexes can be prepared by the reaction of chromium metal with a non-interacting anion such as the perchlorate anion $[ClO_4]^-$ from perchloric acid, $HClO_4$ (figure 1-13).

Figure 1-13 Preparation of a aqueous chromium(II) complex

$$Cr(m) \xrightarrow[N_2]{HClO_4(aq)} \left[Cr-(H_2O)_6\right]^{2+} (ClO_4)_2^-$$
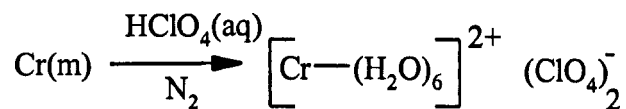
An alternative approach is to make the chromium(III) aqueous complex, this is achieved by the oxidation of the metal in the presence of perchloric acid, figure 1-14.

Figure 1-14 Preparation of a aqueous chromium(III) complex

$$Cr(m) \xrightarrow[O_2]{HClO_4(aq)} \left[Cr-(H_2O)_6\right]^{3+} (ClO_4)_3^-$$
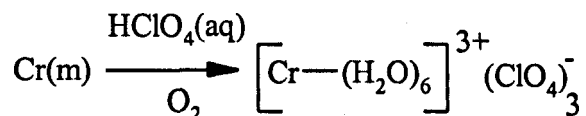
Aqueous chromium(II) solutions can also be prepared from chromium trioxide by forming a chromium(III) solution and then reduction to the chromium(II) solution.

Figure 1-15 Alternative preparation of an aqueous chromium(II) complex

$$CrO_3 + H_2O_2 \xrightarrow{HClO_4(aq)} \left[Cr-(H_2O)_6\right]^{3+}\left[ClO_4^-\right]_3 \xrightarrow[N_2]{Hg/Zn} \left[Cr-(H_2O)_6\right]^{2+}\left[(ClO_4)^-\right]_2$$
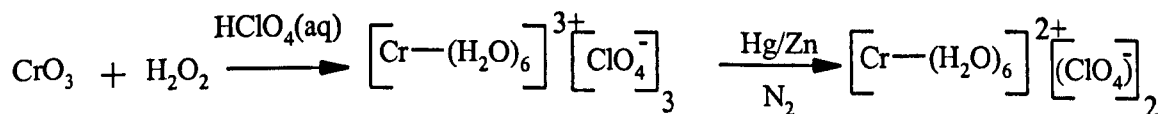
In the absence of oxygen aqueous chromium(II) will slowly decompose to give off hydrogen, this is due to small impurities in the solution.

Aqueous chromium(II) solution is a bright sky blue colour, the UV/Visible electronic spectrum of this solution shows two peaks, a main peak at 407 nm, and a second peak at 537 nm. These peaks are consistent with what would be expected in a tetragonally

27

distorted octahedral complex. Unfortunately no crystal structure has been obtained to prove this due to the instability of the complex. A similar complex, $[Cr(OH_2)_4Cl_2]$, has been prepared, its crystal structure shows two long Cr-Cl distances 275.8 pm, and four normal Cr-O distances, 207.8 pm.

Aqueous chromium(II) complexes can be used to prepare aqueous chromium alkyl complexes. Several routes are available for the preparation of these complexes: preparation by free radical capture; the reaction between chromium(II) and hydrogen peroxide and abstraction reactions of HO•.

The main method of preparation involves the reaction of a carbon-centred free radical and $[Cr(H_2O)_6]^{2+}$. This method was first used by Anet and Leblanc[39] to prepare $[(H_2O)_5\text{-Cr-}CH_2Ph]^{2+}$. A second chromium alkyl was prepared shortly after, $[(H_2O)_5\text{-}Cr\text{-}CHCl_2]^{2+}$ [43].

The simple method of preparation uses a dilute solution of aqueous chromium(II), this is then reacted with the alkyl halide required, R-X, the reaction produces the desired product, $[Cr(H_2O)_5\text{-R}]^{2+}$, and a chromium halide complex, $[Cr(H_2O)_5\text{-X}]^{3+}$. A reaction scheme is shown in scheme 1-8.

Scheme 1-8 Preparation route for an aqueous chromium alkyl complex

$$Cr(m) \xrightarrow[\text{HClO}_4]{\text{air}} Cr(III) \xrightarrow[\substack{\text{amalgam}}]{\text{Zn/Hg}} Cr(II)$$

N$_2$ / HClO$_4$ (over the top arrow from Cr(III) to Cr(II))

$$Cr(III) \xleftarrow[\substack{\text{HClO}_4}]{\text{H}_2\text{O}_2} CrO_3$$

Cr(II) $\xrightarrow[\text{Chloroform}]{\text{CHCl}_3}$

$$(\text{H}_2\text{O})_5 \left[\text{Cr}-\text{CHCl}_2 \right]^{2+} \equiv \left[\begin{array}{c} \text{CHCl}_2 \\ \text{H}_2\text{O} \\ \text{H}_2\text{O} \end{array} \text{Cr}^{3+} \begin{array}{c} \text{OH}_2 \\ \text{OH}_2 \\ \text{H}_2\text{O} \end{array} \right]^{2+} \left[\text{ClO}_4^- \right]_2$$

RED

+

$$(\text{H}_2\text{O})_5 \left[\text{Cr}\cdot\text{Cl} \right]^{2+} \equiv \left[\begin{array}{c} \text{Cl} \\ \text{H}_2\text{O} \\ \text{H}_2\text{O} \end{array} \text{Cr}^{3+} \begin{array}{c} \text{OH}_2 \\ \text{OH}_2 \\ \text{H}_2\text{O} \end{array} \right]^{2+} \left[\text{ClO}_4^- \right]_2$$

GREEN
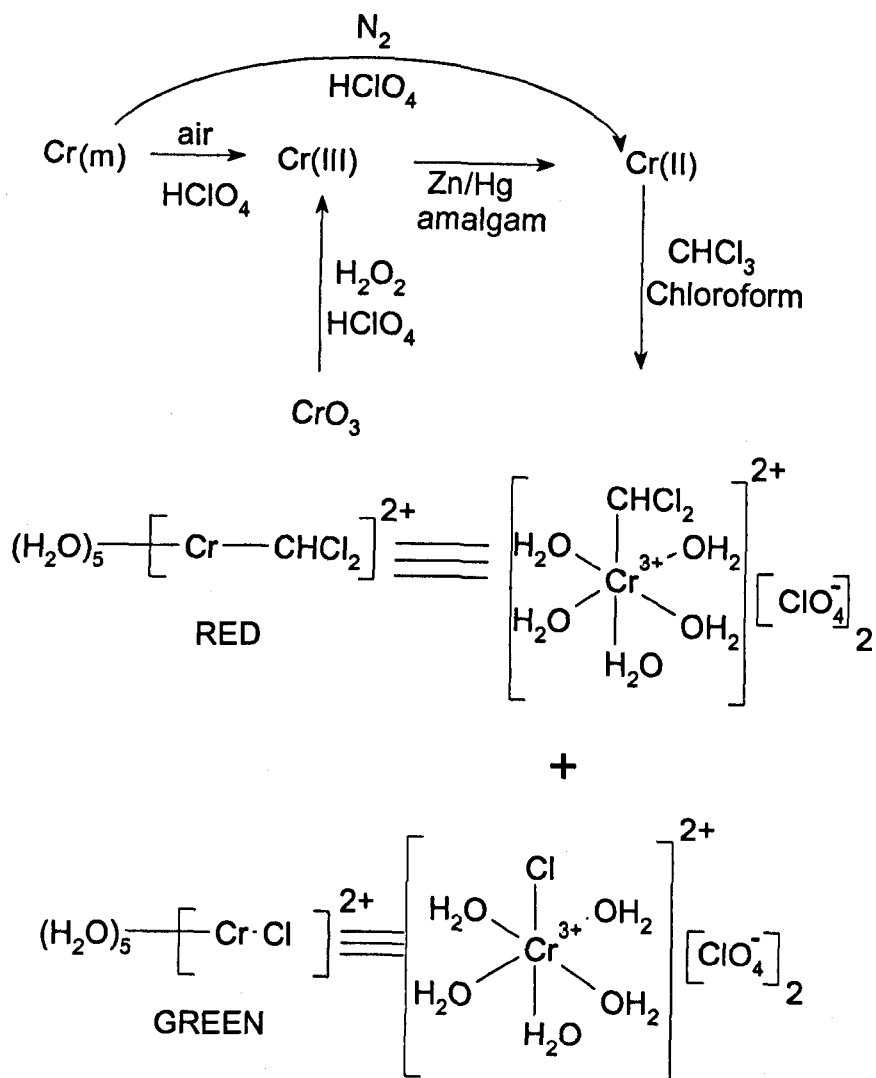
The reaction mechanism for the preparation of $[(\text{H}_2\text{O})_5 \text{-Cr-CHCl}_2]^{2+}$ is shown in

figure 1-16.

Figure 1-16 Mechanism for the preparation of $[(\text{H}_2\text{O})_5 \text{-Cr-CHCl}_2]^{2+}$

$$\text{CHCl}_3 + \text{Cr}^{2+} \longrightarrow \text{CrCl}^{2+} + \cdot\text{CHX}_2$$

$$\cdot\text{CHX}_2 + \text{Cr}^{2+} \longrightarrow [\text{CHX}_2\text{Cr}]^{2+}$$
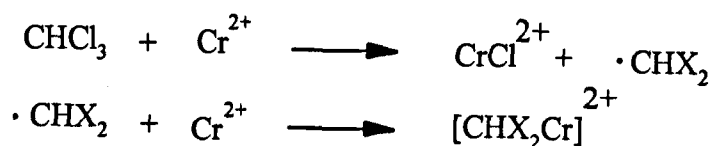
This mechanism only works for "activated" alkyl halides, for example CHCl$_3$ and

PhCH$_2$Br. Some other examples of organochromium complexes prepared by this route

are $[(H_2O)_5CrCH(CH_3)_2]^{2+}$ [44] and $[(H_2O)_5Cr\text{-}c\text{-}C_5H_9]^{2+}$ prepared by Espenson et al[45] in addition to $[(H_2O)_5CrCH_3]^{2+}$ formed by Ardon and co-workers[46].

Pulse radiolysis is another method of preparation for this class of compounds. This has been used to prepare $[(H_2O)_5CrC(CH_3)_2OH]^{2+}$ [47], however, this is formed only in low concentrations, characteristic of this technique. The preparation by Schimdt et al[48] is the preferred method. The mechanism for this is shown in figure 1-17.

Figure 1-17 Preparation of $[(H_2O)_5CrC(CH_3)_2OH]^{2+}$

$$Cr^{2+} + H_2O_2 \longrightarrow CrOH^{2+} + \cdot OH$$

$$OH + (CH_3)_2CHOH \longrightarrow H_2O + \cdot C(CH_3)_2OH$$

$$Cr^{2+} + \cdot C(CH_3)_2OH \longrightarrow CrC(CH_3)_2OH^{2+}$$
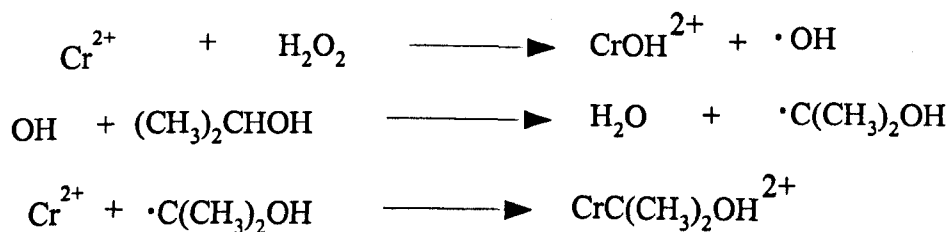
The yield for this reaction is usually ~70 % of the theoretical quantity, the remainder being accounted for in side reactions occurring during the formation of the product.

Few complexes of the general formula $[(H_2O)_5Cr\text{-}R]^{2+}$ have been isolated as solids, if they have been prepared, due to impurities and decomposition over time, it has meant that x-ray crystallographic analysis has not been possible.

The organoaqueous complexes isolated are yellow, orange or red in colour. The UV-visible absorption spectrum is characteristic of the presence of a chromium-carbon bond. The complex $[(H_2O)_5CrC(CH_3)_2OH]^{2+}$ shows a spectrum with peaks typical of the complexes $Cr\text{-}R^{2+}$, with a peaks at λ_{max} 407 nm (ε 700 M^{-1} cm^{-1}) and 311 nm (ε 2500 M^{-1} cm^{-1}). UV-visible spectroscopy can be used to identify the product formed in the reaction and determine its purity.

Decomposition of the product $[(H_2O)_5CrC(CH_3)_2OH]^{2+}$ has been extensively examined[49]. This has lead to the discovery of two parallel decomposition reactions, acidolysis and homolysis. Acidolysis is a non-radical reaction, this corresponds stoichiometrically and mechanistically to the heterolytic cleavage of the chromium-carbon bond. Homolysis is the reverse reaction used in its preparation. Figure 1-18 shows these two mechanisms.

Figure 1-18 Mechanisms of the decomposition of $[(H_2O)_5CrC(CH_3)_2OH]^{2+}$

$$[(H_2O)_5CrC(CH_3)_2OH]^{2+} + H_3O^+ \rightleftharpoons [Cr(H_2O)_6]^{3+} + (CH_3)_2CHOH$$

acidolysis

$$[(H_2O)_5CrC(CH_3)_2OH]^{2+} + H_2O \rightleftharpoons [Cr(H_2O)_6]^{2+} + \cdot C(CH_3)_2OH$$
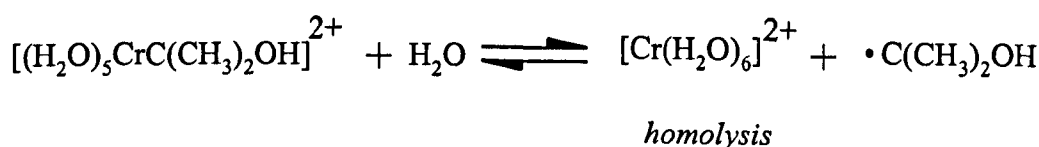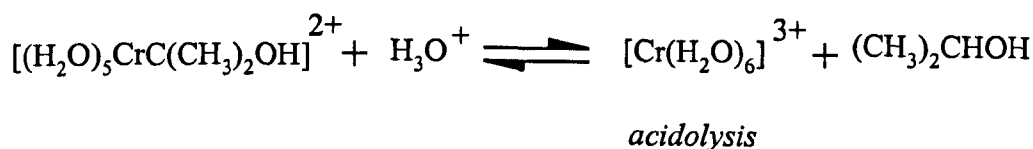
homolysis

Virtually complete suppression of the unfavourable homolysis equilibrium in figure 1-19 can be achieved by addition of a small amount of chromium(II) solution ($\sim 10^{-4}$M). However, the thermodynamically unfavourable homolysis reaction may be drawn to completion by addition of a regent that reacts with chromium(II) or $\cdot C(CH_3)_2OH$. Thus the complex can be prepared and then reacted with a different reagent at a later stage. An example is the reaction of $[(H_2O)_5CrC(CH_3)_2OH]^{2+}$ with the reagent $[Co(NH_3)_5Cl]^{2+}$ as this reacts with both compounds rapidly.

The reactions of chromium(II) solutions and organochromium complexes with other reagents has been investigated by Kochi and Mocadlo[50], who investigated organic peroxides with chromium(II). Bakac and Espenson[51] studied the kinetics and mechanisms of the oxidation of α-hydroxyalkyl chromium complexes by copper(II) and iron(III) ions, other work by them can also be found[52,53].

It has been shown that there are a wide variety of organochromium complexes that can easily be prepared. These complexes can act as a source of radical alkyl compounds and chromium(II) ions in solution. These complexes will be investigated to see if they can be used in the polymerisation of methacrylates, due to their reactivity as well as their stability in water towards hydrolysis.

1.5.1.4.Polymerisation Systems using Chromium Compounds

Polyethylene production world-wide relies largely on chromium-based catalysts[54,55]. If looked at broadly there are two types of commercial catalysts. One, the Phillips catalyst, is prepared by deposition of chromium trioxide on silica followed by activation with hydrogen[56].

Union Carbide has developed catalysts formed by the treatment of silica with low-valent organometallic compounds, chromocene, Cp_2Cr. Theopold[57] noticed a similarity between his work investigating chromium compounds and the Cp_2Cr/SiO_2 catalyst, he then investigated the reactions of chromium(III) alkyls and small olefins. The first catalyst investigated was $[Cp*Cr(THF)_2CH_3]^+BPh_4^-$ with ethylene in dichloromethane. The reaction was carried out at room temperature and 1 atmosphere pressure, it yielded high-density polyethylene, size exclusion chromatography showed Mn of 10-20,000 and PDi of 1.6 to 4.6. Figure 1-19 shows a reaction scheme.

Figure 1-19 Reaction scheme using $[Cp*Cr(THF)_2CH_3]^+BPh_4^-$ catalyst for ethylene polymerisation
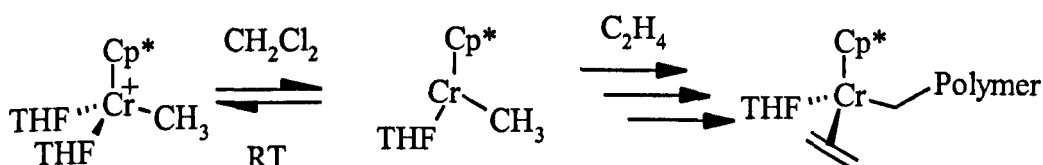
Other compounds included the neutral complex [Cp*CrSi((CH$_3$)$_3$)$_2$], for low temperature polymerisation(-40 °C) and [Cp*Cr(dmpe)CH$_3$]$^+$PF$_6^-$, which was slow due to the phosphine ligand being strongly bound to the metal centre. Their work found that the chromium(III) compounds were responsible for insertion reactions and chain growth. The chromium(II) alkyls were responsible for β-elimination and chain transfer.

There is evidence to show that chromium compounds have been used in the polymerisation of monomers on both laboratory and industrial scales. A huge variety of chromium(II) and chromium(III) complexes can be made, using many different ligands in a variety of solvents. This paves the way into the investigation of other chromium compounds and their use in the polymerisation of vinyl monomers.

1.6. Methods of Analysis for Polymers

Two important methods for examining the physical characteristics of polymers are Size Exclusion Chromatography (SEC) and Thermal Gravimetric Analysis (TGA). Both of these methods will be described briefly in sections 1.6.1 and 1.6.2.

1.6.1. Size Exclusion Chromatography (SEC)

Size exclusion chromatography (SEC), also called gel permeation chromatography, is a technique commonly used to analyse the products of polymerisation reactions.

SEC separates molecules in solution according to their size. This solvent is then pumped through a column containing millions of porous rigid particles. The molecules of different size elute at different rates. Larger molecules elute first as they penetrate fewer pores.

As polymers are not monodisperse species, the width of peaks reflects the distribution of the size of molecules for a polymer solution.

Mw - Weight average molecular weight

Mn - Number average molecular weight

And **PDi** - Polydispersity, representative of the distribution of the polymers size.

Figure 1-20 shows the statistical equations used to calculate these important figures.

Figure 1-20 Equations for Mn, Mw and PDi

$$\overline{Mn} = \frac{\sum NiMi}{\sum Ni}$$

$$\overline{Mw} = \frac{\sum WiMi}{\sum Wi} = \frac{\sum NiMi^2}{\sum NiMi}$$

$$PDi = \frac{\overline{Mw}}{\overline{Mn}}$$

[Mi = mass of a polymer chain, Ni = number of a particular chain, Wi = weight of all chains of mass Mi]

The numbers calculated can be used to describe a polymer, they can give a comparison of the size of other polymers. Information is obtained from the polydispersity (PDi), a measure of the distribution of the polymer. A small number (<1.2) represents a narrow distribution, that is to say that the molecular weights of the polymer chains are all similar.

SEC is an invaluable technique used to obtain data about the size of a polymer formed in a reaction. Polydispersity gives information about whether there is any control over the reaction, a low polydispersity can indicate a controlled polymerisation reaction.

1.6.2. Thermal Gravimetric Analysis (TGA)

A second technique used to analyse polymers is thermal gravimetric analysis. This section will describe what information can be obtained from this technique.

1.6.2.1. An Outline of Thermal Gravimetric Analysis

This is an analytical technique to help examine the structure of the polymer chains end groups. In turn this information can be used to help elucidate the mechanism of the polymers formation. A sample of vacuum dried polymer is placed in a sealed thermal chamber under nitrogen, the mass of polymer used is measured to 4 decimal points. The chamber, and hence the polymer is heated to 130 °C in a few minutes. This is then left for 5 minutes before the temperature is raised at a steady rate per minute, in many cases 5 °C per minute. The temperature increase carries on until the temperature desired is reached. This is where decomposition of the polymer sample is likely to be complete. In the case of PMMA this is usually about 350 °C.

Over the course of the reaction the weight of the polymer sample is monitored with respect to the temperature. As the temperature is raised the polymer is degraded, gases are given of and hence the weight of the polymer decreases. It is this information which can be used to help analyse the polymers end group structure.

1.6.2.2. An Introduction to Thermal Stability

Polymers degrade when chemical changes result from exposure of the material to heat, thermal degradation, exposure to light, light degradation or due to environmental effects. Poly(methyl methacrylate) and its degradation by heat has been extensively studied[58-65] and some of this information will be summarised here.

In the vast majority of its end user applications PMMA undergoes a form of heat treatment, to varying degrees, for example injection moulding, extrusion and thermoforming, hence the large amount of interest in this subject.

The way in which a polymer chain decomposes, or breaks down depends upon the structure of the polymer, and on the presence of impurities.

When the temperature of the polymer reaches the point where primary chemical bonds are being broken that is the point of thermal degradation. PMMA will actually degrade back to monomer, whereas polyethylene will degrade to a variety of decomposition products.

PMMA degrades via a method called chain depolymerisation or unzipping. That is successive units are removed, starting from a weak link within that chain.

1.6.2.3. PMMA Structural Considerations

Poly(methyl methacrylate) undergoes chain unzipping, this will occur from a chain end or along the chain backbone. The unzipping will occur along the whole chain eliminating successive monomer units, or until a termination reaction occurs, blocking depropagation.

For PMMA the synthesis of the polymer controls the types of irregularities in the polymer chain, and the nature of the end groups that are present.

i) PMMA prepared by free radical methods

Normal free radical propagation of PMMA proceeds as shown in figure 1-21.

Figure 1-21 Free radical polymerisation.
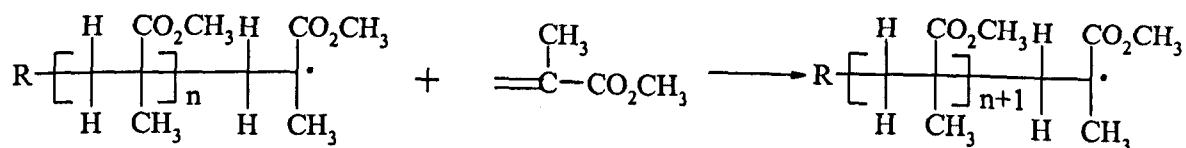
This results in monomer units polymerising in a *head to tail* nature. Upon termination, in the absence of a chain transfer agent various effects are incorporated into the polymer chain. If termination is by recombination, then a head to head link will be formed. If termination is by disproportionation, then unsaturated vinyl group with an equal number of fully saturated end groups are formed. These are shown in figure 1-22.

Figure 1-22 Termination reactions for PMMA
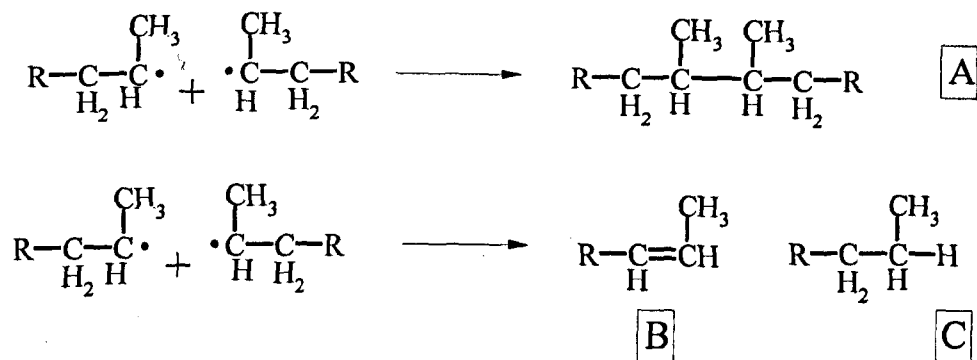
Three products **A**, **B** and **C** are formed, each will have different effects on the thermal stability of the polymer chain.

Thermal gravimetric analysis can be performed on a polymer sample, the nature of the curve obtained will help elucidate the presence of these end groups.

It has been shown [63] that these end groups will decompose within a particular temperature region, this information is summarised in table 1-2.

Table 1-2 Radical polymers end group decomposition temperatures

Structure	End group	Temperature range
A	Head to Head	165-195 °C
B	Unsaturated end group	255-270 °C
C	Saturated end group	300-360 °C

The wide ranges in the temperature are due to the variety in methods of heating the polymer sample.

Figure 1-23 shows a typical TGA trace from a free radical reaction.

Figure 1-23 TGA trace for a typical polymer formed by free radical methods
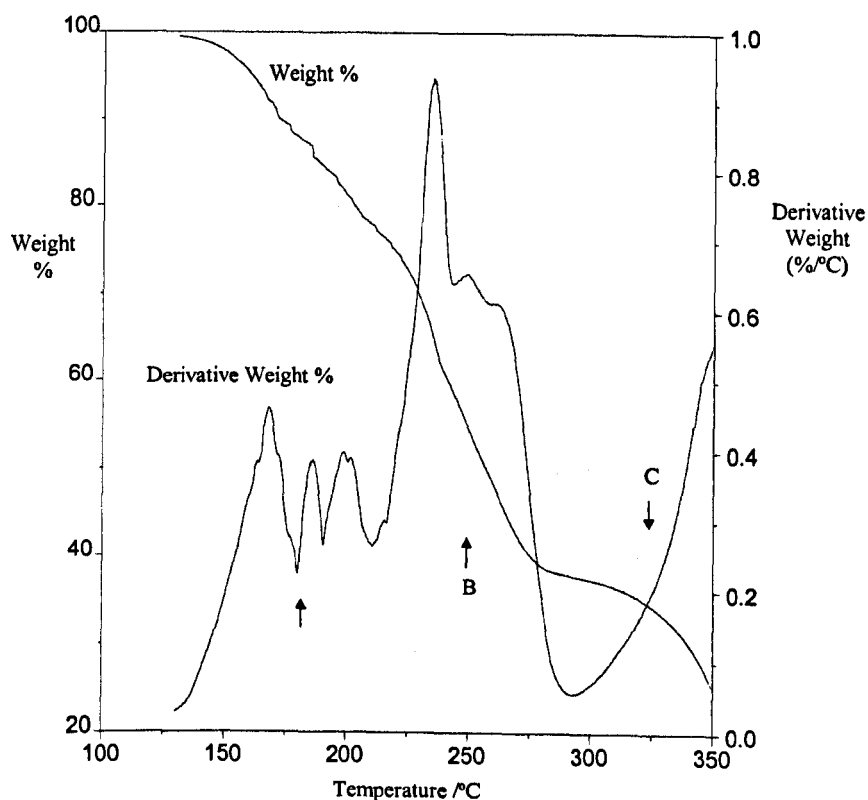
Peak A, B, and C are marked, these correspond to the decomposition of products A, B and C for a polymer formed by a free radical reaction.

ii) Polymerisation of PMMA in the presence of a chain transfer agent

If a mercaptan or other CTA is present this will cause the propagating PMMA chain to be terminated with a high efficiency rate by a proton. Hence chain transfer methods produce a polymer with fully saturated end groups. These have been shown to be the most stable of the end groups in PMMA.

Figure 1-24 Termination by a chain transfer agent of PMMA

$$R-\underset{H_2}{C}-\underset{H}{\overset{CH_3}{C}}\cdot \quad + \quad R'-SH \quad \longrightarrow \quad R-\underset{H_2}{C}-\underset{H}{\overset{CH_3}{C}}-H \quad + \quad R'-S\cdot \quad \boxed{C}$$
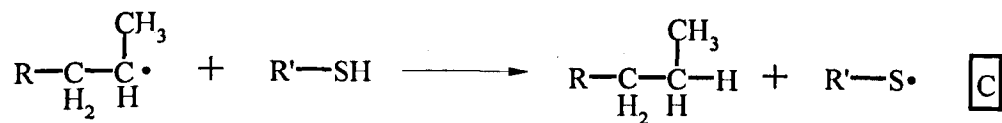
In this case formation of head to head linkages is eliminated, as are the unsaturated end groups. This results in the TGA trace for a chain transfer terminated polymer having just the one transition change (table 1-3).

Table 1-3 Chain transfer terminated end group decomposition temperature

Structure	End group	Temperature range
C	Saturated end group	300-360 °C

This transition is main chain scission, no other peaks are present.

iii) Anionic polymerisation of PMMA

It has been shown that the weak links in a polymer chain are due to head to head linkages and unsaturated end groups. Polymerisation of PMMA by an anionic method results in a termination process where only saturated end groups are possible. This leads to only one transition which should be seen at ~300-360 °C, due to the main chain scission. The presence of unusual peaks in the TGA trace will show that there have been imperfections in the polymerisation process, resulting in some weak links. Figure 1-25 shows a typical polymerisation trace for a polymer prepared by anionic methods.

Figure 1-25 TGA trace for a PMMA sample prepared by anionic methods
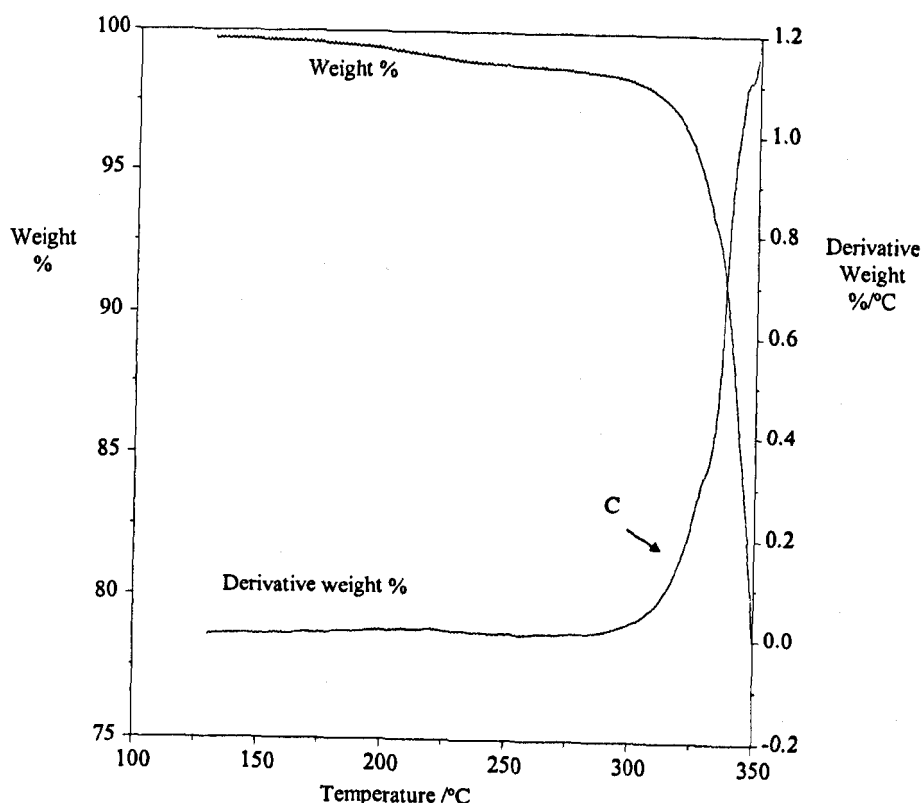
Peak C marks the transition corresponding to the decomposition of saturated end groups.

Polymerisation by anionic methods should reduce the opportunity for weak links. All polymer chains should possess the favoured head to tail links[58], so only one weight loss transition is seen at ~326 °C.

iv) The effect of stereochemistry on a TGA trace of PMMA

Stereochemistry is well known to affect the physical properties of polymers. For example the softening point of polypropylene is 170 °C for the isotactic chain. Due to its stereoregularity, this allows crystals to be formed and increases the softening point. However, the atactic chains are amorphous, this results in a softening point of -20 °C.

Hatada[57] has reported that for anionically prepared PMMA with Mn of <25,000, the degradation in nitrogen is higher than for an isotactic PMMA sample of the same Mn. At greater than Mn=25,000 the isotactic polymer was more stable. Table 1-4 shows a summary of these results.

Table 1-4 Summary of results concerning the effect of stereochemistry on the decomposition of PMMA

PMMA tacticity	Mn	Atmosphere	Decomposition temperature / °C
Syndiotactic	5,000	Nitrogen	391
Isotactic	5,000	Nitrogen	382
Syndiotactic	90,000	Nitrogen	358
Isotactic	95,000	Nitrogen	365
Syndiotactic	25,000	Air	389
Isotactic	25,000	Air	368
Syndiotactic	32,000	Air	318
Isotactic	32,000	Air	341

Knowing some information about the stereochemistry of the polymer it may be possible to predict a TGA trace.

v) The effect of oxygen on a TGA trace of PMMA

The presence of oxygen will modify the results obtained from a TGA trace. This is the reason why most TGA traces are carried out under a nitrogen atmosphere.

PMMA samples with a head to head linkage, when degraded under air will no longer show a transition due to these head to head linkages at 165-195 °C. In addition the transition due to the unsaturated linkages at 255-270 °C will also disappear under air. The TGA trace will show just one transition at ~300 °C instead of the expected 3 peaks.

Oxygen has two roles, one suppressing degradation caused by the weak links at low temperatures, and also enhancing degradation at higher temperatures. Oxygen is an

effective trapping agent for radicals that originate from head to head links as well as those that originate from unsaturated groups.

Thermal gravimetric analysis has been used to help elucidate the mechanism of polymerisation for many PMMA polymer samples within this thesis. As it is possible to tell the difference between a polymer formed by a free radical mechanism, to one formed in the presence of chain transfer agents, or by an anionic method, TGA has been a valuable technique.

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Chapter 2

Polymerisation of MMA using novel chromium(II) and (III) compounds in conjunction with alkyl halides

2. Polymerisation of MMA using novel chromium(II) and (III) compounds in conjunction with alkyl halides

2.1. Introduction

Chromium complexes have been previously reported for the polymerisation of ethylene[1,2]. Mixed metal chromium complexes containing chromium and other transition metals[3-5] have been prepared. There is the scope to investigate these compounds and the polymerisation of vinyl monomers, such as MMA. This chapter discusses the reactions of chromium trichloride tetrahydrofuranate with vinyl monomers and alkyl halides.

These reactions have been investigated due to the redox properties of chromium(II) and chromium(III) complexes. A large variety of chromium complexes have previously been prepared in both oxidation states. In addition the possibility of adding alkyl halide initiators in the presence of vinyl monomers opens possibilities for polymerisation mediated by this kind of complex.

2.2. Results and Discussion

This chapter describes the preparation of some novel chromium compounds as prepared from chromium trichloride, (CrCl$_3$), these compounds were then used in a system for the polymerisation of methyl methacrylate.

2.2.1. Synthesis of chromium trichloride tetrahydrofuranate, CrCl$_3$(THF)$_3$

Chromium trichloride is a purple crystalline compound. In this form it is insoluble in organic solvents, this drastically hinders any possible polymerisation reactions, as it makes them heterogeneous. This can be overcome by solubilising with THF. The organo-soluble compound, CrCl$_3$(THF)$_3$ is prepared from the reaction of chromium trichloride with THF in the presence of a small amount of zinc. The zinc is present as a reducing agent. Experimental details can be found in section 6.4.2-1, this preparation is modified from Herwig and Zeiss[6]. The reaction is carried out under nitrogen with anhydrous solvents as the product is moisture sensitive. The method of preparation uses a soxhlet apparatus and the product is easily formed and collected in quantitative yields. The structure of the compound is shown in figure 2-1.

Figure 2-1 The *mer*-isomer of CrCl$_3$(THF)$_3$

$$
\begin{array}{c}
Cl \diagdown \ \ Cl \\
\ \ \ \ \ | \\
THF - Cr - THF \\
\ \ \ \ \ | \ \ Cl \\
\ \ \ THF
\end{array}
$$
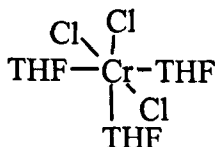
This crystalline product is purple, this compound can be used for further reactions, due to increased solubility.

2.2.2. Reduction of CrCl₃(THF)₃ with zinc mercury amalgam.

A quantity of $CrCl_3(THF)_3$ is dissolved in THF, added to a zinc mercury amalgam and shaken vigorously for 30 minutes. The purple solution turns green and a light blue powder precipitates out of solution, this blue powder was isolated. Experimental details can be found in 6.4.2-2.

The blue chromium(II) compound, *(A)*, is extremely air sensitive and decomposes to unidentifiable compounds instantly upon contact with air. Identification of *(A)* proved difficult because of its extreme air sensitive nature. Crystals were grown from THF solution and characterised by x-ray crystallographic analysis. The structure of *(A)* is shown in figure 2-2.

Figure 2-2 Crystal structure for *(A)*
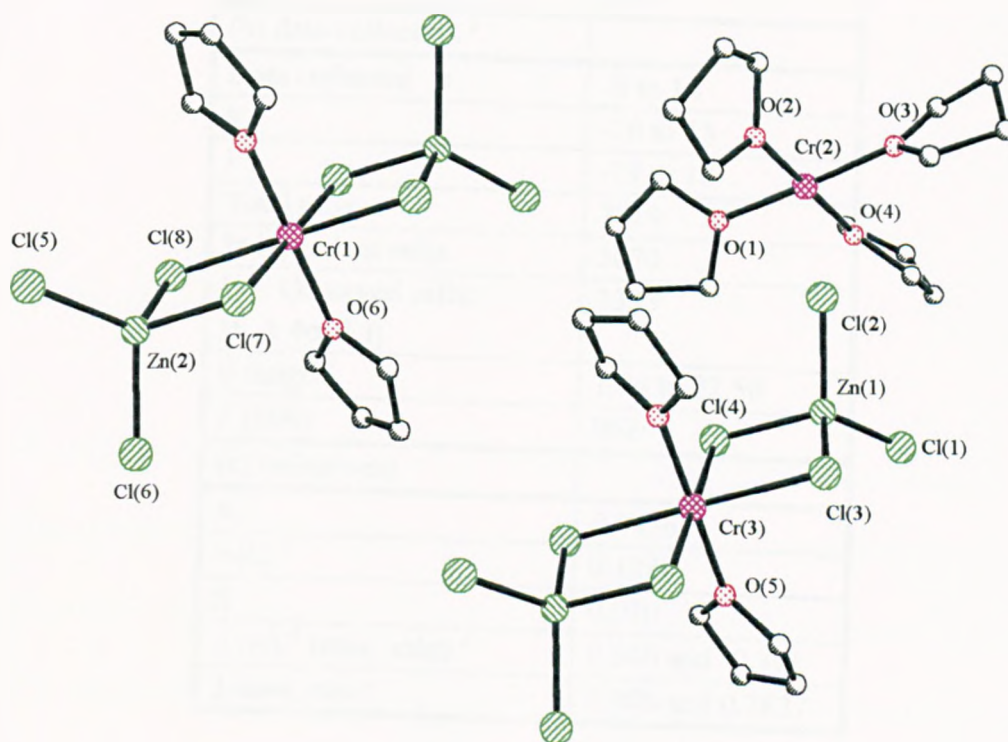
Table 2-1 shows summarised crystallographic data for *(A)*. Full crystallographic details for *(A)* can be found in appendix A.

Table 2-1 Summarised crystallographic data for *(A)*

(a) Crystal parameters	Compound *(A)*
Formula	$C_{12}H_{24}Cl_4CrO_3Zn$
M	475.48
Crystal system	Triclinic
Space group	p1
a/ Å	11.3651
b/ Å	12.2514
c/ Å	14.1689
α/ °	91.8
β/°	92.4
γ/°	95.7
refls for cell detm.	7919
U/ Å³	1960.09(7)
Z	4
dimensions /mm	0.40 x 0.30 x 0.05
D_c /Mg/m³	1.61
μ(Mo-Kα) /mm⁻¹	2.327
T / K	200
(b) data collection [a]	
Data collected h	-8 to 14
k	-16 to 15
l	-19 to 18
Total refls.	7919
Independent refls.	5070
Ind. Observed refls. $[F_o \geq 4\sigma(F_o)]$	3393
θ range/°	1.44 to 22.50
F (000)	968
(c) refinement	
R [b]	0.0436
wR2 [c]	0.1234
S	0.970
Δ /eÅ⁻³ (max, min) [d]	0.540 and -0.391
T max, min [e]	1.000 and 0.7827

Legend for Table 2-1

[a] Data collected on a Siemens 3 circle diffractometer equipped with a SMART CCD area detector; graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). [b] $R = \Sigma |F_o - F_c| / \Sigma F_o$ (for $F_o \geq 4\sigma(F_o)$). [c] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$ for all data. [d] peaks of unassigned residual electron density. [e] By SADABS. [f] $w^{-1} = \sigma^2(F_o^2) + aP + bP$, where $P = [max(F_o^2, 0) + 2F_c^2]/3$, where $max(F_o^2, 0)$ indicates that the larger of F_o^2 or 0 is taken, a and b are values set by the program.

Elemental and ICP analysis was carried out on *(A)*,

[Cl$_2$Zn(μ-Cl)$_2$Cr(THF)$_2$(μ-Cl)$_2$ZnCl$_2$]$^-$[Cr(THF)$_4$]$^{2+}$[Cl$_2$Zn(μ-Cl)$_2$Cr(THF)$_2$(μ-Cl)$_2$ZnCl$_2$]$^-$
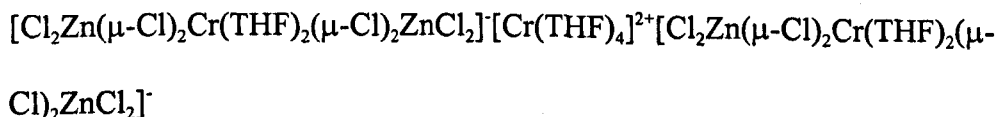
a representation of which is shown in figure 2-3.

Figure 2-3 Representation of *(A)*
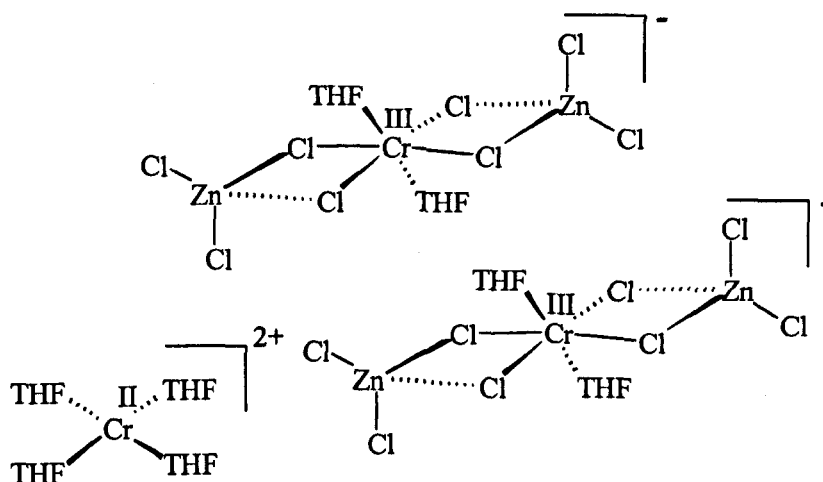
The crystallographic unit cell is C$_{12}$H$_{24}$Cl$_4$CrO$_3$Zn, this was used to determine the theoretical results for ICP analysis; Cr = 10.93 and Zinc = 13.75, the results found; Cr = 5.07 and Zn = 5.69. This result does show that there is one chromium to one zinc atom in the compound as expected, however, overall less metal has been found than calculated. This result suggests that not all of *(A)* is made up from the crystal unit cell of C$_{12}$H$_{24}$Cl$_4$CrO$_3$Zn.

Table 2-2 shows some selected bond angles and lengths found in *(A)*, these are compared to other chromium and zinc compounds (table 2-3).

Table 2-2 Selected bond angles and lengths for *(A)*

Atoms	Bond length [Å]
Cr(1) - O(6)#1	2.052(4)
Cr(1) - O(7)#1	2.5147(14)
Cr(1) - Cl(8)	2.676(2)
Cr(2) - O(1)	2.038(3)
Cr(2) - O(4)	2.064(4)
Zn(1) - Cl(1)	2.208(2)
Zn(1) - Cl(3)	2.286(2)
Zn(2) - Cl(8)	2.280(2)

Atoms	Bond angles [°]
O(6)#1 - Cr(1) - O(6)	180.0
O(6) - Cr(1) - Cl(7)#1	89.52(11)
O(6)#1 - Cr(1) - Cl(8)	92.311(11)
Cl(7)#1 - Cr(1) - Cl(8)	95.00(4)
Cl(1) - Zn(1) - Cl(2)	115.00(7)
Cl(1) - Zn(1) - Cl(3)	111.60(7)
Cl(6) - Zn(2) - Cl(7)	106.76(6)
Zn(1) - Cl(3) - Cr(3)	85.95(5)

Table 2-3 Selected bond angles and lengths for related compounds, $MCl_3(THF)_3$
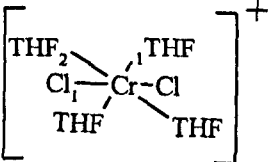
$$
\begin{array}{c}
\text{Cl} \quad \text{Cl} \\
\text{THF} - \text{M} - \text{THF} \\
\text{Cl} \\
\text{THF}
\end{array}
$$

M	M-Cl_{ax}	Average M-Cl_{eq}	M-O_{ax}	Average M-O	Cl_{ax}-M-O_{ax}	Average Cl_{ax}-M-Cl_{eq}	Average Cl_{ax}-M-O_{eq}
Sc	2.406(4)	2.418(3)	2.236(8)	2.156(9)	179.5(3)	92.8(3)	96.4(3)
Ti	2.336(5)	2.351(5)	2.183(2)	2.097(8)	176.8(6)	94.0(8)	91.6(4)
V	2.297(2)	2.330(4)	2.102(3)	2.062(8)	179.64(11)	92.0(5)	93.7(1)
Cr	2.283	2.310(3)	2.077(4)	2.01(2)	179.8(1)	90.9(4)	93.9(0)
Source:-Research by Cotton et al[7]							

Comparing the chromium - chlorine bonds in *(A)* with the above example shows the chromium - chlorine bonds longer than those in the case of $CrCl_3THF_3$, this would be

due to the bridging nature of these Cr-Cl-Zn bonds. Chromium - oxygen bonds fall into the range expected for a metal-oxygen bond.

The compound $[CrCl_2(THF)_4]^+[SnCl_5(THF)]^-$ has been prepared by Janas et al[3], table 2-4 shows some selected bond lengths and angles within the chromium cation.

Table 2-4 Selected bond angles and lengths for the cation $[CrCl_2(THF)_4]^+$

Atoms	Bond length [Å]
Cr-Cl(1)	2.288(3)
Cr-O(1)	2.011(6)
Cr-O(2)	2.029(6)

Atoms	Bond angles [°]
Cl(1)-Cr-O(1)	89.6(2)
Cl(1)-Cr-O(2)	90.0(2)
O(2)-Cr-O(1)	91.2(3)

Chromium is in the +3 oxidation state in this complex, as is chromium(1) in *(A)*. The chromium - chlorine bond again shows that the Cr-Cl bond in *(A)* is longer than would be expected, although similar length Cr-O bonds are found.

Cotton et al[8], prepared by the reduction of $VCl_3(THF)_3$ with zinc, a product they identified as $[V_2(THF)_6(\mu-Cl)_3]_2(Zn_2Cl_6)$, this is shown in figure 2-4.

55

Figure 2-4 Representative structure of [V$_2$(THF)$_6$(μ-Cl)$_3$]$_2$(Zn$_2$Cl$_6$)
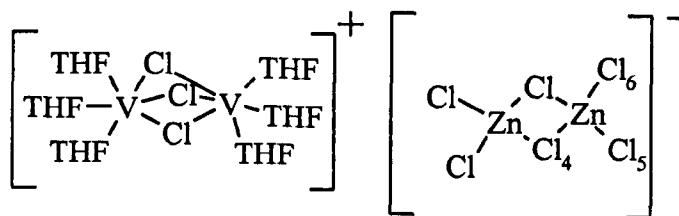
Thus this type of reaction is not unprecedented. In the example shown in figure 2-4 the product shows a vanadium cation with a zinc anion. The product prepared in this work, *(A)*, is interesting as it has been identified as containing a mixed metal anion. Table 2-5 shows some examples of bond lengths found in the anion.

Table 2-5 Selected bond lengths for the anion [Zn$_2$Cl$_6$]$^{2-}$

Atoms	Bond length [Å]
Zn-Zn'	3.251(1)
Zn-Cl(4)	2.349(1)
Zn-Cl(5)	2.211(1)
Zn-Cl(6)	2.211(1)

The anion can be regarded as containing two ZnCl$_4$ tetrahedra sharing an edge. These bond lengths can be compared to those within *(A)*. In *(A)* a terminal Zn-Cl bond is 2.208 Å and a bridging Zn-Cl bond is 2.286 Å. Some degree of shortening has occurred in *(A)*, probably due to the presence of chromium and zinc bridging atoms rather than two zinc atoms.

There is no evidence of chromium-zinc bonding in *(A)* as the metal -metal distances are too long. Indeed it would be unusual to have found this to be the case as very few examples of chromium - metal bonds have been found. *(A)* is the first example of a chromium and zinc mixed metal product and as such is worthy of note in itself. In addition it contains chromium in both the +2 and +3 oxidation states. This compound was subsequently used for further reactions.

2.2.3. The reaction of *(A)* and ethyl-2-bromoisobutyrate.

The reaction of *(A)* with ethyl-2-bromoisobutyrate (figure 2-5) was investigated.

Figure 2-5 Structure of ethyl-2-bromoisobutyrate (R-Br)
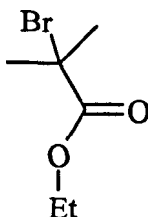
A quantity of *(A)*, partially dissolved in THF was reacted with an excess of ethyl-2-bromoisobutyrate. The reaction at room temperature is complete within one hour (section 6.4.2-3). The blue solution turns purple giving a purple crystalline product on removal of the solvent. Crystals of this compound were grown from a concentrated solution in THF over two weeks. The structure was determined by x-ray crystallography (figure 2-6).

Table 2-6 shows summarised crystallographic data for *(B)*. Full crystallographic details for *(B)* can be found in appendix A. Figure 2-7 shows a representation of *(B)*.

Figure 2-6 Crystal structure of *(B)*
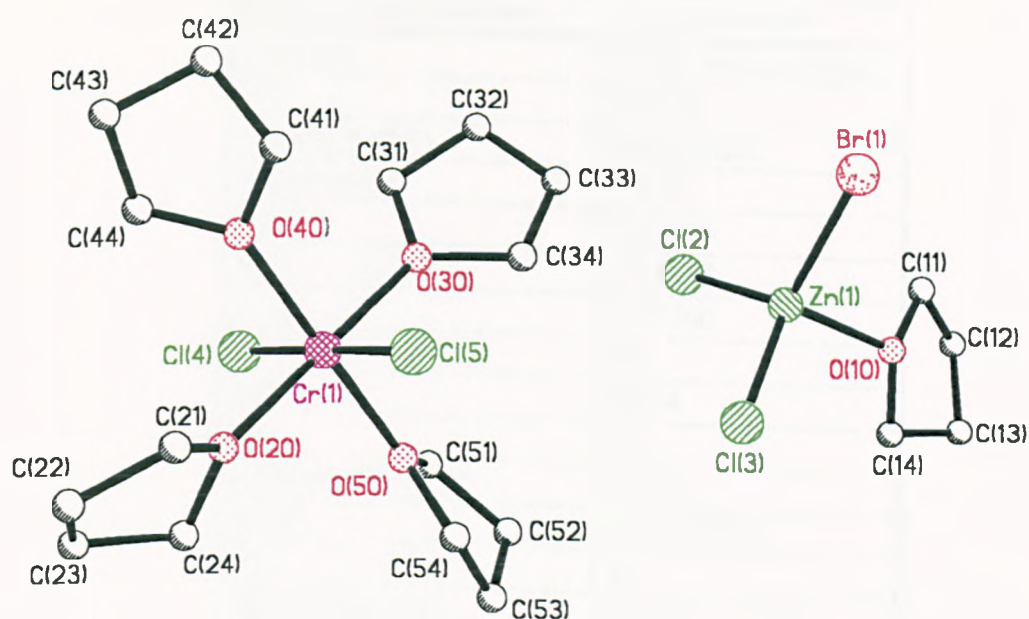
Figure 2-7 Representation of *(B)*
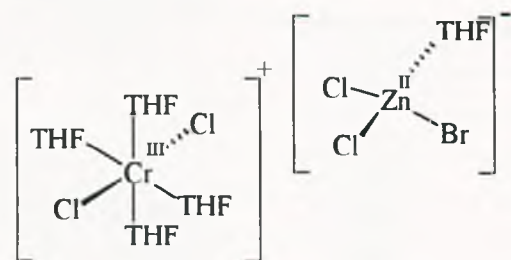
Table 2-6 Summarised crystallographic data for *(B)*

(a) Crystal parameters	Compound *(B)*
Formula	$C_{20}H_{40}BrCl_4CrO_5Zn$
M	699.60
Crystal system	Monoclinic
Space group	$P2_1/c$
a/ Å	14.1656
b/ Å	11.9885
c/ Å	17.3760
$\alpha/\degree$	90
$\beta/\degree$	98.04
$\gamma/\degree$	90
refls for cell detm.	17212
U/ Å^3	2921.85 (11)
Z	4
dimensions /mm	0.3 x 0.1 x 0.05
D_c /Mg/m^3	1.590
μ(Mo-Kα) /mm^{-1}	2.953
T / K	180
(b) data collection [a]	
Data collected h	-12 to 18
k	-15 to 15
l	-23 to 23
Total refls.	17212
Independent refls.	6850
Ind. Observed refls. $[F_o \geq 4\sigma(F_o)]$	3894
θ range/$\degree$	2.07 to 28.65
F (000)	1428
(c) refinement	
R [b]	0.0591
wR2 [c]	0.1532
S	1.007
Δ /eÅ^{-3} (max, min) [d]	0.614 and -1.219
T max, min [e]	0.9300 and 0.5300

Legend for Table 2-6
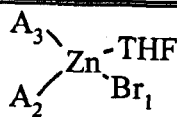
[a] Data collected on a Siemens 3 circle diffractometer equipped with a SMART CCD area detector; graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). [b] $R = \Sigma \lvert F_o - F_c \rvert / \Sigma F_o$ (for $F_o \geq 4\sigma(F_o)$). [c] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{\frac{1}{2}}$ for all data. [d] peaks of unassigned residual electron density. [e] By SADABS. [f] $w^{-1} = \sigma^2(F_o^2) + aP + bP$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$, where $\max(F_o^2,0)$ indicates that the larger of F_o^2 or 0 is taken, a and b are values set by the program.

Based on the crystal structure unit cell structure of $C_{20}H_{40}BrCl_4CrO_5Zn$ the figures for ICP analysis was calculated as:-

ICP anal. Calcd. Cr = 7.43 , Zn = 9.35; Found Cr = 9.71 Zn = 3.55.

There is a significant error in these results. This could be explained by the unfortunate problem whereby the structure, shown in figure 2-6, is not a true representation of the compound formed, but only of one isomer formed in the reaction. It has been found that the chlorine and bromine atoms interconvert, the following data has been obtained from x-ray crystallography.

Table 2-7 Atom occupancy for *(B)*

Atom number	% occupancy
Cl_{2a}	66
Br_{2b}	33
Cl_{3a}	50
Br_{3b}	50

The effect of this is to alter the actual unit cell molecular formula, hence, altering the calculated values expected for elemental and ICP analysis which might account for the error observed.

(B) has been shown to contain a chromium(III) metal centre and a zinc(II) metal centre.

Table 2-8 shows selected bond lengths and angles for *(B)*.

Table 2-8 Selected bond angles and bond lengths for *(B)*

Atoms	Bond length [Å]
Cr(1)-O(20)	1.997(4)
Cr(1)-O(50)	2.004(4)
Cr(1)-Cl(4)	2.293(2)
Zn(1)-O(10)	2.086(4)
Zn(1)-Cl$_{2a}$	2.25(2)
Zn(1)-Br$_{2b}$	2.32(2)
Zn(1)-Br(1)	2.3620(10)

Atoms	Bond angles [°]
O(20)-Cr(1)-O(30)	179.7(2)
O(20)-Cr(1)-O(50)	90.8(2)
O(20)-Cr(1)-Cl(4)	89.63
O(30)-Cr-Cl(5)	90.79
O(10)-Zn(1)-Cl$_{2a}$	101.5(6)
O(10)-Zn(1)-Br$_{2a}$	96.9(6)
Br$_{2b}$-Zn(1)-Br$_{3b}$	117.0(5)

Compound $[CrCl_2(THF)_4]^+[SnCl_5(THF)]^-$ prepared by Janas et al[3], and mentioned in 2.2.2, contains an identical cation, $[CrCl_2(THF)_4]^+$, structural data can be compared. Table 2-4 shows bond angles and bond lengths for this cation.

A comparison of these figures reveals similar results, both compounds have almost identical Cr-Cl bond lengths. In addition the angles between atoms are 90 ° in both cases, consistent with a six co-ordinate octahedral complex. A comparison of the anion is more difficult due to the nature of the halogen atoms and their partial occupancy. The bond angles are consistent with a tetragonal complex, the angles are slightly distorted due to the steric hindrance presented by the halogen atoms, particularly bromine.

A zinc anion was found in the complex $[V_2(THF)_6(\mu\text{-}Cl)_3]_2(Zn_2Cl_6)$ as prepared by

Cotton et al[8] (figure 2-4), although this contains bridging chlorine atoms the complex

is made up of two tetrahedra and can be used to compare the *Zn-Cl bonds*.

Table 2-5 shows some examples of bond lengths found in the anion.

A terminal Zn-Cl bond in this example is slightly shorter in length. This can be

explained by the different electronic properties at the zinc metal centre. The reaction

is shown in figure 2-8.

Figure 2-8 Reaction for the preparation of *(B)*
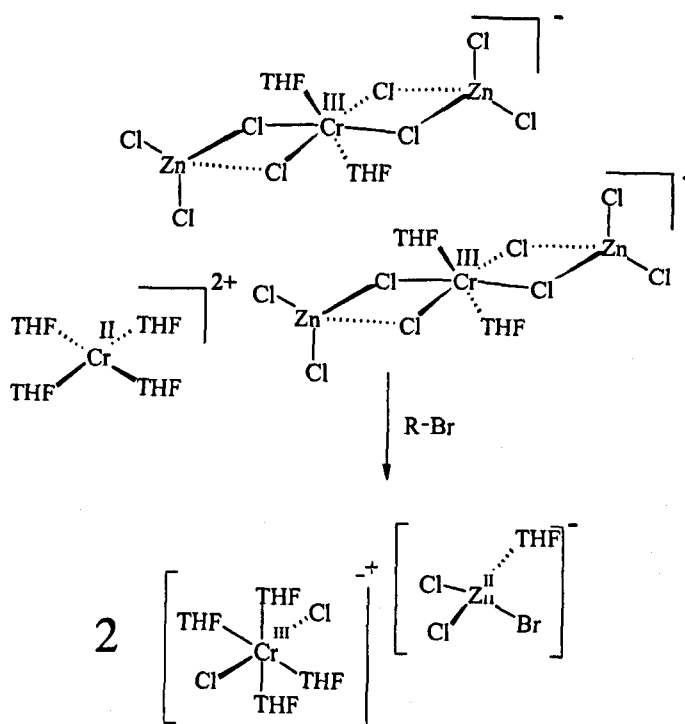
Unusual chromium and zinc halide compounds, *(A)* and *(B)*, have been prepared and

analysed. The complexes do not contain any unusual bond lengths or angles and the

cation in *(B)* is identical to one prepared in earlier research. The complex *(A)* was

subsequently used to investigate the reaction with methyl methacrylate monomer.

2.2.4. Polymerisation of methyl methacrylate using *(A)* in conjunction with ethyl-2-bromoisobutyrate.

This section describes the reaction of the unusual chromium-zinc *(A)* with ethyl-2-bromoisobutyrate initiator in THF with methyl methacrylate. Polymerisations were carried out with *(A)* in THF and methyl methacrylate with ethyl-2-bromoisobutyrate. The reaction was carried out at room temperature for 24 hours, prior to molecular weight and conversion analysis (section 6.6.2).

On addition of MMA to the light blue solution no colour change was observed. However, upon addition of ethyl-2-bromoisobutyrate a purple solution is formed. A series of polymerisations were carried out with a range of reaction conditions, table 2-9.

Table 2-9 Table of quantities for *(A)* with R-Br

Experiment	*(A)* g	*(A)* moles	MMA g	MMA moles	R-Br (initiator) moles	Ratio of [Cr]:[Init]:[MMA]
1	0.57	1.20×10^{-3}	4.68	4.68×10^{-2}	2.7×10^{-3}	1:2:39
2	0.180	3.78×10^{-4}	4.68	4.68×10^{-2}	5.0×10^{-3}	1:13:123
3	0.180	3.78×10^{-4}	14.04	1.40×10^{-1}	5.0×10^{-3}	1:13:375
4	0.250	5.26×10^{-4}	9.36	9.36×10^{-2}	3.6×10^{-3}	1:7:133
5	0.180	3.78×10^{-4}	9.36	9.36×10^{-2}	3.6×10^{-3}	1:10:500
6	0.095	2.00×10^{-4}	9.36	9.36×10^{-2}	1.4×10^{-3}	1:7:500
7	0.095	2.00×10^{-4}	9.36	9.36×10^{-2}	2.7×10^{-3}	1:13:500
8	0.095	2.00×10^{-4}	9.36	9.36×10^{-2}	4.1×10^{-3}	1:20:500

Table 2-10 Table of results for *(A)* with R-Br

Experiment	% Yield	Mn	Mw	PDi
1	65	26,300	66,400	2.53
2	<10	23,700	86,000	3.63
3	<10	5,900	14,200	2.41
4	8	18,200	63,500	3.50
5	3	15,400	27,500	1.78
6	<10	10,800	17,300	1.60
7	<10	10,100	15,800	1.57
8	<10	11,800	16,300	1.39

The yields obtained are low, except for an example whereby a low ratio of initiator to

(A) was used. Molecular weights for this reaction system are varied and the PDi for

the product is between 1.4 and 3.6. These results suggest that an increase in the

amount of initiator results in a lowering of yield. This data can be plotted for an

alternative representation. Figure 2-9 shows a plot of the amount of *(A)* used verses

Mn.

Figure 2-9 Graph of concentration of (*A*) verses Mn from experiment
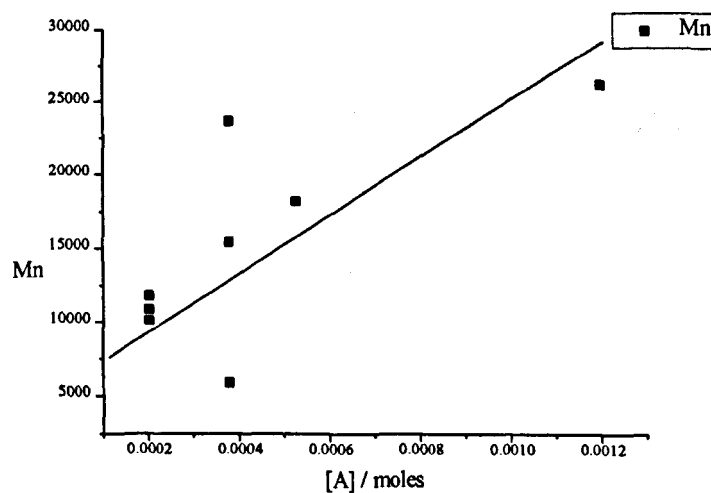
The Mn obtained appears to have a relationship to the amount of *(A)* used. However, a

more appropriate plot is shown in figure 2-10, a plot of the ratio of [initiator]:[MMA]

verses Mn.

Figure 2-10 Plot of ratio [initiator]:[MMA] verses Mn
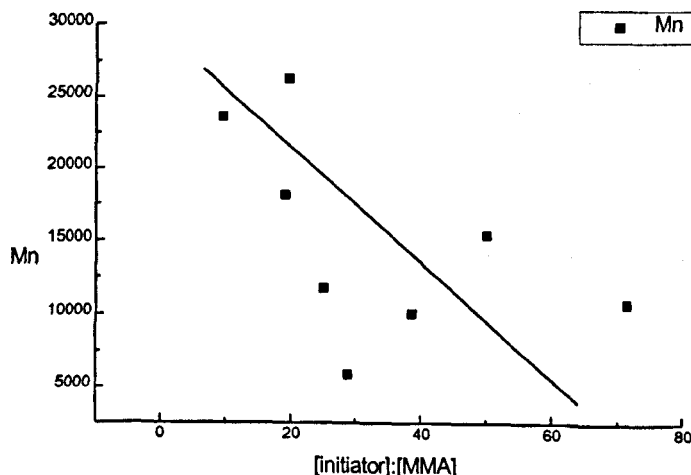
This plot suggests that an increase in the ratio of initiator to monomer lowers the molecular weight of polymer obtained. If the reaction was to proceed by a living polymerisation mechanism then an increase in this ratio should have resulted in an increase in Mn.

2.2.5. Further polymerisation reactions of methyl methacrylate using *(A)* in conjunction with ethyl-2-bromoisobutyrate

The following experiments were similar to those carried out in section 2.2.4, in this case the temperature had been raised to 60 °C. Table 2-11 shows the quantities used for these experiments, table 2-12 contains the results from this work. In these experiments the quantity of chromium has been kept constant and the ratio of monomer has been changed.

Table 2-11 Quantities used

Experiment	*(A)* moles	MMA moles	R-Br (initiator) moles	Ratio of [A] : [Init] : [MMA]
9	8.2×10^{-5}	9.36×10^{-2}	6.8×10^{-3}	1:80:1000
10	8.2×10^{-5}	9.36×10^{-2}	6.8×10^{-3}	1:80:1000
11	8.2×10^{-5}	4.68×10^{-2}	6.8×10^{-3}	1:80:500

Table 2-12 Results obtained

Experiment	% Yield	Mn	Mw	PDi
9	12	5,300	10,600	1.99
10	14	2,000	3,600	1.70
11	10	2,100	4,400	2.13

These results show that an increase in temperature does not affect the yield of the reaction. A higher reaction temperature might have been expected to yield a higher rate of reaction, resulting in higher % conversion, this does not appear to have been the case.

In the following experiments the quantity of *(A)* was changed, but the ratio of initiator to monomer was kept constant.

Table 2-13 Quantities used

Experiment	*(A)* moles	MMA moles	R-Br (initiator) moles	Ratio of [A] : [Init] : [MMA]
12	6.7×10^{-5}	9.36×10^{-2}	3.4×10^{-3}	1:50:1400
13	1.32×10^{-4}	9.36×10^{-2}	3.4×10^{-3}	1:25:700
14	2.00×10^{-4}	9.36×10^{-2}	3.4×10^{-3}	1:12:350
15	2.00×10^{-4}	9.36×10^{-2}	3.4×10^{-3}	1:17:500
16	2.00×10^{-4}	9.36×10^{-2}	3.4×10^{-3}	1:17:500
17	2.00×10^{-4}	9.36×10^{-2}	3.4×10^{-3}	1:17:500

Table 2-14 Results obtained

Experiment	% Yield	Mn	Mw	PDi
12	<10	248,000	489,000	1.97
13	<10	481,000	910,000	1.89
14	<10	348,000	655,000	1.88
15	<10	291,000	461,000	1.58
16	<10	255,000	433,000	1.70
17	<10	190,000	416,000	2.20

In these experiments the molecular weight increases by a factor of 10, relative to the experiments carried out previously, although yields are still low. Molecular weights in these experiments were again the same order of magnitude after 24 hours, polydispersities obtained were ~2. Conflicting results for these experiments has made concluding comments difficult, a comparison of all results was carried out.

A comparison of all results carried out using this system

At this point all data from 2.2.4 and 2.2.5 has been collated, from this graphs have been plotted to try and gather further information on the effect of changing the quantities of materials (figures 2-11 and 2-12).

Figure 2-11 Graph of Mn verses concentration of *(A)*
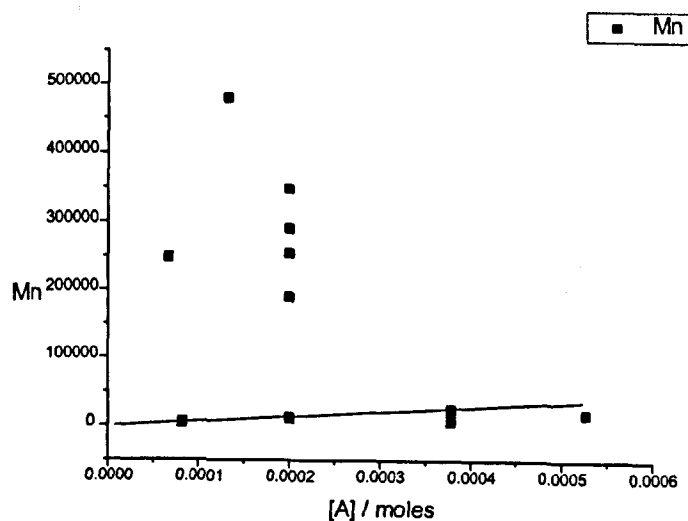
Two sets of data appear to be present, one set of reactions result in a Mn of ~15,000, a second set results in molecular weights obtained of an order of magnitude higher. The results suggest no correlation can be observed. A second plot is the ratio of *(A)* to MMA verses Mn (figure 2-12).

Figure 2-12 Graph of ratio of *(A)* to MMA verses Mn
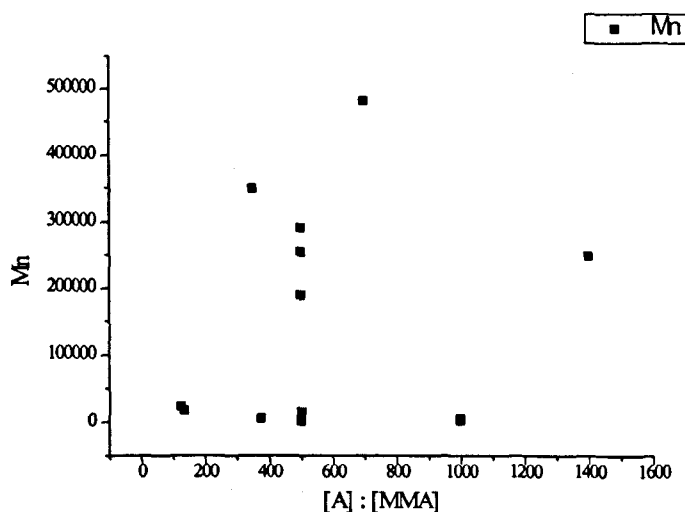
The results obtained from this section when presented in this manner also indicate a random reaction, almost consistent with a free radical reaction. There is no relationship between the quantity of monomer or ratio of monomer to metal. This system was investigated further in an attempt to elucidate the mechanism.

The following plot (figure 2-13) shows a plot of the concentration of [R-Br] verses Mn.

Figure 2-13 Plot of [R-Br] verses Mn for all results
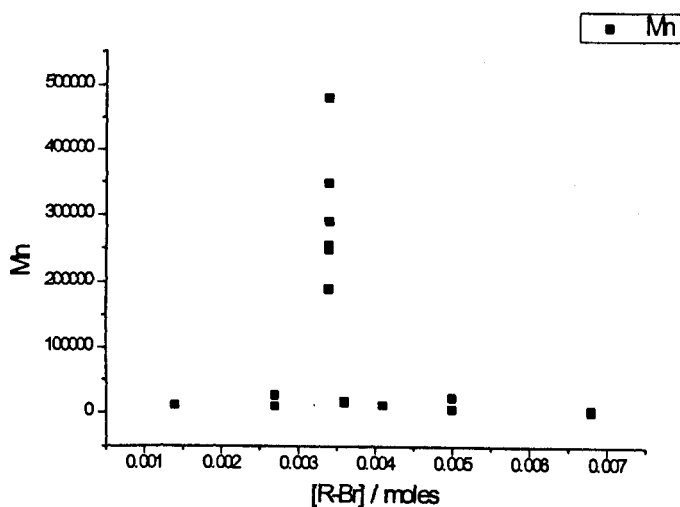
This plot shows that there does not appear to be relationship between the molecular weight obtained and the concentration of initiator used in the polymerisation reaction.

2.2.6. Polymerisation of methyl methacrylate with *(A)* and ethyl-2-bromoisobutyrate; dependence on time on Mn

The polymerisation was carried out as described previously with samples of the reaction solution removed at intervals. Table 2-15 shows the quantities used for such an experiment, table 2-16 shows the results obtained.

Table 2-15 Table of quantities for *(A)* with R-Br and MMA

Experiment	*(A)* moles	MMA moles	R-Br (initiator) moles	Ratio of [*A*] : [Init] : [MMA]
18	1.05×10^{-3}	4.68×10^{-2}	2.7×10^{-3}	1:2.5:45

Table 2-16 Table of results for *(A)* with R-Br and MMA

Experiment number	Time	SEC from	Mn	Mw	PDi
18 /1	35 min	solution	4,600	6,900	1.51
2	75 min	solution	4,700	8,400	1.77
3	120 min	ppt in hexane	5,000	11,000	2.21
4	20 hours	solution	5,800	23,600	4.11
5	96 hours	solution	7,500	48,300	6.45
6a	120 hours	ppt in hexane	8,700	67,200	7.76
6b	5 days	ppt in MeOH/HCl	20,500	85,700	4.18

In this example, after 5 days at 60 °C the percentage yield was calculated to be 45 %. Due to the scale of this reaction there was insufficient sample available to perform gravimetric analysis at each stage.

The reaction reaches 45 % conversion after 5 days. In the case of a living polymerisation reaction 45 % of monomer would have been used, this would result in a polymer of 45 % of theoretical mass. In this example that would be 45 % x (45 x 100) = 2000 (based on [Cr]:[MMA]), the Mn obtained however is 20,000, with a large polydispersity, not characteristic of a polymer obtained by living polymerisation. This indicates that the reaction is unlikely to proceed by a controlled living polymerisation mechanism and some mode of termination is present.

2.2.7. Stereochemistry of PMMA from ethyl-2-bromoisobutyrate and *(A)*

An important aspect of control in polymerisation reactions is control over the stereochemistry of the polymer backbone, this can be measured by ^{1}H NMR.

Table 2-17 shows the stereochemistry of PMMA from experiment 18/6.

Table 2-17 Tacticity results for experiment 18/6

mm	rm	rr
3 %	27 %	69 %

[Statistical results expected for a statistical free radical polymerisation of MMA:-

Isotactic (mm) 4.5 %, Atactic (rm) 17.5 %, Syndiotactic(rr) 78 %.].

This suggests that the reaction does not achieve stereochemical control and may

proceed by a free radical mechanism.

2.2.8. Thermal gravimetric analysis of poly(methyl methacrylate) formed in the reaction of methyl methacrylate and *(A)* and ethyl-2-bromoisobutyrate

Analysis of the PMMA by thermal gravimetric gives information on the polymer end

group, giving information regarding polymerisation mechanism, this has been

extensively examined[9-16], section 1.6.2.

Figures 2-14 to 2-16 show TGA traces for the polymer sample 18 at various stages of

the reaction and using different solvents to precipitate the polymer sample.

Figure 2-14 TGA trace for PMMA sample 18/5 precipitated from hexane.
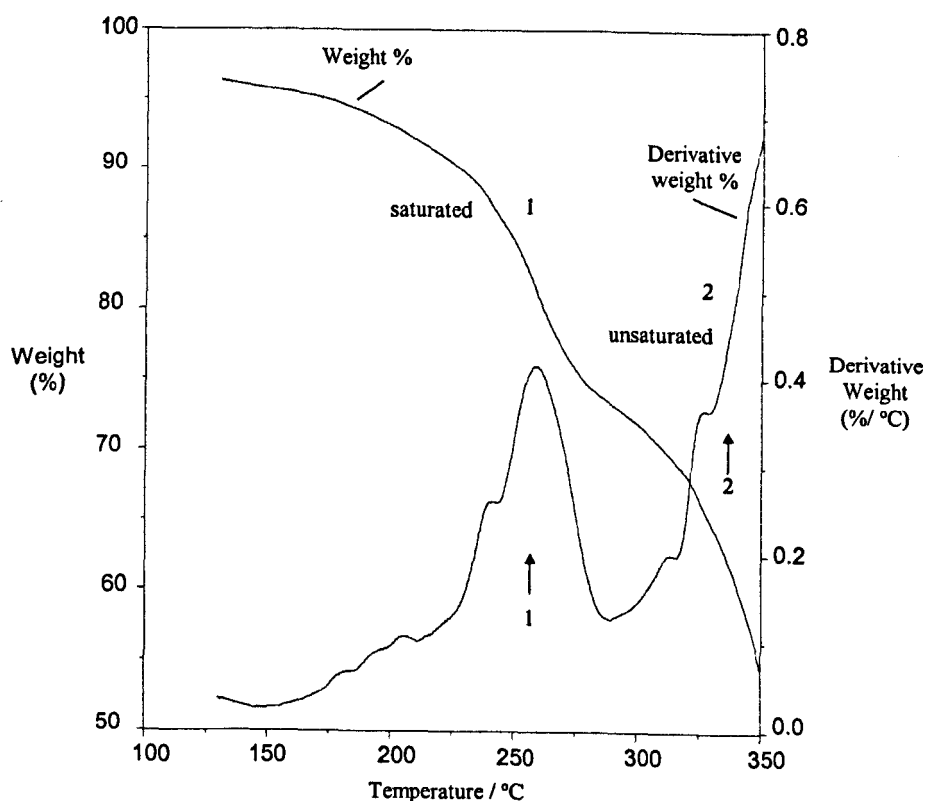
Experiment	Mn	Mw	PDi
18/5	7,500	48,300	6.46

Figure 2-14 shows a PMMA sample from a typical experiment involving *(A)* and ethyl-2-bromoisobutyrate. Two peaks can be seen, marked 1 and 2, the first is a broad transition from ~220 °C to ~270 °C, the second at ~310 °C. The broadness of these transitions is due to the large polydispersity of the polymer sample examined. Peak 1 is in the usual range for a terminally unsaturated end group -CH=CH$_2$. The second transition at ~310 °C is a typical saturated end group, -CH$_2$-CH$_3$.

Figure 2-15 TGA trace for experiment 18/5 precipitated from hexane
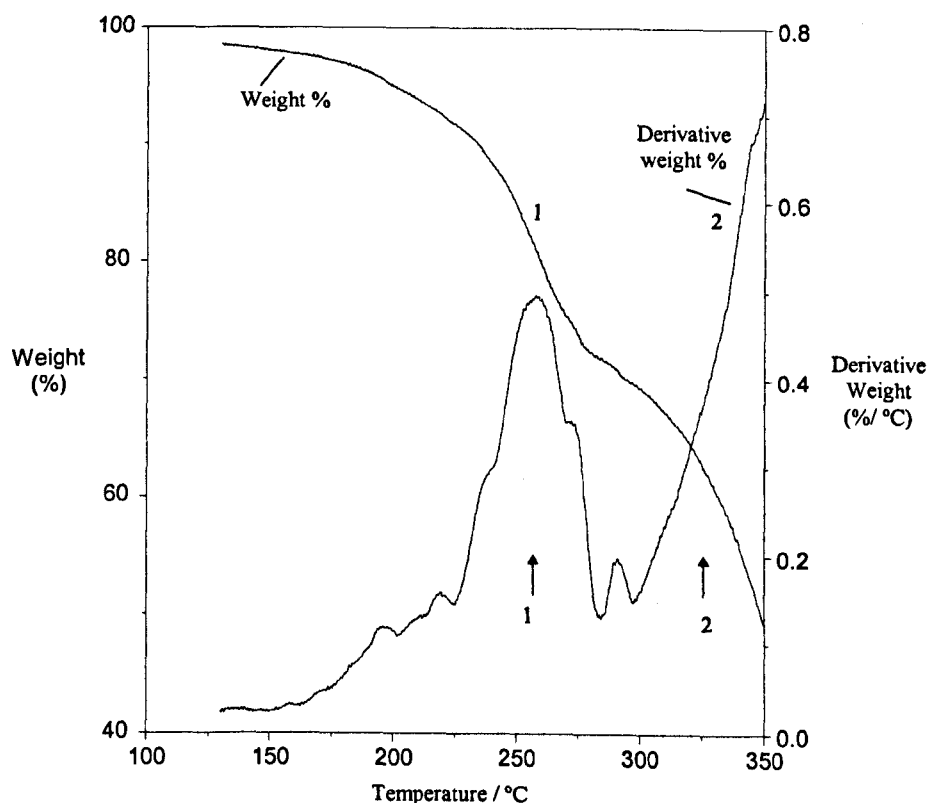
Experiment	Mn	Mw	PDi
151/6	8,600	67,200	7.76

Figure 2-15 is another example of PMMA formed in the presence of *(A)* and ethyl-2-bromoisobutyrate. There are two peaks present, one broad transition at ~240 °C to 280 °C, the second transition is at ~320 °C. These transitions are similar to those shown in figure 2-14, hence the same conclusions can be made, showing a typical unsaturated and saturated end group.

Figure 2-16 TGA trace for experiment 18/6 precipitated from methanol/HCl
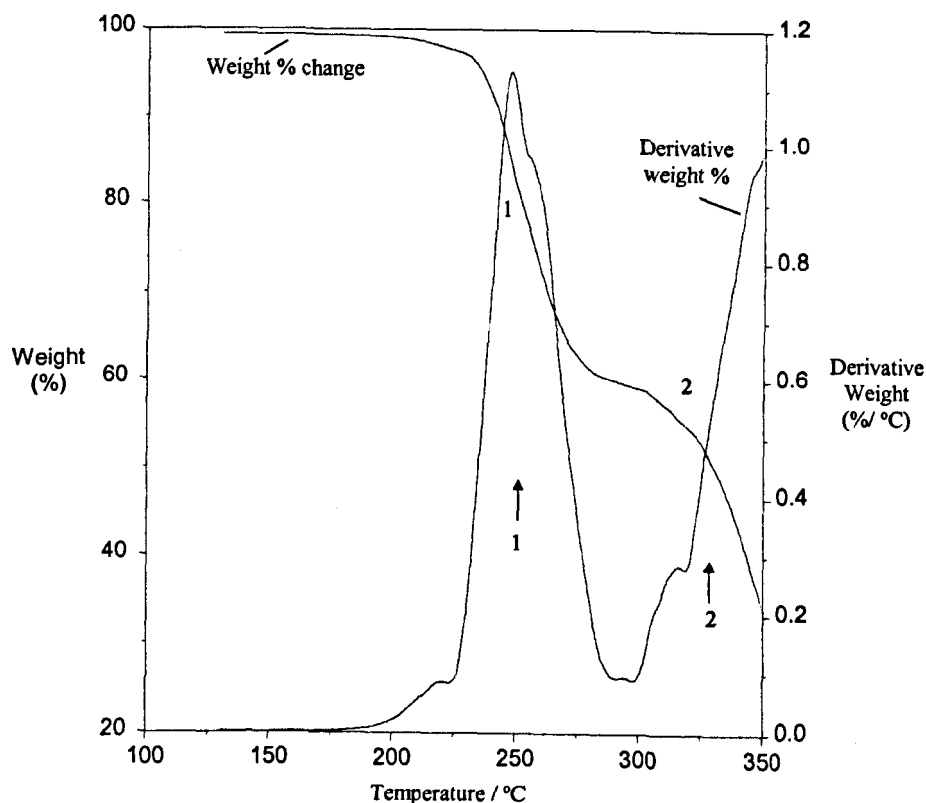
Experiment	Mn	Mw	PDi
18/6	20,500	85,700	4.18

The polymer shown in figure 2-16 has been precipitated in a methanol/HCl mixture. This removes lower molecular weight fractions from the sample leading to a narrower polymer Mn value and sharper peaks should be expected. Figure 2-16 clearly shows a smoother TGA trace with 2 sharper peaks now observable at ~240-270 °C and at 300-350 °C. The first peak shows the presence of an unsaturated end group. In addition the transition at 300-350 °C is likely to be both saturated end groups and main chain scission. The region 170-220 °C shows no peak indicating no weak head to head linkages which would be expected in a free radical reaction. The evidence suggests that this is not a typical free radical polymerisation reaction but may occur by a different mechanism. If the reaction proceeded by an anionic polymerisation

mechanism a TGA trace should only show a saturated head to tail end group peak at 300-360 °C. Alternatively if the mechanism involves chain transfer then only a saturated end group peak at ~360 °C would be present. From the evidence available it suggests that neither of these mechanisms is occurring uniquely.

2.2.9. Control polymerisation of MMA using *(A)* and ethyl-2-bromoisobutyrate

1) The attempted polymerisation of methyl methacrylate using *(A)* in THF.

This experiment was carried out to test whether polymerisation of MMA would take place in the presence of *(A)* without ethyl-2-bromoisobutyrate. A quantity of *(A)* in THF was added to MMA, polymerisation was carried out at 50 °C for 24 hours and the reaction solution examined by SEC. Table 2-18 shows the quantities used.

Table 2-18 Table of quantities

Experiment	*(A)* moles	MMA moles	Ratio [A]:[MMA]
19	1.05×10^{-3}	4.68×10^{-2}	1:45
20	9.1×10^{-4}	4.68×10^{-2}	1:50

The results from these experiments indicated that no polymerisation occurred.

2) Attempted polymerisation of methyl methacrylate using ethyl-2-bromoisobutyrate in THF

This control experiment was carried out to determine if polymerisation is possible using only the initiator and monomer in a THF solution. A quantity of MMA is added to a solution of initiator in THF, giving a ratio of [Init]:[MMA] of 1:100. The reaction was carried out at 50 °C for 24 hours, after this time a sample was removed and

examined by SEC to see if polymerisation had taken place. No polymerisation was found to have occurred.

These control experiments indicate that present in these reactions must be both *(A)* and ethyl-2-bromoisobutyrate with MMA. If only one of these is present with the monomer then no polymer will be formed. This suggests that the mechanism must involve *(A)* reacting with the alkyl halide to allow the polymerisation of MMA.

2.3. Conclusions

This chapter has discussed the formation of some novel chromium compounds, *(A)* & *(B)* prepared from $CrCl_3(THF)_3$ and zinc. *(A)* has been used to mediate polymerisation of MMA in the presence of an initiator, ethyl-2-bromoisobutyrate, acting as R-Br. *(B)* was prepared and analysed by x-ray crystallography to help determine the polymerisation mechanism. Thermal gravimetric analysis was carried out on PMMA samples prepared using this system. Thermal polymerisation has been ruled out by TGA, as has conventional free radical polymerisation.

The polymerisation reaction is likely to initiated by the abstraction of a halogen atom from the initiator (R-Br) or *(A)*. Following this, propagation of monomer and termination by disproportionation occurs, this would account for the terminally unsaturated end groups found by TGA, this mechanism is shown in figure 2-17.

Figure 2-17 Proposed polymerisation mechanism

$$R-Br \longrightarrow R\cdot + Br\cdot \qquad \textit{decomposition of initiator}$$
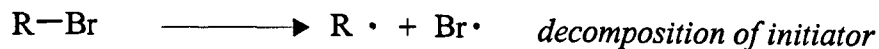
[Decomposition caused by atom transfer with *(A)*]

initiation of monomer

propagation
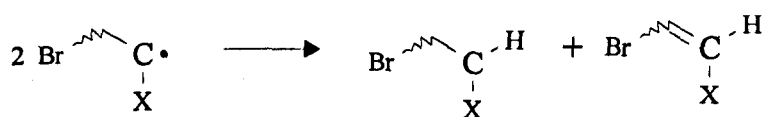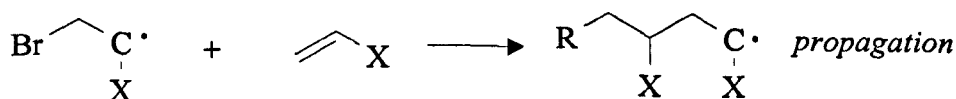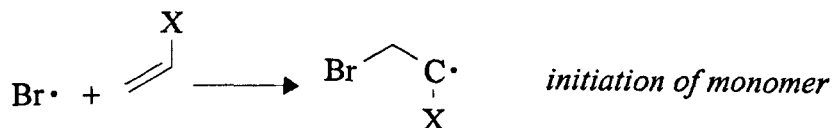
termination by disproportionation

[Termination by this method would give unsaturated and saturated end groups]

The low yields of PMMA obtained are due to the high rate of termination, in addition the difficulty of initiation by this method. The equilibrium of initiation lies with the formation of a stable compound, *(B)*, rather than initiation of monomer. Experiments showed that if large quantities of initiator were used this resulted in low yields, probably due to large quantities of the stable compound *(B)* being formed. Only where low ratios of *(A)* with initiator were used did yields rise. As increased initiator probably resulted in increased termination reactions. Lower amounts of initiator suggest a greater probability of *(A)* removing a halogen atom and then the halogen initiating polymerisation of MMA.

2.4. References

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Chapter 3

Polymerisation of MMA utilising

(A) with Schiff base ligands in

conjunction with alkyl halides

3. Polymerisation of MMA utilising (A) with Schiff base ligands in conjunction with alkyl halides

3.1. Introduction

In recent years progress has been made investigating living radical polymerisation[1]. Transition metal compounds have been used to form carbon to carbon bonds by organic chemists for many years, a review by Iqbal et al[2] discusses the transition metal free-radical reactions in organic synthesis and the progress made by these methods. The review discusses both oxidative and reductive processes using the following metals; titanium, vanadium, manganese, iron, cobalt, copper, niobium, ruthenium and chromium. This development has taken place over the last ten years, it has shown that free radical reactions are, under certain conditions controllable. Recently there has been the emergence of transition metal based radical reactions, this has been largely due to the work of Kharasch[3],Minisci[4] and Kochi[5], who showed that carbon-centred radicals can be generated using organometallic reagents. Transition metal-promoted reactions of carbon centred radical may be divided into oxidative reactions and reductive reactions (section 1.4.1.1).

3.2. Results and Discussion

This chapter discusses work carried out using the chromium-zinc complex *(A)* prepared in chapter 2. A quantity of *(A)* was reacted with nitrogen bonding Schiff base ligands under a nitrogen atmosphere to form a new series of compounds, the reactions of these complexes with methyl methacrylate were then investigated to study polymerisation reactions and investigate the possibility of controlled polymerisation occurring. Crystallographic data and discussion of *(A)* can be found in section 2.2.2. This compound has been utilised in further reactions during this chapter.

3.2.1. Preparation of some unusual ligands

Two classes of ligand compounds were prepared, one based on a diazabutadiene structure, commonly called a DAB ligand, the second is based on a 2-pyridinecarbaldehyde centre (PCA). Figure 3-1 is a representation of a R-DAB ligand, figure 3-2 shows a R-PCA ligand.

Figure 3-1 A DAB ligand
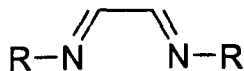
Figure 3-2 A PCA ligand
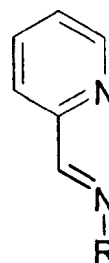
In both cases the alkyl group can be changed very easily to include a wide range of chain lengths and structures. Ligands were prepared via suitable modifications to the published procedure, R-PCA by the method of Bähr et. al [6], R-DAB by that of Emmons[7].

The products formed are yellow coloured oils, unless stated otherwise. An easily prepared example of one of these ligands is the "propyl-PCA ligand (section 6.3). This is prepared from propylamine and 2-pyridinecarbaldehyde. These alkyl-PCA compounds and alkyl-DAB compounds are used frequently as ligands in this chapter because of their ability to stabilise low oxidation state metals and to solubilise metal compounds.

3.2.2. The reaction of (A), dipyridine, methyl methacrylate with ethyl-2-bromoisobutyrate.

Dipyridine has been used previously to stabilise low oxidation states of metal complexes due to its π-orbitals. (A) has been shown to have chromium in both +2 and +3 oxidation states. The presence of dipyridine (DIPY) is expected to help form a stable low oxidation state compound. In turn it is thought likely that this can then react in the presence of initiator and monomer, the aim is to polymerise methyl methacrylate.

A quantity of (A) is dissolved in THF, this is added to a solution of dipyridine in THF, finally a mixture of MMA with initiator is added. The reaction mixture is then left at room temperature for 24 hours. General experimental details are in section 6.6.3 The quantities used and the results obtained are shown in table 3-1.

Table 3-1 Quantities used and results obtained

Experiment	(A) g	(A) moles	DIPY moles	MMA moles	R-Br (initiator) moles	Ratio of [A]:[Init]:[Mon]
1	0.1	2.1×10^{-4}	8.4×10^{-4}	4.67×10^{-2}	3.41×10^{-3}	1:16:220
			Yield %	Mn	Mw	PDi
			< 10	41,500	91,900	2.21

(A) in THF solution is blue, upon addition of DIPY this solution immediately becomes dark purple, addition of MMA and ethyl-2-bromoisobutyrate results in no further colour changes. In chapter 2 work was carried out to investigate the reaction of *(A)* with ethyl-2-bromoisobutyrate and methyl methacrylate, the results of that work indicated that polymerisation took place. This experiment has shown that the addition of dipyridine has not hindered that process, PMMA is still formed, the yield though is still low.

Identification of the reactive species was not possible at this stage. Further reactions could now be carried out using different ligands. To investigate the effect on the reaction and the control of any polymer formed using this system.

3.2.3. The attempted polymerisation of methyl methacrylate using *(A)* with ᵗbutyl diazabutadiene ('Bu-DAB) and ethyl-2-bromoisobutyrate.

The previous section (3.2.2) explained the reaction of dipyridine with *(A)* and initiator and monomer, this resulted in the polymerisation of MMA. The yields obtained during the course of the reaction were low. The following work investigates the use of an R-DAB ligand in this process. This ligand has been chosen due to its different electronic properties compared to dipyridine. The solution was heated to 70 °C for 10 hours, a sample was then removed for analysis by SEC.

Figure 3-3 Structure of t-butyl diazabutadiene

$$t\text{-Bu}-N \quad\quad N-t\text{-Bu}$$
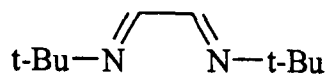
Tables 3-2 shows the quantities of materials used in this reaction.

Table 3-2 Quantities used.

Experiment	(A) moles	'Bu-DAB moles	R-Br (initiator) moles	MMA moles	Ratio [A]:[Init] :[MMA]
2	6.51×10^{-4}	3.11×10^{-3}	6.8×10^{-3}	9.3×10^{-2}	1:10:150

The results obtained by SEC show that no polymerisation occurs. This should be compared to the previous example, where dipyridine was used and polymerisation did occur. As polymerisation does not take place it was decided to analyse the green compound formed to investigate why polymerisation did not occur.

Crystals of the green compound were grown in THF, these were examined by x-ray crystallography (section 6.2.3 and 6.4.2). Analysis of these results lead to the elucidation of an unusual chromium complex (C), figure 3-4.

Full crystallographic data for (C) can be found in appendix A.

Figure 3-4 Crystal structure of (C)
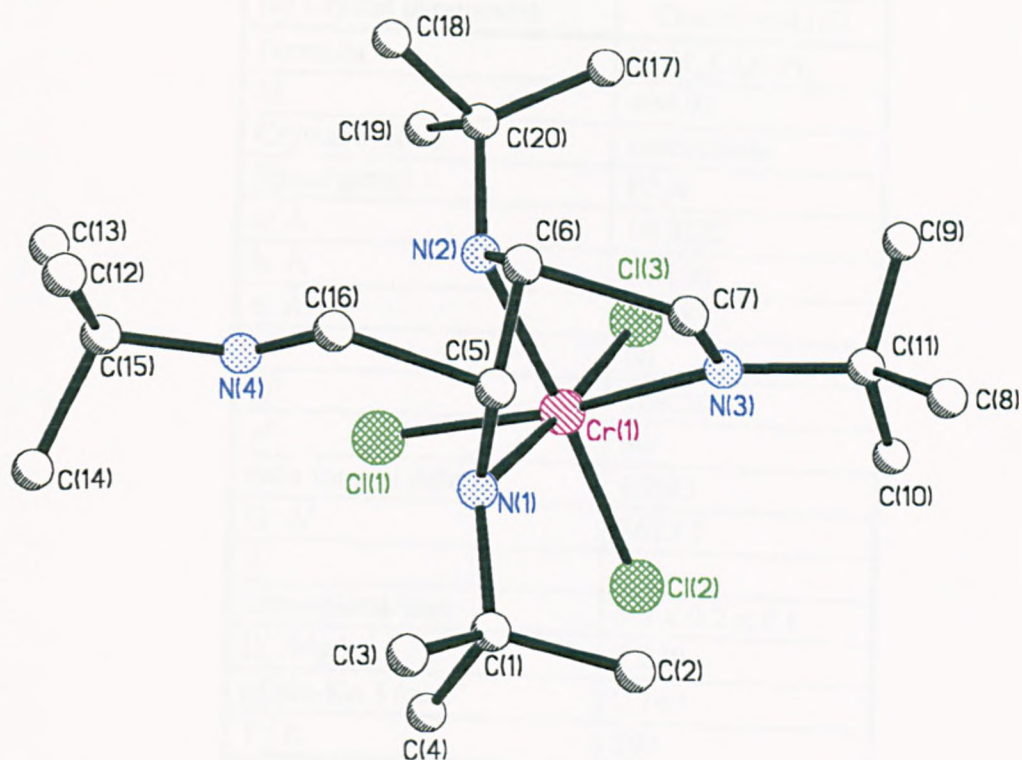
Table 3-3 shows summarised crystallographic data for this compound, labelled *(C)*.

Table 3-3 Summarised crystallographic data for *(C)*

(a) Crystal parameters	Compound *(C)*
Formula	$C_{20}H_{40}Cl_3CrN_4$
M	494.91
Crystal system	monoclinic
Space group	$P2_1/c$
a/ Å	10.3822
b/ Å	19.100
c/ Å	14.2833
α/ °	90
β/°	109.267
γ/°	90
refls for cell detm.	10523
U/ Å^3	2673.7
Z	4
dimensions /mm	0.2 x 0.2 x 0.1
D_c /Mg/m^3	1.229
μ(Mo-Kα) /mm^{-1}	0.740
T / K	293
(b) data collection [a]	
Data collected h	-13 to 10
k	-22 to 24
l	-16 to 19
Total refls.	10523
Independent refls.	3485
Ind. Observed refls. [$F_o \geq 4\sigma(F_o)$]	1819
θ range/°	1.85 to 22.50
F (000)	1052
(c) refinement	
R [b]	0.1876
wR2 [c]	0.2440
S	1.166
Δ /eÅ^{-3} (max, min) [d]	0.968 and -0.370
T max, min [e]	0.9576 and 0.7557

Legend for Table 3-3.

[a] Data collected on a Siemens 3 circle diffractometer equipped with a SMART CCD area detector; graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). [b] $R = \Sigma |F_o - F_c|/\Sigma F_o$ (for $F_o \geq 4\sigma(F_o)$). [c] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$ for all data. [d] peaks of unassigned residual electron density. [e] By SADABS. [f] $w^{-1} = \sigma^2(F_o^2) + aP + bP$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$, where $\max(F_o^2,0)$ indicates that the larger of F_o^2 or 0 is taken, a and b are values set by the program.

A representation of (C) is shown in figure 3-5.

Figure 3-5 Representation of (C)
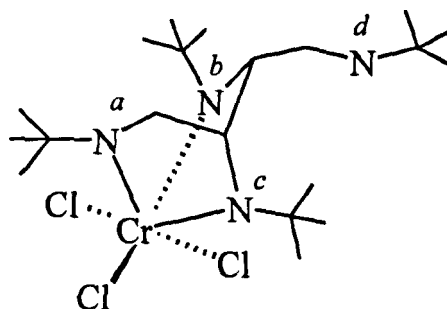
Table 3-4 shows some selected bond lengths and angles found in (C), these are compared to similar chromium compounds (table 3-5).

Table 3-4 Selected bond angles and lengths for (C)

Atoms	Bond length [Å]
Cr(1)-N(3)	2.146(7)
Cr(1)-N(2)	2.158(6)
Cr(1)-N(1)	2.204(7)
Cr(1)-Cl(2)	2.302(3)
Cr(1)-Cl(3)	2.307(3)
Cr(1)-Cl(1)	2.325(3)
N(1)-C(5)	1.471(11)
N(1)-C(1)	1.534(12)
N(2)-C(20)	1.524(11)
C(5)-C(6)	1.396(13)

Atoms	Bond angles [°]
N(3)-Cr(1)-N(2)	82.9(3)
N(3)-Cr(1)-N(1)	85.2(3)
N(2)-Cr(1)-N(1)	74.6(3)

Atoms	Bond angles [°]
N(2)-Cr(1)-Cl(2)	172.2(2)
N(3)-Cr(1)-Cl(3)	173.1(2)
Cl(2)-Cr(1)-Cl(3)	89.11(12)
N(3)-Cr(1)-Cl(1)	166.8(2)
N(1)-Cr(1)-Cl(1)	85.6(2)

Table 3-5 Selected bond angles and lengths for related compounds, $MCl_3(THF)_3$

```
        Cl   Cl
          \  |
    THF — M — THF
          |  Cl
        THF
```

M	M-Cl_{ax}	Average M-Cl_{eq}	M-O_{ax}	Average M-O	Cl_{ax}-M-O_{ax}	Average Cl_{ax}-M-Cl_{eq}	Average Cl_{ax}-M-O_{eq}
Sc	2.406(4)	2.418(3)	2.236(8)	2.156(9)	179.5(3)	92.8(3)	96.4(3)
Ti	2.336(5)	2.351(5)	2.183(2)	2.097(8)	176.8(6)	94.0(8)	91.6(4)
V	2.297(2)	2.330(4)	2.102(3)	2.062(8)	179.64(11)	92.0(5)	93.7(1)
Cr	2.283	2.310(3)	2.077(4)	2.01(2)	179.8(1)	90.9(4)	93.9(0)
Source:-Research by Cotton et al[8]							

Comparing the chromium - chlorine bonds in *(C)* with the above example show very similar bond lengths, the distances found in *(C)*, this demonstrates that there are no unusual bonding properties between chromium and chlorine.

Atoms	Bond angles [°]
N(3)-Cr(1)-N(2)	82.9(3)
N(3)-Cr(1)-N(1)	85.2(3)
N(2)-Cr(1)-N(1)	74.6(3)
N(2)-Cr(1)-Cl(2)	172.2(2)
N(3)-Cr(1)-Cl(3)	173.1(2)
Cl(2)-Cr(1)-Cl(3)	89.11(12)
N(3)-Cr(1)-Cl(1)	166.8(2)
N(1)-Cr(1)-Cl(1)	85.6(2)

The angles in complex *(C)* are not demonstrative of a six co-ordinate octahedral complex. The bond angles shown are all slightly distorted, for example N(2)-Cr(1)-N(1) is 74.6 °, compared with 90 ° for an octahedral complex. This is due to the combination of chlorine and nitrogen bonding to the metal centre and the steric

hindrance introduced as a result of the large dimerised ligand. An important feature of this compound is the unusual ligand bonding to the chromium metal centre, a dimerised 'Bu-DAB, figure 3-6.

Figure 3-6 Representation of new "dimerised" DAB ligand and 'Bu-DAB
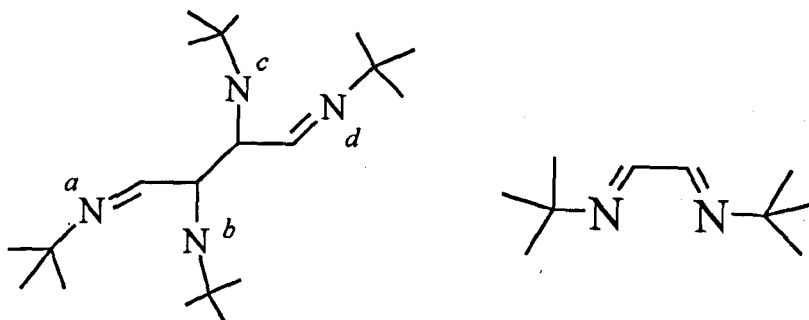
The reaction of *(A)* with 'Bu-DAB has caused the ligand to be reduced and become a new ligand bonding to chromium. Additionally, one end of the chain is not bound, this can then result in different stereoisomers being formed. Kaupp and co-workers[9] reported on the preparation of a zinc-DAB complex, (figure 3-6), the distances found in 'Bu-DAB can be compared to those found in this work.

Figure 3-7 Representation of ZnMe$_2$-(^{t}Bu-DAB)
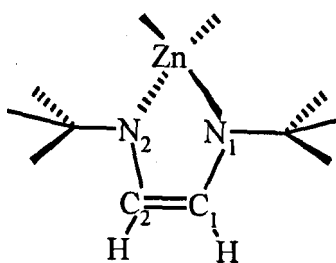
Table 3-6 Selected bond lengths for ZnMe$_2$-(t-Bu-DAB)

Atoms	Bond length [Å]
Zn-N(1)	2.27
N(1)-C(1)	1.25
C(1)-C(2)	1.50

The reaction reported by Kaupp shows, as a side reaction, the dimerisation of 'Bu-DAB, he describes this process as a "collapse" product leading through "escape" of a radical to the formation of a radical product which is in equilibrium with its CC coupled dimer. This coupled dimer is almost identical to the dimerised ligand found in this work. It is thought that the presence of zinc in this reaction has caused the ligand to become dimerised. The presence of chromium has resulted in the dimerisation of 'Bu-DAB, chromium stabilises this product.

3.2.4. Polymerisation of methyl methacrylate using *(A)* with alkyl 2-pyridinecarbaldehyde ligands.

The procedure unless stated otherwise uses a quantity of *(A)* in THF, added to this is a solution of ligand, followed by monomer and subsequently alkyl halide. The temperature is raised, if necessary, and the reaction left for up to 3 days (section 6.6.2). The blue coloured solution immediately becomes dark red or brown upon addition of the ligand. This colour change is markedly different from the reaction carried out in section 3.2.3, where the solution became green upon addition of the 'Bu-DAB ligand.

3.2.4.1. Polymerisation of MMA with *(A)* with ⁿBu-PCA

This reaction was carried out to investigate the suitability of alkyl-PCA ligands with *(A)* and the polymerisation of MMA. The quantities used and results for this reaction are shown in tables 3-7 and 3-8.

Table 3-7 Quantities used

Experiment	(A) moles	ligand moles	MMA moles	R-Br (initiator) moles	Ratio of [A] : [Init] : [Mon]
3	2.47×10^{-4}	6.50×10^{-3}	1.6×10^{-1}	7.5×10^{-4}	1:6:650
4	2.47×10^{-4}	6.50×10^{-3}	1.6×10^{-1}	1.50×10^{-3}	1:12:650

Table 3-8 Results obtained

Experiment	Time	% Yield	Mn	Mw	PDi
3	1 hour	-	57,000	118,000	2.06
	3 hour	-	54,000	108,000	1.99
	24 hour	100	47,000	141,000	2.60
4	2 hour	-	38,000	66,000	1.80
	24 hour	100	37,000	77,000	2.07

The reaction solution is red after addition of all materials, for the first 10 minutes. Following this the reaction mixture changes to a dark brown solution for the remainder of the reaction. This is an important result as it has shown that addition of an R-PCA ligand to (A) improves the yield of the reaction, raising it to quantitative conversion. This figure compares to only ~10 % - 30 % in the presence of alkyl halide, or in the presence of DIPY.

At 100 % conversion Mn should be 65,000, as the ratio of [Cr]: [MMA] is 1:650, if the experiment proceeded by a living polymerisation mechanism[10]. The ratio of [Init] to [MMA] is only 1:100 and 1:50 which would result in Mn of 10,000 or 5,000 respectively. The experimental Mn of 47,000 and 37,000 is lower than expected. Mn does not increase with conversion and PDi obtained is approximately 2.

The experiment was repeated varying the quantities of (A), ligand, monomer and initiator, table 3-9, table 3-10 shows the results obtained from these reactions.

Table 3-9 Quantities used

Experiment	(A) moles	ligand moles	MMA moles	R-Br (initiator) moles	Ratio of [A] :[Init] : [Mon]
5	2.1×10^{-4}	3.1×10^{-3}	5.3×10^{-2}	1.9×10^{-3}	1:9:250
6	4.2×10^{-4}	3.1×10^{-3}	5.3×10^{-2}	1.9×10^{-3}	1:4:125
7	4.2×10^{-4}	3.1×10^{-3}	5.3×10^{-2}	1.9×10^{-3}	1:4:125

Table 3-10 Results obtained

Experiment	Time	% Yield	Mn	Mw	PDi
5	30 min	2.9	28,000	46,000	1.67
	60 min	3.1	20,000	38,000	1.92
	90 min	3.6	20,000	35,000	1.78
	210 min	4.0	25,000	42,000	1.68
	18 hours	22.0	42,000	85,000	2.02
	24 hours	24.9	40,000	82,000	2.05
6	30 min	6.4	35,000	60,000	1.72
	60 min	48	33,000	54,000	1.66
	90 min	12	31,000	54,000	1.72
	210 min	28	28,000	50,000	1.78
	18 hours	45.5	35,000	74,000	2.11
	24 hours	46	31,000	73,000	2.31
7	30 min	7.0	5,000	11,000	1.97
	60 min	5.5	10,000	13,000	1.29
	90 min	3.9	11,000	14,000	1.31
	210 min	5.4	11,000	16,000	1.46
	18 hours	29	28,000	82,000	2.89
	24 hours	30	27,000	78,000	2.89

The data obtained from these experiments can be plotted, Mn as a function of

conversion, figure 3-8.

Figure 3-8 Plot of Mn verses % conversion for experiments 5, 6 and 7
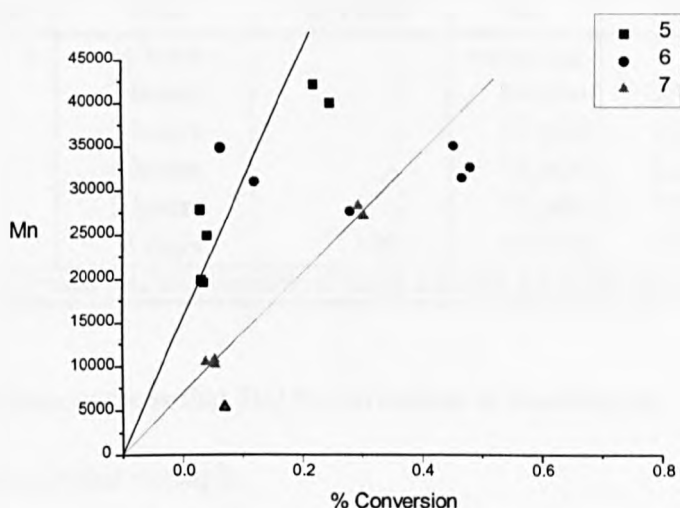
Mn does not appear to be a linear function of conversion according to the data obtained. Mn does increase with percentage conversion, polydispersities are still relatively large.

A further experiment was carried out. In this example *(A)* in THF with the "Bu-PCA ligand gave a purple heterogeneous solution, this was then filtered, leaving a homogeneous solution. Only then was MMA and ethyl-2-bromoisobutyrate added [MMA 50 % w/w], the reaction was carried out at 50 °C for 3 days. Samples were removed at intervals and examined by SEC, tables 3-11 and 3-12 contain experimental data.

Table 3-11 Quantities used

Experiment	*(A)* moles	ligand moles	MMA moles	R-Br (initiator) moles	Ratio of [*A*]:[Init] : [Mon]
8	1.68×10^{-4}	6.50×10^{-3}	5.3×10^{-2}	1.93×10^{-3}	1:11:300

Table 3-12 Results obtained

Experiment	Time	% Yield	Mn	Mw	PDi
8	½ hour	-	monomer		
	2 hours	-	14,000	20,000	1.42
	3 hours	-	17,000	23,000	1.39
	4 hours	-	15,000	22,000	1.44
	5 hours	-	15,000	23,000	1.51
	3 days	100	35,000	65,000	1.90
Conversion data not obtainable at earlier intervals due to the size of samples removed					

This reaction demonstrates that 100 % conversion is possible, the polydispersity of the product is lower in this example.

3.2.4.2. Reaction of *(A)* with ^{n}Bu-PCA, ethyl-2-bromoisobutyrate and MMA in bulk monomer

A quantity of ^{n}butyl-2-pyridinecarbaldehyde is added to *(A)*, followed by MMA then ethyl-2-bromoisobutyrate at 50 °C. Table 3-13 and table 3-14 show the results obtained from this series of reactions.

Table 3-13 Quantities used

Experiment	*(A)* moles	ligand moles	MMA moles	R-Br (initiator) moles	Ratio of [*A*]:[Init] : [Mon]
9	5.26×10^{-4}	1.62×10^{-3}	5.3×10^{-2}	1.1×10^{-3}	1:2:100
10	5.26×10^{-4}	1.62×10^{-3}	5.3×10^{-2}	2.3 x 10-3	1:4:100
11	5.26×10^{-4}	1.62×10^{-3}	5.3×10^{-2}	1.1×10^{-3}	1:2:100
12	5.26×10^{-4}	1.62×10^{-3}	5.3×10^{-2}	2.3 x 10-3	1:4:100
13	5.76×10^{-4}	6.50×10^{-3}	5.3×10^{-2}	1.9×10^{-3}	1:3:100
14	3.15×10^{-4}	6.50×10^{-3}	5.3×10^{-2}	1.9×10^{-3}	1:6:150

Table 3-14 Results of reaction

Experiment	Time / minutes	% Yield	Mn	Mw	PDi
9	180	100	84,000	139,000	1.65
10	180	100	70,000	154,000	2.18
11	180	100	70,000	99,000	1.91
12	180	100	59,000	118,000	1.99
13	240	100	53,000	150,000	2.84
14	240	100	43,000	108,000	2.51

These results show a marked improvement in the efficiency of the reaction. In these examples the reaction is complete in less than 4 hours, this can be compared to ~24 hours if carried out in the presence of THF as solvent.

These results indicate that under these conditions, although there is quantitative yield, there is no control over the molecular weight of the polymers formed. In addition the polydispersity is relatively high, at ~2 for all samples examined.

3.2.4.3. Reaction of (A) with ⁿpropyl-2-pyridinecarbaldehyde imine in THF with methyl methacrylate and ethyl-2-bromoisobutyrate.

A quantity of (A) is reacted with ⁿpropyl-2-pyridinecarbaldehyde imine in THF, this forms a dark purple solution. MMA is then added, followed by ethyl-2-bromoisobutyrate. The temperature of the reaction is raised to 60 °C and the reaction left to proceed for up to 3 days. (Modified from 6.6.3). Table 3-15 show the quantities of materials used, table 3-16 show the results obtained during the reaction.

Table 3-15 Quantities used

Experiment	(A) moles	ligand moles	MMA moles	R-Br (initiator) moles	Ratio of [A]:[Init] : [Mon]
15	2.80×10^{-4}	6.50×10^{-3}	5.3×10^{-2}	1.35×10^{-3}	1:5:200
16	2.80×10^{-4}	6.50×10^{-3}	5.3×10^{-2}	1.35×10^{-2}	1:5:200
17	2.80×10^{-4}	1.3×10^{-2}	1.6×10^{-1}	1.35×10^{-3}	1:5:600

After a period of 24 hours 2 mL of monomer (2.13×10^{-2} moles) were added to 15, 16 and 17. The reaction was then left to proceed for a further 3 days with the extra monomer. The purpose of this was to study the effect on the molecular weight and its distribution of the polymer sample formed.

Table 3-16 Results obtained

Experiment	Time	Mn	Mw	PDi
15	90 min	62,000	132,000	2.14
	4 hours	63,000	150,000	2.38
	24 hours	69,000	141,000	2.05
	*3 days	99,000	301,000	3.04
16	90 min	66,000	147,000	2.22
	4 hour	59,000	133,000	2.23
	24 hours	41,000	113,000	2.74
	*3 days	30,000	83,000	2.82
17	90 min	44,000	103,000	2.33
	4 hours	69,000	133,000	1.94
	24 hours	52,000	120,000	2.29
	*3 days	28,000	95,000	3.44
			* extra monomer added	

The results in table 3-17 suggest that the reaction is not "living", as Mn does not increase with time (results do not show conversion). After the addition of the second portion of MMA the Mn for the experiments increases in some cases. The polydispersity increases in the final sample. This suggests that the additional monomer added has reacted with the catalyst system, but probably not with the

polymer chains already produced. This has resulted in new chains being formed and a broader polydispersity being the end result.

Tables 3-17 and 3-18 show repeat experiments, with THF as solvent, ⁿPropyl-PCA has been used as it will have different electronic and solubility properties compared to ⁿButyl-PCA, used previously.

Table 3-17 Quantities used

Experiment	(A) moles	ligand moles	MMA moles	R-Br (initiator) moles	Ratio of [A]:[Init] : [Mon]
18	1.05×10^{-3}	6.50×10^{-3}	3.2×10^{-2}	1.93×10^{-3}	1:2:30
19	8.41×10^{-4}	6.50×10^{-3}	6.4×10^{-2}	1.93×10^{-3}	1:2:15
20	5.28×10^{-4}	6.50×10^{-3}	1.06×10^{-2}	1.93×10^{-3}	1:4:20
21	6.31×10^{-4}	6.50×10^{-3}	5.3×10^{-2}	1.93×10^{-3}	1:3:84
22	4.21×10^{-4}	6.50×10^{-3}	5.3×10^{-2}	1.93×10^{-3}	1:5:125

Table 3-18 Results obtained

Experiment	Time	% Yield	Mn	Mw	PDi
18	24 hours	60	31,900	84,100	2.64
19	24 hours	50	77,700	258,000	3.32
20	24 hours	80	17,900	34,900	1.94
21	72 hours	80	65,400	167,400	2.56
22	72 hours	100	95,900	191,800	2.00

The results all show that despite a low ratio of [monomer] to [(A)], and [monomer] to [initiator] the Mn obtained is still fairly high. Mn is not less than 10,000 as would have been expected using these ratios. Further work was carried out, tables 3-19 and 3-20 show the quantities used and the results obtained in this example.

Table 3-19 Quantities used

Experiment	(A) moles	ligand moles	MMA moles	R-Br (initiator) moles	Ratio of [A]:[Init] : [Mon]
23	7.07×10^{-4}	6.50×10^{-3}	8.0×10^{-2}	7.7×10^{-4}	1:1:110
24	7.26×10^{-4}	6.50×10^{-3}	8.0×10^{-2}	1.5×10^{-3}	1:2:110

Table 3-20 Results obtained

Experiment number	Time	% Yield	Mn	Mw	PDi
23	1 hour	-	25,000	45,000	1.80
	3 ½ hours	-	27,000	52,000	1.94
	21 hours	-	26,000	54,000	2.07
	45 hours	100	30,000	57,000	1.91
24	1 hour	-	33,000	73,000	2.21
	3 ½ hours	-	35,000	82,000	2.34
	21 hours	-	36,000	88,000	2.45
	45 hours	100	38,000	88,000	2.29
Conversion data not available at earlier times due the size of the samples removed					

Mn remains similar over the course of the reaction and the polydispersity for the reaction has remained broad. Previous experiments have been carried out *in situ*. In the following experiment the catalyst solution is filtered prior to the addition of initiator and MMA. The purpose of this is two fold, one to remove the insoluble materials present and secondly to remove other products, such as any insoluble zinc products in the mixture.

A quantity of *(A)* (0.5 g) in THF (20 mL) is reacted with propyl-PCA ligand (1 mL), this dark purple slurry is filtered, leaving a purple solution. The solution is then reacted with MMA and ethyl-2-bromoisobutyrate, at 50 °C for 3 days, modified from 6.6.3. This experiment uses "relative" amounts of filtered *(A)* with propyl-PCA ligand to study the effects on Mn. The actual quantity of reactive species is unknown

due to only a portion of the filtrate being removed, subsequently only a portion of catalyst solution is actually used.

Table 3-21 Quantities used

Experiment	(A) in THF mL	proportion used	MMA moles	R-Br (initiator) moles	Ratio of [Init] : [Mon]
25	1	1 x	7.8×10^{-2}	3.9×10^{-4}	1:200
26	5	5 x	7.8×10^{-2}	3.9×10^{-4}	1:200
27	10	10 x	7.8×10^{-2}	3.9×10^{-4}	1:200

Table 3-22 Results obtained

Experiment	Time	% Yield	Mn	Mw	PDi
25	3 days	<5	121,000	232,000	1.91
26	3 days	50	213,000	473,000	2.22
27	3 days	100	46,000	165,000	3.61

The least amount of active chromium compound gives only a low yield and the yield appears to be in proportion to the amount of chromium solution used. Mn obtained are still high and do not differ by the factors expected of 1 : 5: 10, if linearly related to the quantity of chromium catalyst.

3.2.4.4.The reaction of (A) with ethyl-2-pyridinecarbaldehyde imine in THF with methyl methacrylate and ethyl-2-bromoisobutyrate

The following experiment investigated the use of a small chain alkyl-PCA ligand, ethyl at 30 °C, table 3-23 and table 3-24 show the results and quantities used.

Table 3-23 Quantities used

Experiment	*(A)* moles	ligand moles	MMA moles	R-Br (initiator) moles	Ratio of [*A*]:[Init] : [Mon]
28	5.28×10^{-4}	2.57×10^{-3}	7.0×10^{-2}	6.8×10^{-4}	1:1.3:132
29	5.13×10^{-4}	2.57×10^{-3}	7.0×10^{-2}	6.8×10^{-4}	1:2.6:136
30	5.30×10^{-4}	2.57×10^{-3}	7.0×10^{-2}	6.8×10^{-4}	1:5:132

Table 3-24 Results obtained

Experiment	Time	% Yield	Mn	Mw	PDi
28	3 days	<10	44,000	101,000	2.29
29	3 days	<10	42,000	93,000	2.24
30	3 days	<10	45,000	119,000	2.67

The yield obtained from this reaction has dropped considerably through the use of a small alkyl chain. This is likely to have been caused by a lack of stability in the resulting catalyst compound.

3.2.5. Polymerisation reaction of *(A)* with more unusual R-DAB and R-PCA ligands

3.2.5.1. Reaction of *(A)* with 2,6-ᵗButyl-phenyl-DAB in THF with methyl methacrylate and ethyl-2-bromoisobutyrate.

The ligand examined in this example(figure 3-9) is sterically hindered and was examined to investigate the effect on percentage yield and Mn in the reaction system.

Figure 3-9 Structure of 2,6-ᵗButyl-phenyl-DAB
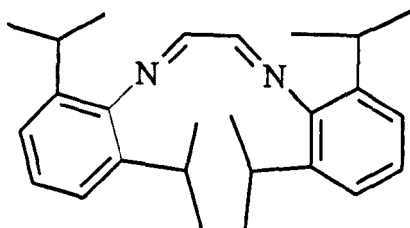
(A) is reacted with a solution of 2,6-'Butyl-phenyl-DAB in THF, this is then filtered to remove insoluble materials, then to portions of this catalyst solution quantities of MMA and ethyl-2-bromoisobutyrate are added. The temperature is then raised to 50 °C. Tables 3-25 and 3-26 show the quantities used and results obtained from this example.

Table 3-25 Quantities used

Experiment	*(A)* in THF mL	proportion used	MMA moles	R-Br (initiator) moles	Ratio of [Init] : [Mon]
31	1	1 x	4.7×10^{-2}	6.8×10^{-4}	1:70
32	0.1	0.1 x	4.7×10^{-2}	6.8×10^{-4}	1:70
33	10	10 x	4.7×10^{-2}	6.8×10^{-4}	1:70

Table 3-26 Results obtained

Experiment	Time	% Yield	Mn	Mw	PDi
31	3 days	0	monomer only		
32	3 days	2	57,000	233,000	4.11
33	3 days	0	monomer only		

The use of 2,6-'butyl-phenyl-DAB results in almost complete hindrance of the reaction as demonstrated by the low yields of PMMA.

This reaction was repeated using different quantities of catalyst and initiator. *(A)* (0.23 g) with ligand (0.35 g) in THF (30 mL) was filtered and portions removed for reactions with MMA and initiator, the reaction was carried out at 60 °C for 24 hours. Table 3-27 shows the quantities used, table 3-28 the results obtained from these reactions.

Table 3-27 Quantities used

Experiment	(A) in THF mL	proportion used	MMA moles	R-Br (initiator) moles	Ratio of [Init] : [Mon]
34	10	4 x	4.68 x 10⁻²	2.0 x 10⁻³	1:25
35	5	2 x	4.68 x 10⁻²	2.0 x 10⁻³	1:25
36	1	1 x	4.68 x 10⁻²	2.0 x 10⁻³	1:25

Table 3-28 Results obtained

Experiment	Time	% Yield	Mn	Mw	PDi
34	20 hours	~5	21,000	175,000	8.19
35	20 hours	~10	28,000	167,000	5.86
36	20 hours	~15	197,000	519,000	2.63

This reaction indicates that the use of 2,6-^{t}Butyl-phenyl-DAB dramatically lowers the yield. The molecular weights obtained are not controlled by the amount of chromium or initiator used in the reaction.

3.2.5.2. Reaction of *(A)* with phenyl-PCA in THF with methyl methacrylate and ethyl-2-bromoisobutyrate

Modified from 6.6.3, a quantity of *(A)* in THF is reacted with phenyl-PCA (figure 3-10), followed by MMA and ethyl-2-bromoisobutyrate. The quantities used are shown in table 3-29, the results obtained in 3-30.

Figure 3-10 Structure of Phenyl-PCA ligand
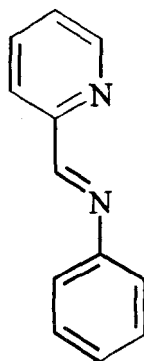
Table 3-29 Quantities used.

Experiment	*(A)* moles	ligand moles	MMA moles	R-Br (initiator) moles	Ratio of [*A*]:[Init] : [Mon]
37	2.1×10^{-4}	7.3×10^{-4}	4.68×10^{-2}	3.4×10^{-3}	1:16:220
38	2.1×10^{-4}	7.3×10^{-4}	4.68×10^{-2}	6.8×10^{-3}	1:32:222
39	2.1×10^{-4}	7.3×10^{-4}	4.68×10^{-2}	1.36×10^{-2}	1:64:222

Table 3-30 Results obtained

Experiment	Time	% Yield	Mn	Mw	PDi
37	40 hours	10	48,000	138,000	2.88
38	40 hours	0	monomer only		
39	40 hours	5	103,000	440,000	4.28

The effect of this ligand has been to dramatically lower the yield of the reaction when compared to the results obtained using ⁿButyl and ⁿPropyl-PCA ligands. This is likely to be due to a combination of steric hindrance and differing electronic properties.

3.2.5.3. Reaction of *(A)* with 3-methyl-phenyl-DAB in THF with methyl methacrylate and ethyl-2-bromoisobutyrate

Modified from 6.6.3, a quantity of *(A)* (0.346 g, 7.3×10^{-4} moles) is reacted with 3-methyl-phenyl-DAB (2.2×10^{-3} moles) (figure 3-11) in THF, to this is added MMA (7.2×10^{-2} moles) and ethyl-2-bromoisobutyrate (6.1×10^{-4} moles). The temperature is raised to 60 °C for 3 days. Table 3-32 indicates the results obtained from the reaction.

Figure 3-11 Structure of 3-methyl-phenyl-DAB
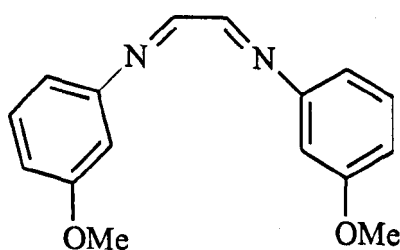
Table 3-31 Results obtained

Experiment	Time	% Yield	Mn	Mw	PDi
40	3 days	~5	13,000	30,000	2.38

The results obtained have shown that a poor yield is obtained when using an alkyl-DAB type ligand. The SEC results obtained have shown that the polydispersity is large at 2.38 with no control over the molecular weight of the polymer formed.

The experiments described in section 3.2.5 used a variety of large bulky Schiff base ligands in the reaction with (A), monomer with initiator. The experiments have shown the remarkable difference in results available by changing the ligand used in the reaction. Section 3.2.4 used straight chain alkyl-PCA ligands. The effect of this was to produce high yields with molecular weights obtained of around 30,000, however there was no real control over the molecular weights obtained from the reactions. Changing the ligand to an alkyl-DAB ligand has resulted, in all examples, poor yields. Ue of a straight chain alkyl-PCA ligand increases the yield dramatically. Bulky R-PCA ligands lowers this figure. In all examples no control over the molecular weight obtained has been achieved.

3.2.6. A comparison of initiators used in the reaction of (A) with propyl-2-pyridinecarbaldehyde imine, MMA and ethyl-2-bromoisobutyrate in THF

Matyjaszewski[11], Teyssié[12] and Percec[13] have reported investigations into the effect of changing the initiator in ATP reactions. This work looked at the effect of using two similar initiators. Figure 3-12 shows two examples the first is based on R-Br, the

second on R-Cl. Due to the difference in the bond strengths of C-Br and C-Cl bonds alone, a difference in the polymer results obtained should be noticeable.

Figure 3-12 Structure of ethyl-2-bromosisobutyrate and ethyl 2-chloropropionate

$$RMM = 195 \qquad RMM = 136$$
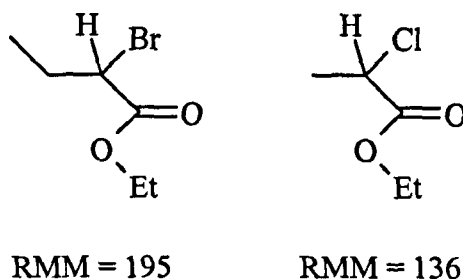
A carbon-chlorine bond will be stronger than a carbon bromine bond. This should lead to the reaction involving the chlorine initiator the reaction being slower and more control over the reaction might be obtained, compared to the bromine initiator. Table 3-32 shows the quantities used and table 3-33 shows the results obtained.

A quantity of *(A)* in THF is reacted with propyl-PCA, this catalyst solution is separated and then to (a) a quantity of MMA with R-Br is added, to (b), MMA and R-Cl initiator. The reaction is carried out at 60 °C for 24 hours. Modified from section 6.6.3.

Table 3-32 Quantities used

Experiment	*(A)* moles	ligand moles	MMA moles	R-X (initiator) moles	Ratio of [A]:[Init] : [Mon]
41A(R-Br)	4.2×10^{-4}	3.16×10^{-3}	7.7×10^{-2}	6.8×10^{-4}	1:1.5:180
41B(R-Cl)	4.2×10^{-4}	3.16×10^{-3}	1.0×10^{-1}	8.8×10^{-4}	1:2:240
42A(R-Br)	3.1×10^{-4}	9.2×10^{-4}	3.0×10^{-2}	2.7×10^{-4}	1:3:1:100
42B(R-Cl)	4.2×10^{-4}	1.3×10^{-3}	4.2×10^{-2}	4.3×10^{-4}	1:3:1:100

Table 3-33 Result obtained

Experiment	Time	% Yield	Mn	Mw	PDi
41A(R-Br)	30 min	-	22,000	34,000	1.57
	2 ½ hours	-	37,000	102,000	2.77
	24 hours	100	66,000	267,000	4.03
41B(R-Cl)	2 ½ hours	-	monomer		
	24 hours	<5	79,000	149,000	1.89
42A(R-Br)	24 hours	80	28,000	80,000	2.84
42B(R-Cl)	24 hours	0	monomer		

This experiment indicates that the use of the chlorine initiator slows the reaction down considerably, as expected due to a stronger carbon-halogen bond. The results do not show greater control over Mn being obtained. It is concluded that the use of the chlorine based initiator slows the reaction down to such an extent that the reaction is not viable.

3.2.7. Investigation of the reactions of chromium(II) chloride with Schiff base ligands, MMA and alkyl-halide initiators.

Work in this chapter so far has focused on reactions involving the unusual chromium-zinc complex prepared, *(A)*. Control experiments have determined that zinc does not take part in this reaction. Its presence in the reaction though, has been unavoidable due to the method of preparation of the low oxidation state chromium compound and its subsequent reaction with nitrogen ligands. The remaining work in this chapter investigates the reactions of chromium(II) chloride with nitrogen bonding alkyl-PCA ligands, MMA and alkyl-halides. Chromium(II) chloride, $(CrCl_2)$ was purchased from Aldrich chemicals in order to investigate these reactions without the presence of zinc compounds. Chromium(II) chloride is a reactive compound and needs to be handled under a dry nitrogen atmosphere.

3.2.7.1. Reaction of chromium(II) chloride with ^{i}Butyl-2-pyridinecarbaldehyde imine, MMA and ethyl-2-bromisobutyrate in THF

A slurry of chromium(II) chloride in THF was reacted with ^{i}Butyl-PCA. This causes the light green/blue slurry to immediately turn dark brown. This is followed by the addition of MMA and then ethyl-2-bromoisobutyrate. The reaction was carried out for 3 days at 60 °C, (table 3-34 and 3-35). Modified from section 6.6.3.

Table 3-34 Quantities used

Experiment	$CrCl_2$ moles	ligand moles	MMA moles	R-Br (initiator) moles	Ratio of $[CrCl_2]$: [Init] : [Mon]
43	7.30×10^{-4}	3.5×10^{-3}	4.7×10^{-2}	6.8×10^{-4}	1:1:64
44	7.30×10^{-4}	3.5×10^{-3}	4.7×10^{-2}	1.7×10^{-3}	1:2:64
45	2.44×10^{-4}	1.2×10^{-3}	4.7×10^{-2}	3.4×10^{-3}	1:14:200

Table 3-35 Results obtained

Experiment	Time	% Yield	Mn	Mw	PDi
43	1 hour	-	4,700	40,000	8.56
	16 hours	-	20,000	89,000	4.48
	72 hours	100	35,000	100,000	2.85
44	1 hour	-	5,500	44,000	8.04
	16 hours	-	26,000	75,000	2.87
	72 hours	100	44,000	86,000	1.94
45	1 hour	-	17,000	71,000	4.28
	16 hours	-	21,000	178,000	8.40
	72 hours	100	82,000	219,000	2.68

This experiment is an important result as it has shown that the use of $CrCl_2$, in place of *(A)*, still results in the polymerisation of MMA in quantitative yield. Samples have been removed over time and examined by SEC. There is preliminary evidence to suggest that the Mn obtained from the reaction increases over time, and the polydispersity decreases as the reaction proceeds. These are two features of living polymerisation and merit further investigation.

3.2.7.2. Reaction of chromium(II) chloride with propyl 2-pyridinecarbaldehyde imine, MMA and ethyl-2-bromisobutyrate

A quantity of $CrCl_2$ was reacted with propyl-PCA ligand, added to this was MMA, followed by ethyl-2-bromoisobutyrate. No THF was added as solvent in this case. This allowed the temperature to be raised to 90 °C for 3 hours, the duration of the reaction (tables 3-36 and 3-37). Modified from section 6.6.3.

Table 3-36 Quantities used

Experiment	$CrCl_2$ moles	ligand moles	MMA moles	R-Br (initiator) moles	Ratio of $[CrCl_2]$: [Init] : [Mon]
46	1.28×10^{-3}	6.78×10^{-3}	4.6×10^{-2}	6.80×10^{-4}	1:0.5:40
47	1.60×10^{-3}	6.78×10^{-3}	4.6×10^{-2}	1.36×10^{-3}	1:1:30
48	1.78×10^{-3}	6.78×10^{-3}	4.6×10^{-2}	2.04×10^{-3}	1:1:25
49	1.39×10^{-3}	4.17×10^{-3}	6.95×10^{-2}	1.39×10^{-3}	1:3:1:50
50	3.7×10^{-3}	1.11×10^{-2}	9.25×10^{-2}	3.7×10^{-3}	1:3:1:25
51	3.73×10^{-3}	1.11×10^{-2}	1.85×10^{-1}	3.7×10^{-3}	1:3:1:50

Table 3-37 Results obtained

Experiment	Time	% Yield	Mn	Mw	PDi
46	15 min	-	31,000	105,000	3.43
	1 hour	-	65,000	143,000	2.20
	3 hour	100	54,000	145,000	2.68
47	15 min	-	39,000	92,000	2.32
	1 hour	-	48,000	103,000	2.15
	3 hour	100	38,000	113,000	3.00
48	15 min	-	33,000	88,000	2.65
	1 hour	-	47,000	109,000	2.33
	3 hour	100	36,000	107,000	2.99
49	20 hours	100	21,000	41,000	1.94
50	20 hours	100	14,000	27,000	1.97
51	2 hours	-	12,000	21,000	1.81
	24 hours	-	13,000	27,000	2.02
	3 days	100	16,000	46,000	2.85

Polymerisation proceeds to 100 % conversion, Mn does not increase with time.

Figure 3-13, plots Mn against the concentration of chromium chloride.

Figure 3-13 Plot of Mn verses concentration of chromium(II) chloride
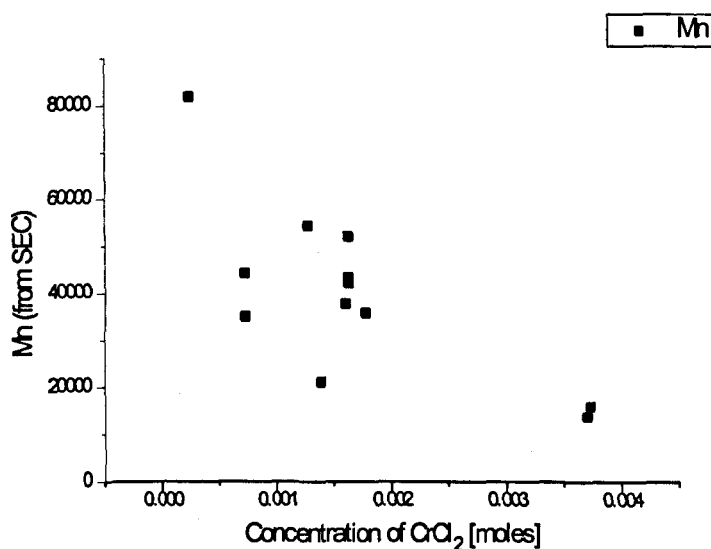
This plot shows that there does not appear to be a relationship between Mn and the

concentration of chromium chloride.

3.2.7.3. Effect of varying the quantity of alkyl-PCA ligand in the reaction

of chromium chloride with ligand, MMA and initiator

The following experiment investigated the reaction of CrCl$_2$, with an alkyl-PCA

ligand, MMA and initiator. In this case the quantity of propyl-PCA ligand added was

carefully monitored. The ratio of CrCl$_2$ to ligand was changed to 1:1, 1:2 and 1:3 to

study any effects on the reaction system. The reaction was carried out under bulk

conditions at 70 °C, (tables 3-38 and 3-39).

Table 3-38 Quantities used

Experiment	CrCl$_2$ moles	ligand moles	MMA moles	R-Br (initiator) moles	Ratio of [CrCl$_2$] : [Lig] : [Init] : [Mon]
52	1.63 x 10^{-3}	4.87 x 10^{-3}	6.82 x 10^{-2}	6.8 x 10^{-4}	1 : 3: 0.4:40
53	1.63 x 10^{-3}	3.24 x 10^{-3}	6.82 x 10^{-2}	6.8 x 10^{-4}	1 : 2: 0.4:40
54	1.63 x 10^{-3}	1.62 x 10^{-3}	6.82 x 10^{-2}	6.8 x 10^{-4}	1 : 1: 0.4:40

Table 3-39 Results obtained

Experiment	Time	% Yield	Mn	Mw	PDi
52	15 min	-	23,000	47,000	2.08
	30 min	-	30,000	66,000	2.20
	180 min	100	43,000	174,000	4.01
53	15 min	-	25,000	59,000	2.35
	30 min	-	33,000	75,000	2.25
	180 min	100	42,000	176,000	4.17
54	15 min	-	21,000	62,000	2.95
	30 min	-	35,000	91,000	2.59
	180 min	100	52,000	247,000	4.77

In the above examples the reactions proceed to 100 % conversion of monomer, giving similar molecular weights and high polydispersities (>4). Higher polydispersity's are characteristic of bulk polymerisation reactions. The quantity of ligand present in the reaction mixture does not, from this evidence, play a significant part in the reaction.

3.2.7.4. Reaction of chromium(II) chloride with pentyl 2-pyridinecarbaldehyde imine with methyl methacrylate and ethyl-2-bromoisobutyrate in THF

The purity of the chromium(II) chloride used was changed from 95 % to 99 % purity.

A sample of chromium(II) chloride in THF is reacted with pentyl-PCA ligand, followed by MMA and initiator, modified from 6.6.3. This is reacted at 60 °C for 24 hours (tables 3-40 and 3-41).

Table 3-40 Quantities used

Experiment	CrCl$_2$ moles	ligand moles	MMA moles	R-Br (initiator) moles	Ratio of [CrCl$_2$] : [Init] : [Mon]
55	6.59 x 10^{-4}	3.38 x 10^{-3}	4.67 x 10^{-2}	1.6 x 10^{-3}	1:2.5:70
56	8.14 x 10^{-4}	3.38 x 10^{-3}	9.34 x 10^{-2}	1.6 x 10^{-3}	1:2:100
57	2.60 x 10^{-3}	3.38 x 10^{-3}	9.35 x 10^{-3}	1.6 x 10^{-3}	1:0.5:4

Table 3-41 Results obtained

Experiment	Time	% Yield	Mn	Mw	PDi
55	24 hours	80	16,000	33,000	2.11
56	24 hours	55	41,000	172,000	4.15
57	24 hours	40	6,600	11,000	1.70

The use of a higher purity chromium(II) chloride starting material makes little difference to the results obtained from the reaction. A similar experiment was carried out using the higher purity CrCl$_2$. Samples were removed over time and examined by SEC (tables 3-42 and 3-43).

Table 3-42 Quantities used

Experiment	CrCl$_2$ moles	ligand moles	MMA moles	R-Br (initiator) moles	Ratio of [CrCl$_2$]: [lig]: [Init]: [Mon]
58	1.23 x 10^{-3}	3.69 x 10^{-3}	1.23 x 10^{-1}	1.23 x 10^{-3}	1:3:1:100
59	1.79 x 10^{-3}	5.37 x 10^{-3}	8.95 x 10^{-2}	1.79 x 10^{-3}	1:3:1:50

Table 3-43 Results used

Experiment	Time	% Yield	Mn	Mw	PDi
58	½ hour	-	13,000	118,000	1.37
	1 ½ hours	-	12,000	23,000	1.90
	24 hours	-	24,000	56,000	2.44
	72 hours	100	23,000	58,000	2.52
59	½ hour	-	7,900	12,000	1.52
	1 ½ hours	-	9,300	19,000	2.06
	24 hours	-	13,000	30,000	2.30
	72 hours	100	12,000	28,000	2.38

The reaction was allowed to proceed for 3 days to quantitative yield. The molecular weights of the polymers are double the expected figures, however, the polydispersities are broad, not characteristic of living polymerisation reactions.

The reactions to date have involved performing the reaction *in situ*. At no point has an identification of the active catalyst been possible. In this example a slurry of chromium(II) chloride in THF has a quantity of pentyl-PCA ligand added to it. This causes the solution to go dark purple, the solution is then filtered and the THF and excess ligand vacuumed off. This results in a quantity of what is believed to be "active catalyst" only. The active compound is then dissolved in THF before the addition of MMA and initiator, (tables 3-44 and 3-45). This reaction is carried out at 60 °C for 24 hours. The active catalyst has not been identified, hence, it is not possible to determine the amount of chromium present in the reaction. As a result the ratios given only represent the ratio of monomer to initiator.

Table 3-44 Quantities used

Experiment	CrCl$_2$ with ligand g	MMA moles	R-Br (initiator) moles	Ratio of [Init] : [Mon]
60	0.11	2.80 x 10^{-2}	2.04 x 10^{-3}	1:15
61	0.12	5.60 x 10^{-2}	2.04 x 10^{-3}	1:30

Table 3-45 Results obtained

Experiment	Time	% Yield	Mn	Mw	PDi
60	24 hours	80	115,000	283,000	2.46
61	24 hours	20	3,100	15,000	4.91

The quantities of monomer and initiator used result in a low ratio of monomer to initiator. The purpose of this was to try and achieve a low molecular weight polymer

product from the reaction. Sample 61 has given a low Mn, however, the large

polydispersity has meant a poor product has been prepared. The experiment has

shown that the isolated catalyst has reacted under these conditions to form PMMA.

The conversion of the reaction has been lowered in these reactions.

3.2.8. The reaction of chromium(II) chloride with propyl 2-pyridinecarbaldehyde imine, MMA and ethyl-2-bromoisobutyrate in toluene

All reactions in this chapter have been carried out with THF, as solvent or under bulk

polymerisation conditions. The following experiment examined the effect of a change

in solvent. The choice of solvent on a reaction system will affect such factors as the

rate of reaction, due to changes in polarity. The second effect is that due to the higher

boiling point of, in this case, toluene (110 °C), compared with THF (66 °C), the

temperature of the reaction can be raised. Chromium(II) chloride is reacted with

propyl 2-pyridinecarbaldehyde in THF, this is then removed under vacuum. Toluene

is then added, followed by MMA and ethyl 2-bromoisobutyrate. The temperature is

raised to 80 °C for the duration of the reaction (tables 3-46 and 3-47), procedure

modified from 6.6.3.

Table 3-46 Quantities used

Experiment	$CrCl_2$ moles	ligand moles	MMA moles	R-Br (initiator) moles	Ratio of $[CrCl_2]$: [Init] : [Mon]
62	4.74×10^{-3}	1.45×10^{-2}	6.8×10^{-2}	6.8×10^{-4}	1:0.1:10

Table 3-47 Results obtained

Experiment	Time	% Yield	Mn	Mw	PDi
62	¼ hour	-	19,000	36,000	1.88
	1 hour	-	27,000	53,000	1.99
	3 hours	-	34,000	71,000	2.06
	5 hours	-	35,000	79,000	2.27
	6 hours	40	37,000	81,000	2.20

This simple reaction has demonstrated that the reaction will still proceed despite a change in solvent. The low yield is attributed to the reaction only being allowed to proceed for 6 hours.

3.2.8.1. The effect of a change of initiator on the course of the reaction of chromium(II) chloride with pentyl-PCA and MMA

In section 3.2.6 the effect of a change in initiator was examined. This effect is examined in the following example involving chromium(II) chloride, pentyl-PCA, MMA and p-toluenesulfonyl chloride (figure 3-14). This initiator was examined as its electronic properties are different from initiators previously examined. Additionally the presence of chlorine is expected to cause the polymerisation reaction to behave differently.

Figure 3-14 Structure of p-Toluenesulfonyl chloride
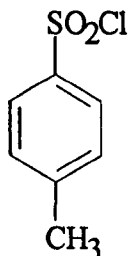
Chromium(II) chloride is reacted with pentyl 2-pyridinecarbaldehyde imine in THF, MMA is then added, followed by the initiator. The reaction is carried out at 55 °C for 24 hours (tables 3-48 and 3-49).

Table 3-48 Quantities used

Experiment	CrCl$_2$ moles	ligand moles	MMA moles	R-X (initiator) moles	Ratio of [CrCl$_2$] : [Init] : [Mon]
63	1.13 x 10^{-3}	4.54 x 10^{-3}	1.29 x 10^{-2}	1.12 x 10^{-3}	1:3:1:100
64	1.16 x 10^{-3}	4.54 x 10^{-3}	3.87 x 10^{-2}	1.15 x 10^{-3}	1:3:1:300
65	1.20 x 10^{-3}	3.60 x 10^{-3}	1.37 x 10^{-2}	1.20 x 10^{-3}	1:3:1:100
66	1.39 x 10^{-3}	4.17 x 10^{-3}	4.76 x 10^{-2}	1.39 x 10^{-3}	1:3:1:300

Table 3-49 Results obtained

Experiment	Time	% Yield	Mn	Mw	PDi
63	18 hours	<5	5,000	12,000	2.37
64	18 hours	<5	10,000	30,000	2.93
65	96 hours	<5	12,000	23,000	1.98
66	96 hours	<5	25,000	67,000	2.65

The use of p-toluenesulfonyl chloride initiator reduces the efficiency of the reaction, resulting in <5 % conversion in 96 hours. Control over the molecular weight or the polydispersity has not been achieved.

3.2.9. The effect of impurities on the reaction of chromium(II) chloride, propyl 2-pyridinecarbaldehyde imine, MMA and ethyl-2-bromoisobutyrate

The following reactions have been carried out to investigate the effect on the polymerisation reaction due to the addition of impurities to the system. The impurities used have been carefully chosen to inhibit certain kinds of polymerisation reactions. As a result information gained from these reactions gives valuable information as to the mechanism of polymerisation.

In the first example water has been added to the system. Water will inhibit an anionic type polymerisation reaction by acting as a source of protons which will terminate the

reaction prematurely. The second example uses phenol. Phenols are used as radical inhibitors and as such should inhibit a radical polymerisation reaction by causing the propagating species M' to become terminated. This could be by combination or disproportionation.

A quantity of chromium(II) chloride in THF is reacted with proply-PCA, this is followed by MMA, then 0.5 mL of water (2.77×10^{-2} moles), finally the ethyl-2-bromoisobutyrate. The reaction is carried out at 60 °C for 3 days (tables 3-50 and 3-51).

Table 3-50 Quantities used

Experiment	CrCl$_2$ moles	ligand moles	MMA moles	R-Br (initiator) moles	Ratio of [CrCl$_2$] : [Init] : [Mon]
67	2.77×10^{-4}	8.30×10^{-4}	2.76×10^{-2}	2.766×10^{-4}	1:3:1:100

Table 3-51 Results obtained

Experiment	Time	% Yield	Mn	Mw	PDi
67	24 hours	-	41,000	107,000	2.62
	72 hours	100	23,000	94,000	4.19

This shows a significant result, as the polymerisation reaction has in no way been affected by the introduction of water. This results indicates that the reaction does not proceed by an anionic mechanism.

In the following experiment, a quantity of chromium(II) chloride is reacted with proply-PCA, followed by MMA and then phenol (0.2 g, 2.12×10^{-3} moles) before the addition of ethyl-2-bromoisobutyrate. The reaction is carried out at 60 °C for 3 days (tables 3-52 and 3-53).

Table 3-52 Quantities used

Experiment	CrCl$_2$ moles	ligand moles	MMA moles	R-Br (initiator) moles	Ratio of [CrCl$_2$] : [Init] : [Mon]
68	8.46×10^{-4}	2.54×10^{-3}	8.46×10^{-2}	8.46×10^{-4}	1:3:1:100

Table 3-53 Results obtained

Experiment	Time	% Yield	Mn	Mw	PDi
68	24 hours	-	37,000	93,000	2.51
	72 hours	100	33,000	86,000	2.64

The results from this reaction have shown that polymerisation is still possible despite the addition of a radical polymerisation inhibitor. These results indicate that this reaction proceeds by an unusual type of polymerisation reaction. Experiments conducted by Matyjaszewski[10,11,14,15], Sawamoto[16-19] have shown an unusual type of polymerisation reaction to be possible in the presence of these inhibitors and using similar polymerisation regents (A metal halide and a Schiff base ligand with an alkyl halide as initiator). It has been described as atom transfer radical polymerisation (ATRP). Their work suggests ATRP reactions result in controlled polymerisation (section 1.5 for details on ATRP). In this case polymerisation has been achieved but not with controlled polymerisation products.

3.2.10. The effect of temperature on the reaction of chromium(II) chloride with propyl-PCA, MMA and ethyl-2-bromoisobutyrate

This experiment was carried out to see if the reaction investigated in this chapter could be carried out at lower temperatures, this experiment was carried out at 27 °C.

The procedure modified from section 6.6.3 reacts chromium(II) chloride with proply-PCA in THF, followed by MMA, finally a quantity of ethyl-2-bromoisobutyrate. The reaction was carried out at 27 °C for 3 days (tables 3-54 and 3-55).

Table 3-54 Quantities used

| Experiment | CrCl$_2$

moles | ligand

moles | MMA

moles | R-Br
(initiator)

moles | Ratio of
[CrCl$_2$] :
[Init] :
[Mon] |
|---|---|---|---|---|---|
| 69 | 1.44 x 10^{-3} | 4.32 x 10^{-3} | 7.2 x 10^{-2} | 1.50 x 10^{-3} | 1:3:1:50 |
| 70 | 1.63 x 10^{-3} | 4.93 x 10^{-3} | 8.1 x 10^{-2} | 1.64 x 10^{-3} | 1:3:1:50 |

Table 3-55 Results obtained

Experiment	Time	% Yield	Mn	Mw	PDi
69	2 hours	-	2,300	8,900	3.79
	72 hours	100	14,000	27,700	1.98
70	2 hours	-	4,200	110,000	2.61
	72 hours	100	15,400	31,000	2.00

This reaction has shown that it is possible to get quantitative yields of PMMA, despite carrying the reaction out at almost room temperature. This result indicates a reactive system, not requiring high temperatures to initiate the polymerisation.

3.2.11. The effect of using styrene monomer in the reaction of chromium(II) chloride with alkyl-PCA, and ethyl-2-bromoisobutyrate

All reactions so far have been carried out using methyl methacrylate. It was decided to test the versatility of the reaction by using styrene. Chromium(II) chloride (0.2 g) in THF (10 mL) was reacted with pentyl 2-pyridinecarbaldehyde imine (1 mL), styrene (5 mL) was then added followed by ethyl 2-bromoisobutyrate (0.3 mL). The reaction was carried out for 3 days at 25 °C.

The colour changes during this reaction are as follows; the blue chromium chloride in THF becomes purple on addition of the ligand, this then becomes green on addition of monomer, there is no further colour change upon addition of the initiator.

After this time a sample is removed and examined by SEC. The result from this showed only monomer, there was no evidence of polystyrene. This result shows a limitation in the choice of monomer for this reaction, this information will be of use in elucidating the reaction mechanism.

3.2.12. Control experiments

3.2.12.1. The polymerisation reaction of chromium(II) chloride compared to zinc(II) chloride

In reaction A; chromium(II) chloride is reacted with propyl-PCA, MMA and initiator. In reaction B; zinc(II) chloride is used with propyl-PCA, MMA and initiator (tables 3-56 and 3-57).

Table 3-56 Quantities used

Experiment	MCl_2	MCl_2	ligand	MMA	R-Br (initiator)	Ratio of [MCl_2] : [Init] : [Mon]
	g	moles	moles	moles	moles	
71 A $CrCl_2$	0.22	1.79×10^{-3}	6.78×10^{-3}	4.67×10^{-2}	2.39×10^{-3}	1:1:25
72 B $ZnCl_2$	0.30	2.20×10^{-3}	6.78×10^{-3}	4.67×10^{-2}	2.39×10^{-3}	1:1:20

Table 3-57 Results obtained

Experiment	Time	% Yield	Mn	Mw	PDi
71 A	½ hour	-	1,400	2,400	1.66
	1 hour	-	3,400	7,500	2.20
	2 hours	-	3,500	9,200	2.65
	24 hours	-	3,000	9,400	3.06
	72 hours	low ~10	2,600	12,000	4.60
72 B	72 hours	monomer only			

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This reaction indicates that chromium must be present for the reaction to proceed and that the presence of zinc does not initiate polymerisation. This result shows that *(A)*, despite containing chromium and zinc, it is likely to be chromium that is the reactive centre. This is due to its ease with which it can be in either a +2 or +3 oxidation state. Zinc on the other hand is limited to just the +2 state and likely to be less reactive in this environment.

3.2.13. Thermal gravimetric analysis of poly(methyl methacrylate) formed from the reactions examined in this chapter

At this stage, the mechanism of polymerisation has not been identified. An examination of the polymers formed during this work should help elucidate the polymerisation mechanism. As discussed in section 1.6 and 2.2.8 poly(methyl methacrylate) can be examined by a technique known as thermal gravimetric analysis (TGA). The importance of TGA has been discussed in section 1.6. Tables 3-58 to 3-60 show a summary of the expected decomposition peaks expected depending on the method of preparation of PMMA.

Table 3-58 TGA results expected for PMMA formed by a radical polymerisation

Type of Peak	Temperature range of peak / °C
Head to Head linkage (combination)	165 - 195
Terminal unsaturated methylene end group	255 - 270
Terminal saturated methyl end group	300 - 360

Table 3-59 TGA results for PMMA formed by an anionic polymerisation

Type of Peak	Temperature range of peak / °C
Stable head to tail linkages only giving terminally methyl saturated end groups only	300- 360

Table 3-60 TGA results for PMMA formed in the presence of a chain transfer agent

Type of Peak	Temperature range of peak / °C
Fully saturated methyl end groups (No Head to Head or unsaturated methylene end groups)	> 360

Figures 3-15 - 3-21 show examples of polymers prepared from the system outlined in this chapter with an interpretation of these results.

Figure 3-15 TGA trace from PMMA formed from experiment 6
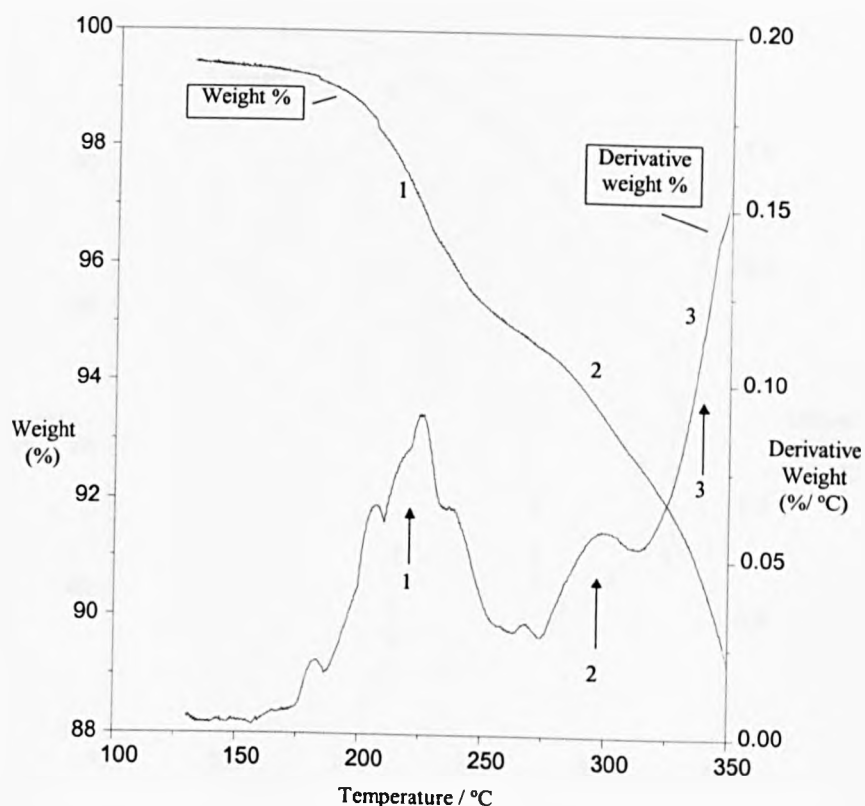
The trace in figure 3-15 is from a PMMA sample formed in the reaction of *(A)* with

ⁿButyl-PCA, MMA and ethyl 2-bromisobutyrate.

The TGA trace shows three peaks clearly, (1) at 200-250 °C, a second (2) at ~290- 310

°C, before the main scission peak can be seen rising from 320 °C, peak (3).

This trace is unusual as it does not contain any of the usual transitions expected if the

polymerisation process occurs by a free-radical or anionic mechanism or one in the

presence of a chain transfer agent.

Figure 3-16 TGA trace from PMMA formed from experiment 8
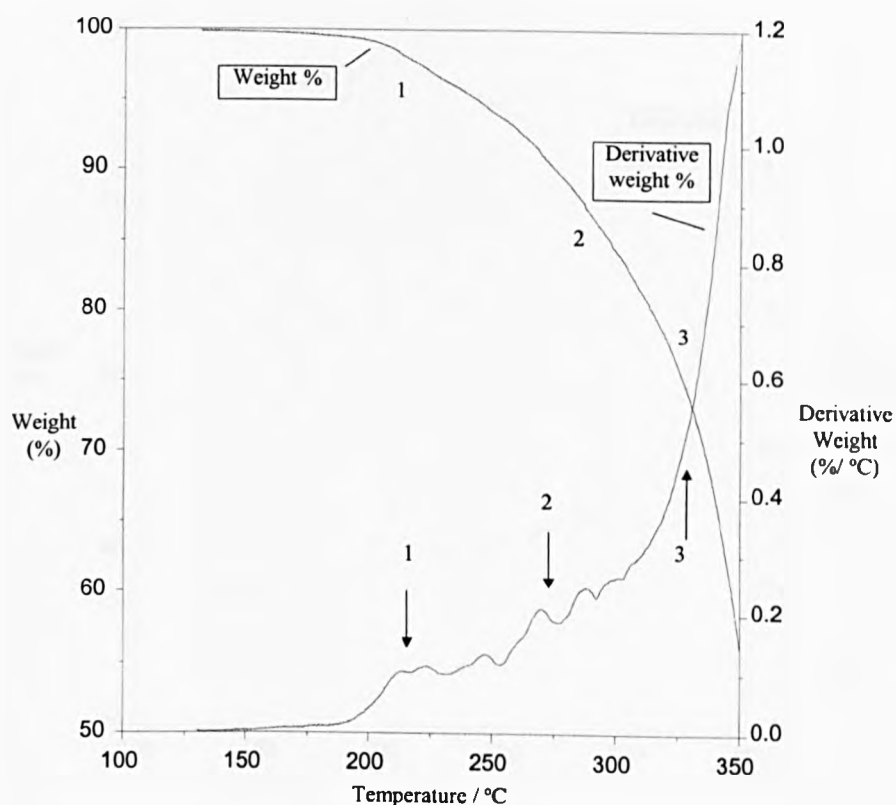
The trace in figure 3-16 is a sample of PMMA formed from the reaction of *(A)* with

ⁿButyl-PCA, MMA and ethyl 2-bromisobutyrate (as figure 3-15). In this example the

two peaks can be seen less cleanly, with the third main chain scission peak(3). The

trace does show that the decomposition transitions do not fall into the traditional

regions expected in a TGA trace of PMMA, if the reaction proceeded by conventional

methods.

Figure 3-17 TGA trace from PMMA formed from experiment 13
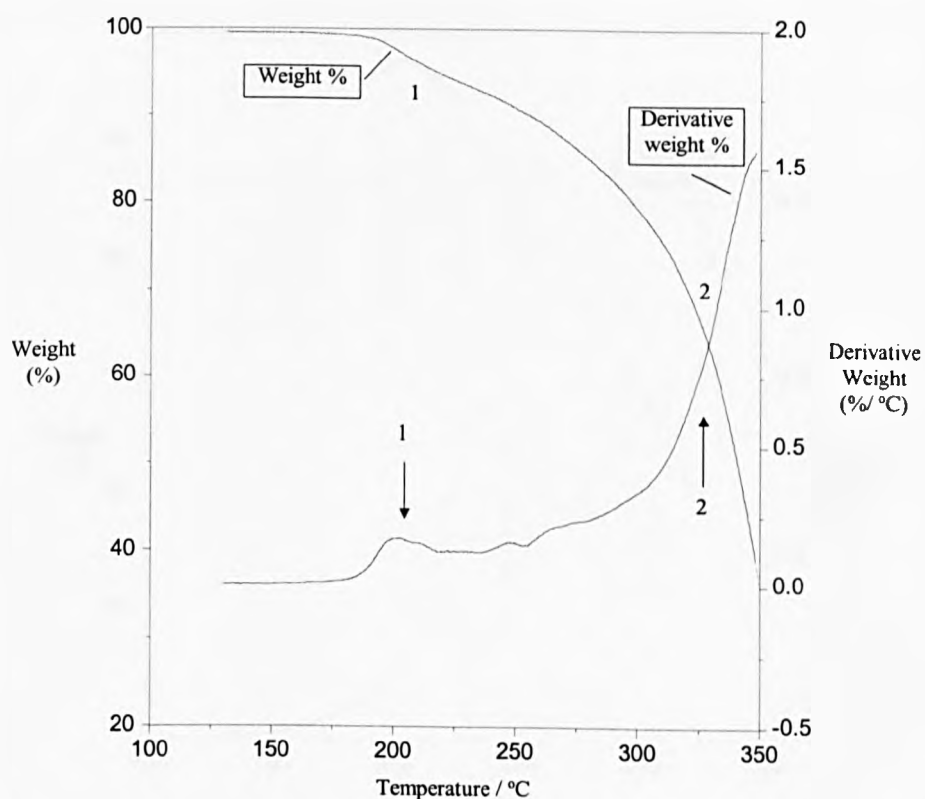
In this example the PMMA has been formed under bulk polymerisation conditions. One transition is visible (1), at 190-210 °C, higher than a head to head linkage should be found, but it is lower than an unsaturated end group. The second is present at 320 °C, marked (2), this refers to decomposition resulting from a saturated methyl end group.

Figure 3-18 TGA trace from PMMA formed from experiment 42A
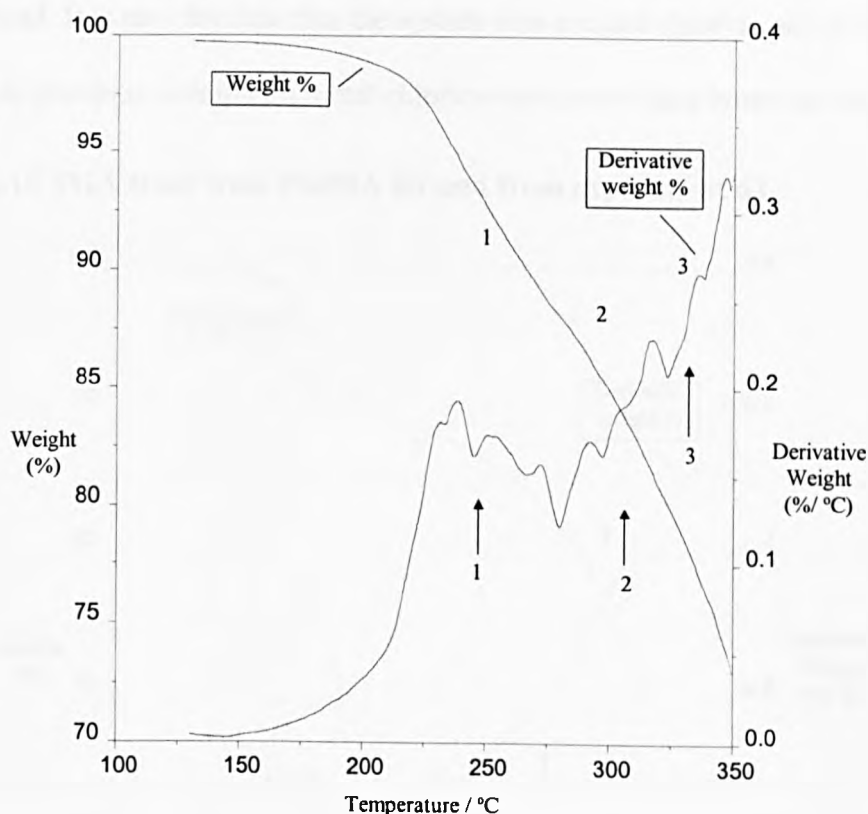
The polymer in figure 3-18 is formed from the reaction of (*A)* with propyl-PCA, MMA and ethyl 2-bromisobutyrate in THF. Two transitions are seen, (1) at 225-275 °C, a second (2) at 290-320 °C. These compare reasonably with figures 3-15 to 3-17. The minor discrepancies can be put down to the differences in molecular weight, and polydispersities between samples. The third transition occurs at 320 °C, and is caused by methyl end groups.

In this reaction the ligand has been changed, but this has not resulted in a major change in the TGA trace. It can be assumed that the polymer formed is not altered by the use of a different ligand.

The following figures, 3-19 to 3-21 show PMMA polymers formed from reactions involving a different initiator. The samples below were formed using p-toluenesulfonyl chloride. This is likely to incorporate a chlorine atom into the

polymerisation reaction. In examples shown previously bromine is likely to have been incorporated. It is now the case that the system uses a metal chloride and a chlorine initiator, in previous examples a metal chloride was used with a bromine initiator.

Figure 3-19 TGA trace from PMMA formed from experiment 63
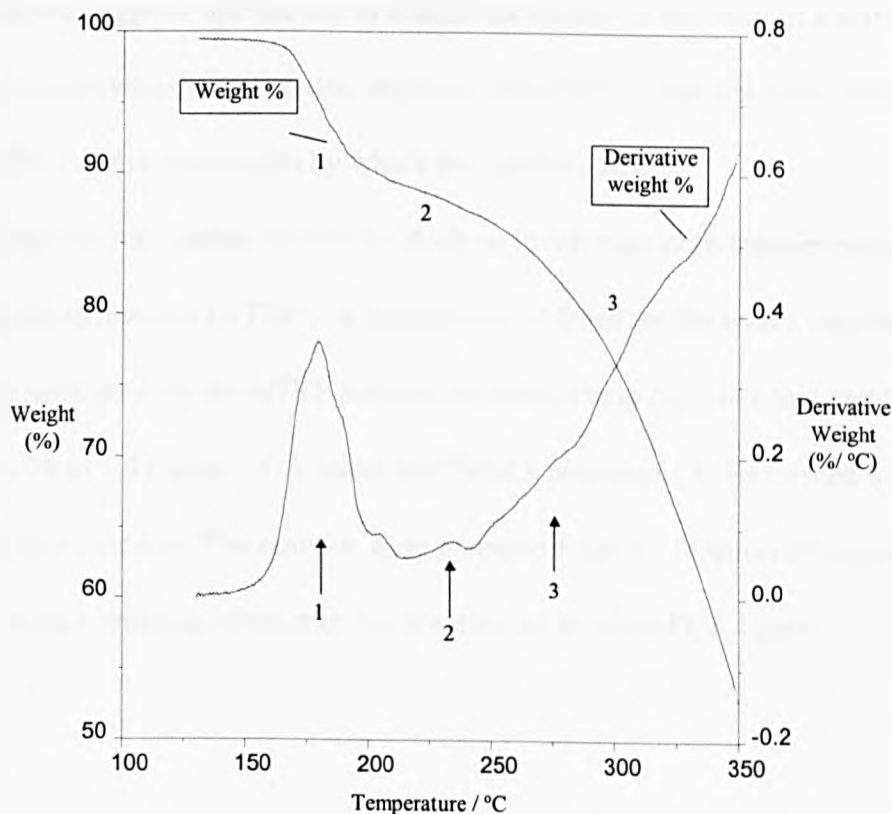
The trace in figure 3-19 is somewhat different to those encountered previously. The yield for this reaction, involving chromium(II) chloride with pentyl-PCA, MMA and using p-toluenesulfonyl chloride was low (<5%). The TGA trace shows 3 transitions, (1) at 160-190 °C (major peak) (2) at 210-240 °C (minor peak) and (3) at 260-300 °C (major peak).

With exception to peak (2), the other transitions (1) and (3), almost fall into the classic categories of free radical polymerisation as described earlier in tables 3-59 to 3-61. The yield in this reaction was low, despite leaving the reaction for 3 days. It is feasible that part of the reaction actually occurred by thermal polymerisation. This would

result in the peaks usually seen by free radical polymerisation, (1) and (3). The small

peak at (2), 210-240 °C could occur as a result of the reaction proceeding by the

mechanism of previous experiments. In this case incorporating part of the chlorine

based initiator compared to the bromine initiator in the previous examples.

This evidence suggests that the use of a different initiator may result in a different end

group, in the previously unrecorded region of 200-250 °C. This transition will be

characteristic of the mechanism by which the reaction occurs.

At this stage the mechanism is thought likely to involve an atom transfer radical

polymerisation reaction (ATRP). A comparison of these results with a reaction

known to have gone by the ATRP mechanism should help elucidate this mechanism.

Figures 3-20 to 3-21 show TGA traces for PMMA polymers (A, B) formed by a

known ATRP reaction. The samples were prepared from the reaction of copper

bromide with a bromine initiator in the presence of an alkyl-PCA ligand.

Figure 3-20 TGA trace from PMMA formed from experiment A
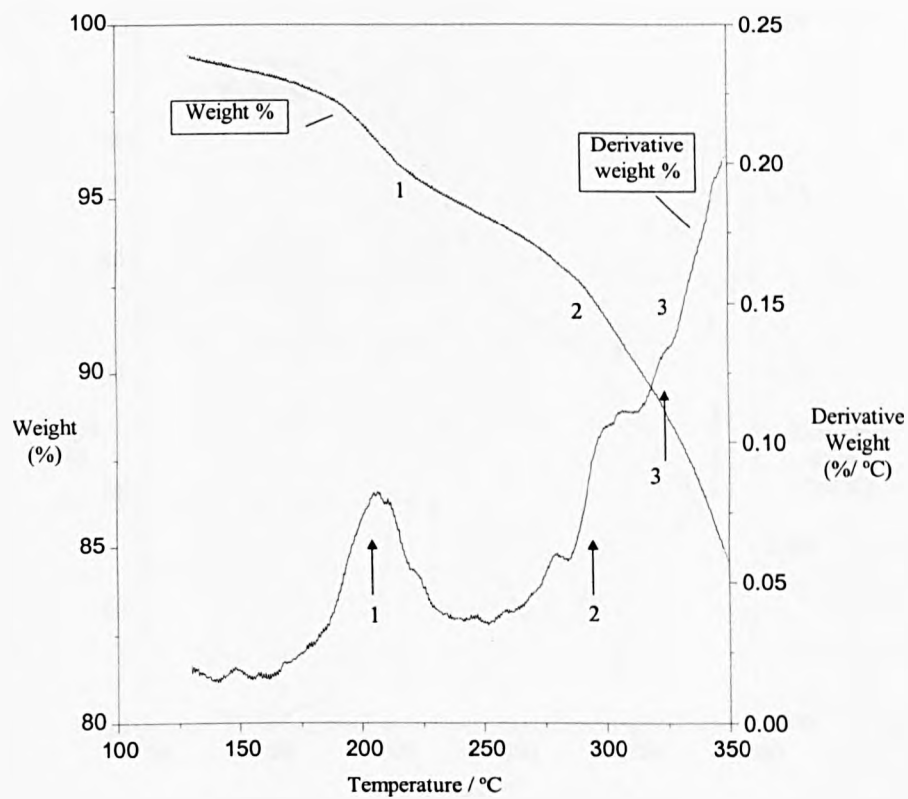
Experiment	Mn	Mw	PDi
A	6,000	7,500	1.25

Figure 3-21 TGA trace from PMMA formed from experiment B
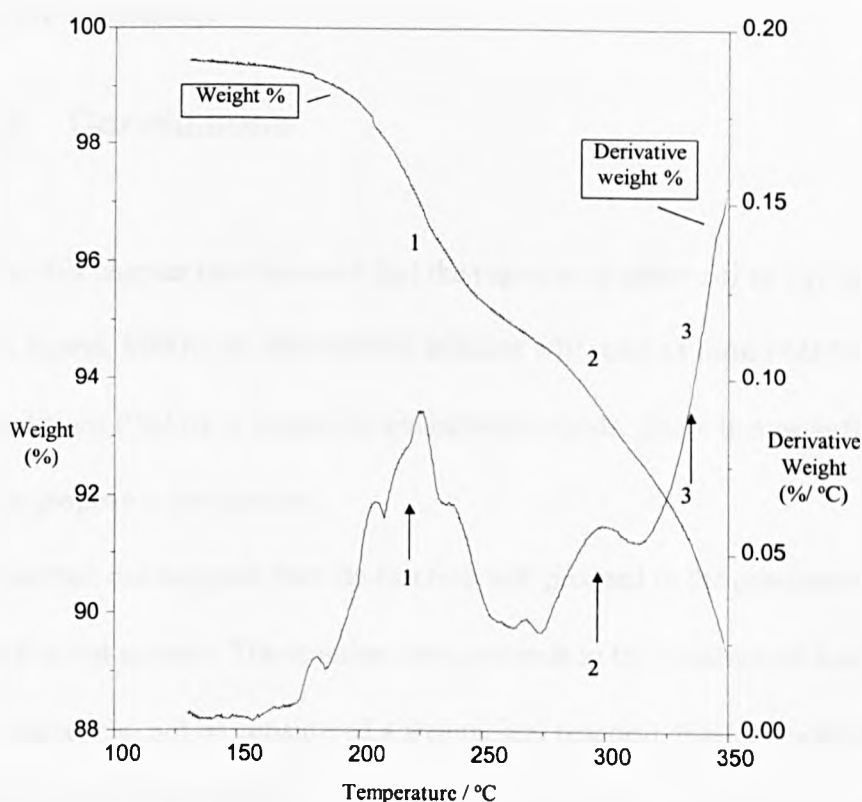
Experiment	Mn	Mw	PDi
B	5,200	6,800	1.30

Figures 3-20 and 3-21 show TGA traces which have three peaks present, (1) at 190-220 °C , (2) at 280-310 °C and (3) at 320 °C. The transitions shown are not consistent with free radical polymerisation transition peaks. These can be compared to the traces and transitions from polymers formed with the chromium system that has been examined.

The transitions are similar to those seen in figures 3-15 to 3-20. Minor discrepancies in peak positions are due to the low molecular weight of the samples used in figures 3-21 and 3-22.

It is concluded from these results that the polymers formed in the reactions using this chromium based polymerisation system have similar end groups present to those

found in ATRP polymers. From this it is probable that the polymers are formed by a similar ATRP mechanism.

3.3. Conclusions

Evidence in this chapter has indicated that the reaction of either *(A)* or $CrCl_2$ with an alkyl-PCA ligand, MMA and alkyl-halide initiator will react to form PMMA. Under certain conditions PMMA is formed in quantitative yields. There is now sufficient evidence to propose a mechanism.

The work carried out suggests that the reaction will proceed in the presence of water, indicating it is not anionic. The reaction also proceeds in the presence of a radical inhibitor, hence, can not be considered a free radical reaction. Evidence obtained by thermal gravimetric analysis shows similar results to polymers formed by known ATRP reactions.

A mechanism proposed for the polymerisation of vinyl monomers using copper complexes was shown in figure 1-8. This mechanism shows a radical reaction with transfer and termination's suppressed by the rapid equilibrium between active and dormant species.

Matyjaszeski described the role of the ligand as to solubilise the copper and the active catalyst, this has been described as 'Cu(I)/bipy' [20]. Since then a number of possible copper species have been described as being in solution[21], these were shown in figure 1-9.

This has shown that more than one equivalent of ligand is required and more than one metal atom may be required in the reaction.

The results in this chapter indicate a system that is resilient to both anionic inhibitors and free radical inhibitors. TGA showed similar results to those obtained by ATRP reactions. From this a similar mechanism may be proposed (figure 3-22).

Figure 3-22 Proposed mechanism for chromium system

$$R-X \;+\; CrX_2\,/\,2\,\text{lig} \;\underset{}{\overset{k_{eq}}{\rightleftharpoons}}\; R\cdot \;+\; CrX_3\,/\,2\,\text{lig}$$

Initiation

$$R\cdot \;+\; MMA \;\xrightarrow{\;k_i\;}\; M^\bullet_1$$

$$M_n-X \;+\; CrX_2\,/\,2\,\text{lig} \;\underset{}{\overset{k_{eq}}{\rightleftharpoons}}\; M^\bullet_n \;+\; CrX_3\,/\,2\,\text{lig}$$

Propagation

$$M^\bullet_n \;+\; MMA \;\xrightarrow{\;k_p\;}\; M^\bullet_{n+1}$$

$$M^\bullet_n \;+\; M^\bullet_m \;\xrightarrow{\;k_t\;}\; M_{n+m}$$
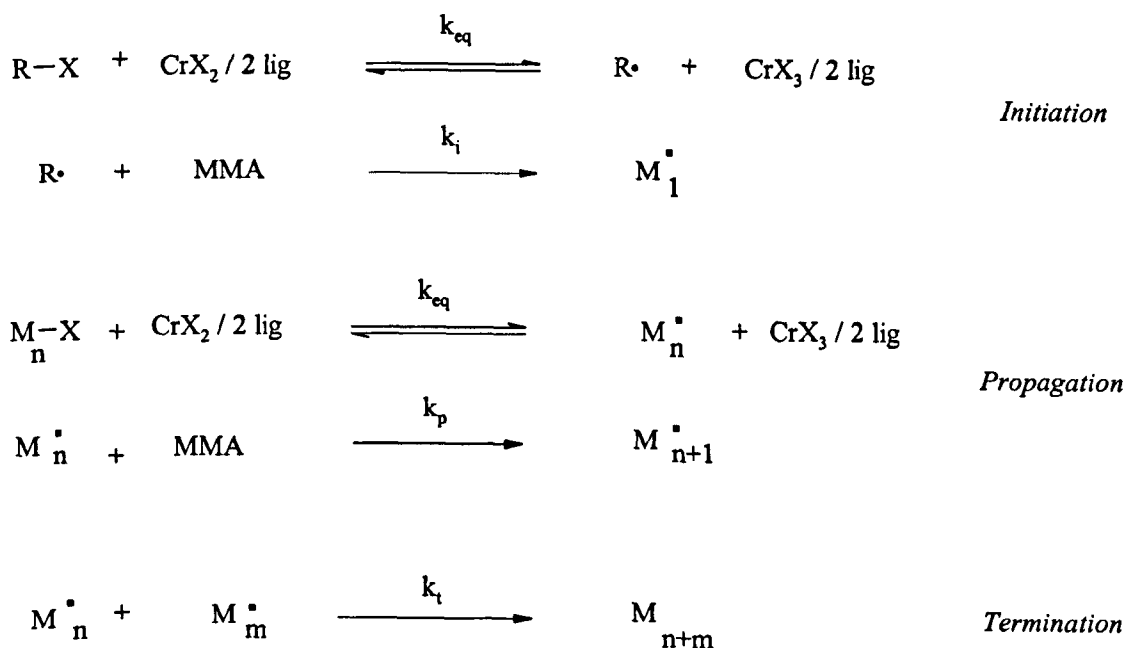
Termination

Termination reactions may be inhibited by the equilibrium between M_n-X and $M_n^\bullet$; this may result in termination by a halogen atom if combination is not possible. Alternatively termination may be occurring by a mechanism resulting in the presence of a terminal saturated methyl group and a halogen atom.

The results for this system demonstrate that although polymerisation is possible, the system is not efficient. No control over the reaction and the molecular weight of the polymer products was achieved as predicted for a living polymerisation reaction.

Possible explanations for this are that the system is not refined. Further work would need to be carried out to investigate other ligands, different initiators and other solvent

systems. This reaction system though does produce a relatively thermally stable form of PMMA compared to that which is poorly made from free radical reactions.

3.4. References

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Chapter 4

An investigation into the polymerisation of methyl methacrylate using aqueous organochromium complexes

4. An investigation into the polymerisation of methyl methacrylate using aqueous organo-chromium compounds

4.1. Introduction

In 1957 Anet[1] prepared the first aqueous organochromium complex. This was an unusual compound as it contained a stable metal-carbon bond. Very few metal-carbon compounds that are stable in water have been prepared. Examples for cobalt[2], rhodium[3] and chromium have been reported.

The first such complex reported was $[Cr-CH_2Ph(H_2O)_5]^{2+}$ [1], followed shortly by $[Cr-CHCl_2(H_2O)_5]^{2+}$ [4]. These compounds have been discussed in 1.5.1.6. It is an important feature that the compounds are prepared by a radical process. The complexes are formed by a homolytic reaction, a consequence of this is that the metal-carbon bonds should be able to be broken homolytically under the right reaction conditions. It is this feature which was examined in this research. Further work was carried out to examine if it could be usefully employed in the polymerisation of MMA under aqueous reaction conditions.

4.2. Results and Discussion

This chapter outlines all of the aqueous chromium compounds and aqueous organochromium complexes that were prepared in section 6.5.4 of the experimental. Also discussed are the attempts at preparing some aqueous chromium complexes and organochromium complexes.

4.2.1. Preparation of hexaaquachromium(III) compounds utilising hexaflurophosphoric acid, (HPF$_6$)

(i) Attempted synthesis of hexaaquachromium(III), [Cr(H$_2$O)$_6$]$^{3+}$ [PF$_6^-$]$_3$ from chromium trioxide, (CrO$_3$)

A solution of chromium trioxide in hexaflurophosphoric acid, (HPF$_6$), was reacted with an aqueous solution of hydrogen peroxide. The chromium trioxide dissolves in HPF$_6$ to give a red solution. Upon careful addition of the hydrogen peroxide the solution becomes green. This result is somewhat surprising, in that the preparation of the hexaaquachromium(III) species, [Cr(H$_2$O)$_6$]$^{3+}$[ClO$_4^-$]$_3$ in aqueous solution as reported by Hanzs[5], the solution was expected to be dark blue. It is noted that this work uses the acid hexaflurophosphoric acid, (HPF$_6$)(aq), as opposed to perchloric acid (HClO$_4$)(aq). Both acids are sources of non-interacting counter ions. Perchloric acid was avoided as it is considered to be more hazardous due to the explosive nature of perchloric salts. The unknown product was analysed by UV/Visible spectroscopy, the results are shown in table 4-1.

Table 4-1 Unknown chromium(III) complex

This work		Reference Stunzi[6]	
λ_{max} / nm	ε (experimental)/ mol^{-1} dm^3 cm^{-1}	λ_{max} / nm	ε / mol^{-1} dm^3 cm^{-1}
424	13.2	408	15.5
606	13.3	575	13.2

The data for the unknown chromium compound formed can be compared to the literature values shown in table 4-1. The reported hexaaquachromium species, $[Cr(H_2O)_6]^{3+}[ClO_4^-]_3$, has λ_{max} peaks at ~20 nm difference compared to those obtained here. This indicates that the product formed may not be the chromium(III) complex, $[Cr(H_2O)_6]^{3+}[PF_6^-]_3$ as aimed for.

It was postulated that the product could be the bridged dimer $[(H_2O)_5Cr(OH)_2Cr(H_2O)_5]^{4+}$, see figure 4-1, however the UV/Visible spectroscopy data for the dimer is reputed to have λ_{max} at 582 nm and 417 nm.

Figure 4-1 Chromium bridged dimer product, $[(H_2O)_5Cr(OH)_2Cr(H_2O)_5]^{4+}$.
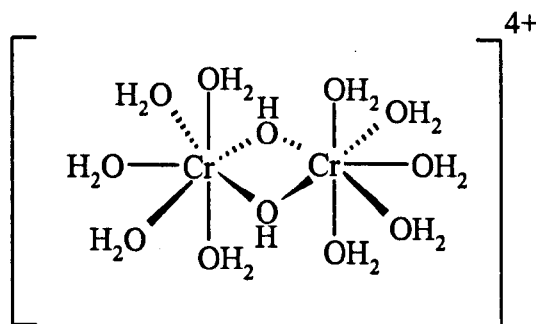
The change of counter-anion was not expected to have made any changes to the structure of the product. The data indicates that the desired hexaaquachromium(III) species, $[Cr(H_2O)_6]^{3+}[PF_6^-]_3$, was not formed. The nature of the counter-ion does seem to have an effect on the structure of the product.

It is considered that there are two possibilities to explain this reaction: (i) A fluorine atom may have been abstracted from the PF_6^- anion and become coordinated to the

chromium metal centre resulting in $[Cr(H_2O)_5F]^{3+}$. Alternatively, (ii) the counter ion PF_6^-, shifts λ_{max} of the two peaks by ~20 nm. This has resulted in the compound being green in colour rather than the dark blue as expected. At this time neither of these possibilities have been unequivocally assigned.

(ii) Attempted synthesis of hexaaquachromium(III), $[Cr(H_2O)_6]^{3+}$ $[PF_6^-]_3$, from chromium metal.

Chromium metal is reacted with hexaflurophosphoric acid in water at ~80 °C, (section 6.5.3). This reaction results in a green solution within a few minutes. UV/visible spectroscopy gave results showing λ_{max} at 424 nm and 609 nm, table 4-2.

Table 4-2 Unknown chromium complex in HPF_6 acid from chromium metal

This work		Reference Stunzi[6]	
λ_{max} / nm	ε (experimental)/ mol^{-1} dm^3 cm^{-1}	λ_{max} / nm	ε / mol^{-1} dm^3 cm^{-1}
424	14.1	408	15.5
609	14.01	575	13.2

This data suggests that the product is not $[Cr(H_2O)_6]^{3+}[PF_6^-]_3$. Although ε values are similar the λ_{max} positions differs by 16 nm and 34 nm respectively. The spectrum is almost identical to the spectrum obtained from the product formed in 4.2.1.i and it is likely that the same product has been formed.

As stated before fluorine abstraction to give a $[Cr-F(H_2O)_5]^{2+}$ species is possible, alternatively, it is feasible that the anion used is having some effect on the position of the λ_{max}. The more likely explanation of the two, however, is that the PF_6^- anion has exerted an effect on the cation, this then leads to the shifting of the peaks, resulting in the colour changes.

4.2.2. Preparation of hexaaquachromium(II) compounds, $[Cr(H_2O)_6]^{2+}[PF_6]_2$ from HPF_6 and $[Cr(H_2O)_6]^{3+}[PF_6]_3$

The chromium complex formed in 4.2.1.ii was reduced in water with a zinc/mercury amalgam under a nitrogen atmosphere (section 6.5.3). The chromium complex in aqueous solution is green and upon reduction for 3 days the solution turns sky blue. Under examination by UV/Visible spectroscopy the following peaks were observed, see table 4-3.

Table 4-3 Cr(II) complex from HPF_6 - reduction by Zn/Hg amalgam

This work		Reference Stunzi[6]	
λ_{max} / nm	ε (experimental)/ mol^{-1} dm^3 cm^{-1}	λ_{max} / nm	ε / mol^{-1} dm^3 cm^{-1}
434	-	-	-
690	~5	714	5
Not in range of our spectrometer		1,052	1.8

The reaction product, according to the spectroscopy data, is very similar to the data expected according to the literature. However, the peak is 24 nm lower than expected. The reason for this could be, as suggested earlier, due to the different counter-anion shifting the peak to its observed position. The complex formed is the chromium(II) species, $[Cr(H_2O)_6]^{2+}[PF_6]_2$, the deviation in the λ_{max} has to be due to the counter-anion, PF_6^-. If a fluorine atom was coordinated it would be expected to have been removed upon reduction.

4.2.3. Synthesis of chromium alkyls from chromium(II) compounds.

(i) The attempted synthesis of $[(H_2O)_5Cr-C(CH_3)_2OH]^{2+}[PF_6^-]_2$.

Hexaaquachromium(II), $[Cr(H_2O)_6]^{2+}$ $[PF_6^-]_2$, was reacted with *iso*-propyl alcohol and

hydrogen peroxide, section 6.5.4. The sky-blue chromium(II) solution, upon addition

of hydrogen peroxide solution becomes deep green. This is in contradiction to the

experiment reported by Bakac and Espenson[7], who found that the solution turns

orange. The reaction according to Espenson et. al. is shown below in scheme 4-1.

Scheme 4-1 Mechanism for the formation of $[(H_2O)_5Cr-C(CH_3)_2OH]^{2+}[PF_6^-]_2$

Overall reaction.

$$2[Cr(H_2O)_6]^{2+} + H_2O_2 + (CH_3)_2CHOH + H^+ \rightarrow [Cr(H_2O)_6]^{3+} + [(H_2O)_5CrC(CH_3)_2OH]^{2+} + 3H_2O$$

Step equation

$$(H_2O)_6Cr^{2+} + H_2O_2 \rightarrow (H_2O)_5CrOH^{2+} + HO\bullet$$

$$HO\bullet + (CH_3)_2CHOH \rightarrow H_2O + \bullet C(CH_3)_2OH$$

$$(H_2O)_6Cr^{2+} + \bullet C(CH_3)_2OH \rightarrow (H_2O)_5CrC(CH_3)_2OH^{2+}$$
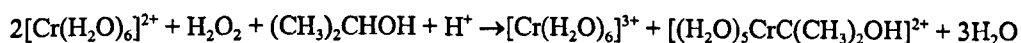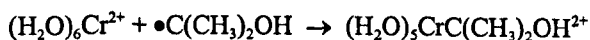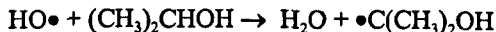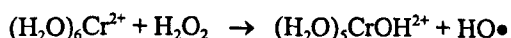
If the concentration of hydrogen peroxide is too strong it is possible that it would react

with the chromium(II) solution before the alcohol. Thus giving a chromium(III)

solution, and not the chromium alkyl compound desired.

The complex formed was examined by UV/Visible spectroscopy and compared to the

literature data, shown in table 4-4.

Table 4-4 UV/Visible data for $[(H_2O)_5Cr-C(CH_3)_2OH]^{2+}$ from Espenson[7]

λ_{max} / nm	$\varepsilon/$ $mol^{-1} \, dm^3 \, cm^{-1}$
311	2.8×10^3
407	6.9×10^2

The reaction results indicate that the chromium-alkyl is not present in this solution. It is thought that the reaction did not proceed due to the use of the PF_6^- anion as opposed to a ClO_4^- anion.

(ii) Synthesis of $[(H_2O)_5Cr-CHCl_2]^{2+}[PF_6^-]_2$.

Chromium(II) aqueous solution, $[Cr(H_2O)_6]^{2+}$, was reacted with chloroform in water, section 6.5.4. The mechanism of this reaction is shown in scheme 4-2.

Scheme 4-2 Mechanism for the preparation of $[(H_2O)_5CrCX_2H]^{2+}$

$$CHCl_3 + [(H_2O)_5Cr]^{2+} \rightarrow [(H_2O)_5CrCl]^{2+} + \bullet CHCl_2$$

$$\bullet CHCl_2 + [(H_2O)_5Cr]^{2+} \rightarrow [(H_2O)_5CrCCl_2H]^{2+}$$
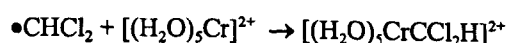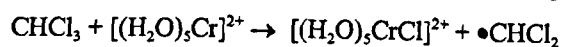
The products are formed by this reaction are both $[(H_2O)_5Cr-CHCl_2](aq)$ and $[(H_2O)_5Cr-Cl](aq)$. Separation of these compounds is achieved using ion exchange chromatography (section 6.5.2).

In this case the first layer eluted is green, which is assigned as $[(H_2O)_5Cr-Cl]^{2+}[PF_6^-]_2(aq)$. The second layer removed, an orange/red solution, is probably the chromium alkyl $[(H_2O)_5Cr-CHCl_2]^{2+}[PF_6^-]_2$ (aq) species. This is expected to bind more strongly to the column than the $[Cr(H_2O)_5Cl]^{2+}(aq)$ species. This product was collected, analysed and used as required as the aqueous solution. The first fraction removed was green, table 4-5.

Table 4-5 UV/Visible data for the green fraction, [(H$_2$O)$_5$Cr-Cl(aq)] complex

This work		Reference Stunzi[6]	
λ_{max} / nm	ε / mol^{-1} dm^3 cm^{-1}	λ_{max} / nm	ε / mol^{-1} dm^3 cm^{-1}
404	-	432	-
605	27.6	605	17.8

The compound is assigned as the [Cr(H$_2$O)$_5$Cl]$^{2+}$ species. The differences in λ values are ascribed to PF$_6^-$ counter ion as opposed to ClO$_4^-$. The red product is the chromium alkyl product, as assigned by UV/Visible spectroscopy, table 4-6.

Table 4-6 UV/Visible data for the red fraction, [(H$_2$O)$_5$Cr-CHCl$_2$] complex

This work		Reference Stunzi[6]	
λ_{max} / nm	ε / mol^{-1} dm^3 cm^{-1}	λ_{max} / nm	ε / mol^{-1} dm^3 cm^{-1}
396	367	396	157
522	99	514	38.7
This peak can not be seen clearly due to its very high extinction coefficient.		266	4,290

Although the λ_{max} values and the ε values are slightly different to those expected from the literature this difference is accounted for by the presence of PF$_6^-$ anion as opposed to ClO$_4^-$.

A final fraction remains on the column, which is likely to be the chromium dimer, [(H$_2$O)$_5$Cr(OH)$_2$Cr(H$_2$O)$_5$]$^{4+}$, formed in small quantities, (figure 4-1). This remains on the column due to its high charge and thus strong coordination to the column under these conditions.

4.2.4. Hexaaquachromium(III) compounds from perchloric acid, (HClO₄)

Following the limited success in the preparation of chromium alkyls via

hexaflorophosphoric acid, (HPF₆) as the source of the anion it was decided to revert

to the original work of Anet and Bakac[1,4]. This would involve the use of perchloric

acid (HClO₄) as a source of ClO_4^-. This work was carried out carefully due to the

hazardous nature of perchlorate salts. Perchloric acid is used as a non-interacting

anion. The water remains coordinated to the chromium metal centre in the same

manner as HPF₆ used previously.

(i) Formation of $[Cr(H_2O)_6]^{3+}[ClO_4^-]_3$ from CrO₃

$[Cr(H_2O)_6]^{3+}[ClO_4^-]_3$ was prepared as outlined in section 6.5.3, and assigned by

UV/Visible spectroscopy, table 4-7.

Table 4-7 Cr(III) complex from HClO₄

This work		Reference Stunzi[6]	
λ_{max} / nm	ε / mol^{-1} dm^3 cm^{-1}	λ_{max} / nm	ε / mol^{-1} dm^3 cm^{-1}
407	17.3	405	-
576	14.7	575	13.9

(ii) Formation of $[Cr(H_2O)_6]^{3+}[ClO_4^-]_3$ from chromium metal

As shown above, the chromium(III) species, $[Cr(H_2O)_6]^{3+}[ClO_4^-]_3$, can be prepared

from CrO₃ It can also be prepared directly from chromium metal by reduction of the

acid in the presence of air, see experimental section 6.5.3. The UV/Visible spectrum

produced from this reaction is identical to that obtained in table 4-7.

4.2.5. Hexaaquachromium(II), [Cr(H$_2$O)$_6$]$^{2+}$[ClO$_4$]$_2$, utilising perchloric acid, HClO$_4$.

Two attempts were made to prepare this compound, (i) from chromium trioxide, and (ii) directly from the oxidation of chromium metal.

(i) The species formed in section 4.2.4.i , [Cr(H$_2$O)$_6$]$^{3+}$[ClO$_4^-$]$_3$, as made from chromium trioxide, is reduced by shaking the aqueous solution with a zinc mercury amalgam under nitrogen for approximately 3 days.

The purple solution turns bright blue, this is assigned to [Cr(H$_2$O)$_6$]$^{2+}$[ClO$_4^-$]$_2$.

(ii) The second method involves the reduction of chromium metal in perchloric acid solution under a nitrogen atmosphere at ~80 °C. This produces a blue solution containing mainly the chromium(II) product, [Cr(H$_2$O)$_6$]$^{2+}$[ClO$_4^-$]$_2$. However, there is also a small quantity of [Cr(H$_2$O)$_6$]$^{3+}$[ClO$_4^-$]$_3$, the chromium(III) aqueous product. The solution is filtered to remove any unreacted metal and then further reduced by shaking with zinc mercury amalgam for 1 hour. This results in a light blue coloured solution. Both reactions result in the chromium(II) aqueous species [Cr(H$_2$O)$_6$]$^{2+}$[ClO$_4^-$]$_2$, this is confirmed by analysis of its UV/Visible spectrum, shown in table 4-8.

Table 4-8 Cr(II) complex

This work		Reference Stunzi[6]	
λ_{max}/ nm	ε / mol^{-1} dm^3 cm^{-1}	λ_{max} / nm	ε / mol^{-1} dm^3 cm^{-1}
714	5.1	714	5
not in range of our spectrometer		1,052	1.8

Method (ii) is preferred as this will result in the chromium(II) product within 4 hours, compared to 3 days if prepared by method (i).

4.2.6. Chromium alkyls from hexaaquachromium(II), $[Cr(H_2O)_6]^{2+}$ $[ClO_4]_2$

Following the successful preparation of the chromium(II) species,

$[Cr(H_2O)_6]^{2+}$ $[ClO_4^-]_2$, work was carried out to prepare a selection of chromium alkyl

compounds.

(i) Preparation of $[(H_2O)_5CrCHCl_2]^{2+}$ $[ClO_4^-]_2$

An acidified solution of $[Cr(H_2O)_6]^{2+}$ $[ClO_4^-]_2$ in a nitrogen atmosphere was reacted

with chloroform at 0 °C. This reacts over an hour to give a reddy brown coloured

solution containing the products $[(H_2O)_5Cr\text{-}CHCl_2](aq)$ (red) and $[(H_2O)_5Cr\text{-}Cl](aq)$

(green).

These are separated on an ion exchange chromatography column as outlined in section

4.2.3. The mechanism of this reaction is shown in scheme 4-2. The green fraction,

$[(H_2O)_5Cr\text{-}Cl](aq)$ is removed first. The second red fraction, was examined by

UV/Visible spectroscopy, table 4-9.

Table 4-9 UV/Visible data from the red fraction.

This work		Reference Stunzi[6]	
λ_{max} / nm	ε / mol^{-1} dm^3 cm^{-1}	λ_{max} / nm	ε / mol^{-1} dm^3 cm^{-1}
399	160	396	157
521	41	514	38.7
This peak can not be seen clearly due to its very high extinction coefficient.		266	4,290

This data was compared to the literature data for the organochromium compound

$[(H_2O)_5Cr\text{-}CHCl_2](aq)$ confirming that the chromium alkyl product has successfully

been produced. The concentration of chromium alkyl present was determined using

the Beer-Lambert law. This product could be routinely made and used in polymerisation experiments as explained later in this section.

(ii) Attempted synthesis of $[(H_2O)_5CrC(CH_3)_2OH]^{2+} [ClO_4^-]_2$.

The chromium(II) solution, $[Cr(H_2O)_6]^{2+} [ClO_4^-]_2$, was reacted with hydrogen peroxide and *iso*-propyl alcohol. The product, $[(H_2O)_5CrC(CH_3)_2OH]^{2+} [ClO_4^-]_2$, has been prepared previously by Espenson[7] and reported to yield a yellow solution. During this reaction the yellow colour, presumably from the chromium alkyl, could be seen briefly. When this solution was transferred to the chromatography column and separated only one green fraction was obtained.

It is feasible that the chromium alkyl is unstable and decomposes too quickly to be isolated by chromatography. Alternatively the complex could react with excess hydrogen peroxide being oxidised to an unidentified chromium(III) complex.

(iii) Attempted synthesis of $[(H_2O)_5CrCH_2Ph]^{2+} [ClO_4^-]_2$.

Benzyl chloride, CH_2ClPh, is added to an acidified solution of $[Cr(H_2O)_6]^{2+} [ClO_4^-]_2$, as originally reported by Anet and Leblanc[1]. This reaction should have produced the red chromium alkyl product $[(H_2O)_5CrCH_2Ph]^{2+} [ClO_4^-]_2$. During this synthesis attempt the solution goes to a reddy brown colour, however, within 10 minutes this colour disappears, turning green. The compound is too thermally unstable to be isolated and so no separation using the chromatography column was possible.

4.2.7. Polymerisation experiments using aqueous chromium alkyls

$[(H_2O)_5CrCHCl_2]^{2+}$ $[Y^-]_2$, (where Y is either PF_6^- or ClO_4^-), was used as a polymerisation initiator/catalyst for the polymerisation of hydroxyethyl methyl methacrylate and methyl methacrylate.

(i) The polymerisation of hydroxyethyl methyl methacrylate (HEMA) with $[(H_2O)_5CrCHCl_2]^{2+}$ $[PF_6^-]_2$

To a solution of Cr-R(aq) in deoxygenated water, hydroxyethyl methyl methacrylate (figure 4-2) was added. The temperature was subsequently raised to the polymerisation temperature, 40 °C. The quantities used are shown in table 4-10.

Figure 4-2 Monomer, Hydroxyethyl methacrylate (HEMA)

RMM = 130.14
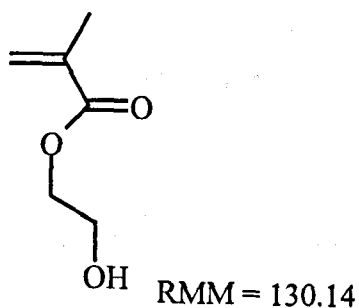
Table 4-10 Quantities used

Experiment	Cr-R cm^3	Cr-R mols	monomer g	monomer mols	THF cm^3	[Mon] : [Cr-R]
1	50	3.4×10^{-5}	5	5×10^{-2}	0	1500:1

This reaction resulted in a yield of PHEMA of ~20 % after 3 days at room temperature. However, the product proved to be insoluble in THF, as a result analysis by SEC was not possible. Although full analysis of the product did not prove possible, the formation of poly(HEMA) demonstrates that chromium alkyl complexes of this type are able to initiate polymerisation of methacrylates.

Further work using the chromium alkyls was carried out. This used the monomer methyl methacrylate, MMA, in place of HEMA, due in part to the ease with which poly(methyl methacrylate) products can be analysed. In addition, hydroxyethyl methacrylate, due to the method of preparing the monomer, is contaminated with a small quantity of ethylene glycol dimethacylate, which is a cross-linking agent. As a consequence there is the possibility that the reaction product contained cross-linked poly(HEMA), due to the presence of the cross-linking agent. A cross-linked polymer would render the polymer insoluble in THF, and thus analysis by SEC would not be possible. MMA does not contain a cross-linking agent so the products formed can be examined by SEC.

(ii) Polymerisation of methyl methacrylate, (MMA) with

$[(H_2O)_5CrCHCl_2]^{2+}[PF_6^-]_2$

Following the experimental procedure outlined in section 6.6.4, polymerisation experiments were carried out using a quantity of the chromium alkyl in THF solution with MMA monomer. The temperature was raised to 40 °C and the reaction allowed to proceed for 2 hours. The red solutions turn green over the time of the reaction. The quantities used during these reactions are shown in table 4-11.

Table 4-11 Quantities used.

Experiment	Cr-R cm³	Cr-R mols	monomer mols	THF cm³	[Mon] : [Cr-R]
2	1	1.5 x 10⁻⁵	1.9x 10⁻³	20	125:1
3	1	1.5 x 10⁻⁵	7.5 x 10⁻³	20	500:1
4	1	1.5 x 10⁻⁵	4.7 x 10⁻²	20	2500:1
5	1	1.5 x 10⁻⁵	9.4 x 10⁻²	20	5000:1
6	5	1.13 x 10⁻⁵	1.81 x 10⁻⁴	42	62:1
7	8	1.81 x 10⁻⁵	1.81 x 10⁻³	42	1000:1
8	8	1.81 x 10⁻⁵	9.04 x 10⁻²	32	5000:1
9	8	1.81 x 10⁻⁵	1.81 x 10⁻¹	22	10000:1
10	0	0	5.0 x 10⁻³	20	/
11	8	1.24 x 10⁻⁵	5.0 x 10⁻³	20	500:1
12	8	1.24 x 10⁻⁵	1.24 x 10⁻²	19	1000:1
13	4	2.56 x 10⁻⁵	2.56 x 10⁻²	17	5000:1

GPC data obtained from these reactions is shown in table 4-12.

Table 4-12 Results obtained

Experiment	% Yield	Mn	Mw	PDi
2	0	/	/	/
3	/	6,900	12,500	1.80
4	/	117,000	192,000	1.63
5	/	131,000	295,000	2.25
6	0	/	/	/
7	60	22,200	44,200	1.99
8	40	124,600	277,000	2.23
9	5	25,400	196,000	7.70
10	0	/	/	/
11	18	27,000	73,000	2.72
12	10	31,600	94,900	3.02
13	0.2	30,200	86,100	2.85

Figure 4-3 shows Mn as a function of concentration of chromium alkyl. No

correlation between Mn and the amount of chromium complex used is observed.

Figure 4-3 Mn against concentration of chromium alkyl
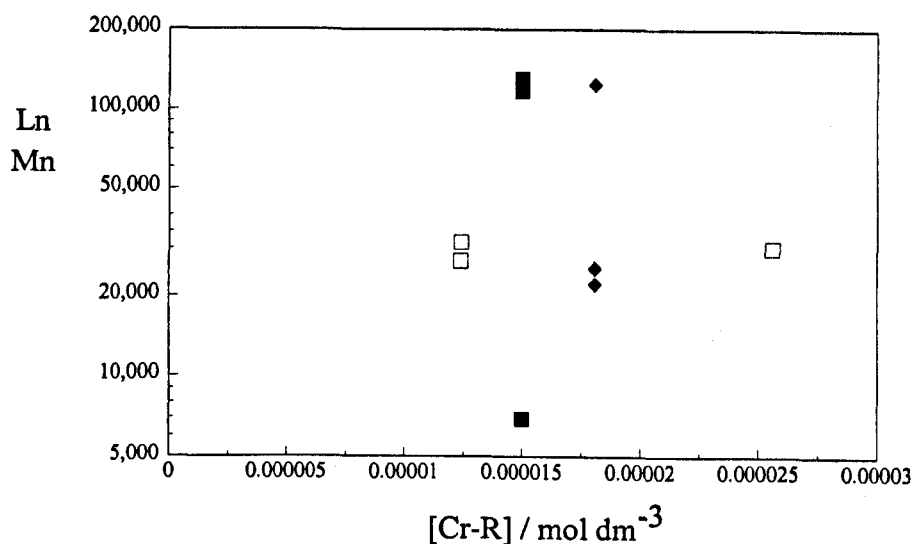
Figure 4-4 shows a plot of Mn against the ratio of [chromium alkyl] to [monomer].

This graph, shows that under these conditions no relationship between Mn and ratio of

monomer to initiator was observed.

Figure 4-4 Mn against ratio of [Cr-R] to [monomer]
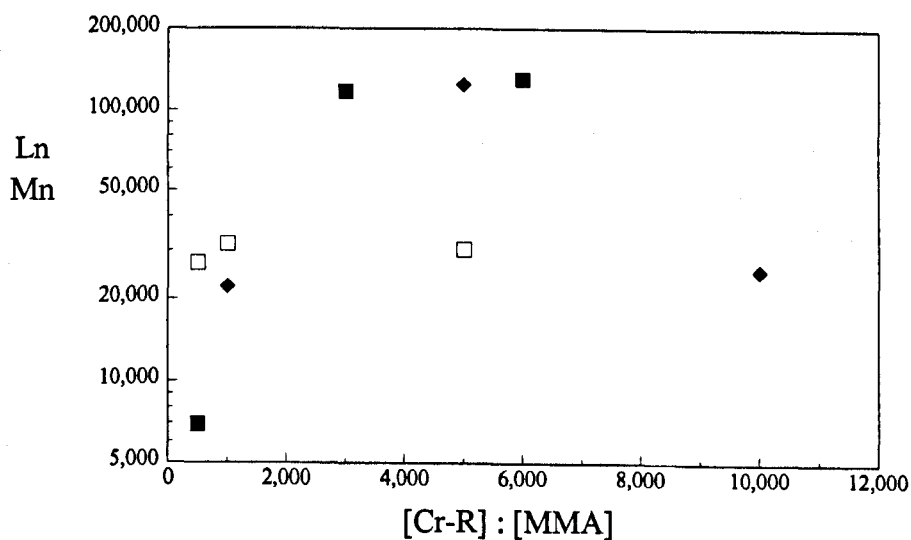
This would suggest that this system does not lead to controlled polymerisation[8] . It is

likely that homolysis of the Cr-carbon bond leads to R•, which initiates

polymerisation. Insufficient experiments were carried out for anything further to be

concluded.

(iii) Polymerisation of methyl methacrylate using $[(H_2O)_5CrCHCl_2]^{2+}$ $[ClO_4^-]_2$.

Polymerisation experiments were carried out using $[(H_2O)_5CrCHCl_2]^{2+}$ $[ClO_4^-]_2$. In this experiment the counter ion, ClO_4^- was employed. Polymerisation experiments were carried out with a quantity of chromium alkyl aqueous solution in THF with monomer (section 6.6.4). Table 4-13 shows the quantities used in this series of experiments. Table 4-14 reports the results obtained from these reactions.

Table 4-13 Quantities used

Experiment	Cr-R cm^3	Cr-R mols	monomer mols	THF cm^3	Ratio [Mon] : [Cr-R]
14	1	3.91×10^{-5}	3.9×10^{-3}	9	100:1
15	1	3.91×10^{-5}	1.95×10^{-2}	7	500:1
16	5	3.64×10^{-4}	1.8×10^{-2}	18	50:1
17	5	3.64×10^{-4}	3.64×10^{-2}	16	100:1
18	3	2.18×10^{-4}	3.64×10^{-2}	16	166:1
19	3	2.18×10^{-4}	3.64×10^{-2}	16	166:1

Table 4-14 Results obtained

Experiment	% Yield	Mn	Mw	PDi
14	<5	-unobtainable-		
15	10	31,600	136,000	4.30
16	8	45,000	69,500	1.40
17	40	42,000	98,900	2.35
18	16	47,400	81,400	1.71
19	8	39,400	75,800	1.92

This data was plotted to see if there was a relationship between Mn and the quantities of the components used. Figure 4-5 shows Mn as a function of concentration of chromium alkyl. From the data available it does not indicate that there is a relationship between Mn and the concentration of chromium alkyl used.

Figure 4-5 Mn against concentration of chromium alkyl
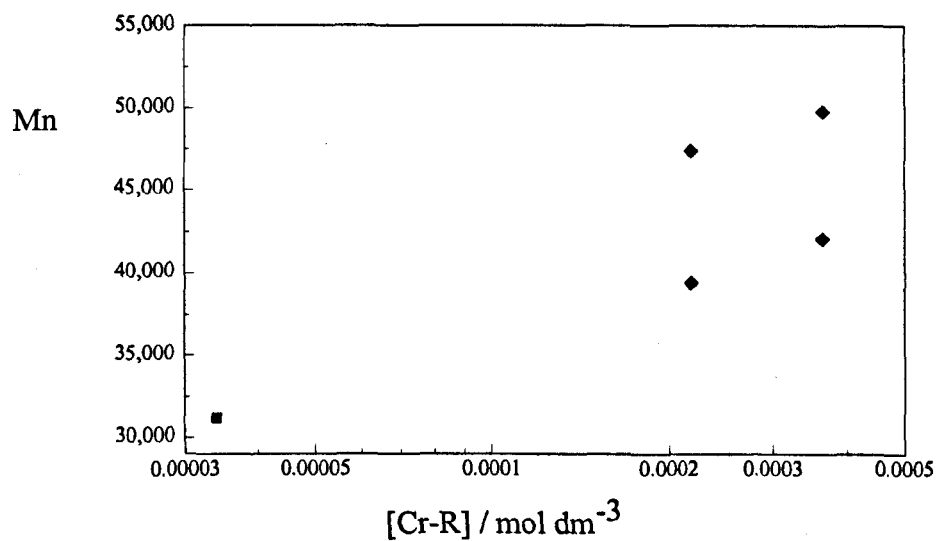
Figure 4-6 shows a graph of Mn verses the ratio of monomer to concentration of

chromium alkyl.

Figure 4-6 Mn against the ratio of concentration of Cr-R to monomer
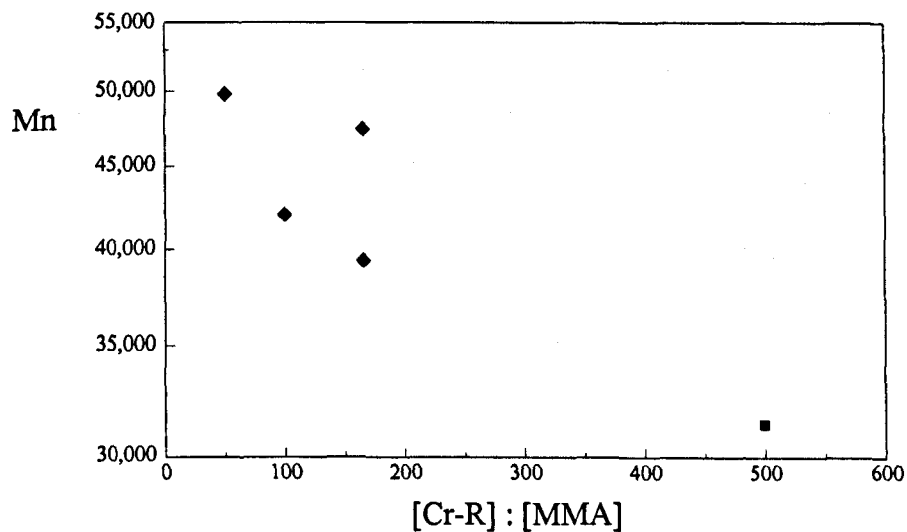
Both figures 4-5 and 4-6 suggest that this polymerisation reaction is not a controlled

polymerisation.

(iv) Dependence of Mn upon time

This experiment was carried out at room temperature. The reaction was sampled over time and analysed by SEC. Table 4-15 shows the quantities used in these experiments, table 4-16 indicates the results obtained from these reactions.

Table 4-15 Quantities used

Experiment	Cr-R cm^3	Cr-R mols	monomer mols	THF cm^3	Ratio [Mon] : [Cr-R]
20(A)	10	1.53×10^{-4}	7.63×10^{-3}	10	50:1
20(B)	10	1.53×10^{-4}	7.66×10^{-3}	10	50:1
21	5	7.65×10^{-5}	7.66×10^{-2}	10	1000:1

Table 4-16 Results obtained

Experiment	Time	% Yield	Mn	Mw	PDi
20(A)	½ hour	/	43,000	97,200	2.26
	1 hour	/	71,400	124,000	1.74
	2 hours	/	68,900	124,000	1.80
	24 hours	/	61,700	118,000	1.91
20(B)	24 hours	?	76,700	262,000	3.40
21	24 hours	20	162,000	390,000	2.40

The information from 20(A) indicates that the reaction does not exhibit an increase in Mn with time. In addition it is noted that the ratio of monomer to chromium alkyl for experiment 20(A) is 50:1, if the reaction was living it would be expected that a Mn (50 x 100, ratio x RMM of monomer) = 5,000 RMM at 100 % conversion would be obtained.

The molecular weights obtained are significantly higher than those expected for a living polymerisation experiment.

An alternative reaction, was to examine the possibility as to whether or not the active species were living, was to add extra monomer to the reaction after the original quantity had been consumed. If Mn is increased upon addition of further monomer

after the original quantity of monomer has been consumed in the reaction, this would suggest that the polymer chains can continue to grow. Table 4-17 shows the quantities used in these reactions, table 4-18 indicates the results obtained.

Table 4-17 Quantities used

Experiment	Cr-R cm^3	Cr-R mols	monomer mols	THF cm^3	Ratio [Mon] : [Cr-R]
22	20	6.4 x 10^{-4}	1.29 x 10^{-3}	10	20:1
23	10	3.2 x 10^{-4}	3.2 x 10^{-2}	10	100:1

Table 4-18 Results obtained

Experiment	% Yield	Mn	Mw	PDi
22	23	54,400	77,800	1.43
23	unobtainable	77,900	152,600	1.96
23*	30	104,000	165,000	1.58
* after 24 hours an extra 2 mL of MMA was added				

The results obtained for reaction 23 indicate that Mn has not increased as would have been expected for living polymerisation. A maximum Mn at 100 % conversion would have been expected at ~10,000, however, this is clearly not the case. From the data obtained it would indicate that the polymerisation reaction using chromium alkyls and monomer does give polymer, but the reaction is not a "controlled polymerisation".

An analysis of the polymers obtained from these reactions would give further evidence in elucidating a mechanism for this reaction. Section 4.2.8 contains a thermal gravimetric analysis (TGA) of several polymer samples.

4.2.8. TGA analysis of polymers obtained using the system of chromium alkyl with monomer

An analysis of polymers by TGA can give structural information on the way that the polymer chain was formed. From this, evidence as to the mechanism of the reaction can be obtained. Section 1.6.2 explains the unzipping process of PMMA and the information that can be obtained from TGA, this is based on work reported by others previously[9-16].

The polymers formed in this section were examined by TGA using the method described in experimental section 6.2.1, 3 examples appear below, figures 4-7 to 4-9.

Figure 4-7 PMMA polymer sample A
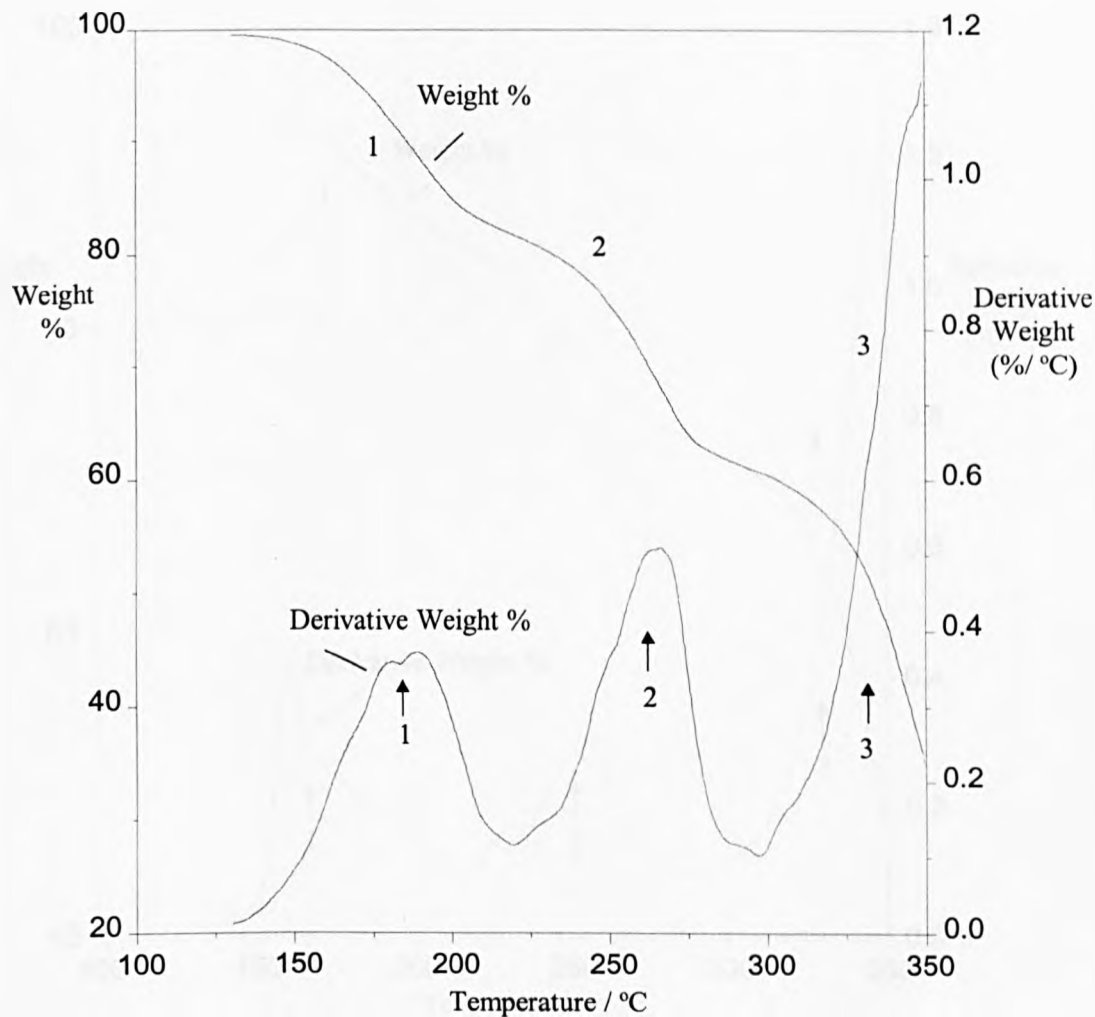
Figure 4-8 PMMA polymer sample B
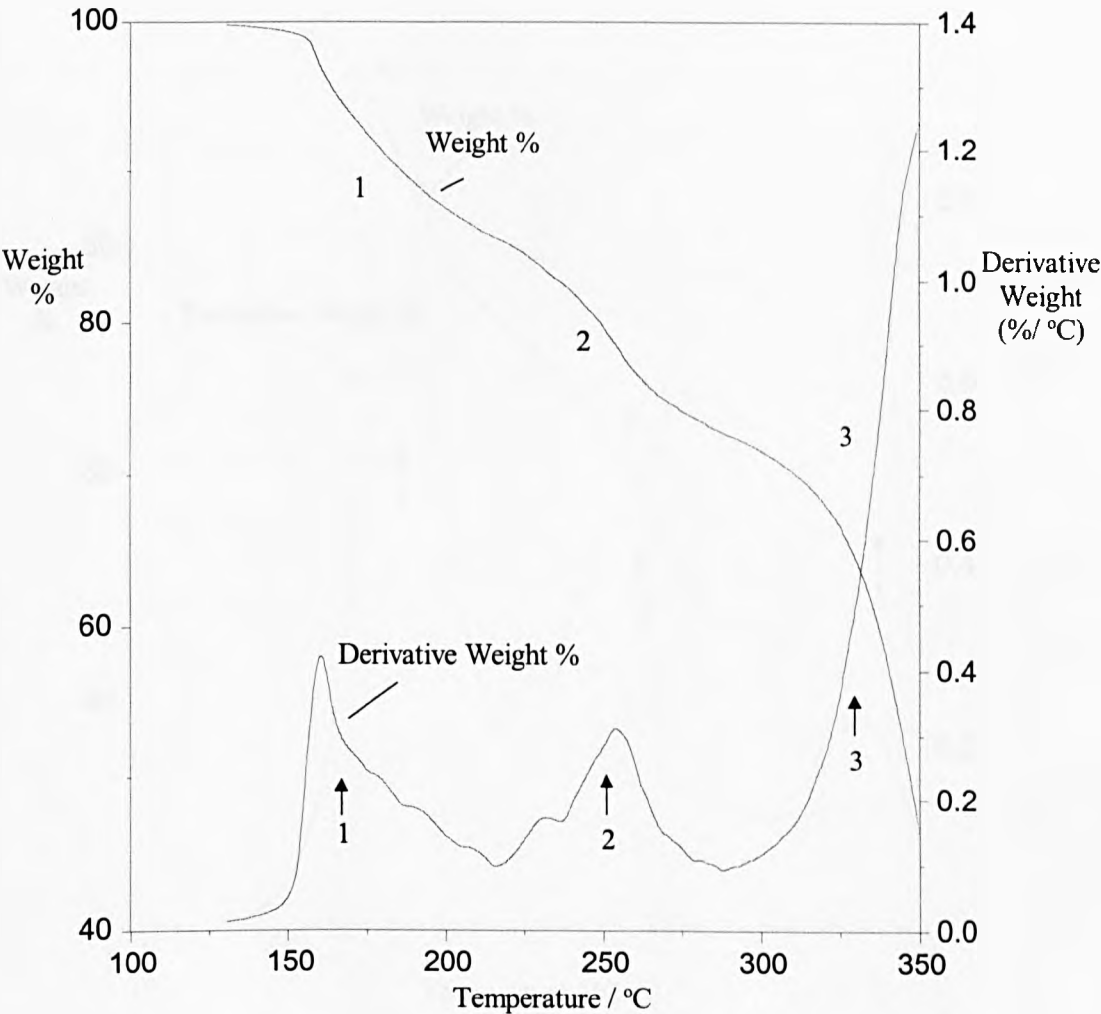
Figure 4-9 PMMA polymer sample C
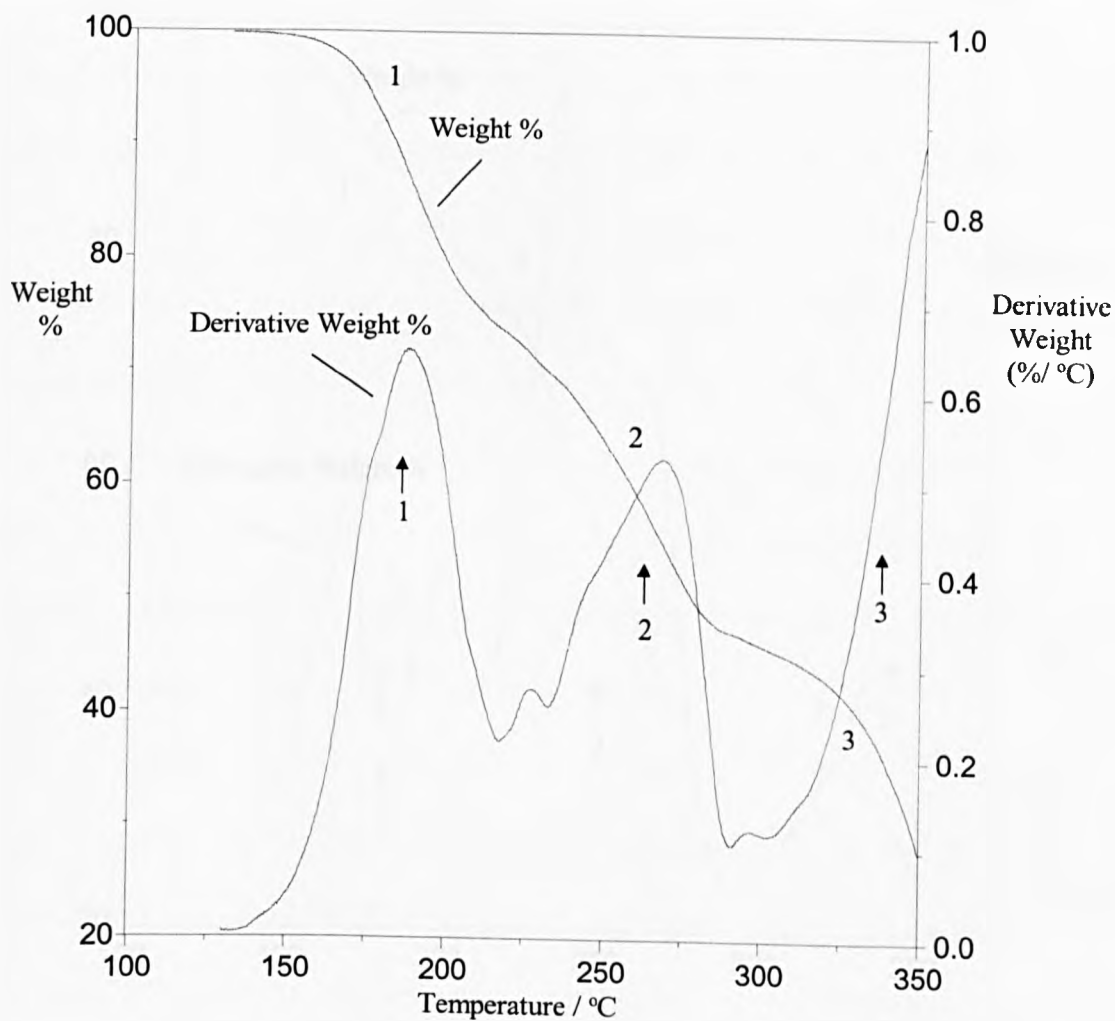
All 3 polymers A, B and C show 3 main degradation bands, (1) at ~150-200 °C and
(2) at ~225-260 °C and a final transition at >300 °C is main chain scission.

Figure 4-10 shows a PMMA polymer sample prepared from a typical free-radical

reaction using AIBN as initiator.

Figure 4-10 Polymer sample of PMMA, prepared by a free radical reaction, D
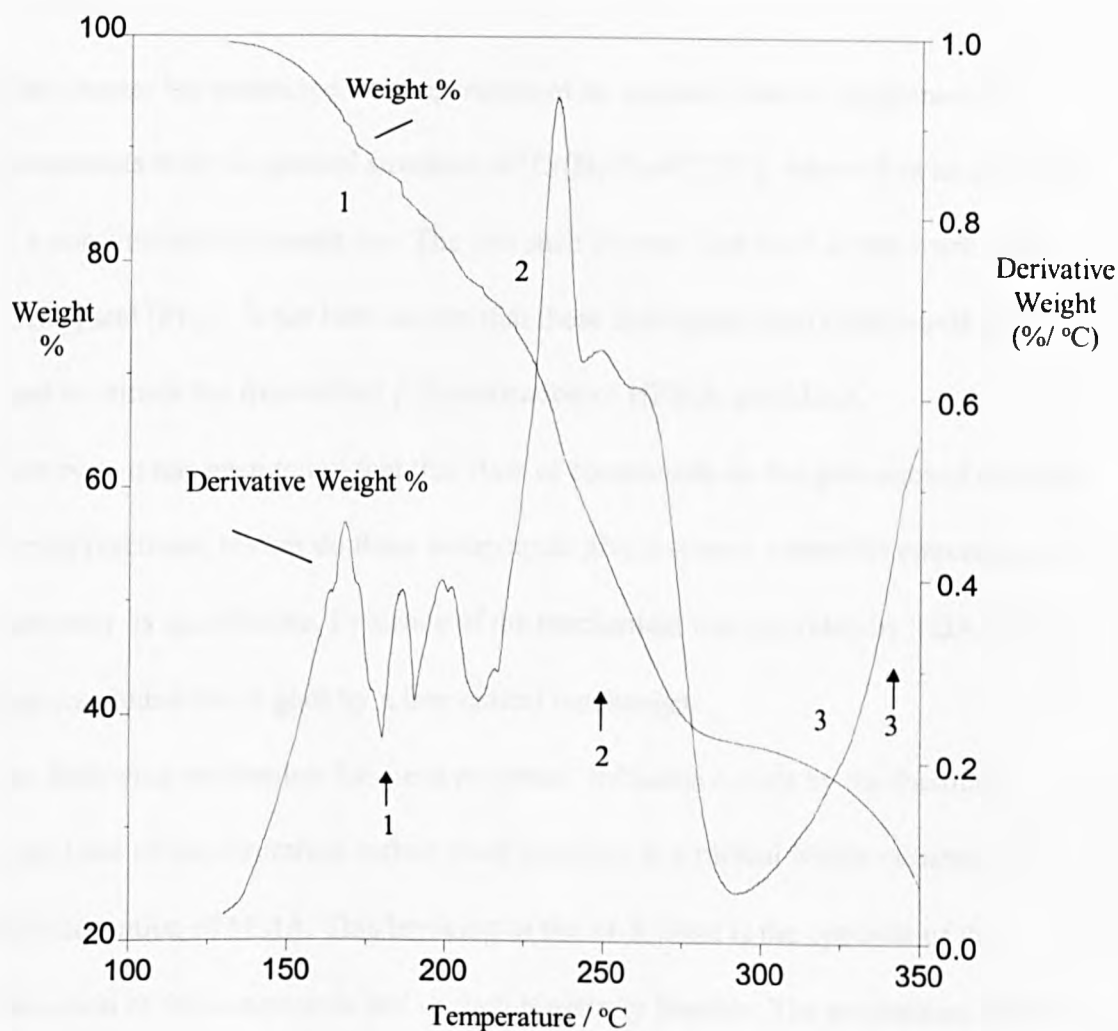
Peak 1 is characteristic of polymer chains terminated by head to head radical

combination reactions. Peak 2 is typical of an unsaturated end group. Peak 3 is due to

a saturated end group. The TGA traces in figures 4-7 to 4-9 are evidence that the

PMMA samples have been formed from a typical *free-radical* reaction carried out at

relatively low temperatures. Figure 4-10, showing a typical PMMA polymer sample

prepared by a free radical reaction, shows the same three characteristic peaks found in

the polymer samples examined.

4.3. Conclusions

This chapter has examined the preparation of an unusual class of organometallic compounds with the general structure of $[Cr(H_2O)_5\text{-}R]^{2+}[X^-]_2$, where R is an alkyl and X a non-interactive counter ion. The two such counter ions used in this work were $[ClO_4^-]$ and $[PF_6^-]$. It has been shown that these chromium alkyl compounds can be used to initiate the free-radical polymerisation of HEMA and MMA.

However, it has been found that this class of compounds do not give control over Mn during reactions, neither do these compounds give a system where the conversion of monomer is quantitative. Evidence of the mechanism was provided by TGA and it was concluded that it goes by a free radical mechanism.

The following mechanism has been proposed. Initiation occurs by the thermal homolysis of the chromium carbon bond resulting in a radical which initiates the polymerisation of MMA. This breaking of the M-R bond is the opposite of the formation of the compounds and as such is entirely feasible. The mechanism is shown in scheme 4-3.

Scheme 4-3 The free radical polymerisation of MMA using chromium alkyls

Decomposition of the chromium alkyl initiator

M-R $\longrightarrow$ M• + R•

Initiation of the monomer
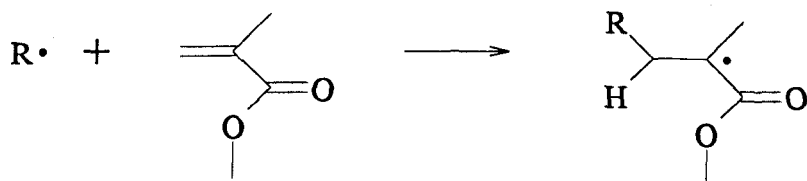
Propagation
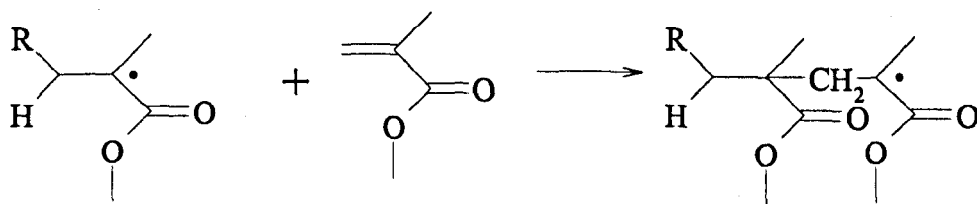
The propagation step is repeated many times before the following termination reactions occur in varying proportions.

Termination by combination.
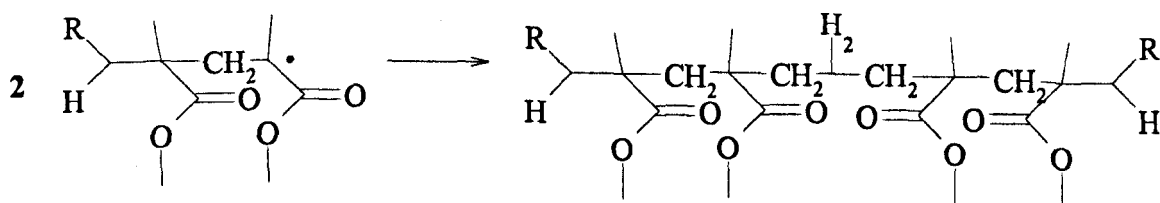
This gives a so called head to head linkage, seen as peak 1 in the TGA traces of

figures 4-7 to 4-10.

Termination by disproportionation.

This gives an unsaturated end group, visible as peak 2 in the TGA traces of figures 4-7 to 4-10. A saturated end group is also formed, this can be seen in a TGA trace at ~300 °C, peak 3.

4.4. References

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Chapter 5

Polymerisation of methyl

methacrylate in the presence of

tributyl aluminium-chromium

acetylacetonate-2,2'-dipyridine

5. Polymerisation of methyl methacrylate in the presence of tributyl aluminium- chromium acetylacetonate-2,2'-dipyridine

5.1. Introduction

In 1976 two Russian scientists, Korshun and Mazurek [1] reported on the polymerisation of methyl methacrylate, which they described as proceeding by a living anionic mechanism [1]. The system used chromium acetylacetonate, 2,2'-dipyridine and tributyl aluminium in toluene with MMA. This system is important to this work for two reasons, firstly it utilises a chromium compound, and secondly the reporting of a controlled living polymerisation reaction. These are preliminary results, Korshun and Mazurek concluded that the mechanism was anionic, as the polymers had characteristics produced by a living polymerisation mechanism. This work aims to examine further this promising system. Some recent examples of anionic polymerisation include work carried out by Antoun [2], Feast [3], Hatada [4], Kurock [5] and Tessyie [6].

5.2. Results and Discussion

It is apparent that this system might not proceed via an anionic pathway. The conclusion that it involved an anionic mechanism was based on Mn increasing with % conversion with linear rate progression, this assumption might be flawed. We decided to investigate this polymerisation method further. We were interested to see whether a chromium-aluminium bond system could be involved and in addition whether

controlled polymerisation, allowing control over Mn and PDi, was present. The effect

of chromium-aluminium on the stereochemistry and the resulting polymer was also of

interest. The following compounds have been used.

Figure 5-1 Compounds used in this chapter
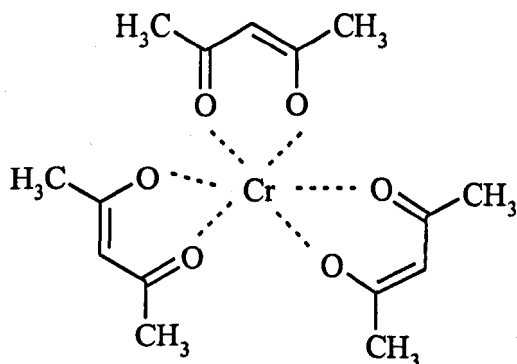
Chromium acetylacetonate
Cr(acac)$_3$
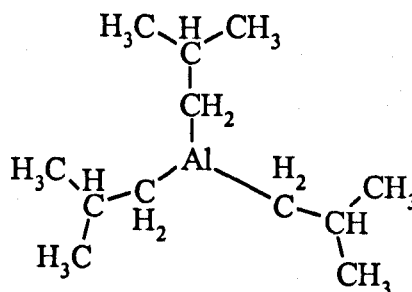
Tri-*iso*-butyl aluminium
TIBA
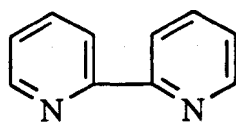
2,2'-Dipyridine
DIPY
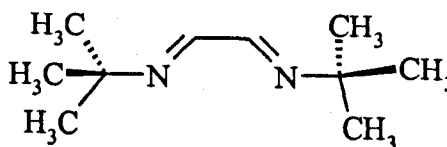
t-Butyl diazobutadiene
^{t}Bu-DAB

5.2.1. Polymerisation of MMA using tributyl aluminium-chromium acetylacetonate-2,2'-dipyridine

Polymerisation of MMA was attempted with a range of polymerisation conditions,

based on the work reported by Korshun and Mazurek. The results from this study are

reported in table 5.1. During the course of the reaction a range of colour changes were

observed.

Chromium acetylacetonate is a purple solid, and purple in toluene solution. This

becomes brown when tri-*iso*-butyl aluminium is added. On addition of DIPY this

becomes reddy/purple. As the solution is warmed to room temperature the solution

becomes darker. No further colour changes are observed upon addition of MMA. The many colour changes are due to changes in both oxidation states and to different compounds being formed. The following work follows the experimental procedure outlined in section 6.6.5.

Table 5-1 Experimental quantities

Experiment	Cr(acac)$_3$ moles	TIBA moles	DIPY moles	MMA moles	Ratio* [Cr(acac)$_3$]:[TIBA]:[DIPY]:[MMA]			
Ideal ratios according to reference [1]					1	3	1.5	
1	2.11 x 10^{-4}	6.70 x 10^{-4}	3.92 x 10^{-4}	1.01 x 10^{-1}	1	3.17	1.85	480
2	2.16 x 10^{-4}	6.70 x 10^{-4}	3.56 x 10^{-4}	1.01 x 10^{-1}	1	3.10	1.65	470
3	1.81 x 10^{-4}	6.70 x 10^{-4}	3.43 x 10^{-4}	5.07 x 10^{-2}	1	3.70	1.89	280
4	4.81 x 10^{-4}	1.68 x 10^{-3}	8.23 x 10^{-4}	5.07 x 10^{-2}	1	3.48	1.71	105
5	5.03 x 10^{-4}	1.68 x 10^{-3}	8.28 x 10^{-4}	5.07 x 10^{-2}	1	3.33	1.65	101
6	1.77 x 10^{-4}	6.70 x 10^{-4}	3.46 x 10^{-4}	5.07 x 10^{-2}	1	3.79	1.96	287
7	2.00 x 10^{-4}	6.70 x 10^{-4}	3.29 x 10^{-4}	5.07 x 10^{-2}	1	3.35	1.64	253
8	1.99 x 10^{-4}	6.70 x 10^{-4}	3.40 x 10^{-4}	5.07 x 10^{-2}	1	3.36	1.71	254
9	1.91 x 10^{-4}	6.70 x 10^{-4}	3.25 x 10^{-4}	5.07 x 10^{-2}	1	3.5	1.70	265
10	1.98 x 10^{-4}	6.70 x 10^{-4}	3.18 x 10^{-4}	5.07 x 10^{-2}	1	3.38	1.6	256
11	2.05 x 10^{-4}	6.70 x 10^{-4}	2.74 x 10^{-4}	5.07 x 10^{-2}	1	3.26	1.34	247
12	1.88 x 10^{-4}	6.70 x 10^{-4}	3.73 x 10^{-4}	5.07 x 10^{-2}	1	3.57	1.99	270
13	1.96 x 10^{-4}	1.00 x 10^{-3}	3.54 x 10^{-4}	5.07 x 10^{-2}	1	5.11	1.81	259
14	2.04 x 10^{-4}	1.00 x 10^{-3}	3.64 x 10^{-4}	2.80 x 10^{-2}	1	4.91	1.79	138
15	1.97 x 10^{-4}	1.00 x 10^{-3}	3.16 x 10^{-4}	5.05 x 10^{-2}	1	5.08	1.6	257
16	2.00 x 10^{-4}	7.00 x 10^{-4}	3.16 x 10^{-4}	2.06 x 10^{-2}	1	3.51	1.58	103
17	1.95 x 10^{-4}	1.3 x 10^{-3}	3.17 x 10^{-4}	2.06 x 10^{-2}	1	6.66 (XS)	1.62	105
18	2.06 x 10^{-4}	2.00 x 10^{-3}	3.46 x 10^{-4}	4.67 x 10^{-2}	1	9.72 (XS)	1.68	227
19	2.07 x 10^{-4}	2.00 x 10^{-3}	2.93 x 10^{-4}	4.67 x 10^{-2}	1	9.65 (XS)	1.45	225

* Molar ratio of [Cr(acac)$_3$] : [TIBA] : [DIPY] : [MMA]

Table 5-2 Results obtained from these experiments

Experiment	Yield %	[Cr]:[MMA]	Mn	Mw	PDi
1	89	480	81,000	181,000	2.23
2	100	470	112,000	242,000	2.17
3	6	280	29,000	117,000	4.10
4	12	105	28,000	178,000	6.47
5	26	101	48,000	312,000	6.71
6	32	287	40,000	75,000	1.90
7	8	253	45,000	185,000	4.14
8	72	254	45,000	99,000	2.21
9	100	265	97,000	244,000	2.51
10	94	256	54,000	127,000	2.35
11	55	247	36,000	74,000	2.05
12	94	270	24,000	34,000	1.40
13	37	259	26,000	73,000	2.83
14	39	138	24,000	51,000	2.11
15	100	257	69,000	229,000	3.32
16	61	103	32,000	57,000	1.79
17	95	105	33,000	77,000	2.30
18	<5	227	839,000	1275,000	1.85
19	<5	225	75,000	163,000	2.18

The data in table 5-1 and 5-2 show the results after 2 hours of polymerisation. The

data suggests, that despite similar conditions being used the results are varied,

particularly the yields obtained over the course of the reactions.

Figure 5-2 shows a plot of Mn w.r.t. the ratio of [Cr(acac)$_3$] to [MMA].

Figure 5-2 Plot Mn verses ratio of moles of Cr(acac)₃ to moles of monomer
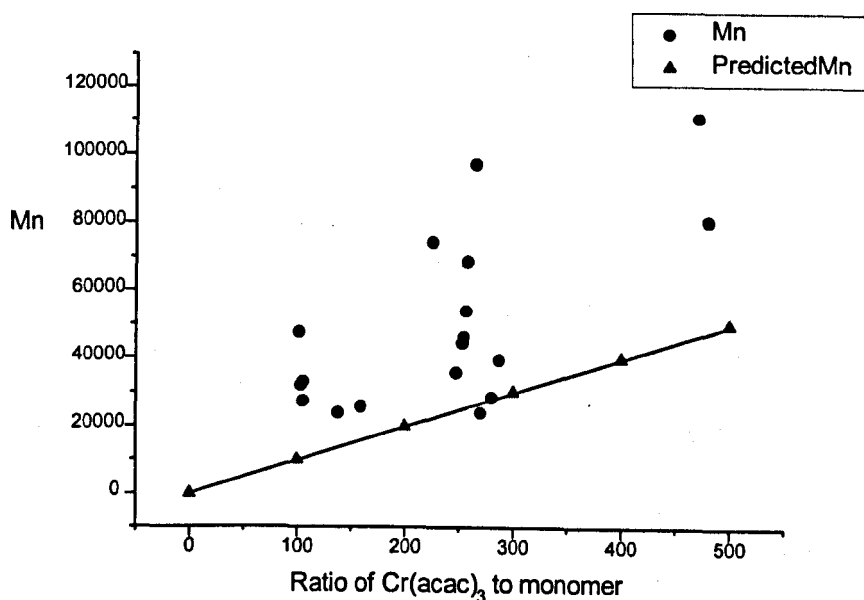
Figure 5-2 also shows the points expected for Mn if the reaction followed a living

polymerisation reaction. The two plots show that there is no relationship between Mn

and the ratio of chromium acetylacetonate to MMA. It is not clear in this analysis, due

to the method of the experiment, if all the chromium is involved in the initiation.

In Figure 5-2 the line showing predicted Mn shows that the actual Mn obtained are

higher than expected. If the reaction was a 'living' reaction as stated by Korshun and

Mazurek, then if 100 % conversion was achieved then these results should fall on the

predicted Mn line. Many factors could be affecting this reaction. Anionic

polymerisation reactions are extremely sensitive to experimental conditions. These

include the presence of water, oxygen and indeed the purity of the reactants. A trace

impurity of any of the above could be affecting these reactions and hence the results

obtained.

The reaction conditions were altered in the following experiments. The chromium

acetylacetonate and TIBA solution in toluene was warmed to room temperature, from

-78 °C, before the addition of DIPY. The result of this was that no polymer was

formed. The experiment was repeated, removing samples at intervals to examine by

SEC and determine percentage conversion by gravimetric analysis.

Table 5-3 Table of quantities for experiment 20

Sample	Cr (acac)$_3$ moles	TIBA moles	DIPY moles	MMA moles	Ratio [Cr(acac)$_3$] : [TIBA] : [DIPY] : [MMA]			
20	1.98×10^{-4}	1.00×10^{-3}	3.40×10^{-4}	5.05×10^{-2}	1	5.04	1.71	254

Table 5-4 Table of yields for experiment 20

Sample	Time / minutes	Conversion %	Mn	Mw	PDi
1	3	4	4,000	5,800	1.42
2	12	11	6,500	17,500	2.70
3	23	20	20,000	53,300	2.70
4	34	34	21,400	61,000	2.86
5	47	53	22,700	75,600	3.33
6	61	45	25,300	81,100	3.23
7	76	47	16,500	78,500	4.76
8	94	60	27,400	89,400	3.26
9 (final)	840	80	30,100	88,000	2.93

Figure 5-3 shows a graph with the results of the experiment as a plot of Mn against

percentage conversion.

Figure 5-3 Plot of Mn against percentage conversion
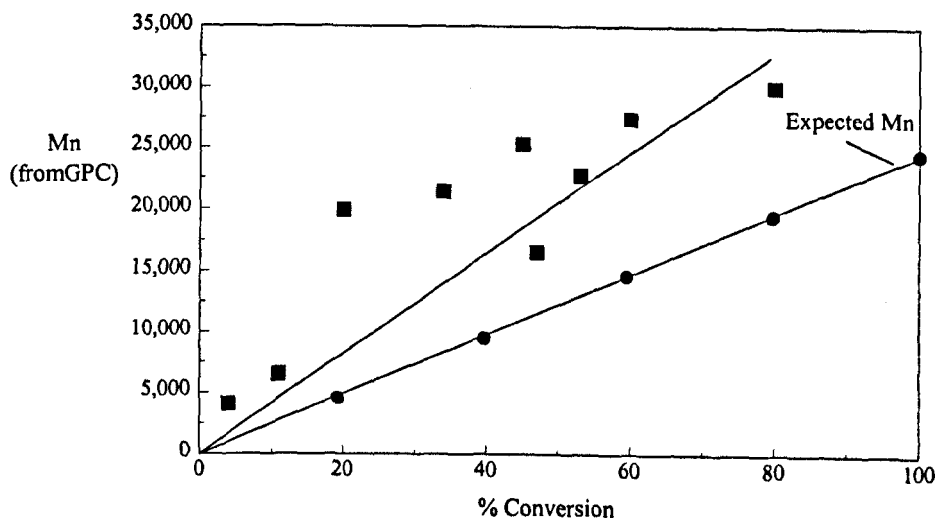
Figure 5-3 shows that the molecular weights achieved were higher than those expected. However, Mn does increase with increasing conversion. This suggests that the reaction does not proceed with the 100 % initiator efficiency.

5.2.2. The effect of changing the alkyl aluminium for the polymerisation of MMA with alkyl-aluminium chromium acetylacetonate-2,2'-dipyridine

The experimental conditions of this polymerisation system were modified to change the alkyl aluminium used. A quantity of chromium acetylacetonate was reacted with tripropylaluminium in toluene at -78 °C. This was followed by the addition of DIPY, then MMA, modified from 6.6.5.

Table 5-5 Table of quantities

Experiment	Cr (acac)$_3$ moles	TPrAl moles	DIPY moles	MMA moles	Ratio [Cr(acac)$_3$] : [TPrAl] : [DIPY] : [MMA]		
21	1.98×10^{-4}	1.00×10^{-3}	3.56×10^{-4}	2.8×10^{-2}	1	5.04	1.79	141
22	2.06×10^{-4}	1.00×10^{-3}	3.44×10^{-4}	5.07×10^{-2}	1	4.85	1.67	246
23	2.03×10^{-4}	1.00×10^{-3}	3.41×10^{-4}	5.05×10^{-2}	1	4.93	1.68	249

Table 5-6 Table of results

Experiment	Yield %	Mn	Mw	PDi
21	<5	5,100	165,000	32.20
22	<5	79,800	115,000	1.43
23	<5	33,100	281,000	8.48

Where tripropyl aluminium is used, instead of triosobutyl aluminium, a significant drop in yield is obtained with high and variable molecular weight distributions.

A quantity of chromium acetylacetonate was reacted with trimethylaluminium in toluene at -78 °C. This was followed by the addition of DIPY, then MMA, modified from 6.6.5.

Table 5-7 Table of quantities

Experiment	Cr (acac)$_3$ moles	Me$_3$Al moles	DIPY moles	MMA moles	Ratio [Cr(acac)$_3$] : [Me$_3$Al] : [DIPY] :[MMA]			
24	3.98×10^{-4}	4.00×10^{-3}	6.53×10^{-4}	3.74×10^{-2}	1	10.05	1.64	94
25	3.98×10^{-4}	4.00×10^{-3}	6.65×10^{-4}	3.74×10^{-2}	1	10.05	1.67	94
26	3.84×10^{-4}	4.00×10^{-3}	6.83×10^{-4}	3.74×10^{-2}	1	10.40	1.78	97

Table 5-8 Table of results

Experiment	Yield %	Mn	Mw	PDi
24	61	34,500	64,200	1.87
25	80	16,000	23,000	1.46
26	90	8,300	11,000	1.32

This result shows the reaction proceeds to relatively high conversion with a PDi below 2.

A quantity of chromium acetylacetonate was reacted with triethylaluminium in toluene at -78 °C. This was followed by the addition of DIPY, then MMA, modified from 6.6.5.

Table 5-9 Table of quantities

Experiment	Cr (acac)₃ moles	Et₃Al moles	DIPY moles	MMA moles	Ratio [Cr(acac)₃] : [Et₃Al] : [DIPY] : [MMA]		
26	2.07 x 10⁻⁴	1.00 x 10⁻³	3.34 x 10⁻⁴	4.67 x 10⁻²	1	4.83	1.61	226
27	2.01 x 10⁻⁴	1.90 x 10⁻³	3.25 x 10⁻⁴	4.86 x 10⁻²	1	9.45	1.62	242

Table 5-10 Table of results

Experiment	Yield %	Mn	Mw	PDi
26	<5	32,000	58,600	1.83
27	<5	47,500	92,800	1.95

Using a less sterically demanding alkyl aluminium has shown that control over the reaction is still not achieved and polydispersities are still high.

5.2.3. The effect of changing the co-ordinating ligand in the system of alkyl-aluminium chromium acetylacetonate

Following the changes in the experiment whereby the alkylaluminium was changed during the experiment, the following experiments investigated the use of different ligands other than DIPY.

a) Triphenyl phosphine

Modified from 6.6.5, in this case the ligand DIPY was substituted by triphenyl phosphine. This has changed the reaction from using a bidentate ligand to a monodentate ligand.

Table 5-11 Table of quantities

Experi ment	Cr (acac)₃ moles	TIBA moles	PPh₃ moles	MMA moles	Ratio [Cr(acac)₃] : [TIBA] : [PPh₃] : [MMA]			
28	2.09×10^{-4}	1.00×10^{-3}	3.54×10^{-4}	5.05×10^{-2}	1	4.79	1.70	242
29	1.98×10^{-4}	6.70×10^{-4}	3.32×10^{-4}	5.05×10^{-2}	1	3.39	1.68	256
30	4.07×10^{-4}	1.50×10^{-3}	6.87×10^{-4}	3.74×10^{-2}	1	3.69	1.69	92
31	4.06×10^{-4}	1.50×10^{-3}	7.02×10^{-4}	1.87×10^{-2}	1	3.69	1.73	46

Table 5-12 Table of results

Experiment	Yield %	Mn	Mw	PDi
28	0	/	/	/
29	83	520,000	891,000	1.71
30	39	66,700	600,000	8.98
31	100	61,300	505,000	8.22

The results show, that the use of this PPh₃ ligand causes some changes to the reaction.

The yields obtained are relatively high in these experiments. However, the molecular

weights and polydispersity's are varied with very large PDi's obtained. This is

possibly due to the monodentate ligand, which does not posses the ability to stabilise

the intermediate, formed from the chromium compound and alkyl aluminium.

b) Butyl-diazobutadiene (^{t}Bu-DAB)

Modified from 6.6.5, in this case the ligand DIPY was substituted by ^{t}Bu-DAB [7].

Table 5-13 Table of quantities

Experi- ment	Cr (acac)₃ moles	TIBA moles	^{t}Bu-DAB moles	MMA moles	Ratio [Cr(acac)₃] : [TIBA] : [^{t}Bu-DAB] : [MMA]			
32	4.09×10^{-4}	4.00×10^{-3}	7.22×10^{-4}	4.67×10^{-2}	1	9.77	1.76	114

Table 5-14 Table of results

Experiment	Time	Mn	Mw	PDi
32	35 min	16,700	26,700	1.65
	70 min	20,100	29,200	1.54
	180 min	28,000	47,500	1.73
	3 days	14,200	81,800	5.86

5.2.4. Thermal gravimetric analysis of poly(methyl methacrylate) formed with alkyl-aluminium chromium acetylacetonate-2,2'-dipyridine

Polymers formed in this section were examined by thermal gravimetric analysis. The results from this analysis were then used in an attempt to determine the kind of mechanism occurring. The TGA process has been discussed in the introduction, experimental details can be found in section 6.2.1. Figures 5-4 to 5-7 show the TGA for PMMA samples A, B, C, and D.

Figure 5-4 PMMA sample A
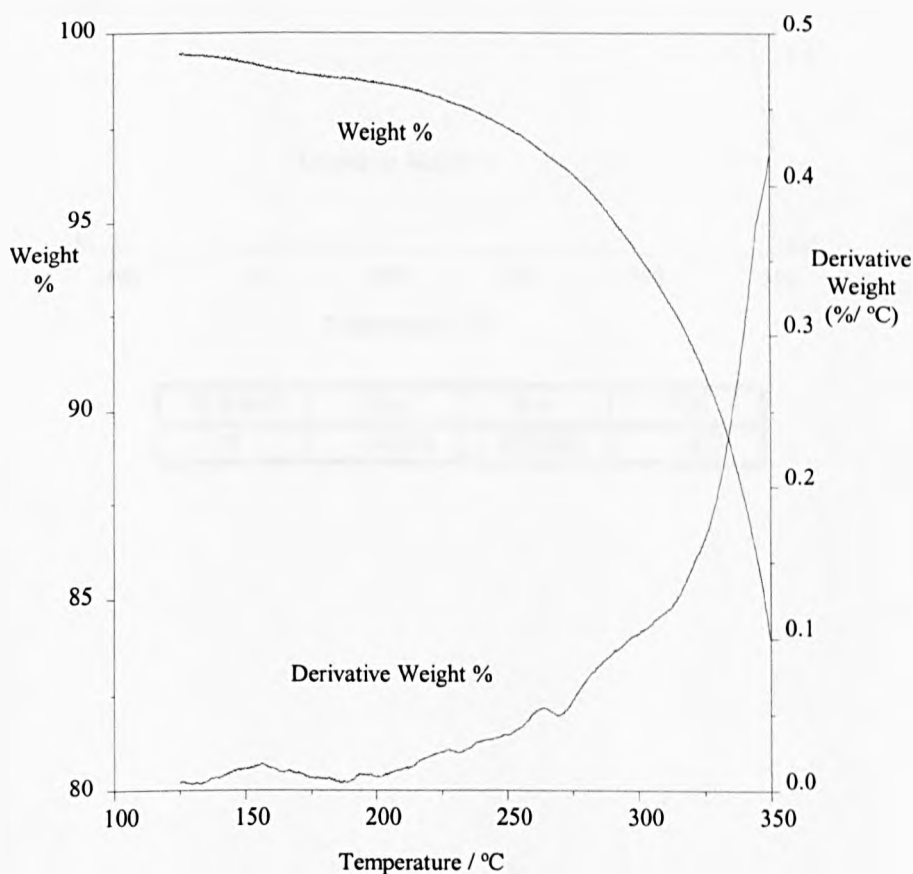
% Yield	Mn	Mw	PDi
90	81,000	181,000	2.24

Figure 5-5 PMMA sample B
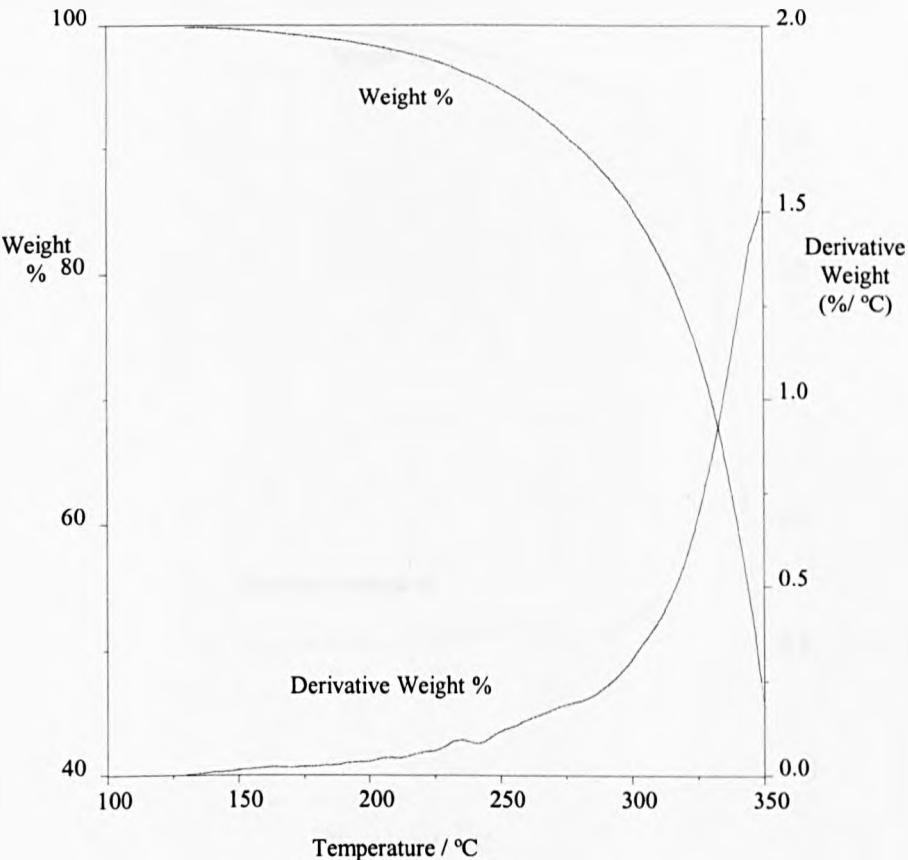
% Yield	Mn	Mw	PDi
8	44,600	185,000	4.14

Figure 5-6 PMMA sample C
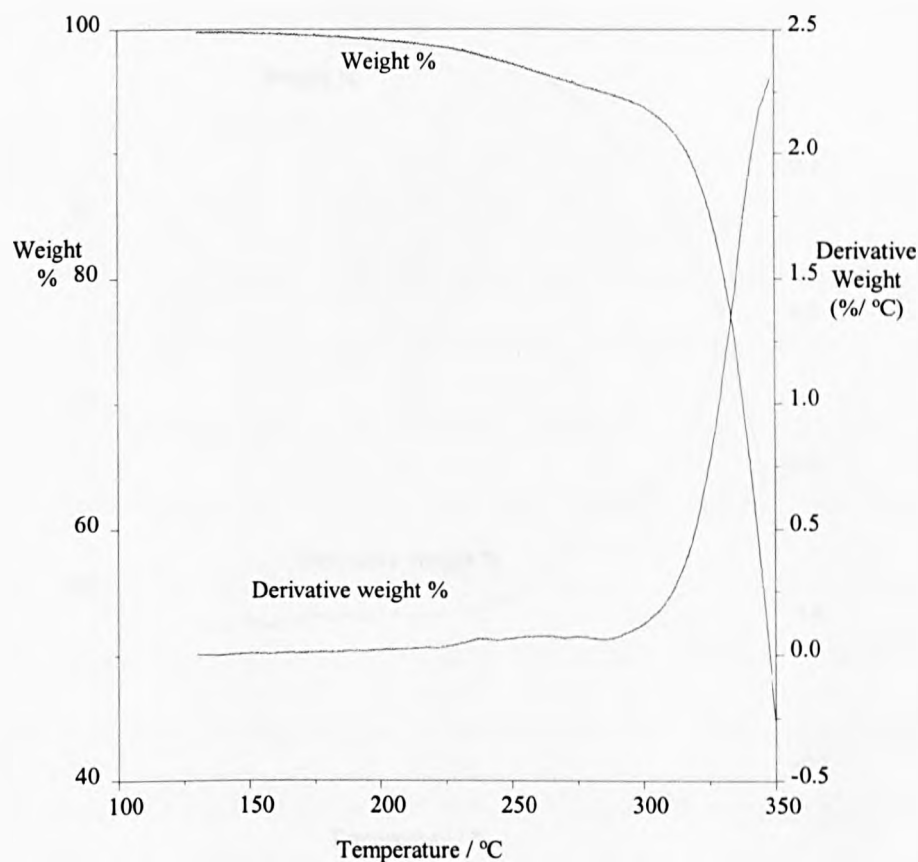
% Yield	Mn	Mw	PDi
94	54,100	127,000	2.35

Figure 5-7 PMMA sample D, from trimethylaluminium.
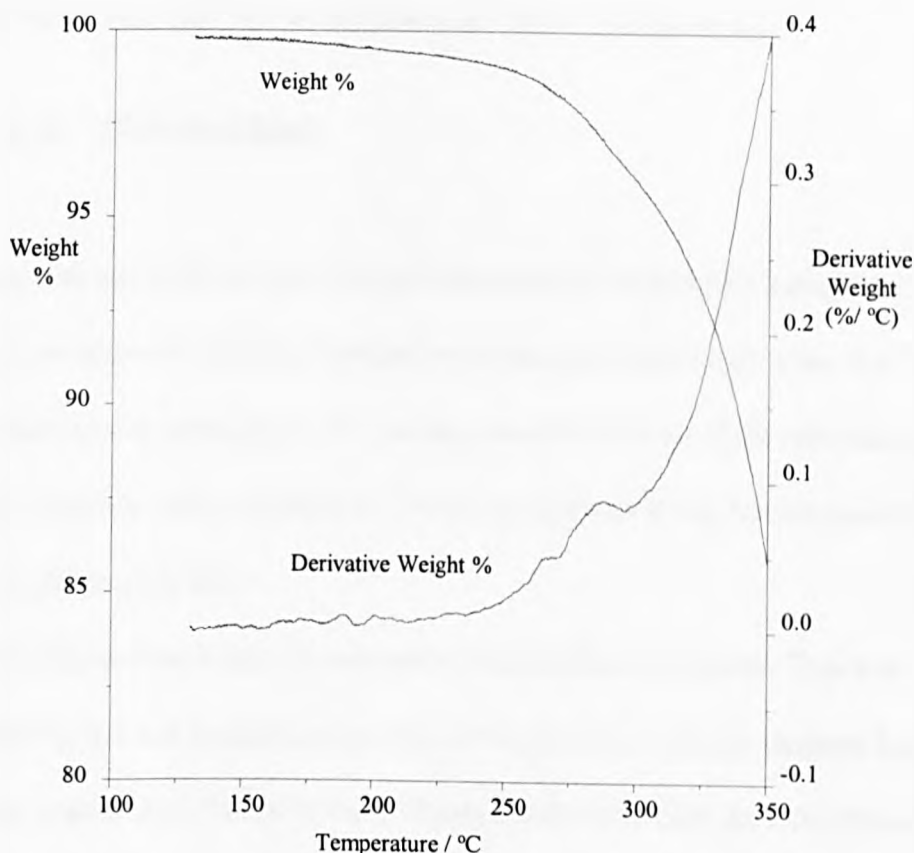
% Yield	Mn	Mw	PDi
61	34,400	64,200	1.89

The traces in figures 5-4 to 5-7 show similar thermal decomposition's. Examples A, B

and C use the method outlined in 6.6.5. Example D uses a procedure modified from

6.6.5, where trimethyl aluminium is used in place of tributylaluminium. The traces

show only the one decomposition transition in these plots, from a point at ~250 °C.

The main point of increase is at ~300 °C, this is consistent with a terminally saturated

methyl group and main chain scission. The results from TGA are consistent with a

polymer structure as might be expected from anionic polymerisation. Anionic

polymerisation results in a polymer with just the one type of end group. This kind of

polymerisation forms a stable head to tail polymer with a saturated methyl group at the end. *As a result only the one transition at ~300 °C will be found.*

5.3. Conclusions

This work has been carried out to try and determine, if as was first thought by Korshun and Mazurek, that the mechanism would give results indicating that 'living' polymerisation was taking place. It was also carried out to see if the reaction system could be improved upon, additionally it was hoped to see if any further aspects of control could be obtained.

This work has indicated that the reaction is indeed anionic in nature. This was confirmed by thermal gravimetric analysis of some of the polymer samples formed using this system. In addition the lack of polymer formed when the catalytic system has been warmed up, before the addition of ligand and monomer. Anionic reactions are very sensitive to the purity of the reagents. This system is no exception and is one of the reasons for the lack of consistency in the results. From TGA investigations, polymers formed by this system have a saturated end group. This will result in a thermally stable polymer, unlike some free radical formed polymers, which can degrade at low temperatures such as 150 °C.

5.4. References

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Chapter 6

Experimental

6. Experimental

6.1. General Experimental Procedures

All reactions were carried out using standard Schlenk line techniques, under an atmosphere of nitrogen, unless stated otherwise. All reagents were used as received, unless otherwise stated. All solvents and monomers were deoxygenated prior to use, by purging with nitrogen for over one hour, or alternatively by carrying out at least three freeze pump thaw cycles in liquid nitrogen. Addition of monomers and solvents was performed by syringe or cannula.

6.2. Characterisation Methods

6.2.1. Characterisation of polymers

Polymer molecular weight data was obtained by size exclusion chromatography, using a Polymer Laboratories modular SEC system. This was equipped with two PLgel 5 μm mixed-C columns (300 x 7.5 mm) and one PLgel 5 μm guard column (50 x 7.5 mm). Low molecular weight polymers were analysed on a similar system equipped with one PLgel 5 μm mixed-E column (300 x 7.5 mm).

Both systems used THF as the eluant at 1 mL min^{-1} and a differential refractive index detector. A LKB Bromma 2141 Variable wave length detector was used for UV analysis.

Calibration was performed using narrow PMMA standards (Mp = 1040-1577000), which were obtained from Polymer Laboratories together with authentic samples of MMA dimer and trimer[1].

Yields of polymerisation reactions were calculated by drying a known mass of reaction mixture to constant weight in a vacuum oven maintained at 80 °C. Alternatively percentage yields were calculated from precipitation of the polymer in appropriate solvent then drying in a vacuum oven at 80 °C. ^{1}H and ^{13}C NMR spectra were obtained using a Bruker ACF 250 MHz spectrometer. Spectra were referenced using the resonance's of residual protons in the deuterated solvents. Deuterated solvents were stored under argon, and kept dry over molecular sieves (3Å).

Thermal Gravimetric Analysis (TGA) is used to perform end-group analysis on polymers. A summary of characterisation by this method can be found in chapter 1, (section 1.6.2).

TGA was carried out on a HiRes TGA 2950 Thermogravimetric analyzer, using a standard dynamic method whereby samples were equilibrated at 125 °C, followed by ROMP at 5 °minute[-1] up to 350 °C. Sample size ranged from 5 mg to 25 mg of polymer powder, pre-dried for two hours in a vacuum oven at 80 °C.

6.2.2. Characterisation of Schiff base ligands

Nuclear magnetic resonance spectra were recorded using a Bruker AC-250 instrument. Spectra were recorded and referenced as described in section 6.2.1.

Mass spectrometry by Chemical Ionistaion (CI), Electron Impact (EI) or Fast Atom Bombardment (FAB) were recorded on a Kratos MS 80 spectrometer. Infra-red

spectra of compounds were recorded as Nujol mulls on a Unicam Mattson 1000 FT-IR spectrometer. Elemental analysis was performed on a Leeman Inc. Spectrometer.

6.2.3. Characterisation of chromium ligand complexes

Crystal structures were solved by direct methods. Suitable crystals were quickly glued to quartz fibres, coated in dry nujol, and cooled in the cold nitrogen gas stream of the diffractometer. Anisotropic thermal parameters were used for all non-H atoms whilst hydrogen atoms were inserted at calculated positions and fixed, with isotropic thermal parameters (U ≈ 0.08 Å), riding on the supporting atom. The structure solutions were carried out using SHELXTL [2] version 5.0 software on a Silicon Graphics Indy workstation, refinements were carried out using SHELXL96 [3] software, minimising on the weighted R factor wR2. Additional material is available from the Cambridge Crystallographic Data Center.

6.2.4. Characterisation of aqueous organochromium complexes

Due to the sensitivity and reactivity of these complexes, analysis was limited to UV/Visible spectrometry on a Unicam 8700 series scanning spectrophotometer. The ultraviolet/visible spectrometer scanned between 200 nm and 850 nm, with a bandwidth of 2 nm and a scan speed of 2000 nm minute^{-1}.

For air sensitive solutions an adapted quartz cell was used, a 1 cm^2 cell with a Youngs tap attached to it to allow it to be degassed and sealed under nitrogen *if necessary*, before being placed in the examination compartment.

Characterisation of complexes could be made by comparison of results from known compounds. For unknown alkyl complexes of unknown concentrations a simple concentration experiment was carried out, allowing the concentration of chromium and the extinction coefficient (ε) for the complex to be determined. This involved the conversion of any chromium(III) species into the chromate anion (CrO_4^{2-}), chromium(VI), whose UV absorption spectrum has been extensively examined, at λ_{372} $_{nm}$ with an absorption coefficient of $\varepsilon = 4830$ cm^{-1} mol^{-1} dm^3.

A known volume of Cr(III) sample (10 mL) was taken, 2 M KOH (~5 mL) was added to make the solution basic, followed by H_2O_2 (30 %, 10 mL), which oxidises the species to CrO_4^{2-} giving an intense yellow solution. This is then slowly brought to the boil for 5 minutes to decompose any excess hydrogen peroxide. The solution is then made up to a known volume e.g. 100 mL, and then diluted again if necessary. Finally its UV absorbance is measured at 372 nm. Hence c can be determined for this solution and the concentration of the original Cr(III) solution can then be calculated.

6.3. Preparation of Schiff Base Ligands

6.3.1. General procedure

Ligands were prepared via suitable modifications to the published procedure, pyridine-2-carbaldehyde-*tert*-butylimine by the method of Bähr et. al [4], 1,4-di-*tert*-butyldiazabutadiene by that of Emmons[5].

6.3.2. Reagents

Reagent	Purity	Source
Glyoxal	40 wt % in water	Aldrich
2-Pyridine carboxladehyde	99 %	Avocado
Diethyl ether	GPR grade	BDH
Amines	98 % +	Aldrich

6.3.3. Preparation of diazobutadiene (DAB) ligands

Figure 6-1 Structure of DAB ligands

general DAB ligand

1

2

3
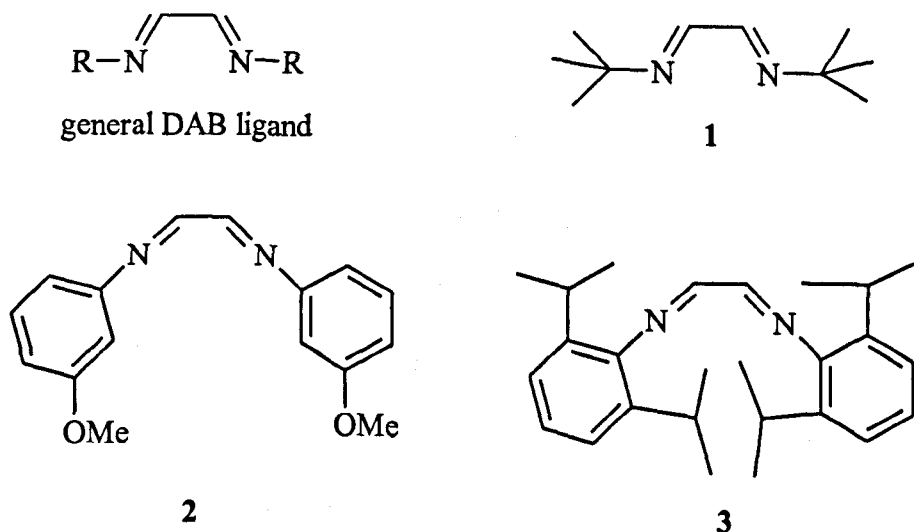
1) 1,4 -Di-t-butyl-1,4 diazabuta-1,3-diene ; t-butyl DAB

To a stirred solution of 40 % aqueous glyoxal (36.25 g, 0.25 mol) in a conical flask was added t-butyl amine (36.5 g, 0.5 mol) dropwise over ten minutes. A pale yellow solid formed immediately which was diluted with water (*ca.* 75 mL) and filtered. The resulting white solid residue was dissolved in diethyl ether (*ca.* 500 mL) and poured over a large excess of $MgSO_4$ (200 g). This suspension was left for 2 hours prior to filtration and the $MgSO_4$ was subsequently thoroughly washed with diethyl ether to give the product as a pale yellow solution. The ether was completely removed by

rotary evaporation to leave a pale yellow crystalline solid. This was purified by recrystalisation from diethyl ether to give 156 g of white needles (93 % yield). Mpt. = 52 °C, lit. Mpt.[5] = 52-53 °C.

^{1}H NMR (250 MHz, 298K d$_6$-acetone). 7.88 ppm (s, 2 H, -CH= N-), 1.23 ppm (s, 18H, (CH$_3$)$_3$-N). ^{13}C NMR (250 MHz, 298K, d$_6$-Acetone) δ = 157.9, 58.3, 29.5 ppm. Mass spectrometry (+EI) (m/z): 169 [M$^+$], Anal. Calcd. for C$_{10}$H$_{20}$N$_2$, C = 71.37, H = 11.98, N = 16.65; Found C = 71.30, H = 11.92, N = 16.69. I.R. (ν C=N) 1630 cm^{-1}.

2) 1,4-(2,6-Diisopropylphenyl)-1,4-diazabuta-1,3-diene

The same procedure was employed as 1), except for substitution of the diisopropylphenyl amine. After recrystalization in diethyl ether yellow crystals were obtained (41 g, 93 % yield). Mpt. = 106 °C, lit. Mpt [6] =104 °C.

^{1}H NMR (250 MHz, 298K d$_6$-acetone) δ = 8.15 (s, 2 H), 7.19 (d, J = 10 Hz, 4 H), 7.13 (t, J = 7.5, 2 H), 2.97 (m, J = 6.1 Hz, 2 H), 1.18 (d, J = 6.95, 12 H). ^{13}C NMR (250 MHz, 298K, d$_6$-acetone) δ = 164.14, 149.18, 137.12, 125.86, 123.89, 30.14, 23.56 ppm. Mass spectrometry (+CI) (m/z): 377 [M$^+$], Anal. Calcd. for C$_{26}$H$_{36}$N$_2$, C = 82.93, H = 9.64, N = 7.44; Found C = 82.89, H = 9.72, N = 7.25. I.R. (ν C=N) 1624 cm^{-1}.

3) 1,4-(4-Methoxyphenyl)-1,4-diazabuta-1,3-diene

The same procedure was employed as **1)**, except for substitution of the 4-methoxyphenyl amine. After recrystallization in diethyl ether brown needles were obtained (26 g, 62 % yield). Mpt = 153 °C, Lit. Mpt [7] = 153-154 °C.

^{1}H NMR (250 MHz, 298K d$_6$-acetone), δ = 8.39 (s, 2 H), 7.42(d, J = 10, 4 H), 7.03(d, J = 9.68 Hz, 4 H), 3.8 (s, 4 H). ^{13}C NMR (250 MHz, 298K, d$_6$-acetone) δ =160.65, 158.36, 144.12, 123.87, 115.37, 55.7. Mass spectrometry (+CI) (m/z): 269 [M$^+$], Anal. Calcd. for C$_{16}$H$_{16}$N$_2$O$_2$, C = 17.62, H = 6.01, N = 10.44; Found C = 17.59, H = 6.09, N = 10.46. I.R. (ν C=N) 1621 cm^{-1}.

6.3.4. Preparation of alkylimine-2-pyridylmethanimine (PCA) ligands

Figure 6-2 Structure of PCA ligands

general PCA ligand

1

2

3

4

5
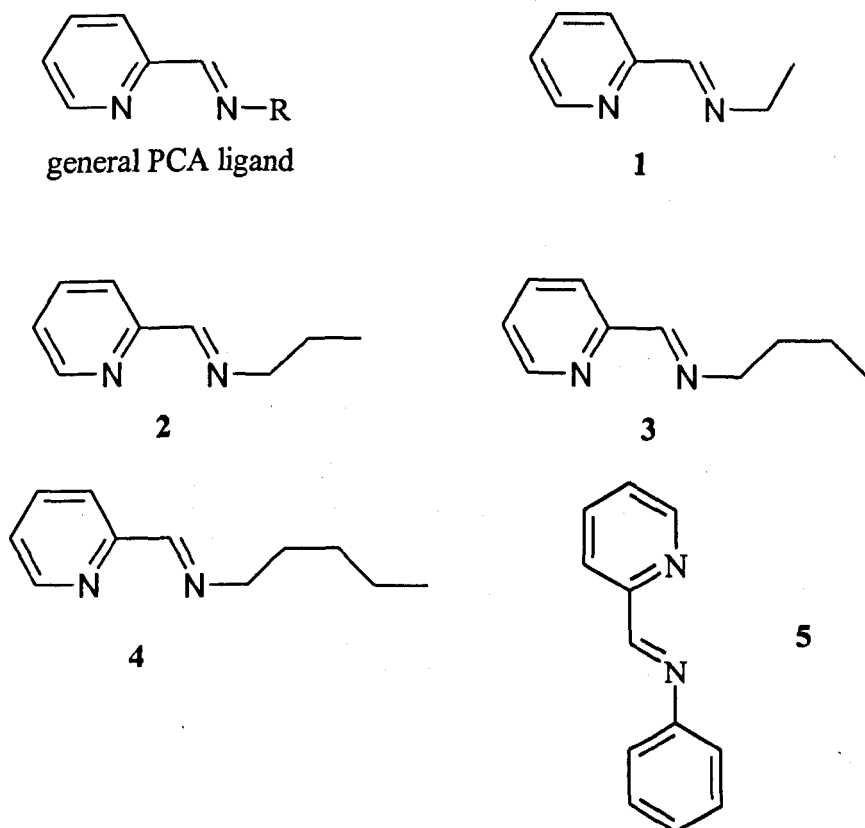
1) Ethyl-2-pyridylmethanimine

To a stirred solution of 2-pyridine carbaldeheyde (10 g, 0.0934 mol) in 20 mL diethyl ether in a conical flask was added ethyl amine (4.2 g, 0.0934 mol) dropwise. The solution was stirred at room temperature for 10 minutes prior to the addition of a large excess of $MgSO_4$ (20 g). This suspension was left for 2 hours to remove all the water from the product. On filtration the $MgSO_4$ was thoroughly washed with fresh diethyl ether and the filtrate, a yellow liquid was retained. The ether was removed by rotary evaporation to leave a pale yellow liquid. This was purified by vacuum distillation at 164 °C at 0.5 Torr to give a yellow oil with a yield of 11.2 g, 90 %.

^{1}H NMR (250 MHz, 298K, CDCl$_3$), δ =8.51 (d , J = 4.0 Hz , 1 H), 8.27 (s, 1 H), 7.84 (d, J = 798 Hz, 1 H), 7.60 (t, J = 8.22 Hz, 1 H), 7.1670 (t, J = 6.10 Hz, 1 H), 3.59 (q, J = 7.30 Hz , 2 H), 1.20 (t, J = 7.00 Hz , 3 H).

^{13}C NMR (250 MHz, 298K, CDCl$_3$) δ = 161.05, 154.42, 149.16, 136.23, 124.32, 120.92, 55.39, 15.80

2) n-Propyl-2-pyridylmethanimine

The same procedure was employed as for **1)**, except for the substitution of n-propyl amine. A yellow oil was obtained in a yield of 11.1 g, 80 %.

^{1}H NMR (250 MHz, 298K, CDCl$_3$), δ = 8.54 (d, J = 5.0 Hz, 1 H), 8.29 (s, 1 H), 7.90 (d, J = 8.9 Hz, 1 H) 7.63 (t, J = 6.4 , 1H), 7.21 (t, J = 3.7 Hz , 1 H), 3.55 (t, J = 8.55 Hz, 2 H), 1.71 (m, J = 7.3 Hz, 2 H), 0.88 (t, J = 4.8 Hz 3 H)

^{13}C NMR (250 MHz, 298K, CDCl$_3$) δ = 161.30, 154.30, 148.99, 136.03, 124.14, 120.75, 62.88, 23.48, 11.46

3) n-Butylimine-2-pyridylmethanimine

The same procedure was employed as for **1)**, except for the substitution of n-butyl amine. A yellow oil was obtained in a yield of 14.4 g, 95 %.

^{1}H NMR (250 MHz, 298K, d$_6$-acetone), δ = 8.62 (d , J = 4.1 Hz , 1 H), 8.33 (s, 1 H), 8.0 (d, J = 7.8 Hz, 1 H), 7.82 (t, J = 7.8 Hz, 1 H), 7.39 (t, J = 4.95 Hz, 1 H), 3.65 (t, J = 5.5 Hz , 2 H), 1.67 (m, J = 7.3 Hz , 2 H), 1.40 (m, J = 5.2 Hz, 2 H), 0.95 (t, J = 7.3 Hz, 3 H).

^{13}C NMR (250 MHz, 298K, d$_6$-acetone) δ = 161.57, 154.62, 149.29, 136.39, 124.47, 121.07, 61.15, 32.70, 20.34, 13.79. Mass spectrometry (+EI) (m/z): 163 [M$^+$]. I.R. (ν C=N) 1649 cm^{-1}.

4) n-Pentyl-2-pyridylmethanimine

The same procedure was employed as for **1)**, except for the substitution of n-pentyl amine. A yellow oil was obtained in a yield of 15.6 g, 95 %.

^{1}H NMR (250 MHz, 298K, CDCl$_3$), δ = 8.59 (d , J = 3.36 Hz , 1 H), 8.32(s , 1 H), 7.95 (d, J = 6.7 Hz, 1 H) 7.69 (t, J = 9.1 Hz, 1 H), 7.25 (t, J = 4.9 Hz, 1 H), 3.63 (dt J = 7.0 Hz, 2 H), 1.68 (q, J = 4.6 Hz, 2 H), 1.31 (m, J = 2.5 Hz, 4 H), 0.86 (m, J = 4.6 Hz).

^{13}C NMR (250 MHz, 298K, CDCl$_3$) δ = 161.81, 154.96, 149.58, 136.62, 124.73, 11.34, 61.76, 30.62, 29.74, 22.70, 14.25.

5) Phenylimine-2-pyridylmethanimine

To a stirred solution of 2-pyridine carbaldeheyde (10 g, 0.0934 mol) in 20 mL diethyl ether in a conical flask was added aniline (8.69 g, 0.0934 mol) dropwise. A pale yellow solid formed immediately which was diluted with water (ca. 100 mL) and filtered. The resulting white solid residue was dissolved in diethyl ether (ca. 500 mL) and poured over a large excess of MgSO$_4$ (50 g).This suspension was left for 2 hours to remove all the water from the product. On filtration the MgSO$_4$ was thoroughly washed with diethyl ether and the filtrate, a clear yellow liquid was retained. The ether was completely removed by rotary evaporation to leave a pale yellow crystalline solid. This was purified by recrystalization from diethyl ether. Yield = 17.5 g, 94 %.

^{1}H NMR (250 MHz, 298 K, d$_6$-acetone), δ = 8.71 (d, J = 3.5 Hz , 1 H), 8.56 (s, 1 H), 8.21 (d, J = 7.5 Hz , 1 H), 7.9 (t, J = 4.6 Hz, 1 H), 7.51 (t, J = 4.6 Hz, 1 H), 7.45 (m, J = 9 Hz, 2 H), 7.34 (m, J = 8.8 Hz, 2 H), 7.3 (m, J = 7.3 Hz, 1 H). ^{13}C NMR (250 MHz, 298K, d$_6$-acetone) δ = 161.76, 155.70, 152.06, 150.58, 137.47, 130.14, 127.48, 126.15, 121.86. Mass spectrometry (+EI) (m/z): 182 [M$^+$]. *Anal.* Calcd. for C$_{12}$H$_{10}$N$_2$, C = 79.1, H = 5.53, N = 15.37; Found C = 78.72, H = 5.44, N = 15.30. I.R. (ν C=N) 1632 cm^{-1}.

6.4. Preparation of Chromium(II) and Chromium(III) Complexes

6.4.1. Reagents

Reagent	Purity	Source
Chromium(II) chloride	95 %	Aldrich
Chromium(III) chloride	99 % sublimed	Aldrich
Tetrahydrofuran	AR grade	BDH
Ethyl-2-bromoisobutyrate	98 %	Aldrich
Toluene	AR grade	BDH

6.4.2. Preparation

1) Chromium trichloride tetrahydrofuranate, CrCl$_3$(THF)$_3$

This preparation is based on the original method by Herwig and Zeiss[8]. To a cellulose thimble was added chromium trichloride (5 g, 0.36 mol) followed by zinc metal powder (<0.1 g). The solid was then extracted by refluxing THF using a soxhlet apparatus for 24 hours under nitrogen. The purple solution is collected and the THF solvent removed under vacuum leaving purple crystals. Yield 12.6 g, 100 %

Figure 6-3 Structure of mer-chromium trichloride tetrahydrofuranate

$$\begin{array}{c} \text{Cl} \quad \text{Cl} \\ \diagdown \quad | \\ \text{THF} - \text{Cr} - \text{THF} \\ | \quad \diagdown \text{Cl} \\ \text{THF} \end{array}$$
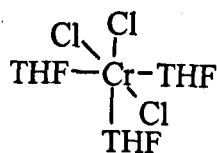
Anal. Calcd. for CrCl$_3$C$_{12}$H$_{24}$, C=38.46, H=6.47; Found C=36.55, H=5.88.

2) (A) - [Cl$_2$Zn(μ-Cl)$_2$Cr(THF)$_2$(μ-Cl)$_2$ZnCl$_2$]⁻[Cr(THF)$_4$]$^{2+}$[Cl$_2$Zn(μ-Cl)$_2$Cr(THF)$_2$(μ-Cl)$_2$ZnCl$_2$]⁻

To a magnetically stirred suspension of chromium trichloride tetrahydrofuranate (2 g, 5.68 x 10^{-3} mol) prepared as explained in (1) in THF a quantity of zinc/mercury amalgam[9] (10 g) is added, this is shaken for 30 minutes. The purple slurry reacts to give a blue powder suspended in a green solution. The blue powder is filtered off from the amalgam and green solution, and then washed in a little cold THF (10 mL). The solid is then dried under vacuum to obtain a sky blue powder, identified as *(A)*, yield 10 g.

Figure 6-4 shows the crystal structure of the product obtained from the reaction. A crystal unit cell was calculated as C$_{12}$H$_{24}$Cl$_4$CrO$_3$Zn.

Figure 6-4 Crystal structure of *(A)*
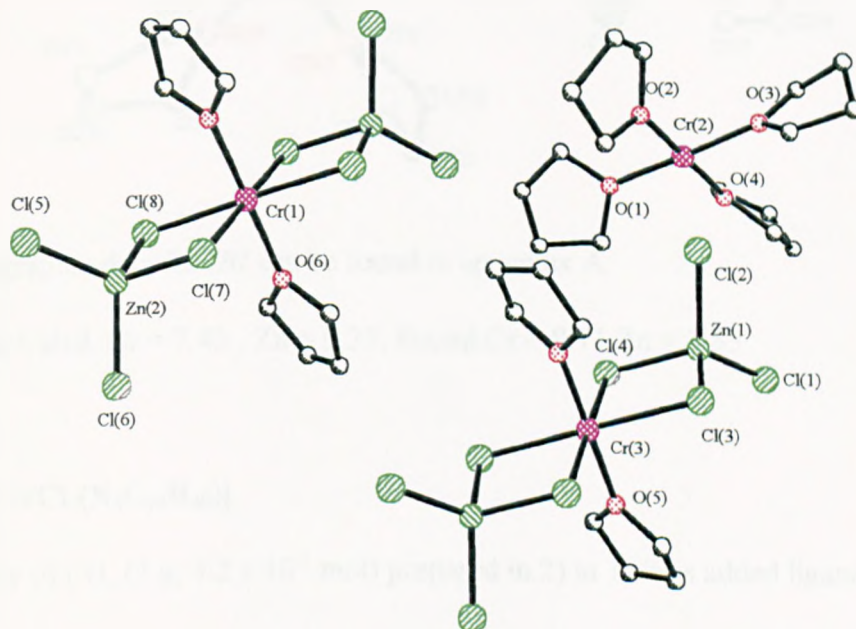
Crystallographic data for *(A)* can be found in appendix A.

Anal. Calcd. for C$_{12}$H$_{24}$Cl$_4$CrO$_3$Zn C = 30.31, H = 5.10; Found C = 27.94, H = 4.58.

ICP anal. Calcd. Cr = 10.93, Zn = 13.75; Found Cr = 5.07 Zn = 5.69.

3) (B) - [CrCl$_2$(THF)$_4$][ZnBrCl$_2$(THF)]$^+$

To a slurry of (A), (2 g, 4.2 x 10^{-3} mol) prepared in 2) in THF is added ethyl-2-bromoisobutyrate (1 mL, 5.1 x 10^{-3} mol). The blue powder reacts to give a purple solution. The purple solution is filtered and the THF removed under vacuum to give a purple powder. Yield 2.9 g, 100 %. A crystal unit cell was calculated as C$_{20}$H$_{40}$BrCl$_4$CrO$_5$Zn.

Figure 6-5 shows the crystal structure of the product obtained from the reaction.

Figure 6-5 Crystal structure of (B)
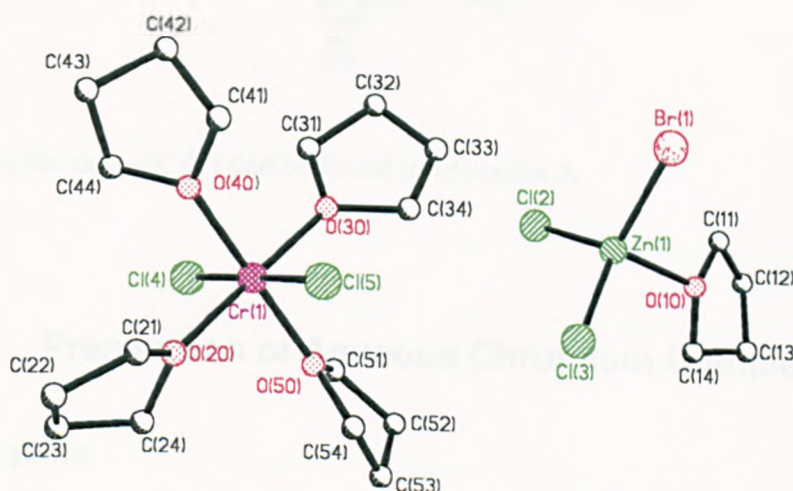
Crystallographic data for (B) can be found in appendix A.

ICP anal. Calcd. Cr = 7.43 , Zn = 9.35; Found Cr = 9.71 Zn = 3.55

4) (C) - [CrCl$_3$(N$_4$C$_{20}$H$_{40}$)]

To a slurry of (A), (2 g, 4.2 x 10^{-3} mol) prepared in 2) in THF is added ligand The blue powder reacts to give a green slurry. The solution has THF added (10 mL) to dissolve the compound, this is then filtered and the THF removed under vacuum to give a green powder. Yield 2.1 g, 100 %. A crystal unit cell was calculated as C$_{20}$H$_{40}$Cl$_3$CrN$_4$.

Figure 6-6 shows the crystal structure of the product obtained from the reaction.

Figure 6-6 Crystal structure of *(C)*
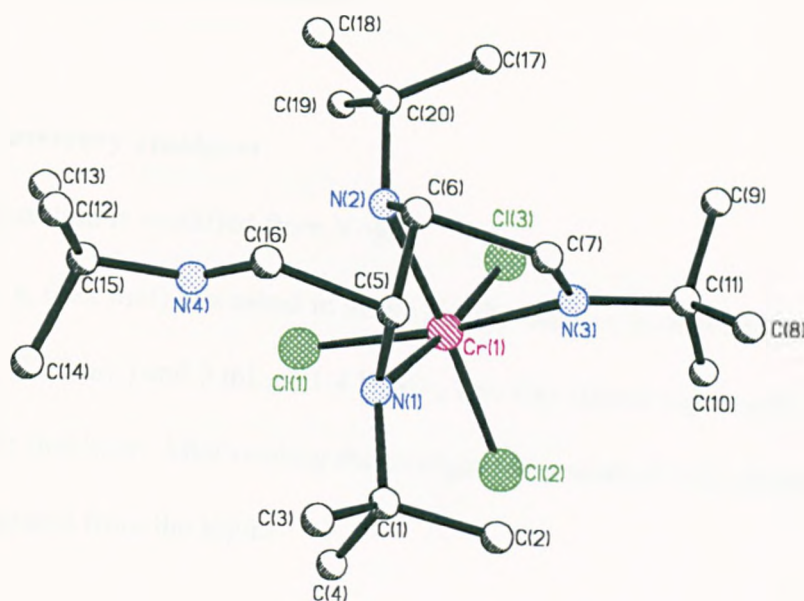
Crystallographic data for *(C)* can be found in appendix A.

6.5. Preparation of Aqueous Chromium Complexes

6.5.1. Reagents

Reagent	Purity	Source
Chromium(VI) trioxide	98 %	BDH
Chromium (chips)	99.5 %	Aldrich
Chromium (powder)	99.5 %, -100 mesh	Aldrich
Hexafluorophosphoric acid	60 wt % in water	Aldrich
Perchloric acid	70 wt % in water	Aldrich
Tetrahydrofuran	AR grade	BDH
Chloroform	AR grade	BDH
Iso-propyl-alcohol	99 % +	Aldrich
Zinc powder	99 % +	BDH
Hydrogen peroxide	30 wt % in water	BDH

6.5.2. Preparation of reagents

1) Zinc/mercury amalgam

The preparation is modified from Vogel[9].

Zinc (15 g, 0.22 mol) is washed in dilute H_2SO_4, the zinc is then added to 300 g of mercury (22.2 mL) and 5 mL of 1:4 H_2SO_4, this was stirred vigorously and heated to ~90 °C for one hour. After cooling the amalgam was washed with dilute acid and the solid separated from the liquid.

2) Dilute hexafluorophosphoric acid, HPF_6(aq)

Hexafluorophosphoric acid (HPF_6) comes as a solution of 60 % by weight in water, this approximates to a solution of 16 mol dm^{-3}. The acid is diluted down to a usable and known concentration.

Upon diluting with distilled water, to an approximately known concentration, a sample of these solutions is taken and titrated against KOH 2 M solution, with phenylphalein as an indicator (colour change clear to pink), to determine the exact concentration. Solutions of concentrations 0.5 - 5 mol acid have been prepared by this procedure. The acid solutions were stored at 4 °C.

3)Dilute perchloric acid, $HClO_4$(aq)

Perchloric acid ($HClO_4$) is 70 % by weight, in water, solution. This approximates to 12 mol dm^{-3}. Solutions of lower concentrations were made using distilled water. The solutions were then titrated against KOH 2 M solution to find out the exact

concentrations. Concentrations of 0.1 to 3 mol acid have been prepared by this method. The acid solutions were stored at 4 °C.

4) Ion exchange chromatography

Once formed, the aqueous organochromium complexes are purified using an *Ion Exchange Chromatography Column* (figure 6-7).

Figure 6-7 Ion exchange chromatography column
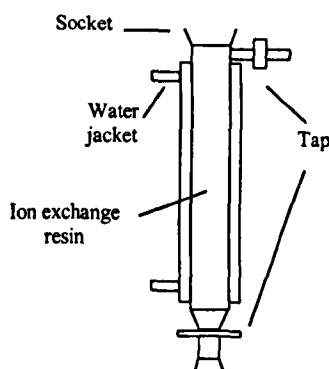
The ion exchange resin used is Sephadex-SP C25 40-120 micron ion exchange resin. This can be used under fairly mild conditions (i.e. acids of <2M). The column is prepared using deoxygenated water and exchange resin, it is ~15 cm by 2 cm, all eluents have also been deoxygenated.

The column is first washed through with water, then it is chilled by running iced water around the jacket on the column. After this a sample of the impure chromium alkyl solution is added (~10 cm^3) and run through to the top of the resin. First water is flushed through, this is then followed by acid solutions of varying, but known strengths to elute the various products (weakest acid first).

In these examples, usually three layers are formed, two are removed, firstly the Cr-Cl(aq) product (green) secondly the Cr-R(aq) product (red/orange). A third is a

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chromium dimer product formed in small quantities, this is not removed under these conditions.

Analysis is performed by UV/Visible spectroscopy on each sample.

6.5.3. Preparation of aqueous chromium(II) and (III) complexes

The preparation of the aqueous chromium complexes is based on work by Anet[10] and Schug and King[11].

1) Preparation of chromium(III) complex, $[Cr(H_2O)_6]^{3+}[PF_6^-]_3$ from CrO_3

An aqueous solution of CrO_3 was prepared (5 g, 0.05 mol, in ~50 mL of distilled water), to this an appropriate excess number of moles of dilute HPF_6 (~2 mol dm^{-3}) acid was added (>0.3 mol). Slowly a slight excess of H_2O_2 (30 % volume) was added (0.5 mol). On addition of this oxygen was given off and the solution went from an orange colour, briefly dark blue, and then to a dark green solution. The product was kept and used in solution.

UV/Visible analysis:- Literature for $[Cr(H_2O)_6]^{3+}[ClO_4^-]_3$ [12] $\lambda_{408\,nm}$ $\varepsilon = 15.5$ mol^{-1} dm^3 cm^{-1}, $\lambda_{575\,nm}$ $\varepsilon = 13.2$ mol^{-1} dm^3 cm^{-1} ; Found $= \lambda_{424\,nm}$ $\varepsilon = 13.2$ mol^{-1} dm^3 cm^{-1}, $\lambda_{606\,nm}$ $\varepsilon = 13.3$ mol^{-1} dm^{-3} cm^{-1}.

2) Preparation of chromium(III) complex, $[Cr(H_2O)_6]^{3+}$ $[PF_6^-]_3$ from Cr (metal)

Chromium metal (5 g, 0.1 mol) in water (~50 mL) has added to it an appropriate

excess number of moles of dilute HPF_6 acid (~2 mol dm^{-3}) (>0.3 mol), and is then

heated to 90 °C in air for one hour. The colourless solution becomes a dark green. The

product was stored and used in solution.

UV/Visible analysis:- Literature for $[Cr(H_2O)_6]^{3+}[ClO_4^-]_3$ [12] $\lambda_{408\,nm}$ ε = 15.5 mol^{-1} dm^3

cm^{-1}, $\lambda_{575\,nm}$ ε = 13.2 mol^{-1} dm^3 cm^{-1} ; Found = $\lambda_{424\,nm}$ ε = 14.1 mol^{-1} dm^3 cm^{-1}, $\lambda_{609\,nm}$ ε

= 14.01 mol^{-1} dm^{-3} cm^{-1}.

3) Preparation of chromium(II) complex, $[Cr(H_2O)_6]^{2+}$ $[PF_6^-]_2$

Chromium(III) solutions as prepared in (1) and (2) were degassed, either by freeze-

pump-thaw methods or by bubbling N_2 through the system for one hour. These were

then added to 10 mL of degassed Zn/Hg amalgam in Schlenk apparatus under

nitrogen. The mixture was then shaken for 72 hours. The resulting solutions formed

were a bright sky blue. The chromium(II) solutions formed are stored over Zn/Hg

amalgam until needed.

Concentration of the chromium(II) solution is determined by UV/Visible

spectroscopy.

UV/Visible analysis:- Literature for $[Cr(H_2O)_6]^{2+}[ClO_4^-]_2$ [12] $\lambda_{714\,nm}$ ε = 5 mol^{-1} dm^3 cm^{-1}, $\lambda_{1052\,nm}$ ε = 1.8 mol^{-1} dm^3 cm^{-1} ; Found = $\lambda_{434\,nm}$, $\lambda_{609\,nm}$ ε = 5 mol^{-1} dm^{-3} cm^{-1}.

4) Preparation of chromium(III) complex, $[Cr(H_2O)_6]^{3+}[ClO_4^-]_3$ from CrO_3

An aqueous solution of CrO_3 was prepared (5 g, 0.05 mol, in ~50 mL of distilled

water), to this an appropriate excess number of moles of dilute $HClO_4$ acid (~2 mol

dm^{-3}) was added (>0.3 mol). Slowly a slight excess of H_2O_2 (30 % volume) was added

(0.5 mol). On addition of this oxygen was given off and the solution went from orange

to a dark blue solution. The product was stored and used in solution.

UV/Visible analysis:- Literature for $[Cr(H_2O)_6]^{3+}[ClO_4^-]_3$ [12] $\lambda_{405\,nm}$ ε = - mol^{-1} dm^3 cm^{-1}, $\lambda_{575\,nm}$ ε = 13.9 mol^{-1} dm^3 cm^{-1} ; Found = $\lambda_{407\,nm}$ ε = 17.3 mol^{-1} dm^3 cm^{-1} , $\lambda_{576\,nm}$ ε = 14.7 mol^{-1} dm^{-3} cm^{-1}.

5) Preparation of chromium(II) complex, $[Cr(H_2O)_6]^{2+}[ClO_4^-]_2$ from Cr(metal)

Chromium metal (5 g, 0.1 mol) in deoxygenated $HClO_4$ acid (2.5 M) solution was

heated to ~90 °C. The reaction is initiated giving off hydrogen, the solution becomes a

dark blue, a mixture of Cr(III) and Cr(II) complexes.

The reaction mixture is filtered under nitrogen, through celite, the filtrate is then

added to ~10 mL of Zn/Hg amalgam and shaken for less than two hours. A bright sky

blue solution of $[Cr(H_2O)_6]^{2+}[ClO_4^-]_2$ results.

UV/Visible analysis:- Literature for $[Cr(H_2O)_6]^{3+}[ClO_4^-]_3$ [12] $\lambda_{405\,nm}$ ε = - mol^{-1} dm^3 cm^{-1}, $\lambda_{575\,nm}$ ε = 13.9 mol^{-1} dm^3 cm^{-1} ; Found = $\lambda_{407\,nm}$ ε = 17.3 mol^{-1} dm^3 cm^{-1} , $\lambda_{576\,nm}$ ε = 14.7 mol^{-1} dm^{-3} cm^{-1}.

6.5.4. Preparation of aqueous organochromium complexes

1) Attempted preparation of [(H₂O)₅Cr-C(CH₃)₂OH]²⁺ [PF₆⁻]₂

Modified from the original preparation by Espenson et al[13]. A quantity of known

concentration chromium(II) solution (5 mL, 0.0046 mols) is diluted with

deoxygenated water (20 mL), added to this is an acidified solution of H_2O_2 (0.5 mL)

and iso-propyl alcohol (0.25 mL, 0.006 mol). The reaction solution goes from a sky

blue to a dark green solution. Ion exchange chromatography yielded only one green

fraction, not an orange solution as expected.

UV/Visible analysis:- Literature[14] $\lambda_{407\,nm}$ $\varepsilon = 700$ M⁻¹ cm⁻¹, $\lambda_{311\,nm}$ $\varepsilon = 2500$ M⁻¹ cm⁻¹ ;

Found N/A.

2) Preparation of [(H₂O)₅Cr-CHCl₂]²⁺ [PF₆⁻]₂

The method was modified from the original preparation by Anet and Leblanc[10]. A

quantity of known concentration chromium(II) solution (5 mL, 0.005 mols) is diluted

with deoxygenated water (100 mL) and cooled to 0 °C. Deoxygenated chloroform (10

mL, 0.12 mol) is then added to this and stirred for two hours at 0 °C.

The solution goes from a light blue to a green within a few minutes, this then changes

over two hours to a red/brown solution. This mixture of products is then purified

using a cooled ion exchange chromatography column (see 6.5.2). The red fraction

removed is the desired product, [Cr(H₂O)₅ -CHCl₂]²⁺ [PF₆⁻]₂ . The product is stored at

0 °C until needed and then used *in situ*.

UV/Visible analysis:- Literature[10] for [(H₂O)₅Cr-CHCl₂]²⁺ [ClO₄⁻]₂

$\lambda_{396\ nm}\ \varepsilon = 157\ mol^{-1}\ dm^3\ cm^{-1}$, $\lambda_{514\ nm}\ \varepsilon = 38.7\ mol^{-1}\ dm^3\ cm^{-1}$ $\lambda_{266\ nm}\ \varepsilon = 4{,}290\ mol^{-1}$ $dm^3\ cm^{-1}$; Found $= \lambda_{396\ nm}\ \varepsilon = 367\ mol^{-1}\ dm^3\ cm^{-1}$, $\lambda_{522\ nm}\ \varepsilon = 99\ mol^{-1}\ dm^{-3}\ cm^{-1}$.

3) Attempted preparation of $[(H_2O)_5Cr\text{-}C(CH_3)_2OH]^{2+}\ [ClO_4^-]_2$

This follows the same preparation as explained in 1) but uses $[Cr(H_2O)_6]^{2+}\ [ClO_4^-]_2$. The product collected is a green solution, not orange as expected.

UV/Visible analysis:- Literature[14] $\lambda_{407\ nm}\ \varepsilon = 700\ M^{-1}\ cm^{-1}$, $\lambda_{311\ nm}\ \varepsilon = 2500\ M^{-1}\ cm^{-1}$; Found N/A.

4) Preparation of $[(H_2O)_5Cr\text{-}CHCl_2]^{2+}\ [ClO_4^-]_2$

This follows the same preparation as explained in 2) but uses $[Cr(H_2O)_6]^{2+}\ [ClO_4^-]_2$. The red fraction removed is the desired product, $[Cr(H_2O)_5\text{ -}CHCl_2]^{2+}\ [ClO_4^-]_2$. The product is stored at 0 °C until needed and then used *in situ*.

UV/Visible analysis:- Literature[10] for $[(H_2O)_5Cr\text{-}CHCl_2]^{2+}\ [ClO_4^-]_2$

$\lambda_{396\ nm}\ \varepsilon = 157\ mol^{-1}\ dm^3\ cm^{-1}$, $\lambda_{514\ nm}\ \varepsilon = 38.7\ mol^{-1}\ dm^3\ cm^{-1}$ $\lambda_{266\ nm}\ \varepsilon = 4{,}290\ mol^{-1}$ $dm^3\ cm^{-1}$; Found $= \lambda_{399\ nm}\ \varepsilon = 160\ mol^{-1}\ dm^3\ cm^{-1}$, $\lambda_{521\ nm}\ \varepsilon = 41\ mol^{-1}\ dm^{-3}\ cm^{-1}$.

6.6. Polymerisation of Vinyl Monomers

6.6.1. Reagents

Reagent	Purity	Source
Tetrahydrofuran	AR grade	BDH
2-Hydroxyethyl methacrylate	98 %	Bisomer
Methyl methacrylate	99 %	ICI
Styrene	99 %	Aldrich
ethyl-2-bromoisobutyrate	98 %	Aldrich
ethyl 2-chloropropionate	99 %	Aldrich
p-toluene sulfonyl chloride	98 %	Aldrich
Chromium acetylacetonate	97 %	Aldrich
Alkyl aluminium	99 % (1 M in toluene)	BDH
2,2'-dipyridyl	98 %	Aldrich

(Other materials used purities as indicated earlier)

6.6.2. Preparation of polymers using chromium compound *A* and *B* with ethyl-2-bromoisobutyrate

This section refers to polymerisation experiments carried out in chapter 2.

1) The polymerisation of MMA using *(A)* and ethyl-2-bromoisobutyrate in tetrahydrofuran

A quantity of *(A)* (0.2 g, 4.21×10^{-4} mol), in THF (10 mL) is stirred vigorously, methyl methacrylate is added (7.5 mL, 0.07 mol), followed by ethyl-2-bromisibutyrate (0.1 mL, 6.8×10^{-3} mol) the temperature is raised to ~60 °C for the duration of the reaction (24 hours). A sample of reaction mixture is removed and precipitated into solvent, (Methanol/5 % HCl or hexane).

Mn values from 10,000 - 500,000, yields of PMMA obtained from 0 % to 50 %.

The quantities used of *(A)*, THF, monomer and initiator are varied during the course of these experiments as was the temperature and the duration of the reaction.

2) The attempted polymerisation of methyl methacrylate using *(A)* in THF

A quantity of *(A)* (0.5 g, 1.05×10^{-3} mol), in THF (10 mL) is stirred vigorously

followed by methyl methacrylate is added (4.68 mL, 4.7×10^{-2} mol), the temperature

is raised to 50 °C for the duration of the reaction (24 hours). A sample of reaction

mixture is removed and precipitated into solvent, (Methanol/5 % HCl or hexane).

Yield 0 %.

6.6.3. Preparation of polymers using *(A)* with nitrogen bonding ligands, THF and alkyl halide initiators

This section refers to experiments carried out in chapter 3.

1) The polymerisation of MMA with *(A)*, R-PCA and ethyl-2-bromoisobutyrate

A quantity of *(A)* (0.12 g, 2.47×10^{-4} mol) in THF (10 mL) has ⁿBu-PCA ligand added

(0.1 mL , 6.5×10^{-3} mol) followed by ethyl-2-bromoisobutyrate (0.12 mL, 7.5×10^{-4}

mol) then MMA (17 mL, 0.16 mol) the temperature is raised to 60 °C for the duration

of the reaction (72 hours). A sample of reaction mixture is removed and precipitated

into solvent, (Methanol/5 % HCl or hexane). Mn values from 10,000 - 500,000, yields

of PMMA obtained from 0 % to 100 %.

The quantities used of *(A)*, THF, monomer, ligand and initiator were varied during the

course of these experiments, as was the temperature and the duration of the reaction.

2) The polymerisation of MMA with CrCl₂, R-PCA and ethyl-2-bromoisobutyrate

A quantity of $CrCl_2$ (0.1 g, 7.3 x10^{-4} mol) in THF (10 mL) has ^{i}Bu-PCA ligand added (0.6 mL , 3.5 x10^{-3} mol) followed by ethyl-2-bromoisobutyrate (0.1 mL, 6.8 x 10^{-4} mol) then MMA (4.68 mL, 4.7 x10^{-2} mol) the temperature is raised to 60 °C for the duration of the reaction (72 hours). A sample of reaction mixture is removed and precipitated into solvent, (Methanol/5 % HCl or hexane). Mn values from 10,000 - 500,000, yields of PMMA obtained vary from 0 % to 100 %.

3) The attempted polymerisation of styrene monomer in the reaction of chromium(II) chloride with pentyl-PCA, and ethyl-2-bromoisobutyrate.

Chromium chloride (0.2 g, 1.6 x10^{-3} mol) in THF (10 mL) is mixed with pentyl 2-pyridinecarbaldehyde imine (1 mL, 5.7 x10^{-3} mol), styrene monomer (5 mL, 0.05 mol) followed by ethyl 2-bromoisobutyrate (0.3 mL, 0.002 mol). The reaction is carried out for 3 days at 25 °C. Yield of was PS 0 %.

6.6.4. Preparation of polymers using aqueous organochromium complexes

This section refers to polymerisation experiments carried out in chapter 4.

1) Polymerisation of 2-hydroxyethyl methacrylate (HEMA)

A quantity of unpurified $[(H_2O)_5Cr-CHCl_2]^{2+}[PF_6^-]_2$ and $[(H_2O)_5Cr-Cl]^{2+}[PF_6^-]_2$ (5 mL) solution is added to 2-hydroxyethyl methacrylate (2 mL, 0.04 mol). The reaction is

left at room temperature for 72 hours. A sample of solid PHEMA was removed, yield ~20 %, Mn unknown.

2) Polymerisation of methyl methacrylate (MMA)

A quantity of MMA (0.20 mL, 1.9×10^{-3} mol) in THF (20 mL) in Schlenk apparatus has a quantity of organochromium complex, $[Cr(H_2O)_5\text{-}CHCl_2]^{2+}[PF_6^-]_2$ added to it (1 mL, 1.5×10^{-5} mol). This is covered in tin foil to avoid any UV light interaction. The temperature is raised to 60 °C for two hours. The solid was precipitated in hexane to obtain a sample of PMMA, yield 0 - 60 %, Mn 10,000 - 50,000.

6.6.5. Preparation of polymers in the presence of the system tributyl aluminium-chromium acetylacetonate-2,2'-dipyridine

This section refers to experiments carried out in chapter 5.

This reaction is modified from that of work carried out by Korshun and Mazurek[15,16]. Chromium acetylacetonate (0.074 g, 2.11×10^{-4} mol) in toluene (20 mL) is cooled to -78 °C (acetone/dry ice bath). Added to this is tri-*iso*-butyl aluminium (0.67 mL, 6.7×10^{-4} mol), this is then left for 30 minutes to react and warm to ~ 0 °C. Following this a solution of 2,2'-dipyridine (0.061 g, 3.92×10^{-4} mol) in toluene (2 mL) is added. The catalyst solution is then left to warm to room temperature (20 minutes), before the addition of methyl methacrylate (10.84 mL, 0.1 mol). The solution was reacted for 2 hours before precipitation of the solution in hexane or a methanol/HCl solution. Yield 90 %. Mn = 81,000 PDi = 2.24.

Mn values obtained from these reactions 5,000 - 200,000. Yields obtained from these reactions varied from 0 - 100 %.

6.7. References

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Chapter 7

Appendix

7. Appendix

Appendix A

7.1. Appendix A - Crystal structure data

1) Crystal structure data for *(A)*, [Cl$_2$Zn(μ-Cl)$_2$Cr(THF)$_2$(μ-Cl)$_2$ZnCl$_2$]$^-$

[Cr(THF)$_4$]$^{2+}$[Cl$_2$Zn(μ-Cl)$_2$Cr(THF)$_2$(μ-Cl)$_2$ZnCl$_2$]$^-$
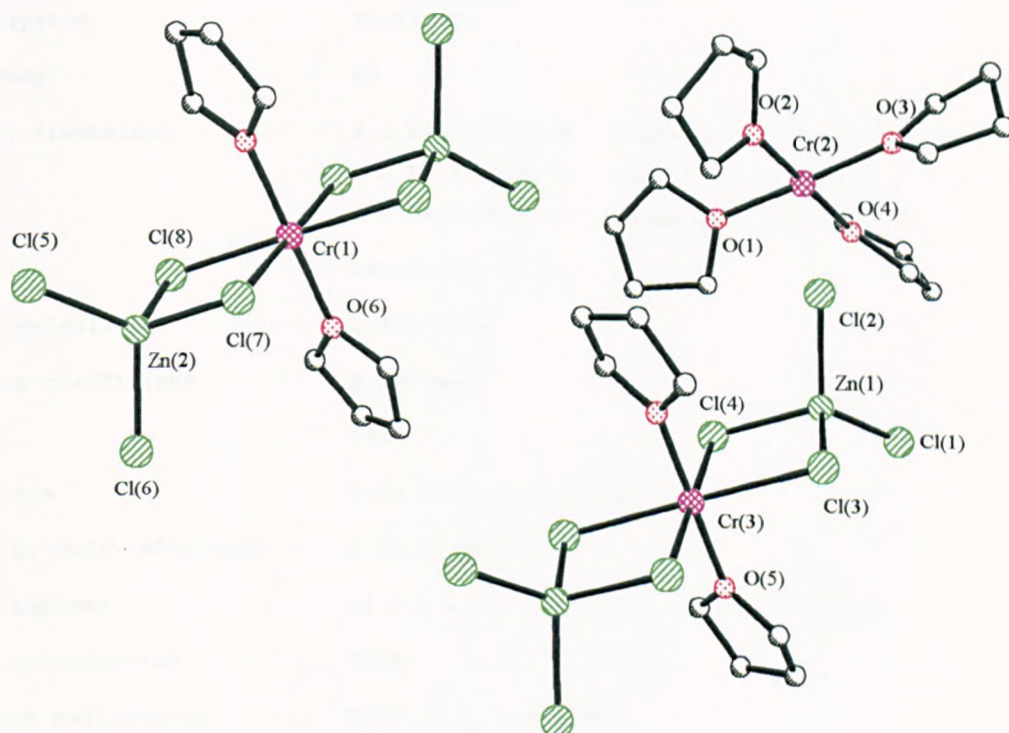
Table 7-1 Crystal Data and Structural Refinement for *(A)*

Table 1. Crystal data and structure refinement for 1(stma).

Identification code	stma
Empirical formula	$C_{12}H_{24}Cl_4CrO_3Zn$
Formula weight	475.48
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$p\bar{1}$
Unit cell dimensions	a = 11.3651(3) Å alpha = 91.7720(10)$^{\circ}$
	b = 12.2514(2) Å beta = 92.3550(10)$^{\circ}$
	c = 14.1689(3) Å gamma = 95.7390(10)$^{\circ}$
Volume, Z	1960.09(7) $Å^3$, 4
Density (calculated)	1.611 Mg/m^3
Absorption coefficient	2.327 mm^{-1}
F(000)	968
Crystal size	0.40 x 0.30 x 0.05 mm
θ range for data collection	1.44 to 22.50°
Limiting indices	$-8 \leq h \leq 14$, $-16 \leq k \leq 15$, $-19 \leq l \leq 18$
Reflections collected	7919
Independent reflections	5070 (R_{int} = 0.0311)
Absorption correction	SADABS
Max. and min. transmission	1.0000 and 0.7827
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5070 / 0 / 362
Goodness-of-fit on F^2	0.970
Final R indices [I>2σ(I)]	R1 = 0.0436, wR2 = 0.1057(for 3393reflections)
R indices (all data)	R1 = 0.0758, wR2 = 0.1234
Largest diff. peak and hole	0.540 and -0.391 $eÅ^{-3}$

Table 7-2 Atomic co-ordinates (x 10⁴) and equivalent isotopic displacement parameters (Angstroms x 10³) for *(A)*

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [Å^2 x 10^3] for 1. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Cr(1)	5000	5300	5000	31(1)
Cr(2)	10066.8(8)	7454.1(7)	2516.5(6)	31(1)
Cr(3)	5000	0	0	32(1)
Zn(1)	2955.2(6)	-2225.7(5)	128.6(5)	38(1)
Zn(2)	7168.7(6)	7124.3(5)	4872.9(5)	35(1)
Cl(1)	2084.3(16)	-3179.4(13)	-1100.0(13)	64(1)
Cl(2)	2230.8(14)	-2681.4(13)	1545.7(11)	51(1)
Cl(3)	4970.3(13)	-2198.2(12)	148.5(11)	48(1)
Cl(4)	2791.6(13)	-343.1(11)	-29.6(10)	41(1)
Cl(5)	8109.8(15)	8122.8(13)	6044.5(11)	57(1)
Cl(6)	7887.4(13)	7516.4(13)	3441.0(10)	48(1)
Cl(7)	7225.5(13)	5237.1(11)	5048.4(11)	44(1)
Cl(8)	5170.6(13)	7184.5(12)	4874.2(11)	47(1)
O(1)	10028(3)	9060(3)	2193(3)	41(1)
O(2)	11024(3)	7960(3)	3752(3)	37(1)
O(3)	10176(3)	5845(3)	2813(2)	36(1)
O(4)	9042(3)	6984(3)	1308(2)	37(1)
O(5)	4955(3)	-118(3)	-1456(3)	43(1)
O(6)	4954(3)	4897(3)	3550(3)	45(1)
C(1)	8995(6)	9654(5)	2078(6)	73(2)
C(2)	9463(6)	10844(5)	2101(6)	66(2)
C(3)	10630(7)	10825(5)	1674(5)	68(2)
C(4)	11084(6)	9813(4)	2087(5)	55(2)
C(5)	10619(5)	8747(6)	4424(4)	55(2)
C(6)	11613(6)	8971(6)	5157(5)	73(2)
C(7)	12542(8)	8486(10)	4860(7)	182(7)
C(8)	12230(5)	7771(5)	4023(5)	58(2)
C(9)	9904(6)	5367(4)	3710(4)	51(2)
C(10)	9688(6)	4144(4)	3482(5)	54(2)
C(11)	10480(6)	3980(5)	2690(4)	52(2)
C(12)	10454(6)	5006(4)	2143(4)	53(2)
C(13)	7877(6)	6353(5)	1279(4)	55(2)
C(14)	7611(6)	6035(5)	264(4)	55(2)
C(15)	8226(7)	6965(6)	-241(5)	67(2)
C(16)	9334(6)	7272(6)	359(4)	66(2)
C(17)	4411(8)	591(8)	-2087(5)	97(3)
C(18)	4437(9)	137(8)	-3033(5)	104(3)
C(19)	5250(11)	-673(9)	-2992(6)	139(5)
C(20)	5445(8)	-937(7)	-2000(5)	90(3)
C(21)	5554(8)	4181(7)	2984(5)	99(3)
C(22)	5042(10)	4233(8)	2018(5)	126(4)
C(23)	4426(9)	5140(8)	1965(6)	111(4)
C(24)	4315(8)	5567(7)	2928(5)	84(3)

Table 7-3 Bond lengths (Angstroms) and Angles (°) for *(A)*

Table 3. Bond lengths [Å] and angles [°] for 1.

Cr(1)-O(6)#1	2.052(4)	Cr(1)-O(6)	2.052(4)
Cr(1)-Cl(7)#1	2.5147(14)	Cr(1)-Cl(7)	2.5147(14)
Cr(1)-Cl(8)	2.676(2)	Cr(1)-Cl(8)#1	2.676(2)
Cr(2)-O(1)	2.038(3)	Cr(2)-O(3)	2.043(3)
Cr(2)-O(4)	2.064(4)	Cr(2)-O(2)	2.067(4)
Cr(3)-O(5)	2.062(4)	Cr(3)-O(5)#2	2.062(4)
Cr(3)-Cl(4)	2.5014(14)	Cr(3)-Cl(4)#2	2.5015(14)
Cr(3)-Cl(3)#2	2.705(2)	Cr(3)-Cl(3)	2.705(2)
Zn(1)-Cl(1)	2.208(2)	Zn(1)-Cl(2)	2.266(2)
Zn(1)-Cl(3)	2.286(2)	Zn(1)-Cl(4)	2.349(2)
Zn(2)-Cl(5)	2.205(2)	Zn(2)-Cl(6)	2.265(2)
Zn(2)-Cl(8)	2.280(2)	Zn(2)-Cl(7)	2.340(2)
O(1)-C(1)	1.449(7)	O(1)-C(4)	1.454(6)
O(2)-C(8)	1.451(7)	O(2)-C(5)	1.455(6)
O(3)-C(9)	1.447(6)	O(3)-C(12)	1.445(6)
O(4)-C(16)	1.444(7)	O(4)-C(13)	1.464(6)
O(5)-C(17)	1.431(8)	O(5)-C(20)	1.419(7)
O(6)-C(21)	1.414(7)	O(6)-C(24)	1.446(8)
C(1)-C(2)	1.500(8)	C(2)-C(3)	1.482(9)
C(3)-C(4)	1.514(9)	C(5)-C(6)	1.500(8)
C(6)-C(7)	1.339(9)	C(7)-C(8)	1.463(9)
C(9)-C(10)	1.516(7)	C(10)-C(11)	1.488(8)
C(11)-C(12)	1.499(8)	C(13)-C(14)	1.489(8)
C(14)-C(15)	1.494(8)	C(15)-C(16)	1.499(9)
C(17)-C(18)	1.437(9)	C(18)-C(19)	1.422(11)
C(19)-C(20)	1.465(11)	C(21)-C(22)	1.470(10)
C(22)-C(23)	1.373(10)	C(23)-C(24)	1.461(9)

O(6)#1-Cr(1)-O(6)	180.0	O(6)#1-Cr(1)-Cl(7)#1	90.48(11)
O(6)-Cr(1)-Cl(7)#1	89.52(11)	O(6)#1-Cr(1)-Cl(7)	89.52(11)
O(6)-Cr(1)-Cl(7)	90.48(11)	Cl(7)#1-Cr(1)-Cl(7)	179.999(1)
O(6)#1-Cr(1)-Cl(8)	92.31(11)	O(6)-Cr(1)-Cl(8)	87.69(11)
Cl(7)#1-Cr(1)-Cl(8)	95.00(4)	Cl(7)-Cr(1)-Cl(8)	85.00(4)
O(6)#1-Cr(1)-Cl(8)#1	87.69(11)	O(6)-Cr(1)-Cl(8)#1	92.31(11)
Cl(7)#1-Cr(1)-Cl(8)#1	85.00(4)	Cl(7)-Cr(1)-Cl(8)#1	95.00(4)
Cl(8)-Cr(1)-Cl(8)#1	179.999(2)	O(1)-Cr(2)-O(3)	177.5(2)
O(1)-Cr(2)-O(4)	90.0(2)	O(3)-Cr(2)-O(4)	90.3(2)
O(1)-Cr(2)-O(2)	88.9(2)	O(3)-Cr(2)-O(2)	91.0(2)
O(4)-Cr(2)-O(2)	177.22(14)	O(5)-Cr(3)-O(5)#2	180.0
O(5)-Cr(3)-Cl(4)	90.03(11)	O(5)#2-Cr(3)-Cl(4)	89.97(11)
O(5)-Cr(3)-Cl(4)#2	89.97(11)	O(5)#2-Cr(3)-Cl(4)#2	90.03(11)
Cl(4)-Cr(3)-Cl(4)#2	180.0	O(5)-Cr(3)-Cl(3)#2	87.61(11)
O(5)#2-Cr(3)-Cl(3)#2	92.39(11)	Cl(4)-Cr(3)-Cl(3)#2	94.68(4)
Cl(4)#2-Cr(3)-Cl(3)#2	85.33(4)	O(5)-Cr(3)-Cl(3)	92.39(11)
O(5)#2-Cr(3)-Cl(3)	87.61(11)	Cl(4)-Cr(3)-Cl(?)	85.32(4)
Cl(4)#2-Cr(3)-Cl(3)	94.67(4)	Cl(3)#2-Cr(3)-Cl(3)	180.000(1)
Cl(1)-Zn(1)-Cl(2)	115.00(7)	Cl(1)-Zn(1)-Cl(3)	112.31(7)
Cl(2)-Zn(1)-Cl(3)	111.60(7)	Cl(1)-Zn(1)-Cl(4)	110.54(6)
Cl(2)-Zn(1)-Cl(4)	106.87(6)	Cl(3)-Zn(1)-Cl(4)	99.24(6)
Cl(5)-Zn(2)-Cl(6)	113.25(7)	Cl(5)-Zn(2)-Cl(8)	112.39(6)
Cl(6)-Zn(2)-Cl(8)	111.65(6)	Cl(5)-Zn(2)-Cl(7)	112.96(6)
Cl(6)-Zn(2)-Cl(7)	106.76(6)	Cl(8)-Zn(2)-Cl(7)	98.84(6)
Zn(1)-Cl(3)-Cr(3)	85.95(5)	Zn(1)-Cl(4)-Cr(3)	89.47(5)
Zn(2)-Cl(7)-Cr(1)	89.33(5)	Zn(2)-Cl(8)-Cr(1)	86.74(5)
C(1)-O(1)-C(4)	108.9(4)	C(1)-O(1)-Cr(2)	127.3(4)
C(4)-O(1)-Cr(2)	123.7(3)	C(8)-O(2)-C(5)	108.8(4)
C(8)-O(2)-Cr(2)	128.1(3)	C(5)-O(2)-Cr(2)	122.3(3)
C(9)-O(3)-C(12)	110.2(4)	C(9)-O(3)-Cr(2)	124.7(3)
C(12)-O(3)-Cr(2)	125.0(3)	C(16)-O(4)-C(13)	109.0(4)

C(16)-O(4)-Cr(2)	125.4(3)	C(13)-O(4)-Cr(2)	125.5(3)
C(17)-O(5)-C(20)	108.5(5)	C(17)-O(5)-Cr(3)	126.3(4)
C(20)-O(5)-Cr(3)	125.3(4)	C(21)-O(6)-C(24)	107.9(5)
C(21)-O(6)-Cr(1)	126.5(4)	C(24)-O(6)-Cr(1)	125.6(4)
O(1)-C(1)-C(2)	105.3(5)	C(3)-C(2)-C(1)	103.0(6)
C(2)-C(3)-C(4)	102.4(5)	O(1)-C(4)-C(3)	104.7(5)
O(2)-C(5)-C(6)	105.3(5)	C(7)-C(6)-C(5)	108.3(6)
C(6)-C(7)-C(8)	111.8(7)	O(2)-C(8)-C(7)	105.1(5)
O(3)-C(9)-C(10)	104.4(5)	C(11)-C(10)-C(9)	103.3(5)
C(10)-C(11)-C(12)	104.1(5)	O(3)-C(12)-C(11)	105.7(5)
O(4)-C(13)-C(14)	105.2(5)	C(13)-C(14)-C(15)	103.2(5)
C(16)-C(15)-C(14)	103.5(6)	O(4)-C(16)-C(15)	105.7(5)
O(5)-C(17)-C(18)	108.3(7)	C(19)-C(18)-C(17)	106.2(7)
C(18)-C(19)-C(20)	108.1(7)	O(5)-C(20)-C(19)	106.3(6)
O(6)-C(21)-C(22)	106.0(6)	C(23)-C(22)-C(21)	109.0(6)
C(22)-C(23)-C(24)	107.7(7)	O(6)-C(24)-C(23)	107.0(6)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1   #2 -x+1,-y,-z

Table 7-4 Anisotropic Displacement Parameters (Angstroms x 10^3) for *(A)*

Table 4. Anisotropic displacement parameters [Å^2 x 10^3] for 1.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2$ [(ha*)^{2}U$_{11}$ + ... + 2hka*b*U$_{12}$]

	U11	U22	U33	U23	U13	U12
Cr 1)	26(1)	33(1)	32(1)	1(1)	5(1)	-1(1)
Cr(2)	35(1)	25(1)	33(1)	7(1)	-3(1)	0(1)
Cr(3)	31(1)	34(1)	29(1)	0(1)	4(1)	-4(1)
Zn(1)	36(1)	35(1)	40(1)	2(1)	4(1)	-8(1)
Zn(2)	32(1)	35(1)	36(1)	0(1)	4(1)	-4(1)
Cl(1)	72(1)	45(1)	71(1)	-16(1)	-23(1)	2(1)
Cl(2)	46(1)	55(1)	55(1)	20(1)	17(1)	4(1)
Cl(3)	35(1)	50(1)	58(1)	-1(1)	8(1)	0(1)
Cl(4)	44(1)	34(1)	45(1)	4(1)	6(1)	-1(1)
Cl(5)	66(1)	50(1)	50(1)	-11(1)	-13(1)	-3(1)
Cl(6)	43(1)	61(1)	40(1)	12(1)	11(1)	8(1)
Cl(7)	37(1)	35(1)	60(1)	8(1)	6(1)	1(1)
Cl(8)	31(1)	50(1)	60(1)	-2(1)	6(1)	5(1)
O(1)	40(2)	26(2)	54(3)	12(2)	-9(2)	-5(2)
O(2)	33(2)	39(2)	39(2)	-1(2)	-5(2)	6(2)
O(3)	54(3)	22(2)	33(2)	8(2)	10(2)	2(2)
O(4)	39(2)	43(2)	26(2)	10(2)	1(2)	-8(2)
O(5)	50(3)	53(3)	26(2)	-4(2)	5(2)	10(2)
O(6)	47(3)	55(3)	36(2)	0(2)	4(2)	17(2)
C(1)	60(5)	45(4)	114(7)	19(4)	-27(5)	10(4)
C(2)	78(5)	31(4)	91(6)	25(4)	-23(5)	13(4)
C(3)	116(7)	33(4)	56(5)	12(3)	25(5)	-2(4)
C(4)	61(4)	37(4)	68(5)	8(3)	29(4)	-1(3)
C(5)	41(4)	77(5)	47(4)	-11(4)	-2(3)	11(4)
C(6)	69(5)	81(5)	68(5)	-18(4)	-19(4)	23(4)
C(7)	73(7)	313(15)	159(10)	-184(11)	-73(6)	107(8)
C(8)	49(4)	65(4)	61(5)	-8(4)	-10(4)	26(4)
C(9)	68(5)	41(4)	46(4)	19(3)	19(4)	10(3)
C(10)	67(5)	31(4)	63(5)	18(3)	7(4)	-2(3)
C(11)	78(5)	30(3)	48(4)	4(3)	5(4)	11(3)
C(12)	76(5)	35(3)	50(4)	1(3)	19(4)	4(3)
C(13)	53(4)	69(5)	39(4)	10(3)	-1(3)	-18(4)
C(14)	55(5)	55(4)	51(4)	9(3)	-5(4)	-10(3)
C(15)	80(6)	79(5)	40(4)	8(4)	2(4)	-8(4)
C(16)	65(5)	93(6)	35(4)	13(4)	-1(4)	-25(4)
C(17)	132(8)	139(8)	30(4)	-1(5)	-13(5)	72(7)
C(18)	140(9)	128(8)	51(5)	-15(5)	-5(5)	61(7)
C(19)	218(13)	172(10)	46(6)	-14(6)	3(7)	117(10)
C(20)	131(8)	95(6)	52(5)	-17(5)	8(5)	47(6)
C(21)	137(8)	124(7)	49(5)	-15(5)	10(5)	80(7)
C(22)	209(12)	135(8)	45(5)	-36(5)	-22(6)	101(8)
C(23)	160(9)	133(8)	52(5)	-16(5)	-7(6)	84(7)
C(24)	122(7)	93(6)	45(5)	-1(4)	-13(5)	53(6)

2) Crystal structure data for *(B)*, [CrCl₂(THF)₄] [ZnBrCl₂(THF)] $[CrCl_2(THF)_4]^{+}[ZnBrCl_2(THF)]^{-}$
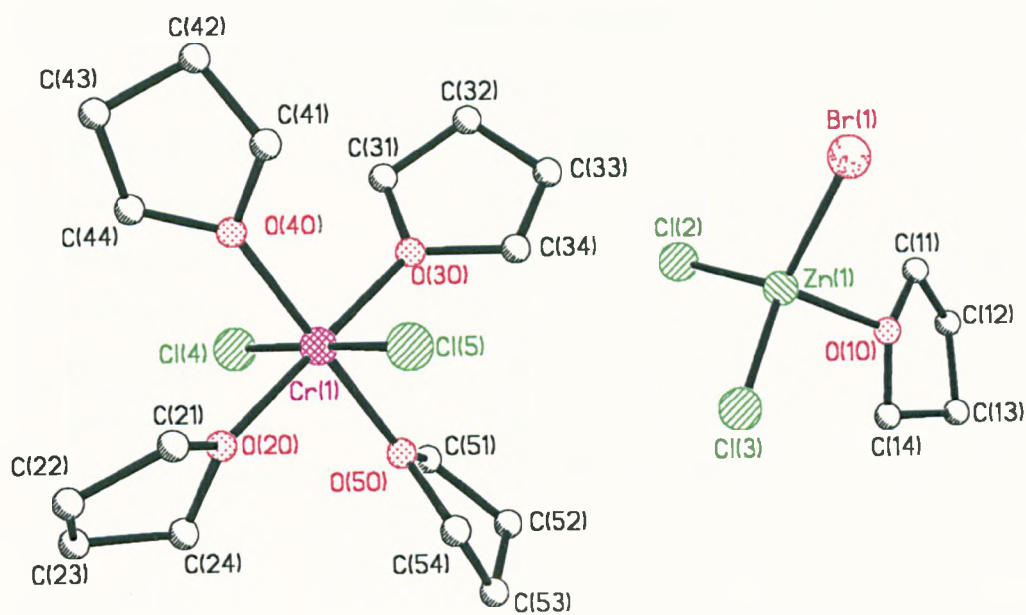
Table 7-5 Crystal Data and Structural Refinement for *(B)*

Table 1. Crystal data and structure refinement for 1(mscr).

Identification code	mscr
Empirical formula	$C_{20}H_{40}BrCl_4CrO_5Zn$
Formula weight	699.60
Temperature	180(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 14.1656(3) Å alpha = 90°
	b = 11.9885(3) Å beta = 98.0410(10)°
	c = 17.3760(3) Å gamma = 90°
Volume, Z	2921.85(11) Å³, 4
Density (calculated)	1.590 Mg/m³
Absorption coefficient	2.953 mm⁻¹
F(000)	1428
Crystal size	0.3 x 0.1 x 0.05 mm
θ range for data collection	2.07 to 28.65°
Limiting indices	-12 ≤ h ≤ 18, -15 ≤ k ≤ 15, -23 ≤ l ≤ 23
Reflections collected	17212
Independent reflections	6850 (R_{int} = 0.0528)
Absorption correction	SADABS
Max. and min. transmission	0.9300 and 0.5300
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6850 / 0 / 309
Goodness-of-fit on F^2	1.007
Final R indices [I>2σ(I)]	R1 = 0.0591, wR2 = 0.1273(for 3894reflections)
R indices (all data)	R1 = 0.1259, wR2 = 0.1532
Largest diff. peak and hole	0.614 and -1.219 eÅ⁻³

Table 7-6 Atomic co-ordinates (x 10^4) and equivalent isotopic displacement parameters (Angstroms x 10^3) for *(B)*

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [Å^2 x 10^3] for 1. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Cr(1)	3073.2(6)	11819.6(7)	-793.5(5)	25(1)
Zn(1)	1978.7(5)	6902.9(6)	1164.2(4)	34(1)
Br(1)	3388.7(5)	5831.2(7)	1249.8(4)	56(1)
Cl2a	1018(16)	6877(16)	17(11)	70(6)
Cl3a	2104(12)	8600(11)	1675(11)	51(4)
Br2b	917(14)	6760(13)	21(9)	48(2)
Br3b	2121(4)	8657(4)	1753(4)	59(2)
Cl(4)	1861.1(11)	12004.6(11)	-1808.0(8)	33(1)
Cl(5)	4286.7(11)	11681.5(12)	228.2(8)	37(1)
O(10)	1193(3)	5960(3)	1859(2)	30(1)
C(11)	950(5)	4847(5)	1593(4)	38(2)
C(12)	36(5)	4562(6)	1889(4)	52(2)
C(13)	-97(5)	5468(6)	2463(4)	54(2)
C(14)	399(5)	6443(5)	2156(4)	47(2)
O(20)	3146(3)	13478(3)	-695(2)	34(1)
C(21)	4035(4)	14139(5)	-567(4)	41(2)
C(22)	3762(5)	15262(5)	-903(4)	47(2)
C(23)	2691(5)	15253(5)	-1127(4)	52(2)
C(24)	2344(4)	14259(5)	-727(4)	43(2)
O(30)	3007(3)	10160(3)	-888.9(19)	26(1)
C(31)	2835(5)	9541(5)	-1620(3)	38(2)
C(32)	3063(8)	8380(5)	-1401(4)	87(4)
C(33)	3029(6)	8252(5)	-593(4)	51(2)
C(34)	3160(6)	9376(5)	-237(3)	46(2)
O(40)	4030(3)	11850(3)	-1545(2)	34(1)
C(41)	4951(4)	11245(5)	-1444(4)	38(2)
C(42)	5180(5)	11096(6)	-2251(4)	52(2)
C(43)	4807(6)	12163(7)	-2640(4)	66(2)
C(44)	3905(6)	12367(7)	-2324(4)	61(2)
O(50)	2103(3)	11758(3)	-59(2)	32(1)
C(51)	1166(4)	11226(5)	-228(3)	35(1)
C(52)	845(5)	11066(5)	552(3)	42(2)
C(53)	1324(6)	12020(6)	1022(4)	60(2)
C(54)	2241(5)	12127(7)	760(4)	54(2)

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Table 7-7 Bond lengths (Angstroms) and Angles (°) for *(B)*

Table 3. Bond lengths [Å] and angles [°] for 1.

Cr(1)-O(20)	1.997(4)	Cr(1)-O(30)	1.997(3)
Cr(1)-O(50)	2.004(4)	Cr(1)-O(40)	2.010(4)
Cr(1)-Cl(4)	2.293(2)	Cr(1)-Cl(5)	2.298(2)
Zn(1)-O(10)	2.086(4)	Zn(1)-Cl3a	2.22(2)
Zn(1)-Cl2a	2.25(2)	Zn(1)-Br2b	2.32(2)
Zn(1)-Br3b	2.335(7)	Zn(1)-Br(1)	2.3620(10)
O(10)-C(14)	1.425(7)	O(10)-C(11)	1.438(7)
C(11)-C(12)	1.497(9)	C(12)-C(13)	1.504(9)
C(13)-C(14)	1.499(9)	O(20)-C(24)	1.467(7)
O(20)-C(21)	1.478(7)	C(21)-C(22)	1.496(8)
C(22)-C(23)	1.513(9)	C(23)-C(24)	1.496(9)
O(30)-C(31)	1.463(6)	O(30)-C(34)	1.464(6)
C(31)-C(32)	1.467(8)	C(32)-C(33)	1.420(9)
C(33)-C(34)	1.483(8)	O(40)-C(44)	1.477(7)
O(40)-C(41)	1.481(7)	C(41)-C(42)	1.493(9)
C(42)-C(43)	1.506(10)	C(43)-C(44)	1.479(10)
O(50)-C(51)	1.465(7)	O(50)-C(54)	1.476(7)
C(51)-C(52)	1.501(8)	C(52)-C(53)	1.510(9)
C(53)-C(54)	1.441(10)		
O(20)-Cr(1)-O(30)	179.7(2)	O(20)-Cr(1)-O(50)	90.8(2)
O(30)-Cr(1)-O(50)	89.3(2)	O(20)-Cr(1)-O(40)	90.3(2)
O(30)-Cr(1)-O(40)	89.6(2)	O(50)-Cr(1)-O(40)	178.6(2)
O(20)-Cr(1)-Cl(4)	89.63(12)	O(30)-Cr(1)-Cl(4)	90.63(11)
O(50)-Cr(1)-Cl(4)	89.25(12)	O(40)-Cr(1)-Cl(4)	89.97(12)
O(20)-Cr(1)-Cl(5)	88.95(12)	O(30)-Cr(1)-Cl(5)	90.79(11)
O(50)-Cr(1)-Cl(5)	90.61(11)	O(40)-Cr(1)-Cl(5)	90.20(12)
Cl(4)-Cr(1)-Cl(5)	178.57(6)	O(10)-Zn(1)-Cl3a	106.6(4)
O(10)-Zn(1)-Cl2a	101.5(6)	Cl3a-Zn(1)-Cl2a	111.8(6)
O(10)-Zn(1)-Br2b	96.9(6)	O(10)-Zn(1)-Br3b	104.8(2)
Br2b-Zn(1)-Br3b	116.5(3)	O(10)-Zn(1)-Br(1)	100.57(10)
Cl3a-Zn(1)-Br(1)	117.0(5)	Cl2a-Zn(1)-Br(1)	116.7(4)
Br2b-Zn(1)-Br(1)	117.0(3)	Br3b-Zn(1)-Br(1)	116.23(14)
C(14)-O(10)-C(11)	109.1(4)	C(14)-O(10)-Zn(1)	120.1(4)
C(11)-O(10)-Zn(1)	116.1(3)	O(10)-C(11)-C(12)	106.3(5)
C(11)-C(12)-C(13)	104.9(6)	C(14)-C(13)-C(12)	102.7(6)
O(10)-C(14)-C(13)	104.2(5)	C(24)-O(20)-C(21)	107.5(4)
C(24)-O(20)-Cr(1)	127.0(3)	C(21)-O(20)-Cr(1)	125.4(3)
O(20)-C(21)-C(22)	104.8(5)	C(21)-C(22)-C(23)	106.8(5)
C(24)-C(23)-C(22)	105.6(5)	O(20)-C(24)-C(23)	102.9(5)
C(31)-O(30)-C(34)	109.6(4)	C(31)-O(30)-Cr(1)	125.3(3)
C(34)-O(30)-Cr(1)	125.1(3)	O(30)-C(31)-C(32)	104.6(5)
C(33)-C(32)-C(31)	108.9(6)	C(32)-C(33)-C(34)	107.1(5)
O(30)-C(34)-C(33)	105.4(5)	C(44)-O(40)-C(41)	107.7(5)
C(44)-O(40)-Cr(1)	126.7(4)	C(41)-O(40)-Cr(1)	125.3(3)
O(40)-C(41)-C(42)	104.5(5)	C(41)-C(42)-C(43)	102.2(5)
C(44)-C(43)-C(42)	103.9(6)	O(40)-C(44)-C(43)	105.8(6)
C(51)-O(50)-C(54)	108.5(5)	C(51)-O(50)-Cr(1)	124.8(3)
C(54)-O(50)-Cr(1)	126.4(4)	O(50)-C(51)-C(52)	104.8(5)
C(51)-C(52)-C(53)	102.7(5)	C(54)-C(53)-C(52)	104.7(6)
C(53)-C(54)-O(50)	105.9(5)		

Symmetry transformations used to generate equivalent atoms:

Table 7-8 Anisotropic Displacement Parameters (Angstroms x 10^3) for (B)

Table 4. Anisotropic displacement parameters [Å^2 x 10^3] for 1.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2$ [$(ha^*)^2 U_{11}$ + ... + $2hka^*b^*U_{12}$]

	U11	U22	U33	U23	U13	U12
Cr(1)	27(1)	24(1)	21(1)	-2(1)	-4(1)	5(1)
Zn(1)	34(1)	39(1)	28(1)	6(1)	2(1)	5(1)
Br(1)	46(1)	73(1)	48(1)	-2(1)	5(1)	11(1)
Cl2a	45(5)	122(13)	39(5)	6(5)	-8(3)	2(4)
Cl3a	93(9)	20(4)	42(4)	11(3)	12(4)	-19(5)
Br2b	42(4)	66(3)	32(3)	7(2)	-4(3)	11(3)
Br3b	64(2)	46(2)	65(3)	-3(1)	5(2)	8(2)
Cl(4)	34(1)	33(1)	27(1)	1(1)	-8(1)	6(1)
Cl(5)	37(1)	44(1)	25(1)	-5(1)	-9(1)	6(1)
O(10)	31(2)	29(2)	31(2)	-2(2)	7(2)	6(2)
C(11)	44(4)	35(3)	36(3)	0(3)	10(3)	3(3)
C(12)	42(4)	55(4)	60(5)	8(4)	6(4)	-6(3)
C(13)	46(4)	68(5)	51(4)	-2(4)	21(4)	-2(4)
C(14)	44(4)	45(4)	56(4)	-7(3)	19(4)	10(3)
O(20)	25(2)	23(2)	53(3)	-6(2)	-1(2)	1(2)
C(21)	24(3)	35(3)	63(4)	-4(3)	1(3)	-4(3)
C(22)	46(4)	43(4)	53(4)	4(3)	7(4)	-8(3)
C(23)	58(5)	37(4)	59(5)	15(3)	-3(4)	9(3)
C(24)	31(4)	31(3)	63(4)	-10(3)	-1(3)	5(3)
O(30)	39(2)	22(2)	17(2)	-1(1)	-4(2)	7(2)
C(31)	57(4)	31(3)	25(3)	-8(2)	-3(3)	-3(3)
C(32)	192(11)	30(4)	37(4)	-10(3)	8(5)	29(5)
C(33)	72(5)	30(3)	47(4)	4(3)	-6(4)	-10(3)
C(34)	78(5)	34(3)	24(3)	10(3)	4(3)	20(3)
O(40)	34(2)	41(2)	26(2)	5(2)	4(2)	5(2)
C(41)	25(3)	42(4)	46(4)	-5(3)	0(3)	3(3)
C(42)	31(4)	87(5)	37(4)	-17(4)	8(3)	4(4)
C(43)	59(5)	103(7)	38(4)	3(4)	12(4)	-6(5)
C(44)	70(6)	77(5)	38(4)	26(4)	14(4)	15(4)
O(50)	36(2)	37(2)	24(2)	-10(2)	2(2)	-5(2)
C(51)	32(3)	37(3)	35(3)	-4(3)	2(3)	-2(3)
C(52)	46(4)	39(4)	40(4)	1(3)	7(3)	-3(3)
C(53)	74(6)	70(5)	38(4)	-15(4)	17(4)	-17(4)
C(54)	56(5)	78(5)	29(3)	-22(3)	7(3)	-3(4)

3) Crystal structure data for (C), [CrCl₃(N₄C₂₀H₄₀)]
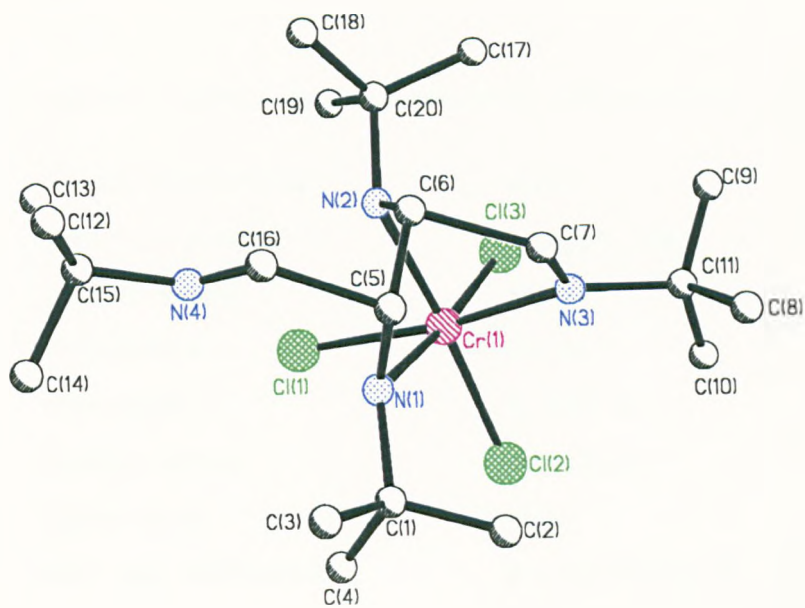
Table 7-9 Crystal Data and Structural Refinement for *(C)*

Table 1. Crystal data and structure refinement for 1(stbum).

Identification code	stbum
Empirical formula	$C_{20}H_{40}Cl_3CrN_4$
Formula weight	494.91
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 10.3822(9)$ Å alpha $= 90^{\circ}$
	$b = 19.100(2)$ Å beta $= 109.267(2)^{\circ}$
	$c = 14.2833(12)$ Å gamma $= 90^{\circ}$
Volume, Z	2673.7(4) Å^3, 4
Density (calculated)	1.229 Mg/m^3
Absorption coefficient	0.740 mm^{-1}
F(000)	1052
Crystal size	.2 x .2 x .1 mm
θ range for data collection	1.85 to 22.50°
Limiting indices	$-13 \leq h \leq 10$, $-22 \leq k \leq 24$, $-16 \leq 1 \leq 19$
Reflections collected	10523
Independent reflections	3485 ($R_{int} = 0.1136$)
Absorption correction	SADABS
Max. and min. transmission	.9576 and .7557
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3485 / 0 / 253
Goodness-of-fit on F^2	1.166
Final R indices [$I>2\sigma(I)$]	R1 $= 0.0963$, wR2 $= 0.2057$(for 1819reflections)
R indices (all data)	R1 $= 0.1876$, wR2 $= 0.2440$
Largest diff. peak and hole	0.968 and -0.370 eÅ^{-3}

Table 7-10 Atomic co-ordinates (x 10^4) and equivalent isotopic displacement parameters (Angstroms x 10^3) for (C)

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for 1. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Cr(1)	4653.4(16)	2332.7(9)	2561.0(10)	48(1)
Cl(1)	3404(3)	3061.3(15)	1278.2(17)	67(1)
Cl(2)	4185(3)	1331.9(15)	1610.3(19)	76(1)
Cl(3)	6669(3)	2445.7(16)	2225(2)	77(1)
N(1)	2818(7)	2326(4)	3013(5)	39(2)
N(2)	4846(7)	3239(4)	3501(5)	38(2)
N(3)	5629(8)	1816(4)	3949(5)	44(2)
N(4)	1897(10)	3707(6)	3272(7)	85(3)
C(1)	1732(12)	1750(6)	2822(8)	67(3)
C(2)	2355(13)	1059(6)	3258(9)	89(4)
C(3)	643(11)	1963(6)	3285(9)	89(4)
C(4)	1015(11)	1721(7)	1691(8)	89(4)
C(5)	3261(13)	2585(6)	4040(7)	82(4)
C(6)	4493(12)	2952(7)	4326(7)	82(4)
C(7)	5296(13)	2130(7)	4605(8)	101(5)
C(8)	6402(15)	839(6)	5149(9)	111(5)
C(9)	8084(14)	1582(9)	4754(11)	132(6)
C(10)	6715(19)	786(8)	3507(10)	202(11)
C(11)	6712(14)	1252(6)	4331(7)	71(4)
C(12)	725(12)	4444(7)	4171(8)	87(4)
C(13)	1499(16)	4902(8)	2860(13)	149(7)
C(14)	-351(14)	4066(9)	2464(10)	145(7)
C(15)	965(11)	4272(7)	3203(9)	72(4)
C(16)	2416(15)	3372(8)	4053(9)	126(7)
C(17)	7300(11)	3477(6)	4458(8)	79(4)
C(18)	5520(11)	4374(6)	4388(9)	89(4)
C(19)	6078(13)	4121(6)	2889(9)	85(4)
C(20)	5974(11)	3787(6)	3821(8)	56(3)

Table 7-11 Bond lengths (Angstroms) and Angles (°) for *(C)*

Table 3. Bond lengths [Å] and angles [°] for 1.

Cr(1)-N(3)	2.146(7)	Cr(1)-N(2)	2.158(6)
Cr(1)-N(1)	2.204(7)	Cr(1)-Cl(2)	2.302(3)
Cr(1)-Cl(3)	2.307(3)	Cr(1)-Cl(1)	2.325(3)
N(1)-C(5)	1.471(11)	N(1)-C(1)	1.534(12)
N(2)-C(6)	1.453(11)	N(2)-C(20)	1.524(11)
N(3)-C(7)	1.254(11)	N(3)-C(11)	1.522(12)
N(4)-C(16)	1.244(13)	N(4)-C(15)	1.431(13)
C(1)-C(2)	1.511(14)	C(1)-C(4)	1.540(14)
C(1)-C(3)	1.542(14)	C(5)-C(6)	1.396(13)
C(5)-C(16)	1.74(2)	C(6)-C(7)	1.76(2)
C(8)-C(11)	1.530(14)	C(9)-C(11)	1.49(2)
C(10)-C(11)	1.48(2)	C(12)-C(15)	1.519(14)
C(13)-C(15)	1.48(2)	C(14)-C(15)	1.48(2)
C(17)-C(20)	1.499(14)	C(18)-C(20)	1.545(13)
C(19)-C(20)	1.513(13)		

N(3)-Cr(1)-N(2)	82.9(3)	N(3)-Cr(1)-N(1)	85.2(3)
N(2)-Cr(1)-N(1)	74.6(3)	N(3)-Cr(1)-Cl(2)	96.1(2)
N(2)-Cr(1)-Cl(2)	172.2(2)	N(1)-Cr(1)-Cl(2)	97.7(2)
N(3)-Cr(1)-Cl(3)	92.9(2)	N(2)-Cr(1)-Cl(3)	98.6(2)
N(1)-Cr(1)-Cl(3)	173.1(2)	Cl(2)-Cr(1)-Cl(3)	89.11(12)
N(3)-Cr(1)-Cl(1)	166.8(2)	N(2)-Cr(1)-Cl(1)	85.6(2)
N(1)-Cr(1)-Cl(1)	85.6(2)	Cl(2)-Cr(1)-Cl(1)	94.46(11)
Cl(3)-Cr(1)-Cl(1)	95.07(11)	C(5)-N(1)-C(1)	112.8(7)
C(5)-N(1)-Cr(1)	105.9(6)	C(1)-N(1)-Cr(1)	127.4(6)
C(6)-N(2)-C(20)	112.9(7)	C(6)-N(2)-Cr(1)	101.9(6)
C(20)-N(2)-Cr(1)	129.9(6)	C(7)-N(3)-C(11)	115.1(8)
C(7)-N(3)-Cr(1)	107.9(7)	C(11)-N(3)-Cr(1)	136.4(6)
C(16)-N(4)-C(15)	122.2(10)	C(2)-C(1)-N(1)	111.3(9)
C(2)-C(1)-C(4)	113.2(10)	N(1)-C(1)-C(4)	106.6(9)
C(2)-C(1)-C(3)	109.2(10)	N(1)-C(1)-C(3)	109.5(9)
C(4)-C(1)-C(3)	106.9(9)	C(6)-C(5)-N(1)	114.5(9)
C(6)-C(5)-C(16)	88.9(10)	N(1)-C(5)-C(16)	107.9(9)
C(5)-C(6)-N(2)	113.8(9)	C(5)-C(6)-C(7)	86.5(10)
N(2)-C(6)-C(7)	107.0(8)	N(3)-C(7)-C(6)	119.0(9)
C(10)-C(11)-C(9)	108.9(13)	C(10)-C(11)-N(3)	109.6(9)
C(9)-C(11)-N(3)	109.9(10)	C(10)-C(11)-C(8)	110.7(13)
C(9)-C(11)-C(8)	108.8(10)	N(3)-C(11)-C(8)	108.8(10)
N(4)-C(15)-C(13)	108.6(11)	N(4)-C(15)-C(14)	107.1(11)
C(13)-C(15)-C(14)	109.9(12)	N(4)-C(15)-C(12)	114.2(9)
C(13)-C(15)-C(12)	108.5(12)	C(14)-C(15)-C(12)	108.5(11)
N(4)-C(16)-C(5)	120.3(10)	C(17)-C(20)-C(19)	112.5(10)
C(17)-C(20)-N(2)	111.8(9)	C(19)-C(20)-N(2)	107.3(8)
C(17)-C(20)-C(18)	110.3(9)	C(19)-C(20)-C(18)	106.1(10)
N(2)-C(20)-C(18)	108.6(8)		

Symmetry transformations used to generate equivalent atoms:

Table 7-12 Anisotropic Displacement Parameters (Angstroms x 10³) for *(C)*

Table 4. Anisotropic displacement parameters [$\text{Å}^2 \times 10^3$] for 1.
The anisotropic displacement factor exponent takes the form:
$$-2\pi^2 [(ha^*)^2 U_{11} + \ldots + 2hka^*b^* U_{12}]$$

	U11	U22	U33	U23	U13	U12
Cr(1)	62(1)	57(1)	29(1)	-7(1)	21(1)	-1(1)
Cl(1)	91(2)	75(2)	35(1)	9(1)	23(2)	24(2)
Cl(2)	117(3)	60(2)	50(2)	-14(1)	25(2)	9(2)
Cl(3)	84(2)	102(3)	66(2)	18(2)	53(2)	26(2)
N(1)	33(5)	47(5)	41(5)	-10(4)	18(4)	-24(4)
N(2)	53(5)	31(5)	40(4)	-23(4)	29(4)	-24(4)
N(3)	53(6)	47(6)	36(5)	11(4)	18(4)	13(4)
N(4)	103(8)	109(9)	51(6)	22(6)	34(6)	71(7)
C(1)	58(8)	70(10)	70(8)	-9(7)	16(7)	-19(7)
C(2)	101(10)	47(9)	111(10)	12(7)	26(8)	-33(8)
C(3)	58(8)	89(10)	124(11)	-3(8)	35(8)	-36(8)
C(4)	74(9)	102(11)	80(9)	-25(8)	13(7)	-27(8)
C(5)	121(11)	101(11)	36(6)	-13(6)	43(7)	-73(9)
C(6)	79(9)	137(12)	45(7)	-32(7)	42(7)	-68(9)
C(7)	136(13)	131(12)	53(8)	41(7)	55(8)	105(10)
C(8)	166(14)	62(10)	111(11)	49(8)	53(10)	44(9)
C(9)	68(10)	194(18)	135(14)	47(13)	34(10)	55(11)
C(10)	310(2)	185(19)	78(10)	-28(11)	14(13)	190(18)
C(11)	92(10)	74(9)	41(7)	15(6)	13(7)	35(8)
C(12)	80(9)	109(11)	78(9)	-16(8)	33(7)	35(8)
C(13)	135(14)	127(15)	217(19)	91(14)	100(14)	37(12)
C(14)	115(13)	148(16)	114(12)	-41(11)	-39(11)	44(11)
C(15)	49(8)	85(10)	65(8)	3(7)	-5(7)	28(7)
C(16)	174(15)	156(15)	64(9)	21(9)	62(10)	121(13)
C(17)	52(8)	94(10)	91(9)	-10(8)	24(7)	-30(7)
C(18)	86(10)	80(10)	104(10)	-42(8)	35(8)	-44(8)
C(19)	112(11)	54(8)	112(10)	2(7)	66(9)	-27(8)
C(20)	55(8)	53(8)	70(7)	-18(6)	33(7)	-21(6)

Appendix B

7.2. Appendix B - UV/Visible spectroscopy examples

Examples of spectra obtained from chapter 4.

Figure 7-1 UV/ Visible spectrum for $[Cr(H_2O)_6]^{2+}[ClO_4^-]_2$

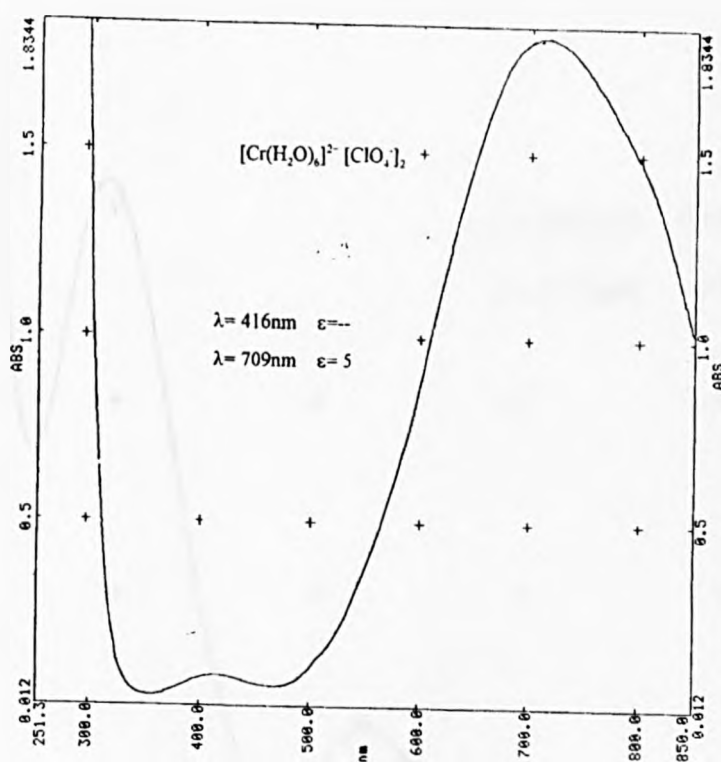**Figure 7-2 UV/ Visible spectrum for $[(H_2O)_5\text{-}Cr\text{-}CHCl_2]^{2+}[PF_6^-]_2$**

$[(H_2O)_5\text{-}Cr\text{-}CHCl_2]^{2-}\ [PF_6^-]_2$

$\lambda= 396nm \quad \varepsilon=367$

$\lambda= 522nm \quad \varepsilon=99$